Synthesis and mechanism study of Au nanowires and their derivatives

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Synthesis and Mechanism Study of Au Nanowires and Their Derivatives

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Abstract

This thesis summarizes my postgraduate research on the mechanism studies of the novel nanowire and nanowire related structures, rational design and synthesis based on the mechanism understanding, and structural transformation at the nanoscale. The research was carried out mostly based on the ultrathin gold nanowires (Au NWs) structures. Two main systems were studied: the Active Surface Growth mechanism which yields then substrate-bound Au nanostructures and the ultrathin Au NWs synthesized in the colloidal organic mediate. We systematically studied Active Surface Growth mechanism, and demonstrated it to be an effective method for enriching the synthetic capability of the Au nanostructures. On the other hand, gold and silver (Ag) was grown onto the colloidal ultrathin Au NWs, giving novel nanobracelets structures and alloy wires with novel twisting morphologies. .

In detail, we performed system investigation on the Active Surface Growth mechanism of the substrate-bound Au NWs (**Chapter 2**). Hairy Au NWs was previously synthesized with the colloidal Au@SiO₂ (silica encapsulated Au nanoparticles (NPs)) substrate. By transforming the system to the wafer substrate, we had a much controllable system to investigate the growth mechanism of such novel type of Au NWs. The symmetric breaking during the Au deposition was discovered to be closely related to the existence of the

substrate, as well as the blockage effect of the strong thiol-ended ligand, 4-mercaptoenozoic acid (4-MBA) for the Au deposition. The different degrees of absorption of the ligands between the areas touched the substrate (the active surface) and the rest on the exposed Au surface led to the formation of a constantly more active surface on the Au nanoparticles (or other nanostructures), and from where the nanowires emerged. Controlling experiments was performed to identify the Au deposition sites, and distinguishing this mechanism from the traditional VLS growth. The relationship between the diameter of the Au NWs and the ligand concentration as well as the Au reduction rate was also determined.

In **Chapter 3**, we further screened the effect of the ligands, especially the different moieties, on the Active Surface Growth of the surface-bound Au NWs. We found the ligand criteria for facilitating such growth was the strong thiol group and the planar backbone of molecules. The generality of the ligands allowed the construction of the substrate surface with desirable surface properties. Typically the superhydrophobic coating could be obtained with naphthalenethiol ligands.

In **Chapter 4**, we investigated the seed effects on the active surface formation and NWs growth. We observed splitting of the active surface when the seeds were in odd shape. A principle that analog to the Rayleigh instability could be employed to explain this behavior of the dynamic active surface. We

also looked at the relation between the bundle formation and the seed density. After we have gained the knowledge on the system, by changing the combination of the seed morphology and the ligand amount, a variety of the Au nanostructures can be generated on the substrates. With careful design and choosing the seeds, nano-brushes, nano-curtains and nano-flowers have been demonstrated here.

Seeded growth has been widely employed in the nanoscale synthesis, and has already provided many novel and complex structures. We further grown the Au onto the pre-synthesized Au NWs rings, and obtained the chain-like nanobracelets (**Chapter 5**). Ultrathin Au NWs were first synthesized and transferred to aqueous phase and forming coiled rings with reported methods in our group. With the presence of the 11-mercaptopodecanoic acid (11-MUA), Au deposition on to these rings and forming blocks that hold together by the wires. By adjusting the ligand environment, the block number can be changed. In some mixed ligand cases, smooth thicker wires could be obtained. The mechanism discussion of the growth kinetics and thermodynamics was performed. Generally such type of the overgrowth included the heterogeneous nucleation on the wires, the expansion of the islands and the lateral growth of the islands. Ligands adjust the relative rate of these three processes in a similar way like the active surface, leading to such unconventional structures.

In **Chapter 6**, we further studied the behavior of the ultrathin Au NWs by

growing Ag onto it and obtaining surprisingly double helix twisting structures. Different from the Au, Ag addition induced the structural transformation of the nanowires, most probably by the diffusion of Ag into the lattice to form Au-Ag solid solution which changed the lattice structures. The ultrathin Au NWs were previously all considered as single crystal NWs while our result strongly suggested that, there exist more than one types of lattices, which would behave quite differently in the presence of the Ag (0). The synthesis conditions of the Au NWs influenced the lattices and the percentage of each type of the lattice a lot. Such unconventional behavior of twisting not only provided the novel morphology of the nano-building blocks but also the more insights of our understanding on the oleylamine-stabilized ultrathin Au NWs.

Chapter1 Introduction

Nanostructure growth and transformation are of great importance as they are the starting points towards the complex nanodevices and applicable functional materials. Understanding the mechanism of the existing synthesis is essential for rational design of nanostructures and constructs new nano-morphologies.

Thermodynamics and kinetics are at the center of the mechanism discussions. Thermodynamics deals with the driving force of a system moving from the initial state to the product state, whereas kinetics concerns with the barriers of the specific pathways in this process. For a simple illustration, Figure 1-1 shows the potential energy landscape of two competitive reactions, where C is the thermodynamically favored product and D is the kinetically favored one. The rate constant is exponentially dependent on the activation energy E_a (Eq. 2).^[1] Thus, the reaction of the red pathway is significantly faster, leading to D as the main product. On the other hand, upon establishment of equilibrium, the molecules would have experienced the different product states multiple times and eventually accumulate at the most stable state. The equilibrium constant is exponentially dependent on the driving force ΔG° (Eq. 1).^[1] For a typical chemical reaction, one often needs to distinguish between the thermodynamic control and the kinetic control).^[2]

While thermodynamic and kinetic analyses are common in the traditional fields of chemical science,^[2d, 3] they are to date rare in nanoscience. This is

Figure 1-1. Simple energy landscape illustrating the choice between the thermodynamically and kinetically controlled products.

because there are often multiple concurrent processes in a typical nanoscience phenomenon, unlike a typical chemical reaction. However, it is still possible to compare the various forms of nanostructures using simple standards such as the surface to volume (S/V) ratio and the strength of interactions. Simple geometric analysis and logical deduction can provide powerful predictions, which can then be subjected to experimental verification. The typical approach in chemistry is to establish the mechanistic hypothesis on the basis of a few key observables, making sure it is also consistent with the control experiments and the trapped intermediates. In nanoscience, traditionally there has been great attention to the physical characterization of nanocrystals. Notwithstanding the importance of the shape and internal structure, a static state is often not a sufficient basis for interpreting the overall process. At least, an initial hypothesis would remove the ambiguity, so that one can interpret the various

factors affecting the observables under a specific scenario. The deductions from the analysis, when feasible, can be then tested by experiments.

1.1 Interactions to be considered.

In a chemical reaction, the stability of the molecules is usually evaluated on bases such as bond energy and computational simulations.^[4] However, the same standards cannot be easily applied in nanoscience. Because typical nanostructures contain a huge number of atoms, conventional methods of simulation would be too costly in terms of computation time. Moreover, unlike molecules with identical composition, a collection of NPs, regardless how uniform, always have a certain distribution in terms of size, shape, surface ligand density, and even chemical composition. Lastly, in typical nanoscale phenomena, there are uncertainties at molecular detail. For example, during aggregation, the contact area between the NPs and the ligand density therein are of critical importance to the stability of the resulting cluster, but such properties are wildly variable in the mixture and very difficult to characterize. With these limitations, the discussion at the nanoscale shall focus on the dominant factors and major trends.

1.1.1 Type and strength of interactions.

For a NP suspended in a solution, there are cohesive interactions within the NP and surface interactions with the environment. Depending on the material, the cohesive interactions include metallic, covalent, or ionic bonding, van der

Waals interactions, H-bonding, *etc.* The surface atoms can directly interact with the environment, or via ligands. Thus, the surface interactions include the NP-solvent, NP-ligand, ligand-ligand, ligand-solvent interactions. In experimental studies, it is often difficult to distinguish these interactions. Therefore, the surface energy can be considered as a whole, including the contributions from the ligands and interfacial defects.

Hydrophobic interaction often plays important roles in nanoscience.^[5] Take the aggregation of two carbon nanotubes (CNTs) in water as an example, the process is favorable because it reduces the exposed surface area. The un-aggregated CNTs are not stable because their incapability of H-bonding leads to disruption of the highly dynamic H-bonds among the water molecules, restricting their mobility and giving a structured "cage" around their nonpolar surface (mostly entropic contribution).^[6] While there are only van der Waals interactions between the CNTs in the product state, part of the stability of the aggregate originates from the reduction of the unfavorable CNT-water interactions in the initial state. Given the "invisible" contribution (there is no real hydrophobic force between the aggregated CNTs); the term "hydrophobic interaction" is typically used to designate the driving force of the overall system. This interaction is well established in biological systems, but not yet broadly recognized in the field of nanoscience.

One can often invoke the relative strength of interactions to compare the

stabilities of different states. For example, the formation of defects in nanocrystals or the lattice mismatch between the neighboring domains reduces the number of bonding interactions therein (Section 1.3.1). The reduction of interactions in terms of quality and/or quantity gives rise to unstable states. And when comparing the amorphous and crystalline states of a same material, In general, ordered packing is energetically favorable due to the dominant enthalpic contribution.

1.1.2 Surface energy at the nanoscale.

In nanoscience, the surface energy is often the key contributing factor, because the amount of materials and their chemical composition are typically not changing in many nanoscale processes. When considering the possible states of NPs with different size and shape, the main difference is the amount of their surface atoms/molecules, which have less favorable interactions than the internal ones do. To illustrate this point, we use water droplet as a simple model (Figure 1-2).

A molecule on the surface of a water droplet has poor interactions with the surrounding air, but strong H-bonding with the neighboring molecules inside the droplet. Thus, on average it experiences a net force perpendicular to the water-air interface, *i.e.*, the surface tension. Balancing the surface tension around the droplet leads to a spherical shape. From a chemist's point of view, the surface molecules are experiencing weaker interactions than the interior

Figure 1-2. The essence of surface energy: The minimization of system energy requires the minimization of the number of the surface atoms with unfavorable interactions. This principle applies to all nanostructures, though in crystals the facets are also important.

ones do (and an additional entropic term if they have less mobility). In order to maximize the favorable interactions within the droplet, it should minimize the number of surface molecules, *i.e.*, minimize its S/V ratio in the form of a sphere (Figure 1-2).

Similarly, the spherical shape of nanometer-sized liquid droplets can also be explained on the basis of their surface energy. Given the higher percentage of the surface molecules on a smaller domain, the surface energy would play an even more significant role.^[7] Maximizing the cohesive interactions within the NP (metallic bonds, ionic bonds, *etc.*) would drive the system towards the minimized S/V ratio.

Considering the less interactions on a surface, the surface energy is defined as the unit energy required to create a new surface.^[8] In experiments, the

surface is often interacting with a media (gas or solvent) or another solid, thus the surface energy is reduced when there are strong surface interactions (in quality and quantity). The term “interfacial energy” instead of “surface energy” is also used when emphasizing the interactions of the surface with their environment or the neighboring domain. Typically, the interactions between the surface and the media (solvent molecules) should be weaker than the cohesive interactions within the NP. Otherwise, the system would seek to maximize the solvent-NP interface, meaning that the NPs would be dissolved.

For two juxtaposed domains of condensed phase, their interface is an important component of the total interfacial energy. It basically depends on the strength of the interactions at the interface, more specifically, on the quality of the bonding interactions between the domains, the matching of the opposing lattices (affecting the number of bonding interactions and/or bond distances), the interfacial defects, as well as entropic contributions. For a liquid droplet on a solid surface, the liquid domain would adopt a configuration with minimized total interfacial energy. Suppose there are only poor bonding interactions at the solid-liquid interfaces, maximizing the cohesive interactions within the droplet would become a better option. This leads to a poor wetting property.

In short, while interfacial energies are difficult to measure for nanostructures, the major trends can be deduced by comparing them on the basis of bonding interactions. For many structures, the S/V ratio is a convenient standard, which,

admittedly, is not as rigorous as the interfacial energy. But in contrast to the latter, it can be easily calculated from the experimentally observed structures.

1.2 Growth of single-domain nanoparticles.

1.2.1 Effects of ligands.

Ligands play a pivotal role in NP synthesis. The process of ligand binding to a NP surface has a thermodynamic driving force and encounters kinetic barriers,^[9] which should not be confused with the thermodynamic and kinetic factors of nanocrystal growth that will be discussed below.

In a colloidal solution, ligands are dynamically adsorbing to and detaching from the NP surface.^[10] In their presence, the growth of the underlying facet is attenuated because the growth materials cannot be directly deposited on top of the ligands. The material deposition has to “wait” until ligand dissociation exposes the crystal surface. Thus, the ligand affinity determines the “on”/“off” ratio of the ligand,^[11] which in turn governs the rate of facet growth (the kinetics).

Interacting both with the solvent and with the crystal surface, the ligand layer also modulates the thermodynamic stability of the facets, influencing the end states of nanocrystal growth.

1.2.2 Thermodynamic analysis.

Figure 1-3. The lowest energy structure of a nanocrystal can vary, depending on the relative stability of its facets.

To evaluate the stability of NPs, one needs to compare the overall shape (*e.g.*, cube vs. cuboid), the different facets, and the sharpness or roundedness of the edges and corners. For simplicity, we first analyze the surface energy of one nanocrystal with an invariant volume (no growth or aggregation). In comparison to liquid droplets and amorphous NPs, the minimization of surface energy in nanocrystals is more complex because they have different types of facets. The facets have different density of surface atoms, charges, ligands, leading to different stability.

If all of the facets of a nanocrystal are equally favored, then a spherical shape would be preferred because it has the lowest S/V ratio (Figure 1-3). On the other extreme, a polyhedron with sharp edges and corners will be preferred if only one type of facets is favored, for example, octahedra with (111) facets, cubes with (100) facets, *etc.* Most nanocrystals are in between these two

extremes, with a range of surface energies for the different types of facets. When the stability difference among the facets is reduced, more than one type of facets will appear and the resulting polyhedron should gradually appear rounder, with truncated edges and corners.

The system seeks to minimize the total surface energy, that is, the sum of the facet area weighted by their respective surface energy:

$$\Delta G = \sum \gamma_i A_i \quad (3)$$

where γ is the surface energy of a given facet, and A is its area (Figure 1-4). Thus, we arrive at the classic Wulff construction (the Gibbs-Wulff Theorem).^[12] In experiments, the observation of nanocrystals adopting rounder shapes is sometimes associated with the removal of the ligand or the reduction of its concentration. This reduces the stability difference among the facets, thus leading to less sharp edges and corners.

Not considering ligand modification, the relative stability of the facets can be evaluated on the basis of the bonding interactions within the facets, which depends on the surface packing efficiency. In fcc metal nanocrystals, for example, the (111) facets are normally the most stable ones, because the atoms thereon have the largest number of neighbors, and thus the largest number of metallic bonds per atom. On this basis, it is generally agreed that $\gamma_{(111)} < \gamma_{(100)} < \gamma_{(110)} < \text{other higher index facets}$.^[13] For ionic crystals, charge balance is of great importance. For example, NaCl crystals prefer the (100) facets over the (111)

facets, because the former are charge neutral whereas the latter are dominated by one type of charges. However, for most of the colloidal nanocrystals, the surface ligand is an important factor, if not the dominant one. Indeed, a wide variety of ligands are known in the literature for stabilizing the specific facets of nanocrystals.^[14]

It is not always easy to determine if a nanocrystal is thermodynamically or kinetically controlled. A rule of thumb is that those with high aspect ratio are likely not the most stable form, in particular, when there is inequivalent growth of the equivalent facets. In single-crystalline fcc nanocrystals, for example, there are always multiple equivalent facets (eight (111) facets, six (100) facets, *etc.*). Without invoking additional factors (Section 1.2.4), they should remain as equivalent. For some nanowires (NWs) and nanorods with high aspect ratio, it would be implausible to invoke enormously different surface energies for explaining the large difference in the respective facet area (Wulff construction). In other words, should a NW flow like liquid, it would withdraw into a near spherical polyhedron to reduce its S/V ratio. A faceted grain with equal area of the equivalent facets should be more favorable than a wire with a high aspect ratio (Figure 1-3).

On the other hand, determining the thermodynamically favored shape of semi-liquid (*e.g.*, polymer NPs formed above their glass transition temperature) or amorphous NPs is easy. Without the influence of facets, the S/V ratio is a

Figure 1-4. Schematics illustrating the different scenarios to achieve minimal energy structures: a) via the flowing of liquid; b) via the dynamic dissolving and re-depositing of the growth material (brown arrows) or the rapid migration of the surface atoms (green arrows); and c) when the minimal energy form is achieved in every step.

good standard of evaluation.

Means to achieve thermodynamic control.

In chemical reactions, the thermodynamically controlled product is obtained when the system is in equilibrium. In contrast, there are several different scenarios where a NP can reach its minimal energy shape (Figure 1-4): (1) the

NP is a liquid or has a sufficient structural fluidity, so that it can flow into the minimal energy shape; (2) the material of the NPs is continuously dissolving and re-depositing, reaching an equilibrium; (3) the surface atoms are rapidly migrating, equilibrating the external facets;^[15] (4) during the growth of the NP, in every step its shape is the minimal energy form, so that the final shape is also thermodynamically controlled. It should be noted that there are differences in these equilibria. For example, the internal defects are easily adjusted in Scenario 1, but not in Scenario 2, 3 and 4 (See Section 1.2.4). Moreover, the dissolution-redeposition equilibrium will lead to the exchange of materials among the NPs (Ostwald ripening), giving a broad size distribution.

The detailed steps in reaching the lowest energy shape can be subjected to kinetic analysis. The lack of prominent barriers in some cases could mean that the driving forces are subtle and accumulative. For example, in the shape evolution of an irregular droplet to a sphere (Figure 1-4a), the interfacial tension pushes the droplet towards gradually more favorable forms. If one analyze at molecular detail in very short time interval, the dynamic process would seem random. But the thermodynamic control is like the “invisible hands” providing the direction of progress, where the exact pathway is hard to predict and often meaningless. After oscillating for a few times, the droplet would eventually settle at the spherical shape. Similarly, despite the dynamic and chaotic steps in forming the spherical NPs atom by atom, the underlying

thermodynamic control exerts its effects in a subtle and consistent manner.

Defining the right system.

Proper definition is of great importance when discussing “the minimum energy state of NPs”. The discussion above only considers a single NP, and their ligands are inexplicitly included because they contribute to the facet stability.

If we consider all NPs in the solution, the collection is obviously not at the minimum energy state, regardless of the shape of the NPs. The system would seek the minimum total surface energy by reducing the number of particles. Ostwald ripening is a possible means to exchange materials among the NPs and reduce the system energy.^[16] In this context, the thermodynamically stable final state would be one giant particle with minimized surface.

The discussion on thermodynamics can be confusing if the boundaries are ill-defined. For example, if the NPs can react with the residue reactants, air, or water in the environment, their chemical instability can further complicate the discussion of shapes. Basically, the definition is critically dependent on what are included in the system and the applicable time frame.

In many cases, we are interested in the shape of colloidal NPs, not their chemical changes. In practice, the product NPs can be isolated before they have enough time for ripening or degradation.

Figure 1-5. a) Plot of monomer concentration against time, illustrating the initial accumulation of the monomers, the nucleation stage, and the subsequent growth of the nuclei (modified with permission from ref. [20e], [24a], copyright 2009 Wiley-VCH, 1950 American Chemical Society); b-d) Kinetic analysis of crystal growth: b) all nuclei are generated at roughly the same time and grow at a same rate; c) with over-supply of monomers, continual homogeneous nucleation leads to polydispersed NPs; d) heterogeneous nucleation occurs only on the pre-existing seeds.

1.2.3 Kinetic analysis.

Unlike the thermodynamics, the kinetics of NP growth is influenced by a variety of factors at the different levels of fundamental processes, for example, the random encountering of the growth material, the formation of stable nuclei, and the isotropic diffusing of growth materials towards the nuclei. In the following, the effects are discussed separately.

During the growth of a nanocrystal, the atoms/molecules are deposited onto a nucleus, but it is also possible that they will re-dissolve in the solution or migrate on the surface. These processes are akin to the reverse chemical reactions in concept. It is important to note that the reversibility is critical to the formation of facets. In a homogeneous solution, the diffusion of growth materials towards the nucleation center is isotropic in nature (on average or upon accumulation). In order for the facet stability to exert its influence, the growth material must sample over multiple locations, making re-dissolving a necessary condition. In other words, if the deposition is a one-way process, uniform over-coating will only lead to isotropic structures (spheres). Experimentally, at the beginning of the growth, the initial fast reaction rate typically leads to rapid deposition and negligible re-dissolution. Indeed, the intermediates trapped before the formation of faceted NPs (such as cubes and octahedra) were often smaller spheres.^[17] In this context, the initial stage of nanosphere formation is kinetically controlled. At the later stage, slower reaction rate and the dissolving–deposition dynamic would help establish the

stable facets.

Nucleation and growth.

Regardless of materials composition, the typical growth of NPs shares a similar process. A chemical reaction gives free atoms or molecules, which are then fed to the growth. The basic process of how these free atoms or molecules join with each other has been described in the classic theory of nucleation and growth (Figure 1-5a).^[11, 14c, 18]

Basically, there is a main kinetic barrier in forming nuclei in a homogeneous solution (the homogeneous nucleation).^[19] It arises because the nuclei, being extremely small and not thoroughly solvated, are less stable than both the well solvated atoms/ions and the subsequently formed NPs. The Gibbs free energy of forming a spherical nucleus can be expressed as the sum of the volume energy and the surface energy,^[14c, 19-20]

$$\Delta G = \frac{4}{3}\pi r^3 G_V + 4\pi r^2 \sigma \quad (4)$$

where G_V is the energy per unit volume (negative in value); σ is the surface energy per unit area of the nucleus (positive); and r is the radius. Addition to the nucleus is energetically unfavorable until it reaches a critical radius. At this inflection point,

$$r^* = -\frac{2\sigma}{G_V} \quad (5)$$

Thus, for the overall growth, the nucleation barrier is the amount of energy required to form a nucleus with the critical radius r^* :

$$\Delta G^* = \frac{16\pi\sigma^3}{3(G_V)^2} \quad (6)$$

This barrier forces the growth material to build up in the solution, making the solution oversaturated (the accumulation stage, Figure 1-5a). Initially, the clusters formed by the random collision of the monomer species are too small to be stable. As a result, they dissolve in the solution regenerating the monomers. With the increasing oversaturation, at a certain point the collision becomes so intense that many clusters are able to reach beyond the critical size, giving stable nuclei (the nucleation stage) and consuming the growth materials. This stage only lasts for a short period until the oversaturation drops below the critical level, stopping the formation of new nuclei. Now with the stable nuclei, the deposition of the monomers on them (the heterogeneous nucleation) is energetically favorable, and the growth will last as long as the solution is oversaturated (the growth stage).

In experiments, the kinetic pathways of NP growth and the control of the NP size distribution are mainly dependent on how the nucleation barrier is crossed. In an extreme case, the chemical reactions are instantaneously finished. The resulting oversaturation of the growth materials leads to rapid homogeneous nucleation. Should there be no kinetic barrier for the nucleation, the aggregation of the monomer species would be similar to the step-growth polymerization of organic monomers,^[21] leading to polydispersed atomic clusters. However, the kinetic barrier causes the initial clusters to re-dissolve except those above the

critical size, making those emerge from the nucleation uniform in size. A good example is the formation of noble metal NPs via the rapid reduction of metal salts using NaBH_4 .^[22] The nucleation consumes a significant portion of the monomer species, preventing continual homogenous nucleation. Given the large number of nuclei and the diminished growth materials, it would be difficult to grow large NPs. To this end, using more starting materials is usually not a good strategy, because their higher concentration would lead to faster initial reactions and thus a higher oversaturation. Therefore, the extra materials would contribute to the increased number of nuclei instead of the additional growth on the individual NPs.

If the chemical reactions are still ongoing after the initial nucleation event, it is possible that they may build up enough growth materials for continuous homogeneous nucleation. Thus, the new nuclei that emerge later would have less time to grow, leading to polydispersed NPs (Figure 1-5c). To achieve uniformly sized NPs, the rate of producing the growth materials should be kept slower than that of its consumption (heterogeneous nucleation on the existing nuclei). This prevents the buildup and suppresses the homogeneous nucleation, allowing all nuclei to emerge at roughly the same time and grow at the same rate (Figure 1-5b).

Temperature is a convenient variable for controlling the growth kinetics. Its main effect is on the reaction rates, though it also affects the saturation level of

the growth material, reaction equilibrium, *etc.* The “hot-injection” method used for the synthesis of quantum dots is a good example.^[23] The injection of room temperature reactant causes a major drop of the temperature (*e.g.*, from 300° to 180° within seconds).^[23a] With the initial burst nucleation and the rapid drop of the temperature, the oversaturation is quickly brought below the critical level. The subsequent growth is dominated by the heterogeneous nucleation on the initial nuclei. The burst nucleation, the separation of the nucleation and growth processes, together with the “size-distribution focusing” effects lead to the NPs with the extremely narrow size distributions.^[11, 18b, 24]

Seeding.

Given a same amount of starting material, the size of the resulting NPs is inversely proportional to the number of nuclei in the system. But it is usually very difficult to control the number of nuclei formed during the homogeneous nucleation. To solve this problem, pre-fabricated NPs can be used as seeds, so that the number of NPs in the solution can be pre-determined. If all of the seeds grow at a same rate and there are no newly formed nuclei, the product NPs will have a uniform size distribution (Figure 1-5d).

The amount of seeds is also of importance. If the seed concentration is extremely low, there must be regions in the solution where the produced growth material cannot reach any seeds by diffusion.^[25] It is also possible that severe aggregation of NPs may greatly reduce the number of nucleation centers

Figure 1-6. TEM images of a) 50 nm Ag nanocubes synthesized using PVP as the ligand; b) Ag octahedra obtained with sodium citrate as the ligand. The scale bar in the inset is 20 nm. c) SEM and d) HRTEM image of tris-octahedral nanocrystals and the model of a (221) facet. Reprinted with permission from ref. [17a], [28a], and [29], respectively, copyright 2010 Wiley-VCH, 2010 American Chemical Society, and 2008 Wiley-VCH.

