Construction of complex nanostructures in solution phase

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CONSTRUCTION OF COM- PLEX NANOSTRUCTURES IN SOLUTION PHASE

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Abbreviations

DMF	N,N-dimethylformamide
THF	Tetrahydrofuran
EtOH	Ethanol
PS	Polystyrene
PAA	Poly(acrylic acid)
P4VP	Poly (4-vinylpyridine)
PEG	Polyethylene glycol
NPs	Nanoparticles
QDs	Quantum dots
AuNRs	Au nanorods
AuNWs	Au nanowires
CNT	Carbon nanotube
AuNPs@PSPAA	PSPAA encapsulated Au nanoparticles
SERS	Surface-enhanced Raman scattering
DLVO theory	Derjaguin Landau Verwey and Overbeek theory
PVP	Polyvinylpyrrolidone
CTAB	Cetyl trimethylammonium bromide
TMAOH	tetramethylammonium hydroxide

TOPO	Tri octyl phosphine oxide
APS	Ammonium peroxydisulfate
SDS	Sodium dodecyl sulfate
AA	Ascorbic acid
CMC	Critical micelle concentration
TEM	Transmission electron microscopy
SEM	Scanning electron microscopy
HRTEM	High-resolution transmission electron mi- croscopy
UV-vis	Ultraviolet-visible spectroscopy
XPS	X-ray photoelectron spectroscopy

Abstract

In this thesis, the main work explored a new methodology for preparation of complex nanostructures in solution phase. There are two strategies, namely 1) block copolymer assisted nanoparticle (NP) self-assembly and 2) oil/water interface assembly. Based on these strategies, we successfully developed 1) core-shell system, which utilized amphiphilic block copolymer as shell and a wide range of inorganic NPs as core materials; 2) emulsion system, which utilized emulsified oil droplets as soft templates to compress nanofilaments into nanoring structures.

At first, we described core-shell systems in chapter 2. Various NPs including metal, metal oxide and semiconductor NPs, could be encapsulated within uniform polymer shells. Mechanism studies demonstrated that one block of the polymer is extremely hydrophobic and the other is extremely hydrophilic, so that the polymer forms micelles including hydrophobically functionalized NPs. The micelles are covered with long ionic PAA chains in extended conformation, which introduces charge and steric repulsion against aggregation. After encapsulation, we further demonstrated that the presence of polymer shell maintained structural integrity of nanoclusters, allowing them to be isolated, enriched and then characterized. Anisotropic polymer coating was also achieved for both hydrophobic and hydrophilic NPs. Triblock copolymer P4VP-PS-P4VP encapsulation achieved demonstrated our polymer encapsulation was applicable to other block copolymers.

In chapter 3, based on the established core-shell system, we successfully prepared Au nanosprings by manipulating ultrathin AuNWs inside polymer shells. The ultrathin AuNWs were dispersed in THF/DMF/water mixture and coated with a layer of PSPAA shell. A large amount of water was then added to the solution to de-swell the polymer shells. This led to a significant increase of polymer/solvent interfacial tension and the contraction of the polymer nano-droplet. Thus, as the cylindrical polymer shells transformed to become a spherical droplet, the incorporated AuNWs were forced to coil into rings. The obtained Au nanosprings uncoiled when the polymer shells were removed or swelled by organic solvent. Obviously, these results suggested that elastic potential energy of the nanosprings was converted back to kinetic energy. This was the first evidence of energy storage in colloidal NPs.

Emulsion system was also utilized for assembly of complex nanostructures (Chapter 4). We found that the oil droplets could exert sufficient force to straight bundles of AuNWs to compress them into perfect nanorings. The mechanism could be explained as solvent-shifting process. Surfactant greatly influenced the morphologies of final rings. As a proof of concept, we successfully achieved Au@Ag@Ppy nanorings by using as-synthesized Au nanorings as templates. Furthermore, Au nanoring composed of close-packed monolayer free-standing films were achieved by simply using Ppy modified Au nanorings self-assembly at water/oil interface.

Finally, in chapter 5, we demonstrated that the as-synthesized Au nanorings could be fused into coherent Au nanorings. The method was very simple. Heating as-synthesized Au nanorings together with reductant in SDS aqueous solution for a short time gave fused rings. Importantly, we found that the fused

nanorings had single-crystalline dominant structure, and a few crystal defects presented within small range. Further studies revealed that single crystal parts of nanoring had the same lattice orientation with as-synthesized Au nanorings. Zipper mechanism was proposed for explanation of lattice orientation preserved fusion, which was confirmed by perpendicular growth of Ag nanorods on fused nanorings.

Chapter 1 Introduction

1.1 Nanoscience/nanotechnology

Nanoscience/nanotechnology study the control of matter on a scale between 1 - 100 nm, and the fabrication of devices on this same length scale. As scaling down to nano-size, material properties are significantly different with the bulk counterparts. One direct impression is that more functions can be packed within a small volume. In fact, far more than this, nanomaterials can have a series of novel properties including mechanical, electrical, magnetic, optical, kinetic as well as thermodynamic properties owing to their small size. There are four main reasons why nanomaterials can have different properties: (1) large fraction of surface atoms; (2) high surface energy; (3) spatial confinement; (4) reduced imperfections which do not exist in the corresponding bulk materials. These differences render many promising physical and chemical properties, and enable nanomaterials to be promising in application over broad areas such as sensing, labeling, optical imaging, magnetic resonance imaging (MRI), cell separation, and treatment of diseases.¹⁻⁵ In the history of scientific research and development, there is no other topic like nanoscience, giving rise to so exciting and full of imagination. The presented new nano-world has merged into various aspects of human life, and induced significant changes in the areas of biology, informa-

tion, materials, environment and energy. The whole world is experiencing and will continue experiencing the industrial revolution brought by nanotechnology.

In recent decades, researchers have made significant breakthrough in nanotechnology development. Starting from just simply searching for new properties on nano-material, nano-study has come into a golden age of diversity, ranging from nanomaterial synthesis and modification to new material development, from free arrangement of materials to assembly of atomic molecules, from mechanism investigation to functionalized nano-object manipulation. Just like the prediction by Nobel laureate Richard Feynman in his famous talk “There’s Plenty of Room at the Bottom” in 1959,⁶ nanoscience/nanotechnology has already had an enormous number of technical applications.

Generally, nanomaterials are composed of nanoscale building blocks, which are divided into 1) zero dimensional nanostructures⁷⁻⁸ (three dimensions are at nanoscale, e.g. semiconductor quantum dots (QDs)⁹, clusters, and NPs¹⁰⁻¹¹); 2) one dimensional (1D) nanostructure (two dimensions are at nanoscale, e.g. nanofibres, nanowires, nanotubes, nanorods¹²); 3) two dimensional (2D) nanostructure (only one dimension is at nanoscale, e.g. nanofilms and nanodisks¹³). Numerous methods were developed to yield various nanoscale inorganic materials, which were widely used as building blocks. The most widely used one is wet chemistry technology based on chemical reactions in solution that yield NPs with a wide range of sizes and shapes. As such, metal NPs with different novel

morphologies have been widely studied;¹⁴ QDs, a new class of inorganic fluorescent nanoparticles, have been facilely prepared via organic or aqueous phase routes;¹⁵⁻¹⁶ magnetic NPs, which are widely applied in biotechnology/biomedicine, have been synthesized by a number of suitable methods.¹⁷ The development of these methodologies not only provides sufficient amount of nanomaterials for exploring their unknown properties and potential applications, but also supply high quality building block for constructing complex nanostructures.

1.2 Construction of complex nanostructures via self-assembly

Owing to the increasing demands in energy, material and biomedical fields, novel nano-objects with small size as well as improved performance are strongly needed.^{4,18-23} Thus, the innovation trending shifted from synthesis of nanoscale building blocks to construction of the complex nanostructures by using such building blocks.^{10,14-16,24-28} Besides the enhancement in mechanical properties of the whole composite, complex nanostructures allow multiple tasks to be performed simultaneously or in sequence. Even more, complex nanostructures can also exhibit new electronic, magnetic and optical properties as a result of interactions between the excitons, magnetic moments or surface plasmons of individual NPs. The rapid development in nanoscience and nanotechnology, especially in instrument precision, provides great opportunity for researchers to ex-

exploit collective properties of the complex nanomaterials and further apply these properties in functional devices.

Constructing complex nanostructures is not an innovative idea. However, the ability of controlling the sizes, three-dimensional (3D) morphologies, spatial couplings, as well as the environmental response behavior of the complex nanostructures still remain challenge.²⁹⁻³³ Self-assembly technology, known as a process in which disordered components are orderly organized without external direction, has been described as a simple and low-cost method to overcome the aforementioned problems.³⁴⁻³⁸ Usually, self-assembly is realized through supramolecular chemistry that constituent parts are spontaneously connected and integrated by specific and/or non-covalent interactions, such as Van Der Waals interactions, electrostatic interactions, molecular surface forces, entropic effects, and so forth. These novel connection fashions provide the opportunity to tune the dimensions of complex structures, from 1D fibers, 2D films, to 3D bulk materials.³⁹⁻⁴⁴ Beyond this, due to the weak interactions of self-assembly, such complex nanocomposite can sensitively response to environmental variation by a reversible disassembly process, which gives rise to the birth of smart materials.⁴⁵⁻⁴⁶ Self-assembly technology also shows a tremendous flexibility in achieving the complex structures from various macromolecular and small molecular building blocks, and producing the complex structures over macroscopic and microscopic scales. The complex structures may have defined size, mole-

cular weight, and stoichiometric ratio of different components.⁴⁷⁻⁵¹

Self-assembly of inorganic NPs, which are widely used as functional materials, are playing an increasingly important role in current materials science for their broad range of applications.³⁵⁻³⁸ Specifically, the NPs are not limited to spherical particles, but refer to nanometer-sized inorganic materials with different shapes, such as nanodots, nanorods, nanocubes, nanodisks and nanostars. These NPs, made of metals, metallic oxides or semiconductors, display unique size-dependent and shape-dependent physical and chemical properties resulting from the quantum confinement effects and surface effects.⁵²⁻⁵⁵ CdSe nanodots, a good example of semiconductor nanomaterial, exhibit strong size-dependent photoluminescence (PL). Their PL can be tuned from green to red by fine controlling the nanodot sizes during the synthetic process.⁵⁶ The shapes of nanostructures also determine their properties. A typical case is gold nanorods (AuNR). By varying the aspect ratio, the plasmonic absorption of AuNR shifts from visible to near infrared range (NIR).⁵⁷ Therefore, considering these unique properties, it is promising to utilize inorganic NPs as crucial building blocks for complex nanostructures self-assembly to obtain specific functionalities, multifunctional integration and functional modulation.

