Colloidal synthesis and applications of surface-bound metal nanowires

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Colloidal Synthesis and Applications of Surface-Bound Metal Nanowires

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Abbreviations of Chemicals

2-MBA	2-mercaptobenzoic acid
3-MBA	3-mercaptobenzoic acid
4-MBA	4-mercaptobenzoic acid
4-MPA	4-mercaptophenol
4-MPAA	4-mercaptophenylacetic acid
11-MUA	11-mercaptoundecanoic acid
APTES	3-aminopropyltriethoxysilane
APTMS	3-aminopropyltrimethoxysilane
CTAB	hexadecyltrimethylammonium bromide
DMF	N,N-dimethylformamide
HAuCl ₄	hydrogen tetrachloroaurate (III)
NaBH ₄	sodium borohydride
Na ₂ PdCl ₄	sodium chloropalladate(II)
PVP	Polyvinylpyrrolidone
TEOS	tetraethylorthosilicate

Abstract

This thesis focuses on the development and application of a new type of nanowire growth where ultrathin metal nanowires selectively grow from the interface between seeds and oxide substrate. Under this active-surface growth mode, surface-bound metal nanowires can achieve nanowire-substrate hierarchical structures such as vertically aligned metal nanowires which show excellent performance in fixed-bed catalysis. By modifying the reaction conditions, this unique growth mode can also be applied in the growth of bimetallic segmented nanowires as well as chiral nanostructures. The synthesis of these surface-bound nanowires is carried out at room temperature in aqueous solution using solid seeds. This approach of promoting anisotropic growth of nanocrystals into nanowires is novel and previously unknown in the literature (**Chapter 1**). It shows potential for fabrication of complex nanostructures as building blocks in nanodevices.

By employing strong thiol ligands, the nanowires grow from only one side of the seeds. Interestingly, the width of emerging nanowires is independent of the size of the seeds but dependent on the dynamic competition between the ligand diffusion and metal deposition processes (**Chapter 2**). By carrying out designed experiments, a mechanism is proposed that can explain these unusual phenomena. The strong binding of thiol ligands in this system blocks the

deposition of metal on the exposed surface of the seeds, while in turn forcing selective deposition of metal at the ligand-deficient interface between metal seeds and oxide substrates. Subsequently, the instant binding of ligands inhibits the growth of newly-formed surface at the perimeter of the interface, thus conferring the interface higher “activity” for metal deposition.

This method for growing surface-bound metal nanowires is facile and scalable. It can be applied on different kinds of oxide substrates and even trumpet shells to form conductive films. By growing Au nanowires on glass fibres, they can be used in a column for fixed-bed catalysis (**Chapter 3**). With the high loading Au surface and loose packing of glass fibres, both high catalytic capability and fast flow of reaction solutions can be achieved in the system. For the conversion reaction of 4-nitrophenol to 4-aminophenol, the continuous flow catalysis can be achieved with a processing rate about 100 times that of the best literature rate.

This active-surface growth is not limited to the fabrication of Au nanowires. For example, it can also be applied to the growth of surface-bound ultrathin Pd nanowires which cannot be synthesized by any reported methods (**Chapter 4**). With the understanding of the growth mechanism, it is demonstrated that the “active” metal-substrate interface allows the deposition of another metal even when their lattices mismatch. The growth of Pd nanowires can be controlled from the interface of Au seeds and substrate, as well as the interface of Au

nanowires and substrate, thus producing Pd nanowires with Au tips or Au-Pd bimetallic segmented nanowires.

Fabricating chiral nanostructures is one of the important research objectives in nanoscience and nanotechnology. Metallic chiral nanowires are rarely reported because the assembly of symmetric metal atoms in an asymmetric way is difficult. **Chapter 5** demonstrates that the strong binding of ligands (4-mercaptobenzoic acid) in the current system can be made use of to induce the growth of chiral nanowires such as spiral nanowires when the reaction conditions are altered. When excess ligands are present in the system, the uneven binding of ligands at the seed-substrate interface is proposed to induce imbalanced growth rate of Au at this interface. This imbalanced rate makes the growth of emerging nanowires to tilt towards another direction. Thus, the propagation of the curving results in the final chiral structures. Based on the analysis, it is also shown that other thiol ligands can also be used to synthesize chiral nanowires. With the additional understanding of active-surface growth mechanism, further insights can be gained on how different nanocrystals are formed.

This active-surface growth mode is facile as it is able to be applied to different substrates. It can also fabricate a variety of nanowires such as pure metal, bimetallic, chiral nanowires. One of its potential applications in fixed-bed catalysis has also been explored. Active-surface growth mode shows

promising capabilities for the fabrication of complex nanostructures as building blocks in future nanodevices.

Chapter 1 Introduction

1.1 Anisotropic nanocrystals

The study of nanocrystals has been the focus of attention for decades. As the basic building blocks in nanotechnology, nanocrystals are being explored for many applications, which more often than not, demand complex geometries beyond the simple shape of an isotropic sphere. The various degree of anisotropy in structures leads to morphological variety of nanocrystals. Nanowires (NWs) are an extreme case in anisotropic nanostructures (Figure 1-1c), caused by the disparity in the rate of growth along different directions during their formation.

To generate anisotropic nanocrystals, symmetry breaking process must be induced during nanocrystal growth. However, this process is non-trivial. In the growth of nanocrystals, the diffusion of materials towards a nucleation centre is often isotropic (Figure 1-1). Hence, there is a clear gap between the initial state and final anisotropic geometry. The link between them is the factor of symmetry breaking. Identifying this factor is a key to understanding the variety of nanocrystal geometries.

This introduction aims to summarize and categorize the origins of anisotropy of the shape of nanoparticles (NPs). In particular, the fundamental mechanisms

for the growth of NWs will be the main focus. Through the categorization of different methodologies, an overview and understanding of such growth processes will be presented so as to support the theme of this thesis.

Figure 1-1 Schematics illustrating the growth of anisotropic nanocrystals. All the nanocrystals are grown starting from their nuclei. The isotropic diffusion of growth materials in the surrounding environment towards the nuclei should have resulted in the nuclei simply growing bigger. Anisotropic factors which break this symmetric growth can therefore achieve the formation of various geometries. With different growth rates (red versus black arrows), three kinds of anisotropic structures can be obtained: (a) polyhedron crystals, (b) plates, and (c) nanowires.

1.2 Significance of anisotropic nanocrystals

Anisotropy in nanostructures is an intriguing phenomenon and useful in material science and technology. With larger surface area and greater structure diversity as compared to their isotropic counterparts, anisotropic nanostructures not only exhibit excellent electronic, optical and chemical properties, but also provide new technology to industrial applications.

1.2.1 Properties

Anisotropic nanomaterials have shown numerous promising and novel properties. One example is the excitonic lasing action that Yang *et al.* reported in ZnO NW array on sapphire.^[1] The vertical ZnO NW array was prepared by using chemical-vapour-deposition (CVD) method via vapour-liquid-solid (VLS) mechanism. The wide band-gap and large aspect-ratio of ZnO NWs makes the array suitable for room-temperature ultraviolet lasing.

Other than lasing property, anisotropic nanostructures also show waveguiding properties. Among the semiconductor NWs, SnO₂ NWs have proved to be excellent sub-wavelength waveguides.^[2] Their single crystal nature, large refractive index, and high flexibility allows them to act as optical linking elements in a device.

Nanocrystals with diameter less than 10 nm have widely been used as catalysts for catalytic reaction due to their large surface-to-volume ratio (S/V).^[3]

Besides near-spherical nanocrystals, ultrathin nanoplates can also be used as catalysts. Zheng *et al.* have reported the facile synthesis of freestanding ultrathin Pd nanoplates. These nanoplates show excellent electrocatalytic property for the oxidation of formic acid which is better than commercial Pd black.^[4]

1.2.2 Applications

Anisotropic nanostructures such as semiconductor or metallic NWs that have well-controlled components and morphologies have been applied for use in electronic and optical devices. One-dimensional (1D) metallic nanostructures are widely used as transparent electrodes for electronic devices due to their high conductivity and large aspect ratio. The Cui group has reported scalable preparation of transparent electrode with Ag NWs on flexible substrates of polyethylene terephthalate.^[5] Using a similar Ag NW electrode, the Yang group can achieve the visibly transparent polymer solar cell with 4% power-conversion efficiency.^[6]

Dye-sensitized solar cells (DSSC) are another significant type of solar cell. Semiconductor NWs like ZnO have shown their excellent electron-transporting ability as electrode in DSSC devices. For example, the Yang group has developed a DSSC device by using a dense array of crystalline ZnO NWs as anode.^[7] Their rapid electro-transporting ability and large surface area for

loading of DSSC dye makes the high performance of device with a full Sun efficiency of 1.5%.

In addition, the aligned ZnO NWs have been shown to convert nanoscale mechanical energy into electric power, which acts as piezoelectric nano-generators. The Wang group has pioneered the study in this field, and reported that the charge separation across a NW was created due to a strain field when the NW was bent.^[8] This unique property allows the ZnO NWs to be used in the electrical devices.

Another important application for anisotropic nanocrystals is their use as sensors. The high S/V confers anisotropic nanostructures high sensitivity to species adsorbed on the surface. For example, the Cui group used functionalized Si NWs as highly sensitive sensors for detection of PH change and biological species like streptavidin in the solution.^[9]

1.3 General conditions for synthesizing anisotropic nanocrystals

The fabrication approaches for anisotropic nanocrystals have been limited thus far. Top-down approaches such as nanolithographic techniques^[10] can be used to prepare uniform anisotropic nanostructures of high quality. However, further effort is needed to further develop a low cost, practical and highly

efficient technique. Bottom-up methods such as colloidal synthesis are promising because they are easily scaled up, low cost and easily operated. Although a number of colloidal syntheses of anisotropic nanostructures have been reported, there is still a big challenge in using these methods to achieve well-controlled morphology with high yield.

During the nanocrystal growth, the process of crystallization is the main essence in controlling growth and dictating the resulting morphology. The nanocrystal growth process includes two parts: nucleation and growth (Figure 1-1). Normally, this process occurs in a solution phase where the growth materials can move freely. During nucleation, when the concentration of growth materials reaches over-saturation, aggregation of growth materials (atoms, ions or molecules) in the system form clusters (*i.e.* nuclei) with sphere-like shapes which is favoured by thermodynamic control. These newly-formed nuclei will then serve as seeds for the further crystal growth. With the continuous supply of the growth materials, the seeds grow to larger structures. As the surrounding environment for a seed is homogeneous, the isotropic diffusion of growth materials to the seed should result in uniform growth and the emerging nanocrystal maintains a sphere-like shape. Uneven adsorption of growth materials on nuclei surface breaks the symmetry of crystal growth and leads to anisotropic structures (Figure 1-1). Obviously, factors leading to this uneven adsorption will in turn break the crystal symmetry. Controlling these factors can

help in the synthesis of more complicated nanostructures and other kinds of materials.

With different growth rates in different orientation, anisotropic structures can be divided into three categories. When the difference in growth rates in all directions is small, the nanocrystals will be polyhedron with stable facets on their surfaces, which are often found in single-crystalline nanocrystals (Figure 1-1a). The resulting structures are nearly spherical but are strictly still considered anisotropic as the growth rates of the faceted surfaces are not totally equivalent. If growth rates in two directions are much slower than the others, 2-dimensional nanoplates can be obtained (Figure 1-1b). If growth rates in all directions are unfavored except two ends, 1D structures such as nanorods or NWs can be obtained (Figure 1-1c). Ultrathin NWs are the most distinctive structures, being the extreme case in such anisotropy. In this case, two ends of nanocrystals grow much faster than the rest to gain the extremely large aspect ratio.

Controlling the growth rates in different directions is a challenge, especially more so in all of the seeds to achieve high uniformity and yield. So far, methodological approaches employed to break the symmetry can be summarized as following: (a) VLS and solution-liquid-solid (SLS) process; (b) templated growth; (c) defects in the seeds suppress (such as five-fold twinning defects) or promote growth of nanocrystals at these sites (such as

screw-dislocation-driven growth); (d) oriented attachment; (e) ligand binding.; (f) oxidative etching. In the following sections, these basic mechanisms and the key evidences will be discussed in detail.

1.4 Basic mechanisms

1.4.1 VLS & SLS process

VLS process typically occurs in a vacuum chamber during CVD method, but a variation of this process known as SLS process can also occur in solution. The key factor in both cases is the molten seed that acts as the catalyst (Figure 1-2a,b), making high temperature a necessity. The growth materials preferentially dissolve in the seed and then nucleate to form a nanocrystal. The initial nucleation can either occur at the seed-substrate interface in the VLS process (Figure 1-2a), or at the seed-solution interface in the SLS process (Figure 1-2b). The continuous growth via the seed confines the emerging nanocrystal and pushes the seed along, producing a NW. Competitive growth may occur on the surface of nanocrystals, directly on the substrate, or particles may form on their own (homogeneous nucleation). In order to suppress these processes, the supply of growth materials in the gas phase (or solution) must be slow enough, so that they can sample over various locations without depositing. This argument explains the typical use of low pressure gas phase or diluted

reactant concentrations in solution phase.

The molten seed provides a spatial confinement favouring the growth of NW, whose diameter is highly dependent on the size of the seed. The molten seed is usually highly symmetric, but when sitting on a substrate, the seed-substrate interface breaks its symmetry, favouring unidirectional growth. For a molten seed suspended in a solution, the initial nucleation at the seed-solution interface is random but usually at one site per seed. The subsequent nucleation on the seed-nanocrystal interface is more favourable than that on a new location of the seed-solution interface,^[11] thus locking the site of growth. If more than one nucleation site is present, branched NWs will be obtained (Figure 1-2b). In summary, the anisotropy of nanocrystal arises from the use of catalytic seed and the preferential growth at a particular location of the seed surface in both VLS and SLS processes.

Figure 1-2 (a,b) Schematics illustrating (a) VLS and (b) SLS process.

1.4.2 Templated growth

In this process, growth materials are deposited around (or inside) the template, so that the resulting structure is dictated by the shape of the template (Figure 1-3). Hard templates are usually solid and structurally stable during growth. On the other hand, soft templates are usually made of surfactant micelles; there is no agreement in the literature on whether the templates are being created during growth or whether their structure is dependent on the emerging nanocrystal. When a nanocrystal is grown on a template, three interfaces are formed, namely the template-nanocrystal, nanocrystal-solvent, and template-solvent interfaces. Whether the nanocrystal can attach to the template depends on the relative strength of the three interfaces.^[12] In other words, the “wetting” of the nanocrystal on the template is a prerequisite.

Diffusion of the growth materials is usually not a problem when growing on the outer surface of the template. For growth inside the channels or cavities of a template, the inner surface must have a higher affinity for the nanocrystal than the outer surface. This is typically achieved using different chemical groups on the surfaces. For a long channel, the growth should start from multiple sites on the channel wall (or from the seeds introduced thereon). It would be impossible that these nuclei or seeds would have matching lattice orientation. As the emerging domains merge, a single piece of polycrystalline nanocrystal forms. A competitive process that occurs is the homogenous nucleation of growth

materials outside the templates. It is conceivable that the diffusion of materials into the template channels is a very slow process. Thus, one needs to reduce the rate of introduction of growth materials to avoid their homogeneous nucleation.

The size of the nanocrystals is controlled by the template channel. Given a cylindrical template with uniform channels such as anodic aluminium oxide (AAO) channel, uniform NWs or nanorods can be obtained.

Nanocrystal growth with pre-synthesized seeds is also possible, especially for hard templates with an open end. For soft templates, the presence of seeds is likely to affect the formation of micelles, as the seeds and micelle molecules may cooperatively assemble into seed-micelle composite structures due to their strong affinity. With free-standing seeds, however, it is difficult to achieve one seed per channel.

Given the above analysis, the rapid formation of ultrathin single-crystalline NWs^[13] from soft templates is possible in reality but difficult to explain in theory. The dynamic formation of the template via surfactant self-assembly is a possible explanation, but has not been fully proven yet.

In summary, in templated growth the anisotropy of nanocrystals originates from the template. The structure of a template is dependent on its formation process, which is case specific. For example, the formation of AAO channels,^[13-14] the creation of hollow silica cavity,^[15] and the self-assembly of surfactant micelles^[16] have very different mechanisms.

Figure 1-3 Schematic illustrating templated growth of nanocrystals.

1.4.3 Five-fold twinning defect

The essence of this defect-driven growth is the presence of five-fold twinning defects at the nucleation step of nanocrystal growth, usually in terms of seed NPs of decahedron morphology (Figure 1-4). Decahedron structures can be viewed as an assembly of five face-centred cubic (fcc) tetrahedrons bound with $\{111\}$ facets joined via twin boundaries. However, it is impossible to fill the space of a decahedron object with only tetrahedra because an angular gap of 7.35° in cross section will emerge. To close this gap, the empty space must be compensated by lattice distortion which increases the distance between adjacent atoms, generating lattice strain. For five-fold twinned seeds, the internal lattice strain would greatly increase if the seeds are grown in the transverse direction (perpendicular to the five-fold symmetry axis). This unfavourable transverse growth restricts the size of the crystals in the transverse direction and in turn

forces the crystal growth along symmetric axis. With the assistance of ligands to protect newly-formed lateral surfaces, the nanocrystals grow to be wire-like structures with five-fold symmetry in the centre.

This growth mechanism is based on the initial defects in a crystal seed. To obtain high quantities of five-fold-twinned NWs with the same morphology, the same amount of five-fold-twinned seed particles are necessary. However, a question that remains unclear is how to precisely control the occurrence of identical defects in the numerous seeds during nucleation step.

Figure 1-4 Schematic illustrating templated growth of nanocrystals. Reprinted with permission from ref 63. Copyright 2003 from American Chemical Society.

1.4.4 Screw-dislocation-driven growth

This process is also based on the initial defects present on a crystal (seed) surface. A line defect originating from screw dislocation creates step edge on a crystal surface (Figure 1-5b).^[17-18] Addition of atoms at this step edge will perpetuate the line defect rather than form a complete layer. Thus, the line

defect spirals around the dislocation axis and improves the rate of crystal growth in that direction. The screw-dislocation-driven growth only requires low activation barriers to propagate the line defects. A competitive growth mode is known as layer-by-layer (LBL) growth where atoms nucleate on perfect crystal surfaces and form complete new layers (Figure 1-5a). This growth mode must overcome high activation barriers for growing new layers of atoms, favoured with large supplies of the growth materials. Thus, the supply of growth materials must maintain low to suppress the LBL growth mode in the system.

In screw-dislocation-driven growth, the growth rate of line defects dictates the final structure of the nanocrystals. If the growth rate at the core of a dislocation is much faster than the outer edge, NWs composed of step bunching can be obtained (Figure 1-5c). The side surface of NWs is free of defects, so their growth is energetically unfavoured where it is required high energy to generate a new nucleation site for LBL growth mode. If the growth rate at the core and outer edge is at the same level, the line defects spiral up to be pyramid-like structures (Figure 1-13c).

There is a strain generated with screw-dislocation, forcing the crystals to twist along its dislocation axis (Eshelby twist^[19]). With increasing step height (Burgers vector), the centre of NW becomes hollow when the lattice strain is more than the energy cost of creating an inner core (Figure 1-13b).