(in the form of clusters of NPs), leading to a similar situation. The consequence is the local buildup of the growth material, causing homogeneous nucleation. The resulting nuclei will then participate in the subsequent growth competing with the seeds and giving NPs with different sizes. Whether such

buildup can occur depends on the seed concentration, the rate of mass transport (diffusion, convection, *etc.*), and the production-consumption dynamic of the growth material. Thus, stirring and the viscosity of the solution are also factors.

With these background knowledge, one can appreciate why nanoparticle syntheses are often less reproducible than chemical reactions. The homogeneous nucleation is highly sensitive to the experimental conditions such as temperature, stirring (affecting solution homogeneity), impurity (leading to premature nucleation or aggregation of nuclei), *etc.* Such sensitivity could be responsible for the variation among the different batches of syntheses.

Kinetic control of nanocrystal shapes.

The relative stability of the facets can be modulated by selecting facet specific ligands or surfactants. It has been widely postulated that the preferential formation of stable facets is a result of rapid growth at the unstable facets.^[14c, 26] Basically, the atoms newly added to an unstable facet can establish better bonding interactions than those added to a stable facet do. The former process encounters a lower barrier and is thus faster (Eq. 2). Flanked by the stable facets, the filling of the unstable facets reduces and eventually eliminates their area, leading to nanocrystals with only stable facets. As proposed in the literature, polyvinylpyrrolidone (PVP) passivates the Ag (100) facets leading to Ag nanocubes;^[17a, 27] citrate ions passivate the Ag (111) facets yielding Ag octahedra;^[28] high index facets like the Au (221) facets can be generated in

tris-octahedral nanocrystals by using hexadecyltrimethylammonium chloride (CTAC) as the ligand (Figure 1-6).^[29]

In the thermodynamic arguments (Section 1.2.2), the emergence of facets depends on their relative stability. In contrast, the kinetic arguments here emphasize on the relative rate of growth.^[30] These two trends may or may not coincide. Considering the complex role of ligands, there is likely no simple dependence between the two.

Inducing anisotropy in nanocrystals.

In the literature, many nanocrystals are highly anisotropic, with the shape of rod, wire, or plate.^[14c, 26, 31] As discussed above, such structures are likely thermodynamically unfavorable. The key to understanding the kinetic process is to identify the anisotropy factor that is responsible for the inequivalent growth of the equivalent facets.

While some lattices are intrinsically symmetric with multiple equivalent facets, the presence of defects can break their symmetry. The preferred growth at the defect sites (or unfavorable growth) thus induces anisotropy during the crystal growth (Figure 1-7. Specifically, if there is a stacking fault between the crystal planes ((111)^[32], (100)^[33], etc.), the growth along the fault plane at the edges would be more favorable than the deposition perpendicular to the plane, thus leading to plate-like nanocrystals (Figure 1-7a,b). On the other hand, if a nucleus has a 5-fold twinning defect, it can grow into a NW because the

Figure 1-7. Defect-induced anisotropic growth. (a,b) Schematics and TEM images of Ag nanoplates, where the growth is promoted by the stacking fault between the (100) planes. (c,d) The growth of Ag NWs as a result of the 5-fold twinning defect and the favored (100) facets. (e,f) The growth of ZnO "Christmas trees" driven by the screw-dislocation defect. Reprinted with permission from ref. [33c], [34] and [35a], respectively, copyright 2012 Wiley-VCH, 2005 American Chemical Society, and 2008 AAAS.

longitudinal growth is preferred whereas the induced strain among the twinning defects would restrict the lateral growth (Figure 1-7c,d).^[34] Furthermore, the presence of screw-dislocation on a facet would greatly favor

the material deposition thereon, making its growth many times faster than the other seemingly equivalent facets. Thus, the unidirectional growth leads to highly anisotropic NWs or nanotubes (Figure 1-7e,f).^[35]

The facet-specific binding of surface ligands can also induce anisotropic growth of nanocrystals.^[14a] It has been proposed that the effects are exerted by the selective passivation of facets, for example, the binding of hexadecyltrimethylammonium bromide (CTAB) on the Au(100) surface leads to the formation of nanorods.^[36] Similarly, the preferential adsorption of CO on the Pd (111) facets was proposed to confine the Pd deposition between the two stabilized planes, giving rise to ultrathin nanosheets.^[37] On the other hand, amphiphilic ligands are proposed to form cylindrical micelles^[38] that can template the formation of rod- or wire-like nanocrystals (see also Section 1.3.3).^[31b, 39] The cylindrical micelles break the symmetry among the equivalent facets, leading to anisotropic growth. In the literature, such ligands include CTAB,^[40] oleylamine,^[41] oleic acid,^[42] *etc.*

In the above two categories, defects and ligands are the anisotropy factors only after they come into existence. That is, the existing defects and ligand organization are already anisotropic before they promote the anisotropic crystal growth. To obtain a collection of uniform NPs, such factors must be consistently present in all individual NPs. Thus, for many systems there is a gap in explaining the inequivalent growth of the equivalent facets, that is, how

exactly the specific type of defects or specific ligand passivation are consistently generated in/on the initial symmetrical nuclei. A possible explanation is that those nanocrystals without the anisotropic factor are outcompeted and may either re-dissolve or remain in the sample as impurity nanocrystals.

In vapor-liquid-solid (VLS) or solution-liquid-solid (SLS) growth,^[31a, 43] the growth material is dissolved in the molten seed and the nucleation occurs specifically at the seed-nanocrystal interface. The molten seed confines the cross-sectional width of the emerging nanocrystal, making it the anisotropy factor. It thus promotes the unidirectional growth of the nanocrystals into NWs (as opposed to plates or spheres). Recently, our group reported a system with similar growth behavior but fundamentally different mechanism. Ultrathin Au NWs are directly grown from Au seeds anchored on a substrate in an aqueous solution at room temperature.^[44] The seeds are far from molten and the size of the emerging NWs is independent of the size of the seeds. The strong ligand in the system prevents Au deposition on the seed except the seed-substrate interface. Thus, selective growth at this interface breaks the symmetry of the nanocrystals, leading to unidirectional growth of NWs. The size of the NWs depends on how fast the new NW domain emerges and how fast the ligands passivate its surface.

1.2.4 Complex cases.

In the above cases, the mechanistic proposals can be clearly assigned as either thermodynamically or kinetically controlled scenarios. As shown in the examples below, sometimes there are mixed controls by thermodynamics and kinetics. Thus, the arguments can get entangled. Careful and case-specific analysis is often necessary to elucidate the overall process.

For nanocrystals with thermodynamically controlled facets, their formation should be independent of the growth pathways. It is akin to the flowing of water on a tilted floor. The local bumps can easily alter the pathway of flowing, but under the influence of the “invisible hands” of the thermodynamics, water is always collected at the lowest basin (the global minimum state). However, if several phenomena are considered together (*e.g.*, defects and facets in the following example), the energy landscape would become more complex, and it is possible for the system to arrive at the local minimum states (*i.e.*, dents in the floor).

Twinning defects can occur in the nuclei at the early stage of nanocrystal growth.^[45] In the theoretic framework of nucleation and growth (Figure 7a),^[14c, 18a] once the nuclei grow beyond the critical size, normally there is no pathway for them to be completely dissolved (except extensive Ostwald ripening). Thus, the internal defects will always remain. Even when the external facets of the nanocrystals reach equilibrium by dissolution-redeposition, the overall shape is

Figure 1-8. The effects of oxidative etching. a) Schematics illustrating the growth process, where the twinned NPs are selectively dissolved by oxidative etching. b) TEM images of the Ag NPs obtained at 10 min (left), 2 h (middle) and 44.1 h (right). Inset: photograph of the reaction mixture at 2 h; it is nearly colorless because most of the Ag NPs are dissolved. Reprinted with permission from ref. [48], copyright 2004 American Chemical Society.

permanently altered by the internal twinning defects.^[46] In other words, the specific pathway directs the system to a local minimum state. Modified Wulff construction can be applied to analyzing such twinned nanocrystals.^[47]

A contrary example is the selective growth of single-crystalline Ag NPs by introducing oxidative etching (Figure 1-8).^[48] In the presence of Cl^- and O_2 , the nuclei with twinning defects are more prone to etching than those with a single-domain do. The latter eventually emerges to give single-crystalline NPs.

In a sense, the oxidative etching makes the system more reversible, helping the individual NPs approach the global minimum state. Hence, the thermodynamics exerts its effect at the critical stage of forming the nuclei. At the later stage of growth, though having no twinning defects is still favorable, the absence of pathway would mean that the thermodynamics has no further control over the defects.

In nanocrystals with five-fold twinning defects (decahedra or pentagonal NWs), the presence of defects is unfavorable for the lattice energy, but its presence leads to the maximized formation of (111) facets, which is favorable for the surface energy.^[3, 49] It is conceivable that for very small NPs, the surface energy would dominate; and for large nanocrystals, the defect-induced strain becomes intolerable and so the lattice energy would dominate.^[50] However, it is inappropriate to use thermodynamic arguments for analyzing large nanocrystals, because even if the thermodynamics is favorable, it will be too late to induce or remove the defects. The thermodynamic control, if exist, must occur at a stage when the nanocrystals can still sample over the various forms, more specifically, when some of the nuclei can be re-dissolved before reaching the critical size (Figure 1-8a), or if small nanocrystals can somehow change their internal structure by “flowing” (Section 1.2.2).

It should be noted that the static states (*e.g.*, the shape of nanocrystals) are usually insufficient for distinguishing if thermodynamics or kinetics dominates.

For example, spherical NPs can form either because of the isotropic diffusion kinetics (Section 1.2.3), or because their facets are equally stable (Section 1.2.2 Figure 5); faceted grains can form either because of the stable facets (Section 1.2.2), or because of the rapid growth at the unstable facets (Section 1.2.3). Study of the trapped intermediates and in situ investigation of other observables are often necessary to help establish the process.^[51]

1.3 Growth of hybrid nanostructures.

Over the past few decades, single-component nanostructures have been extensively studied. Recently, the research focus of the field has started to shift towards multi-component or hybrid nanostructures, *i.e.*, structures with at least two domains with different compositions.^[52] For such nanostructures, the additional interface between the domains must be considered.

1.2.1 Thermodynamic analysis.

The conformations of double-domain particles can be analyzed as the “wetting” of one material over another. For thermodynamic analysis, only the final state is of importance, whereas how the domains are formed (by flowing or growth) is of less importance.

The simplest case is to consider the merged states of two immiscible liquid droplets (1 and 3, Figure 1-10). The interfacial energies of such droplets in a third immiscible solvent (2) have been previously investigated.^[53] Basically, there are three interfaces (with area of A_{12} , A_{23} , and A_{13}) that have different

Figure 1-9. Equilibrium configurations for two immiscible liquid droplets (1 and 3) in a third immiscible solvent (2). Reprinted with permission from ref. [53], copyright 2013 American Chemical Society.

interfacial energies (σ_{12} , σ_{23} , and σ_{13}). The two-component system seeks to minimize the overall interfacial energy ($A_{12}\sigma_{12} + A_{23}\sigma_{23} + A_{13}\sigma_{13}$). The situation is akin to a three-party tug-of-war, where the competition among the three terms is complex but the basic principle is straightforward. Whether one droplet can engulf the other can be predicted on the basis of the spreading coefficients (Figure 1-9),

$$S_i = \sigma_{jk} - (\sigma_{ij} + \sigma_{ik}) \quad (7)$$

Basically, if the droplet 1 “hates” (has poor interactions with) the solvent 2 but the droplet 3 “likes” both 1 and 2, then 3 will engulf 1. On the other hand, if the droplet 1 “hates” 3, then they will form separated domains maximizing their own internal interactions (in the form of spherical domains). Partial encapsulation will result for the intermediate cases.

This analysis can be extended to nanostructures because it is based on geometric considerations. A requirement is that the interfaces should have uniform properties (ligand density, charges, *etc.*), so that the interfacial energy is proportional to the interfacial area. Unlike bulk droplets, the interfacial energies of nanostructures cannot be readily measured. But one can often deduce their trends on the basis of the bonding interactions at the interface, as will be discussed in the following sections.

For two juxtaposed liquid droplets, they can flow into the equilibrium configuration where the total interfacial energy is minimized. When growing a polymer domain on the surface of a solid NP, the core NP cannot adopt different shapes. If the polymer can flow, it would be safe to assume that this particular domain has adopted a lowest energy configuration with respect to the solid domain. In contrast, bi-component NPs where both domains are solid can also reach the lowest energy configuration. They are normally synthesized by solution growth of an extra domain on top of an existing solid particle (*e.g.*, growth of silica on Au NPs). As discussed in Section 1.2.2 and Figure 6, the new domain can approach the lowest energy configuration if there is dissolution-redeposition equilibrium and/or surface diffusion of the growth material, or if the equilibrium structures are obtained in every step during the growth of the new domain.

Core-shell NPs.

Figure 1-10. a) Schematics illustrating the embedding of the ligand 2-mercaptobenzimidazole (MBIA) during the growth of the Ag domain on Au NPs, where the Au-Ag interfacial energy depends on the amount of the embedded ligands. b) TEM images of the different types of Au-Ag hybrid NPs, including (i) concentric, (ii) eccentric, (iii) acorn, and (iv) hetero-dimer structures. Polymer encapsulation is used to protect the NPs after their formation. Scale bars are 20 nm, Reprinted with permission from ref. [62], copyright 2012 American Chemical Society.

Encapsulating NPs in inorganic or polymer shells is a popular method for stabilizing NPs in a colloidal solution. The key issue is to establish strong bonding interactions between the core and the shell, so that the interfacial energy can be greatly reduced (Section 1.1.2).

If the two domains are of the same type (metal-metal, oxide-oxide, *etc.*), there are often strong bonding interactions between them, leading to a small interfacial energy. But it is normally difficult to predict the trend of the

interfacial energy. When two nanocrystal domains have epitaxial relationship, the trend can be easily predicted on the basis of their lattice mismatch. Basically, larger mismatch leads to larger strain and sometimes more defects, which reduce the quality and quantity of the interfacial interactions, resulting in a higher interfacial energy. The dependence of the growth modes on lattice mismatch has been extensively studied and reviewed.^[54] Encapsulation can be easily achieved if the shell has a small lattice mismatch with the core, for example, in Pd@Au,^[55] Pd@Pt,^[54b] and CdSe@CdS^[56] core-shell nanocrystals.

For dissimilar materials, surface modification is often needed to improve the interfacial interactions. For example, silica cannot readily form effective bonding with Au; it prefers homogeneous nucleation yielding pure silica NPs. This problem can be solved by introducing ligands that can bond to both materials, for example, one that contains a –SH group for bonding with Au and –COOH or –Si(OH)₃ group for interacting with silica.^[57] Similarly, hydrophobic polymers usually do not have strong interactions with NPs, but with a right choice of ligand, the encapsulation can be easily achieved.^[53a] Such a ligand must have a group that can form strong bonding with the core NP (–SH or –NH₂ for Au,^[58] –COOH for Fe₂O₃,^[59] *etc.*) and a hydrophobic tail for interacting with the polymer (via hydrophobic interactions, Section 1.1.1).^[60]

A special case of double-modification has also been shown to work, where a layer of hydrophobic ligands was used to coat the NPs, followed by a layer of

amphiphilic PVP. These treatments make the surface of several types of NPs amenable for the growth of polar ZnO.^[25] With strong interactions between the NP-ligand, ligand-PVP, and PVP-ZnO layers, the apparent NP-ZnO interfacial energy, when considered as a whole, is greatly reduced.

It should be noted that the discussion here focuses on the core-shell interface. The external facets or outline of the shell is governed by the thermodynamics and kinetics of the shell growth, as has been discussed in Section 1.2.

Janus NPs.

In the intermediate case between completely wetting (full encapsulation) and completely non-wetting, Janus (two-faced) NPs with two juxtaposed domains are often obtained.^[61] It is normally difficult to deduce from their shape whether they are thermodynamically or kinetically controlled (Section 1.3.2). Analysis for the complex cases will be presented in Section 1.3.4.

In one example from our laboratory, we reported the continuous tuning of the Ag domain on spherical Au cores, giving a series of hybrid structures that were assigned as the near-equilibrium configurations (Figure 1-10).^[62] The interfacial energy between any two nanocrystals (*e.g.*, Au and Ag) is usually not considered as tunable, because the nature of interaction and the lattice mismatch cannot be modified. In our system, however, ligands were embedded in between the Au-Ag layers and their amount can be tuned. A larger number of the ligand-induced defects lead to weaker interactions and thus, a higher interfacial

energy. Uniform hybrid NPs with either core-shell, eccentric, or Janus structures were obtained with high purity. For these configurations, we find it very difficult to propose distinctive kinetic pathways (Figure 1-12) with a clear underlying trend. In contrast, the continuous change in the “wetting” of the Ag domain on the Au NPs can be easily explained in the thermodynamically controlled scenario. It is possible that the equilibrium structures are obtained in every step during the growth of the new domain. Basically, the growth of Ag domain occurred in such a way that the Au-Ag interface was optimized by the “invisible hands” of the thermodynamics. Admittedly, more experiments are imperative to make a clearer distinction of the T-K problem.

1.3.2 Kinetic analysis.

In a thermodynamically controlled scenario, the configuration of the hybrid nanostructures (core-shell, eccentric, or Janus) is independent of the growth pathways. Nevertheless, it is still of importance to understand how the kinetically controlled scenarios are avoided (via kinetic analysis), that is, what is the course of action that allows the growth material to sample over the various forms. For kinetically controlled systems, it is of crucial importance to know the key process and the nature of the activation barrier.

Here, we focus on the choice of the hybrid configuration, not the general control of the growth process. The latter can determine, for example, the extent of the homogeneous nucleation and the amount of material in the shell, which

Figure 1-11. The effects of interfacial energy in the nucleation and growth of ZnO on Au NPs. (a-b) Schematics illustrating the competitive nucleation pathways when the Au–ZnO interfacial energy is either (a) high or (b) low. (c-d) Plots of ZnO solubility versus time, highlighting the different growth behavior when the Au–ZnO interfacial energy is (c) high or (d) low. Reprinted with permission from ref. [25], copyright 2013 American Chemical Society.

are the preconditions for the choice of structural configuration.

For polymer domains or shells, one can easily adjust their fluidity to design pathways. The glass transition temperature (T_g) of a polymer depends on its chemical composition and the degree of polymerization, cross-linking, and swelling. To render the polymer liquid-like, for example, one can raise the temperature over the T_g or greatly reduce the T_g by swelling. A uniform

polymer shell can be created when it is highly swollen by a good solvent, for example, N,N-dimethylformamide (DMF) for polystyrene-block-poly(acrylic acid) (PS-b-PAA).^[53a] Quick addition of water can then extract the DMF, causing deswelling of the PS domains. As a result, the PS became glassy with a low fluidity, trapping the core-shell nanostructures at kinetically stable states.^[63] Similarly, chemical cross-linking can also be used to this end.^[58a, 64]

In typical core-shell NPs, the shells are not formed instantaneously, but are sequentially built up by solution deposition. Thus, there is a fundamental similarity among different systems in how the free atoms/molecules join with each other and with the cores (*i.e.*, seeds). In contrast to Section 1.2.3, here the seeds have a different chemical composition from the growth material. Thus, the growth must be described by a modified nucleation and growth model as follows.

Taking the growth of ZnO domain on the ligand-modified Au NPs as an example (Figure 1-11),^[25] it is only possible when the interfacial energies are suitable. That is, the thermodynamics must allow it. More specifically, the heterogeneous nucleation of ZnO on the Au surface (path β) must be more favorable than the homogeneous nucleation, otherwise the latter process will dominate. On the other hand, the path β is always less favorable than the heterogeneous ZnO nucleation on the ZnO surface (path α), because there is essentially no interfacial energy between two domains of a same material. From

the kinetics perspective, these requirements constitute the “activation” barriers for the formation of a newly added domain, where the relative height of the barriers depends on the interfacial energy between the new domain and the underlying surface. Figure 1-11c presents the basic concept that, during the growth, the oversaturation of the growth material must reach certain levels before these pathways become allowed.

With these considerations, the buildup of ZnO in solution would reach such a level that ZnO would first form a small domain on the Au NP. Once this happens, the subsequent ZnO deposition would occur more favorably on the existing ZnO domain than on a fresh location of the same Au NP. This typically leads to a single ZnO domain per each Au NP. On the other hand, if the ZnO-Au interfacial energy can be greatly reduced using appropriate ligands/surfactants, the threshold for path β would then approach that for path α (Figure 1-11b). When this difference is small enough, random fluctuation of concentration or local buildup of ZnO would be sufficient to give new nucleation sites on the Au surface, leading to multiple nucleation sites and eventually a merged shell.^[65]

In this model, the rate of deposition is conceivably the key factor. At one extreme, if the rate is so slow that the choice between paths α and β is always true, then the most favorable configuration would be obtained in every step and the thermodynamics would dominate. At the other extreme, if the deposition is so rapid that paths α and β are equally probable, a meta-stable core-shell

Figure 1-12. a) Schematics and representative TEM images illustrating the formation of the merged Au nanoshell on the silica NPs, by first decorating them with seeds. b) Schematics and representative TEM images (viewing from different directions) illustrating the kinetically controlled overgrowth of Ag on the Pd cubes. Reprinted and modified with the permission from ref. [66d], [66e], and [68c], copyright 2007 American Chemical Society, 2004 Adenine Press, and 2012 American Chemical Society.

structure might be obtained even if the interfacial energy is unfavorable. A huge oversaturation may allow both pathways and/or make the re-dissolution process negligible, but it should also lead to extensive homogeneous nucleation.

The growth conditions can be designed to achieve rational pathways. For example, small Au NPs can be decorated on the surface of silica^[66] (or NaYF₄^[67]) NPs. Using them as the seeds, Au deposition would lead to a rough but complete metal shell (Figure 1-12a). Without these initial seeds, a very different result will be obtained (rarely any heterogeneous nucleation), because a newly formed Au domain would have a high silica-Au interfacial energy. The presence of the seeds permits numerous nucleation sites on each silica NP, eventually giving a merged shell that is thermodynamically unfavorable. Suppose that the Au shell can flow, it would contract into a single domain in order to reduce the Au-silica interface.

By modulating the rate of the chemical reaction producing the growth materials, the Xia group demonstrated the versatile synthetic control of bi-metallic NPs.^[68] As shown in Figure 14b, Ag was selectively grown on 1 to 6 faces of the Pd cubes, whereby an increasing number of the faces were coated with the increasing reaction rate. It was proposed that the faster reaction caused more faces to become the “active growth sites” (see Section 1.3.1), where the initially coated Ag layer facilitated the subsequent deposition, whereas the rest of the faces remained inactive due to the lattice mismatch between Pd and Ag.^[68c]

Figure 1-13. Schematics illustrating (a-b) the templated growth of nanocrystals and (c-d) the templated assembly of NPs. The template-NP interfaces are highlighted in red. The diffusion of the growth material or NP is not a limiting factor for (a) and (c); but the random nucleation or adsorption of NPs inside a template can easily cause problems.

1.3.3 Templated growth.

In essence, templated growth of nanocrystals can be viewed as the growth of the crystalline domain on the surface of the template, making it a bi-component system.^[69] Should the template-nanocrystal interfacial energy be high, the formation of the interface would be both kinetically and thermodynamically unfavorable, leading to homogeneous nucleation of free nanocrystals in the solution unaffected by the template. Thus, for all known cases of templated growth, the interfacial energy must be low enough to allow conformal coating

or at least multiple nucleation sites that can eventually lead to a merged domain. As discussed in Section 1.3.1 and Figure 11, there are three interfaces (template-solvent, template-nanocrystal, and nanocrystal-solvent). Therefore, the shape of the nanocrystals depends not only on the shape of the template but also on the interfacial energies.

Templated growth has been widely postulated for many anisotropic nanocrystals, particularly nanorods and NWs.^[31b, 69b, 70] Unfortunately, the detailed processes are difficult to characterize and has so far remained elusive. There is a battery of questions to be asked. First and foremost, the template-nanocrystal interface is of pivotal importance, but it is often poorly understood, for example, the exact interactions between the CTAB head group with the Au surface.^[71] With more insights, one may hopefully be able to tune the interface, expand the scope of the templates, and improve the synthetic control. Second, for the growth of nanocrystals inside templates (*e.g.*, cylindrical micelles), the diffusion of the growth materials is a major problem (Figure 1-13b).^[69b] Should nucleation occur near the opening of the micelle, the newly generated nanocrystal domain will block the supply of the growth material. Last, the complex interplay between the template and the emerging nanocrystal has not been fully established. For example, the assembly of the CTAB micelles may occur simultaneously as a result of the growth of the Au nanorods; and the dynamic motion of the CTAB molecules in the cylindrical

micelles may allow porosity in the micellar wall and thus, the diffusion of the growth materials across it.

We note that the colloidal growth of ultrathin NWs,^[31a, 41] often proposed to be the result of templated growth, is very different from the growth of most other nanocrystals. The scope of the applicable templates is extremely narrow. The width of the ultrathin NWs is unusually monodispersed and rarely tunable.^[41, 72] What stops their lateral growth when a certain width is reached? Growing long NWs from short NW has not been demonstrated. The NWs have not been shown to grow from a bulk crystal surface. More insights in the templated growth may help elucidate these mysteries and improve the synthetic design.

1.3.4 Complex T-K problems.

With multiple components and multiple processes in a system, it is conceivable that its energy landscape is significantly more complex than that of the single-component systems. In the deposition of shell materials on core NPs, for example, one need to consider the coordination and dissociation of ligands on the cores, the nucleation and growth of the shell materials, the core-shell configuration, and the ligand coordination to the shells. Given the different processes and their possible interplay, mixed T-K arguments are rather common in such systems.

A good example is the growth of conformal silica shells on Au nanorods.^[73]

Figure 1-14. Schematics and TEM images illustrating the formation of (a-c) amorphous and (d-f) faceted shells on anisotropic seeds. The growth can be judged on the extent of growth (a) at the different directions when the shell is amorphous, or (d) at the equivalent facets when the shell is faceted. (b,c) TEM images of the silica-coated Au nanorods, with thin and thick silica shells, respectively. (e,f) Side and vertical view of the Ag-coated Au nanorods, where the Ag shells are faceted. Reprinted with permission from ref. [73] and [76], copyright 2011 American Chemical Society, 2012 Royal Society of Chemistry.