Through self-assembly, inorganic NPs with different properties can be integrated into supramolecular complex structures with enriched functionalities.⁵⁸⁻⁶⁰ The advanced self-assembly technology provides a great

deal of flexibility to tune the spatial distance between NP building blocks and further control energy and/or charge transfer within the regular structures.⁶¹ It should be emphasized that the reversibility of assembly-deassembly between these inorganic NPs or other discrete components grants practicable stimulus-response ability to environment.⁶²⁻⁶³ This environmental response nanocomposite, further manipulated into diversified switches, depicts the prototypes of next generation nano-devices.

The development of NP self-assembly is inspired by the rapid progress in NP fabrication and surface modification. Currently, the synthesis of NPs is well established so that it is possible to supply a large number of NPs with specific components, sizes, shapes, and surface characteristics. Particularly, the surface characteristics of NPs are significantly important since the surface of NPs directly links to intermolecular interactions, which is the main driven force for self-assembly.⁶⁴ Hence, functionalization of NP surface with specific ligand is necessary before assembly. A great many successful technologies have been developed to modified target molecules onto NP surface. For example, mercapto-compounds can be selectively conjugated on the ends of Au nanorods,⁶⁵ followed by asymmetric polymerization on NPs to produce Janus composite NPs.⁶⁶ Profiting from the tremendous progress in surface modification technologies, a large toolbox is presented for researchers to design and realize the expected surface characteristics, and hence the final self assembly architectures.

1.3 Block copolymer based self-assembly of complex nanostructures

Recently, amphiphilic block copolymers attract great interest and have been extensively studied. They are widely used as crucial components for preparation of polymer colloids with various morphologies and functionalities.⁶⁷ In a certain solvent system, the amphiphilic polymers aggregate to form micelles with insoluble blocks as cores and soluble blocks acting as coronas.⁶⁸⁻⁷⁰ Also, in oil/water mixed solution, the polymers can play a role as stabilizers for the formation of oil droplets, known as emulsions.⁷¹⁻⁷³ Usually, the polymers have specific functional groups presented in the backbones, which allow them to connect with a secondary component via noncovalent interactions such as hydrogen bonding, electrostatic and hydrophobic interactions. Thus, complex nanostructures can be achieved through self-assembly process. Following this strategy, a large number of interesting novel nanostructures have been prepared.⁷⁴⁻⁷⁸ Taking advantages of these studies, block copolymer self-assembly have been explored in more depth and applied in the construction of inorganic/organic complex hybrid nanostructures in attempt to develop novel functional nanomaterials.

The utilization of block copolymers in the preparation of inorganic/organic hybrid complex nanostructures with synergetic functions of the two components can be dated back to 1990s.^{79,80-87} The conceivable approach involves *in situ* synthesis of inorganic NPs, such as QDs,⁸⁸ metal NPs and silica particles,⁸⁹⁻⁹² using self-assembled block copolymers as templates or nanoreactors. Inorganic

block polymer self-assembly is another growing technique to obtain inorganic/organic complex nanostructures with novel morphologies and properties.⁹³⁻⁹⁴

Besides the above approaches, multi-component system based on well-studied block copolymer self-assembly has been intensively studied in order to incorporate inorganic components into the complex structures in a designed fashion. This approach, which involves co-assembly of multi-components with a broad range of inorganic NPs, provides a great deal of flexibility for potential functional material development. Two strategies are often used: 1) concurrent self-assembly of block copolymers with a second component;⁹⁵⁻¹⁰¹ and 2) sequential self-assembly of inorganic NPs with assembled block copolymer micelles.¹⁰²⁻¹⁰⁶ Many researchers have demonstrated that complex nanostructures produced from block copolymers are particularly useful as functional materials that cannot be achieved by using other synthetic techniques.

1.3.1 Core-shell structures

As we known, for application of nanostructures, especially for biological area, NPs should possess long term colloidal stability, favorable water-dispersion and tailored surface chemistry for covalent coupling to antigens, antibodies, enzymes or DNA/RNA hybridization. Long time stability of NPs without aggregation or precipitation is an urgent requirement for almost all the applications of nanomaterials, and is crucial to avoid degradation such as partial oxidation or undesired sintering of NPs. However, due to the anisotropic dipolar attraction, NPs are easily aggregated by slight disruptions in the chemical envi-

ronment that causes the loss of specific properties associated with single-domain nanostructures. NPs coated with surface ligands often show only short-term stability because of the loss of their surface ligands; it has been demonstrated even strong thiol ligands can dissociate or undergo exchange with other ligand on gold surfaces, let alone weaker ligands on the surface of QDs or magnetic NPs. Therefore, it is of great importance to develop efficient approaches to improve the chemical and colloidal stability of NPs. On the other hand, various high quality and monodispersed colloidal NPs are coated with surfactants that render their surface hydrophobic, thus synthesis of these NPs needs to be conducted in organic solvent at high temperature.^{25,107} How to transfer high quantity NPs into aqueous solution then becomes another key issue to utilize NPs. In addition to stability and water-solubility, stable functionalization of NPs would be particularly important since only a few bio-active molecules can be selectively attached to a NP, limiting the application of NPs. Consequently, it may be necessary to modify the surface of NPs, such as introducing functional organic groups on the NP surface which allows deliberate interaction of the NPs with molecules, other NPs and bulk surfaces.

To overcome these limitations, several methods have been developed to render the NPs soluble in aqueous media, while preventing aggregation and providing positions where functional molecules can be attached are based on ligand exchange. The original surfactants of the NPs are directly replaced by a new ligand molecule which contains a functional group such as thiols, phosphines or carboxyl on one end and a polar group on the other end to render NP water-solubility.¹⁰⁸⁻¹¹⁴ This strategy is widely used to generate different kinds of stable and water-soluble NPs. However, the low ratio of ligand exchange and

desorption of new ligands always destabilize the system and lead to aggregation of the NPs. Thus appropriate ligand molecules have to be individually chosen for each material. Meanwhile, based on a coating or encapsulation method, the substituted strategies are also developed. This involves functionalization of the surface of NPs, and then encapsulation with different matrixes, including organic and inorganic materials.¹¹⁵⁻¹¹⁸ These matrixes or shells can prevent the dissociation of surface ligands, thereby enhancing the stability and dispersibility of the NPs. For example, metal, semiconductor and magnetic NPs can be embedded in silica shells, which provided the particle with mechanical and chemical stability.¹¹⁹⁻¹²² Shell encapsulation also facilitates NP surface modification. Normally, repeatability of surface modification of bared NPs is limited and the resulting NPs also show poor dispersion in aqueous solution.¹²³⁻¹²⁴ Hence tremendous progress in the generation of organic shells has been made. The advantages of organic shells are: (a) improving the long-term stability of NPs; (b) adjusting the solubility and amphiphilicity of NPs; (c) tailoring the properties of NPs, as well as (d) enhancing the compatibility and processability.^{112,125}

Block copolymers are known to perform self-assembly in selected solvents, forming stable crew-cut aggregates named as micelles or micelles like aggregates^{67-68,126-128} This typical kind of polymers have attracted considerable attention over the past few years. Previously, Taton et al. have encapsulated gold NPs,¹²⁹ magnetic NPs,¹³⁰ QDs⁹⁷ and multi-component NPs¹³¹ by amphiphilic diblock polymers through self-assembly. The resulting NPs have a well-defined core-shell structure, good solubility and stability in water and aqueous buffers, which is crucial to their potential application in biomedical fields. Using the modified method, as shown in Figure 1-1, our group have

singly encapsulated small AuNPs (about 5 nm) by diblock copolymer with long hydrophilic chains.¹⁰¹ Following up, we are trying to find out a general and facile method to encapsulate different NPs via self-assembly of amphiphilic block copolymers. If a large range of NPs with various morphologies and different sizes, including metal, oxide, rare earth and semiconductor QDs could be encapsulated in our system, resulting in highly stable and water soluble core-shell nanostructure, the scope of nanomaterial application will be extend to various areas.

Figure 1-1. Encapsulation of AuNPs. a) Schematic drawing showing the mechanism for encapsulation of AuNP. b) TEM image of 5 nm AuNPs encapsulated by PS₁₀₈PGA₁₀₈ after centrifugation. The polymer shells appear white in contrast to the stain in the background. c) SEM images of 32 nm AuNPs encapsulated by PS₁₃₂PAA₇₂. (Reprinted with permission from ref. 101. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.)

Compared to previously reported methods of encapsulation, our encapsulation approach has several advantages. First, due to the thermodynamically controlled process, the polymer shells with uniform thickness were easily prepared with only one-step synthesis, which involved only simple heating and cooling. Second, the potential encapsulations of different kinds NPs by polymer shell render the NPs soluble in aqueous solution, prevent salt-induced aggregation and allow directly isolation by centrifugation, which makes the separation of NPs possible.¹³² Third, a protective shell which possesses the abundant functional groups, -COOH, not only serving to protect NPs against degradation, but also providing positions for further functionalization. The carboxylic acid moieties are ideal for attaching biomolecules such as peptides, proteins, antibodies and nucleic acids, to the NP complexes through standard bioconjugation techniques. Last but not the least, our method avoided mixing of two solution phases, which could induce aggregation caused by regional inhomogeneity, thus rendering the NPs unusable for many purposes.

1.3.2 Polymer-assisted construction of complex nanostructures

In addition of core-shell structures, polymer-encapsulation approach also provides a novel way to manipulate morphologies of encapsulated nanostructures. In the past several years, our group has developed a robust method for finely controlling the assembly of various NPs together with PSPAA micelles. For example, we reported a facile approach for the synthesis of Janus-shaped hybrid nanostructures via the assembly of block copolymers and AuNPs in the presence of hydrophobic (L_A) and hydrophilic ligands (L_B) (Figure 1-2).⁹⁸ The binding competition between L_A and L_B on the surface of AuNPs broke the symmetry of surface attachments of the block copolymers (PSPAA) on the AuNPs. By varying the ratio of two competitive ligands, the morphology evolved from homocentric to slightly eccentric and then to highly eccentric.

Figure 1-2. Schematic diagram showing the formation of homocentric (a and b) and eccentric (a, c, and d) AuNP@polymer. TEM images of purified AuNP@polymer (e-f) evolved from homocentric to slightly eccentric and then to highly eccentric. (Reprinted with permission from ref. 98. Copyright 2008 American Chemical Society.)