In screw-dislocation-driven growth, the anisotropy of nanocrystals arises

from the presence of dislocation defects, promoting the unidirectional growth of crystals. Dislocation defects are conventional but not easily controlled. It is conceivable that there are rarely any means^[20] to confer dislocation defects onto nanocrystals.

Figure 1-5 (a-c) Schematic illustrating (a) LBL growth on a perfect crystal surface. (b) a line defect of screw dislocation. (c) screw-dislocation-driven growth of a NW. Reprinted with permission from ref. 17. Copy right 2010 from American Chemical Society.

1.4.5 Oriented attachment

This growth process involves the attachment of faceted nanocrystals along similar directions to form wire-like structures (Figure 1-6). The attachment is usually driven by the electric or magnetic dipole interaction between nanocrystals.^[13, 21] When nanocrystals with dipoles on their surface collide, the matching of the dipoles with specific facets allows them to assemble together and their common dipole orientation makes them rotate and align in a chain.

Nanocrystals in solution are continuously added to the two ends of the chain, and the interface between them eliminated with the supply of growth materials in solution. During the fusion process, the surface ligands are removed and the lattice of interfaces may rearrange to match each other, resulting in single-crystalline NWs.^[22] With an extended growth period, the NWs become longer and the NPs in the system would be exhausted.

This end-to-end addition can maintain the constant width of the NWs, which is dependent on the diameter of the seed nanocrystals. Dipole-dipole interaction is the key factor in symmetry-breaking process. Thus, this oriented-attachment mechanism is usually occurs in semiconductor nanostructures where long-lived dipoles can be formed on their surfaces.

Figure 1-6 Schematic illustrating oriented-attachment process.

1.4.6 Ligand binding

Capping ligands with affinity to specific crystal facets prefer to bind to these facets during nanocrystal growth (Figure 1-7). A dense layer of strong-binding ligands stabilize the specific facets and hamper the addition of growth materials to them, reducing their growth rate. However, as the binding of the ligands at other facets are relatively weaker, the growth at these other facets is much faster, leading to the anisotropy. With crystal growth, the preferred facets enlarge and become dominant on the surfaces of the final structures.

This selective ligand shielding is proposed to allow the formation of nanoplates or NWs. However, seed nanocrystals are usually bound with equivalent facets on their surface. For NW growth, it seems impossible for the binding of ligands to occur for all the equivalent facets except for two.

When more than one ligand is present in the system, the system will become more complicated. The difference between their binding affinities and co-packing mode on the surface has to be taken into consideration if these ligands preferentially bind to the same facets. If ligands preferentially bind to different facets, the growth rate of different facets will be then controlled by the ratio of ligands, leading to various shapes.

Figure 1-7 Schematic illustrating nanocrystal growth controlled by ligand binding.

1.4.7 Oxidative etching

This process is based on the stability of different crystal surfaces. It is proposed that high-energy surfaces such as twinning defects are easily etched by oxidants like oxygen, while low-energy surfaces like single-crystalline surfaces are more stable. Thus, nanocrystals with defects are easily decomposed in solution but the formation of single-crystalline crystals is favoured.

When single-crystalline NPs are used as seeds, their surfaces are usually bond with equivalent facets protected by ligands. Without any reason, the isotropic supply of growth materials should simply grow nanocrystals into larger sizes. However, oxygen or other oxidants dissolved in the solution are believed to be capable to oxidize the surface atoms of metal nanocrystals and

dissociate the capping ligands. If the capping ligands on one part of nanocrystal surface are removed, surface atoms at this part become more active than the rest. The growth materials are preferentially deposited on this part of surface, promoting the growth of nanocrystals to form rod-like structures (Figure 1-8).

Anisotropy induced by oxidative etching is actually a facet activation process. By activating one of the equivalent facets, the growth rates at nanocrystal surfaces become imbalanced. The width of resulting nanorods is determined by the size of this active surface.

Figure 1-8 Schematic illustrating the growth of nanowires via oxidative-etching process.

The important features of the mechanisms for anisotropic growth have been summarised in Table 1-1. For the anisotropic growth of metallic nanocrystals, five mechanisms are usually employed: templated growth, five-fold twinning defects, screw-dislocation driven growth, ligand binding and oxidative etching. In addition, controlling the growth of seed NPs with identical defects is difficult

to achieve and only a few examples can be found via these mechanisms (see Section 1.4.3 and 1.4.4). Thus, it is still challenging to develop the anisotropic growth methods for metallic nanocrystals.

Table 1-1. Summary of the mechanisms for anisotropic growth of nanocrystals.

Mechanisms for anisotropic growth	Features
VLS	Molten seeds on substrate; vapor deposition; at seed-substrate interface; unidirectional growth; single-crystalline
SLS	Molten seeds in solution; growth at the seed surface; branched NWs; single-crystalline
Templated growth	Hard or soft templates; single- or poly-crystalline
Five-fold twinning defect	Seeds with twinning defects
Screw-dislocation-driven growth	Seeds with screw-dislocation defects
Oriented attachment	Dipole-dipole interaction
Ligand binding	Ligands with strong affinity to some sets of crystal facets
Oxidative etching	Stability of different surface facets; oxidants are needed

1.5 Key evidences and mechanistic variations

1.5.1 VLS process

The VLS process was first proposed by Wagner *et al.* for the growth of Si NWs.^[23] This process was then further developed and has been widely employed to grow single-crystalline NWs. There is a direct evidence for this VLS growth mode. The Yang group has reported the in-situ observation of VLS growth of Ge NWs under high-temperature TEM characterization (Figure 1-9a-f).^[24] In this case, it can be clearly observed that the nucleation of Ge nanocrystal on the molten Au seed occurs, as well as its subsequent growth to form a NW.

As surface-bound metal droplets are the prerequisite for this growth process, it allows the bonding of NWs to specific positions on a substrate to form patterned array whereby the seeds could be pre-arranged.^[25-27] With lattice-matched substrates, epitaxial growth of NWs from the substrate surface lead to vertically-aligned NWs (Figure 1-9g,h). NWs can also be grown without extra metal catalysts, where the precursors also serve as catalyst droplets for the NW growth. In this case, precursors with low melting point, such as Zn, are preferred and it has been used for synthesis of ZnO^[28] NWs. Without the pre-arranged catalyst droplets, the growth sites are random and the defects or impurities on substrate would promote the nucleation and growth thereon.

The width of the NWs is constrained by the size of molten seeds. For thin or ultrathin NWs, seeds with small sizes are necessary. The Lieber group has employed laser ablation to obtain very small molten seeds for the growth of crystalline Si and Ge NWs with width less than 10 nm (Figure 1-9i).^[29] However, in the case of Si NW, a layer of silica was formed to block the surface of resulting Si NW due to the ultra-high temperature (1200°C). This laser-assisted approach can also be applied in a broad-range synthesis of binary and ternary III-V, II-VI, IV-IV group semiconductor NWs.^[30-31] Recently, the Gradečak group developed a method to control the width in-situ along individual III-V nitride NWs, such as InN, GaN, InGaN.^[32] This control was achieved by modulating the size of molten seeds during the NW growth via changing the supply of III and V gas sources (Figure 1-9j). This process was then developed and has since been widely employed to grow single-crystalline NWs.

The nature of high temperature involved in VLS process makes it easy to grow semiconductor NWs,^[33-34] but the drawback of this methodology is that it is difficult to be applied for metal NWs^[35] or other materials with low melting point.

Although CVD is the most popular method for VLS growth, some modifications of synthetic approaches have also been reported. One modification is using chemical beam epitaxy (CBE) system as gas source in the

VLS growth.^[34, 36] By using the CBE system, the supply of the precursors can be well controlled, synthesizing segmented nanowires such as InAs/InP.^[34]

VLS growth can also be applied to the synthesis of chiral structures, such as ZnO,^[37] carbon nanotube (CNT)^[38] helices and CrSi₂ nanowires^[39] and some driving forces have been discovered such as anisotropic extrusion, surface charge or defects.^[40]

Figure 1-9 VLS process. (a-f) in-situ TEM images recording the growth

process of Ge NW via VLS process. (g,h) SEM images of vertical ZnO arrays grown on sapphire substrates. (i) Core-shell Si-SiO₂ NW produced after laser ablation. (j) Schematics and TEM image showing the width of *m*-GaN can be controlled by modulating the supply of Ga flux via adjusting H₂ flow. Reprinted with permission from ref. 1, 24, 29, and 32, respectively. Copyright 1998 and 2001 from AAAS, and 2001, 2012 from American Chemical Society.

1.5.2 SLS process

The SLS process was first reported by Buhro *et al.* on the synthesis of III–V semiconductor NWs (InP, InAs and GaAs) by using In or Ga NPs as seeds (Figure 1-10a,b).^[41] Subsequently, the Kuno group reported the high quality of ultrathin single-crystalline CdSe,^[42] CdS,^[43] CdTe^[44] NWs by using Bi NPs or even Bi salt as catalysts.

SLS growth normally involves the use of molten metallic catalysts in an organic solvent with boiling point below 400 °C. Thus, the catalyst particles are limited to elements with low melting point, such as Bi, In, Sn and Ga. Korgel *et al.* later found that the melting point of small Au NPs ($d = 2$ nm) is lower than 400 °C due to their high surface energy. By using these molten Au NPs as catalysts, single-crystalline Si NWs can be easily synthesized (Figure 1-10c).^[45]

The nucleation at seed-solution interface can occur at more than one site to

form branched NWs. Kuno *et al.* reported the synthesis of straight and branched CdSe NWs by changing supply rate of growth materials (Figure 1-10d,e).^[42] With high supply of trioctylphosphine selenide, more branched NWs were obtained (Figure 1-10e).

In a related work, Korgel *et al.* used supercritical fluid as the solvent for SLS process. Under high temperature ($> 400^{\circ}\text{C}$) and high pressure, Si^[46] and Ge^[47-48] NWs have been synthesized (Figure 1-10f,g).

Figure 1-10 SLS process. (a) TEM image of the growth of InP NWs by using In as seeds. (b) TEM image of GaAs NWs synthesized by with In seeds. (c)

SEM image of Si NWs synthesized in hot octacosane by Si_3H_8 decomposition with Au seeds. (d,e) TEM images of (d) straight and (e) branched CdSe NWs by reacting CdO and trioctylphosphine selenide with Au/Bi seeds. (f,g) low- and high-magnification TEM images of Si NW obtained by decomposition of diphenylsilane in supercritical hexane with Au seeds. Reprinted with permission from ref. 41, 42, 45, and 46, respectively. Copyright 1995 and 2000 from AAAS; and 2004, 2008 from American Chemical Society.

1.5.3 Templated growth

AAO and silica nanostructures have been widely used as hard templates for nanocrystal growth due to their well-confined channels. The growth of nanocrystals in the templates is usually achieved by electrochemical deposition or redox reactions which are suitable for metallic nanostructures. After the nanocrystal growth, a template removal step is necessary via etching process. Uniform and aligned structures such as nanorods and NWs are usually obtained. By using multiple step deposition, segmented rods or wires can be obtained.^[49] Keating et al. has reported the synthesis of segmented multimetal micro-size rods by using AAO templates (Figure 1-11a,b).^[50] The resulting rods can be used as barcodes which can be easily identified via optical microscopy. As shown in Figure 1-11c-e, the Yin group has reported the scalable synthesis of

metal nanorods by using uniform etched silica nanotubes as template.^[15, 51]

Stucky and coworkers have shown that various types of helical silica nanotubes can be prepared by confining the silica-surfactant assembly in different-sized AAO channels. By backfilling these silica nanotubes with Ag, helical Ag NWs with different mesostructures were obtained.^[52]

Templated growth can also be performed by soft templates such as assembly of small organic molecules. In the use of soft templates the packing of the amphiphilic molecules should be loose to allow the diffusion of growth materials, but also dense enough to hinder the growth of nanocrystals. The Kim group has used the self-assembled organic compound calyx[4]hydroquinone (CHQ) as the template to grow Ag NWs in aqueous solution under ambient condition (Figure 1-11f,g).^[53] The embedded single-crystalline NWs can be grown to be 0.4 nm in width and more than 1 μm in length.

Three groups have reported the synthesis of Au NWs via templated growth mechanism under similar reaction conditions. The Yang group reported Au ions and oleylamine can form 1D mesostructures in organic solution to confine the subsequent growth in wire shapes (Figure 1-11h,i).^[16] The formation of ordered Au-oleylamine mesostructures was further confirmed by characterization via small angle X-ray scattering and diffraction. At the same time, The Sun group also proposed the micelle template mechanism for growth of Au NWs.^[54] In this case, the authors demonstrated that the width of the emerging Au NWs was

controlled by solvent combination (oleylamine and oleic acid). The addition of oleic acid is proposed to interact with oleylamine and co-assembled into micelles with alternating channel structures. The Xia group proposed that oleylamine and AuCl salts can form polymer-like [(oleylamine)AuCl] complex in organic solution.^[55] The Au ions inside the polymer strands would be reduced to form NWs by oleylamine in the presence of Ag NPs. From TEM characterization, polymer-like wires can be observed. Moreover, the data from small angle X-ray diffraction showed that layers spacing of 4.4 nm are present in the polymer-like structures, which is similar to the case reported by the Yang group.

Bio-molecules have also been used as templates for directing NW growth.^[56] Metal NWs can be synthesized by using DNA,^[57-58] short peptide chain,^[59] and tobacco mosaic virus.^[60-61]

Figure 1-11 Templated growth. (a,b) Optical image and schematics of segmented Au-Ag nanorods obtained by electro-deposition of Au and Ag in the pores of anodic aluminium oxide film. (c-e) TEM images of (c) hollow silica nanotubes, (d) Au nanorods grown in the silica tubes, and (e) freestanding Au nanorods obtained after removal of the silica shells. (f,g) HRTEM and

schematic showing the formation of ultrathin Ag NWs in the pores of assembled calix[4]hydroquinones. (h,i) TEM image and schematics of ultrathin Au NWs synthesized by mixing HAuCl_4 and oleylamine. Reprinted with permission from ref. 15, 16, 50, and 53, respectively. Copyright 2001 from AAAS; and 2008 and 2011 from American Chemical Society.

1.5.4 Five-fold twinning defect

This growth process is usually observed in metallic NWs with pentagonal twinning defects in the centre. The Xia group has performed intensive research on the synthesis and mechanism study of pentagonal Ag NWs (Figure 1-12a).^[62-65] Generally, pentagonal Ag NWs were synthesized via polyol reactions where Ag ions were reduced by ethylene glycol in the presence of polyvinylpyrrolidone (PVP) at high temperature. As discussed in Section 1.4, these Ag NWs were grown from the decahedral seeds with five-fold twinning defects (Figure 1-12b). The twinning defects would generate internal lattice strain to confine the crystal growth in the transverse direction. By investigating the crystal structure of the cross-sections of Ag NWs, Sun *et al.* have observed the lattice distortion induced by internal strain.^[66] A body-centred tetragonal lattice can be found in the cross-sections, which may come from the distortion of fcc lattice. From the TEM images, it can be clearly observed that a highly

strained core is covered by a relatively stable shell (Figure 1-12c-e).

Beside the twinning defects, the ligand PVP also plays an important role in the formation of Ag NWs. They are believed to stabilize the newly-formed lateral {100} facets and block the adsorption of growth materials on these facets.^[62] PVP with different degree of polymerization can dramatically affect the final structure of Ag NWs.^[64]

The five-fold-twinning-driven growth mechanism can be applied in the synthesis of Pd NWs.^[67-68] For growing Pd NWs, PVP and halide are essential for stabilize the lateral surface of the emerging NWs. The Zheng group proved that the tips of the Pd NWs are more active than the lateral surface during NW growth. Au NPs can be formed preferentially on the tips of each Pd NWs rather than lateral surface which is protected by PVP and halide ions (Figure 1-12f,g).^[68]

Figure 1-12 Five-fold twinning defect. (a) SEM image of Ag NWs synthesized by reducing AgNO_3 with ethylene glycol in the presence of PVP. (b) TEM image of decahedral Ag seeds. (c-e) HRTEM images of (c) cross-section obtained by cutting a Ag NW, (d) the centre and (e) the edge of the cross-section, showing that most of the defects are in the centre. (f,g) TEM images of (f) Pd NWs obtained by reducing PdCl_2 with PVP in the presence of NaI and (g) Au NP grown on tip of Pd NWs suggesting the activity at the tip of

NWs. Reprinted with permission from ref. 63, 66, and 68, respectively.

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1.5.5 Screw-dislocation-driven growth

This growth process can be visually recognized from the distinct emerging plate-like structures. As shown in Figure 1-13c, the dislocation line defects occur on the surface of zinc hydroxy sulfate nanoplates and spiral up along the axial centre to form chiral structures.^[69] For NWs, dislocation-driven growth can be confirmed via the lattice twist along a NW which was originated from Eshelby twist (Figure 1-13a,e).^[20] This lattice twist causes regular bending which appeared as periodical band contours under TEM characterization (Figure 1-13a). Moreover, the lattice twist was believed to induce regular rotating branches along the dislocation axis to form helical NWs (Figure 1-13d,f,g).^[70-71]

The methodology for screw-dislocation-driven growth can be extended towards different phase conditions such as in solution or gaseous form. This self-perpetuating process is a general principle for crystal growth, independent of material components. Screw-dislocation-driven growth has been confirmed in the growth of metal nanostructures such as Au,^[69] Cu,^[72] Ti^[73] and

semiconductor nanostructures such as ZnO,^[20, 74] PbS,^[70, 75] PbSe,^[71] CdS/CdSe,^[76] AlN,^[77] InN,^[78] GaN,^[79] FeOOH,^[80] and CNT^[81].

Figure 1-13 Screw-dislocation-driven growth. (a,b) Schematics and bright-field and dark-field TEM images of dislocation-driven growth of ZnO (a) NWs and (b) nanotubes. (c,d) Schematics and SEM images of dislocation-driven growth of (c) zinc hydroxy sulfate nanoplates and (d)

pine-tree-like PbS NWs. (e) Schematics illustrating the Eshelby twist in a dislocated NW. (f,g) Low- and high-magnification TEM images of PbSe chiral branched NWs. Reprinted with permission from ref. 17, 69-71, and 74, respectively. Copyright 2008 from Macmillan Publishers Limited; 2008, 2010 from AAAS; and 2010, 2011 from American Chemical Society.

1.5.6 Oriented attachment

The dipole-induced attachment of semiconductor NPs usually leads to 1D nanostructures. Penn *et al.* pioneered the use of oriented attachment to explain the observation of TiO₂ chains, which is the result of coalescence of TiO₂ NP tips (Figure 1-14a).^[82] The Kotov group subsequently synthesized single-crystalline CdTe NWs under the oriented attachment mechanism (Figure 1-14b).^[83] The observation of intermediate stage of the particle-wire transition supports the hypothesis of oriented-attachment growth, where CdTe NPs assemble into pearl-like chains (Figure 1-14c).

By tuning the shape of the seed NPs, NWs with different morphologies can be obtained. For example, with octahedral shapes, PbSe NPs can assemble together through the {111} facets along the <100> axis to build helical NWs (Figure 1-14d-f).^[84] When the seeds were of star-like shapes, they can also align along <100> axis to merge to form radially branched NWs (Figure 1-14g,h).