When the shells are very thin, the overall shape resembles that of the initial Au nanorods. When the shells grow thick, however, the silica outline gradually approaches spherical shape, suggesting the diminishing structural influence of the internal core (Figure 1-14a-c). We can analyze the T-K problem by comparing the transverse growth (silica thickness of α) to the longitudinal

growth (silica thickness of β). At one extreme, when $\alpha = \beta$, the uniform silica shells would suggest indiscriminate deposition (likely because the deposition is irreversible). Although the overall shape does appear rounder, it is solely because the equal increase of length and width leads to a decreased aspect ratio. Another evaluating characteristic is that the lateral surface should remain parallel to the side surface of the Au nanorods (as in straight cylinders), not curved like that of ellipsoids. Such a growth can then be assigned as kinetically controlled. At the other extreme, when the silica outline is exactly a sphere ($\alpha > \beta$), the growth is obviously thermodynamically controlled (Section 1.2.2). Intermediate cases between the two extremes are likely, as the increase of shell thickness is gradual and the reversible dissolution during the silica deposition is usually not extensive.

This method of analysis may be applied to other core-shell systems. Ideally, the shell should be amorphous or without selective facets, for example, the coating of polymer shells on Ag nanocubes^[74] and Au nanorods,^[75] and the heteroepitaxial growth of Pd on Pt nanocubes (control experiments without the seeds gave non-specific NPs).^[54b] In a different case, the formation of cuboidal Ag shells on highly anisotropic Au nanorods^[76] requires unequal growth of the Ag (100) facets, suggesting underlying thermodynamic influence (Figure 1-14d-f).

Assigning solid shells as the thermodynamically controlled configuration

may seem difficult to comprehend. While the effects of the “invisible hands” of thermodynamics can be recognized, there is still a gap in appreciating the exact underlying pathways. A possible explanation is that the reversible deposition and dissolution processes and a subtle difference of the rates may help guide the overall shape towards a form with the lowest surface energy, even though each monomer species does not “know” the overall shape. In this aspect, these cases are similar to the control of spherical shape in Section 1.2.2 and the control of configuration of the hybrid Ag-Au NPs in Section 1.3.1 (Figure 1-10).

In the above analyses, the surface properties of the cores are considered as uniform, in particular the ligand layer. If there are multiple ligands forming segregated patches on the core, the situation would become more complex. The competition of hydrophobic and hydrophilic ligands has been employed to adjust the coating of PS-*b*-PAA on Au NPs, where the polymer only attached to the areas covered with the hydrophobic ligands.^[77] The ratio of polymer coverage per NP can be tuned by adjusting the ratio of the two ligands. The sequence of ligand introduction was shown to affect the final polymer-Au configuration, suggesting the pivotal role of the ligand kinetics. However, the details of ligand kinetics have yet to be established due to limits of the characterization methods.

1.4 Summary and outlook.

In the formation of nanostructures, the microscopic processes are random

and dynamic. Among the chaos, orderly nanostructures are known to emerge, including their regular shape, size uniformity, and extensive superstructures. Such ordering is the basis of nanoscience and nanotechnology; and understanding its origin is of pivotal importance. We must start from the fundamental principles in growing and assembling the basic building blocks, before sophisticated nanostructures can be made for advanced applications. To establish the mechanistic proposals on the basis of energy terms is a first step towards rational design and systems approach.

Using simple geometric analysis and logical deduction, it is indeed possible to compare the relative stability of nanostructures during their growth, assembly and shape evolution. The detailed processes therein were articulated and carefully analyzed, so that the mechanistic proposals were unambiguously presented. The fundamental differences between the thermodynamically and kinetically controlled scenarios can be a useful tool in mechanistic proposals.

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Chapter 2 Vertically Aligned Au Nanowire Array on Substrate: A Mechanism Study

2.1 Introduction

One-dimensional nanomaterials, typically nanowires, have attracted significant research interest over the years.^[1] Semiconductor nanowires are potential photonic materials owing to their unique optical and electronic properties, while metallic nanowires are considered as good candidates of interconnects in nanoelectronic devices according to their high electric conductivity.^[1a, 1b, 2] In addition, nanowires are often fabricated into hierarchical assemblies, such as aligned arrays, in order to make functional components in chemical sensors, piezoelectric generators and field-emission devices.^[3]

Many synthetic strategies have been developed to synthesize nanowires with various chemical compositions. For certain materials, nanowires could be fabricated by reorganization of 0D nanoparticles through oriented attachment.^[4] Template-assisted methods are more general in terms of materials. It makes use of porous materials or lithography techniques to construct hard template, which confine the growth of the materials to produce nanowires.^[1c, 5] Vapor-liquid-solid (VLS) growth, and subsequently solution-liquid-solid growth

as well as supercritical fluid-liquid-solid growth have been widely used to obtain semiconductor nanowires and nanowire arrays.^[1b, 6] These methods usually employ metal nanoparticles as catalysts. Epitaxial growth of the nanowire is achieved as the supersaturation accumulated at the catalyst-crystal interface. For noble metal nanowires, many of them are directly synthesized in solution by wet chemistry reductions.^[2b, 7] Organic small-molecule ligands or surfactants are usually used to induce anisotropy deposition of metal. In certain cases, the ligands selectively absorb on certain facets and subsequently lower the surface energy of those facets^[7a], while in other cases they are considered acting like soft template that restrict growth of the wires^[7c]. Although the wet chemistry synthesis has the advantage of the quantitative production, post-synthesis assembly of nanowire usually is not simple.

Recently our group developed an aqueous phase synthesis of substrate-bounded ultrathin gold nanowire with the presence of thiol aromatic ligand.^[8] The Au NWs were able to grow from Au seeds attached on the colloidal silica particles. Here we report a novel type of Au NW array formed on substrate (Figure 2-1) using similar method. With substrate-based synthesis, the effects of ligands were closely investigated without interference from the nanoparticle aggregation as in colloidal system. The growth mode of the Au NW was also revealed to be unique. It followed a novel active surface growth mode. During the Au NW growth, gold was deposited only at the root of

existing Au NW, which is the interface of Au and the surface modified substrate, and pushed the seed to the top of the whole wire. This active surface was maintained throughout the whole process, becoming the anisotropic factor that leads to the wire formation.

2.2 Materials and Methods

2.2.1 Materials

All solutions were prepared using deionized water (resistivity $> 18 \text{ M}\Omega \text{ cm}^{-1}$). 4-mercaptobenzoic acid (MBA, 90%, Sigma Aldrich), hydrogen tetrachloroaurate(III) (HAuCl_4 , 99.9%, Au 49% on metals basis, Alfa Aesar), trimethyl(methylcyclopentadienyl)platinum(IV) (98%, Sigma Aldrich), 3-aminopropyltriethoxysilane (APTES, Sigma Aldrich), sodium citrate tribasic dihydrate (99.0%, Sigma Aldrich), L-ascorbic acid (Sigma Aldrich) and ethanol (analytical grade) were used as received. Copper specimen grids (200 meshes) with formvar/carbon support film (referred to as TEM grids in the text) were purchased from Beijing XXBR Technology Co.

2.2.2 Methods

Characterization. Transmission electron microscopy (TEM) images were collected on a JEM-1400 (JEOL) operated at 100 ~ 120 kV. Field emission scanning electron microscopy (SEM) images were collected on a JEOL

JSM-6700F. High-resolution TEM (HRTEM) images were taken from JEOL 2100 F field emission transmission electron microscopy operated at 200 kV.

Preparation of TEM Samples. TEM grids were treated with oxygen plasma in a Harrick plasma cleaner/sterilizer for 45 s to improve the surface hydrophilicity. The hydrophilic face of the TEM grid was then placed in contact with the sample solution. A filter paper was used to wick off the excess solution on the TEM grid, which was then dried in air for 30 min.

Synthesis of Au NWs on wafer substrate. To prepare the vertical Au NWs on Si/SiO₂ wafer, a Si wafer (about 0.6 cm²) was pretreated with O₂ plasma for 10 min to improve its surface hydrophilicity. The wafer was then functionalized with amino group by reacting with APTES solution (5 mM) for 1 h.^[9] Subsequently, the wafer was soaked in excess citrate-stabilized Au seeds (3-5 nm) solution for 2 h to ensure the adsorption of Au seeds and rinsed with water twice to remove the excess Au seeds. The seeds-adsorbed wafer was then immersed in a reaction solution containing the ligand MBA (550 μM), HAuCl₄ (1.7 mM) and L-ascorbic acid (4.1 mM) for 15 min. Finally, the wafer was rinsed with ethanol and dried in air. The SEM image of the product was shown in Figure 1a. The generation of a thin conductive film on Si/SiO₂ wafer is similar to that of vertical Au NWs. All reaction conditions were unchanged except that the substrate was first functionalized with amino group by reacting with lower APTES solution (10 μM) for 0.5 h.

For preparing Au NWs with 15 nm AuNPs as seeds (Figure 2-1d, e), all reaction conditions were unchanged except that citrate-stabilized AuNPs with diameter of 15 nm were used as seeds ^[10] during the incubation with the amino-functionalized Si wafer.

To investigate the concentration-dependent growth of Au NWs, two sets of experiments were carried out: (a) Varying the ligand concentration. For the preparation of Au NWs or spherical NPs on Si/SiO₂, all reaction conditions were unchanged except that the concentration of MBA was lowered to 55 μ M, 28 μ M and 5.5 μ M, respectively; (b) Varying the concentration of HAuCl₄ and L-ascorbic acid (their relative ratio was kept unchanged). For the preparation of Au NWs or spherical NPs on wafer (Figure 2-4a-c), all reaction conditions were unchanged except that the concentration of HAuCl₄ and L-ascorbic acid was lowered to (a) 0.6 mM and 1.4 mM; (b) 1.7 mM and 4.1 mM and (c) 8.6 mM and 20.7 mM, respectively.

To identify the site of Au NW growth, a two-stage reaction was carried out. The substrate was first grown in a solution of 550 μ M MBA for 5 min, and then rapidly transferred without drying to a solution of 28 μ M MBA and grown for another 5 minutes. The concentrations of HAuCl₄ (1.7 mM) and L-ascorbic acid (4.1 mM) were constant in both stages. The resulting Au NWs had thin heads and thick tails (Figure 2-3e). Conversely, when the growth was carried out first with low concentration of 4-MBA (55 μ M) and then with high concentration

(550 μM), the resulting Au NWs had thick heads and thin tails (Figure 2-3g).

This phenomenon was also observed by changing the concentrations of HAuCl_4 and L-ascorbic acid with fixed ligand concentration as shown in Figure 2-4 d-e.

Grow Au NW on paper substrate. The process was similar to the growth on wafer substrate, except the pre-treatment of the papers. Filter paper can be directly soaked in the seed solutions for prolonged time. After rinsing, the paper can directly be used for NWs growth. Alternatively, similar APTES treatment as above can be used, but multiple rinses after that must be required. To prepare silica treated paper, the paper piece was soaked in the mixture solution of 2-propanol (2.5 mL), H_2O (0.5 mL), tetraethoxysilane (TEOS) (0.6 mL of 2 $\mu\text{L/mL}$ aqueous solution) and $\text{NH}_3\cdot\text{H}_2\text{O}$ (90 μL) for overnight, and rinsed to proceed from APTES treatment.

Preparation of Au NW cross-section. The cross-sections of Au NWs were prepared by using FEI NovatechTM Nanolab DualBeamTM 600i, combining ultra-high resolution field emission scanning electron microscopy (SEM) and precise focused ion beam (FIB) and deposition. Firstly, the Si wafer with Au NWs lying on its surface was properly loaded into the FIB chamber. Protective deposition of a Pt layer to the area of interest was applied by using electron beam induced deposition to protect the Au NW from ion beam damage during subsequent milling. The electron beam (5 kV and 0.4 nA) for protective deposition is not strong enough to fully dissociate the precursor

trimethyl(methylcyclopentadienyl)platinum(IV), so this protective layer is in amorphous state, containing a considerable amount of coordination compounds from the precursor. Then a thin lamellar for TEM characterization was cut out by FIB milling. Finally, low energy cleaning was carried out to remove the amorphous layer on the cut surface.

2.3 Results and discussion

Chips of Si wafer were used as substrates for growing Au NWs. Its top thermal oxide layer was functionalized with amino groups using 3-aminopropyltriethoxysilane (APTES) to facilitate the subsequent adsorption of citrate-stabilized Au seeds ($d = 3\text{-}5\text{ nm}$).^[9, 11] After adsorbing Au seeds (Figure 2-1b), the substrate was immersed in a water/ethanol ($v/v = 1:1$) solution containing ligand MBA ($550\text{ }\mu\text{M}$), HAuCl_4 (1.7 mM), and reducing agent L-ascorbic acid (4.1 mM). After 15 min, the substrate was retrieved, rinsed with water, and then dried. The gilding of the substrate surface confirmed Au deposition (Figure 2-1c). As revealed by scanning electron microscopy (SEM), the wafer surface was covered with a dense layer of vertically aligned Au NWs. At the edge of a scratch mark (Figure 2-1a), it can be clearly observed that the Au NWs were over $1\text{ }\mu\text{m}$ in length, with uniform width and height. Such length is remarkable considering the short 15 min growth. Though these Au NWs were roughly parallel to each other, they were not perfectly straight, unlike the typical single-crystalline NWs.^[12] Figure 2-1d shows the UV-vis

Figure 2-1. (a,b) SEM image of (a) vertically aligned Au NWs on a Si/SiO₂ substrate, (b) Au seeds ($d = 3\text{-}5\text{ nm}$) adsorbed on the substrate; (c) A photograph of the resulting Si wafer in sample a; (d) UV-vis spectra of the Au NWs before growth, after growth before drying and after drying, the sample was taken by grow Au NWs on glass pane. (e) SEM image of Au NWs synthesized using 15 nm AuNPs as seeds; (f) TEM image of the Au NWs scratched from sample d.

spectrum of the Au NWs grown on the glass substrate, which has exactly the

same morphology as the wafer-grown ones. Before the growth, although there were Au seeds, no significant absorption can be observed as there is only a thin layer of particles. The wet sample has a peak at around 500 nm, corresponding to the transverse Au surface plasma peak. After drying in air, the scattering effect of the Au layer led to a much higher base-line (red), and also the peak red-shifted and became broader compare to the wet sample. This might due to the aggregation (or say, sticking) of the near Au NWs during the drying process.

Despite the complex hierarchical structure, the synthesis was facile and reproducible. The method only involved the mixing of a few solutions in correct ratio and then treating the seed-adsorbed substrate at room temperature. It can be easily scaled up without significant change in the resulting nanostructures.

Unlike the typical solution methods for growing NWs,^[12-13] in our system the NWs cannot grow without the substrate: when free Au seeds (3-5 nm) were used without being adsorbed to the wafer substrate, the seeds simply grew larger with nearly-spherical shape, but NWs were not formed.^[14] Hence, it appeared that the adsorption of the seeds on the silica surface was essential. We must identify the anisotropic factor that is responsible for shifting the near-spherical growth mode to the NW growth. The presence of the substrate in itself was clearly insufficient in this role.

The width of the Au NWs was found to be independent of the size of the seeds. When large 15 nm AuNPs were used, they ended up on the top of the

Figure 2-2. (a,b) Schematics illustrating (a) the specific conditions used for the syntheses of Au NWs on Si/SiO₂ substrates, (b) because of the strong ligands, the Au deposition selectively occur at the Au-substrate interface.

resulting thin Au NWs (Figure 2-1d). Obviously, the formation of the Au NWs has caused the 15 nm seeds to be elevated from the substrate. Therefore, the initial Au deposition must have occurred at the Au-silica interface. After these Au NWs were scratched off and characterized by transmission electron microscopy (TEM), the diameter was measured as 6 nm (Figure 2-1e), the same as those prepared from smaller seeds. There was no obvious increase in the size

of the 15 nm seeds, which roughly retained their spherical shape. It was surprising that each Au NW was grown from an Au seed but its diameter was much smaller.^[15] Normally, in colloidal synthesis the seeds are the heterogeneous nucleation centers; the nanocrystals grown around them are usually larger.^[16] In solid-state growth such as via the VLS mechanism, the entire molten seed is the catalyst, making it hard to grow smaller structures.^[17]

2.3.1 Ligand dependence

We found that the diameter of Au NWs was dependent on the ligand concentration. When the MBA concentration was decreased from 550 to 55 and 28 μM , the resulting nanostructures became teeth-like with shorter Au NWs. However, their average diameter increased from 6 to 13, and then 17 nm (Figure 2-3a-c). Upon further decrease of the ligand concentration to 5.5 μM , Au deposition on the seeds formed an overcoating layer (*i.e.*, near-spherical growth mode) without any sign of NW formation (Figure 2-3d).

Study of the Au NWs by high-resolution TEM (HRTEM) showed that they were polycrystalline with frequent occurrence of random twinning defects (Figure 2-5a). Hence, the unidirectional growth of Au NWs was not consistent with screw-dislocation driven growth, which is an orderly process.^[18] Occasionally, single-crystalline segments can also be observed, as illustrated by the Fourier transform analysis of a local section (Figure 4b and inset). The Au NWs were cut by focus ion beam (FIB) to reveal their cross sections, which

were circular in all of the observed cases (Figure 2-5c).^[14] There was no preferred surface facet that we could identify. Thus, these Au NWs with nonspecific surface facets were distinctively different from those synthesized in the presence of oleylamine and CTAB, whose side surfaces were bound with specific facets.^[12, 19] In this aspect, the NW growth is different from the conventional growth models.

After the initial Au deposition at the seed-substrate interface, it is essential to understand if the subsequent growth occurred at the top seed-Au NW interface or the bottom Au NW-substrate interface. We can devise the reaction conditions to distinguish the temporal evolution of the Au NWs. To clearly observe the width control, 5 nm Au seeds were used. The substrate was first grown in 550 μM of MBA, and then rapidly transferred without drying to a solution of 28 μM of MBA. The resulting Au NWs had thin heads and thick tails (Figure 2-3e). Conversely, when the growth was carried out first with low and then with high ligand concentration, the resulting Au NWs had thick heads and thin tails (Figure 2-3g). Therefore, the Au growth must have occurred at the Au-substrate interface after the seed has been elevated from the substrate. This is clearly different from the VLS mechanism, where the materials deposition selectively occurs at the interface between the NWs and the molten seeds.^[17]

Figure 2-3e provides additional evidence that Au deposition did not occur on the ligand covered surface. It appeared that once the thin sections were formed,

Figure 2-3. (a-e) SEM and TEM (shown in the insets) images of the AuNWs grown on Si/SiO₂ substrates at different ligand concentrations: (a) 550 μ M, (b) 55 μ M, (c) 28 μ M, (d) 5.5 μ M of MBA, and (e) the AuNWs grown first in 550 μ M MBA solution for 5 min and then in 28 μ M MBA solution for 5 min; (f) Schematics illustrating the specific conditions used in the syntheses of the AuNWs as shown in e and g, yellow stars indicate the active site of growth; (g) SEM and TEM images of the AuNWs grown first in 55 μ M MBA solution and then in 550 μ M MBA solution. All experiments were carried out using 5 nm Au seeds, so that the width control can be clearly observed. All scale bars = 100 nm.

they cannot grow thicker even when the ligand concentration was reduced during the second growth stage. This was probably because the densely packed ligand molecules on their surface cannot easily dissociate. This result was consistent with the absence of seed growth in Figure 1d, e.

2.3.2 Mechanism discussion

In contrast to the absence of lateral growth, the continued longitudinal growth at the Au-substrate interface was obviously promoted by an anisotropic factor. Probably, it was because of insufficient ligand coverage at this interface (Figure 2-2b). Hence, the uniqueness of the “active” Au NW-substrate interface lies in its confined environment, which restricts ligand coordination and allows continued Au deposition. Because the ligand MBA binds strongly to Au,^[20] its instant absorption inhibits Au deposition at the perimeter of the active site, inducing anisotropic growth and forcing the nanocrystals to be pushed upward. This model also explains why the Au NWs can be randomly polycrystalline but have circular cross-section with uniform diameter. Without specific surface facets or internal lattice order, it is normally inconceivable how the polycrystalline domains with different lattice orientation would be able to coordinate with each other to form the orderly shape of wires.

The partial activation of the seed surface cannot easily occur: When free colloidal Au seeds were used, their surface facets were equivalently blocked by the ligand (*vide supra*).^[14] Even when the seeds were anchored on a substrate, if the ligand concentration was too low, the insufficient ligand density on the seeds caused them to grow near-isotropically into larger spheres (Figure 2-3d).

Following this theory, the control of Au NW width (Figure 2-3a-c) can be interpreted as the effectiveness in switching off the lateral growth at the active

site. In doing so, the rate at which the fresh Au NW is being generated from the active site must also be of importance. If ligand coordination cannot keep up with the new Au NW section being pushed upward, the Au NW must be able to grow thicker. The increase in the length of Au NW (dL) should be proportional to the amount of Au deposition and inversely proportional to the cross-section of the Au NWs. Hence:

$$dL = \frac{\mu dt M}{\rho} \cdot \frac{4}{\pi D^2} \quad (1)$$

where μ is the Au deposition rate, t is time, M and ρ are the molar mass and density of Au, and D is the diameter of the NW. On the other hand, the ligand coverage on the newly formed Au NW section must be able to keep up with the growth:

$$dL = \frac{\gamma dt}{k} \cdot \frac{1}{\pi D} \quad (2)$$

where γ is the ligand diffusion rate, k is the ligand density on NW surface.

Combining Eq. (1) and (2) gives:

$$D = \frac{4Mk}{\rho} \cdot \frac{\mu}{\gamma} = a \cdot \frac{\mu}{\gamma} \quad (3)$$

where a is a constant. Hence, D is proportional to μ and inversely proportional to γ . Because of the complex environment of the Au-silica interface, further analysis of μ is not possible. Nevertheless, the trends are clear: faster ligand diffusion towards the active site should lead to thinner Au NWs; whereas faster Au deposition should lead to thicker Au NWs. Hence, the polycrystalline nature of the domains is not an issue in this unique growth mode. Given the

Figure 2-4 SEM images of the AuNWs grown with 55 μM MBA as ligand from 5 nm Au seeds on wafer substrates by varying HAuCl_4 and L-ascorbic acid concentrations (constant ratio): (a) 0.6 mM and 1.4 mM, respectively; (b) 1.7 mM and 4.1 mM; and (c) 8.6 mM and 20.7 mM; (d) the AuNWs grown from 5 nm Au seeds, first in a solution of 1.7 mM HAuCl_4 and 4.1 mM L-ascorbic acid for 5 min and then transferred into a solution of 0.6 mM HAuCl_4 and 1.4 mM L-ascorbic acid for 5 min; (e) the AuNWs grown from 5 nm Au seeds, first in a solution of 0.6 mM HAuCl_4 and 1.4 mM L-ascorbic acid for 5 min and then transferred in a solution of 1.7 mM HAuCl_4 and 4.1 mM L-ascorbic acid for 5 min. All scale bars = 100 nm.

homogeneous solution environment, the diffusion rates around the seeds or Au NWs should be similar and thus, the highly uniform diameter among the individual NWs can be explained.

Keeping all other conditions unchanged, lower ligand concentration should give lower ligand diffusion rate. As shown in Figure 2-3a-d, Au NWs with larger diameter were obtained, consistent with Eq. 3. To further test our proposal, we modulated the rate of Au deposition by adjusting the concentration of HAuCl_4 and L-ascorbic acid: At the same ligand concentration, faster Au deposition led to thicker Au NW sections whereas slower deposition led to thinner ones (Figure 2-4).^[14] The morphology of the Au NWs changed from particles to wires when the concentration of the HAuCl_4 and L-ascorbic acid increased from 0.6 mM to 8.6 mM. Then trend of the changing Au reduction rate half-way was also fit the trends and inverse with the ligands concentration change case. The nanowires possessed a big head when changed from a concentrated growth solution to a diluted growth solution (Figure 2-4e), but have a big tail if it was transferred from a more diluted solution to a concentrated one (Figure 2-4f).

Our results also ruled out that the ligand 4-MBA might form templating cylindrical micelles: At a constant ligand concentration, the diameter of the presumed micelles should not change. Thus, by only changing the rate of Au deposition, the diameter of the resulting Au NWs should have remained constant. However, this speculation is inconsistent with the observations.^[14]

Therefore, these results support a dynamic competition between Au deposition and ligand binding. Changing the rate of one process can tilt the

Figure 2-5. HRTEM images of (a) the substrate end of a typical ultrathin AuNW, (b) a single-crystalline segment (Inset: Fourier transform pattern along the $[011]$ zone axis), (c) a typical cross-section of a AuNW, prepared by FIB.

balance of this competition, causing the width of the Au NWs to be adjusted. With this understanding, it is obvious that under our unique growth mode the Au NWs can grow thinner than the original seeds. It is also easy to recognize that the initial contact area of the seeds with the substrate is not of importance, because the width of Au NWs can be quickly adjusted during their growth. This

is supported by the fact that the thick Au NW sections can be simply grown from the thin ones and vice versa (Figure 2-3e, g).

Under ambient conditions, we can now achieve seeded growth on a substrate, mimicking the popular VLS growth mode but with a drastically different mechanism: In the VLS growth, the growth material is first dissolved in the molten seed and subsequently nucleates onto the wire at the seed-wire interface.^[17] The fact that the growth materials are supplied to the molten seed means that the newly grown segment is always next to the seed. In our method, the growth material is supplied to the active Au-substrate interface and hence, the newly grown segment is always next to the substrate (Figure 2-3). Under the VLS mechanism, the size of the wire is highly dependent on the size of the seed and the surface ligands (if any) should have no effect on the nucleation event inside the molten droplet. Our new growth mechanism does not require molten seeds and thus, allows ambient growth conditions. Moreover, the size of the growing wire is independent of the size of the seed. Instead, the size of the wire depends on how fast the ligands shut off the lateral growth and how fast Au is being supplied to the growth site (Eq. 3).

2.4 Extension to other substrates

The facile synthesis of substrate-anchored Au NWs can be easily extended to other oxide substrate such as glass, generating a uniform conductive film.^[14] By simple immersion in a solution, this method can be easily applied to

Figure 2-6. SEM images of (a) Au NWs grown from the filter paper substrate; b) Parchment paper with both sides grown with silica; c) A4 paper and d) plastics with both sides grown with silica. All scale bar = 100 nm.

substrates with complex surface morphology such as a trumpet shell, making its surface conductive.^[14] This feat is difficult to achieve by traditional methods such as spin-coating or doctor-blading.