Our group also demonstrated that through controlling aggregation kinetics, polymer encapsulated dimmers and trimmers of AuNPs were obtained.¹³²⁻¹³⁴ The polymer shells maintained the stability of the assembled AuNP, preventing

aggregation and disintegration during subsequent purification, enrichment, and application. As proof of concept, the AuNP dimmers were utilized as catalyst for growth of diametric zinc oxide NWs (Figure 1-3).¹³³

Figure 1-3. a) TEM image of AuNP dimmers encapsulated within PSPAA micelles; b) SEM picture of ZnO NWs grown by using an enriched sample of AuNP dimmers. (Reprinted with permission from ref. 133. Copyright 2008 American Chemical Society.)

Furthermore, based on the controlled aggregation of AuNPs, we developed a high purity separation of AuNP or Au/Ag NP dimmers and trimmers (Figure 1-4).^{132,134} The spatially isolated colloidal nanoclusters provided a platform for measurement of the ensemble-averaged surface-enhanced Raman scattering (SERS) enhancement factors (EF).¹³⁵ By tuning ionic strength, a linear AuNP chain structures obtained and block copolymer served as a stable shell to prevent de-assembly.¹³⁵⁻¹³⁶ Considering most of these complex nanostructures

composed of metal NPs, extension of polymer co-assembly with other inorganic NPs may give a new story on the promising functional materials. Additionally, incorporation of two or more types of NPs in the same polymer micelles produced multi-functional nanomaterials. For example, magnetic NPs and QDs were successfully encapsulated within PSPAA micelles. The obtained complex nanostructures displayed both magnetic and PL properties, which can potentially be utilized as bio-lab in many biological applications.¹³⁷

Figure 1-4. A typical setup of separation of AuNP dimmers. (B) The result of A after 20 min centrifugation. (C) Separation result of A pre-enriched trimmer sample. (a1, b2, and c3) TEM images of the respective fractions indicated in A-C. (Reprinted with permission from ref. 132. Copyright 2009 American Chemical Society.)

1.4 Nanosprings and nanorings

1.4.1 New concept of nanospring

Spring is an elastic object with particular function of storing and releasing mechanical energy. It is normally made of resilient metal. The mechanical function of spring performs by deforming and returning its shape upon application and removal of external force. There are quite a few categories of springs in practice. Helical spring (Figure 1-5a) is probably the most classic one with unique helical configuration, which can shorten or lengthen its length to response an axial force. It is widely used as vehicle suspension and force measurement. Torsion spring (Figure 1-5b), consisting of wire coiled into a tight ring, rotates its ends to response to a torque or twisting force. It is commonly found in clips. The hairspring is composed of a coplanar spiral wire (Figure 1-5c), extensively used in mechanical watches and marine chronometers. Although most of springs are helical or spiral configuration, a few types of spring are not stick

to helical or spiral. Any object with ability of storing and releasing mechanical energy can be regarded as spring. For example, gas spring, composed of the compressed gas can be applied for pneumatic shock absorbers (Figure 1-5d). Even a bow-shaped object, made of a simple resilient rod can be considered as a spring.

Figure 1-5. Schematic of several types of springs in practice (a) helical spring, (b) torsion spring, (c) hairspring, (d) gas spring.

One common interest in current nanoscience and nanotechnology is to fabricate mechanical nanodevices. The mechanical component, which has ability of storing and releasing mechanical energy in nanoscale, is highly desired in many of these devices. Therefore, scientific community has been driven to explore similar nanoobjects with spring function. Once they are achieved, it shall definitely expedite the birth of some new device. Furthermore, it is conceivable that the excellent mechanical properties of nanospring would allow widespread application of nanospring in nanoengineering,¹³⁸⁻¹³⁹ such as resonating elements and novel reinforcements in high strain-composites.^{139,140} Particularly,

nanosprings are expected to be in the future functional nano-robot, an extreme case of device miniaturization. The movements of the nano-robots may not only be powered by (fuel) engine or battery, but also promoted by nanospring components.

The classical top-down approaches, such as lithographic patterning, and direct writing techniques have created various 3D periodic structures as small as microsprings. However, no successful top-down method has been reported when size further decreases to nanoscale. Downsizing the bulk spring into nanoscale still remains challenge. Researchers therefore put more effort in seeking other methodologies for making nanosprings.¹⁴⁰ From the morphological viewpoint, as shown in Figure 1-5, most of springs exhibit unique structural configurations such as helicity and periodicity. The structure mimicking, which prepared nanostructure with particular helical configurations, is considered as a simple way to achieve spring in nanoscale. Hence, an increasing attention has been paid on the creation of helical, spiral or coiled nanostructures.

Generally, helical structure, spiral or coiled structures all consist of wires/belts. Preliminary experimental evidence showed that such nanostructures could be observed in nanowire/nanobelt synthesis system. Since the synthesis methodology for 1D nanostructure has been well developed, the relationship between the spring and 1D wire/belt inspires researchers to look for a synthetic strategy analogous with 1D nanostructures manipulation to obtain nanosprings. In the last two decades, a large number of helical nanosprings derived from nanowires/nanobelts were synthesized. These successful fabrication methods provide model systems to investigate factors governing nanospring formation. Meanwhile, the obtained nanosprings give excellent platform to study nano-

spring behavior and gain valuable information on the potential applications including MEMS, motors, electromagnets generators and related equipment.

From the perspective of functions, a nano-object with ability of storing and releasing mechanical energy also is considered as nanospring. Therefore, the range of nanospring becomes broad. It is not limited to be helical or other popular spring morphologies, but also can be designed with whatever morphologies posing spring properties. Even a bended nanorod or deformed nanoring may be employed as spring.¹⁴¹⁻¹⁴² In addition to a variety of structural nanosprings, functional springs may give a new direction to design nanosprings and realize the functionalization of springs in nanoscale.

1.4.2 Nanosprings and nanorings

For traditional nanospring, the conceivable strategy is morphology mimicking, so that helical nanostructures have attracted major interest for a period. Various helical nanostructures were synthesized with a broad range of materials. For example, helical carbon nanocoils,¹⁴³⁻¹⁴⁵ helical nanosprings of GeTe,¹⁴⁶ SiC,¹⁴⁷ SiO₂,¹⁴⁸ MgB₂,¹⁴⁹ PbS¹⁵⁰⁻¹⁵² and ZnO¹⁵³ were prepared by vapor phase synthesis. The asymmetric growth is caused by anisotropic and inhomogeneous catalyst activity, dislocation, or determined by the native structural property of materials.

Generally, the competitions between elastic and interfacial effects contribute to spontaneous assembly of nanowires/nanobelts into helical, ring or racket shape. Thus similar to helical structure, the rings from coiled nanowires/nanobelts are also potential nanosprings.

Vapor phase synthesis can be applied to ring nanostructures, and most studied nanorings are CNT nanorings. At early stage, CNT rings are usually obtained occasionally in the process of synthesis of CNTs. Smalley group first observed CNT rings when they characterized the laser-grown single-walled CNT.¹⁵⁴ The proposed formation mechanism claims that single tube bended, the two ends nearly touched to each other and then stick to a metal catalyst to become welded together to maximize Van Der Waals interactions and alleviate bending strain. Compared to single tube rings, those composed of well-organized bundles are more common.¹⁵⁵⁻¹⁵⁸ Colomer group found that the double-walled CNT forming rings were not tori but coils, and packed in a triangular arrangement with the bundles.¹⁵⁶ By floating chemical vapor deposition, bundles of SWNT rings was obtained with yield higher than 70%.¹⁵⁷ A similar mechanism with helical CNTs may lead to the ring growth.¹⁵⁹

ZnO nanorings were formed based on the polar charge induced self-coiling,¹⁶⁰⁻¹⁶¹ and SnO₂,¹⁶² GaN,^{89,163} AlN,¹⁶⁴ ZnSe,¹⁶⁵ K₂Ti₆O₁₃,¹⁶⁶ Na₂Ti₆O₁₃¹⁶⁷ nanorings were also formed by the spontaneous self-coiling of polar nanobelts. Significantly, this mechanism is not only applied to vapor phase, but also to solution phase to generate Ag₂V₄O₁₁,¹⁶⁸ Ag_{1.2}V₃O₈¹⁶⁹ and CuO¹⁷⁰ nanorings under hydrothermal conditions. Bundled Si₃N₄ nanorings were synthesized and structurally characterized, revealing that the coiled NWs were bi-layer consisting of a crystalline layer and an amorphous layer. This in turn indicated that the growth rates difference between the two layers caused the NW coiled and nanorings formed.¹⁷¹

Post treatment methods have been also regarded as one of the most powerful tools to get nanorings. A widely used method is acid treatment, coiling

single-walled CNTs into rings under ultrasonic irradiation.¹⁷²⁻¹⁷⁴ The formation of rings involved a balance between the tube-tube Van Der Waals interaction and the strain energy resulting from the coiling-induced curvature. Using a similar method, the closed CNT rings with different shapes, such as circular, oval, and even closed ribbon-like structures were obtained on SiO₂/Si substrate.¹⁷⁵ The rings were formed during sonication process. The difference in shape on substrate may be related to the competition between the surface tension from solvent and the strain from ring itself. Meanwhile, Van Der Waals interaction between the rings and substrate stabilized ring shape. Also, this difference of ring morphologies may demonstrate the elasticity of CNT rings. Chemical functionalization is another efficient post treatment to produce nanorings from the straight CNTs. Oxygen-containing groups were functionalized to the ends of cut SWNTs using H₂SO₄/H₂O₂ etching. The rings with average diameter around 540 nm were produced via covalent ring-closure reactions.¹⁷⁶ By integrating dip pen nanolithography and nano-affinity templates, Mirkin group achieved self-assembly of CNT ring array on a gold substrate.¹⁷⁷ They found that SWNTs were attracted to the boundary between hydrophilic and hydrophobic self-assembled monolayers on a gold substrate, due to strong Van Der Waals interaction between SWNTs and carboxylic acid moieties. The long SWNTs coiled into rings at the interface of the self-assembled monolayers to minimize the tension from nanotube bending.

Figure 1-6. TEM images of (a) circular CNT rings after removal of PSPAA shell. (b) PSPAA encapsulated CNT rings; (c, d) TEM images, and (e) schematic illustration of CNT rings undergoing consecutive steps of structural conformational transformation. (Reprinted with permission from ref. 178. Copyright 2011 American Chemical Society.)