In oriented-attachment growth, the width of the emerging NWs is controlled by the size of seed NPs.^[83-89] Changing the reaction conditions may affect the seed size, leading to NWs with varying width. The Peng group showed that the width of CdSe NWs was affected by the composition of mixed ligands dodecylamine (DDA) and octadecylamine (ODA).^[90] With a higher ratio of DDA, short NWs with small diameter were obtained, while longer and thicker NWs were grown at higher percentage of ODA (Figure 1-14i,j). However, the author could not observe the seed clusters due to their small sizes.

In some cases, metal NWs are proposed to be grown via oriented attachment mechanism such as Au^[91] and bimetallic Au-Ag NWs.^[92] The authors observed that NWs emerged along with the exhaustion of seed NPs during the reaction. This observation supported the hypothesis of oriented attachment. It is known that long-lived dipole moments should not be generated on metal NP surface due to their free-electron cloud. Without the common dipole, the seed NPs should aggregate randomly to form branched nanostructures rather than NWs.

Figure 1-14 Oriented attachment. (a) TEM image of titania chains obtained via hydrothermal coarsening of titania NPs. (b,c) TEM images of (b) single-crystalline CdTe NW, and (c) pearl-like intermediate state of CdTe NW. (d-f) TEM images of helical single-crystalline PbSe NWs synthesized by

oriented-attachment of octahedral nanocrystals. (g,h) TEM images of (g) star-shape PbSe nanocrystal seeds and (h) the resulting branched NWs grown from these seeds. (i,j) TEM images of emerging CdSe NWs obtained by reacting cadmium acetate and selenourea with different ratio of dodecylamine and octadecylamine. Reprinted with permission from ref. 82-84 and 90, respectively. Copyright 2002 from AAAS; 1999 from Elsevier Science Ltd; and 2005 and 2006 from American Chemical Society.

1.5.7 Ligand binding

Ligands such as PVP and hexadecyltrimethylammonium bromide (CTAB), oleylamine are theorized to show strong affinity to specific facets of crystals. As discussed above, PVP has strong affinity to the $\{100\}$ facets of Ag, which can stabilize the $\{100\}$ size facets during the growth of Ag NWs (Figure 1-12a). By using PVP as ligands, single-crystalline Ag nanocubes were also synthesized using a modified method from the preparation of Ag NWs (Figure 1-15a).^[93] The resulting nanocubes were bound with six $\{100\}$ facets which were stabilized by PVP. It is proposed that PVP preferentially binds to the $\{100\}$ facets of fcc Au seeds to hinder the further growth of these facets. Thus, the fcc seeds were grown with maximized $\{100\}$ surface facets.

Similar to the strong binding of PVP to $\{100\}$ facets of Ag, CTAB possesses

strong affinity to the {100} facet of Au.^[94] The Murphy group reported that Au nanocubes were fabricated by using CTAB as ligands and ascorbic acid as reducing agent.^[95]

Besides organic molecules, certain gases can also be employed as ligands. The Zheng group has proved that CO can act as ligands in the growth of ultrathin Pd nanoplates (Figure 1-15b).^[4] It is believed that CO was adsorbed to the {111} facets of Pd to block the growth on these facets, resulting in Pd plates with 1.8 nm in thickness. In this case, CTAB also help to form the hexagonal shape of the plates by stabilizing the {100} facets at the edges.

In some cases, the presence of ligands can help to form unconventional structures such as helical NWs. The José-Yacamán group synthesized helical Au-Ag bimetallic NWs (Au/Ag = 3:1) in oleylamine solution.^[96] These ultrathin NWs showed “fan” type of contrast under TEM characterization (Figure 1-15c). This unique contrast suggested that the NWs can be regarded as the packing of two or three strands of Boerdijk-Coxeter-Bernal (BCB) helices composed of tetrahedra.^[40]

Ultrathin Au-Ag bimetallic (Au/Ag = 1:1) NWs synthesized in a polar solution using PVP as ligand were reported by our group.^[97] These NWs were 2 nm in width and they also showed “fan” type of TEM contrast, indicating the occurrence of BCB structures. Coated with a layer of metal, the straight NWs twisted to form double helices (Figure 1-15d). We proposed that a significant

lattice strain was generated upon metal coating. This strain caused original BCB structure to untwist to be normal fcc structure. Given the high aspect ratio, NWs tended to self-wind to give double helices.

Figure 1-15 Ligand binding. (a) TEM images of Ag nanocubes synthesized by reducing AgNO_3 with ethylene glycol in the presence of PVP. (b) TEM image of Pd nanoplates synthesized by using CO as reducing agent in the presence of CTAB. (c) TEM and HRTEM (inset) image of helical Au-Ag alloy NWs synthesized by using oleylamine as ligand. (d) TEM images of self-winded

helical alloy NWs, evolved from the straight Au-Ag NWs synthesized in the presence of PVP (inset). Reprinted with permission from ref. 4, 39, 93, and 97, respectively. Copyright 2010 from Nature publishing group; 2002 from AAAS; and from American Chemical Society.

1.5.8 Oxidative etching

The Xia group reported the oxidative etching process in a controllable growth of Ag NPs (Figure 1-16a-c).^[98] The synthetic route is modified from that for Ag NWs in Figure 1-12a. Single-crystalline Ag truncated cubes and tetrahedral were formed in ethylene glycol in the presence of PVP and a trace amount of NaCl (Figure 1-16c). They observed that both single-crystalline and twinned seeds were present in the early stage of reaction (Figure 1-16b). With increasing reaction time, more single-crystalline NPs were in the solution whereas twinned NPs become less. They proposed the twinned NPs were easily etched by oxygen in the presence of chloride ions, which in turn promoted the growth of single-crystalline NPs. Both oxygen and chloride ions are essential. Without oxygen or chloride ions, twinned NPs were formed and then grown into NWs. The authors also applied this etching process in the selective growth of single-crystalline Pd truncated cubes.^[99] Later they reported that the presence of citric acid or citrate ions can suppress the etching process to synthesize

uniform Pd icosahedra.^[100]

The Xia group also showed that oxidative etching can occur in single-crystalline NPs. For instance, Pd nanorods were grown from cubic seeds (Figure 1-16d,e).^[101] The reaction condition for these nanorods were modified from that for Pd nanocubes^[99], and KBr was introduced as ligand. It is proposed that the {100} surface facets of cubic seeds were protected by PVP and bromide ions. During the reaction, the localized oxidative etching at one of these facets removed the surface ligands. The Pd atoms were preferentially added to this exposed facet. When the growth rate of Pd was much faster than the etching rate, Pd nanorods were obtained (Figure 1-16e). The bromide ions are crucial for the nanorod growth. Using other halide ions such as chloride and iodide will not be able to induce the formation of nanorods.

In another case, the Mourzina group reported that ultrathin Au NWs were grown via oxidative etching mechanism (Figure 1-16f).^[102] These NWs were synthesized by simply dissolving AuCl in oleylamine and hexane. The authors showed that oxygen played a key role in the NW growth. Without oxygen, only Au NPs were observed (Figure 1-16g).

Figure 1-16. Oxidative etching. (a-c) (a) Schematics illustrating the etching/growth process in single-crystalline Ag NPs; (b) TEM image of twinned Ag NPs obtained after 10 min reaction; (c) SEM image of the single-crystalline

Ag NPs obtained after 46 h reaction. (d,e) TEM images of Pd nanocubes and nanorods controlled by the amount of reducing agents: (d) 0% and (e) 72.7% ethylene glycol in solution. (f,g) TEM images of (f) Au NWs synthesized by mixing AuCl and oleylamine in hexane with oxygen, and (g) Au NPs obtained with the same procedure but without oxygen. Reprinted with permission from ref. 98, 101, and 102, respectively. Copyright 2004, 2007 from American Chemical Society; and 2011 from Wiley-VCH Verlag GmbH & Co.

1.6 Summary

In this chapter, reported growth mechanisms and methodologies of anisotropic nanostructures, particularly nanowires, have been summarized. Most known growth methods for anisotropic structures have been explained, but fundamental questions still remain. In addition, a colloidal method for surface-bound metal nanowires has yet to be reported. In the next chapters, a new nanowire growth mechanism, named as active-surface growth, will be demonstrated. With this unique growth mechanism, surface-bound metal nanowires can be fabricated and applied in fixed-bed catalysis and conductive film. Further extensions of this method to bimetallic and chiral structures are then subsequently covered.

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Chapter 2 Colloidal Synthesis of Surface-Bound Ultrathin Gold Nanowires: A New Type of Nanocrystal Growth

2.1 Introduction

Controlling where and how nanocrystals grow is of fundamental importance for nanoscience and nanotechnology. For metallic nanocrystals, such control is often realized by exploiting the facet-specific binding of surface ligands, so that preferred growth of certain facets determines the shape of nanocrystals.^[1-3] Because of the intrinsic symmetry of crystal lattice, a metallic nanocrystal always has multiple sets of equivalent facets. Without a reason they should grow equivalently.

Nanowire (NW) is a special type of nanocrystal with extremely large anisotropy.^[2-11] Any metallic NW must grow from a small primary nucleus with multiple sets of equivalent facets, before transitioning to an anisotropic growth mode. Thus, a prominent question is why the two ends of a wire grow so much faster than the rest of the equivalent facets. It cannot be solely explained by the difference in the binding affinity of ligands. Thus, additional factors have been proposed in the literature: (a) templated growth using surfactant micelles;^[12-16]

(b) the five-fold twinning defects in pentagonal NWs can confine the transverse growth and promote the longitudinal growth;^[17-20] (c) the screw-dislocation on a facet can induce the preferred growth of nanocrystals at the defect sites;^[21-23] and (d) during the oriented attachment of nanocrystals, the interactions between the facets can lead to linear growth of NWs.^[24-26] In addition, in the vapour-liquid-solid (VLS) growth under high temperature, the molten seeds confine the cross-sectional width of the nanocrystal, catalyzing its linear growth.^[27-31] Thus, VLS growth is almost always used to grow semiconductor NWs, but rarely applied to grow metallic NWs. In contrast to these known systems, we now present a new origin for the anisotropy in metallic NW growth.

In the conventional growth of metal NWs in solution, there are several common characteristics: The known surface ligands are all weakly binding, including oleylamine,^[12-15, 32-33] hexadecyltrimethylammonium bromide (CTAB),^[7, 34-36] polyvinylpyrrolidone (PVP),^[5, 17, 19-20, 37-39] and their analogues.^[40-41] On the other hand, seeded growth of NWs was rarely reported,^[16, 18, 34] particularly for ultrathin metal NWs ($d < 10$ nm). Without seeds, the known factors above for inducing anisotropic nanocrystal growth cannot be easily applied to a substrate. This is probably the reason why solution growth of anchored NWs on a substrate has so far not been demonstrated.

Here, we report a new type of NW growth in polar solution under ambient

conditions. We employ a thiol ligand system, including 4-mercapto-phenylacetic acid (4-MPAA), 4-mercaptobenzoic acid (4-MBA), 3-mercaptobenzoic acid (3-MBA), and 4-mercaptophenol (4-MPN). By using these strong-binding ligands, Au seeds anchored on oxide substrates can “catalyze” the growth of ultrathin AuNWs (Figure 2-1 and 2-15). The growth mode is similar in appearance to the VLS growth in chemical vapour deposition, but the underlying mechanism is radically different. The strong-binding ligand is of critical importance, but not because it has affinity to any special facet: Au can be continuously deposited at the Au-substrate interface because ligands cannot effectively bind there, whereas the instant binding of strong ligands inhibits the growth at the perimeter of this active site, pushing the nanocrystals upward into anisotropic NWs. Such partial activation of seed surface can generate “hairy” nano-hybrids and even vertically aligned AuNWs. Under this active-surface growth mode, the diameter of the resulting NWs is, surprisingly, independent of the size of the seeds, but dependent on the dynamic competition between ligand diffusion rate and Au deposition rate.

Figure 2-1 (a) Schematics illustrating the colloidal synthesis of AuNWs on Au@silica. (b) TEM image of the product nanocomposites using 4-MPAA as ligands in the presence of PVP; the inset shows a scaled-up reaction.

2.2 Materials and Methods

2.2.1 Materials

Hydrogen tetrachloroaurate(III) (HAuCl_4 , 99.9%, Au 49% on metals basis, Alfa Aesar), 4-MPAA (97%, Alfa Aesar), 4-MBA (90%, Sigma Aldrich), 4-MPN (90%, Alfa Aesar), 3-MBA (95%, Sigma Aldrich), 2-mercaptobenzoic acid (2-MBA, 95%, Sigma Aldrich), 3-aminopropyltriethoxysilane (APTES, Sigma Aldrich), trimethyl(methylcyclopentadienyl)platinum(IV) (98%, Sigma Aldrich), sodium citrate tribasic dihydrate (99.0%, Sigma Aldrich), PVP (99%, Alfa Aesar), L-ascorbic acid (Sigma Aldrich), 11-mercaptoundecanoic acid (11-MUA, Sigma Aldrich), tetraethylorthosilicate (TEOS, Sigma Aldrich), CTAB (Sigma Aldrich), Ammonia (25%-28% w/w, Chemical Reagent), 2-propanol (HPLC grade) 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 XinXing BaiRui (T10023).

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. Ultraviolet-visible (UV-vis) spectra were collected on a Cary 100 spectrophotometer. High resolution TEM (HRTEM) images were taken from

JEOL 2100 F field emission transmission electron microscope operated at 200 kV.

Sheet resistance of the large conductive AuNW film was measured by using KEITHLEYTM 2636A Dual-channel System SourceMeterTM Instrument and KEITHLINKTM Sheet Resistivity Four Point Probe. For an accurate measurement, all four tips of the probe head were placed firmly in contact with a spot on the AuNW film and the average sheet resistance of 10 measurements collected. Here, the sheet resistances at three different spots were measured to be: 53.8, 45.1 and 76.5 Ω/sq , showing an overall average sheet resistance of 58.5 Ω/sq on the AuNW film.

Preparation of TEM Samples. TEM grids were treated with oxygen plasma in a Harrick plasma cleaner/sterilizer for 45 s to allow the surface to become more hydrophilic. The sample solution was then placed in contact with the hydrophilic face of the TEM grid. Then, the excess solution was wicked off using a filter paper and the TEM grid was air-dried for 30 min.

Synthesis of citrate-stabilized Au nanoparticles (AuNPs). Citrate-stabilized Au AuNPs with diameter in 15 nm and 35 nm were synthesized according to established literature procedure^[42] with minor modification. For a typical synthesis of 15 nm AuNPs, 100 ml HAuCl₄ solution (0.1 mg/mL) was added to a 250 mL round bottom flask. This solution was then heated to boil under stirring. 2.4 mL of sodium citrate tribasic dihydrate (1 wt%)

was added to the solution and heated for another 30 min. The dark-red solution that results suggests the formation of AuNPs. For the synthesis of 35 nm AuNPs, the procedure is the same as for 15 nm AuNPs except that 1.5 mL of sodium citrate tribasic dehydrate solution was added.

Synthesis of silica coated AuNPs (Au@silica). Synthesis of Au@silica (core@shell) was carried out using Stöber method with modifications.^[43] As-synthesized 35 nm citrate-stabilized AuNP solution (3 mL) was concentrated to 6 μ L by centrifugation for 8 min at 4000 g. The supernatant was then removed and the residual NPs re-dispersed into 500 μ L of water. The resulting solution was transferred to 2.5 mL 2-propanol dropwise under vigorous stirring, after which 20 μ L 11-MUA (2 mM in ethanol) was added. After 5 min, 600 μ L TEOS (8.96 mM in water) was added, followed by 90 μ L of ammonia (25-28 wt%). Concentric core-shell Au@silica nanocomposites were obtained after 12 h of reaction at room temperature. To isolate the product, the reaction mixture was then centrifuged for 9 min at 5200 g and the supernatant removed, after which the residual NPs were re-dispersed in ethanol. In the main text, we also show that silicon wafer with a thermal SiO₂ layer can also be used for growing AuNWs. Thus, the nature of the silica was not a critical factor for AuNW growth.

Synthesis of Au@silica with adsorbed seeds ($d = 3-5$ nm).^[44] The Au@silica synthesized as above (1.5 mL) was concentrated to about 6 μ L by

centrifugation for 9 min at 5200 g, and then added into a solution containing 500 μL of H_2O , 500 μL of ethanol and APTES (1 mM). After a 1 h reaction with vigorous stirring, the surface of the Au@silica was functionalized with amino groups. These NPs were purified twice with ethanol by centrifugation for 9 min at 5200 g. In a typical synthesis of citrate-stabilized Au seeds ($d = 3\text{-}5$ nm), a 50 mL flask was filled with 0.3 mM of sodium citrate tribasic dehydrate, 0.2 mM of HAuCl_4 , and 20 mL of water. 600 μL of ice-cold NaBH_4 solution (0.1 M) was then added with vigorous stirring. The colour of the solution turned from orange-yellow to brownish-red. To the resulting seeds solution (500 μL), the purified amino-functionalized Au@silica was added, and the mixture was incubated for 2 h. The product was then isolated by centrifugation for 8 min at 5200 g and re-dispersed in ethanol.

Synthesis of colloidal nanocomposites with AuNWs attached on Au@silica. The nanocomposites can be obtained in the same reaction system using either 4-MPAA, 4-MBA, 4-MPN or 3-MBA as the ligands. 500 μL of Au@silica with adsorbed seeds was concentrated to about 6 μL by centrifugation for 8 min at 5200 g and then added into a water/ethanol (v/v = 1:2) solution containing the ligand (0.7 mM), PVP (21 mM), HAuCl_4 (0.7 mM for 4-MBA, 1.2 mM for all other ligands) and L-ascorbic acid (3.6 mM). The total volume of the reaction mixture is about 2 mL. The mixture was then vigorously stirred for 15 min. Centrifugation was then done for 4 min at 4000 g

to purify the products and subsequently re-dispersed in water. For the preparation of nanocomposites with short AuNWs (Figure 2-4), the reaction conditions were unchanged (the ligand is 4-MPAA) except that the concentration of HAuCl_4 was reduced to 0.3 mM.

Our method can be easily scaled up to 30 mL (about 15 times of the samples in Figure 2-1b). The synthetic approach is unchanged except for the scaled up volume of the reaction solution.

Synthesis of AuNWs on Si/SiO₂ substrate. A Si wafer (about 1 cm²) was treated with O₂ plasma for 10 min to allow its surface to become more hydrophilic. APTES solution (5 mM) was then used to functionalize the wafer surface with amino group by immersion for 1 h. The wafer was then soaked in a solution of excess 3-5 nm citrate-stabilized Au seeds for 1 h. This was to ensure that Au seeds were adsorbed, after which it was rinsed with water twice to remove excess Au seeds. Then, the seed-adsorbed wafer was immersed in a water/ethanol (v/v = 1:1) solution containing the ligand (550 μM), HAuCl_4 (1.7 mM) and L-ascorbic acid (4.1 mM) for 15 min. Finally, ethanol was used to rinse the wafer, which was then air-dried.

For synthesizing AuNWs using 15 nm AuNPs as seeds, all conditions in the reactions were the same except that 15 nm citrate-stabilized AuNPs were used as seeds^[42] during incubation with the amino-functionalized Si wafer.

Experiments were carried out with different ligand concentrations to

investigate the concentration-dependent growth of AuNWs. For the preparation of spherical NPs or AuNWs on Si/SiO₂ in Figure 2-17b,c, all reaction conditions were the same except that the concentration of 4-MBA was decreased to 28 μ M and 5.5 μ M, respectively.