Besides the wafer substrates, this Au NWs growth was also applicable for other substrates, such as papers. The difficulty of applying to the soft substrate like papers or other plastics would rise from the adsorption of the Au NPs seeds.

APTES has been widely used for the modification of oxide substrates or the silicon substrate, but does not work well with papers. A key problem is the degree of hydrolysis of the APTES is hard to estimate, given the low activity of the $-OH$ of the cellulose. Moreover, the paper we used, typically filter papers are highly porous and the wash of the APTES can be very difficult. Residual APTES caused the aggregation of Au NPs seeds in the seed adsorption step, which is unfavorable for growth of Au NWs arrays. If no APTES was used, although the paper itself had the ability to physically absorb the Au NPs, it lacks of effective interaction to hold the particles or wires; therefore, straight Au NWs could not be obtained (Figure 2-6a). Also, for commercialized papers like A4 printing paper, there might be unknown ingredient used to treat the paper. So wires were also difficult to grow; only the wire-like grasses were observed (Figure 2-6c).

To overcome such Au seeds attachment problem, a layer of silica can be first grown onto the surface followed by the APTES treatment, prior to the seed attachment. This method worked with parchment papers (Figure 2-6b) and certain types of plastics materials (transparency film) (Figure 2-6d). Generally speaking, the surface chemistry of these soft materials varies from one to another and the surface compatibility must be solved case by case.

2.5 Conclusion

We discovered a novel type of nanowire growth and proposed a new mechanism. The anisotropic growth of the nanocrystals was a consequence of both the strong surface ligands and the ligand-deficient interface between Au and substrate. To the best of our knowledge, this anisotropic factor has not been previously known in the literature. The unique ability to create nanowire-substrate hierarchical structure by solution methods opens windows for new synthetic strategies and mechanistic insights. The surface-adsorbed ultrathin nanowires are of importance for catalysis, conductive film, and nanoelectronic device.

2.6 Bibliography

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Chapter 3 Exploring the Parameters in the Growth of Substrate-Bound Ultrathin Au Nanowires

3.1 Introduction

Synthetic control of nanomaterials is the main thrust in nanoscience and nanotechnology. The ability to control their shape, size, and location is of critical importance for their applications in electronic,^[1] optical,^[2] and magnetic devices.^[3] In particular, anchoring metal nanowires (NWs) on substrates can greatly improve the amount of catalyst loading per unit area of substrate, leading to excellent catalytic performance in fixed-bed catalysis.^[4] Moreover, it provides a means to effectively collect the charges at the nanoscale junctions or surfaces.^[5] These potentials are being actively explored for applications.

Previously, we reported the growth of vertically-aligned Au NWs from seeds anchored on a substrate, directly giving interconnected hybrids.^[6] This approach cannot be achieved by adapting the traditional growth of colloidal NWs, because one cannot align the facets, defects, or surfactants of the anchored seeds, which determines the direction of NW growth. Indeed, growing ultrathin NWs from prefabricated colloidal seeds have not been demonstrated in the first place, despite it provides an obvious route for synthesizing NW-containing hybrids.

In our method, a strong ligand, 4-mercaptobenzoic acid (4-MBA), was used to passivate any exposed Au surface in the solution, inhibiting further Au deposition thereon. Thus, the Au growth occurs selectively at the Au-substrate interface (active surface) where the ligands cannot reach. As such, the NW diameter is independent on the size of the seed, but depends on the dynamic competition between the rate of Au deposition at the active surface and the rate of ligand adsorption on its perimeter. The ligand-dependent growth at room temperature in aqueous solution makes this growth mode obviously different from the vapor-liquid-solid (VLS) mechanism, where the dissolution of growth materials in the molten seed is essential.

In this work, we systematically vary the growth parameters, especially the substrates and ligands, so as to investigate the window of applicability of this growth mode and the consistency with the previously proposed mechanism. The results show that a strong ligand, *i.e.* the thiol-ended ligands, must be used to induce the growth of the long NWs. Weak ligands such as the amine-based one only gives spherical growth. More specifically, among the strong ligands, only the aromatic ligands work but not aliphatic ones. The substrate window is broader, and almost all types of oxide substrate regardless of the surface morphology can be used.

3.2 Materials and Methods

3.2.1 Materials

Materials and Characterization Methods. All solutions were prepared using deionized water (resistivity $> 18 \text{ M}\cdot\text{cm}^{-1}$). 4-mercaptobenzoic acid (MBA, 90%), 2-naphthalenethiol (99%), 1-naphthalenethiol (99%), biphenyl-4-thiol (BP4T) (97%), 2-phenylethanethiol (2-PET) (98%), butanethiol (BuSH) (99%), 1-decanthiol (DoSH) (99%), 1-dodecanethiol (DodSH) (99%), 1-octadecanethiol (OctdSH) (99%), 3-mercaptopropanoic acid (3-MPA)(99%), 16-mercaptohexadecanoic acid (16-MHDA) (99%), 3-aminopropyltriethoxysilane (APTES, 98%), sodium citrate tribasic dihydrate (99.0%), L-ascorbic acid (99%) were purchased from Sigma Aldrich and used as received. Hydrogen tetrachloroaurate(III) (HAuCl_4 , 99.9%, Au 49% on metals basis, Alfa Aesar), 4-ethylthiophenol (4-ETP)(97% Alfa Aesar), sodium borohydride, and ethanol (analytical grade) were used as received. Copper specimen grids (200 mesh) with formvar/carbon support film (referred to as TEM grids in the text) were purchased from Beijing XXBR Technology Co.

Field emission scanning electron microscopy (SEM) images were collected on a JEOL JSM-6700F.

Transmission electron microscopy (TEM) images were collected on a JEM-1400 (JEOL) operated at 100 kV.

SERS spectra were collected directly from the substrate on a PeakSeeker Pro

spectrometer (Raman Systems Inc.) using a red laser ($\lambda = 785$ nm) at 290 mW.

3.2.2 Methods

Synthesis of Au seeds 5 nm AuNP seeds are synthesized based on the reported method,^[7] basically, 1.47 mg of sodium citrate and 1.97 mg of $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ were dissolved in 20 mL water. Then, 0.6 mL of ice-cold NaBH_4 solution (0.1 M) was added with vigorous stirring. The solution turned from orange-yellow to brownish-red, indicating the formation of AuNP. The seed solution could be used directly after 2 hours.

60 nm Au NPs are synthesized based on the reported method.^[8] Citrate-stabilized AuNP with a diameter of 40 nm was first synthesized by reducing boiling 100 mL $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ (0.1 mg/ml) with 0.75 mL sodium citrate solution (1% wt), followed by 11 cycles of addition of extra $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$, sodium citrate and NaOH solution as well as boiling water.

Synthesis of Au NWs on wafer substrate. The method of the synthesizing Au NWs was followed the one reported.^[6] A Silicon wafer (about 1 cm^2) was pretreated with O_2 plasma for 10 min to form a thermal layer. The wafer was functionalized with amino group by reacting with APTES solution (5 mM) for 1 h. Subsequently, the wafer was soaked in excess citrate-stabilized Au seeds (3-5 nm) solution for 2 h to ensure the adsorption of Au seeds and rinsed with water twice to remove the excess Au seeds. The seeds-adsorbed wafer was then immersed in a reaction solution containing the ligand 4-MBA (550 μM),

HAuCl₄ (1.7 mM) and L-ascorbic acid (4.1 mM) for 15 min. Finally, the wafer was rinsed with ethanol and dried in air. The SEM image of the product was shown in Figure 1a.

Synthesis of Au NWs on other bulk substrate. All reaction conditions were kept the same except the change of respective substrate (glass, *etc.*)

Synthesis of Au NWs on colloidal SiO₂ substrate. AuNP@silica was used as the colloidal substrate and synthesized using the Stöber method with modifications. As-synthesized 35 nm citrate-stabilized gold nanoparticles (AuNPs) was first synthesized according to established literature procedure.^[9] The AuNPs solution (3 mL) was then concentrated to a total of 6 µL by centrifugation at 4000 g for 8 min. After the removal of supernatant, the residual NPs were re-dispersed into 500 µL of water. The resulting solution was transferred to 2.5 mL 2-propanol dropwise under vigorous stirring, after which 20 µL 11-MUA (2 mM in ethanol) was added. After 5 min, 600 µL TEOS (8.96 mM in water) was added, followed by 90 µL of ammonia (25-28% w/w). Concentric core-shell AuNP@silica were obtained after 12 h of reaction at room temperature. To isolate the AuNP@silica, the reaction mixture was centrifuged at 5200 g for 9 min and the supernatant removed. The residual NPs were re-dispersed in ethanol.

The AuNP@silica as synthesized were functionalized with amino group by APTES. AuNP@silica solution (1.5 mL) was concentrated to ~6 µL by

centrifugation at 5200 *g* for 9 min. After the removal of the supernatant, the isolated NPs were added into a solution containing 500 μ L H₂O, 500 μ L ethanol and APTES (1 mM). Amino-functionalized AuNP@Silica were obtained after 1 h reaction with vigorous stirring. The NPs were purified twice by centrifugation in ethanol at 5200 *g* for 9 min. Consequently, the concentrated NPs were added into the Au seeds solution (500 μ L) and incubated for 2 h to ensure that a single layer of Au seeds has been fully attached onto the Au@silica NPs. To isolate the (AuNP@silica)@seeds, the mixture was centrifuged at 5200 *g* for 8 min and the isolated NPs were re-dispersed in 500 μ L ethanol.

(AuNP@silica)@Au NWs can be obtained in the same reaction system using 4-MPAA, 4-MBA, 4-MPN or 3-MBA as ligands. The as-synthesized (AuNP@silica)@seeds solution (500 μ L) was concentrated to $\sim$ 6 μ L by centrifugation at 5200 *g* for 8 min. The concentrated solution was then added into a reaction solution containing the acting ligand (0.7 mM), PVP (21 mM), HAuCl₄ (1.2 mM) and L-ascorbic acid (3.6 mM) under vigorous stirring. The (AuNP@silica)@Au NWs were obtained after 15 min of reaction. The resulting nanocomposites were then purified by centrifugation at 4000 *g* for 4 min. The concentrated NPs were collected by removing the supernatant and re-dispersing in water.

Preparation of the Au NWs (nanostructures) with ligands other than 4-MBA,

all reaction conditions were kept the same except the ligands was changed to the one investigated. When mixed ligands were used, the seed concentration for incubation was reduced to 1/100 but the total concentration of the ligands was still kept at 0.55 mM

For preparation of the superhydrophobic surface, the reaction was allowed to proceed for prolonged time.

3.3 Results and Discussion

In a typical growth, a piece of Si wafer was treated with O₂ plasma to render its surface hydrophilic and to present surface Si–OH groups for the chemical adsorption of 3-aminopropyl-triethoxysilane (APTES). The APTES treatment provided surface –NH₂ groups which allowed the subsequent adsorption of Au seeds, usually the citrate-stabilized Au nanoparticles of 3-5 nm in diameter. Then, the seed-decorated substrate was immersed in the reactant solution containing the ligand 4-MBA (0.55 mM), the Au precursor HAuCl₄ (1.7 mM), and the reducing agent L-ascorbic acid (4.1 mM). After 15 min, the substrate was retrieved, rinsed, and dried in air. Typically, a dense forest of ultrathin Au nanowires ($d = 6$ nm, $l = 1$ μ m) would form on the substrate surface. In the following, the reaction parameters are systematically varied to study the generality of the Active Surface Growth mode.

Figure 3-1. SEM images of a) Au nanowires grown in the EtOH: H₂O = 9:1 (v/v); b) Au nanowires grown in the EtOH: H₂O = 1:3 (v/v); c) Au nanowires grown in the EtOH: H₂O = 1:9 (v/v); d) photograph of the growth solution in (a) and e), in (c), 2 min after mixing all the components,

3.3.1 Solvent

The initial solvent used in our method was the mixture of ethanol and water (v/v = 1:1).^[6] Slight change of the solvent ratio (16:13) did not lead to obvious changes in nanowire arrays. When the water content was increased (1:3), the rate of reduction was greatly accelerated, as manifested by the rapid color change of the solution (Figure 3-1e). Control experiments showed that the color change was the result of H_{AuCl}₄ reduction by ascorbic acid (independent of the

substrate) and the formation of colloidal Au particles. In general, faster HAuCl_4 reduction leads to oversupply of Au atoms, promoting homogeneous nucleation and causing the solution to turn black. The growth on the resulting Au seeds consumes the Au atoms, competing with the nanowire growth on the substrate. This leads to short teeth-like nanorods (ethanol/water = 1:3, Figure 3-1b) or even no nanowire growth (ethanol/water = 1:9, Figure 3-1c). The variation of diameter in the teeth-like nanorods reflects the initial oversupply of Au atoms (thick section) and the dramatic decrease of Au supply as it was quickly consumed by the competitive growth in the solution.^[6]

On the other hand, when the water content was decreased (ethanol/water = 4:1 and 9:1), the rate of Au reduction slowed but Au nanowires were still able to form with longer time (Figure 3-1a). The nanowires were about 5 nm in diameter, similar to those obtained at 1:1 ethanol/water mixture, but they were only 0.2 μm in length at 15 min of growth, presumably due to the slower rates of Au reduction and nanowire growth.

When ethanol was replaced with other water-miscible organic solvents, Au nanowires were able to grow in most cases (Table 3-1 and Figure 3-2, 3-3). Given the different polarity of the solvents, the rate of HAuCl_4 reduction varies, leading to different window of solvent ratios. Typically, the solution color should be controlled such that it turned from yellow to colorless, but not to black. Too much water leads to fast reaction and oversupply of Au atoms,

Figure 3-2. SEM images of the AuNWs grown with a) Methanol:H₂O = 16:13 (v/v); b) Isopropanol:H₂O = 16:13 (v/v); c) dioxane:H₂O = 16:13 (v/v) and d) DMF:H₂O = 16:13

Figure 3-3 SEM images of the AuNWs grown with a) THF: H₂O = 2: 9 (v/v); b) THF: H₂O =1: 9 (v/v); c) DMSO:H₂O = 1:3 (v/v); d) acetone:H₂O = 9:1 (v/v); e) acetone:H₂O = 16:13 (v/v); f) acetone:H₂O = 1:9 (v/v); g) acetonitrile:H₂O = 1:9 (v/v); h) acetonitrile:H₂O = 16:13 (v/v); i) acetonitrile:H₂O = 1:9 (v/v).

whereas too little water slows the Au reduction to a halt.

In short, while the initial intention of the organic solvent was to dissolve the 4-MBA ligand, another important function was revealed, namely to reduce the rate of Au reduction and thus avoid homogeneous nucleation. The ready tuning of solvent ratio provides a facile means to control the rate of nanowire growth. The broad scope of the solvent is consistent with its passive role in our mechanism.

Table 3-1 Au nanowire growth in different solvents

Solvent:H ₂ O	Ratio & Result					
	9:1	4:1	16:13	1:3	2:9	1:9
MeOH			√			
EtOH	√ ^a	√	√	teeth-like ^b	-	× ^d
Isopropanol			√			
Dioxane			√			
DMF			√	√		
THF			× ^c		√	× ^d
Acetone	× ^c		√			× ^d
Acetonitrile	√ ^a		√			× ^d
DMSO	× ^c		× ^c	√		× ^d
Ethylene Glycol			√			

a: slow reaction, Figure 1a and 1d left

b: as shown in Figure 1b

c: no reaction takes place, solution remains yellow for a prolonged time

d: reaction too fast, as shown in Figure 3-1d and 1e

Figure 3-4 SEM images of the AuNWs grown with a) hydroquinone (41 mM, aq); b) hydroquinone (4.1 mM, aq); c) H_2O_2 (1.08M); d) H_2O_2 (4.32M) and e) H_2O_2 (9.05M, EtOH: H_2O =1:9 (v/v))

3.3.2 Reducing agent

The reducing agent can also be changed. As shown in Table 3-2 and Figure 3-4, ascorbic acid, hydroquinone, and H_2O_2 can be used for the Active Surface Growth. The fact that different reducing agents can be used indicates that they

only participate in the chemical reduction of HAuCl_4 , not directly in the nanowire growth.

Initial attempts using H_2O_2 failed. By greatly increasing its concentration (9 M) and the water content (ethanol/water = 1:9), the rate of Au reduction became fast enough to allow the growth of Au nanowires.

When strong reducing agents, such as NaBH_4 , N_2H_4 , and NH_2OH , were used, the solution quickly turned black, suggesting rapid Au reduction and homogeneous nucleation. Attempts to slow the reduction by reducing reductant concentration and changing solvent ratios were unsuccessful. The reaction was still too fast even in nearly neat organic solvents.

In general, the reducing agent should have a low enough reduction potential to reduce Au^{3+} to Au^0 , but the reaction rate should not be too fast, in order to prevent immediate homogenous nucleation.

Table 3-2 Au nanowire growth with different reducing agent

Reducing agent	Result
L-ascorbic acid (4.1 mM),	√
Hydroquinone (4.1 mM)	√
Hydroquinone (41 mM)	√
H_2O_2 (1.08 M)	×
H_2O_2 (4.32 M)	teeth-like
H_2O_2 (9.05 M, EtOH:H ₂ O=1:9)	√
NaBH_4 (0.41 mM)	×, fast reduction
N_2H_4 (0.016 mM)	×, fast reduction
NH_2OH (1 μL/mL)	×, fast reduction

Figure 3-5. a) SEM images of the Au nanowires grown from glass (SiO_2) substrates. b) TEM images of the Au nanowires scratched from a). c) Photograph of 1: glass pane; 2: sapphire; 3: LaAlO_3 ; 4: ITO; 5: FTO and 6: tausonite substrates before and after nanowires growth (see SEM images in Figure 3-6)

3.3.3 Substrate

In the conventional VLS mechanism, growing vertical nanowires typically requires epitaxial contact between the nanowire and the underlying substrate. As such, successful growth depends critically on the nature of the substrate, leading to a lack of generality. In contrast, our growth mechanism is independent of the substrate. The origin of selective growth was the lack of

Figure 3-6. SEM images of the AuNWs grown from a) Al_2O_3 ; b) SrTiO_3 ; c) LaAlO_3 ; d) glass (SiO_2), e) ITO and f) FTO substrates.

ligand at the Au-substrate interface, meaning that the substrate itself only plays a passive role.

To test this expectation, we studied substrates with different chemical composition, including common glass panes (SiO_2), indium tin oxide panes (ITO), fluorine doped tin oxide panes (FTO), sapphire chips ($\alpha\text{-Al}_2\text{O}_3$),

tausonite chips (SrTiO_3), and lanthanum aluminate chips (LaAlO_3). These substrates were rinsed with water and dried. The subsequent plasma and APTES treatment, seed adsorption, and the growth process were the same as with the Si wafer substrate. SEM characterization showed that the resulting Au nanowires were formed in all cases, with no obvious difference from those grown on Si/SiO₂ wafer (Table 3-3, Figure 3-5, 3-6).^[10] Obviously, the Au nanowire growth was independent of the chemical composition or the lattice constant of the underlying substrate.

Considering the small interface between the 6 nm nanowire and the substrate, the area or curvature of the substrate should not be a major factor. Colloidal nanoparticles were thus tested as the substrate, which had much larger local curvature than a typical bulk substrate with a rough surface. Silica-coated Au nanoparticles (Au@silica , $d_{\text{Au}} = 35 \text{ nm}$; $d_{\text{overall}} = 90 \text{ nm}$)^{[11],[12]} were used. They were functionalized with APTES and decorated with Au seeds, with about 120-160 seed particles on each Au@silica . A similar ligand, 4-mercapto-phenylacetic acid (4-MPAA, 0.7 mM) was used to passivate the Au surface. The reduction of HAuCl_4 by ascorbic acid was carried out in the presence of surfactant polyvinylpyrrolidone (PVP, 21 mM) to prevent aggregation, resulting composite with ultrathin Au nanowires ($d = 6 \text{ nm}$) decorated on the surface of the colloidal nanoparticles. Despite the different substrate, the resulting nanowires were similar to those grown on bulk

substrates. The solution turned from the red color of Au@silica to the grey color of colloidal Au nanowires. The synthesis can be easily scaled up to 30 mL without significant change in the resulting nanostructures.

With MPAA as the ligand, long and flexible Au nanowires were formed. In contrast, when 4-MBA was used, the resulting nanowires tend to aggregate like dirty hair to form large bundles, leading to octopus-like hierarchical nanocomposites. Considering that PVP is not needed for the growth on bulk substrates, we believe that it only acted as a surfactant to prevent the aggregation of the nanocomposites in this colloidal synthesis. In its absence, ultrathin Au nanowires can still form, but most of the Au nanowires and Au@silica were lost due to severe aggregation.^[10]

Table 3-3 Result of growing Au NWs on different substrates

Substrate	Result
Si/SiO ₂ wafer	
No APTES	√
1 μL/mL APTES	√
0.01 μL/mL APTES	√
1 μL/mL CNPTES	√
1 μL/mL MPTES	low coverage
Silica (colloidal)	√
glass	√
Al ₂ O ₃	√
SrTiO ₃	√
LaAlO ₃	√
ITO	√
FTO	√

3.3.4 Seed adsorption.

The adsorption of seeds on a substrate is essential for the Active Surface Growth. In the absence of substrate, colloidal Au nanoparticles under the same growth conditions led to direct overcoating on the seeds, giving spiky nanoparticles with increased size but no nanowires (Figure 3-7).^[10] This result is well consistent with the mechanism, considering the unhindered binding of ligands and the lack of active surface.

In the previous discussion, the linker molecule between the Au seeds and the substrate was APTES. The molecule is selected because the $-NH_2$ group can coordinate to Au whereas the $-SiOH$ groups after hydrolysis can bond to any oxide surface via condensation reactions. The surface density of APTES on the Si/SiO₂ substrate was reduced by lowering the APTES concentration during the surface treatment step. No obvious change was observed in the nanowire growth (Table 3-3).

When APTES was replaced with other linkers such as 3-mercaptopropyltriethoxysilane (MPTES) and 3-cyanopropyl-triethoxysilane (CNPTES), the seeds were not uniformly adsorbed on the substrate, likely because of their different rate of hydrolysis and efficiency in adsorption. But Au nanowires were still obtained in both cases (Table 3-3 and Figure 3-7b,c).^[10] Thus, the generality of the linker molecules suggests that they do not participate directly in the nanowire growth. Their role is to anchor the seed nanoparticles

Figure 3-7. SEM images of the AuNWs grown from substrates which treated with a) 0.01 $\mu\text{L/mL}$ APTES (aq) solution; b) CNPTES in $\text{H}_2\text{O}:\text{Methanol} = 1:3$ (v/v) solution; c) MPTES in $\text{H}_2\text{O}:\text{Methanol} = 1:3$ (v/v) solution and d) Without any treatment.

so as to create the active surface.

To further investigate the anchoring effects, a drop of seed solution was directly dried on a Si/SiO_2 substrate. Thus, there was no linker between the seed and substrate, but the steric effects of the substrate should be the same. With direct drying, the seeds easily aggregated and cannot be distributed uniformly on the substrate, but Au nanowires were still able to form at the places with scattered seed adsorption (Figure 3-7d).

Figure 3-8. SEM images of the Au particles grown with 0.55 mM a) 4-aminobenzoic acid and b) oleylamine as ligand, c) 4-mercaptophenylboronic acid; d) 4-nitrobenzenethiol.

3.3.5 Ligand

The primary role of the ligand 4-MBA is to passivate the exposed Au surface so that the growth can occur at the active surface. Too little ligands led to nonselective deposition and overcoating of the Au seeds, whereas too much ligand led to precipitation on the substrate preventing Au deposition. Within the window, the ligand concentration directly affected the nanowire diameter,

which was a result of the competition between the rate of Au deposition and the rate of ligand coordination on the freshly generated Au surface.^[6]

The ligands were found to play an additional role of preventing homogeneous nucleation. We compared two similar molecules, 4-MBA and 4-aminobenzoic acid (4-ABA), with $-SH$ and $-NH_2$ as the end group, respectively. Given their similar molecular structure, the packing within the ligand layer should be quite similar. In experiments with the same reactants but without the substrate and seeds, 4-ABA gave a black solution containing large Au particles in 30 s, whereas the reaction with 4-MBA remained colorless for at least 2 h. Thus, it is understandable that nanowires cannot be grown on a substrate using 4-ABA as the ligand (Figure 3-8a), because the rapid nucleation of Au in the solution outcompeted the growth on the substrate.

The exact reasons how 4-MBA can inhibit the homogeneous nucleation is unclear; we speculate that the stronger ligand may stabilize the Au^0 atoms preventing their nucleation. Given to the strong affinity between the Au and the $-SH$, there is a great possibility that the Au (Au^{III} , Au^I and Au^0) would form some types of complex in this case. From simple deduction of the thermodynamic energy landscape, the redox potential of the Au^{III} and Au^I in the complex would be less negative compare to the free ions, as the complex could stabilize the structure. More energy would be required to bring them into transition state. This stabilization probably counts for the slow reduction rate

Figure 3-9. SEM images of the Au nanowires formed with a) 4-MBA; b) 4-MPAA; c) 3-MBA and d) 2-MBA as ligand. e-f) TEM images of the Au nanowires or nanostructures synthesized on the colloidal substrate with 3-MBA and 2-MBA. g) Schematic illustration of the packing status of the 3 ligands above which have the same moieties but at different substitution positions.

when the ligand was present in this case. When the HAuCl_4 and ascorbic acid are mixed in absence of the 4-MBA, fast reduction and homogeneous

nucleation occurred and the growth solution soon turned color, while the control experiment with 4-MBA present could stay colorless. In general, the ligands that will cause the supernatant to turn black in short time are not suitable for growing nanowires. In the following, we focus our discussion on ligands that can prevent homogeneous nucleation.

Thiol-ended ligands with similar structures as 4-MBA were tested. More specifically, 4-MPAA (Figure 3-9a, b) has an extra $-\text{CH}_2-$ between the benzene ring and the $-\text{COOH}$ group, breaking their π -p conjugation; 4-nitrobenzenethiol (Figure 3-8c), and 4-mercaptophenylboronic acid (Figure 3-8d) have $-\text{NO}_2$, and $-\text{B}(\text{OH})_2$ groups, respectively. Au nanowires were formed in all cases. Hence, the hydrophilic substituent group at the diametric side of the $-\text{SH}$ group appeared to have little effects on the nanowire growth.