Our group also demonstrated that nanoring structures were able to serve as nanospring, which will be detailed in this thesis. We have successfully squeezed ultrathin gold NWs inside a polymer case caused them to coil up into tiny springs. Ultrathin gold NWs were first encapsulated with a styrene–acrylic acid block copolymer (PSPAA) dissolved in DMF-THF-H₂O, and then diluted the system with water to shrink the polymer shells. The micelle shrinkage triggered the coiling up of the NW, giving a structure resembling that of torsion springs. The two important factors in the process were encapsulation and polymer shell shrink. Since the encapsulating method has been successfully extended to various nano-objects, it is conceivable that this approach is potential for generating ring-like nanosprings made of various nanowire/nanobelt. Using the modified method, single-walled CNTs were encapsulated in PSPAA, and then coiled into ring structure by contraction of polymer shells (Figure 1-6).^{95,178} Here, it is noted that the coiled rings showed reversible structural transformation in a colloidal solution, and were able to mimic the reversible elastic motions of typical macroscopic rings. Although elastic motion of nano-objects has been studied using rings and helical nanostructures,¹⁴² most of the prior reports were based on the manipulation of individual nanostructures. Our method may provide a new strategy to manipulate an entire population of rings in a colloidal solution. The indirect shape control means that one does not have to act on a single nanostructure which requires perfect dexterity and spatial resolution.

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Chapter 2 General Method for Encapsulating Nanoparticles with Block Copolymers

2.1 Introduction

NPs are the foundation of nano science and technology. Owing to their small size and size-dependent properties, they have been applied in many areas such as sensing, labeling, imaging, cell separation and photodynamic therapy.¹⁻⁵ A major challenge in the application of NPs is the generality: it would be desirable to use one type of NP for many applications and to use many types of NPs in a single application. The predominant use of NPs is in the biomedical research, and thus, a general process to render NPs soluble and stable in an aqueous environment is of utmost importance.

A great variety of methods have been developed for the synthesis of colloidal NPs involving many different solvents. The NPs are typically passivated on their surface by ligands or surfactants, so that they remain stable in the particular solvent system during and after the synthesis. Change of solvent is often difficult as the polarity change easily destabilizes the NPs. Hence, unless the NPs are directly synthesized with biocompatible ligands in an aqueous solution, there is often a need to modify their surface chemistry to render them soluble in water with minimal aggregation. In most cases, the surface passivation of NPs requires excess ligands to be present in the solution, which is not always realis-

tic in biological applications. Without excess ligands, the ligands on the NP surface could easily dissociate. Even a strong thiol-based ligand could dissociate from a Au surface, not to mention ligands bound by weak coordination or ionic interactions. With the loss of surface ligands, both the chemical and colloidal stability of NPs are compromised. The materials of the NPs could react and/or dissolve in the media, and the NPs could aggregate with themselves or with other substances present in the system.

A direct approach of surface modification is to exchange the surface ligands, so that NPs can be transferred from the as-synthesized solution to the media of intended application. Such a process typically involves two different ligands and two different solvents. In particular, the new ligand and its functionalized NPs have to be stable in both solvents to minimize NP aggregation during the exchange of solvents. For each type of NPs, the affinity of their surface ligands is highly specific; a complete ligand exchange, at the minimum, requires the incoming ligand to be stronger or at least similar to the original one. On the other hand, the colloidal stability of NPs depends on the packing of the ligands and their solvent-facing chemical group, among other factors. Thus, the selection window for suitable incoming ligands is quite narrow. While obtaining NP samples free of aggregation is always not trivial, a larger problem is that each time the ligand and solvent exchange have to be specifically studied and a successful approach can only be applied to a specific system. Only a few general processes exist in the literature, and it remains a challenge to apply these methods to NPs synthesized from both polar and nonpolar solvents.

In comparison, coating NPs with a shell has several advantages. The encapsulated NPs with their surface ligands are protected so that their chemical

and colloidal stability do not depend on the excess ligands in the media. Preventing ligands from dissociation and exchange is of importance for applications such as surface enhanced Raman scattering (SERS), where the Raman signals are derived from the surface ligands. To render the encapsulated NPs stable in aqueous solution, typically polymers, proteins, or inorganic materials (e.g., silica) have been attached to the NP surface by either chemical reaction or deposition. While the water-facing surface of these shell materials must have charge, polar, or H-bonding functionalities for water solubility, their interface with the embedded NPs is also important in order for the encapsulation to work in the first place. For example, it is difficult to chemically link proteins to non-polar NP surface; surface initiators are necessary for grafting polymers; for silica encapsulation, NPs need to be functionalized with vitrophilic compounds in order for silica adsorption. Typically, if the NP-shell interface has a high surface tension, incomplete encapsulation will result⁶⁻¹¹. Since the core-shell interactions are often highly specific to both core and shell materials, most encapsulation methods have to be specifically developed and fine-tuned.

Here, we report a general approach to encapsulate a variety of NPs in shells of polystyrene-*block*-poly(acrylic acid) (PSPAA). The NPs only have to be functionalized with a hydrophobic ligand so that PSPAA can self-assemble on their surface via hydrophobic and Van Der Waals interactions. Since these interactions are non-specific to chemical groups, a wide range of NPs with very different surface ligands are compatible with the encapsulation process. The PSPAA shells protect the surface ligands and render the NPs highly soluble in water in the absence of excess ligands.

Previously, the PSPAA encapsulation of AuNPs,^{6,12} γ -Fe₂O₃¹³, QDs,¹⁴ and CNTs¹⁵ has been reported, where the slow addition of water to solublized PSPAA in an organic solvent induced the polymer self-assembly. We also reported a modified approach to induce PSPAA self-assembly by heating NPs and PSPAA in mixture solvents,^{6,11,16-17} by which AuNPs, AuNWs, and CNT bundles were encapsulated. In this section, we extend the method to encapsulate 19 types of NPs not yet reported. We focus our discussion on the mechanistic interpretation of the PSPAA self-assembly and on minimizing aggregation during the process.

2.2 Experimental section

2.2.1 Materials and characterization

All chemical reagents were used without further purification. Hydrogen tetrachloroaurate(III) hydrate (HAuCl₄ · 3H₂O), 99.9% (metal basis Au 49%) was purchased from Alfa Aesar; oleylamine (70% teach) was purchased from Acros, 2-dipalmitoyl-sn-glycero-3-phosphothioethanol (sodium salt) (ligand 1) were purchased from Avanti Polar Lipids; amphiphilic diblock copolymer polystyrene-*block*-poly(acrylic acid) (PS₁₅₄-*b*-PAA₆₀, M_n = 16000 for the polystyrene block and M_n = 4300 for the poly(acrylic acid) block, M_w/M_n = 1.15,) was purchased from Polymer Source, Inc.; all other chemicals were purchase from Aldrich. Deionized water (resistance > 18.2 M/cm) was used in all reactions. Copper specimen grids (300 mesh) with formvar/carbon support film (referred

to as TEM grids in the text) were purchased from Beijing XXBR Technology Co.

Preparation TEM sample: TEM grids were treated with oxygen plasma in a Harrick[®] plasma cleaner/sterilizer for 1 min to improve the surface hydrophilicity. The product solution was diluted (300 μ L solution added to 1200 μ L DI water) and then centrifuged at designed speed (depend on size of NPs) for 30 min to remove the empty micelles. Then a sample solution was carefully mixed with stain solution ($[(\text{NH}_4)\text{Mo}_7\text{O}_{24}] = 6.8 \text{ mM}$) on the surface of a plastic Petri dish, the hydrophilic face of the TEM grid was then placed in contact with the sample solution. A filter paper was used to wick off the excess solution on the TEM grid, which was then dried in air for 5 min. TEM images were collected from a JEM-1400 Transmission Electron Microscopy (JEOL) operated at 120 kV.

Preparation of hydrophilic NPs: All hydrophilic NPs were prepared by known procedures and stabilized by different ligands in aqueous solution: citrate-Au NPs¹⁸, PVP-Ag nanocubes¹⁹, CTAB-Au nanorods²⁰, citrate-Ag triangles²¹, citrate-Pt NPs²², tetramethylammonium hydroxide (TMAOH)- Fe_3O_4 NPs²³, poly ethylene glycol (PEG)- Cu_2O nanocubes²⁴.

Preparation of hydrophobic NPs: Hydrophobic NPs were prepared according to the literature and coated with ligands that render them hydrophobic: oleylamine-Au NPs²⁵, oleic acid- Fe_2O_3 NPs²⁶, oleylamine-FePt NPs²⁷, Trioctyl phosphine oxide (TOPO)-CdSe/ZnS dots²⁸, oleylamine- NaYF_4 NPs and nanorods²⁹.

2.2.2 Encapsulation of nanoparticles

Encapsulation of hydrophilic NPs: In a typical encapsulation, as-synthesized hydrophilic NPs were purified and separated by centrifugation and then re-dispersed in water. In a 4 mL vial, 180 μ L (~ 4.75 nM) of NP solution was added to 820 μ L of polymer solution which was prepared by mixing 740 μ L DMF with PSPAA (80 μ L, 8 mg/mL in DMF). Finally, 40 μ L of ligand 1 (See structure in Table 2-1) in EtOH was added to the mixture to give total volume of 1040 μ L, where the DMF/H₂O volume ratio was 4.5/1 and concentration of PS₁₅₄-*b*-PAA₆₀ is 28.5 μ M. The mixture was heated at 110 °C for 2 hrs and then allowed to slowly cool down to room temperature.

Encapsulation of hydrophobic NPs: In a typical encapsulation, hydrophobic NPs were purified and separated by centrifugation and re-dispersed in THF. In a 4 mL vial, 250 μ L water was added to the 750 μ L THF solutions which contained hydrophobic NPs (about 0.01 mM) and PS₁₅₄-*b*-PAA₆₀ in THF (80 μ L, 8 mg/mL) under vortex. The total volume of the final mixture solution was 1000 μ L, where the THF/H₂O volume ratio was 3/1 and concentration of PS₁₅₄-*b*-PAA₆₀ was 28.5 μ M. The mixture was heated to 60 °C for 2 hrs and then allowed to slowly cool down to room temperature in the oil bath.

2.3 Results and discussions

2.3.1 Overview of general method for encapsulation of nanoparticles

Figure 2-1. Schematic illustration of general method of encapsulating different NPs by using block copolymers; (a) encapsulation of hydrophilic NPs; (b) encapsulation of hydrophobic NPs.

Figure 2-1 shows a schematic illustration of the preparation procedure for diblock copolymer-encapsulated NPs. In our method, for hydrophilic NPs, hydrophobic ligands were used to render the hydrophilic NPs surface hydrophobic, upon which an amphiphilic diblock copolymer PSPAA attached to form an encapsulating shell. The hydrophilic NPs, PS₁₅₄-*b*-PAA₆₀, and proper ligands in DMF/H₂O (final volume ratio 4.5/1) were mixed in a given sequence; the mixture was heated to 110 °C for 2 hrs and then slowly cooled down to induce

self-assembly of copolymer into spherical micelle. For hydrophobic NPs, due to its hydrophobicity, encapsulation process accomplished without addition of any ligands.