To identify the site of AuNW growth, a two-stage reaction was carried out. The substrate was first grown in a solution of 550 μ M 4-MBA for 5 min, and then rapidly transferred without drying to a solution of 28 μ M 4-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 AuNWs had thin heads and thick tails (Figure 2-21a). Conversely, when the growth was carried out first with low concentration of 4-MBA (55 μ M) and then with high concentration (550 μ M), the resulting AuNWs had thick heads and thin tails (Figure 2-21b).

Generation of a thin and uniform conductive film on oxide substrate.

The generation of a thin and uniform conductive film is similar to that of vertical AuNWs on Si/SiO₂ wafer. When a glass slide (about 1 cm²) was used as substrate, it was first functionalized with amino group by reacting with APTES solution (10 μ M) for 0.5 h. Subsequently, the slide was soaked in excess citrate-stabilized Au seeds ($d = 3\text{-}5$ nm) solution for 1h, and rinsed twice with water to remove the excess Au seeds. The seed-adsorbed slide was then put into a solution containing the ligand (600 μ M), HAuCl₄ (1.5 mM) and

L-ascorbic acid (4.5 mM) for 15 min. For the preparation of AuNW film on other oxide substrates such as SrTiO₃, LaAlO₃, and sapphire, all reaction conditions were unchanged except for the substrate.

Our method can be easily scaled up to prepare a conductive AuNW film on larger substrates (about 532 cm²) and trumpet shell. The synthetic approach for both is the same as that on glass slide except for the scaled up volume of the reaction solution.

Preparation of AuNW cross-section. The cross-sections of AuNWs were prepared by using FEI NovatechTM Nanolab DualBeamTM 600i, combining ultra-high resolution SEM and precise focused ion beam (FIB) and deposition. Firstly, the Si wafer with AuNWs 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 AuNW from ion beam damage during subsequent milling. The electron beam (5kV and 0.4nA) 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.

Control Experiments. Some control experiments were carried out to

elucidate the growth mechanism of AuNWs. (1) when Au@silica were used as precursor directly in the reaction solution, numerous small AuNPs were formed by homogeneous nucleation, as shown in Figure 2-6; (2) In the absence of colloidal substrate Au@silica, spherical AuNPs were obtained from free seeds, as shown in Figure 2-7; (3) only AuNPs were observed when the ligand concentration is as high as 1.4 mM, with all other conditions unchanged (Figure 2-9); (4) In the absence of the thiol-ligands, only core-shell nanocomposites were obtained, as shown in Figure 2-11; (5) 2-MBA and 11-MUA were used as ligand to grow AuNWs, with the same concentration as 4-MPAA in Figure 2-1b, but only core-shell nanocomposites were observed (Figure 2-12); (6) colloidal Au@silica with attached NWs can be synthesized without PVP surfactant, with all other conditions unchanged, as shown in Figure 2-13; (7) when CTAB was used as ligands, only freestanding NPs and nanorods were obtained, as shown in Figure 2-14.

Figure 2-2 (a-b) TEM images of (a) Au@silica using 35 nm AuNP as core and (b) seed-adsorbed Au@silica.

2.3 Results and Discussions

2.3.1 Growth of ultrathin AuNWs on colloidal substrates

We used core@shell nanocomposites (Au@silica)^{[43, 45-46],[47]} ($d_{\text{AuNP}} = 35 \text{ nm}$; $d_{\text{overall}} = 90 \text{ nm}$) as model substrate for growing the ultrathin AuNWs using 4-MPAA as ligands (Figure 2-2a). The core-shell NPs can be easily recognized among the messy NWs, but the internal AuNPs did not play an active role as confirmed by control experiments using silica NPs. The silica surface was functionalized with amino group using APTES to facilitate the subsequent adsorption of citrate-stabilized Au seeds ($d = 3\text{-}5 \text{ nm}$). The resulting seed-adsorbed Au@silica nanocomposites were confirmed by TEM characterization (Figure 2-2b). About 120-160 seeds were found attached to the

surface of each Au@silica nanocomposites. After purification, the seed-adsorbed Au@silica were mixed with 4-MPAA (0.7 mM), surfactant PVP (21 mM), HAuCl₄ (1.2 mM), and reducing agent L-ascorbic acid (3.6 mM). The reaction mixture was then stirred at room temperature for 15 min, during which its colour turned from red to grey. The resulting ultrathin AuNW on Au@silica were then isolated by centrifugation; after being re-dispersed in water, they were stable for weeks.

As shown in Figure 2-1b, the nanocomposites with long and flexible AuNWs AuNWs formed messy entangled clusters. The ultrathin AuNWs were very uniform in width ($d = 6$ nm). Most of them were over 1 μ m in length and seem to extend from the silica surface. The UV-vis spectrum of this sample showed stronger absorption at around 400 nm than that of the original seed-adsorbed Au@silica (Figure 2-3). This new absorption probably arose from the AuNWs, as it was consistent with that of ultrathin AuNWs synthesized in organic systems.^[14, 32]

Figure 2-3 UV-vis spectra of (a) AuNWs on Au@silica and (b) seed-adsorbed Au@silica.

To confirm the attachment of the AuNWs to the silica surface, we restricted AuNW growth by lowering HAuCl_4 concentration (0.3 mM; all other conditions unchanged). With the shorter AuNWs, the colloidal nanocomposites with AuNWs attached on Au@silica were less entangled, resulting in individual nanocomposites and their small clusters (Figure 2-4). The ultrathin AuNWs were clearly anchored end-on to the silica surface, and each nanocomposite had about 15 wavy AuNWs of about 100 nm in length (Figure 2-4b). During the NW growth, the solution contained very few free seeds; after the growth, few free-standing NWs were observed. Hence, the AuNWs originated from the surface-bound seeds. The 4-MPAA-derived AuNWs could be easily coated

with silica shells without additional ligands (Figure 2-5). Previously, ligands with terminal -COOH groups were known to be amenable for silica adsorption.^[43] Thus, the direct silica coating was in support for the presence of 4-MPAA ligands on the resulting NW surface.

Figure 2-4 (a-d) TEM images of short AuNWs on Au@silica using ligand 4-MPAA in the presence of PVP: (a) large area view of nanocomposites, (b) the isolated and (c,d) entangled nanocomposites.

Figure 2-5 TEM image of the sample in Figure 2-1b was coated with silica.

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 stirring of the mixture at room temperature. It can be easily scaled up to 30 mL (Figure 2-1b inset) without significant change in the resulting nanostructures.

Unlike the typical solution methods for growing NWs, in our system the NWs cannot grow without the seeds: A control experiment using Au@silica nanocomposites under identical conditions did not give any AuNW (Figure 2-6).

More intriguingly, when free Au seeds were used without being adsorbed to the Au@silica, the seeds simply grew larger but NWs were not formed. (Figure 2-7). Hence, it appeared that the adsorption of the seeds on the silica surface was essential.

Figure 2-6 TEM image of NPs which were obtained from a control experiment carried out using Au@silica without seeds, under otherwise the same reaction conditions as for Figure 2-1b. Homogeneous nucleation in the solution led to the formation of the small AuNPs observed.

Figure 2-7 TEM image of AuNPs which were obtained from a control experiment carried out using free Au seeds ($d = 3\text{-}5\text{ nm}$) without silica substrate, under otherwise the same reaction conditions as for Figure 2-1b.

Interestingly, the diameter of the ultrathin AuNWs was found to be independent of the size of the Au seeds used. When 15 nm AuNPs were used in place of the 3-5 nm seeds, the resulting AuNWs were still 6 nm in diameter (Figure 2-8). This observation was surprising, because in typical seeded growth the size of the NWs was always larger than the seeds from which they grew.^[1, 29-30, 48-51] With the large seeds, we can easily determine their position after the

AuNW growth. As shown in Figure 2-8b, not all of the seeds were able to grow AuNWs. Most of the tips of the AuNWs that we observed retained the 15 nm AuNP seeds. However, given the small size of the Au@silica and the high density of surface-bound seeds, it is hard to determine if the attachment of the AuNWs to the silica surface was through these seeds. This independence of the seeds will be discussed in more details in the later parts.

Figure 2-8 (a,b) Low- and high-magnification TEM images of AuNWs on AuNP@silica using 15 nm AuNPs as seeds.

Another interesting issue is that the ligand concentration is one of the main limiting factors. If ligand concentration was increased (the concentration of 4-MPAA was changed from 0.7 mM to 1.4 mM while the concentration of PVP was unchanged), AuNWs did not form. Instead, uniform Au nanospheres of 6

and 33 nm in diameter were obtained (Figure 2-9). It appeared that the high 4-MPAA concentration prevented AuNW growth by blocking the active surface on the seeds. This led to the homogenous nucleation of Au nanospheres in the solution. The divergence in the diameters of the highly uniform nanospheres suggested that they were thermodynamically controlled,^[37, 52-54] probably a result of the strong surface ligand.

Figure 2-9 TEM image of NPs which were obtained from a control experiment carried out using 1.4 mM 4-MPAA as ligand, under otherwise the same reaction conditions as for Figure 2-1b. Two kinds of Au NPs of 6 nm and 33 nm in diameter were obtained and no wires were observed.

The 4-MPAA ligand was not unique in forming AuNWs. Similar AuNWs can be obtained when 4-MPN, 4-MBA, and 3-MBA were used (Figure 2-10). A

common feature of these ligands is that they all have a thiol group, an aromatic body, and a hydrophilic end group. The AuNWs formed using 4-MPN have the same uniform width of 6 nm (Figure 2-10c). Those derived from 4-MBA tend to aggregate into large bundles, leading to octopus-like nanocomposites (Figure 2-10a). Upon close inspection, however, the width of the individual AuNWs in the bundle was also around 6 nm (Figure 2-10b). In contrast, when 3-MBA was used, the width of the resulting AuNWs was variable along each NW (Figure 2-10d). Obviously, these ligands played a critical role. Without them but with PVP still present, the surface-bound seeds simply grew larger and fused together into a shell, rather than formed NWs (Figure 2-11).

Figure 2-10 TEM images of the colloidal nanocomposites synthesized from seed-adsorbed Au@silica using the following ligands: (a,b) 4-MBA; (c) 4-MPN; and (d) 3-MBA.

Figure 2-11 TEM image of nanocomposites (Au@silica)@Au_shell which were obtained from a control experiment carried out in the absence of thiol-ligands.

When the ligand used in the synthesis was unsuitable, such as 2-MBA or 11-MUA, the seeds simply grew larger and fused into a granular shell (Figure 2-12). A plausible explanation is that these ligands cannot pack as densely as

4-MPAA and thus, allows Au deposition on the entire seed surface. Specifically, 2-MBA has the -COOH group on the ortho-position of the thiol group, possibly causing disorder in ligand packing. It is probable that 3-MBA was an intermediate case between 2-MBA and 4-MBA. It is thus proposed that the packing of ligands plays an important role in this growth mechanism.

Figure 2-12 TEM image of (Au@silica)@Au_shell which were obtained from a control experiment carried out by using (a) 2-MBA and (b) 11-MUA. Scale bars = 100 nm.

In our system, PVP acted as a surfactant to prevent the aggregation of the nanostructures. In its absence, 4-MPAA still induced the formation of ultrathin AuNWs, but most of the AuNWs and Au@silica were lost due to aggregation. In Figure 2-13, the resulting AuNWs were 6 nm in diameter, same as those in Figure 2-1b, indicating that PVP did not play a key role in controlling the

AuNW width. Although CTAB is previously known for directing NW growth, the replacement of the thiol ligands with CTAB in a control experiment gave freestanding Au nanorods independent of the seed-adsorbed Au@silica (Figure 2-14).

Figure 2-13 TEM image of AuNWs on Au@silica which were obtained from a control experiment carried out in the absence of PVP.

Figure 2-14 TEM image of NPs which were obtained from a control experiment carried out by using CTAB as ligand in the presence of (AuNP@silica)@seeds. Many Au nanorods and nanoplates were observed.

2.3.2 Growth of ultrathin AuNWs on bulk substrates

Compared to the colloidal substrates, the growth of surface-bound AuNWs on bulk substrates is more suitable for further studying the growth mechanism because the product ultrathin AuNWs are not easily aggregated. As colloidal stability is not an issue, reaction conditions can be changed easily and PVP can be excluded.

Here, we use 4-MBA as ligands to grow surface-bound AuNWs on Si wafer, where the thermal SiO₂ layer can be similarly functionalized by APTES. After adsorbing Au seeds, the substrate was immersed in a growth solution containing 4-MBA, HAuCl₄, and L-ascorbic acid. After 15 min, the substrate was retrieved, rinsed with water, and then dried. As revealed by SEM, this surface was covered with a dense layer of vertically aligned AuNWs. At the edge of a scratch mark (Figure 2-15), it can be clearly observed that the AuNWs were over 500 nm in length, with uniform width and height. Though these AuNWs were roughly parallel to each other, they were not perfectly straight like typical single-crystalline NWs.

Figure 2-15 SEM image of vertically-aligned AuNWs on a Si/SiO₂ substrate.

By growing the AuNWs on bulk substrates, we can clearly observe and analyze the orientation of NW growth. When large 15 nm AuNPs were used to grow AuNWs, they ended up on the top of the resulting thin NWs (Figure 2-16a). Obviously, the formation of the AuNWs 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. It was interesting that each AuNW was grown from a Au seed but its diameter was much smaller.^[55-56] This phenomenon is the same as the AuNW grown on colloidal substrates (Figure 2-8). Normally, in colloidal synthesis the seeds are the heterogeneous

nucleation centres; the nanocrystals grown around them are usually larger.^[1] In solid-state growth such as *via* the VLS mechanism, the entire molten seed is the catalyst, making it hard to grow smaller structures.^[27]

Figure 2-16 SEM image of AuNWs synthesized using 15 nm AuNPs as seeds.

We found that the width of AuNWs was dependent on the ligand concentration. When the 4-MBA concentration was decreased from 550 to 28 μM , the resulting nanostructures became shorter and thicker. However, their average diameter increased from 6 to 17 nm (Figure 2-17a,b). Upon further decrease of the ligand concentration to 5.5 μM , Au deposition on the seeds formed an over-coating layer without any sign of AuNW formation (Figure 2-17c).

Figure 2-17 (a-c) SEM images of the Au nanostructures grown on Si/SiO₂ substrates at different ligand concentrations: (a) 550 μ M, (b) 28 μ M, and (c) 5.5 μ M of 4-MBA.

2.3.3 Crystal structure analysis

Study of the AuNWs by HRTEM showed that they were polycrystalline with frequent occurrence of random twinning defects (Figure 2-18). Hence, the unidirectional growth of AuNWs was not consistent with screw-dislocation driven growth, which is an orderly process.^[11, 21-23] Occasionally, single-crystalline segments can also be observed, as illustrated by the Fourier transform analysis of a local section (Figure 2-19 and inset). The AuNWs were

cut by FIB to reveal their cross sections, which were circular in all of the observed cases (Figure 2-20). There was no preferred surface facet that we could identify. Thus, these AuNWs 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.^[6, 34, 57-58] In this aspect, the NW growth is different from the conventional growth models.

Figure 2-18 (a,b) HRTEM images of two continuous parts along a typical ultrathin AuNW. Scale bars are 5 nm.

Figure 2-19 HRTEM image of a single-crystalline segment (Inset: Fourier transform pattern along the $[011]$ zone axis).

Figure 2-20 (a-d) HRTEM images of cross-sections of AuNWs cut by FIB. Many circular structures were observed, representing the cross-sections of the AuNWs.

2.3.4 Growth mechanism

After the initial Au deposition at the seed-substrate interface, it is essential to understand if the subsequent growth occurred at the top seed-AuNW interface or the bottom AuNW-substrate interface. We can devise the reaction conditions

to distinguish the temporal evolution of the AuNWs. To clearly observe the width control, 3-5 nm Au seeds were used. The substrate was first grown in 550 μM of 4-MBA, and then rapidly transferred without drying to a solution of 28 μM of 4-MBA. The resulting AuNWs had thin heads and thick tails, where the head portion is defined as the segment further away from the substrate (Figure 2-21a). Conversely, when the growth was carried out first with low and then with high ligand concentration, the resulting AuNWs had thick heads and thin tails (Figure 2-21b). 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.^[27]

Figure 2-21a provides additional evidence that Au deposition did not occur on the ligand covered surface. It appeared that once the thin sections were formed, 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 2-8 and 2-16.

Figure 2-21 (a) SEM image of the AuNWs grown first in 550 μM MBA solution for 5 min and then in 28 μM MBA solution for 5 min. (b) SEM image of the AuNWs grown first in 55 μM MBA solution and then in 550 μM MBA solution.

In contrast to the absence of lateral growth, the continued longitudinal growth at the Au-substrate interface was obviously promoted by an anisotropic factor. This is deduced to be the result of insufficient ligand coverage at this interface (Figure 2-22b). Hence, the uniqueness of the “active” AuNW-substrate interface lies in its confined environment, which restricts ligand coordination and allows continued Au deposition. Because the ligand 4-MBA binds strongly to Au and packs well,^[59-62] its instant adsorption inhibits Au deposition at the perimeter of the active site, inducing unidirectional growth and forcing the nanocrystals to be pushed upward. Such partial activation of the seed surface cannot occur when their surface packing is not optimal (Figure

2-11 and 2-12a,b) or when the ligand density is too low (Figure 2-17b,c). This active-surface growth model also explains why the AuNWs 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.

Figure 2-22 (a,b) Schematics illustrating (a) the specific conditions used for the syntheses of AuNWs on Si/SiO₂ substrates, (b) because of the strong ligands, the Au deposition selectively occur at the Au-substrate interface.

Following this theory, the control of AuNW width (Figure 2-17a,b) 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 AuNW is being generated from the active site must also be of importance. If ligand coordination cannot keep up with the new AuNW section being pushed upward, the AuNW must be able to grow thicker. The increase in the length of AuNW (dL) should be proportional to the amount of Au deposition and inversely proportional to the cross-section of the AuNWs. 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 AuNW 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 Equation (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 AuNWs; whereas faster

Au deposition should lead to thicker AuNWs. Hence, the polycrystalline nature of the domains is not an issue in this unique growth mode. Given the homogeneous solution environment, the diffusion rates around the seeds or AuNWs 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 2-17b, AuNWs with larger diameter were obtained, consistent with Equation (3). Therefore, these results support a dynamic competition between Au deposition and ligand binding. Changing the rate of one process can tilt the balance of this competition, causing the width of the AuNWs to be adjusted. With this understanding, it is obvious that under our unique growth mode the AuNWs 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 AuNWs can be quickly adjusted during their growth. This is supported by the fact that the thick AuNW sections can be simply grown from the thin ones and *vice versa* (Figure 2-21).

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.^[27] 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 materials are supplied to the active Au-substrate interface and hence, the newly grown segment is always next to the substrate (Figure 2-21). Under 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 (Equation 3).

2.3.5 Extension and application of the active-surface growth

The facile synthesis of substrate-anchored AuNWs can be easily extended to other oxide substrates such as sapphire, SrTiO₃, and LaAlO₃ (Figure 2-23). Moreover, this method can generate a thin and uniform conductive film with reasonable transparency (Figure 2-24). Further work is in progress to reduce contact resistance and improve transparency.^[20, 63] The ultrathin width of the AuNWs is of importance for reducing cost (58.5 Ω/sq at about 0.02 USD\$/cm²). The solution method can be easily applied to substrates with complex surface morphology. Figure 2-25 shows that a trumpet shell coated

with AuNWs, which is difficult to achieve by traditional methods such as spin-coating or doctor-blading. In addition, it is possible to construct 3-dimensional NW networks by growing the ultrathin AuNWs on an oxide substrate with channels or pillars (Figure 2-26), which are potentially used for catalysis or nano-electronics.