As a further step, we selected ligands without hydrophilic substituent. When 1-naphthalenethiol and 2-naphthalenethiol were used as ligand, Au nanowires were able to grow on the bulk substrate (Figure 6a, 6c), but severe aggregation occurred for the growth on the colloidal substrates ($\text{Au}@\text{SiO}_2$). Apparently, the hydrophobic ligands did not influence the growth of nanowires and their final morphology, but greatly reduce the colloidal stability of the particles suspended in aqueous solvent. Considering that the two ligands are not amphiphilic, these results are further evidence against the possibility that the nanowires are templated by micelle-like nanostructures.

To study the effects of ligand packing, we selected 3-MBA and 2-MBA to compare with the original 4-MBA. These ligands have the same anchoring group; the only difference is the relative position of the –SH and –COOH groups, which may affect the ligand coordination and their packing. When 3-MBA was used, nanowires were able to form (Figure 6c and 6e, for bulk and colloidal substrates, respectively). It is important to note that these nanowires have varying diameter, with thinner sections close to the substrate, likely because of less effective ligand inhibition. As a result, there was continual lateral growth in addition to the longitudinal growth. When 2-MBA was used, the seeds grew larger with few very short nanowires (Figure 3-9d and 3-9f). These results were similar to experiments with low ligand concentration. On these bases, we speculate that the polar –COOH group at the *ortho* position of 2-MBA likely disrupts the packing among the aromatic rings. In the literature, it is known that the affinity of ligand depends on: 1) the bond strength at the anchoring point (e.g., –SH group with the Au surface), the binding rate for the thiol-ended ligands are closely related to the adsorption kinetics, which should not vary too much for all the thiol-ended ligands; and 2) the packing with the neighboring molecules.^[13] In other words, ligands crowded in a patch are more difficult to dissociate because of their interactions with neighbors. Thus, the poor packing of 2-MBA led to weak ligand inhibition and nonselective Au deposition. In comparison, the packing among the 3-MBA molecules was

intermediate between 2-MBA and 4-MBA. It is good enough to induce the Active Surface Growth mode, but not enough for complete inhibition of the lateral growth. Figure 3-9g-i illustrate the adsorption of the three ligands on a gold surface, highlighting the important position of the -COOH group and its effect on molecular packing.

We also compared 2-naphthalenethiol, 1-naphthalenethiol, and biphenyl-4-thiol. All three ligands have two aromatic rings and a -SH group, except that the last one has two conjugated but non-coplanar benzene rings. The first two ligands gave normal Au nanowires of 6 nm in diameter, but biphenyl-4-thiol gave only short and wedge-shaped nanorods (Figure 3-10e). As illustrated in Figure 3-10b, d, f, the packing of biphenyl-4-thiol was less compact, leading to weak ligand control, whereas the orientation of the naphthalene-moieties was not important for their packing.

Aliphatic ligands with terminal -SH were also studied, including 3-mercaptopropanoic acid (Figure 3-11c), 1-mercaptohexadecanoic acid (Figure 3-11d), butanethiol (Figure 3-11e), octadodecanethiol (Figure 3-11f), 11-mercap-toundecanoic acid (Figure 3-12a), ethanethiol (Figure 3-12b) and decanethiol (Figure 3-12c). The former three have -COOH group whereas the latter three have no functional group other than the -SH . In general, the aliphatic ligands cannot be used for the Active Surface Growth. They only led to overcoating of the seed nanoparticles. There were a few exceptions, where

Figure 3-10. SEM images and schematic illustration of the Au nanowires (Au nanostructures) formed with a, b) 1-naphthalenethiol; c, d) 2-naphthalenethiol; e, f) biphenyl-4-thiol as ligand.

3-mercaptopropanoic acid (Figure 3-11c), decanethiol and dodecanethiol can work within a narrow window of conditions, giving thick nanowires and overgrown heads (Figure 3-12d, 3-12e).^[10] Apparently, the aliphatic ligands are

Figure 3-11. SEM images of the nanowire (nanostructures) formed with a) 2-phenylethanethiol; b) 4-ethylbenzenethiol; c) 3-mercaptopropanoic acid (3-MPA) and d) 16-mercapto-hexadecanoic acid, e) butanethiol and f) octadodecanethiol. g) Schematic illustration of the possible ligand packing of the aliphatic ligands and aromatic ligands.

not effective in inhibiting Au deposition on the seeds. This trend is opposite to the previous reports that *n*-alkanethiol ligands usually pack better than aromatic

ones in self-assembled monolayers (SAM).^[14] The main difference between the two systems is that typical SAM was achieved at a long time scale (several hours). Over a prolonged period, *n*-alkanethiol ligands would adapt straight conformation, forming dense packing in the typical SAM. In contrast, it typically takes 15 min to grow 1 μm nanowires, which is about 1.1 nm per second. To form nanowires, ligands must immediately inhibit the newly generated Au surface. We speculate that the aromatic ligands with less conformational freedom may pack better than the aliphatic ones at the short time scale.^[15]

It is important to note that the lack of growth on the seeds was a result of competitive growth (e.g., Figure 3-9a). When the ligands cannot pack well and nanowires fail to form, Au was still able to deposit on the seeds, for example when using 2-MBA (Figure 3-9d), biphenyl-4-thiol (Figure 3-10e), and the aliphatic ligands (Figure 3-11). The rapid growth of the nanowire at the active site is expected to deplete the Au atoms nearby, causing area on Au to be outcompeted. In the absence of nanowire growth, slow Au growth (in comparison to Figure 3-8b) can still occur on the seeds during the dynamic ligand dissociation/association.

We further tested 2-phenylethanethiol and 4-ethylthio-phenol as the ligand (Figure 3-11a, b). The former has two methylene moieties between the benzene ring and $-\text{SH}$ group and thus, a higher conformational freedom is expected. It

Figure 3-12 SEM images of the nanoparticles formed with a) 11-mercaptopundecanoic acid, b) ethanethiol, c) decanethiol (0.55 mM), d) decanethiol (0.275 mM), e) dodecanethiol (0.275 mM), and f) CTAB (0.55 mM).

gave thick nanowires ($d = 12$ nm) with very large heads, suggesting weak ligand inhibition. In contrast, the latter ligand has an ethyl substituent at the *para*-position, whose conformations would unlikely affect the packing of the aromatic backbone. It gave normal nanowires with slightly grown seeds, indicating strong ligand inhibition. Thus, limiting the conformational freedom of the ligands helps their packing at the short time scale.

In the literature, the mechanisms proposed for the ligand-directed growth of nanorods and nanowires include facet control, micelle template.^[16] In our system, we believe the roles of the thiol-ended ligands are very different for the following reasons: 1) non-amphiphilic ligands (e.g., naphthalenethiol) are able to grow nanowires and some amphiphilic ligands (e.g.,

16-mercaptohexadecanoic acid) cannot (Figure 3-12f); 2) when using CTAB as the ligand, there was no sign of nanowires; 3) the polycrystallinity of the nanowires and their circular cross section^[6] are inconsistent with screw-dislocation^[17] and facet control.^[18]

On the basis of these results, we believe that the key characteristic of good ligands for the Active Surface Growth include (a) a strong anchoring group for the Au surface; (b) an aromatic backbone that is directly linked to the –SH group, so as to minimize the conformational freedom, so as to achieve good packing in a short time scale; (c) the substituents should not be steric hindered to the –SH group and also not aurophilic.

3.3.6 Mixing Ligands

We have shown above that the packing of ligand in a short time is of key importance for establishing the Active Surface. Good ligands can pack well and thus give the thin nanowires, while bad ligands could not. We then tested the case with both the good and bad ligands were present. Intermediate case between the full inhibitions and the full exposure of the Au surface was expected, which potentially can provide more structural varieties. However, as each ligand has its own solubility, ligand binding affinity etc., and thus the optimum concentration, such combination would not be easily screened and obtained.

In one example, when 4-MBA and 3-mercaptopropanoic acid were mixed in

Figure 3-13. SEM images of the Au nanowires formed with a) 4-MBA: 3-MPA=1:1, b) enlarged SEM of (a); c) 4-MBA: 3-MPA = 3:1, d) enlarged SEM of the Au nanowires surface in (c). e) Schematics illustrating the effect of ligand coverage on the nanowire growth and the direction of Au growth. Cone-like structures are obtained when ligand coverage is incomplete.

1:1 ratio, we obtain comma-like nanostructures with a very big head. The diameter at the head can be several hundreds of nanometers (Figure 3-13a) and

an ultrathin tail (Figure 3-13bb). The big head can be attributed to the simultaneous lateral growth during the longitudinal growth of the nanowires. Obviously, the presence of the “bad” ligand enables this lateral growth, which is completely shut off when only the “good” ligands were used. The correlation of the wire diameter with the time supports that Au nanowires are grown from the interface of the substrate and the existing nanowires, as the thin tails were formed latest. Another character of the nanowires obtained by mixed ligand is their rough surface. Traditional growth theory of the ligand-capped surface requires the ligand dissociate from the binding site prior to the deposition of Au. This would only leads to the smooth surface, which has less surface area compare to the rough one. The presence of this rough surface thus implies another unconventional mode, where the ligand embedment occurs. The embedding of the ligands causes the increased interfacial energy during the growth of the outer layers, leading to the evenly distributed roughness.

The ratio of mixing the ligand can also be changed to tune degree of the lateral growth. By increasing the 4-MBA: 3-MPA ratio to 3:1, the diameter of Au nanowires obtained only changed slightly from the head to tail (Figure 3-13d). The lateral growth was suppressed due to the increased amount of 4-MBA. The wires can grow into sufficient long and form vertical arrays, and the surface of these wires was also rough.

3.3.7 Superhydrophobic surface

Superhydrophobic (SH) surface are desired in many applications, as they are usually easily cleanable, sometimes even becoming self-cleaning and anti-contamination.^[19] A surface is superhydrophobic if its contact angle (CA) exceeds 150 °.^[19-20] Hydrophobic surfaces with increased roughness, usually by imposing micro or nano-scale structures, are the common candidates to form SH surfaces. Natural SH surface such as the lotus leaf or water striders usually contains hierarchical rough structures. In general, SH surfaces can be formed with the polymeric materials. Nanowire-based structures including carbon nanotubes,^[21] Silicon nanowires, silicon oxide wires,^[22] and other metal oxides^[23] have also been used. Metal nanowire-based structures are rare. Some metallic SH surface includes the AAO-templated Pt nanowires with flouroalkylsilane modification, and sputtered Au on to the lotus-like PDMS arrays.^[24]

In the present system, we would expect the existence of the ligand on the dried Au nanowires surface. The present of ligand 4-MBA and 2-naphthalenethiol on the dried substrate containing the Au nanowire array can be confirmed using the solid state surface enhanced Raman spectroscopy (SERS) respectively (Figure 3-14a, b). We would also expect the surface property of the substrate to be affected by the surface property of the wires

Figure 3-14. a-b) SERS spectra of the Au nanowires (on substrate) prepared with a) 2-NpSH and b) 4-MBA; c) SEM images of the surface made with 2-NpSH as ligand, 60 nm AuNP as seed and grown for prolonged time. d) Contact angle of the surface inset: digital graph of the Au coated piece; e) contact angle evolution when the growth time increases. SEM images of the Au nanowire surface at 30s (f), 3min (g) and 1 hour (h)

which in turn is decided by the ligands. Since the 2-naphthalenethiol ligand is hydrophobic, the Au nanowires formed with 2-naphthalenethiol shall also be

hydrophobic in nature. On the other hand, the Au nanowires array can be considered as nanoscale rough. Theoretically the Au nanowire array constructed using hydrophobic ligands such as the 2-NpSH can be made superhydrophobic.

Figure 3-14d shows the CA of the Au surface prepared with 2-naphthalenethiol as ligand and 60 nm AuNPs as seed. The CA for the surface is $151^{\circ} \pm 2^{\circ}$, qualifying superhydrophobic. The citrate-stabilized Au nanoparticles are hydrophilic, so as the APTES treated wafer surface covered with $-\text{NH}_2$. Figure 3-14e illustrates the CA of the surface at different time during the nanowires growth. The change of the CA indicated that the hydrophobicity of the surface was increasing during the growth process, as nanowires layer became thicker. The surface property gradually changed from hydrophilic to hydrophobic and then became superhydrophobic. The SEM image shown that the ultralong nanowires were all fallen down and no longer be strictly vertical, and the networks formed by the wires covered up the original hydrophilic surface, as a nanoscale rough layer (Figure 9f-g). The choice of the 60 nm AuNPs as seeds also helped to increase the roughness. Since the seeds are much larger in diameter than the wires, a two-level roughness is formed with this hierarchical structure.

As we discussed above, many ligands could induce the nanowire formation, therefore the surface property is expected to be well tunable. Other than controlling the time of growth, which adjust the coverage of the Au nanowires

Figure 3-15 Contact angle measured with Au coated substrate formed with a) 4-MBA and 5 nm seed, b) 4-MBA and 60 nm seeds and c) 2-NpSH with 60 nm seeds after the growth of polypyrrole. d) Au coated substrate formed with 4-MBA and 5nm seeds after silica growth.

on the substrate, surfaces with different CAs can theoretically be prepared by choosing different ligands. Using hydrophilic ligands such as 4-MBA can yields a hydrophilic surface, but it has almost the same surface morphology as the 2-naphthalenethiol case (Figure 3-15b). The surface property of the Au coating is also accessible by further surface modifications such as polypyrrole coating and silica coating, and the later gave a superhydrophilic surface (Figure 3-15d).

3.4 Conclusion

In summary, we explore the generality of the substrate bound Au nanowires

growth in terms of the solvent, substrate and ligand. The solvent mainly affect the growth by affecting the reduction rate, and a variety of organic solvent can be used to replace the ethanol with shift of the window of the combination in this system. Various oxide substrates were demonstrated to be capable for the Au nanowire growth. This generality enables the potential application including preparation of electrode or conductive coating. The generality of ligands were also studied. Aromatic ligands which do not containing any aurophilic substituents are capable to induce the Active Surface growth. Aliphatic ligands, or ligands whose backbone aromatic groups are connected by an σ bond would have a problem of packing which compromise their ability to inhibit Au deposition, and thus failed to generate a constant Active surface for nanowire growth. Substituent group on the benzene ring should have minor effect.

Addition of an unfavorable ligand to 4-MBA would turn on the lateral growth, giving thicker nanowires with big heads. This however can provide additional controls for rational design and synthesis of complex nanostructures.

The generality of the ligand and their diverse properties also give rise to the mean of adjusting the surface property of the Au surface coating. The surface preparation method is mild and easy, and the surface properties are readily adjustable. Typically, superhydrophobic surface that has never been reported before can be obtained if the hydrophobic ligands were employed and. large seed was used to construct two-level hierarchical structures.

3.5 Bibliography

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Chapter 4 Exploring Exotic Au nanostructures via the Active Surface Growth Mechanism

4.1 Introduction

Synthetic control of nanostructures is of great importance for nanoscience and nanotechnology. Expanding this frontier will lead to new structures, new pathways, and new methodologies, opening new windows for extraordinary properties and applications.^[1] While such a goal is far and unclear, we can appreciate how the synthetic advances in organic chemistry have ushered a new age of pharmaceutical industry.

Traditionally, the top-down approaches construct nanostructures based on templates, such as in the lithography methods,^[2] where nanostructures are formed on a substrate and their shapes are dictated by the photomask. Precise control can be achieved but the nanostructures are mostly limited to 2-dimensional patterns and reaching higher resolution becomes increasingly difficult. On the other hand, the bottom-up synthesis (nanosynthesis) usually involves wet chemistry and colloidal synthesis.^[3] The methods are in general more scalable, but developing synthetic control is more challenging. While the effects of facets and seeding have been extensively studied in the past two

Figure 4-1. Schematic illustration of the factors affects the active surfaces (highlight in yellow) and the competition between the active surface expansion and the restriction of ligand binding in both the isotropic and anisotropic case

decades, controlling the structural features in multi-component and multi-domain nanostructure is only just beginning.

In colloidal synthesis, the use of seeds can control the number and size uniformity of the resulting nanostructures, but the shapes of the seeds are rarely inherited in the product, whose shape is controlled by its own external facets. In particular, the nanowire (NW) growth, being extremely anisotropic in nature, is hardly compatible with the intrinsic structure of colloidal seeds. Except a few examples of thick NWs,^[4] the seeded growth was rarely demonstrated,

especially for ultrathin (< 10 nm) NWs. Controlling seeded growth on a substrate surface is even harder, not to mention oriented NW arrays.

At high temperature, the vapor-liquid-solid (VLS) mechanism provides a facile route to NW arrays on a substrate,^[5] where the surface-anchored seeds can dictate the diameter, location and density of the resulting NWs. As such, complex patterns of NW arrays have been created. However, using seed structure to determine the emerging NWs is still difficult, due large to the molten seeds during the VLS growth. Indeed, non-spherical seeds were rarely used for giving unusual clusters of NWs.^[6] Controlling non-molten seeds is indeed possible in VLS methods,^[7] but the added difficulty has prevented the use of rods and wires as seeds.

Previously, we reported the ligand-induced Active Surface Growth mode, where forest of Au NWs can be grown from a substrate under ambient conditions. As such, the seeds can maintain their structural features during the growth, opening a window for manipulating the NW growth using different seeds (Figure 1). In this work, we exploit this unique system for a new type of synthetic control of NW-substrate hybrids. More specifically, ordering of NWs in the form of lines and rings has been achieved with higher spatial resolution (in terms of specific arrangements in small clusters of NWs) than the traditional methods. Our study also reveals the principles underlying the evolution of the active surface during the NW growth, a phenomenon similar to the breaking of

continuous fluid under the influence of Rayleigh instability. On these bases, a number of curious nanostructures have been synthesized. Though these structures by themselves are not immediately useful, the synthetic capability and mechanistic understanding are critical step-stones towards increasingly sophisticated nanostructures.

4.2 Materials and Methods

4.2.1 Materials

All solutions were prepared using deionized water (resistivity $> 18 \text{ M} \cdot \text{cm}^{-1}$). 4-mercaptobenzoic acid (MBA, 90%, Sigma Aldrich), hydrogen tetrachloroaurate(III) (HAuCl_4 , 99.9%, Au 49% on metals basis, Alfa Aesar), 3-aminopropyltriethoxy-silane (APTES, Sigma Aldrich), sodium citrate tribasic dihydrate (99.0%, Sigma Aldrich), L-ascorbic acid (Sigma Aldrich) and ethanol (analytical grade) were used as received. Copper specimen grids (200 mesh) with formvar/carbon support film (referred to as TEM grids in the text) were purchased from Beijing XXBR Technology Co.

Characterization. Transmission electron microscopy (TEM) images were collected on a JEM-1400 (JEOL) operated at 100 ~ 120 kV. Field emission scanning electron microscopy (SEM) images were collected on a JEOL JSM-6700F.

4.2.1 Methods

Preparation of TEM Samples. TEM grids were treated with oxygen plasma

in a Harrick plasma cleaner/sterilizer for 45 s to improve the surface hydrophilicity. The hydrophilic face of the TEM grid was then placed in contact with the sample solution. A filter paper was used to wick off the excess solution on the TEM grid, which was then dried in air for 30 min.

Synthesis of Au NWs on wafer substrate with Au nanorods as seed. The method of the synthesizing Au NWs was followed the previous report. A Si wafer (about 0.6 cm²) was pretreated with O₂ plasma for 10 min to form a thermal layer. The wafer was then functionalized with amino group by reacting with APTES solution (5 mM) for 1 h. Subsequently, a drop of Au nanorod solution was dropped on the wafer and left drop under ambient condition. The seeds-adsorbed wafer was then immersed in a reaction solution containing the ligand MBA (550 μM), HAuCl₄ (1.7 mM) and L-ascorbic acid (4.1 mM) for 15 min. Finally, the wafer was rinsed with ethanol and dried in air.

For preparing Au NWs with other nanoparticles as seeds, all reaction conditions were unchanged except that the typical nanoparticles were used as seeds and the process of applying seeds were slightly different.

The Au nanorods (NR-40-600-100, diameter = 40±4 nm) was purchased from the *NanoSeedz*TM. The rod solution was concentrated 10 times with centrifugation before applied to the wafer.

60 nm Au NPs were synthesized follow the previous reported multi-step growth of the nanoparticles. In a typical procedure, 15 nm AuNPs was

synthesized by adding 1.5 mL sodium citrate solution (1% wt) into 50 mL boiling HAuCl₄ solution (0.1 mg/mL). After 25 min, 50 mL H₂O (boiling), 0.1 mL 6.6 mg/mL NaOH solution (dropwise), 0.5 mL sodium citrate solution (1% wt) (quick) and 0.5 mL HAuCl₄ solution (10 mg/mL) were added and heated for 20 min. In the third cycle, 100 mL H₂O, 0.2 mL NaOH, 1 mL citrate and 1 mL HAuCl₄ were added in sequence via the same way. The addition cycle was repeated twice, followed by additional 14 cycles (each cycle using 0.2 mL NaOH, 1 mL sodium citrate and 1 mL HAuCl₄, followed by 20 min incubation at refluxing). In total, there were 4 cycles with the addition of water, and 14 cycles without addition of water. The resulting solution was cooled to room temperature in the oil bath. When 60 nm Au nanoparticles were used as seed, the as-synthesized particles were first concentrated by centrifugation followed by soaking the wafer with seeds for 2 hr.

Au nanorings were synthesized following the reported method. 100 μ L oleylamine and 3 mg HAuCl₄.3H₂O were added into 2.5 mL THF, then 150 μ L TIPS was added to the mixture and this solution were incubated at room temperature overnight. The nanowires was purified by gradient centrifugation with 200 μ L on 1 mL THF:CHCl₃ =1:4 (v/v) solution. The middle part solution was washed with ethanol and redispersed in 600 μ L THF. Finally, 220 μ L of the purified Au NWs was mixed with 30 μ L of 1% oleylamine in THF solution. Then, 1 mL of SDS solution (8 mM) was quickly injected under vertex. The

resulting mixture was heated at 60 °C for 2 h to evaporate THF. The nanorings were first concentrated, followed by directed drying on the substrates.

The aggregated Au nanoparticles were prepared by addition of 1M NaCl into the 15 nm Au nanoparticle solutions; the obtained solution was purple in color and could be directly used for incubation of the wafer.

The ice-frozen Au nanochains were prepared following the method that was reported before. A drop of 15 nm AuNP solution was left in the -20 °C fridge and frozen. After that the Si wafer was left dry at room temperature and it contains the nanochains on it was readily used to grow Au NWs.

For preparation of the segmental Au nanowire, multi-stage reaction was carried out similar to what has reported. For instance, a wire with the middle part thick (ABA type) can be synthesized as below: The substrate was first grown in a solution of 550 mM MBA for 5 min, and then rapidly transferred without drying to a solution of 28 mM MBA and grown for another 5 minutes, followed by transferring it back to a solution of 550 mM. The concentrations of HAuCl₄ (1.7 mM) and L-ascorbic acid (4.1 mM) were constant in all stages. Similarly the BABA type nanowire was synthesized by starting with an additional stage in 28 mM 4-MBA solution. The thicker stage could also be prepared with a solution containing 550 mM 4-MBA and concentrated HAuCl₄ (8.5 mM) and L-ascorbic acid (20.5 mM). The multi-stage reactions were also used to prepare innovative structures by using Au nanorods as seed.

To grow the Au nano-flowers, about 1/100 (150 uL) of the growth solution (containing 550 mM 4-MBA, 1.7 mM H₂AuCl₄ and 4.1 mM L-ascorbic acid) was applied on the substrate treated with 100 times diluted Au seed solution, majority of the growth solution was removed 5 min after the addition, leaving only a thin layer. The wafer then was left dry naturally to yield nano-flowers.

4.2.3 Seed concentration

1. 5 nm seed: conc. = 65 nM.

$$\text{Density per area} = 3.25 \times 10^{-14} \text{ mol/cm}^2$$

2. 15 nm AuNP (citrate Au): conc. = 4.87 nM

$$\text{Density per area} = 7.305 \times 10^{-15} \text{ mol/cm}^2$$

3. 40 nm AuNP (citrate Au): conc. = 0.258 nM

$$\text{Density per area} = 1.032 \times 10^{-15} \text{ mol/cm}^2$$

4. 60 nm AuNP: synthesized with 15 nm AuNP as seed: conc. = 0.608 nM.

4.3 Results and Discussion

In our method, understanding the growth mechanism is critical for synthetic design. Previously, we found that the special mode of Active Surface Growth was induced by the strong ligand 4-mercaptobenzoic acid (4-MBA), which inhibited deposition on all exposed seed surface except the seed-substrate interface. Thus, there is only one site where the nanowire grown from, which is the active surface. The NW diameter was determined by the dynamic

competition between the deposition of Au and the ligand.

$$D = \alpha \frac{\mu}{\gamma}$$

Where, μ is the rate of Au deposition and γ is the ligand diffusion rate and α is a constant which can be determined as

$$\alpha = \frac{4Mk}{\rho}$$

where M is the molar mass of the Au, ρ is the density of the Au and k is the ligand density on the Au surface. ^[8]

The seed particle is a key component of the active site. The initial active surface was on the seed particle at the side facing the substrate (Figure 4-1).

We start to investigate the interesting possibility from an odd-shaped active surface. Au nanorods were adsorbed on the substrate surface, creating a non-spherical active surface with aspect ratio. Suppose that the shape of the active surface is maintained during the growth, the belt contact should lead to the formation of nanosheets. Briefly, the Au nanorods solution was concentrated by centrifugation, and approximately 20 μL of the concentrated solution was dropped and dried on the wafer substrate that had been treated with O_2 plasma and 3-aminotriethoxysilane. Then the wafer was put into the growth solution that contains 4-MBA, HAuCl_4 and L-ascorbic acid and grown for 15 min. After growth it was rinsed with ethanol and dried at the ambient condition.