The hydrophobic NPs were dispersed in H₂O/THF (final volume ratio THF/H₂O = 3/1) together with amphiphilic diblock copolymer (PS₁₅₄-*b*-PAA₆₀), where THF was used as a good solvent for both hydrophobic NPs and polymer, due to its poor polarity than DMF. Table 2-1 provides an overview of NPs@PSPAA prepared from various conditions respectively. The generality is clear.

Table 2-1. Summary of different types of NPs encapsulation by PSPAA.

NPs	Surface surfactant	Solvent	Ratio of solvent/H ₂ O	^a Ligand	Temp-erature	Reference
Au NPs	Citrate	DMF	4.5/1	1 or 2	110 °C	Figure 2-2a
Au NPs	Citrate	Aetone	8/1	2	25 °C	Figure 2-7a
Au NPs	Citrate	Aetonitrile	8/1	2	25 °C	Figure 2-7b
Ag nanocubes	PVP	DMF	4.5/1	1 or 2	110 °C	Figure 2-2b
Au nanorods	CTAB	DMF	4.5/1	1 or 2	110 °C	Figure 2-2c
Ag triangle NPs	Citrate	DMF	4.5/1	1 or 2	110 °C	Figure 2-2d
Pt NPs	Citrate	DMF	4.5/1	1	110 °C	Figure 2-2e
Fe ₃ O ₄ NPs	TMAOH	DMF	4.5/1	3	110 °C	Figure 2-2f
Cu ₂ O	PEG	DMF	4.5/1	1	110 °C	Figure 2-2g
Fe ₂ O ₃ nanorods	Phosphate	DMF	4.5/1	1	110 °C	Figure 2-2h
Au NPs	Oleylamine	THF	3/1	-	60 °C	Figure 2-3a
Au NPs	Oleylamine	Aetone	3/1	-	RT	Figure 2-7c
Au NPs	Oleylamine	Aetonitrile	3/1	-	RT	Figure 2-7d
γ -Fe ₂ O ₃ NPs (23 nm)	Oleic acid	THF	3/1	-	60 °C	Figure 2-3b
γ -Fe ₂ O ₃ NPs (12 nm)	Oleic acid	THF	3/1	-	60 °C	Figure 2-3c
FePt NPs	Oleic acid /Oleylamine	THF	3/1	-	60 °C	Figure 2-3d
CdSe/ZnS NPs	TOPO	THF	3/1	-	60 °C	Figure 2-3e
NaYF ₄ NPs	Oleic acid	THF	3/1	-	60 °C	Figure 2-3f
NaYF ₄ nanorods	Oleic acid	THF	3/1	-	60 °C	Figure 2-3g

^aStructure of Ligand 1, 2, 3 showing below:

2.3.2 Encapsulation of hydrophilic nanoparticles

In previous work, hydrophilic noble metal NPs, including Au and Ag NPs with different shapes and stabilized by different surfactants, have been successfully encapsulated by PS₁₅₄-*b*-PAA₆₀ in the presence of thiol group ligands.^{6,30} Here we further examined the versatility of our method by using different hydrophilic NPs, including noble metal NPs and metal oxide NPs. Figure 2-2 shows the TEM images of different hydrophilic NPs encapsulated within PSPAA micelles. It can be seen that a PS₁₅₄-*b*-PAA₆₀ shell was formed on the surface of the NPs during the encapsulation process. We first illustrated that our approach was general for those hydrophilic metal NPs. As shown in Figure 2-2 a-e, hydrophilic metal NPs, although they were synthesized under different conditions with various morphologies (sphere, rod, cube and spiky) and stabilizers (negatively charged citrate, positively charged CTAB and neutral PVP) including citrate-Au, CTAB-Au nanorods, PVP-Ag nanocubes, and citrate-Pt spiky NPs, have been successfully encapsulated by PSPAA. These results indicated that our method could be extended to most of hydrophilic metal NPs with different morphologies and stabilizers.

Figure 2-2. TEM images of different types of hydrophilic NPs encapsulated by $PS_{154}\text{-}b\text{-}PAA_{60}$ in DMF/ H_2O mixture, showing (a) citrate-Au NPs, (b) PVP-Ag nanocubes, (c) CTAB-Au nanorods, (d) citrate-Ag triangular NPs, (e) citrate-Pt NPs, (f) TMAOH- Fe_3O_4 NPs, (g) PEG- Cu_2O NPs, (h) Fe_2O_3 nanorods. All scale bars are 100 nm.

Further, we also examined the versatility of our method by using metal oxide in different shapes and with stabilizers. As shown in Figure 2-2 f-h, metal oxides NPs, such as TMAOH- Fe_3O_4 , PEG- Cu_2O and phosphate- Fe_2O_3 spindle were also encapsulated by PSPAA. Noted that a small amount of

TMAOH-Fe₃O₄ aggregation was observed, which occurred in the synthesis step. This result suggested that avoiding aggregation during synthesis was prerequisite for encapsulating NPs. Based on these results, we believed that the method described in this section could be readily extended to other kinds of hydrophilic NPs. Additionally, as confirmed by TEM images, the perfect core-shell structures could be seen and no obvious shape change or aggregation could be found after encapsulation. These encapsulated NPs could be stable and well dispersed in water after purification. The sample remains stable for a few months under ambient conditions.

2.3.3 Encapsulation of hydrophobic nanoparticles

We further demonstrated that our method was general to hydrophobic NPs. Although synthetic methods for hydrophilic NPs of metals, metal oxides, and QDs in aqueous solution are well developed, their applications so far are restricted due to the low-monodispersity and uniformity. Most syntheses for high quality, monodispersed NPs involved non-aqueous solvents and coating with monolayer of hydrophobic surfactants. Therefore, it is of great importance to find an effective way to improve the stability and water-solubility of these NPs. Figure 2-3 shows the various hydrophobic NPs have been successfully encapsulated in PS₁₅₄-*b*-PAA₆₀ micelles by using our method. Each micelle consists hydrophobic NPs surrounded by a shell of fairly consistent thickness. The encapsulated hydrophobic NPs also showed high colloidal stability, and no aggregation was observed even after a few months under ambient conditions. Although a few groups have reported that encapsulating multiple particles in a

shell is common for some hydrophobic NPs such as iron oxide and QDs,^{13-14,31} our method could give singly encapsulated, fairly monodispersed NPs.

Figure 2-3. TEM images of different types of hydrophobic NPs encapsulated by PS₁₅₄-*b*-PAA₆₀, (a) oleylamine-Au NPs, (b) 23 nm and (c) 8 nm oleic acid-Fe₂O₃ NPs, (d) oleylamine-FePt NPs, (e) TOPO-CdSe/ZnS dots, (f) NPs and (g) nanorods of oleic acid NaYF₄. All scale bars are 100 nm.

Figure 2-4. (a) UV-vis absorption spectra of hydrophobic AuNPs and AuNPs@PSPAA; (b) fluorescence spectra of the CdSe/ZnS QDs and CdSe/ZnS@PSPAA.

Characteristic surface plasmon bands were noted in the UV-vis absorption spectra of encapsulated oleylamine Au NPs. As shown in Figure 2-4a, compared with un-encapsulated AuNPs in THF, the UV-vis absorption peak of the AuNPs@PSPAA is red shifted from 526 nm to 535 nm in H₂O. This is resulted from the increasing of refractive index of the surrounding medium, leading to a decrease in surface plasmon resonance energies, which is similar with pervious results.^{6,12} The fluorescence emission peaks for the QDs before and after encapsulation remained the same at 524 nm (Figure 2-4b), indicating no obvious change in their physical properties. However, the quantum yield of the encapsulated QDs is 50% less than that of uncoated QDs.

2.3.4 Multi -core encapsulation

In addition to successful singly encapsulation of NPs, we also demonstrated multiple encapsulations, showing our method can be extended to con-

trolled aggregation and organization of NPs. We found that the linear aggregation of citrate AuNPs confined within the PSPAA micelles, as shown in Figure 2-5a, could be obtained by increasing of ionic strength of DMF/H₂O solution. By increasing the initial concentration of NPs, some structures containing multiple particles were observed. In the case of FePt NPs, as shown in Figure 2-5b the edge of the core region presented darker than the centre, suggesting that the FePt NPs were radically arranged at the interface between the polymer core and the shell, which was similar with the previously reported composites in which QDs were encapsulated in PSPAA block copolymer micelles.³² Multiple oleylamine-Au NPs were encapsulated when the initial concentration of NPs increased (Figure 2-5c). This result may suggest that increasing numbers of NPs in the initial solution led to the relative large micelles contained multiple particles for most of the hydrophobic NPs, As shown in Figure 2-5d, we also observed close-packing nanostructure when extremely monodispersed NPs were used, indicating our method could be applicable to control organization of NPs.

Figure 2-5. TEM images of different types of aggregation of NPs encapsulated by PS₁₅₄-*b*-PAA₆₀, (a) linear aggregation of citrate-Au NPs, (b) FePt NPs assembled at the spherical interface between the polymer core and the shell, (c) multi-core oleylamine-Au NPs and (d) close-packing nanostructure. All scale bars are 100 nm.

2.3.5 Mechanism study

The overall goal of our study is to develop a simple method which can be used to encapsulate a variety of NPs synthesized from different methods and stabilized by different surfactants. To accomplish the encapsulation, a critical step is to transfer NPs dispersed in different solution to a common solvent (DMF or THF) where the encapsulation is carried out. At this step, the original NPs had to get rid of excess surfactants. On one hand, although excess amount of surfactant is essential for the synthesis of high quality monodispersed hydrophilic NPs and often have no effect on the encapsulation, they may have strong affinity to bind with NPs, leading to aggregation or un-encapsulation in some case. For example, after purification, CTAB stabilized Au nanorods could be encapsulated by PS₁₅₄-*b*-PAA₆₀ in presence of ligand 1, while a control experiment showed that encapsulation cannot be achieved without pre-purification. This result attributed to removing the excess surface surfactants by purification, for some surfactants have strong affinity on NP surface and hamper ligand exchange. On the other hand, free surfactants such as long-chain amine/acid and TOPO are usually used to stabilize as-synthesized hydrophobic NPs in organic solvent.

However these excess hydrophobic surfactants would induce aggregation due to their low solubility in the mixture of water and THF. Encapsulation of as-synthesized oleylamine stabilized AuNPs gave PSPAA micelle containing a large number of AuNPs. This aggregation was caused by addition of excess of oleylamine in the solution probably (Figure 2-6a). The degree of aggregation was reduced after oleylamine AuNPs were purified once EtOH (Figure 2-6b).

We found that oleylamine stabilized Au NPs must be pre-isolated with EtOH at least 3 times by centrifugation in order to obtain single encapsulation. Addition of oleylamine to the solution which contained 3 times purified oleylamine stabilized AuNPs, AuNPs tended to aggregation again (Figure 2-6c). These results also confirmed that the elimination of free oleylamine could avoid the aggregation of NPs.