Figure 2-23 (a-c) SEM images of AuNWs obtained by using 4-MBA as ligand on (a) sapphire, (b) SrTiO₃, and (c) LaAlO₃ substrate.

Figure 2-24 (a) Photograph of a conductive film (532 cm^2) made of ultrathin AuNWs on a large glass slide. Sheet resistance at the three different spots was measured to be: (1) 53.8; (2) 45.1; and (3) 76.5 Ω/sq . (b) SEM image of AuNWs grown on a scale-down sample with similar transparency as sample (a).

Figure 2-25 (a) Photograph of a trumpet shell before (inset) and after coating a AuNW film. (b) SEM image of AuNWs on sample **a** (a small chip was removed for characterization). (c) Point to point resistance of AuNW-coated trumpet shell measured by digital multi-meter; It shows the resistance is 117 Ω from the tip to the edge.

Figure 2-26 (a-d) SEM images of AuNWs grown on ordered silica pillar arrays (diameter of each pillar is 300 nm): (a,b) top view, (c,d) side view.

2.4 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 nano-electronic device.

2.5 Bibliography

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Chapter 3 Strategy for Nano-Catalysis in A Fixed-Bed System

3.1 Introduction

Nanoparticles (NPs) have been extensively explored for use in catalysis. Being small, they offer many advantages over conventional bulk catalysts.^[1-7] They have a large surface area and sometimes unusual facets, both of which can greatly improve catalytic performance. However, a major disadvantage in using NPs is to load a sufficient quantity of the tiny NPs and to maintain their small size. Because a smaller size means larger surface energy, NPs tend to aggregate and coalesce together to reduce their surface to volume ratio (S/V).^[8-11]

NPs can be directly employed as a colloid in catalytic reactions.^[1, 12-16] Their capping ligands are essential for the colloidal stability, but can suppress the surface reactions. Generally speaking, the presence of salt and/or wrong ligands (*i.e.*, reactants or products) can cause their aggregation. After the catalysis, colloidal NPs are very difficult to separate, often leading to serious aggregation during the centrifugation or filtration step. Thus, recycling them is a major problem.

By anchoring NPs on a support material, their recyclability can be greatly

improved.^[3-4, 17-24] However, the process of anchoring NPs is not trivial. The NPs must be securely anchored (linked via strong ligands or embedded in shells^[25-26]) and have sufficient space between them in order to avoid aggregation. At the same time, the ligands and shells should not block the surface reactions. Dispersing such supported catalysts in a reaction mixture can ensure their accessibility and easily allow sufficient reaction time. However, recycling them after each batch of reaction is still tedious and wasteful. The method is hence only used in laboratory evaluation of catalysts. In industrial applications, catalysts are often loaded in an immobilized support (fixed bed) to achieve maximum recyclability in continuous-flow reactions, which are amenable for automated process.^[27] Given the much shorter contact time with reactants, there need to be more catalysts with higher efficiency.

The processing rate of a fixed-bed system is determined by the lower rate of (a) the physical flow rate, and (b) the overall rate of chemical reactions. More catalysts can lead to faster reactions, but often cause slower flow rates. There is also a limit in increasing the surface density of NPs on a support. Thus, the traditional approaches to overcoming this limit are to use more support materials and/or smaller support particles, both of which reduce the flow rate. Even when high pressure is used, the flow rate is still a major limitation for improving the processing rate.

An innovative approach is to use nanoscale fibrous^[25] or porous structures^[28]

as the catalyst support, because they have a large surface area but also sizeable pores. Using anodic alumina membrane with pores of 200 nm in diameter, improved flow rate has been achieved. Employing external pressure, nearly 100% reduction of 0.4 mM of 4-nitrophenol was achieved at a flow rate of 17.4 mL/min.^[28]

Here, we show that growth of vertical Au nanowires (AuNWs, $d = 5$ nm) on glass fibres can greatly improve the catalyst loading per unit support area (Figure 3-1). With this new loading mode, we can afford to have very large pores in the support structure, which vastly increases the flow rate (Figure 3-2). Using a simple column, the catalytic performance is significantly improved; 20 mM of 4-nitrophenol was reduced at a flow rate of 32 mL/min, a 100 times increase over the best literature examples.

Figure 3-1 (a) Photograph of the catalytic fibres. (b-d) low- and high-magnification SEM images of sample (a).

Figure 3-2 (a) Reaction scheme of the catalysis. (b,c) Photographs showing the setup and the complete reduction of 6 mL of 4-nitrophenol (20 mM) in 40 s. The total Au in the column is 13 mg.

3.2 Materials and Methods

3.2.1 Materials

Hydrogen tetrachloroaurate (III) (HAuCl_4 , 99.9%, Au 49% on metals basis, Alfa Aesar), 4-mercaptobenzoic acid (4-MBA, 90%, Sigma Aldrich), 3-aminopropyltrimethoxysilane (APTMS, Sigma Aldrich), sodium citrate tribasic dihydrate (99.0%, Sigma Aldrich), 4-nitrophenol (Sigma Aldrich), sodium borohydride (NaBH_4 , Sigma Aldrich), L-ascorbic acid (Sigma Aldrich), glass fibre (Sigma Aldrich) and ethanol (analytical grade) were used as received.

3.2.2 Methods

Characterization. Transmission electron microscopy (TEM) images were collected on a JEM-1400 (JEOL) operated at 100 kV. Field emission scanning electron microscopy (SEM) images were collected on a JEOL JSM-7600F. Ultraviolet-visible (UV-vis) spectra were collected on a Cary 100 spectrophotometer. The loading amount of the catalyst on supports was calculated based on the data collected on an Agilent 7700x inductively coupled plasma mass spectrometer (ICP-MS) equipped with a 3rd generation He reaction/collision cell (ORS3) to minimize interferences.

Preparation of citrate-stabilized AuNPs. 0.2 mL sodium citrate (1 wt%) and 14 mL aqueous solution of HAuCl_4 (0.3 mM) was added in a 50 mL flask.

Then 0.6 mL of ice-cold NaBH_4 solution (0.1 M) was added into the above solution with vigorous stirring. The colour of the solution was changed from orange-yellow to brownish-red, indicating the formation of AuNPs. The size of the resulting AuNPs is 3-5 nm, as shown in Figure 3-3.

Figure 3-3 TEM image of 3-5 nm citrate-stabilized AuNPs.

Preparation of AuNWs on glass fibres. To prepare vertical AuNWs on glass fibres, glass fibres (600 mg) were cleaned with piranha solution (H_2O_2 :

H₂SO₄ = 1:3) to make its surface more hydrophilic. The glass fibres were then functionalized with amino group by reacting with APTMS solution (5 mM) for 0.5 h. Subsequently, the fibres were soaked in excess citrate-stabilized AuNPs ($d = 3\text{-}5\text{ nm}$) solution for 0.5 h to ensure the adsorption of Au seeds and rinsed with water twice to remove the excess Au seeds. The seed-adsorbed fibres were then immersed in a water/ethanol (v/v = 1:2) solution (120 mL) containing the ligand 4-MBA (0.6 mM), HAuCl₄ (1.1 mM), and L-ascorbic acid (2.4 mM) for 15 min. Finally, the resulting fibres were rinsed with ethanol and dried in air. The loading of Au on glass fibre was calculated to be 2.2 wt% on the basis of ICP measurements.

For preparing catalytic fibres with lower loading ratio of Au (1.6 wt%), all reaction conditions were the same except that 1 g glass fibres were used as supports.

Preparation of AuNPs on silica spheres. 1 g of silica spheres ($d = 60\text{ }\mu\text{m}$) were incubated with APTMS solution (5 mM) for 0.5 h to be functionalized with amino group. Subsequently, the silica spheres were soaked in excess citrate-stabilized AuNPs ($d = 3\text{-}5\text{ nm}$) solution for 0.5 h to ensure the adsorption of Au seeds and rinsed with water twice to remove the excess Au seeds and residue chemicals.

Catalytic reactions using catalytic fibres monitored by successive UV-vis spectra. To test the catalytic performance of the catalytic fibres, a few pieces of

the catalytic fibres (2.2 wt% Au) were weighed (1.0 mg) and then added to the aqueous solution of 4-nitrophenol (2.5 mM) and NaBH₄ (250 mM). The reaction process was recorded by UV-vis spectra at 2 min interval, as shown in Figure 3-4. (The reaction solution was shaken before each run to ensure full contact of catalysts with the reactants)

Reduction process of 4-nitrophenol (2.5 mM) and NaBH₄ (830 mM) was also been monitored at 1 min interval. As shown in Figure 3-5, it took only 5 min to fully catalyse the reaction.

Catalytic reactions using citrate-stabilized AuNPs monitored by successive UV-vis spectra. To test the catalytic performance of the “clean” AuNPs ($d = 3\text{-}5\text{ nm}$), 350 μL of as-prepared AuNPs solutions were added to an aqueous solution of 4-nitrophenol (2.5 mM) and NaBH₄ (250 mM). The reaction process was recorded by successive UV-vis spectra at 0.5 min interval.

Catalytic performance of the catalytic fibres in a column. 600 mg of the catalytic fibres were packed in a column ($d = 1\text{ cm}$) to reach about 3 cm in height (Figure 3-2b). Then, aqueous mixture of 4-nitrophenol (20 mM) and NaBH₄ (2 M) was added into the column. As shown in Figure 3-2b,c, the reaction mixture remained yellow until it was allowed to flow through the catalyst bed. The exiting solution was completely colourless, indicating the full reduction of 4-nitrophenol. It took 40 s for fully catalyzing 6 mL of reaction mixtures without external pressure (flow rate = 9 mL/min).

Vacuum suction can be used to improve the flow rate in our system. In this case, 1.2 g of catalytic fibres were loosely packed into a column of 10 cm high for the reduction of 4-nitrophenol. Only 80 s was needed to convert 43 mL of 20 mM 4-nitrophenol to 4-aminophenol (*i.e.* 32 mL/min).

For studying the performance of the catalytic column over an extended period, a column with 195 mg of catalytic fibres and lower catalyst loading (1.6 wt% Au) was used (the setup is shown in Figure 3-11). 4-nitrophenol (10 mM) was reduced at a flow rate of 3.6 mL/min. Over 140 h, a total turnover number (TON) of 16,229 was achieved.

Control experiment using AuNP-adsorbed glass fibres. The glass fibres with adsorbing Au seeds but before the growth of AuNWs were used as control sample. 600 mg of the seed-adsorbed glass fibres were packed into a column with the same height ($h = 3$ cm). Then, an aqueous mixture of 4-nitrophenol (1 mM) and NaBH_4 (0.1 M) were then added into the column. Under the same flow rate (9 mL/min), the exiting solution had almost the same yellow colour as the starting solution (Figure 3-9).

Comparison of the flow rate in glass fibre and silica spheres systems. To compare flow rate issues, several control experiments have been conducted. Catalytic fibres were packed in a column with a height of 3 cm. In contrast, silica sphere with AuNPs were packed in two columns with a height of 0.3 and 4.5 cm (optimal condition), respectively (Figure 3-8). Cotton wools were

packed at the bottom of all the catalyst beds in the experiments to ensure comparable volume. The flow rates were recorded for reduction of 20 mM of 4-nitrophenol: 9 mL/min for catalytic fibres, 1.2 mL/min for silica spheres column in which reaction was not completed ($h = 0.3$ cm), and 0.04 mL/min for silica spheres column ($h = 4.5$ cm), as shown in Table 3-1.

3.2.3 Calculations

Calculation of turnover frequency (TOF) and turnover number (TON).

TOF is defined as the number of molecules of reactants that a Au atom can convert to product per unit of time; TON is defined as the total number of molecules of reactants that a Au atom can convert to product.

Comparison of Au surface area in the AuNPs and AuNWs adsorbed on support surface. For comparison, AuNPs and AuNWs are assumed to have the same density on support surface and AuNWs are grown to be 1 μm in length (Figure 3-7). The calculations do not take into account the interface area of AuNPs and AuNWs in contact with the support surface, which are difficult to determine. Under these assumptions: The surface area of one AuNP = $4\pi r^2 = 78.5 \text{ nm}^2$. The surface area of one AuNW = $2\pi rl = 15700 \text{ nm}^2$. Thus, AuNWs would have 200 times the surface area of AuNPs.

Height of column packed with silica spheres of ideal catalytic capability.

When 1 g of 60 μm silica spheres were packed in a column ($d = 1$ cm), the

height of the column is 2.2 cm. Thus, the total volume of the silica-sphere bed occupied = 1.7 cm^3 .

$$\text{Volume of silica spheres (1g)} = 1 \text{ g} / (2.65 \text{ g/cm}^3) = 0.38 \text{ cm}^3$$

According to the above data, the density of packed silica spheres in the column = $0.38 \text{ cm}^3 / 1.7 \text{ cm}^3 = 22 \%$

The volume of silica spheres ($d = 60 \text{ }\mu\text{m}$) in column is based on the assumption: namely the highest known TOF (0.43/s) and the highest surface density (5 nm AuNPs on silica with 30% coverage). In order to process 20 mM of 4-nitrophenol at 9 mL/min, the weight of Au in this column = 1.4 mg.

$$\text{Number of AuNPs on one silica sphere} = [0.3\pi \times (3 \times 10^{-4})^2 \text{ nm}^2] / (\pi \times 2.5^2 \text{ nm}^2) = 1.7 \times 10^8$$

$$\text{Weight of the AuNPs on one silica sphere} = (4/3) \pi \times 2.5^3 \text{ nm}^3 \times 1.7 \times 10^8 \times 19.28 \times 10^{-18} \text{ mg/nm}^3 = 2.1 \times 10^{-7} \text{ mg.}$$

$$\text{Number of silica spheres adsorbed with 1.4 mg of Au} = 1.4 \text{ mg} / 2.1 \times 10^{-7} \text{ mg} = 6.6 \times 10^6$$

$$\text{Volume of silica spheres} = (4/3) \pi \times (3 \times 10^{-3})^3 \text{ cm}^3 \times 6.6 \times 10^6 = 0.76 \text{ cm}^3$$

$$\text{Total volume of silica spheres in column} = 0.76 \text{ cm}^3 / 22 \% = 3.5 \text{ cm}^3$$

$$\text{Height of the column} = 3.5 \text{ cm}^3 / (\pi \times 0.5^2 \text{ cm}^2) = 4.5 \text{ cm}$$

Comparison of surface area in glass fibres and monolith structures. 600 mg of glass fibres with 10 μm in width were packed in a column ($d = 1 \text{ cm}$) to

reach 3 cm of height. Thus, surface area of these glass fibres = $\pi \times 0.001 \text{ cm} \times [(0.6 \text{ g} / 2.65 \text{ g/cm}^3) / (\pi \times 2.5 \times 10^{-7} \text{ cm}^2)] = 942 \text{ cm}^2$

Here, the monolith^[14] with square channels (diameter of square cells = 0.05 cm and wall thickness = 0.01 cm) was assumed to be packed in a column with a same height.

The surface area of each channel = $0.05 \text{ cm} \times 4 \times 3 \text{ cm} = 0.6 \text{ cm}^2$

The number of channels can be estimated = $(\pi \times 0.5^2 \text{ cm}^2) / (0.05 + 0.005)^2 \text{ cm}^2 = 262$

Thus, internal surface area of the monolith = $0.6 \text{ cm}^2 \times 262 = 157.2 \text{ cm}^2$

Therefore, surface area of glass fibres is about 6 times that of monolith structures.

3.3 Results and Discussion

3.3.1 Synthesis of AuNWs on glass fibres

We use thin glass fibres ($d = 10 \text{ }\mu\text{m}$, $l > 10 \text{ cm}$) as catalyst support because they are robust, inexpensive, and can easily form porous network with reasonable surface area. The method of growing ultrathin AuNWs on oxide substrates has been previously reported.^[29] In a typical synthesis, glass fibres (600 mg) were cleaned using piranha solution, washed, and then functionalized with APTMS. With amino groups on the glass fibre surface, small Au seeds ($d =$

3-5 nm) were easily adsorbed. Finally, the fibres were immersed in a solution of 4-MBA (0.6 mM), HAuCl_4 (1.1 mM), and L-ascorbic acid (2.4 mM) to grow AuNWs. Upon immersion, the glass fibres quickly turned grey (< 1 min) and the colour further darkened over time. After 15 min, the resulting black fibres (catalytic fibres) were rinsed with ethanol to remove the ligands on the AuNWs and then dried (Figure 3-1). The equivalent amount of Au used in the reaction was about 17 mg. On the basis of ICP measurement, the amount of Au loaded on the glass fibres was 2.2 wt% (or a total of 13 mg).

SEM characterization of the glass fibres confirmed that a dense layer of vertical AuNWs have grown on their surface, similar to the report in Chapter 2.^[29] The AuNWs were 5 nm in width and about 1 μm in length (Figure 3-1d). The glass fibre shown in Figure 3-1b was completely covered with the AuNW layer, where the difference in colour was due to the viewing angle in SEM. The layer was so dense that we had to find the cracks in the layer in order to characterize the constituent AuNWs (Figure 3-1d). The layer was also uniform at the multiple locations that we have characterized, which is consistent with the uniform black colour of the glass fibres.^[30] In this method, the presence of strong 4-MBA ligand inhibited the homogenous nucleation of Au to give colloidal NPs^[29] and thus, most of the reduced Au participated in the growth of AuNWs.

3.3.2 Catalytic performance of catalytic fibres

To evaluate the catalytic performance of our system, we use a well-known model reaction, where 4-nitrophenol was reduced to 4-aminophenol using NaBH_4 as the reductant. This reaction cannot proceed in the absence of Au catalyst. It has been widely used because the conversion of yellow 4-nitrophenol to colourless product can be easily monitored. Briefly, a few pieces of the catalytic fibres were weighed (1.0 mg with 2.2 wt% Au) and then added to the aqueous solution of 4-nitrophenol (2.5 mM) and NaBH_4 (250 mM) (Figure 3-4a,b). As shown by the UV-vis spectra (Figure 3-4c), the absorption peak at 400 nm gradually decreased with time and two new peaks appeared at 226 and 305 nm, indicating the formation of 4-aminophenol.^[31] On the basis of the peak at 400 nm, the reaction was completed after 14 min, where the average TOF was about 0.09/s ($k = 6.5 \times 10^{-3} \text{ s}^{-1}$). Higher TOF of 0.26/s was achieved when a higher concentration of NaBH_4 (830 mM) was used, as shown in Figure 3-5. For a fair comparison, the TOFs below were calculated based on the total amount of Au in the system (the same is done for literature values), not the amount of surface atoms.

Figure 3-4 (a,b) Photographs showing the colour change of the reaction mixture (2.5 mM of 4-nitrophenol and 250 mM of NaBH_4) (a) before and (b) after the addition of 1.0 mg catalytic fibres (2.2 wt% Au). (c) Successive UV-vis spectra recorded with 2 min interval.