Figure 4-2b shows SEM image of the wires grown from the Au nanorods. All the nanorods were lifted by the wires from the substrate surface, same as the

Figure 4-2. a) Schematics illustration of the growth of NWs from the Au nanorods seed. Two possible scenarios: islands of the active surface during the initial growth and the Rayleigh instability. b) SEM images c) TEM image of the nanostructures formed with nanorods as seed; d) SEM image of the seeds on the substrate before growth. e) and f) TEM image e: change of the active surface illustrates the Rayleigh instability effect; f: only two islands on the rod started to grow, illustrates the island effect.

particle seed case. Nevertheless, the shape of seeds does change significantly as

compare to before (Figure 2d), with the rod outline still identifiable. Bundles of ultrathin NWs can be observed growing from each seed. The fact that ultrathin NWs were able to form suggest rapid ligand inhibition of the expansion of the active site (Figure 4-1, Eq. 2). There is also slight growth of small gold whiskers on top of the rod surface, making the rods appear hairy. This minor growth could be due to the incomplete ligand exchange at the initial stage of the growth. However, without a substrate that maintaining these active surfaces, it would soon diminish. .

Obviously, the belt active surface was not maintained during the growth of the NWs, because their ultrathin diameter is very different from the rods. In the TEM image (Figure 4-2c), no sheet but bundles of ultrathin NWs with uniform diameter (~6 nm) were formed. Multiple NWs must come multiple active surfaces, which is inconsistent with the supposed continuous line of active surface. On the basis of the conceived initial state and the separated NWs in the final state, we speculate the growth mode as in Figure 4-2a.

4.3.1 Rayleigh instability

There could be two possible explanations for the change of the active surface: (1) the few spots along the belt active sites were the first to grow whereas the remaining part was outcompeted and inhibited by ligand coordination; (2) the extended belt active surface broke into separate domains due to the Rayleigh instability. In scenario 1, active sites should lead to single NWs space out due to

the competition among the NWs. As shown in Figure 4-1, the spherical active surface is always restricted by the ligands binding. Other than the initial active sites which are self-promoting, the rest of the contact would not grow NWs. In experiments, most seeds have dense bundles of NWs grown from, indicating a large number of the initial growth sites; in a few cases, there are two bundles (Figure 4-2f).

The other possible explanation originates from the tendency of Au NWs to minimize their surface area and surface energy. Being a solid, a NW cannot change its shape after formation; the selectivity occurs only at the active surface during the growth. At any moment, the new segment formed would like to have smallest surface area, meaning the circle to area ratio of the cross section should be minimized. Cylindrical NWs are thus preferred. In this very growth mode, the cross section of the Au NWs is defined by the shape of the active surface, which is dynamic. The old materials are pushed up, and new materials are constantly added to form a “new” active surface from time to time.

The dynamic active surface thus would like to minimize its periphery to be circular rather than a rounded rectangular initially defined by the nanorod. Meanwhile, the kinetics prevented the complete change of the belt active surface to a large sphere. The diameter of the NWs is also required to be thin as determined by the Au reduction and ligand concentration. As a result, the active surface breaks into many small circles.

Figure 4-3. a) Schematic illustration of the splitting of the active surface. When the reduction rate is high and the active surfaces are few due to the low seed density, in order for all of the Au (0) to be deposited, the active surface would either grow larger or give thicker wire (top) or increase in number to give bundles (bottom). Due to the Rayleigh instability and the restriction of the ligand, the larger active surface is not the case in the present system. b-e) SEM images of the nanostructures formed with b) 60 nm Au nanoparticles, inset: TEM image of the sample after sonication; c) aggregates of 15 nm Au nanoparticles (formed with NaCl addition); d) Au nanoparticle chains formed by freezing 15 nm Au nanoparticle solution.

Such phenomenon is the same as the Rayleigh instability effect, which

describes the liquid stream in free fall breaking into droplets. The droplets are in a local minimum state when each of them contract from a segment of the cylindrical stream whose length and diameter satisfy $l \geq 9r/2$. Random fluctuation (coming from the local imbalance of Au deposition and ligand adsorption) would help overcome the kinetic cost of forming the intermediate wavy cylinder with larger surface, and the subsequent contraction would be downhill, preventing the reverse process. The dynamic active surface behaves similarly but in a 2D manner. The initially belt active surface keeps on evolving, and eventually separated into small circular ones, leading to the formation of bundles of nanowires. In some case, such can of the active surface can be supported by the transformation of the sheet to bundles of wires (Figure 4-2e).

A similar phenomenon could be observed when using large nanoparticles as seed. In the previous work we reported that the nanowire with similar diameters formed when the seed size was changed from 5 nm to 15 nm. The initial active surface would not increase too much in that case. When the nanoparticle size further increased to 60 nm, things can be very different. Instead of one wire from each seed, a bundle of the Au NWs extended from each particle (Figure 4-3b). Each wire in the bundle had the diameter of about 6 nm, same as all the present case. The wire diameter was still decided by the Au reduction and ligand diffusion rate, which were kept unchanged. Such bundle formation could be attributed to two factors, the low density of the 60 nm Au nanoparticles on

the substrate and the Rayleigh instability effect. Though the seed solution used for incubation was concentrated, it was still much lower than that of the 5 nm particles (see the calculation in 4.2.3); and due to the size difference, the seeds adsorbed were intrinsically less in number. Therefore the number of initial growth sites would be insufficient. On the other hand, the Au that reduced per time was still the same as 5 nm seed case, as both the HAuCl_4 and the L-ascorbic acid concentration were not changed. All of the Au (0) formed in the solution has to find somewhere to go. In order for that amount of the Au to be deposited, either the diameter of each wire increases or the number of the wires increase. Since the ligand concentration in the solution requires the formation of NWs with certain diameter, and the active surface is dynamic, the larger initial active surface split into many small ones during the growth. Hence we would see the diameter of the initially grown Au nanowire was thick, but soon split to bundles of many thinner ones (Figure 4-3a)

When the aggregated Au clusters were used as seed (Figure 4-3c), the phenomenon of the increasing active surface became more obvious. The nanoparticles were purposely aggregated with salt in the solution and the resulting giant aggregates were irregular in shape. When the aggregates were casted on the flat substrate, there were only several touch points for each aggregate. Au NWs could only grow from those touched points where the initial active sites exists. The number of the active surface in this case is even less than

the 60 nm Au nanoparticle case, therefore the total number of the active surface quickly increased to fulfill the deposition of the Au (0) generated in the solution. The final bundles became even bigger, more expansion and splitting happened during the growth. This is similar to the bundle formation when no seed was used. These bundles may be void at the center, which would be discussed in detail below.

The aggregated Au nanocluster results suggested that bulk or macroscale Au structure might also be employed as the seed, so long as they provide active surface at the initial contacting sites. If the sites are much less compare to the Au reduction, the number of the new active surface can split from the existing active surface when they are grown larger. Shen *et al.* synthesized huge Au nanoparticle chains by utilizing the ice channel templates formed when freezing the colloidal solution.^[9] Using this long chain as seed, we could get a comb-like nano-brush (Figure 4-3d), a micro-size object that contains regular nano-level structure.

4.3.2 Seed density

We have shown that the seed morphology would not affect the formation of the nanowires. However, the seed density does, as what happened with the 60 nm Au nanoparticle seed. The initial seed density decided the number of the initial active surface. Bundling occurs when there is insufficient active surface for the Au to grow. Moreover, considering there is no intrinsic driving force for

Figure 4-4. a) Schematic illustration of the origin of vertically aligned Au nanowire arrays. SEM images of nanowires grown with substrate treated with b) 5 nm Au seed solution; c) 10 X diluted 15 nm Au seed solution; d) 100 X diluted 15 nm Au seed solution, e) no seed solution. f) left: the bottom of the Au NWs bundles grown from on seed (bottom view); upper right: the tips of the AuNWs bundles; lower right: the bottom of the Au NWs bundles (top view).

the polycrystalline Au NWs to grow perpendicular to the substrate, the seed

density also affects the alignment of the wires. In fact, under the high magnification, the NWs formed are not perfectly straight (Figure 3b). This is different from the VLS growth of the nanowires, in which the epitaxial growth guided the lattice of the wires, and the long range crystallinity ensures the perfect straight nature (except bending) of the wires. The vertical alignment was most probably due to the steric hindrance among the wires and the charge repulsion between the NWs (Figure 4-4a). If the seed density was high, each wire was restricted by its neighbors and would have only the space above it to extend to.

When the seed number was reduced, however, the wires had sufficient space to extend to every direction, they would not maintain the vertically arrays. Theoretically, the NW extension direction should be vertically straight, as the growth material was fed from the bottom. However, whether NWs is being pushed by its neighbors and the shear force will determine the direction of growth. Another problem in investigating the growth direction is that the SEM sample observed is after drying, where the capillary force at the end of drying process would cause the “aggregation” of the NWs. Figure 4c & 4d show the examples that the nanowires were grown from substrate that treated with diluted seed solution. In Figure 4-4c, the 15 nm Au seed solution (which in nature is more diluted than the 5 nm seed solution) was diluted 10 times, and the obtained nanowires were not straight anymore. The seed solution was

further diluted to 100 times, and in this case no obvious vertically aligned nanowire array was presented (Figure 4-4d). Whereas as mentioned above, when the seed density decreased, the number of the initial active sites also decreased, leading to the bundle formation with the concentration of ligand and Au reduction rate was kept the same. It should also be noted that with decreased number of seeds absorbed, the wires obtained could be much longer (several microns).

When the seed density reduced to 0, *i.e.* no seed was added, the bundle formation was the severest. No Au homogeneous nucleation in the solution because the strong ligand inhibit the formation of initial nuclei. Some nuclei can form on the substrate by the heterogeneous nucleation, and the Au NWs growth still happens with these nuclei as seeds. However due to the extremely low density of the nucleation sites and the relatively high reduction rate, the active surface will expend in order for more Au to deposit similar as the Au nanoparticle cluster case. According to the Rayleigh instability, the increased active surface will become unstable and split in our growth mode. This size increasing and splitting kept on happening, due to the deficiency of active surfaces. Eventually, under this condition the wires grew into huge bundles, with the bottom diameter can extend to microns (Figure 4-4e) and a small tip (Figure 4-4f, upper right). These bundles also have another character of being void at the center. SEM image of the bottom view of the bottom of the bundle

shows clearly the holes at the center (Figure 4-4f, left). Consider the density of the wires and their closely packed; it is not surprise that the mass transportation at the center would be severely affected when the bundle became larger and larger. With no growth at the center, the active surfaces there would diminish as indicate in the scheme in Figure 4-3a, meanwhile actives surfaces kept on expanding and splitting at the outer rim, making the bundles thicker and thicker, until the number of the active surface is enough compare to the reduction rate.

The studies above show correlation of the active surfaces and the seeds, especially the seed densities. The bundle formation can be viewed as the competition between the seed and the reduction. So now we have a few controlling parameters that could control the nanostructures formed on substrate using the Active Surface Growth mode. By adjusting the seeds type, concentration and growth solution, we could rationally design and synthesize desired complex Au nanostructures.

4.3.3 Design Au nanostructures on substrate

The synthetic design could base on changing one or more of the three main parameters. The reduction rate and ligand controls the diameters, while the seed controls the active surface number and positions. Moreover, the seed morphology could also be incorporate into the final nanostructures, allowing the build-up of complexities.

Figure 4-5. a) Schematic illustration of the formation of segmental nanowire. SEM images of b) nanowires with middle part thicker (transferring to a low ligand growth solution in the middle of the growth) (ABA type); c) nanowires with head and middle part thicker (BABA type); and d) BABA type nanowire which the second thick section was constructed with increasing HAuCl_4 concentration instead of reduced ligand concentration.

Wires with a big head or big tail were demonstrated in the previous paper. We could continue this adjustment for another round and obtain the wires with the middle part thick or wires with two big ends but the middle part thin (Figure 4-5a). By first immersing the substrate in a growth solution that contained 0.55

mM 4-MBA for 5 minutes growth, and then transferring it to a growth solution that contained 0.028 mM 4-MBA for another 2 minutes growth before taking it back to the 0.55 mM 4-MBA growth solution, wires with the middle part thick and both end thin was generated (Figure 4-5b). Furthermore, wires with alternative thick segment and thin segment for two cycles were also possible to be generated (Figure 4-5c). Besides adjusting the ligand concentration, the width of the nanowire could be controlled by the Au reduction rate, which in turn could be controlled by the HAuCl_4 concentration and the ascorbic acid concentration. Changing the gold reduction rate could generate segmental wires, as shown in Figure 5d, the second thick section was generated by increasing the HAuCl_4 concentration 5 times. Theoretically, this kind of changing of thickness could be continued as many rounds as possible to obtain necklace-like chain structures. In practice, the mass transportation problem which is the deficiency of the HAuCl_4 around the growth sites when the wire density is high and the wire become longer and the problems associated with washing need to be solved to continue the growth.

Another type of the complex nanostructures is to utilize morphologies of the seeds. As shown above, almost all kinds of the Au nanostructures are capable to be grown from, giving that they could attach to the surface. Besides the nanospheres, rod and nanowire aggregates have also been shown to from comb-like structures. Other seed morphology could be employed, such as the

Figure 4-6. SEM images of the nanostructures formed with a) Au nanorod as seeds, starting with 0.028 mM ligand solution and transferring the 0.55 mM ligand solution for 5 min growth; b) Au nanorod as seeds, starting with 0.55 mM ligand solution and transferring to 0.028 mM ligand solution for 5 min growth. SEM images of c) nanocages with Au nanorings formed during the phase transfer of oleylamine stabilized Au nanowires as seed; and d) nanoflowers grown with 1/100 volume of the growth solution on the substrate treated with 100 times diluted Au seed solution, majority of the growth solution was removed 5 min after the addition. nanowires and nanorings. In one case, the Au nanorings can result

nanocage-like structures (Figure 4-6). The reason that nanocage formed instead of nanotube is the same as the one explained for the nanorod case, the active surface could not maintain a ring shape during the growth process due to the instability effect.

If we use the rod as seeds and adjust the wire thickness simultaneously, more irregular shapes could be obtained. Figure 4-6a shows a comb-like structure that was first grown with low ligand concentration and then transfer to dilute ligand solution. Short wires were obtained as the growth process was terminated by simply taking out the substrate half-way. Alternatively, if the substrate was first put in high ligand solution and then transferred to low ligand solution, the bottom of the wire began to expand (Figure 4-6b). Some of the enlarged tails even merged together.

Other than the above controlling methods, poor mass transportation can also be used for making irregular nanostructures. As a demonstration, nanoflowers were synthesized when the concentration of the growth solution changed and the Au precursors became deficient (Figure 4-6d). After growing in normal growth solution to obtain the wire part, the substrate was only left with a thin layer of growth solution. The wire become firstly very thick and split due to the increasing of the concentration of the growth solution as the solvent kept on evaporated. Lastly, as the Au in the solution was consumed, only the outer ring part was able to grow. The inner center stopped growing.

Further extension of synthesis may include combine the nanowire growth with the complex substrate for making useful devices. As the Active Surface Growth is a solution based method, the growth solution can reach cavities and crevices therefore the Au deposition and Au NWs could also happened at those place on substrate where usually not accessible for the conventional top-down fabrication and eventually forming continuous 3D networks.

One potential application of the Au NWs is to make the transparent conductor film. We demonstrate this by directly growth the Au NWs on a big glass substrate. A few problems should be resolved for this case; firstly the conductivity of the Au film was in tens of ohms per square, which is still not good enough. Another one is the uniformity of coating during the synthesis.

There could be more innovating nanostructures with this growth mechanism, owing to its feasibility. We have shown that this growth is applicable for the bulk substrates, and there could be more which we haven't tested due to the time and resources constrain. To our confidence, almost all kinds of Au nanoparticles and nanostructures could be utilized as the seed for the nanowire growth, and a wide range of the Au nanostructures could be generated from the combination of the seed and wires, and also the derivatives of wires. The effect of the seed density on the nanowire assembly properties is also interesting, and it could help to generate vertical arrays or networks of wires or wire bundles. All the parameters can be combined to give a large space for rational

nanostructure design and synthesis.

4.4 Conclusion

In summary we have studied the effect of the seeds on the Active Surface Growth mode, and developed a general synthetic methodology of synthesizing substrate-bounded gold nanowire and nanostructures based on the understanding of the mechanisms. The seed morphology defines the initial outline of the active surface, but during the growth, the dynamic active surface split following the Rayleigh instability, leading to bundle formation. The seed density is another key factor. When the initial seed density is low, there would be insufficient active surface to facilitate the Au deposition. The active surfaces thus expand outwards. But under the influence of the Rayleigh instability and the mass transportation, the active surface split into many smaller ones and migrate from inside out.

We also designed and obtained a series of Au nanostructures based on this mechanism, as this feasible method does not restrict to a single morphology formation. Most of them here shown are just proof-of-concept structures, and there would be numerous unique Au nanostructures based on this method, due to its compatibility over a wide range of seed, ligands and substrates.

4.5 Bibliography

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Chapter 5 Synthesis and mechanism investigation of the Au nanobracelets

5.1 Introduction

Designing and synthesizing of novel and complex nanostructures with unique properties have long been an attractive field.^[1] A variety of nanostructures with various compositions has been developed in the recent a few decades.^[2] While most of the nanostructures to-date synthesized are still of high symmetric, many efforts have been imposed to obtain the low symmetric ones, such as the nanowires.^[3] On the other hand, hierarchical nanostructures are also desired, as they are usually of lower symmetry and possess unique properties.^[4] Sequential growth can be one useful method to prepare the complex structures. Although for the bottom-up wet chemistry approach, it is usually difficult to directly obtain the complex structures as there are not sufficient parameters to control the nucleation and growth, the complexity could be build up.

The oleylamine-stabilized Au NWs has been a common method for preparing the 1-D noble metal nanostructures. There have been quite a few reports of the synthesis protocols, with slight variation from on to another for

the fine tuning of the synthesis.^[5] Generally it is well accepted that, the ligand oleylamine is the key reagent that induces the anisotropic growth of the Au during the synthesis. Most of the literature believed that the oleylamine functioned like the soft channel template and restrict the deposition of Au to the lateral directions.^[6] But there are also proposals states that the wire was formed due to the oriented attachment of the oleylamine capped small Au NPs.^[7] Despite this synthesis route has been discovered and developed for years, the diameter control of this growth method was not well investigated. Apart from a few reports, most of the oleylamine-stabilized Au NWs reported were ~2 nm diameter, and the mechanism behind such control was not clear yet. The further process of the oleylamine stabilized Au NWs was also not fully explored yet, especially for the deposition of Au on the oleylamine stabilized surface. Even for the reported thicker wire (~9 nm) synthesized with oleylamine, it was quite impossible to be the thickening of the thin wire by co-axial growth.^[5b] Further growth on the oleylamine stabilized surfaces not only can provide us basic scientific understanding on this ligand protection, but also offer a new route for synthetic control. The Au NWs have already been a highly asymmetric structure,^[8] and further growth may bring more complexity.

The oleylamine was commonly used at a capping agent in many nanoscale syntheses.^[9] For synthesis the Au NWs, sometimes it can also function as the reducing agent, as it has a reductive C=C double bond. It binds to the

nanoparticles with the amine group, which can coordinate with the Au.^[10] On the other hand the thiolated ligands, such as the mercaptoudecnoic acid (11-MUA) were generally considered stronger ligands, owing to the semi-covalent Au-S bond.^[11] When the nanoparticles grown from a ligand protected surface, it was believed, the deposition could only happen after the ligand left the surface and expose the bare bottom surface for the new comer to form interactions.^[12] Therefore, ligands protection typically inhibits the growth of nanoparticles on that surface. When we have two different types of ligands present in one system, due to the different ligand dynamics, the two ligands might have different ability for preventing the Au deposition. Thus there would be a difference of growth between the more active and the less active surfaces. We have reported the creation the active surface with the APTES (with amine group bind to Au) and the thiol-ended mercaptobenzoic acid ligands, and the different growth rate of Au at the lateral side and the end created an “active surface”, leading the formation of the Au NWs vertically aligned on the substrate.^[13] A similar phenomenon may be created with an amino group ended ligand and a thiolated ligand.

5.2 Materials and Methods

5.2.1 Materials

All chemical reagents were used as purchased without further purification. Hydrogen tetrachloroaurate(III) hydrate, 99.9% (metal basis Au 49%) was

purchased from Alfa Aesar; 11-mercaptoundecanoic acid, L-ascorbic acid, was purchased from Sigma Aldrich. Oleylamine (approximate C18-content 80-90%) was purchased from ACROS Organics. Sodium hydroxide was purchased from Sinopharm Chemical Reagent Co. Ltd; Deionized water (resistance > 18.2 MΩ/cm) was used in all reactions. All other chemicals were purchased from Sigma Aldrich. Copper specimen grids (300 mesh) with formvar/carbon support film were purchased from Beijing XXBR Technology Co.

5.2.2 Methods

Preparation of TEM samples. TEM grids were treated by oxygen plasma in a Harrick[®] plasma cleaner/sterilizer for 1 min to improve the surface hydrophilicity. A sample solution was dropped on the hydrophilic surface of the TEM grid. Finally, a filter paper was used to wick off the excess solution on the TEM grid, and the grid was dried in air for 30 min.

Characterization. TEM images were collected on a JEM-1400 (JEOL) Transmission Electron Microscope operated at 100 kV. UV-Vis spectra were collected from a Cary 100 UV-vis spectrophotometer.

Preparation of Au NW rings. The method used here was based on our previous report.^[14] The Au NWs were synthesized using oleylamine as the ligand.^[5a] After purification, they were dispersed in 250 μL of THF and 0.3 μL of oleylamine was added. After mixing, 1 mL of aqueous SDS solution (8 mM) was added quickly to induce emulsification, and the mixture was then heated at

60 °C for 2 h to remove THF.

Preparation of the nanobracelet chains. The phase transferred Au NWs (20 μL) was added into a reaction solution (1.5 mL) containing the ligand MBA (500 μM) (100 μL of 1 mM in EtOH), HAuCl_4 (1.5 mM) (6 μL of 50 mM) and L-ascorbic acid (3.75 mM) (75 μL of 10 mM) and grown for 15 min. The obtained sample can be directly drop-cast for TEM characterization

5.3 Results and Discussion

The chain-like nanobracelet was synthesized by growth the Au onto the existing ultrathin Au NWs rings with the presence of the ligand 11-MUA. This unconventional morphology would be very interesting in terms of the complexity, and its mechanism of formation could also provide great insights of the property of the oleylamine-stabilized Au NWs. Theoretically, such growth should be able to carry out for the straight Au NWs, as the ring structure didn't provide any other guide for Au deposition. The ring structure was chosen merely because of the solubility issue, as the Au NWs were synthesized in the hydrophobic environments, and the phase transfer process typically would always coil them due to the emulsion formation.

A typical nanobracelet was shown in Figure 5-1. It was clear that blocks had facets, and were connected by the thin wires in between. The sizes (here typically refer to the length) of the blocks were not as uniform, probably due to the random seeding process. However, the diameters of these blocks were

surprisingly uniform, with only slight variations. Similar growth time may be an explanation, which allows those nucleate at a same time ended up to be almost similar in diameters. There are still many unsolved question about such unique growth mode, and we will discuss some of them in the following section 5.3.3.

5.3.1 Ligand effect

The ligand is undoubted the key effect to cause such kind of block growth. 11-MUA was typically used here. As the thiolated ligand, it is believed to bind to the Au NWs surface strongly. Therefore, during the growth process, this binding would inhibit and slow down the further deposition.

The nucleation and the growth processes are all affected by the MUA concentration. MUA would also bind to the free $\text{Au}^{3+}/\text{Au}^+$ ions, so as to slow down the Au deposition process. If no MUA was added, the nucleation and the Au reduction processes were both became extremely fast. As shown in Figure 5-2, the whole nanowire ring was covered with particle-like islands, indicating severe heterogeneous nucleation. However, under such condition, the growth on the ring was not last for a long time and eventually yielded a very thick ring. This was because that, under such fast reduction condition, the Au (0) accumulated in the solution would soon become huge in number and the system energy would become strong enough for the homogenous nucleation. This would consume the Au and compete with the growth on the nanowires, and the

Figure 5-1. Scheme illustrating and the TEM image the synthesis process of the Au nanobracelet.

fast exhausting of the Au prevented the formation of the extreme thick nanorings.

When MUA was present in the system, the reaction rate would be slowed down and thus the Au deposition would be mainly on the Au NWs rings. However, this would still not be able to explain the uniformity and the segments. Why the diameter of the block was exactly the same and why there is also breakages in between the blocks would be two main questions to ask.

Figure 5-2. TEM images of the chain-like Au nanobracelets formed with different concentration of the MUA ligands (as initial addition).

In order to further explore the effect of the MUA ligands, the concentration of the ligands was changed from 0 mM to 3 mM, and tried to cover the whole spectrum of the growth behaviors. As shown in Figure 5-2, the result is very surprising. Even when the MUA ligand concentration was very low, it was still quite different from the no MUA case. At 0.1 mM, the ligands were already capable to induce the block-like growth. In fact in this case, it is more like an even expansion of the thin wires. There was few break points could be observed. When the MUA concentration gradually increased to 2 mM, the breakage number kept increase. Another trend was that, the diameter of the blocks kept decreasing from 0.2 to 2 mM. This was easy to understand, as the increasing of the ligand concentration would also slow down the Au deposition rate, or the in

situ capping of the ligand onto the newly formed blocks would prevent the nanowires become thicker and thicker.

At the 1 mM and 2 mM ligand concentration, the blocks also began to appear slight different from the 0.2 case. At such ligand concentration, the edge of the blocks was rounded up while in the 0.2 mM case, a clear cut block edge that was almost perpendicular to the center wire could be observed. Such round implied that, the facet control was not promoted by the MUA ligands, but remain an unsolved problem.

However, when the MUA ligand concentration increased to 3 mM, the appearance of the Au blocks became not clear at all. It was hardly to tell if there were any separated blocks, though some breakages could still be observed. At this end, the Au deposition became similar to the low ligands case, as compare to the 0.1 mM case. The only difference was the diameter of the wires were much thinner than the 0.1 mM case, which was understandable as the ligand concentration was much higher therefore the deposition rate was much slower here.