Figure 2-6. TEM images of oleylamine Au NPs encapsulated by PS₁₅₄-*b*-PAA₆₀, which the initial oleylamine-Au NPs were purified (a) 1 time, (b) 2 times, (c) 3 times with addition of 5 μL 1% oleylamine.

Choice of Solvent: The nature of the solvent used to dissolve both block copolymer and NPs in the initial step is a prerequisite factor of the encapsulation. Solvent chosen for encapsulation of hydrophilic NPs is DMF, which is a good solvent for polymer and hydrophilic NPs. High boiling point of DMF allowed PSPAA to assemble easily. Importantly, the ligand exchange process is performed at relatively high temperature so that dynamic solvation of ligands favors exchange of original surfactants with hydrophobic ones through mass action. Solvent chosen for encapsulation of hydrophobic NPs is THF, which is a

good solvent for polymer and most of hydrophobic NPs. A prerequisite of our strategy for encapsulating hydrophobic NPs is that the hydrophobic NPs must be stable and well dispersed in the encapsulation medium, which is a mixture of THF and water. The hydrophobic NPs could be easily dispersed in THF, minimizing the particle-particle aggregation during the encapsulation processes. It should be noted that when DMF was used, hydrophobic NPs were aggregated compared to THF; it may attribute to less polarity of THF. We further demonstrated that other solvent also could be used for encapsulation (Figure 2-7).

Effect of Water Content: Regarding a bad solvent for the hydrophobic block of the copolymer, water works as precipitant while mixing with the solution of block copolymers in the good solvent. Previous report showed that addition of water was necessary to induce self-assembly of block copolymer. In our system, the volume ratios of common solvent to H₂O determined the aggregation level of NPs, as well as the morphology of NP-block copolymer assemblies.

Figure 2-7. TEM images of citrate-Au NPs encapsulated by PS₁₅₄-*b*-PAA₆₀, which prepared at room temperature in (a) Acetone/H₂O = 8/1, (b) Acetonitrile/H₂O = 8/1; oleylamine-Au NPs encapsulated by PS₁₅₄-*b*-PAA₆₀ prepared in (c) Acetone/H₂O = 3/1, (d) Acetonitrile/H₂O = 3/1. All scale bars are 100 nm.

Figure 2-8. TEM images of citrate-Au NPs encapsulated by PS₁₅₄-*b*-PAA₆₀, when (a) DMF/H₂O = 8/1, (b) DMF/H₂O = 1/1. All scale bars are 100 nm.

In the case of hydrophilic AuNPs, aggregation was obtained with 8/1 of DMF/H₂O (Figure 2-8a), while poor encapsulation was occurred when 1/1 DMF/H₂O. (Figure 2-8b). According to the Derjaguin Landau Verwey and Overbeek theory (DLVO theory),¹¹ the stability of NPs in solution is controlled by two factors, namely electrostatic repulsion (V_{elec}) and Van de Waals attraction (V_{vdw}). Weakening V_{elec} between NPs usually causes aggregation. It is noted that tuning the electrostatic repulsion between NPs by ionic strength, especially polarity can finely control the aggregation of NPs. A decrease in the dielectric constant of the medium surrounding NPs can cause a decrease of V_{elec} . Various polar organic solvents with small dielectric constant, including acetonitrile, EtOH, acetone and DMF were introduced to aqueous solution to control the aggregation of NPs.¹¹ In our system, it has been known that the dielectric constant of water ($\epsilon = 80$) is higher than that of DMF ($\epsilon = 38.2$) and THF ($\epsilon = 7.5$). As the water content decreases, dielectric constant of the solution becomes

lower. Consequently, the electrostatic repulsion among NPs decreases, thus aggregation of NPs at lower water content is observed (Figure 2-8a). On the other hand, when the water content increased within a certain range, the high dielectric constant may contribute to the non-aggregation of NPs in solution. However, if water content continues increasing, the solvent obtains poorer quality for hydrophobic PS block. As a response, the stretching degree of PS chain decreases, resulting in a negative influence on the interaction between PS chain and surface hydrophobic ligand. PSPAA assemblies surrounding NPs are limited and partial encapsulated nanostructures was observed (Figure 2-8b).

Compared to hydrophilic NPs, nanostructure of hydrophobic NP-block copolymer assemblies were different. When the ratio of THF/H₂O increased to 8/1, as shown in Figure 2-9a, some large spherical micelles containing a large amount of hydrophobic AuNPs were obtained. Similarly, when the ratio of THF/H₂O was 4.5/1, large spherical micelles containing multi-NPs still could be observed (Figure 2-9b). When the ratio of THF/H₂O decreased to 1/2, some partial encapsulated structure as well as large micelles contained multi-core could be observed (Figure 2-9c). The UV-vis spectra indicates these aggregations were similar (Figure 2-9d).

Figure 2-9. TEM images of encapsulated oleylamine-Au NPs prepared in (a) THF/H₂O = 8/1, (b) THF/H₂O = 4.5/1, (c) THF/H₂O = 1/2. (d) UV-vis spectra of oleylamine-Au NPs before (black), and after encapsulation in THF/H₂O = 4.5/1 (green) and THF/H₂O = 1/2 (red), respectively.

Similar to hydrophilic AuNPs, increasing of THF content in solution resulted in lower dielectric constant. Thus the decrease of electrostatic repulsion caused aggregation of hydrophobic NPs. However, it should be noted that structure of large spherical micelles obtained in high ratio of THF/H₂O was distinct from that obtained in same ratio of DMF/H₂O. It is well known that the

morphology of block-copolymer aggregates can be controlled by many factors including the variation of common solvent composition. Since THF is less polar than DMF, the stretching degree of the PS chain increases in THF. In order to reduce the total free energy of the system, large compound micelles with spherical assembly of reverse micelles were formed.

To further clarify the difference in morphology when same ratio of DMF or THF was used, a series of experiments were carried out. When we used citrate stabilized AuNPs instead of oleylamine stabilized AuNPs in 4.5/1 of THF/H₂O, aggregation was still observed. These results indicated that the aggregation of NPs was really induced by decreasing of dielectric constant rather than solubility of NPs. Also, large compound micelles in Figure 2-10a suggested the reverse micelles were obtained in the case of citrate stabilized AuNPs. When oleylamine stabilized AuNPs were replaced by citrate stabilized AuNPs@PSPAA (as-product in Figure 2-2a) or oleylamine stabilized AuNPs@PSPAA (as-product in Figure 2-3a), the degree of aggregation decreased and all regular core-shell structure transformed into large compound micelles in THF/H₂O = 4.5/1 solution (Figure 2-10b, c). In absence of NPs, polymer PSPAA still assembled into large compound micelles in THF/H₂O = 4.5/1 solution (Figure 2-10d). This observation demonstrated that the formation of large compound micelles at high ratio of THF/H₂O was not related to the core material. In order to encapsulate NPs with regular PSPAA shells, it is important to rationally control water content in solvent system. It is also interesting that large compound micelles could transform into regular core-shell structure. As shown in Figure 2-10e, the well-defined core-shell nanostructures were observed by encapsulation of large compound micelles in THF/H₂O = 3/1 solution.

This result also indicated that the morphologies of NP-block copolymer assemblies were determined by the ratio of THF/H₂O during encapsulating process.

Figure 2-10. TEM images of PSPAA encapsulated composites with starting NPs: (a) citrate-Au NPs (b) citrate-Au NPs@PS₁₅₄-b-PAA₆₀ (c) oleylamine-Au NPs@PS₁₅₄-b-PAA₆₀. TEM images of (d) PSPAA free micelles prepared in solution of THF/H₂O = 4.5/1, (e) single PSPAA encapsulated citrated AuNPs treated in solution of THF/H₂O = 3/1.

When the ratio of THF/H₂O decreased to 1/2, some partially encapsulated structure and large micelles containing multi-core could come out together, while non-aggregates could be found in low ratio of DMF/H₂O. We believed that this difference was probably caused by low solubility of hydrophobic NPs in solution when water content increased. As shown in Figure 2-11a, when

oleylamine AuNPs were replaced by citrate AuNPs, only partial aggregation could be found. Also, no aggregates were obtained at high water content when oleylamine stabilized AuNPs@PSPAA was used. These results suggested that the oleylamine AuNPs became lower soluble at higher water content compared to water-soluble NPs, which may contribute to the formation of multi-core encapsulation. As shown in Figure 2-11b and d, when we introduced small amount of oleylamine to citrate stabilized AuNPs or oleylamine stabilized AuNPs@PSPAA, the aggregates formed again during the encapsulation process. These results further confirmed that it was residual oleylamine that contributed to the aggregation in high water content solution.

Figure 2-11. TEM images of PS₁₅₄-*b*-PAA₆₀ encapsulated (a) citrate-AuNPs (b) oleylamine-AuNPs@PS₁₅₄-*b*-PAA₆₀ in solution of THF/H₂O = 2/1; PS₁₅₄-*b*-PAA₆₀ encapsulated (c) citrate-AuNPs and (d) oleylamine-AuNPs@PS₁₅₄-*b*-PAA₆₀ with addition of 5 μL 1% oleylamine in the solution of THF/H₂O = 2/1.

Role of ligand: Our encapsulated method was based solely on noncovalent interactions between NPs and block copolymers. For hydrophilic NPs, due to their hydrophilic surface, it is necessary to introduce hydrophobic ligands to take the place of original hydrophilic surfactants on NP surface. A various li-

gands were found to be applicable for encapsulation of hydrophilic NPs. Usually, a typical ligand could be binding-ended molecules with hydrophobic groups. Figure 2-12 summarized the ligands used for different kinds of hydrophilic NPs. Several types of hydrophilic metal NPs, including negatively charged citrate-AuNPs, positively charged CTAB-AuNRs, and neutral PVP-Ag nanocubes, were found to be encapsulated in presence of thiol ended ligands. These results suggested that the charge for the surface surfactant was not an important factor in our system. It is noted that in some cases, the as-synthesized NPs must first get rid of the excess capping surfactants which have strong affinity to disrupt the ligands exchange and finally disrupt the encapsulation process. Using ligand 1, citrate stabilized Pt spiky NPs could be encapsulated after removal of surface surfactants; while encapsulation of PVP stabilized Pt NPs could not be proceeded, for PVP have stronger affinity than citrate which block new ligand linked to attach on the surface of NPs. It seems that substitution of ligands plays the most critical role in the process of encapsulation. Further experiments demonstrated that other types hydrophilic NPs, Fe_2O_3 , Cu_2O could also be encapsulated by using appropriate ligands.

Figure 2-12. Ligands used in encapsulating hydrophilic NPs.