This value is compared to the best examples in the literature for the same model catalysis. When AuNPs ($d = 15$ nm) were embedded in the porous silica shells of magnetic NPs, the TOF was estimated to be 0.02/s on the basis of total Au.^[32] When $d = 3$ -5 nm AuNPs were anchored on silica microspheres, it took 60 min to fully reduce 1.5 mM of 4-nitrophenol. The TOF is estimated to be 0.03/s.^[26] For colloidal catalyst, the best performance involved AuNPs ($d = 2$ -3 nm) stabilized by an ionic polymer. It took about 16 min to fully reduce 0.6 mM of 4-nitrophenol (estimated TOF = 0.07/s).^[13] Large citrate-stabilized AuNPs ($d = 20$ nm) gave about 0.02/s TOF.^[16] While citrate is a weak ligand favouring the catalytic reaction, the large NPs have small S/V. To our surprise, we were not

able to find literature rates on using small and “clean” colloidal AuNPs (of which surface is not hampered by strong ligands, polymer, or shells) as catalyst.

Figure 3-5 Successive UV-vis spectra recording the reduction of 2.5 mM of 4-nitrophenol by using 830 mM of NaBH_4 after the addition of 1.0 mg catalytic fibres (2.2 wt% Au) at 1 min interval.

To understand the unusual catalytic performance in our system ($\text{TOF} = 0.09/\text{s}$), we tried to prepare a best control catalyst. HAuCl_4 was reduced in the presence of sodium citrate using NaBH_4 . The resulting AuNPs were 3-5 nm in diameter and capped only with weak ligands (Figure 3-3).^[30] When these colloidal NPs were directly used as catalyst, 2.5 mM of 4-nitrophenol was fully reduced in 3 min ($\text{TOF} = 0.43/\text{s}$), as shown in Figure 3-6. Being small and with

all surfaces available for the catalysis, this simple control sample has better performance than all of the above systems.

In comparison, for the vertical AuNWs ($d = 5$ nm) grown on glass fibres, the catalytic performance was reasonably good but still not comparable to the small and clean AuNPs. This is likely because the AuNWs have a lower S/V than (about 67% of) the colloidal AuNPs and the molecular diffusion may not be efficient in the dense forest of AuNWs. Moreover, some residues of 4-MBA will remain on the AuNW surface even after washing.

Thus, batch-wise reactions are not the best platform for exploiting the advantages of our new method. The exceptional catalyst loading per unit support area is of great importance for continuous flow catalysis. For industry applications, the top concerns are to achieve an “automated” mode of continuous flow, and to improve the processing rate and recyclability. One can always use more catalysts for faster reactions, so long as the catalysts are recyclable.

Figure 3-6 (a,b) Photographs showing the colour change of the reaction mixture (2.5 mM of 4-nitrophenol and 250 mM of NaBH₄) (a) before and (b) after the addition of citrate-stabilized 3-5 nm AuNPs. (c) Successive UV-vis spectra recorded with 0.5 min interval.

3.3.3 Catalytic performance of catalytic column

The catalytic fibres can be loosely packed into a simple column as a proof-of-concept demonstration. Specifically, 600 mg of the fibres with AuNWs were packed in a column ($d = 1$ cm) to reach about 3 cm in height (Figure 3-2b). Then, aqueous mixture of 4-nitrophenol (20 mM) and NaBH₄ (2 M) was added into the column. As shown in Figure 3-2b,c, the reaction mixture remained yellow until it was allowed to flow through the catalyst bed. The exiting solution was completely colourless. Aliquots taken from the solution showed no absorption at 400 nm, indicating the completed reaction. Without using external pressure, it took only 40 s to process 6 mL of the concentrated reaction mixture. The estimated TOF was about 0.05/s, a respectable number considering their short contact time with the flowing reactants.

In comparison to the batch-mode reaction, our ability to carry out continuous flow reaction with recyclable catalyst avoids the recycling step, which is costly in both time and money. Considering the time of recycling, the batch-mode

reactions would be much slower in overall processing rate than our continuous-flow method. Given the small size of our column ($d = 1$ cm), the processing rate we have achieved is exceptional.

In a fixed-bed system, the flow rate depends on the crevices among the support particles. Typically, silica or polystyrene microspheres with large surface area are used as the support material. For 60 μm spheres, the crevices among them should be about only a few μm in width, similar in size to the pores among gel fibres.^[33-34] It is known that the solution inside a gel flows very slowly. Hence, the more support materials used, the slower the flow rate. In contrast, the crevices inside a loose column of glass fibres can be much larger (Figure 3-7a,b).

Without external pressure, our catalytic column ($d = 1$ cm, $h = 3$ cm) can achieve a 9 mL/min flow rate, whereas a thin $h = 0.3$ cm column of silica spheres gave only a 1.2 mL/min rate (Figure 3-8a,b). It is impossible to load enough catalyst in such a short column. In order to process 20 mM of 4-nitrophenol at 9 mL/min, there need to be a lot more catalysts and a lot more support materials. Assuming optimal conditions, namely the highest known TOF (0.43/s, *vide supra*) and the highest surface density (5 nm AuNPs on silica with 30% coverage),^[35] the column of 60 μm silica spheres needs to be at least 4.5 cm in height. Without external pressure, the flow rate through such a column was only 0.04 mL/min, clearly not matching with the catalytic

capability (Figure 3-8c). If $\text{TOF} = 0.04/\text{s}$, then a column of 45 cm high would be needed. Even with high external pressure, the flow rate through such a column is very slow.

Figure 3-7 (a,b) Schematics illustrating the difference of pores among (a) loosely packed silica spheres and (b) glass fibres. The crevices are highlighted in yellow. (c,d) Schematics illustrating the difference in terms of available catalytic surface for (c) AuNPs and (d) AuNWs loaded on a support surface. Under the assumption of a same surface density, AuNWs would have 200 times the catalytic surface area of AuNPs.

Figure 3-8 (a-c) Photographs of (a) catalytic fibres packed in the column with 3 cm in height, (b,c) AuNP-adsorbed silica spheres ($d = 60 \mu\text{m}$) packed in a column with (b) 0.3 cm and (c) 4.5 cm in height.

An alternative approach is to directly adsorb $d = 3\text{-}5 \text{ nm}$ AuNPs on a loose network of glass fibres. Indeed, the glass fibres after adsorbing the seeds and before the growth of AuNWs are a perfect control sample. A similar column packed with these fibres ($h = 3 \text{ cm}$) was tested (Figure 3-9). Under a same flow rate (9 mL/min), even when a low concentration of 4-nitrophenol (1 mM instead of 20 mM) was used, the exiting solution had almost the same yellow colour as the starting solution. Thus, the catalytic capability of this control sample was much less than $1/20$ of the column with AuNWs.

Table 1. Comparison of the flow rate using catalytic fibres or silica spheres adsorbed with AuNPs*

	Catalytic Fibres	Silica Spheres with AuNPs	
Bed Height (cm)	3	0.3	4.5
Flow Rate (mL/min)	9	1.2	0.04

* The catalytic fibres or 60 nm silica spheres decorated with AuNPs ($d = 3\text{-}5$ nm) were separately packed into columns ($d = 1$ cm) with different bed heights.

These simple estimates illustrate the difficulty in improving the catalytic performance while matching the physical flow rate with the catalytic capability. While the NPs have large S/V, their small size necessitates a large quantity in order to present sufficient catalytic surface. However, more catalyst means more support materials and thus, slower flow rate. For the two fixed-bed systems in the literature,^[25, 28] the slow flow rate would make it difficult to use more support for more catalysts.

Figure 3-9 (a,b) Photographs showing the catalysis using 600 mg of glass fibres adsorbed with Au seeds. These fibres were packed in a column for the reduction of 4-nitrophenol (1 mM) with 0.1 M NaBH₄ (a) before and (b) 20 s after the reaction solution was allowed to flow through. It is shown that the reaction was incomplete after flowing through this column.

Our innovative approach is to grow vertical AuNWs on the support. Assuming a same surface density on the support, AuNWs of 5 nm in diameter and 1 μm in length would have 200 times the surface area of $d = 5\text{ nm}$ Au spheres (Figure 3-7c,d). This allows large crevices in the support structure and easily balances the flow rate with the catalytic capability.

In industry, monolith with large and straight pores is often used as catalyst support. The pore size (and thus flow rate) is easily tunable, but the structure has only a small surface for adsorbing catalyst (in comparison to using particles or fibres as support). For example, a similar sized column ($d = 1\text{ cm}$, $h = 3\text{ cm}$) with 0.5 mm pores^[36] would have only 1/6 of the surface area as the glass fibres used in our system. Thus, to load a same amount of catalyst, a longer column is needed. This would be problematic if 3-5 nm AuNPs are used as the catalyst, because the column needs to be 1200 times longer than our system. Of course, if AuNWs can be directly grown inside the monolith pores, the size of the monolith can be reduced. This is indeed possible because of our facile growth using a solution method.

External pressure can be applied to any fixed-bed system to improve the flow rate, but it usually cannot resolve the issues discussed above. It can also be applied to our system. With minor modifications, the processing rate can be greatly improved: 1.2 g of the catalytic fibres (total 26 mg of Au) were loosely packed into a column of 10 cm high and vacuum suction was applied (Figure

3-10). It took only 80 s to process 43 mL of 20 mM 4-nitrophenol (*i.e.* 32 mL/min).

The performance of the catalytic column was studied over an extended period. Due to the high activity of the column, we had to load less catalyst to cut down the required time and chemicals (Figure 3-11). A column with 195 mg of catalytic fibres and lower catalyst loading (total 3.1 mg of Au) was used (Figure 3-12). 10 mM of 4-nitrophenol was completely reduced at a flow rate of 3.6 mL/min. Over 140 h, a total TON of 16,229 was achieved with only slight loss of activity (Figure 3-13).

Figure 3-10 (a,b) Photographs showing the setup and the complete reduction of

43 mL of 4-nitrophenol (20 mM) in 80 s with vacuum suction. The total Au in the column is 26 mg.

Figure 3-11 Photographs showing the setup for catalytic test over an extended period. A column with 195 mg of catalytic fibres and lower catalyst loading (1.6 wt% Au) was used for the reduction of 4-nitrophenol (10 mM) with NaBH_4 (1 M).

Figure 3-12 (a,b) SEM images of low- and high-magnification of a sample with 1.6 wt% of Au loaded on glass fibre. This sample was used for studying the catalytic performance over a long period.

Figure 3-13 Graph showing the total turnover number versus time for the reduction of 4-nitrophenol (10 mM) with NaBH_4 (1 M) by using 195 mg of catalytic fibres (total 3.1 mg of Au).

NPs are problematic for industrial catalysis, because to load them with a sufficient quantity requires a huge support surface. Our careful analysis of the problem showed that there is no conventional solution. By directly growing vertical AuNWs on an oxide substrate, the available catalytic surface increased by about 200 times. This allowed highly porous support structure to be used for improved flow rate. This strategy of using 3-dimensional catalyst structure is conceivably applicable to other systems. It would help bridge the laboratory tested nano-catalysts to industrial applications.

3.4 Conclusion

In summary, our new capability of growing dense Au nanowire forest is immensely advantageous for fixed-bed catalysis. The solution method of growing Au nanowires on glass fibres is simple, reliable, and scalable. In comparison to the best examples in the literature, our system can catalyze the same model reaction with reasonable turnover frequency but greatly improved processing rate.

3.5 Bibliography

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Chapter 4 Synthesis of Surface-Bound Palladium and Bimetallic Segmented Nanowires

4.1 Introduction

Metallic nanowires (NWs) have attracted much interest in the recent years because their large anisotropy and electrical conductivity makes them suitable candidates as linkage in nanoelectronic devices.^[1-3] Their narrow width cuts down on the usage of precious metal and confers high sensitivity for applications such as sensors.^[4-5]

Besides “top-down” methodologies such as nanolithography,^[6] great efforts have been devoted to “bottom-up” approaches like growth of metallic NWs in colloidal systems which are scalable and low cost. While important advances have been made in Au and Ag NWs,^[7-13] the approaches for synthesis of PdNWs are still quite limited. To date, three solution methodologies have been reported for the fabrication of PdNWs: (1) PdNWs can be synthesized via oxidative etching process.^[14] It is proposed that oxygen or other oxidants can etch one surface of single-crystalline Pd nanoparticles (PdNPs) in the presence of halide ions, which is believed to remove the capping ligands from this

surface. Thus, newly-formed Pd atoms in the solution would preferentially deposit on this de-protected surface, leading to the fast growth of crystal in this direction; (2) five-fold twinning defect in the centre of PdNPs induce lattice strain which constrain the growth of NPs in the transverse direction. With the help of halide ions, NPs are grown along the pentagonal axis to form NWs;^[15] (3) templates such as hollow silica tubes can serve as a mould to shape the growth of Pd and allow the Pd nanostructures to follow the shape of templates. Given a cylindrical cavity, PdNWs can be synthesized.^[16] It is conceivable that exploration of new methodologies can create more complex and diverse nanostructures for use in nanodevices.

On the other hand, bimetallic nanostructures composed of distinct metal elements have been of much interest. They can show the properties of two different components and may exhibit enhancement in physical or chemical properties due to the metal-metal hetero-junction.^[17]

Here, we report the synthesis of PdNWs via the active-surface growth mode (Figure 4-1). By using the strong thiol ligands, PdNWs with 4 nm in diameter can be grown from surface-bound seeds on Si wafer. Based on our understanding of the growth mechanism, the methodology can be extended to fabricate segmented Au-Pd NWs.

Figure 4-1 Schematics illustrating the growth of surface-bound PdNWs from Pd seeds.

4.2 Materials and Methods

4.2.1 Materials

Hydrogen tetrachloroaurate (III) (HAuCl_4 , 99.9%, Au 49% on metals basis, Alfa Aesar), sodium chloropalladate(II) (Na_2PdCl_4 , Alfa Aesar), 4-mercaptobenzoic acid (4-MBA, 90%, Sigma Aldrich), 3-aminopropyltrimethoxysilane (APTMS, Sigma Aldrich), sodium citrate tribasic dihydrate (99.0%, Sigma Aldrich), sodium borohydride (NaBH_4 , Sigma Aldrich), L-ascorbic acid (Sigma Aldrich), Ethanol (analytical grade) were used for preparing 4-MBA solution. Deionized water (resistance $> 18.2 \text{ M}\Omega/\text{cm}$) was used in all reactions. Copper specimen grids (300 mesh) with formvar/carbon support film were purchased from Beijing XXBR Technology Co.

4.2.2 Methods

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

electron microscopy (SEM) images were collected on a JEOL JSM-7600F. In a typical experiment, high-resolution scanning transmission electron microscopy (STEM) imaging was conducted at a 2-us/pixel scanning rate with 70 um C2 aperture, spot size 9, a high-angle annular dark-filed (HAADF) detector, and 146 mm camera length. Under such conditions, a spatial resolution of ~ 1.0 Å was obtained.

Preparation of citrate-stabilized Pd seeds. A 50 mL flask was filled with 0.2 mL sodium citrate (1 wt%) and 14 mL aqueous solution of Na_2PdCl_4 (0.4 mM). Then 0.6 mL of ice-cold NaBH_4 solution (0.1 M) was added with vigorous stirring. The solution turned from brown to gray, indicating the formation of PdNPs. The size of the resulting PdNPs was about 3-5 nm, as shown in Figure 4-2.

Figure 4-2 TEM image of citrate-stabilized Pd seeds.

Synthesis of PdNWs on Si/SiO₂ substrate. A Si wafer (about 1 cm²) was treated with O₂ plasma for 10 min to improve its surface hydrophilicity. The wafer was then reacted with APTMS (5 mM) to functionalize the surface with amino group, and incubated with excess citrate-stabilized Pd seeds ($d = 3-5$ nm) solution for 0.5 h to ensure their adsorption of Pd seeds. The PdNP-adsorbed wafer was then rinsed with water and immersed in a water/ethanol ($v/v = 1:2$) solution of ligand 4-MBA (2.0 mM), Na₂PdCl₄ (2.4 mM) and L-ascorbic acid (4.3 mM). After a 30 min reaction, the wafer was washed using ethanol and dried in air. For growing PdNWs on large Si wafer (about 35 cm²), all the reaction procedures were same but the reactant concentrations were scaled up.

For preparing PdNWs using 3-5 or 15 nm AuNPs as seeds, all reaction conditions were the same except that citrate-stabilized AuNPs with diameter of 3-5 or 15 nm^[18] were used as seeds to be adsorbed on the amino-functionalized Si wafer.

Synthesis of Au-Pd segmented NWs on Si/SiO₂ substrate. A plasma-treated Si wafer (about 1.2 cm²) was immersed in an APTMS solution (5 mM) for 0.5 h. Subsequently, the wafer was incubated with excess citrate-stabilized Au seeds ($d = 3-5$ nm) solution for 0.5 h and then rinsed with water twice to remove the excess Au seeds. The seed-adsorbed wafer was then soaked in a water/ethanol ($v/v = 1:2$) solution containing 4-MBA (350 μ M), HAuCl₄ (1.7 mM) and L-ascorbic acid (4.1 mM) for 20 s. The AuNW-attached

wafer was then rinsed with ethanol to remove the residue reagents and then immersed in a water/ethanol ($v/v = 1:2$) solution containing 4-MBA (2.0 mM), Na_2PdCl_4 (2.4 mM) and L-ascorbic acid (4.3 mM) for 30 min. The wafer was then rinsed with ethanol and dried in air.

4.3 Results and Discussion

4.3.1 Synthesis of surface-bound ultrathin PdNWs

In the previous chapters, we reported a new method to induce AuNW growth by employing the thiol ligands with strong affinity to Au. This method is highly feasible and scalable for the growth of surface-bound ultrathin AuNWs. The underlying mechanism for this growth mode (named as active-surface growth mode) is that the strong-binding ligands block the deposition of Au atoms on all the seed surface except for the area at the seed-substrate interface, leading to the extension and growth of a AuNW. From the high-resolution TEM characterization on a cross-section of resulting NWs, the cross-section is almost spherical in shape, indicating that there is no preferential binding of the ligands on specific facets. Based on the proposed mechanism, this method is not only applicable to the growth of AuNWs, but also fabrication of other metal NWs whose surface can be capped with thiol ligands. By modifying reaction conditions, it is shown that surface-bound PdNWs can indeed be synthesized

via the active-surface growth mode.

Figure 4-3 (a,b) low-and high-magnification SEM images of a dense layer of PdNWs on Si wafer. Inset: a photograph of the resulting Si wafer.

Figure 4-4 (a,b) TEM images of ultrathin PdNWs detached from substrates by sonication: (a) highly concentrated and (b) lower concentrated samples.

To synthesize PdNWs, reaction conditions would have to be modified as from Chapter 2. A reaction solution containing ligand 4-MBA (2.0 mM), Na_2PdCl_4 (2.4 mM) and L-ascorbic acid (4.3 mM) was used to immerse the wafer after seed-adsorption, instead of a reaction solution containing HAuCl_4 . Also, the wafer substrate was immersed for a longer period (30 min).