The “U” shape trend of the MUA ligands effect indicated the ligand effect must be complex, compare to the linear behavior in the active surface mechanism. As mentioned above, the effect of MUA can include two parts: 1) affect the rate of the Au reduction; 2) affect the Au deposition on the already formed Au surface. However, there was another key factor missed if only the

MUA was considered. The residual oleylamine (OA) on the Au NWs during the initial synthesis and the phase transformation may play important role, by either compete or cooperate with the MUA ligand. A main difficulty in investigate the quantity of the residue OA was hard to estimate. Similarly the interaction between the MUA and the OA was also difficult to justify. Theoretically the OA should be replaced by the MUA as the thiolated ligands are generally considered as stronger. However, as this was an aqueous solution, the rate of displacement might be much lower than in the good solvent. If no ligand exchange or the degree of ligand exchange was not strong, then the nucleation process must include the OA-protected surface. In fact, it was highly suspected that, the origin of the nanobracelet growth should be closely related to the difference of the surface activities between the OA ligands and the MUA ligands. Detailed discussion will be presented in the section 5.3.3.

5.3.2 Seed and solvent effect

The seed, which is the Au NWs ring, is quite special in terms of the template growth of the nanostructures. These rings were formed due to the emulsification process during the phase transfer, since the Au reduction could only take place in the aqueous solution. Although the rings were formed by the coiling of single nanowires, there was no natural fusion between the coiled wires. Therefore when the Au started to deposit and grow these wires thicker, the coils became could not maintain the bending and become loose. However, uncoiling was still

not like to happen, probably due to the multiple nucleation centers on each coil.

Problems about the seeds arises from the fact that it was hard to keep the seed concentration the same across the batches, while the seed concentration do affect the growth of the blocks or even the growth mode. A simple deduction would be that, if the number of the seeds increased, there would be less nucleation sites and slower growth for each seed since the rest of the condition was unchanged. The concentration of the gold precursor and ascorbic acid, together with the ligand concentration decided the ability of the Au deposition, including the nucleation and the following growth.

The experiment results however disagree with this argument. Figure 5-3a to 3c shown the trend of changing the initial seed concentration in the synthesis. Figure 5-3b was arbitrary assumed as 1, which is the normal seed density we used for growth this nanobracelet, while Figure 5-3a was 4.5 times more concentrate than 3b and Figure 4-3c was only 1/10 of 3b. The wires in the three cases were not quite different at number of blocks, only the diameters of the blocks are different. Therefore we could claim that, the seed density would not decide the total number of the nucleation centers but only relate to the nucleation sites on each wire. This could be rationalized, as when the Au starts to nucleate, they would not know the nucleation situation on other wires or even the other places on the same wires. Therefore simple division could not be used to obtain the total nucleation centers at a given Au/AA/MUA concentration.

Figure 5-3. TEM images of the nanobracelet generated with a) 4.5 times of seed as compare to b, b) normal seed concentration obtained from purification process, and c) 1/10 of seed as compare to b; e) normal 1 mM MUA in aqueous solution, f) 50% THF/water solvent and g) additional 0.1 μ L oleylamine.

When the nucleation event finished and the growth process took up, the blocks in the dense seed case could not grow thick due to the lack of materials.

The seed experiments also imply another special behavior of the growth, that the growth on-wire in this case is much faster than the lateral growth of the blocks. Therefore only the wire thickness was affected but the gap length was not quite obvious here.

The on-wire growth is different from the lateral growth in terms of the surface activities that the incoming Au (0) encountered. In order for the lateral

growth to proceed, the Au deposition must in compete with the MUA binding on the newly formed blocks. While the on-wire growth concerns with the “old” nanowire surface.

However as mentioned above, it was hard to decide the ligands that protect the “old” surface as it was not clear when the MUA was able to replace the OA, and to which degree it can replace OA or even mix with OA. The aqueous environment would prevent the ligand exchange by reducing the ligand dynamics of the OA. Carrying on the experiment at 50% THF/water solvent however did not give very different result (Figure 5-3e and 3f). On the other hand, adding more OA into the system does give quite different result. The gaps are almost diminished. It can then hypothesize that the newly added OA absorbed on the wire surface and prevent the MUA attachment. Since the MUA inhibit the Au deposition while Au could deposit freely on the OA-stabilized surface, the on-wire extension was greatly promoted in one with supplementary OA, leading to the absolute diminishing of the gaps.

5.3.3 Mechanism Discussion

With the existence of the Au NWs rings as seed, the deposition of Au reduced by ascorbic acid should follow the heterogeneous nucleation process, which requires low energy compare to the homogeneous nucleation. However, due to the great length of the Au NWs, there must be multiple nucleation centers on each ring, and these nucleation centers should be total decided by

random. Generally the number of the total nucleation centers should be closely related to the reduction rate and the MUA concentration, just like the active surface in section 2.

As mentioned above, the whole growth process should at least include three parts: 1) the nucleation on the Au NWs; 2) the on-wire growth started from the nucleated islands and expand along the wires; and 3) the lateral growth that expand perpendicular from the wire direction. Each of the three processes is affected by multiple factors, and changing any of the reaction conditions might also affect more than one of the three processes. Thus the growth system become quite complex as it is hard to obtain the clear-cut result with only single variable.

Figure 5-4 illustrates 4 different types of growth mode that could happen for the Au deposition after nucleation, and also their results under different nucleation conditions. If there is no difference in the favorability between the on-wire direction (red arrows) and the lateral growth (green arrow), then the final structures originate from the island nucleated on the wire would be a perfect sphere. The number of these spheres would be decided by the original nucleation number. A1 illustrate the one with deficient nucleation, the final structure would be similar to pearl-necklace, with the spheres randomly scattered on the thin wire. If the nucleation event was violate and a lot of such islands were created, there was possibility that the spheres encounter each other

Figure 5-5. TEM images of the Au nanobracelets formed at a) 60°C, b) room temperature and c) 0 °C.

soon after the growth started, they may merged together as shown in A2. The final structure then would be similar to the segment/blocks on the wires. The condition that fulfilled mode A would be the no-MUA case. Without extra ligand, the newly formed Au blocks were spherical in shape, indicating that the on-wire growth was comparable with the growth on the fresh surface without any ligands.

This thus provides the rational for mode B and D. When there were ligands around, ligand would function in twos ways: 1) slow down the reduction rate by binding to the Au ions and 2) slow down the Au deposition by binding to the existing Au surfaces (de-activate the surface). Therefore the rate of the lateral growth would always be slower when there was MUA around. Mode B describes the situation that the lateral growth was extremely slow compare to the growth on-wire. In such case the newly formed blocks formed the flat spindles, as the inner part have more time to grow thicker than the edges. In Mode D, the lateral growth was slightly faster but the ligand still have certain

Figure 5-4. Schemes illustrating the growth modes: A) same on-wire (red arrow) and lateral growth (green arrow). A1 and A2 correspond to the low nucleation and high nucleation condition; B) on-wire growth is much stronger than the weak lateral growth. C) lateral growth is much stronger than on-wire growth and D) both the on-wire growth and lateral growth are strong, but the ligand has facet control. The on-wire growth was terminated after a while, left only with the lateral growth.

facet control after a while, therefore the effect of spindle become less obvious

and the blocks can grow thicker. Mode C describes another extreme, where the lateral growth is much faster than the on-wire expansion. It may happen if the Au reduction was faster. Since the surfaces of the original wire and the newly formed blocks were generally different in terms of capping agent, there response to the ration rate change might not be linear. The block surface may be more sensitive than the on-wire expansion as it has a larger area (available for deposition).

There is another concern when deal with the final structures. As shown in Figure 5-4, when there are too many nucleation centers, the final structures would be strongly affected. The nearby blocks may fuse together when they encounter each other. In some cases, although the final structure was uniformly thickened wire, there are characteristics stacking faults occurs as darker ring along the line. These stacking faults may come from the faster deposition of the Au at the gap region when the two blocks approached. Therefore for the mode D, there may still be controversy whether it is an isolated mode or it comes from the mode C with many nucleation centers. However, since the nucleation was random, therefore it was hard to have some blocks that are close together while they are separated far away from the rest. The fusion of the blocks, however did take place in such synthesis. When the temperature of the reaction was increased, the effect of the fusion or at least surface smoothing due to the faster surface diffusion or ripening can be observed (Figure 5-5).

Figure 5-6. TEM images of the Au nanobracelets formed with a) 6-mercaptohexanol, b) 11-MUA and c) 16-mercaptohexadecanoic acid.

Now we can examine how the growth affected when the reaction conditions was changed. Firstly when the ligand concentration was adjusted, as in the section 5.3.1, the trend of the morphologies change was like a “U” shape as the ligand concentration increase. Let’s consider the low ligand condition. At such condition, the lateral growth should be strong, at least should be comparable with the on-wire expansion. Meanwhile as there were less ligand the reduction rate was high and therefore there would be many nucleation centers. So the final structure would be close to the demonstration in D2: Large blocks with very less gaps. As the ligand number increasing, the nucleation would be suppressed, so as the lateral growth. So the diameter of the blocks decreased, and the gaps become large. The configuration changes from D2 to D1. When the ligand concentration further increase, now the lateral growth is strongly suppressed and now the on-wire expansion is more favorable than the lateral

Figure 5-7. TEM images of the Au nanobracelets formed at different reduction rate: a) the seed/HAuCl₄/ascorbic acid ratio between a1 and a2 is 3:1; b) the seed/HAuCl₄/ascorbic acid ratio between b1, b2 and b3 is 2:3:5.

growth. The growth mode then changed from D1 to B1.

When the ligand type was changed, we could observe another trend. The hydrocarbon chain of the ligand can be increased to 16 or decreased to 6, and a continuous change from separated blocks to smoothie thickening took place (Figure 5-6). The short chain ligand gives very smooth thickening, indicating that there are a lot of nucleation centers, and in this case the on-wire expanding was more favorable than the lateral expansion and the blocks could fuse when the encounter each other. The faster ligand dynamics may allow such fusion to proceed more easily. The very long-chain ligand is on the other end. Firstly the

solubility of the 16-MDHA was low and due to its long chain, the ligand dynamics shall not be as strong as the 6-MHN, therefore each block grown to a very big one and even have facet structures. But few of them would mix together. The common MUA system lies at the center of the two extreme, with separated but slightly rounded blocks.

In the active surface growth mechanism (Section 2), the reduction rate adjusts the system in an almost completely reverse way as the ligand concentration do. Here we would expect at least a similar behavior. In fact within some range, this was true. Figure 5-7 shows two different sets of experiments. As the concentration of the Au precursor and the reducing agent decreased, the growth mode switched to the B mode, while increase the Au and ascorbic acid drives the growth from B towards D or even C mode.

We have mentioned above that the residual OA may affect the growth of blocks but it was difficult to quantify them. Addition of extra OA during growth however led to the uniform thickening of the wires. If the MUA was in competition with the OA on the nanowires, then this growth mode could be explained. The OA addition strongly promotes the on-wire expansion. Assume MUA was inhibiting the lateral growth; meanwhile it also inserted onto the nanowires and stops the on-wire expansion. This effect may not be obvious when the MUA was in excess, as the effect of the MUA on the lateral growth would be stronger, but be strongly suppressed when there was extra OA in the

system. So with the extra OA, the on-wire expansion dominates. The effect of mixing MUA with 3-mercaptopropanic acid may be similar, and ended up to have the very uniform and thick bending wires.

Since all the reaction parameters could be changed half-way during the reactions, these condition-change reactions may also provide further support to arguments. When the MUA was added half-way through the reaction, the lateral growth was expected to be suppressed. Therefore the growth mode should switch from D to B (Figure 5-8a). On the other hand, dilution of the Au and ascorbic acid concentration and adding new Au sources would result the combination of mode D together with mode B. The later reduction mainly focuses on the on-wire expansion as the lateral growth rate was not comparable with the ligand binding rate now (Figure 5-8c). However, if no extra Au was supplied, the dilution would suppress both the lateral growth and the on-wire expansion process. The final mode would look more like the C mode instead (Figure 5-8b).

5.4 Conclusion

In summary, we have synthesized a novel nanobracelet structure and investigated its formation mechanism. The nanobracelet was formed by growing Au onto the ultrathin Au NWs rings formed by phase transferring to aqueous solution. The HAuCl_4 was reduced by the L-ascorbic acid and form the separated blocks with the presence of the MUA ligands. The MUA ligands were

the key factor that induces such growth. The growth mode after initial nucleation could be divided into the on-wire expansion and the lateral growth that is perpendicular to the wire axis. The difference of the two growth directions created a variety of the structures, while these two growth directions are affected by the ligands. The lateral growth rate depends on the competition between the Au reduction rate and the MUA ligand absorption rate, while the on-wire expansion affected less by the MUA ligand. However, it is remain unsure whether there is ligand exchange between the OA on the original wires and the MUA. Though there are other arguments state that the dynamics of OA should not be high under such aqueous condition.

The nanobracelets, as one type of complex nanostructures, are potentially applicable as catalysis or SERS substrates. Other applications based on its plasmonic effect or conductive effect could also be explored in the future.

5.5 Bibliography

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Chapter 6 Twisting the Ultrathin Au Nanowires by Ag Alloying

6.1 Introduction

Ultrathin nanowires (NWs) have been synthesized with a variety of the compositions and diameters.^[1] Many approaches have been developed, such as the template method,^[2] the chemical deposition (including the Vapor-Liquid-Solid deposition)^[3] and the direct e-beam construction^[4] *etc.* Among them, the synthesis of the ultrathin gold nanowires (Au NWs) is usually achieved with the solution-based wet chemistry method.^[5] The Au NWs with the diameter less than 2 nm can be typically synthesized in a hydrophobic environment. A number of the synthetic protocols have been reported in the past a few years, most of them involving oleylamine as the ligand.^[5a, 5c, 6] The oleylamine ligand could function as both the reducing agent and the capping agent, as many literatures proposed that it formed channel-like templates to induce the anisotropic deposition of the Au.^[5a]

The literature reported oleylamine-stabilized Au syntheses are slightly varied at the solvent conditions or the reducing agent used. While these syntheses are more or less different, many of them proposed that the ultrathin Au NWs

produced under such condition are single crystal in nature. The growth direction was along the $\langle 111 \rangle$ direction. However, as many literatures mentioned, there is problem associate with the characterization of the ultrathin NWs, especially those thinner than 2 nm.^[5b] These NWs are found not stable during the TEM characterization. When irradiate by the electron beam, the thin wire quickly break down into small segments. This problem raises the ambiguity associate with the nanowire lattice structures, and may lead to overlook of the some details.

Transformation from one type of nanostructures to another can be very useful in terms of creating novel and unconventional nanostructures. One common method of nano-transformation is to grow a second material on the preformed nanostructures. Core-shell nanoparticles of a variety of compositions have been widely formed by growing the shell block onto the existing core nanoparticles.^[7] The shape of the nanoparticles can also be altered during the shell growth, giving rise to different properties or even enhanced properties. Janus or heterodimers can also be obtained in a similar way, usually with modified experiment conditions.^[8] Encapsulation can do similar effect as growth.^[9] Sometimes it can give even more innovative products, for example, nanocoils have been obtained by polymer encapsulating of Au NWs or restrict carbon nanotubes in nano-emulsions.^[10] The growth induced nano-transformation can also create complex structures if the original

nanostructures are one dimensional. Double helix of nanowires was reported by coated Pt/Pd onto the Au-Ag alloy NWs.^[11] In this case, the growth of the shell outside the initial wires induced the twisting, as the initial Au-Ag NWs have the special type of the Boerdijk-Coxeter-Bernal (BCB) lattice. The strain in this naturally twisted lattice was built up as the shell grown thicker. In order to release the strain, the wire twisted back to become double helix. Therefore the initial lattice structure was crucial for determining the morphology of the final products. By applying the nano-transformation on the existing morphology and analyzing the outcome changes, we would be able to reveal more on some of the structures that are difficult to characterize.

Furthermore, while one-step reactions most of time yield only single component products or simple and highly symmetric nanostructures, further development or modification are often used to increase the complexity of the nano building blocks, which are desired for the development of potential applications as well as the more complex nano devices.

Ag has very low lattice mismatch with the Au (0.24%). Au-Ag core-shell nanoparticles with epitaxial lattice have been widely reported during the past few decades. There are also plenty of reports of the Au-Ag alloy nanostructures. Usually the two metals are co-reduced together to form the alloy. Au-Ag alloy nanowires have also been reported, with the co-reduction process, the obtained the wires are straight in nature but have the phenomenal BCB type of lattice.

6.2 Materials and Methods

6.2.1 Materials

All chemical reagents were used as purchased without further purification. Hydrogen tetrachloroaurate(III) hydrate, 99.9% (metal basis Au 49%), H₂O₂ (35% v/v), Hydroquinone (99%) was purchased from Alfa Aesar, Oleylamine (approximate C18-content 80-90%) was purchased from ACROS Organics. Deionized water (resistance > 18.2 MΩ/cm) was used in all reactions. All other chemicals were purchased from Sigma Aldrich. Copper specimen grids (300 mesh) with pure carbon support film were purchased from Beijing XXBR Technology Co.

6.2.2 Methods

Preparation of TEM samples. TEM images were collected on a JEM-1400 (JEOL) Transmission Electron Microscope operated at 100 kV. A sample solution was dropped on the hydrophilic surface of the TEM grid. Finally, a filter paper was used to wick off the excess solution on the TEM grid, and the grid was dried in air for 30 min.

Synthesis of Au NWs. The method used here was based on the previous report.^[6c] 3 mg of the H₂AuCl₄ was dissolved in the hexane (2.5 mL) containing 100 μL of the oleylamine. After addition of 150 μL of triisopropylsilane (TIPS), the mixture was left unaffected for 5-10 hours. The color of the solution turned from orange yellow to almost colorless and then began to appear brownish and

finally dark brown. The solution can be used for two weeks.

For preparation of the Au NWs in THF, the solvent could be replaced directly with same amount of THF.

Purification of the Au NWs. The Au NWs can be purified with gradient centrifugation reported before.^[12] 200 μL of the as-synthesized solution was put on top of the centrifugation solution (1 mL) made of 20% CHCl_3 :THF (v/v), and centrifuge at 8.1g for 30 min. The middle colored layer (about 400 μL) was collected and washed with 1 mL EtOH at 5.2 g for 8 min. The purified Au NWs can be dispersed in THF.

Preparation of the twisted Au NWs. The purified Au NWs (originally 200 μL) were dispersed with 600 μL of THF. 100 μL of the solution was further diluted 10 times into 1 mL solution. 40 μL of oleylamine was added to maintain the ligand concentration the same as the Au NWs growth solution. Then 15 μL of AgNO_3 solution (100 mM in H_2O) and 40 μL of H_2O_2 were added in sequence. The reaction mixture was left for 15 minutes. For TEM characterization, it can be directly dropped onto the TEM grids, or can be concentrated by centrifugation with 2X volume of EtOH at 5.2g for 8 min.

Preparation of the twisted bundles. The procedure was almost the same as the normal growth condition, only except that the H_2O_2 was added 10-30 min later after mixing the AgNO_3 with the Au NWs.

Preparation of the NWs incubated with Ag NPs. Oleylamine-stabilized

Ag NPs were first synthesized with reported method.^[13] 1 mmol of AgNO₃ was dissolved in 20 mL of oleylamine to form a solution (ultrasonication may be needed), which was slowly heated to 180 °C under nitrogen flow. NP growth was carried out at this temperature for 1 h. To wash the Ag NPs, 500 µL of the solution was taken out and washed with EtOH for 2-3 times. The Ag NPs used for incubation was calculated to contain the same amount of Ag with the AgNO₃ used for normal synthesis.

Incubation of the Au NWs with dodecanethiol. The purified Au NWs can be directly dispersed into the dodecanethiol contained THF solution and incubated at room temperature.

6.3 Results and Discussion

Here we report a novel type of twisted nanowires synthesized from the ultrathin Au NWs. The ultrathin nanowires were synthesized following the reported methods. Despite the literatures reports that these ultrathin Au NWs are single crystals in nature, the transformation of the wire upon Ag deposition does suggest other unknown structural properties. The as-synthesized NWs were purified by gradient centrifugation and re-dispersed in THF. Oleylamine was also added again to stabilize the wires. AgNO₃ was then added as aqueous solution, followed by the addition of H₂O₂ as the reducing agent. The solution turned yellow or sometimes brown due the formation of Ag particles, and significant amount of bubbles were formed, signature the reduction of Ag. The

Figure 6-1 a) Scheme illustrating the transformation of the ultrathin Au NWs into double helix Au-Ag nanowires. TEM images of b) ultrathin Au nanowires and c) double helix Au-Ag nanowires. d) point EDX results of the nanowires. Scale bar = 50 nm.

color would fade a little bit after a few minutes, but still be pale yellow. The twisted NWs can be collected by centrifugation with ethanol, and re-dispersed in THF.

Figure 6-1b & 6-1c shows the as-synthesized ultrathin Au NWs and the twisted nanowires. The as-synthesized Au NWs are generally around 1.6 nm in width, similar with previously reported. After the Ag alloying, the width of the nanowires increases to about 2.05 nm. The stability of the nanowires under electron beam also improved. It has been widely reported that the ultrathin nanowires break into short segments during the TEM observation, probably due to the heating and electron activation. Figure 6-1b does include a significant number of such breakages. The twisted nanowires on the other hand are more resisting to such breakage, probably due to the slight increase in diameter and the improved strength of the solid solution compare to the pure Au NWs. The length of both the as-synthesized Au NWs and the alloying wires can extend to micro meters. Besides the double helix twists, there were also twists formed by three strands of wires or more. The triple twists may because of the turning back of one of the two twisted strand (Figure 6-1a, 1), or a nearby straight wire is captured by a twist (Figure 6-1a, 2). The quadruple twist due to the further twisting of a twisting wire could also be observed occasionally.

However, the alloying wires usually form tangled networks and twisted together, making it hard to determine the exact length as well as the yield of twisting. It is almost impossible to observe one single twisted wire, and the crossing of wires making it hard to distinguish. This is easy to rationalize as the long wires can easily tangle during twisting. This tangling causes it difficult to

characterize the yield of the twisting. Another problem associates with the inhomogeneity of the twisting. For some cases, it can be observed that the wire is not twisting as a whole and the twisting only began from a long distance to the end. Therefore even if a straight section of wire is observed, it cannot conclude that it is an untwisted wire. Only the 100% yield can be claimed, if all observed parts of the wires are twisted.

The nanowire twisting happens surprisingly fast, though it concerns the movement of such a long wire over the micrometer scale. TEM samples prepared only 5 seconds after the mixing of all ingredients already showed significant yield of the twisted wires. This indicates that both the Ag reduction and the change of the wire conformation are extremely fast. Simply mixing of the AgNO_3 and the H_2O_2 would have not reaction, yet the reduction is quite strong (large volume of bubbles) when there was ultrathin Au NWs presented. Therefore it might assume that the Au NWs acted as the role of catalyst for the reduction of Ag under such circumstances.

The EDX result of the twisted NWs confirmed that they were Au-Ag alloy (Figure 6-1d). There is always significant amount of the by-product Au NPs during the synthesis of the ultrathin Au NWs. However, EDX results shown that there was no Ag deposition on these particles. Although there were excess of Ag precursors, they would rather form homogeneous nucleated Ag NPs, instead of getting deposit on the Au NPs and form core shell structures. This implies the

core-shell structure is most probably not favorable under such condition. Therefore it is also quite impossible to form the Au@Ag coaxial core shell nanowires. An alloy nanowire is a more reasonable explanation for the Ag deposition on the Au NWs. The ultrathin NWs, compare to the Au particles, are much thinner and less stable structures, which may facilitate the Ag reduction and alloying process. Ag get reduced on the Au NWs and immediately diffused into the wires, and cause the change of the lattice structures of the thin wire and yield the twists.

6.3.1 Ligand effect

There might also be argument that it was the ligand, oleylamine that function a wired way to altering the morphology of the nanowires and leads to the twisting. There was reported case that the organic polymer encapsulation can mechanically restrict the nanowire inside the polymer micelles and formed coils. Therefore the ligands effect must be excluded as well. The concentration of the ligands (oleylamine) was adjusted from 0.5% (v/v) to 32%, and it was found that the nanowires twisted and formed double helix under both extreme conditions (Figure 6-2a and 6-2b). The difference came from the gaps in the pitches, which were maintained by the existence of the ligands. Without sufficient oleylamine, the wire collapsed together and the separation disappeared. Other than this, oleylamine seems not significantly affect the twisting of the wire, as the results were almost the same when the concentration

Figure 6-2. TEM images of the Au-Ag NWs synthesized with a) 0.5% (v/v) oleylamine, b) 32% oleylamine, c) 4% octadodecylamine and d) dodecylamine as capping agents. Scale bar = 50 nm.

of the oleylamine increases from 1% (v/v) to 32%. The quantity of the Ag NPs by-products was also controlled by the ligands amount. Since oleylamine would bind to Ag (I) too, the rate of reduction would be slowed down if more oleylamine was present in the system and thus there would be fewer particles. Therefore it was quite clear that the oleylamine functionalize as the capping

agent which stabilize the nanowires as colloids, but would have no significant effects on the twisting. Other ligands that have similar functions would thus do the same work. Indeed, when the ligands was switched to octadecylamine and dodecylamine, the saturated amino hydrocarbon, similar double helix of Au-Ag wires can also be obtained (Figure 6-2c and 6-2d).

6.3.2 Effect of Ag and Ad sources

The twisting of the nanowires is thus strongly related to the Ag addition. The Ag amount does affect the yield of the twists very much. Only when sufficient amount of Ag precursor was added, twisted NWs could be observed (Figure 6-3a). Above the threshold, the yield of the twisted nanowires can roughly be related to the total AgNO_3 added into the system and has been mentioned above, excess amount of the Ag would form the Ag NPs by-product (Figure 6-3b). It should be noted that, when the AgNO_3 amount added was decreased to half, only the yield decrease to half but not the whole twisting degree decreased.

However, although there is no “half-twisted nanowires”, the pitch length of nanowires twists varies greatly from one wire to another, and can even be different within one single wire. Sometimes the head can circle very big. This further indicates the different degree of twisting within the wire. The fact that the whole twist wire only to one direction means that there is an underline regularity associated with the process, which drives the wire turns only to one direction. Such regularity should be a constant torsion that comes from the

strain caused by Ag diffusion or the lattice structure reconstruction.