The successful encapsulation of hydrophobic NPs was performed without any ligands, probably because the hydrophobic surface molecules could induce self assembly directly. The hydrophobic surface molecules played a determining major role in the encapsulation of hydrophobic NPs. Further controlled experiments were performed to confirm this proposes. Hydrophobic NPs could not be encapsulated after substitution of their original hydrophobic surface molecules with hydrophilic PAA (Figure 2-13a)

Another interesting observation is that introduction of hydrophilic ligand during the encapsulation led to a binding competition between hydrophobic and hydrophilic ligand and give eccentrically core-shell nanostructure as a product. Base on this strategy, we prepared a series of eccentrically core-shell NPs with the PSPAA self-assembly on partial surface of metal NPs (Janus NPs). As shown in Figure 2-13b, we also extent this eccentrically core-shell NPs to hydrophobic metal oxide NPs. By introduction of hydrophilic ligand (PAA) to compete with the surface hydrophobic molecule (oleylamine) on Fe_2O_3 , we successfully prepared partial encapsulated $\text{Fe}_2\text{O}_3\text{NPs@PSPAA}$. These eccentric structures are determined by competitive functionalizing the surface of NPs with hydrophobic and hydrophilic patches. The adsorption of different ligands is dictated, obviously, by the binding affinity with NPs. However, one type of ligand with higher concentrations would create higher probability to adsorb on surface of NPs, even the ligand is weaker than the other. In addition, the packing efficiency leads to the ligand with long aliphatic chains adsorbing on surface with low curvature, while short ligand prone to functionalizing sites with high curvature. The packing of long PS chains preferentially on flatter surfaces should also promote the ligand segregation which thus minimizes the interfacial

energy. With regard to different systems, some of the factors were expected to play influential role in the formation of NP@PSPAA with various morphologies. A more detailed theoretical and experimental demonstration on the eccentric encapsulation was discussed in literatures.⁷

Figure 2-13. TEM images of PAA functionalized hydrophobic Fe_2O_3 NPs encapsulated by PSPAA, PAA concentration in solution is (a) 2 mg/mL and (b) 0.4 mg/mL.

Synthesis of metal oxide and semiconductor NPs in polar or nonpolar solvent were well-developed. They provided crystalline near-monodispersed particles with tunable size falling in a milligram to gram scale. The existed method enabled us to obtain core-shell structures of different types of materials that are very stable either in the solid state or in colloidal solution. It is conceivable that these nanostructures could be applied to various applications. Our previous studies have shown that the polymer-encapsulated AuNPs can tolerate saturated NaCl or CsCl solution at $\text{pH} = 10$, which allowed us to separate dimmers and

trimmers with excellent purity. Since different types of NPs have been encapsulated by PSPAA, our method was clearly shown potential for synthesis of dimmers or trimmers of different types of NPs with high purity. Base on this strategy, our approach also could be used as a simple method for controlled organization of nanomaterials in solutions. As shown in Figure 2-14, we successful separated Fe_2O_3 NPs@PSPAA with high purity of monomer (Figure 2-14b), dimmers and trimers (Figure 2-14c), as well as mutil-core@PSPAA (Figure 2-14d) complex nanostructures. Also as illustrated previously, the long PAA arms on NP form a thick hydrophilic layer where biomolecules can be securely attached. We anticipate that these various encapsulated NPs could be used as carriers for targeted drug delivery, as tags for biomolecular sensors *in vivo* imaging.

Figure 2-14. TEM images of Fe_2O_3 NPs@PSAA, (a) as-synthesized without separation; separated (b) monomers, (c) dimmers and trimers, and (d) multi-cores.

2.4 Encapsulation of nanoparticles with triblock polymers

2.4.1 Crew-cut ABA triblock copolymer micelles

It has been known for many years that ABA amphiphilic triblock copolymer also can self-assemble in certain medias to form crew-cut aggregates of multiple morphologies, which is quite similar with amphiphilic diblock polymers cases.³³⁻³⁶ Among these ABA triblock copolymers, poly(4-vinylpyridine)-*b*-polystyrene-*b*-poly(4-vinylpyridine) (P4VP₄₃-*b*-PS₂₆₀-*b*-P4VP₄₃) are intensively studied. In a selected medium, the relative short hydrophilic blocks were supposed to form the shell and the short hydrophobic blocks folded into corona (Figure 2-15). Extensive studies revealed that apart from spherical micelles, some complex aggregated morphologies such as rods, vesicles, lamellae, tubes, disks, onions and ring shapes had been obtained through building hydrogen bonding between one of the block and small molecular surfactant by continuous heating of the micellar solution.³⁷⁻⁴⁰

Figure 2-15. Schematic showing structures of (a) ABA triblock copolymer P4VP-PS-P4VP and (b) its corresponding crew-cut micelles formed in selected mixture.

In section of 2.3, it is clear that in solution phase, self-assembly of diblock copolymers and NPs has been explored as a promising synthetic tool for generating multifunctional nanostructures. It is conceivable that this strategy also applied to the ABA amphiphilic triblock polymers system. Since triblock copolymer ($P4VP_{43}\text{-}b\text{-}PS_{260}\text{-}b\text{-}P4VP_{43}$) can form spherical aggregates, it is reasonable to extend our previous encapsulating method to triblock copolymer system. Furthermore, compared to diblock polymer PSPAA, $P4VP_{43}\text{-}b\text{-}PS_{260}\text{-}b\text{-}P4VP_{43}$ is easier to form rods, vesicles and other complex shapes, which provides new strategy to contracture many novel structures.

2.4.2 Encapsulating nanoparticles with triblock copolymers

Triblock copolymer encapsulation was carried out by modifying our previously published procedures. We used the same concentration of $P4VP_{43}\text{-}b\text{-}PS_{260}\text{-}b\text{-}P4VP_{43}$ instead of PS-*b*-PAA for encapsulating citrate-AuNPs, while other parameters of reaction were remained. As shown in Figure 2-16a, all citrate-AuNPs had a well-defined core/shell structure with uniform P4VP-PS-P4VP shell thickness; and each polymer micelle contained only one AuNP. Also there was no obvious aggregation of AuNPs observed. From UV-vis spectra (Figure 2-16b), the absorption of AuNPs@P4VP-PS-P4VP was slightly red shift over the bare AuNPs. This red shift was attributed to the in-

creasing refractive index of the surrounding medium, similar as the pervious AuNPs@PSPAA case, leading to a decrease in surface plasmon resonance energies.

Figure 2-16. (a) TEM image of citrate-Au NPs encapsulated by P4VP-PS-P4VP shells. (b) UV-vis spectra of citrate-AuNPs before and after encapsulating with P4VP-PS-P4VP, respectively.

2.4.3 Mechanism study

For mechanism study, ligand 2 was used instead of ligand 1 (ligand 1, 2 as illustrated in table 2-1), both small size (20 nm) and large size (40 nm) AuNPs encapsulated with P4VP-PS-P4VP were achieved. From TEM images, there was no obvious aggregation observed (Figure 2-17a). The UV-vis spectrum confirmed this observation, for the spectrum was similar with 20 nm AuNPs encapsulation (Figure 2-17b). Ligand 2 was SERS-active reporter. When they were uniform attached on the metal NP surface, their Raman signal can be

greatly enhanced. The P4VP-PS-P4VP encapsulated AuNPs with ligand 2 were characterized by solution Raman spectroscopy. Figure 2-17c, d showed the SERS signals of ligand 2 on AuNPs (20 nm and 40 nm); the peaks were consistent with reported values in the literature.⁴¹ No extra peak could be assigned to the Raman signals of polystyrene, suggesting that most of the NP surface was covered by the Raman reporter. For 20 nm AuNPs, the SERS signal was weak, which further confirmed no AuNP aggregation present during encapsulating process. The SERS signal provided information that AuNPs were covered by hydrophobic ligand. This information suggested that PS blocks of P4VP-PS-P4VP must be in the inner layer of the shell, giving hydrophobic interaction stabilized core-shell structures. The obtained core-shell nanostructures were stable in aqueous solution, indicating outer layer of the shell must be hydrophilic P4VP block.

Figure 2-17. (a) TEM image of 40 nm citrate-AuNPs encapsulated by P4VP-PS-P4VP. (b) UV-vis spectrum of citrate-AuNPs before and after encapsulating with P4VP-PS-P4VP. SERS spectra of (c) 20 nm and (d) 40 nm citrate-AuNPs@P4VP-PS-P4VP.

Based on these results, we proposed that the P4VP-PS-P4VP chain was folded into U shape, whose PS block attached to AuNP surface and left the hydrophilic P4VP tails outside (Figure 2-18).

Figure 2-18. Schematic showing the proposed structure of P4VP-PS-P4VP encapsulated NPs.

2.4.4 Generality of triblock copolymer encapsulation

We further tested the generality of ABA triblock polymer encapsulation method. For this purpose, both hydrophilic and hydrophobic NPs were used as core materials. As shown in Figure 2-19a, b, CTAB-Au NRs and PVP-Au nanocubes were successfully encapsulated using the same method as citrate-Au NPs. Each uniform P4VP-PS-P4VP micelles contained one NP and no aggregation observed, suggesting the surface charge of NPs might not affect the encapsulating process. For hydrophobic NPs (oleylamine- Fe_2O_3 , TOPO-CdSe/ZnS), THF was used as solvent instead of DMF to avoid aggregation induced by low solubility. As shown in Figure 2-19c, d, these hydrophobic NPs were singly encapsulated by P4VP-PS-P4VP with uniform shells, indicating triblock polymer

encapsulating method was also applicable for hydrophobic system. All of these results demonstrated the generality of ABA triblock copolymer encapsulating method.

Figure 2-19. TEM images of P4VP-PS-P4VP encapsulated (a) CTAB-Au nanorods, (b) PVP-Ag nanocubes, (c) oleylamine-Fe₂O₃ NPs and (d) TOPO-CdSe/ZnS QDs.