As shown in Figure 4-3, the yield of substrate-bound PdNWs is quite high: a dense layer of resulting PdNWs fully covered the substrate surface, obscuring the wafer substrate. The PdNWs NWs form bundle-like structures with random growth directions but we can still identify that each bundle wires composed of several thin PdNWs (Figure 4-3b). To clearly observe the morphology of these PdNWs, they were removed from the substrates by sonication and then characterized by TEM. From TEM images in Figure 4-4, PdNWs were observed as separated wavy structures rather than bundle-like structure. The diameter of PdNWs was measured as 4 nm and their length of up to 200 nm. This solution method for fabricating surface-bound ultrathin PdNWs is facile and scalable and can be easily to be applied onto large substrate surface. Si wafer with surface area of about 35 cm^2 (35 times of the sample in Figure 4-3) was used as substrate to grow PdNWs (Figure 4-5). The morphology of the resulting NWs is roughly the same as that in Figure 4-3.

Figure 4-5 (a,b) Low-and high-magnification SEM images of PdNWs on large Si wafer (35 cm^2 , a small chip was removed for characterization). Inset: a photograph of the resulting Si wafer.

Figure 4-6 (a) Schematics and (b) TEM image of PdNWs grown with Au seeds ($d = 3\text{-}5\text{ nm}$), detached from substrate by sonication.

4.3.2 Synthesis of surface-bound PdNWs with Au tips

The nature of active-surface growth mode is that ligands cannot effectively block the seed surface at the seed-substrate interface, promoting the crystal growth at this interface; The newly-formed lateral NW surfaces are exposed and blocked by the excess ligands in the solution shortly while the NW-substrate interface is still more “active”, allowing the continuous growth thereon. Given an “active” surface, bimetallic crystalline NWs can be formed even lattices of the seed and NW crystals are mismatched.

Based on the above analysis, the PdNWs with Au tips can be synthesized by using AuNPs as seeds (4.7% mismatch) under otherwise the same reaction conditions as for NWs using Pd seeds (Figure 4-6). By using 3-5 nm AuNPs as seeds, the morphologies of the emerging PdNW sections are almost the same that shown in Figure 4-4. The diameter of Au seeds at the end is similar to that of PdNW segments, thus it is difficult to distinguish the Au seeds at the end of the PdNWs.

A possible competitive process in the PdNW growth was homogenous Pd nucleation to form small particles. If these PdNPs happen to adsorb on the wafer surface, they may then serve as seeds for the subsequent growth of PdNWs through the same active-surface growth mode, resulting in PdNWs without Au tips. To identify whether Au seeds are at the end of PdNWs, larger size of AuNPs ($d = 15$ nm) were employed as seeds. As shown in Figure 4-7b,

almost every thin PdNW is bonded with a bigger AuNP ($d = 15$ nm) at the tip.

This implies that the chance of the competitive process is minimal.

Under the active-surface growth mode, the seed surface is protected by the ligands (*i.e.* 4-MBA) which would hamper or block the deposition of growth materials on the seed surface. Thus, there is no obvious change in the size of the seed on the tip. From Figure 4-7b, the diameter of the tip part is measured to be about 15 nm which is equivalent to that of the Au seed particles used. Moreover, the diameter of the NWs is independent of the size of the seeds.

Under the active-surface growth mode, it has been shown that the width of emerging NWs is following the equation:

$$D = a \cdot \frac{\mu}{\gamma} \quad (1)$$

where D is the diameter of NWs, a is a constant, μ is metal deposition rate, and γ is ligand diffusion rate. The growth of PdNWs (with or without Au tips) also follows this rule: Given a fixed ratio of Pd-deposition and ligand-binding rates (which is related to the concentration ratio of Na_2PdCl_4 , 4-MBA and L-ascorbic acid), the width of resulting PdNW segments is unchanged. Thus, the diameter of the PdNW segments is always around 4 nm if they are grown in a solution of 4-MBA (2.0 mM), Na_2PdCl_4 (2.4 mM) and L-ascorbic acid (4.3 mM). In this system, the “active” interface between Au seed and substrate can induce the growth of PdNWs and only one tip of a PdNW is attached with AuNP, indicating the unidirectional growth of the PdNW (Figure 4-7a). From the

energy dispersive X-ray spectroscopy (EDS) analysis, it can be confirmed that the head part is only composed of Au and the tail part is only composed of Pd (Figure 4-7c,d).

4.3.3 Synthesis of surface-bound segmented Au-Pd NWs

NW-substrate interface can also be employed to grow another metallic section of NWs, producing bimetallic segmented NWs such as segmented Au-Pd NWs (Figure 4-8). In this case, seed-adsorbed Si wafer was first immersed in a reaction solution to grow AuNW segments and then immersed into another reaction solution to achieve the growth of PdNW segments beneath the existing AuNWs. The resulting segmented NWs were removed from substrate and characterized by TEM (Figure 4-9).

Figure 4-7 (a) Schematics illustrating the synthesis of PdNWs with Au tips ($d = 15$ nm). The black arrow indicates the growth direction of the NWs. (b) TEM image of the resulting PdNWs with Au tips by using 15 nm Au seeds, under the same reaction conditions as for PdNWs in Figure 4-3. The resulting PdNWs were detached from substrate by sonication. (c,d) EDS analyses of (c) the head part and (d) tail part of a typical nanowire in **b**. The EDS analyses (atomic ratio) have been shown in **c** and **d**.

Figure 4-8 Schematics illustrating the synthesis of segmented surface-bound Au-Pd NWs.

Figure 4-9 (a) TEM image of segmented Au-Pd NWs detached from substrate

by sonication. (b,c) EDS analyses of (b) the thick part and (c) thin part of a typical nanowire in **a**. The EDS analyses (atomic ratio) have been shown in **b** and **c**.

Figure 4-10 (a,b) HAADF-STEM images of (a) a segmented NW grown from a 15 nm Au seed adsorbed on Si wafer, and (b) the connection interface between the Au and Pd segments. The white arrows in (b) indicate the interface of two segments.

The control of the thicknesses of different segments can be achieved, which would allow easy identification of the two segments. The thickness of the emerging AuNWs would be about 7 nm when the reaction solution is composed of 4-MBA (350 μ M), HAuCl₄ (1.7 mM) and L-ascorbic acid (4.1 mM). As mentioned previously, the resulting PdNWs were of around 4 nm in thickness when they were grown in a reaction solution of 4-MBA (2.0 mM), Na₂PdCl₄ (2.4 mM) and L-ascorbic acid (4.3 mM). The latter growth of Pd cannot form a shell on the existing Au segments because the ligands on the lateral surface of Au segments would block the deposition of Pd. Thus, the resulting bimetallic NWs should possess thicker ends of about 7 nm and thinner ends of about 4 nm. In Figure 4-9, the thickness at the two ends of the NWs is different along each individual NW. Based on the analysis, we can deduce that the thick ends ($d = 7$ nm) of the NWs are attributed to Au segments while the thin ones ($d = 4$ nm) are Pd segments. EDS analysis has been employed to show that the NWs are composed of two segments: The thick end of the NWs are only composed of Au while the thin ends are only composed of Pd (Figure 4-9 b,c).

The structure of segmented NWs was further confirmed by using high-resolution STEM. From the HAADF-STEM images of a typical Au-Pd segmented NW with a Au head, Au and Pd segments can be easily distinguished via a clear interface (Figure 4-10). It is observed that a thin Pd NW segment was grown after the thick Au segment. In addition, the absence of Pd layer coated on the Au segment supports our arguments that metal deposition can only occur at the NW-substrate interface. Upon characterization of the Au-Pd interface, it is illustrated that the Pd segment was grown following the lattice of Au but with a twist at the interface probably due to the lattice mismatch (Figure 4-10b).

4.4 Conclusion

The active-surface method has been proven to be extendable towards the growth of Pd nanowires. By using a strong ligand, ultrathin surface-bound Pd nanowires can be grown in polar solution at ambient condition. This method is facile, scalable and reproducible. With the understanding of the growth mechanism, we can also apply this method to the growth of PdNW with Au tips as well as Au-Pd segmented bimetallic NWs. This system could open up new opportunities in nanostructure synthesis and potential application in catalysis and nanodevices.

4.5 Bibliography

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Chapter 5 Ligand Induced Growth of Chiral Gold Nanowires

5.1 Introduction

Chirality has been a prominent issue for material science and technology. Similar to chiral molecules, chiral nanocrystals have drawn increasing attention due to their fascinating properties such as rotation of polarized light^[1-5] and future potential in applications such as plasmonic sensors.^[4]

To obtain chiral nanocrystals, chiral factors have to be introduced to break the symmetry during the crystal growth. Great efforts have been devoted to synthesizing chiral nanocrystals but the methodologies are still limited^[6]: (1) The attraction of surface charge between segments along a wire leads to the coiling structures in semiconductors such as ZnO nanowires (NWs)^[7-9] and CrSi₂ nano-webs;^[10] (2) The strain generated by spiral propagation of line defects in screw-dislocation promotes the growth of “pine-tree-like” helical structures;^[11-12] (3) During the growth of carbon nanotubes (CNTs) via vapour-liquid-solid (VLS) process, the imbalance of growth velocity at the circumference of liquid catalysts is supposed to cause the emerging carbon CNTs to twist, which is invoked by asymmetric extrusion of the growth

materials or anisotropic contact angle of the catalyst droplets on the tip of CNTs;^[13-16] (4) Employing chiral templates such as helical polymers can confine crystal growth and achieve chiral nanostructures^[17-18] but the preparation of chiral templates is not trivial; (5) The fusion of faceted semiconductor nanocrystals via oriented attachment can cause the formation of chiral NWs.^[19]

The assembly of isotropic metal atoms are often highly symmetric, thus chiral nanostructures are rarely reported and extremely interesting in their formation mechanism. Of the known methods, the José-Yacamán group reported the template-free growth of helical alloy NWs by mixing HAuCl_4 , AgNO_3 and oleylamine.^[20] In addition, our group was also able to synthesize ultrathin Au-Ag alloy NWs in polar solution in the presence of polyvinylpyrrolidone (PVP). By coating with a layer of metal, the alloy NWs can wind around themselves to form double-helices.^[21]

As discussed previously in Chapter 2, an unconventional growth of ultrathin AuNWs has been demonstrated via active-surface growth mode. By immersing a seed-adsorbed Si wafer into the reaction mixture containing 4-mercaptobenzoic acid (4-MBA, 0.6 mM), HAuCl_4 (1.7 mM) and L-ascorbic acid (4.1 mM), surface-bound AuNWs with 6 nm in width can be obtained (Figure 5-1a). The resulting NWs are roughly straight although they are polycrystalline. We have proposed and proved that the binding of ligands on the

exposed Au surfaces promotes the NW growth and the width of the resulting NWs is controlled by competition between ligand binding and Au deposition.^[22]

Here, we report the fabrication of chiral NWs based on the active-surface growth mode, where spiral NWs were obtained (Figure 5-2 and 5-3). These NWs of 3 nm width were grown from the surface-bound seeds in a water/ethanol mixture in the presence of high concentration of ligand 4-MBA. With carefully-designed control experiments, we propose that the uneven binding of ligands at the Au-substrate interface induces the imbalance of growth rates of this interface, causing the growth orientation of the NWs to tilt and resulting in chiral (or twisted) structures. This ligand-induced growth is a general method for chiral NW growth using different thiol ligands and potentially can be applied in other metal NWs to achieve chiral nanostructures.

Figure 5-1 (a) TEM image of roughly-straight ultrathin AuNWs detached from

Si wafer surface by sonication. These NWs were synthesized in a reaction solution containing 4-MBA (0.6 mM), HAuCl_4 (1.7 mM) and L-ascorbic acid (4.1 mM). (b) Schematics illustrating the active-surface mechanism for the growth of NWs in (a).

Figure 5-2 SEM image of the ultrathin AuNWs with chiral (or twisted) structures.

Figure 5-3 (a-d) TEM images of ultrathin chiral (or twisted) AuNWs: (a) a large view of the resulting NWs, (b,c) spiral NWs and (d) a typical zigzag-like NW. This sample was synthesized by dipping seed-adsorbed Si wafer into a reaction solution of 4-MBA (1.0 mM), HAuCl_4 (0.5 mM) and L-ascorbic acid (1.2 mM), and corresponds to sample C in Table 1. The resulting NWs were detached from the wafer surface by sonication.

5.2 Materials and Methods

5.2.1 Materials

Hydrogen tetrachloroaurate (III) (HAuCl_4 , 99.9%, Au 49% on metals basis, Alfa Aesar), 4-MBA (90%, Sigma Aldrich), 3-aminopropyltrimethoxysilane (APTMS, Sigma Aldrich), sodium citrate tribasic dihydrate (99.0%, Sigma Aldrich), 4-nitrobenzenethiol (Sigma Aldrich), L-ascorbic acid (Sigma Aldrich), ethanol (analytical grade) were used for preparing solutions of thiol ligands. Deionized water (resistance $> 18.2 \text{ M}\Omega/\text{cm}$) was used in all reactions. Copper specimen grids (300 mesh) with formvar/carbon support film were purchased from Beijing XXBR Technology Co.

5.2.2 Methods

Characterization. Transmission electron microscopy (TEM) images were collected on a JEM-1400 (JEOL) operated at 100 kV. High resolution TEM (HRTEM) images were taken from JEOL 2100 F field emission transmission electron microscope operated at 200 kV.

Synthesis of chiral AuNWs bound on Si/SiO₂ substrate using 4-MBA as ligands. A Si wafer (about 1 cm^2) was treated with O₂ plasma for 10 min to improve the hydrophilicity of the surface. The wafer was then functionalized with amino group by reacting with APTMS solution (5.0 mM) for 0.5 h. Subsequently, the wafer was soaked in excess citrate-stabilized Au seeds ($d =$

3-5 nm) solution for 0.5 h to ensure the adsorption of Au seeds and rinsed with water twice to remove any excess. The seeds-adsorbed wafer was then immersed in a water/ethanol (v/v = 1:2) solution containing the ligand 4-MBA, HAuCl₄ and L-ascorbic acid for 15 min. Finally, the wafer was rinsed with ethanol and dried in air. By modifying the reagent concentrations in the reaction solution, chiral (or twisted) AuNWs with different morphologies can be obtained.

Synthesis of straight and chiral AuNWs using 4-nitrobenzenethiol as ligands. The synthetic route is the same as that for AuNWs using 4-MBA as ligands, except for the change in reagent concentrations. For the growth of straight AuNWs, a chip of seed-adsorbed Si wafer (1 cm²) was dipped into a reaction mixture containing 4-nitrobenzenethiol (0.4 mM), HAuCl₄ (1.8 μM) and L-ascorbic acid (5.2 mM). The TEM image of the resulting AuNWs detached from substrate by sonication is shown in Figure 5-10a. For the growth of chiral AuNWs, the reaction mixture was changed to a solution of 4-nitrobenzenethiol (0.8 mM), HAuCl₄ (1.8 μM) and L-ascorbic acid (5.2 mM). The TEM image of the resulting AuNWs is shown in Figure 5-11b.

Synthesis of straight and chiral AuNWs using naphthalenethiol as ligands. The synthetic procedure is the same as that for AuNWs using 4-MBA as ligands, except for the concentrations of reagents. For the growth of straight AuNWs, a chip of seed-adsorbed Si wafer (1 cm²) was dipped into a reaction

mixture containing naphthalenethiol (0.4 mM), HAuCl_4 (1.8 μM) and L-ascorbic acid (5.2 mM). The TEM image of the resulting AuNWs detached from substrate by sonication is shown in Figure 5-12a. For the growth of chiral AuNWs, the reaction mixture was changed to be a solution of naphthalenethiol (1.5 mM), HAuCl_4 (1.8 μM) and L-ascorbic acid (5.2 mM). The TEM image of the resulting AuNWs is shown in Figure 5-12b.

5.3 Results and Discussion

5.3.1 Growth of surface-bound chiral AuNWs

Chiral AuNWs were grown from Au seeds adsorbed on Si wafer using the same preparation procedure as discussed in Chapter 2. Then, a chip of seed-attached Si wafer was immersed in a modified reaction solution of 4-MBA (1.0 mM), HAuCl_4 (0.5 mM) and L-ascorbic acid (1.2 mM) for 15 min. For TEM characterization, the chiral AuNWs were detached from substrate surface by sonication. As shown in Figure 5-3, the resulting AuNWs are of about 3 nm in width, smaller than that (6 nm) of straight AuNWs (Figure 5-1a) which were fabricated in a solution of 4-MBA (0.6 mM), HAuCl_4 (1.7 mM) and L-ascorbic acid (4.1 mM). In this system, most of the resulting NWs are irregularly twisted with about 50% of spiral NWs (Figure 5-3b,c) and 10% of zigzag-like NWs (Figure 5-3d). As compared to the straight NWs (Figure 5-1a), the

concentration of ligand ($C_{4\text{-MBA}}$) for the chiral AuNWs is higher (about twice of that for straight NWs), whereas both the concentrations of HAuCl_4 (C_{HAuCl_4}) and L-ascorbic acid ($C_{\text{L-ascorbic acid}}$) for the growth of chiral NWs are much smaller than the straight ones.

The growth of chiral AuNWs follows the active-surface growth mode which has been applied in the growth of straight NWs. One of the characteristics for this growth mode is that the width of resulting NWs is dependent on the competition between ligand binding and Au deposition rate, following the Equation:

$$D = a \cdot \frac{\mu}{\gamma} \quad (1)$$

where D is the diameter of NWs, a is a constant, μ is Au deposition rate, and γ is ligand diffusion rate. Ligand diffusion rate is proportional to $C_{4\text{-MBA}}$ and Au deposition rate is proportional to both C_{HAuCl_4} and $C_{\text{L-ascorbic acid}}$. Thus, Equation (1) can be modified to:

$$D \propto \frac{C_{\text{HAuCl}_4} \cdot C_{\text{L-ascorbic acid}}}{C_{4\text{-MBA}}} \quad (2)$$

From Equation (2), it is conceivable that the width of emerging NWs correlates to the reactant ratio $[(C_{\text{HAuCl}_4} \cdot C_{\text{L-ascorbic acid}}) / C_{4\text{-MBA}}]$. With a smaller reactant ratio in the system, the emerging NWs should become thinner. The reactant concentrations and ratios for the straight and chiral AuNWs have been summarized in Table 1. It is true that the chiral NWs generated in all cases

possess thinner width ($d = 3$ nm) with much smaller reactant ratio (ranging from 0.4 to 3.0, versus 11.6 for straight NWs).

Table 1. Summary of reactant concentrations and ratios for straight and chiral (or twisted) AuNWs.