The Ag reduction is thus the key for nanowire turning to the twists. The question remain becomes whether the Ag (I) or the Ag (0) takes the effect for nanowire twisting, and what is the effect of the anion. Two other easily accessible Ag salt, AgClO_4 and CF_3COOAg were used to replace AgNO_3 as the Ag precursor, and both of them could give the double helix nanowires indistinguishable to the AgNO_3 ones (Figure 6-3c and 6-3d). Therefore the effect of the anion can be excluded. Simply incubating the ultrathin Au NWs with the AgNO_3 solution sometimes could lead to a very low yield of the double helix nanowires (Figure 6-3f). However, this result must be treated with caution since the oleylamine is reductive. As the yield of incubating of Ag (I) was not comparable with the case that involves reducing agent, it could be deduced that Ag (0) is the key agent that cause the nanowire transformation.

On the other hand, incubating the Au NWs with the oleylamine-stabilized Ag NPs could give a much higher yield (Figure 6-3e). Both the simple incubation and with presence of H_2O_2 would yield twisted wires. The transferring of Ag (0) to the Au NWs is believed through Ostwald ripening, and promoted by the oxidative etching under the ambient condition. If the environment is oxygen and water free, the color of the Ag NPs could keep more than 20 hours. Under the normal air condition, the yellow color of the Ag NPs would quickly disappear after being added into the Au NWs solution. Particularly when H_2O_2 .

Figure 6-3. TEM images of the Au-Ag NWs synthesized with a) 1 μL of 100 mM AgNO_3 and 10 μL H_2O_2 , b) 30 μL of 100 mM AgNO_3 and 40 μL H_2O_2 , c) 15 μL of 100 mM AgClO_4 and 40 μL H_2O_2 . And d) 15 μL of 100 mM CF_3COOAg and 40 μL H_2O_2 . TEM images of the ultrathin Au NWs after incubation with e) oleylamine stabilized AgNPs and f) 15 μL of 100 mM AgNO_3 solutions.

was also added, then color faded immediately with a lot of bubbles formed,

indicating the fast etching of Ag NPs with the H_2O_2 . The change of the Au NWs started as soon as the color of the Ag NPs disappearing. But generally speaking, the rate of change is slower than that of the normal Ag reduction method with H_2O_2 . This thus allowed us to observe the intermediates that are normally not able to catch.

6.3.3 Reducing agents and other metals

Since reducing agent H_2O_2 is both oxidative and reductive, other reducing agents were used to replace it, so as to eliminate the potential effects originating from its oxidative property. Hydroquinone (HQ) has no oxidative property and can also result the twisting of the nanowires (Figure 6-4a). Therefore the oxidative nature of H_2O_2 should not be critical in the process. The HQ treated nanowires case, however, did appear different. In contrast to the H_2O_2 case where the final wires are always thin and uniform, HQ has no oxidative power therefore the Ag deposition continues after the twisting, and sometimes gives thicker wires. The color of the solution for the HQ case was yellow due to the formation of the Ag NPs by-products, while H_2O_2 can etch the excess amount of the Ag NPs.

When a very strong reducing agent, for example NaBH_4 was used, no twisting was found (Figure 6-4b). As mentioned above, for H_2O_2 reduction, reaction only took place when the Au NWs were present. Therefore the ultrathin NWs may act as catalyst and the Ag reduction might initially happen on the Au

NWs. Although the H_2O_2 reduction was also considered as quite fast (twisting in 5 s), the transformation of the Au NWs could happen. The reduction with NaBH_4 is even faster and does not need the Au catalyst. Therefore Ag (0) would have no time to diffuse into the Au NWs but homogeneous nucleate to form Ag NPs.

Such type of the nanowire transformation, however, is only applicable for the Ag addition. Under the similar condition, when HAuCl_4 was used, only thickening of some segments occurs (Figure 6-4e). This is easy to understand as for such a long wire, Ag deposition cannot be uniformly grown on every site along the wire. And the rate of diffusion for Au (0) is not high enough for generating a uniform coating. If a stronger reducing agent, such as the TIPS were used, the excess Au would form Au NPs and would not cause any twisting as well. Other noble metal such as Pt and Pd also yielded no twisting (Figure 6-4c and 6-4d) in several different stoichiometry conditions. This is quite different from the previous reported case,^[11] where the reduction of the Pt, Pd and Au with the presence of Au-Ag nanowire led to the double helix wires. Thus these two types of the twisted NWs should be fundamentally different and may even be complementary. Although the Au deposition could not induce nanowire twisting, the obtained Au-Ag twisted nanowires could be thickened by the further growth of Au (Figure 6-4f). In this case, the deposition is quite uniform.

Figure 6-4. TEM images of the Au-Ag NWs synthesized with a) 15 μL of 100 mM AgNO_3 and 40 μL of 100 mM hydroquinone, b) 15 μL of 100 mM AgNO_3 and 40 μL of 100 mM NaBH_4 , c) 15 μL of 100 mM H_2PtCl_4 and 40 μL of 100 mM hydroquinone, and d) 15 μL of 100 mM K_2PdCl_4 and 40 μL of 100 mM hydroquinone, e) 15 μL of 100 mM HAuCl_4 and 40 μL H_2O_2 . f) TEM image of the HAuCl_4 grown on the double helix Au-Ag nanowires. scale bar = 50 nm.

The synthesis of the ultrathin Au NWs here involved the use of the reducing

agent TIPS. One may argue that only such nanowires synthesized the specific condition can form such unique type of alloy nanowires, as the defects and twining in the lattice should be closely related to the synthesis condition. The reducing agent used in the synthesis of the ultrathin Au NWs may left in trace amount and cause the nanowire twisting in the following A reduction. Several literature protocols were followed to synthesize Au NWs without TIPS, and grown Ag to see if there was any twisting. The result shown that, such twisting behavior by Ag reduction is quite general for the oleylamine-stabilized ultrathin Au NWs. Despite the yield of the nanowires was not as high due the synthesis capability and the yield of the twisting was also not as good as the TIPS reduced nanowires, double helix twist could still be found in the other systems that have no TIPS at all.

6.3.4 Synthesis conditions of the ultrathin Au NWs

In fact, the yield of the nanowire twisting, although is difficult of quantify due to the tangling, are qualitatively different from one system to another and even varies among the different batches and different time of the same batch of ultrathin Au NWs synthesized. The yield of twisting of the Au NWs synthesized in hexane (Hex-Au NWs) was significantly different from those synthesized in THF (THF-Au NWs). For the Hex- Au NWs, a near 100% yield can be achieved for most of the batches, but the yield for the THF-Au NWs usually would not over 50%. The Au NWs synthesis procedure and the following

Figure 6-5. TEM images the Hex-Au NWs incubated in 0.1% oleylamine THF solution for a) 12 hrs, b) 36 hrs and c) 84 hrs. d) Hex-Au NWs incubated in THF

workup and the Ag growth processes were exactly the same except the solvent during the Au NWs synthesis. Such difference implies that the twisting behavior is closely related to structure of the Au NWs which might be influenced strongly by the environment conditions during the synthesis. Indeed the reduction of the HAuCl_4 in THF by TIPS is usually much faster than in hexane, probably due to the difference in the solvent polarity. The oleylamine behavior would also be different in these two solvents, especially for the THF

which would contain a significant amount of water. The as-synthesized Hex-Au NWs always accompanied with a lot of the Au NPs by-product, making the solution reddish brown, While the THF-Au NWs were much higher in purity and containing few particles. These evidences support the argument that these two types of the NWs are different in terms of the lattice structure. At least there are two types of lattice, one could be twisted and the other not. The Hex-Au NWs contains mainly the former one and the THF-Au NWs probably have both in comparable amount.

We then purposely altered the synthesis conditions in order to produce NWs that deviated from the standard protocols. Temperature is a main factor that could be tuned, and it will affect the nanowires synthesis in many ways. It was found that when the synthesis of the Hex-Au NWs was carried at 60 °C, no long NWs would form. Only short wires appeared and they could not form any twists, but this may also because they are short enough to release the torsion by rotation. When the synthesis temperature was reduced gradually to 50 °C and 40 °C, a continuously trend can be observed. At the lower temperature of 40 °C, the length of the nanowires was comparable with the room temperature sample, and the twisting rate was still high. However, at 50 °C, the yield of the twisting decreased significantly, although the Au NWs appeared to be in similar length with the 40 °C ones.

Other common solvent systems, such as toluene and dioxane, were also

attempted for synthesizing the ultrathin Au NWs. Though ultrathin Au NWs could form in these systems, there was almost no twisting of nanowires after the following Ag growth. This further supports the existence of different lattices for the appeared-the-same ultrathin nanowire, and the solvent environment during the Au reduction would strong affect the lattice structures of the Au NWs formed. The typical explanation of the formation of the Au NWs involves the packing the oleylamine ligand into micelle like channels, which would spatially restrict the Au deposition and leading the linear extension the wires. Solvent polarity and solubility of the oleylamine would affect such packing, which in turn affect the ripening process. If there is any structural strain accumulated and preserved by the oleylamine coating, a slight different solvent environment may help to relieve it by formation of incomplete ligands coatings.

The effect of ripening could also be illustrated with the incubation experiments. During the purification, the surface oleylamine that stabilized the Au NWs would be partially removed. Therefore if no extra ligand was added, severe ripening effect would occur. There was no obvious difference between the decreased oleylamine concentration and the high oleylamine concentration. When the Hex-Au NW was purified and incubated in the 0.1% oleylamine THF, the yield decreased gradually. At 84 h, very little twisting could be observed (Figure 6-5c). It suggests that the lattice structure of the nanowire changes with the incubation time. If the nanowires were incubated in a ligand deficient

environment, then the ripening can be quite fast. Larger nanoparticles appeared after one day (Figure 6-5d). Interestingly, those NWs that survived the ripening almost all become twists after Ag treatment.

6.3.5 Mechanism discussion

We can now make a rough summary: there are at least two different types of lattice structures of the ultrathin Au NWs. One of them could be twisted by the Ag, presumably by the invasion of the Ag (0) and forming the Au-Ag solid solution, while the other would not be twisted. The reconstruction of the lattice would either strain or release the preserved strain of the ultrathin Au NWs, causing the nanowires twisting.

We then examined the HRTEM of the ultrathin Au NWs and the twisted Au-Ag NWs. Although the Au NWs are not stable under the TEM beam, some pieces of the evidences could still be collected. As shown in Figure 6-6, the HRTEM image of the Au NWs before Ag deposition includes **three** different types of structures. Firstly, there are sections that the wire grows along the $\langle 111 \rangle$ zone axis. They are single crystal in nature, same as the literature reports (Figure 6-6b). However, significant amount of twinning structures are also observed. The twin planes are the (111) planes and these sections contain a lot of the stacking faults. Lastly, there are sections that the lattices become too complex to be clearly assigned as any types of simple lattice planes. These blocks typically contain fan-like lattice structures, which is similar to the

Figure 6-6. a) TEM images of as-synthesized Au NWs. b-d) enlarged part in a. (b) shows a single crystal lattice similar to the literature reports. (c) shows a highly twinned structures and d) shows irregular lattices structure similar to the B-C-B type of lattice.

simulated Boerdijk-Coxeter-Bernal (BCB) type twisted lattice.

The mechanism of the Ag addition induced twisting remains unclear. When Ag (I) was added together with reductant, it would commonly expect the reduction and the nucleation of Ag (0). A common observation is the formation of Au@Ag nanoparticles when Ag is reduced in the presence of the Au NPs. Since there is very little lattice mismatch (0.1%) between these two noble metals, heterogeneous nucleation shall happen in an epitaxial manner. However this is the case here. If the Ag formed a conformal coating outside the Au NWs, the nanowires should keep straight and the thickness of the resulting coaxial core-shell wire should be determined by the amount of Ag addition and have no obvious limit. The facts that Pt and Pd reduction could not induce such

twisting further support such argument. Pt and Pd both has larger lattice mismatch with Au, if it was the strain induced twisting similar the Wang *et al.* reported case, then these two metals should do an even better job.

As stated above, on order for the nanowire to twist, a constant torsion must be applied throughout the whole wire. Otherwise the wire would not twist to one direction but become zigzagging. Given the length of the Au NWs, it remains a great question why would such unbalancing of force was exerted for the whole wire. There are several possible explanations. One hypothesis would be that the lattice of the original wire was regularly twisted like the BCB lattice, therefore when the Ag addition relaxes such strain and it turns to the other direction (original BCB). Given the fact that Ag could diffuse into the lattice and also on the surface of the Au NWs, there could be also another hypothesis that the Ag altered the lattice structure of the Au when diffuse inside, and cause the whole lattice structure of the NWs to switch from common single crystal phase or stacking phase to the BCB like phase, making the wire twist (induced BCB).

The first original BCB hypothesis can explain well why the nanowire twists. BCB lattice has itself internal chirality, therefore has a constant turning direction. However, characterization of BCB remains a great challenge, owing to the stability of the ultrathin Au NWs as well as the complex lattice pattern of such highly twined structures. Also according to the literature report, Au, Pt and

Pd were capable to “untwist” the BCB lattice but Ag could not. This is exactly the reverse case here, where only Ag addition caused the nanowire to twist.

The lattice change argument (induced BCB) based on the fact that the nanowires are extremely thin, therefore the diffusion rate of Ag inside the nanowire is expected to be very fast. The fact that the final twisted nanowire is sufficiently thin and smooth also supports this argument. Given the long length of the nanowire, it would be impossible to have uniform coating (uniform nucleation sites). The core-shell coating in the literature report indeed was not as smooth as this case.

The yield of the nanowire twisting also provides clues for the mechanism. Ostwald ripening gradually leads to formation of thicker wires and eventually larger particles which have lower surface to volume ratio. The decreasing twisting yield suggests that the as-synthesized were originally in a relatively higher energy state and unstable. Its lattice structure would change slowly by diffusion and Ostwald ripening. After incubation, the Ag diffusion would not alter the lattice structure that drastically, therefore the yield would decrease.

6.3.6 Dodecanethiol studies

In order to further study the mechanism of the NWs twisting mechanism, we explore the effect of adding dodecanethiol into the system. As a thiolated ligand, dodecanethiol is expected to be a stronger capping agent that could bind to the Au NWs than oleylamine. An interesting observation is the ultrathin Au NWs

Figure 6-7. TEM images of Au NWs incubated with a) 1 mM, c) 0.05 mM e) 0.01 mM dodecanethiol, b, d, f) Au-Ag NWs obtained by grow Ag on the NWs in (a) (c)and (e respectively; g-h) Au-Ag helix NWs incubated with dodecanethiol after the Ag growth. The original Au NWs was synthesized in hexane (g) and THF (h).

become zigzagged when sufficient dodecanethiol was added instead of

oleylamine after the purification (Figure 6-7a). Such zigzagging behavior was highly improbable to be the result of shear force, such as 11-mercaptoundecanoic acid which is another thiolated ligand, would not cause this when binds to the ultrathin nanowires. A possible explanation is the strong interaction between the dodecanethiol and the surface Au/Au⁺ might cause the deformation of the NWs.

Such dodecanethiol-stabilized Au NWs would not further form NWs twists when treated with Ag (Figure 6-7b). When the concentration of dodecanethiol was reduced to half, then roughly half of the Au NWs were affected and became zigzagging wires. Growth Ag onto this type of half-zigzagged wires would result interesting “half twisting-half zigzagging” wire coils. The parts that were not affected by dodecanethiol would still twist, and sometimes even carried along the zigzag sections (Figure 6-7c and 6-7d). Further reduction of the concentration of the dodecanethiol added would have most of the Au NWs unaffected. And the Ag growth after this yielded almost the same NWs twists like those without dodecanethiol (Figure 6-7e and 6-7f). It seems that the two treatments, Ag deposition and the dodecanethiol incubation are in competition with each other. If the Ag deposition was done first, then the twisted NWs would not be further altered by the dodecanethiol either (Figure 6-7g).

The situation of the THF- Au NWs is also worthy noted. As we know the THF-Au NWs have lower yield of twisting, therefore there would be straight wires left in the Ag treated sample. Direct incubation of this sample in the

dodecanethiol environment, however, shown no obvious change. Those straight wires remain straight in such environment. Two possible scenarios can be proposed: 1) there are Ag deposition on those straight wires in the THF-Au NW case, but somehow for this type of Au NWs, no structure transformation take place; 2) Both the Ag deposition and the dodecanethiol change the conformation of the Au NWs by relaxing any possible strains built during the synthesis, and the straight wires does not have such strains, therefore be inert to both of the treatment. Given the fact that the THF-Au NWs would be altered by the dodecanethiol treatment after long incubation, the first scenario is more valid here.

In addition to the normal twists, there is also bundle formation sometimes in the samples. Generally the bundle formation was due to the hydrophobic nature of the oleylamine-stabilized nanowires. Since the AgNO_3 was added as the aqueous solution and the H_2O_2 also contained 65% of water, the solvent environment became slightly more polar; therefore the NWs aggregated and form bundles. If the H_2O_2 was not added immediately after the mixing the AgNO_3 with the nanowire solution, the significant quantity of bundles would be observed. However, even the wire bundled, the twisting happens. Although the movements of the nanowires in the bundles were restricted by their neighbors, making them hard to form real twists, the whole bundle still is affected by the structural transformation of the single wires. Fringes can be observed regularly

on the bundle. These fringes are the diffraction patterns that associate typically with the spiral bundles that are usually observed in the twisted silica nanowires.

6.4 Conclusion

In summary, we have synthesized the nanowire twists from ultrathin Au NWs. The twists were induced by the formation of the Au-Ag alloy in the presence of Ag (0), which has never been reported before. It is highly suspected that the twisting originates from the lattice structure of the ultrathin Au NWs, which has been widely in the literature as the single crystal. However, from our HRTEM studies as well as the control experiments, more complicated microstructures such as the BB type lattice exist in these thin wires. The microstructures are closely associated with the synthetic conditions, and also affect the yield of the twisting. Ag alloying process or dodecanethiol binding would both relax the lattice, however in two different ways. The complicated microstructures have never been reported in this type of nanowires, and potentially have the application such as the nanocatalysis.

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Chapter 7 Summary and Outlook

7.1 Summary

There is no doubt to predict that the development of the nanoscience would follow the track that all of the currently highly developed fields, for example the organic synthesis, had gone through, where the initial random or coincident discoveries accumulate the knowledge at the early stage and systematic directions and rational design come in to give the emerge of the field. In such sense, gaining the synthetic capability to construct the nanoscale building blocks and studying the basic mechanisms for the current synthetic methodologies would both be critical not only for generating useful materials but also the progress of the whole field. In this thesis, we have been focusing on the synthesis of the one dimensional nanomaterial, Au nanowires and its derivatives, as well as the mechanism studies of the formation of these unusual nanostructures.

We first developed and studied the mechanism of the Au NWs synthesized with the Active Surface Growth mechanism. Synthesis of one dimensional nanostructures has been quite a challenge in the nanoscale due to the intrinsic symmetry of many crystal lattices. Breaking such symmetry usually requires

innovative designs. Though in our case the initial discovery was made by accident with the colloidal substrate, we were capable to extend this synthesis to the substrate-based system, and investigate the underlying reasoning of this novel growth. With advances of the substrate system, including the aggregation-free and the ease of characterization, we confirmed such growth was induced by difference of Au deposition between where the ligand 4-MBA adsorbed and the substrate contacts where APTES with amine group was attached to the Au seeds. The relatively more active site at the interface of the wire bottom became the active surface for the continuous deposition of Au while the lateral growth was blocked by the ligand. We studied the exact site of the growth by tuning the ligand concentration and the reduction rate, and also the correlation of the nanowire diameter with the two parameters. Moreover, the substrate generality was extended to other materials such as papers *etc.*

Followed with the initial discovery and the study of the Au NWs and the active surface mechanism, we carried on the survey of the ligands which are suitable for this type of the growth. It was found that the thiolated ligands with an aromatic backbone would be the good candidates. The flexibility of the backbone was crucial for the coverage of the ligand to the Au surfaces. And the aliphatic ligands are not capable to provide sufficient coverage. The ligand generality could also be used for producing the unconventional materials. Thicker nanowires with conical morphology were achieved by mixed use of the

good and bad ligands. The hydrophobicity of the substrates was decided by the thickness and morphology of the Au coating as well as the surface properties of the Au NWs which can be adjusted with the ligand hydrophobicity. In such sense, surfaces from hydrophilic to superhydrophobic were generated.

Next, the seed variety was also surveyed in terms of seed type, size and density. The Rayleigh instability of the active surface was discovered by using rods as initial seeds. There is no requirement for the seed morphology for the growth of the nanowires, and even huge aggregate architecture of the Au NPs was tested eligible for growth the nanowires and yielded large comb-like structure. With the understanding of the ligand selectivity, seed variety and growth mechanism we were able to achieve the programmable growth or rational design of the Au nanostructures. The change of the seed morphology could lead to nanowires with different head, while the tail of the nanowires can also be tuned larger or smaller with the ligand concentration. Preliminary result of the segmental nanowires can be produced by adjusting the ligand concentration several times. More innovative architectures include nanoflowers was achieved by combining the change of ligand density and control of material deficiency.

The active surfaces were achieved by the substrate and the strong ligand in the substrate-bounded nanowire cases. Similar controls could then be attempted in the colloidal system. This time, the growth of the Au on the preformed

ultrathin Au NWs was studied. With the competitions between the oleylamine stabilized Au surface and the 11-MUA absorbed surface, nanobracelets were produced. The key idea was to rationalize the different growth rates of the lateral growth and on-wire extension. Since there were no pre-attached ligands, the situation became more complex and the nucleation rate should also be taken into account. With the combined effect of the nucleation and ligand effects, the trend for increasing the MUA concentration with the product morphology exhibits an unusual “U” shape relationship, with the two extremes gave evenly thickening of the NWs and the moderate amount ligand yielded the segmental growth similar to bracelets. The kinetics control here can be quite useful for further studies on controlled growth.

Finally, we observed nanowires twists when growing Ag onto the preformed Au NWs. The system was different from the above as there was nanoscale transformation induced by not by ligand but the Ag growth. Nevertheless, the mechanism behind such transfer is still of importance for both understanding the oleylamine-stabilized ultrathin Au NWs and the Ag deposition behaviors. The ligand effects were carefully excluded, and such unique transformation of straight wire into double strand helix was found closely associating with the change of the Au NWs lattice. The Ag addition is probably the cause of twisting, but even the Ag diffusion inside the lattice is not directional; therefore there must be another explanation for the constant torsion that leads to the twisting.

As most of the literature reported that this type of the Au NWs are single crystal in nature, this result do raise another possibility that more complex lattice would take place in such system.

7.2 Outlook

On the basis of the understanding of the Au nanowire synthesis and the distinctive ability of these mythologies in developing novel and innovative structures, as well as the strategies developed in this thesis, several future works were proposed in following:

(1) Electrochemical synthesis of the Au NWs and Au nanostructures. The active surface mechanism for growth of the nanowires relies on the competition between the Au deposition rate and the ligand absorption rate. While the later could be adjusted by the concentration of ligand in the solution, the former was usually more difficult to control with the traditional wet chemistry synthesis. The electrochemistry on the other hand can provide better controls in terms of fine tuning the rate of reduction. With the electrochemical reduction, we may be able to precisely control the nanowire diameters. Another advantage of using electrochemistry was that it can make the adjustment immediately by changing the voltage applied. Therefore the segmental wires may be achieved better than what we obtained from the current solution control. Furthermore, Au nanostructures may be obtained in a similar way as the idea of 3D printing. With programmable changing of the reduction rate, a variety of the Au

nanostructures are expected to obtain on various substrates

(2) Patterned nanowire arrays or nanostructure arrays. Nanowire arrays are desired in many situations as functional materials. Also in many cases patterns of the nanowire arrays are preferred for deices. A few preliminary studies had been carried out for growing the nanowires into patterns by using the photolithography. Areas covered by the photoresist would be free of the nanowires. In chapter 4, nanorods could be used as seed to generate odd shaped nanostructures. By combining the substrate fabrication methods together with the controlling parameters for nanostructure growth, we can obtain the arrays of rod-seeded nanostructures. Furthermore, patterns may also be constructed by the E-beam fabrications, so as to obtain finer structures (Figure 7-1). Other chemical templates may also been employed as well.

Figure 7-1 Some possible combinations of the nanostructures with lithography work.

(3) Au nanobracelets for SERS studies. In chapter 5, we demonstrated the synthesis of the Au nanobracelets. We have been mainly focused on the mechanism study of the synthetic control. The potential application of this novel Au nanostructure has yet been fully explored. It has been widely studied that hot-spots of the SERS enhancement exist between the aggregated dimers or the curvature of the plasmonic nanoparticles. The spacing between the segments of the nanobracelets is potential hot-spot. SERS active molecule may be employed as the ligand and attached directly during the formation of the nanobracelets. Ligand exchange method could also be employed to attach the SER active molecules. The current nanobracelets are tangled together as they are prepared from the phase transferred nanorings. The method of phase transfer without causing ring structure could be developed to obtain more feasible and regular structure for the analytical studies and applications.

(4) Double helix networks for catalytically applications. The double helix nanowires were synthesized in chapter 6. Au NWs and Au-Ag nanoparticles have both been reported used as catalyst. We have done some preliminary exploration on its catalytic ability on the reduction of 4-nitrophenol. It was found that the double helix can accelerate the reduction rate compare to the pure Au NWs. Moreover, the chiral structure of the ultrathin nanowire may provide possible route to transfer the chirality into the chemical synthesis.

Figure 7-2. The Pd was able to grow on the Au NWs and forming dendritic structures when using N_2H_4 as reducing agent.

(5) Pd/Pt double helix wires. Au has been shown to grow on the twisted Au-Ag nanowires in chapter 6. Other noble metals especially the Pd or Pt could also be explored due to their potential catalytic abilities. Recently the Pd was shown to be able to grow on the Au NWs (Figure 7-2). The double helix Pd and Pt coaxial nanowire could be useful in the field of catalysis, as the Pd and Pt are better catalysts and have been widely employed in many protocols.

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List of Patents

1. Hongyu Chen, Jiating He, **Yawen Wang**, “Method For Forming Gold
Nanowires On A Substrate And Gold Nanowires Formed Thereof”, PCT
patent application.
2. Hongyu Chen, Jiating He, **Yawen Wang**, “supported gold nanowires for
fixed-bed catalysis”, submitted.