	Sample	$C_{4\text{-MBA}}$	C_{HAuCl_4}	$C_{\text{L-ascorbic-acid}}$	Reactant ratio [*]
		(mM)	(mM)	(mM)	
Straight NWs		0.6	1.7	4.1	11.6
	A	0.2	0.5	1.2	3.0
Chiral or twisted NWs	B	0.7	0.5	1.2	0.9
	C	1.0	0.5	1.2	0.6
	D	1.4	0.5	1.2	0.4
	E	2.3	0.9	2.0	0.8
	F	3.8	1.3	2.7	0.9
	G	5.8	1.7	4.1	1.2

^{*} Reactant ratio = $(C_{\text{HAuCl}_4} \cdot C_{\text{L-ascorbic acid}}) / C_{4\text{-MBA}}$

5.3.2 Effect of ligand concentration

For the growth of chiral NWs in Figure 5-3 (sample **C** in Table 1), the ligand concentration (1.0 mM) is much higher than that for straight NWs (0.6 mM). To

figure out if the ligand concentration plays a key role in the growth of chiral NWs, control experiments have been carried out. When ligand concentration was increased to 1.4 mM, the resulting NWs (sample **D** in Table 1) were curved or twisted but became shorter, so it is hard to observe large chiral nanostructures (Figure 5-4). A large amount of freestanding AuNPs were present in the sample, suggesting that the ligand concentration is too high to promote the growth of NWs but is able to shut off the growth of the seed NPs. It is interesting that the width of these NWs is unchanged ($d = 3$ nm) at a smaller reactant ratio (0.4 versus 0.6), which implies that increasing ligand concentration in the system cannot further decrease the NW width. If the ligand concentration was decreased to 0.7 mM (but still higher than 0.6 mM for straight NWs), the resulting AuNWs (sample **B** in Table 1) were less twisted which have irregular twisted segments bounded at their tips (Figure 5-5a,b). When the ligand concentration was decreased even further (0.2 mM, lower than that for straight NWs) in sample **A**, most of the emerging NWs were with similar morphologies as those in Figure 5-4a but a small quantity (about 10%) of AuNWs were observed to grow with twisted heads NWs (Figure 5-5c,d). In this case, the NWs are 3 nm in width, the same as that in sample **D**. It is observed that the width of NWs was unchanged (3 nm) when the ligand concentration decreased from 1.4 (sample **D**) to 0.2 (sample **A**).

Obviously, ligands in this system play a role more than constraining the

transverse growth of NWs. On the basis of the above experiments, the variation of ligand concentration influences the appearance of the emerging NWs. The fewer the ligands present in the system, the greater the amount of NWs that are less twisted. However, the absolute concentration of the ligands is not a necessary factor because twisted NWs can still be obtained at a low ligand concentration (0.2 mM).

Figure 5-4 TEM image of AuNWs (sample **D**) synthesized using higher ligand concentration (1.4 mM), compared to sample **C**. The samples were detached from Si wafer by sonication for characterization.

Figure 5-5 (a-d) TEM images of (a,b) AuNWs (sample **B**) synthesized using ligand concentration of 0.7 mM; (c,d) AuNWs (sample **A**) synthesized using lower ligand concentration of 0.2 mM. The samples were detached from Si wafer by sonication for characterization.

5.3.3 Effect of reactant ratio

Compared to the straight NWs, the reactant ratios for the growth of chiral (or twisted) NWs are much smaller (Table 1). The reactant ratio for chiral NWs

(0.6, sample **C**) is about 1/20 of that for the straight NWs (11.6), while that for the less-twisted NWs (3.0, sample **A**) is 1/4. Thus, the occurrence of the chiral (or twisted) AuNWs is proposed to be dependent on a smaller reactant ratio but not smaller than 0.4, which may result in short wires and a large quantity of NPs. It is also postulated to be independent of the absolute concentration of the reactants. To test this hypothesis, three samples (**E-G**) with different reactant concentrations but similar reactant ratios were employed for AuNW growth (Table 1). All the ligand concentrations in these samples are higher than that of sample **D**, and the reactant ratios are kept around 0.9. As shown in Figure 5-6, chiral nanostructures such as spiral and helical NWs can be obtained in sample **E-G**. It is interesting that the concentrations of both HAuCl_4 and L-ascorbic acid for sample **G** are the same as that for straight NWs, but the ligand concentration for sample **G** is much higher (Table 1). It is conceivable that this relative high concentration of ligands lowers the reactant ratio and induces the growth of chiral (or twisted) NWs. The results support our argument that the growth of chiral AuNWs is controlled by the reactant ratio (more precisely, relative high ligand concentration).

Figure 5-6 (a-f) TEM images of the AuNWs synthesized at different reaction conditions: (a,b) sample **E** from a solution of 4-MBA (2.3 mM), HAuCl₄ (0.9 mM) and L-ascorbic acid (2.0 mM); (c,d) sample **F** from a solution of 4-MBA (3.8 mM), HAuCl₄ (1.3 mM) and L-ascorbic acid (2.7 mM); (e,f) sample **G**

from a solution of 4-MBA (5.8 mM), H₂AuCl₄ (1.7 mM) and L-ascorbic acid (4.1 mM). The samples were detached from Si wafer by sonication for characterization.

5.3.4 Crystal structure analysis

In this system, the morphologies of the emerging AuNWs are irregular but regular NWs such as zigzag-like and spiral NWs can also be observed (Figure 5-3b-d). In the literatures, it is reported that special type of ordered crystal structures may cause NWs to twist.^[20-21, 23] To find out if these zigzag-like structures are attributed to specific internal lattice order, HRTEM characterization has been carried out. Upon characterization on crystal structure of a typical zigzag-like NW, It is observed that the NW is polycrystalline with face-centred-cubic (fcc) crystalline domains (Figure 5-7), which is of similar crystal structures with straight NWs discussed in Figure 2-18. The crystal structure at the kinks is irregular even along the same NW. In some cases, twin boundaries can be found at some sharp kinks, connecting two straight segments of NWs (Figure 5-7a). However, the lattices at the most of kinked parts are twisted which may be caused by the bending pose of the NW (Figure 5-7b). Thus, it is difficult to confirm the lattice structure at these kinks. With the characterization on another NW, a single-crystalline straight segment was

observed, connecting with other segments via single-crystalline kinks (Figure 5-8). Lattice distortion can also be observed which may be induced by the strain generated from the twisted morphology. From the result of the crystal structures of the zigzag-like NWs, the lattice structures at the kinks are different and should be identified case by case. In this system, the formation of zigzag-like NWs cannot be simply assigned to any internal lattice order.

From the HRTEM images of a typical spiral NW, the spiral NW is not perfect planar structure, and only parts of the lattice were clearly observed at a certain focus length (Figure 5-9b). By comparing the present lattices, it is obvious that the wire grew epitaxial from the spherical seed surface and the lattice was roughly maintained even with large curvature (Figure 5-9b). The same phenomenon can also be observed at the subsequent part of the spiral NW, where even the lattices in two separated concave segments are matched (Figure 5-9c). In addition, it is possible that a curve segment with single-crystalline structure is present (5-9d).

We did not observe any specific facets bounded on the side surface of the zigzag-like or spiral NWs. Without specific surface facets or internal lattice order, the polycrystalline nature of the segments is not an issue for the formation of the orderly shape of wires. Hence, the influence of specific crystal structures can be ruled out for the growth mechanism.

Figure 5-7 (a,b) HRTEM images of two parts along a typical zigzag-like NW;

Twin boundary is highlighted by black arrow in (a).

Figure 5-8 HRTEM image of a zigzag-like NW; the single-crystalline kinks are highlighted by black arrows and the lattice distortions are highlighted by dashed rectangle.

Figure 5-9 (a-d) HRTEM images of three continuous parts along a typical spiral NW.

5.3.5 Growth mechanism

As discussed above, the relative high concentration of ligands in the system is the key factor for growth of chiral AuNWs. In the literatures, ligands have two effects in controlling the growth of nanocrystals: (1) they have strong affinity to each other forming micellar templates to confine the crystal growth;

(2) binding ability of ligands on specific crystal facets slows down the growth on these facets which in turn promote the growth on the other facets, resulting in the anisotropic nanostructures. In this system, ligands have short hydrophobic groups, making them unlikely to form stable micellar templates. Based on the irregular NW structures, template growth mechanism can be ruled out. On the other hand, it has been shown that no preferred facets are present on the NW surface. It is conceivable that the ligand (4-MBA) plays an unconventional role in formation of chiral NWs.

Thus, we proposed a growth mechanism for the chiral (or twisted) NWs based on our previous understanding of active-surface growth: When excess ligands are present in the system, the ligand diffusion and strong binding at the interface between seed and substrate can hamper the deposition of Au at this interface, slowing down the growth rate of Au (Figure 5-10a); It is possible that the ligand binding is uneven at this interface because they cannot easily “squeeze” in or packed well due to the steric hindrance. This uneven binding at the interface induces an imbalanced growth rate of Au, which allows the growth direction of NW to tilt and the emerging NWs to curve (Figure 5-10b). If one site of the interface is always faster than the other sites, the NW would coil up to be spiral nanostructures (Figure 5-3b,c).

This proposed mechanism can explain the morphological variation of the emerging NWs when the reactant ratio is changed by modifying ligand

concentrations (samples **A-D**). When the reactant ratio is high (ligand concentration is low), it is not likely for the ligands to diffuse in the seed-substrate interface as discussed in Chapter 2 (straight NWs). With the increasing ligand concentration, the possibility for the ligands to diffuse in the interface increases, resulting in the NWs with different degree of chirality in shape (samples **A-C**). When the ligand concentration is too high, more ligands “squeeze” in the interface and shut off Au growth, leading to short and curved NWs as well as a large quantity of NPs (sample **D**).

Figure 5-10 (a,b) schematics illustrating the growth mechanism of chiral NWs.

(a) Ligands “squeeze” in the seed-substrate interface to bind to the seed,

hampering the deposition of Au at this site (black arrows) and slowing down its growth rate (white arrows); (b) The imbalanced growth rate of Au at the interface makes the growth direction of NW to tilt (green arrows).

A similar growth mechanism has been proposed for the growth of helical and spiral carbon nanotubes via VLS process.^[14] The authors reported that the asymmetric extrusion at the circumference of catalytic droplets originated from the inhomogeneous catalytic activity of the seeds. In our system, the imbalanced growth at the interface is assigned to the presence of strong-binding ligands. When the ligand concentration in the reaction solution is high enough, the uneven binding of strong ligands would occur at the seed-substrate interface. It is conceivable that even temporary uneven binding of ligands can induce the difference in the growth rate of Au at the interface (Figure 5-10b).

When the growth of NW occurs, the “active” growth surface is changed from seed-substrate interface to NW-substrate interface. Thus, the uneven binding of the ligands at the newly-formed interface between NW and substrate is able to be changed. It is possible that the variation of the uneven binding site allows the growth of “fresh” interface to vary with time, resulting zigzag-like or helical NWs (Figure 5-3d and 5-6d,f). This proposed mechanism can explain the co-presence of zigzag, spiral, helical and even irregularly-twisted NWs when the ligand concentration is high.

5.3.6 Extension of the growth mechanism

As discussed above, the growth of chiral NWs occurred due to the strong binding of ligand 4-MBA in the system. Thus, it is possible to synthesize chiral or twisted NWs by using other ligands which also possess strong binding affinity to Au. For instance, straight and chiral AuNWs can be synthesized by using 4-nitrobenzenethiol as ligands (Figure 5-11). When the AuNWs was grown in a reaction solution of 4-nitrobenzenethiol (0.4 mM), HAuCl₄ (1.8 mM) and L-ascorbic acid (5.2 mM), the resulting NWs are straight (Figure 5-11a). If the concentration of 4-nitrobenzenethiol was increased to be 0.8 mM with the concentrations of other reactants unchanged, the emerging NWs were twisted and spiral NWs can also be observed (Figure 5-11b). Another example is using naphthalenethiol as ligands to fabricate AuNWs. In this case, straight NWs can also be obtained with low concentration of naphthalenethiol (Figure 5-12a). When the ligand concentration became higher (1.5 mM) with other reactant concentrations unchanged, the AuNWs grew to be spiral shape (Figure 5-12b).

Figure 5-11 TEM images of AuNWs synthesized by using 4-nitrobenzenethiol as ligands. (a) a reaction solution containing ligand (0.4 mM), HAuCl₄ (1.8 mM) and L-ascorbic acid (5.2 mM); (b) a reaction solution containing ligand (0.8 mM), HAuCl₄ (1.8 mM) and L-ascorbic acid (5.2 mM).

Figure 5-12 TEM images of AuNWs synthesized by using naphthalenethiol as ligands. (a) a reaction solution containing ligand (0.4 mM), HAuCl₄ (1.8 mM) and L-ascorbic acid (5.2 mM); (b) a reaction solution containing ligand (1.5 mM), HAuCl₄ (1.8 mM) and L-ascorbic acid (5.2 mM).

5.4 Conclusion

In summary, we have developed a versatile process to synthesize chiral ultrathin Au nanowires. It is interesting that the growth of chiral NWs can be easily induced by increasing ligand concentration to lower the reactant ratio. We show that ligands play an unconventional role in this system, where the uneven binding of ligands at the metal-substrate interface leads to its imbalanced growth in the presence of concentrated ligands. Other ligands such as 4-nitrobenzenethiol and naphthalenethiol can also be used as ligand to synthesize the chiral NWs. With the additional understanding of the active-surface growth mechanism, we now have further insights for how different nanocrystals may be formed. It is hoped that this scalable and facile methodology to generate chiral NWs will also be useful for future applications such as in nanodevices.

5.5 Bibliography

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Chapter 6 Summary and Outlook

6.1 Summary

Developing new synthetic methodologies and exploring new nanostructures is essential for nanoscience and nanotechnology. This thesis summarizes my postgraduate research work on the study of an unconventional nanocrystal growth: with the help of strong-binding ligands, unidirectional growth of metal nanowires occurs precisely at the interface between solid metal seeds and substrate. This growth method can be applied in the preparation of complex nanostructures, fabrication of transparent, conductive film and fixed-bed catalysis.

This growth process of nanowire is unique: (1) nanowires can grow from substrate-bound seeds to create hierarchical structures like “hairy” nano-hybrids on colloidal particles or nanowire forests on bulk substrates using aqueous solution and ambient conditions. (2) the width of the emerging nanowires is dependent on the dynamic competition of ligand diffusion and metal deposition but independent of the size of solid seeds. The vertically-aligned nanowires have similar appearance to vapour-liquid-solid process, but the underlying mechanism is totally different. On the basis of experimental evidences, we

propose and test that only one end of the nanowires is “active” towards gold deposition, whereas the remaining surface of seed or nanowire is inhibited by the strong ligands. Because ligands cannot easily enter or pack well at the gold-substrate interface, the preferred growth at the active site and the instant binding of strong ligands at its perimeter are responsible for the rapid unidirectional growth. The polycrystalline nature of the nanowires and their circle cross-sections suggest that the ligands do not preferential bind to any specific facets.

We report for the first time that surface-bound ultrathin Au and Pd nanowires can be synthesized via active-surface growth mechanism. Furthermore, the growth of bimetallic segmented nanowires is possible in our system. Au-Pd segmented nanowires can be synthesized by successively immersing the seed-adsorbed substrate into two reaction solutions. One can easily control the width of the each segment by tuning the ratio of ligand diffusion and metal deposition rates (related to the concentration ratio of the reactants), as well as the length of each segment via modifying the reaction time. The success in the preparation of the segmented nanowires supports our proposed mechanism that the growth of nanowires always occurs at the metal-substrate interface.

It is conceivable that fabrication of chiral metallic nanowires is non-trivial. One has to further break the structural symmetry of a nanowire to make it chiral. Here, we show that chiral Au nanowires such as spiral nanowires can be

synthesized by increasing ligand concentrations in the growth of surface-bound nanowires. We proposed that the imbalanced growth rate of Au at the gold-substrate interface is induced by the uneven binding of ligands when high ratio of ligands is present in the system. The growth of chiral nanowires is not limited to ligand 4-mercaptobenzoic acid, and several thiol molecules can also be used as ligands to synthesize chiral nanostructures.

In terms of applications, this method can be used to build hierarchical nanowire-oxide structures and grow a conductive film on any oxide surface such as glass, sapphire, or even trumpet shell. Lowering the density of seed nanoparticles on substrate surface can lead to a thinner nanowire film which possesses potential for application in transparent electrodes.

The hierarchical structures have also shown excellent performance in fixed-bed catalysis. For industry application of nano-catalysts, there is a dilemma: in order to increase the catalytic capability, more support materials and/or smaller support particles are needed, both of which reduce the flow rate. Even when high pressure is used, the flow rate is still a major limitation for improving the overall processing rate. A new strategy has been demonstrated based on the growth of surface-bound Au nanowires. By growing vertical Au nanowires on loose network of glass fibres, continuous flow catalysis can be achieved with a processing rate about 100 times that of the best literature rate.

6.2 Outlook

On the basis of the understanding and application of the surface-bound metal nanowires in this thesis, several topics of works are proposed in the following:

(1) Enlarge the scope of the active-surface growth method. This method is general for growing surface-bound metal nanowires. We have shown that aromatic thiol molecules can be employed as ligands due to the close-packing via π - π interaction. In the future, different kinds of ligands can be tried such as aliphatic thiol molecules and other strong ligands. Other than Au and Pd nanowires, this growth method is possible to be applied in the synthesis of other metallic nanowires such as Ag and Pt.

(2) Explore industry-related reactions by using catalytic fibres. We have shown that the catalytic fibres can catalyse the conversion of 4-nitrophenol to 4-aminophenol at an exceptional processing rate. We see great possibility in their application to common reactions in the industry requiring metal nanoparticles for catalysis, such as Suzuki coupling reactions, Heck reaction, reduction and oxidation of alcohols. Noble metals have been extensively used for heterogeneous catalysis. The performance of our system can be further optimised and conditions specially tuned for each reaction and requirements. According to our previous results, the fibre-supported Au nanowires with high surface area can be used as scaffold for further growth of other metal nanoparticles thereon. For instance, Au nanowires can be decorated with other

noble metal nanoparticles such as Ag, Pd, or Pt. These bimetallic structures possess potential for further improving the catalyst surface area and may exhibit novel metal-metal hetero-junction for efficient catalysis. Based on the different constraints regarding low cost, efficiency and recyclability, we trust that this system is able to be scaled up and conditions customized to the various levels of trade-offs required. The system is expected to be of highly beneficial use due to its higher efficiency and recyclability and also conceivably open up a new direction for the way nano-catalysis is performed in the future.

(3) Application of our nanowire-growth method in fabrication of circuits. In our system, ultrathin nanowires are grown from the substrate-bound seeds. Thus, it is possible to control the location of the nanowires to build a circuit by adsorbing the seeds at specific positions. There are several methods to control the location of the seeds. It is possible to use nanoimprint lithography to functionalize the substrate surface with patterned 3-aminopropyl-trimethoxysilane and then adsorb the Au seeds thereon. Another alternative method is to “draw” a linear pattern with seed solutions on the amine-functionalized substrate. A template can also be used to confine the exposed surface of the amine-functionalized substrate for the adsorption of the seeds. After the seed adsorption, one can easily build the circuits by immersing the substrate into a reaction solution or inversely drop the concentrated reaction solution on the substrate surfaces.

6.3 Conclusion

Over the course of my postgraduate research, a novel methodology has been developed for the synthesis of surface-bound ultrathin Au nanowires that involves a brand new active-surface growth mechanism. In terms of synthetic applications, this methodology can be extended to Pd nanowires, bimetallic segmented nanowires as well as chiral Au nanowires. For practical industrial applications, we are able to synthesize nanowire conductive films which would be highly useful for electronics devices, and also able to grow these films on oxide substrates as well as seashell. The use of this methodology in fixed-bed nano-catalysis is also expected to be greatly beneficial in industrial applications. This work is hoped to open up a new growth opportunity in the field of nanotechnology and provide some new insights in the growth of anisotropic nanocrystals.

List of Publications

1. **Jiating He**, Yawen Wang, Yuhua Feng, Xiaoying Qi, Zhiyuan Zeng, Qing Liu, Wei Shan Teo, Chee Lip Gan, Hua Zhang, and Hongyu Chen*, "Forest of Gold Nanowires: A New Type of Nanocrystal Growth", *ACS Nano*, **2013**, 7, 2733.
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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.