2.4.5 Complex nanostructures of NPs@P4VP-PS-P4VP

Compared to diblock copolymers, triblock copolymers P4VP-PS-P4VP are easier to form complex nanostructures with various morphologies,⁴²⁻⁴⁴ such as cylinders, vesicles and rings by changing the parameters of systems. So by varying these parameters, the morphologies of micelle could be fine-tuned.⁴⁵⁻⁴⁷

In the fabrication of inorganic NPs doped complex nanostructures, great control over micellar shape and size is very important to obtain the desired functions and properties in practical application possibilities. The micelles may serve as template but be highly desirable to control the morphology. For this purpose, we simply varied organic solvent to water ratio to tune the morphologies of final NP-triblock copolymer assemblies. As shown in Figure 2-20, when DMF/H₂O was 6/1, AuNPs@P4VP-PS-P4VP self-assembles were mostly regular core-shell structures. When DMF/H₂O was 3/1, the morphologies of co-assemblies AuNPs@P4VP-PS-P4VP were cylindrical micelles. Continuing decreasing the ratio of DMF/H₂O gave AuNPs incorporated vesicles as major product. As we know, the self-assembly morphologies of the aggregates were controlled by the equilibrant among stretching of the core-forming chains in the core, interfacial tension between core and solvent, and interactions of the corona chains. Thus, all the changes such as composition of solvent, block lengths of copolymers and additives, would influence the equilibrant in the system and the final morphologies of the aggregates. As water content increased, the interfacial energy between PS core and solvent increased.⁴⁸ In order to minimize the interfacial energy, the average surface area per corona chain would decrease. One way to decrease this value was by increasing the stretching degree of PS

blocks. Thus, the spherical micelles with lower PS stretching degree, changed their structure into rods. When the stretching of PS blocks had reached a critical value, the rods had to transform into other shapes, like bilayers or vesicles, to reach the most stable stage.

Figure 2-20. TEM images of different morphologies of AuNPs@P4VP-PS-P4VP obtained in different ratios of DMF/H₂O (a) 8/1, (b) 6/1, (c) 4/1 and (d) 3/1, respectively.

2.6 Conclusions

In this section, a general method for encapsulation various NPs, including hydrophobic and hydrophilic NPs within block polymer micelles was developed. The obtained core-shell nanostructure was highly stable and soluble in aqueous conditions. Because of the simplicity of this process, we believed that this method could be extended to large-scale production. This procedure had shown a significant generality and should be applicable to many different types of NPs with unique properties. Furthermore, we demonstrated this method was applicable for other types of block copolymers, such as triblock copolymers. The well developed encapsulation method provided solid methodology for constructing block polymer based complex nanostructures.

2.7 Bibliography

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Chapter 3 Mechanical Nanosprings from Ultrathin Au Nanowires

3.1 Introduction

A dream goal of nanoscience is to fabricate nanodevice resembling a macroscopic device. The common strategy in fabricating such nanodevice is to mimic the structure and concept of macroscopic devices to achieve novel functions. Coiled springs are elastic metal objects with structural memory. Their ability to store and release mechanical energy has led to their widespread applications. Likewise, controlling mechanical energy at nanoscale would make an important step towards nano-engineering. A large number of research efforts have been devoted to mimicking coiled springs in nanoscale, but the methodologies are still quite limited. Most of the coiled nanofilaments in the literature were directly synthesized by gas-phase deposition of a material on a substrate at a high temperature. The structural twisting was proposed to be caused either (a) by dislocation-driven growth mode;¹⁻⁸ (b) by the surface charge imbalance on oxide NWs or nanobelts;⁴⁻⁶ or (c) by the anisotropy in the extrusion of CNTs from catalytic particles.⁷⁻⁸ Single-wire studies have demonstrated mechanical flexibility of several helical nanosprings.^{5,8} In addition, CNTs are known to spontaneously coil under various treatments,⁹⁻¹² likely to maximize packing among the overlapping loops. However, these methods are generally not appli-

cable for coiling metallic filaments, which has been rarely reported.¹² Just as in macroscopic springs, metal would be a favored material owing to its flexibility and resilience.

Here, we report a new approach to induce the coiling of pre-fabricated AuNWs in high yield, giving a structure resembling that of torsion springs. The mass transformation of straight wires to circular rings is achieved in a colloidal solution by modulating the contraction of encapsulating shells made of polystyrene-*block*-poly(acrylic acid) (PSPAA). Unlike most of the existing nanosprings, the *induced* coiling stored elastic energy in the stressed AuNWs. As a proof-of-concept demonstration, this energy was released when the nanosprings spontaneously un-coiled upon removal or swelling of the polymer shells.

3.2 Experimental section

3.2.1 Materials and characterization

All chemical reagents were used as purchased without further purification. Hydrogen tetrachloroaurate(III) hydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), 99.9% (metal basis Au 49%) was purchased from Alfa Aesar; Triisopropylsilane (TIPS) was obtained from Sinopharm; amphiphilic diblock copolymer polystyrene-*block*-poly(acrylic acid) ($\text{PS}_{154}\text{-}b\text{-PAA}_{49}$, $M_n = 16000$ for the polystyrene block and $M_n = 3500$ for the poly(acrylic acid) block, $M_w/M_n = 1.15$) was purchased from Polymer Source, Inc.; all other chemicals were purchased from Aldrich. 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 (referred to as TEM grids in the text) were purchased from Beijing XXBR Technology Co.

TEM images were collected from a JEM-1400 Transmission Electron Microscopy (JEOL) operated at 120 kV. UV-VIS-NIR spectra were collected from Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer.

Preparation of TEM samples: $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ was used as the negative stain in all TEM images reported in this paper, so that the polymer shells appear white against the stained background. TEM grids were treated with oxygen plasma in a Harrick plasma cleaner/sterilizer for 1 min to improve the surface hydrophilicity. The hydrophilic face of the TEM grid was then treated with 0.1% (3-aminopropyl)triethoxysilane (APTES) aqueous solution for 15 min to functionalize it with amine groups and then washed with water to remove the un-reacted chemicals. After drying in air, the grid was placed face-down on a droplet of sample laid on a plastic Petri dish. A filter paper was used to wick off the excess solution on the TEM grid, which was then dried in air for 5 min. Finally, a 1% aq. stain solution was cast on the grid, the excess solution was removed by using a filter paper and the grid was dried in air. In most cases the amine-functionalized surface was able to trap the PSPAA micelles (intermediates in particular) as discussed in the main text. However, since the stain solution contains mostly water, it may have induced some loosely bound AuNW@PSPAA to change their conformations (for example, from straight to racket shape or to

coils). The Au nanosprings are stable in water and are thus not expected to be affected during the stain treatment.

3.2.2 Preparation of Au nanosprings

Preparation of ultrathin Au nanowires: Ultrathin Au nanowires (AuNWs) were prepared following a previously reported method.¹³ 100 μL oleylamine and 3 mg $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ were added into 2.5 mL hexane to form a yellow solution. Then 150 μL TIPS was added to the mixture and this solution were incubated at room temperature for 4-5 hrs.

Purification of AuNWs: High purity AuNWs were separated by using organic density gradients.¹⁴ To make a step gradient, 650 μL pure THF was added to a centrifuge tube (polystyrene tube, 1.5 mL), then 650 μL 20% CHCl_3 solution (a volume ratio of CHCl_3 :THF = 1:4 was used to make the 20% CHCl_3 solution) was carefully added below the THF layer by inserting the tip of a pipette to the bottom of the centrifuge tube. The as-synthesized AuNWs (200 μL in hexane) was then carefully layered on top of the density gradient and the tube was centrifuged at 14000 rpm (16000 g) for 30 min. The resulting solution showed clear layers of different color. The dark-brown layer (bottom layer) was separated from the centrifuge tube and purified in ethanol to remove the excess oleylamine. The precipitate was then readily dispersed in 400 μL THF.

Preparation of Au nanosprings: The encapsulation method used here was modified from our previous report on the encapsulation of Au NPs.¹⁵ The above

400 μL AuNWs THF solution was added to 400 μL of polymer solution which was prepared by mixing 320 μL DMF with PS₁₅₄-*b*-PAA₄₉ (80 μL , 8 mg/mL in DMF); then, 100 μL of water was added under vortex (DMF/THF/H₂O = 4:4:1, water content 11%). The resulting mixture was incubated at room temperature for 24 hrs. Finally, 450 μL of water was quickly added (total volume of 1.35 mL, water content 41%). The solution was centrifuged at 13000 rpm (13700 *g*) for 15 min to separate the Au nanosprings from the supernatant. Since the centrifugation took 15 min, no additional time was required for allowing the nanosprings to equilibrate. The collected solution of Au nanosprings (about 10 μL) was further diluted by water (1.5 mL), and then centrifuged again to remove the excess DMF, THF and empty micelles. After re-dispersed in water, the product was stable in solution for weeks.

3.2.3 Trapping of the coiling intermediates.

For mechanistic studies, a sample was directly isolated by centrifugation before the addition of 450 μL of water. The concentrated solution was then used for TEM sample preparation (micelles were trapped by the amine-functionalized grids). It was possible that the later addition of aqueous stain solution may have induced some of the loosely bound AuNW@PSPAA to change conformation, leading to the low yield (72%) of the single-wire core-shell structures.

In a different control experiment, 900 μL of the as-prepared sample (DMF/THF/H₂O = 4:4:1) was added 140 μL of water (23%). The resulting mixture was then centrifuged and used for TEM sample preparation.

3.2.4 Swelling of the polymer shell of Au nanosprings

An as-synthesized solution of Au nanosprings (dispersed in water) was concentrated to ~ 10 μL by centrifugation. The dark brown solution collected from the bottom of centrifuge tube was dispersed in 900 μL pure THF and incubated for 12 hrs at room temperature. The solution was then centrifuged at 13000 rpm (13700 g) for 15 min to isolate the AuNWs from the supernatant for characterization.

Procedures for swelling the PSPAA shells were analogous to the above process. A swelling solution of DMF/THF/H₂O (4:4:1, water content 11%) was prepared by mixing 320 μL DMF with PS₁₅₄-*b*-PAA₄₉ in DMF (80 μL , 8 mg/mL), 400 μL THF and 100 μL water. The concentrated solution of Au nanosprings (10 μL in water) was added; the mixture was incubated for 12 hrs, and then centrifuged to isolate the uncoiled AuNW@PSPAA. The excess PSPAA was used to stabilize the polymer shells. Without it, the polymer shells would dissolve away.

3.3 Results and discussions

3.3.1 Preparation of Au nanosprings

Surface-templated self-assembly of PSPAA provides a facile route to fabricate uniform shells on various types of NPs, where PS blocks attach to hydrophobically functionalized particle surface and PAA blocks dissolve in water facing outwards.¹⁵⁻²⁰ The minimization of PS-solvent interface typically makes free PSPAA micelles spherical in shape. On Au nanorods, as shown in Figure 3-1, the encapsulating PSPAA micelles were often thinner on the ends and thicker on the sides; this deformation of the shell structure manifested sizeable surface tension.¹⁹⁻²¹ We were intrigued by the notion that, conversely, the cores might be made to deform with the force exerted by polymer shells. Thus, we tested this idea on ultrathin AuNWs¹³⁻¹⁴ that were expected to have low flexural strength.

Figure 3-1. A typical TEM image of PSPAA encapsulated Au nanorods. The micelles were often thinner on the ends and thicker on the sides, manifesting sizeable tension at the PS-solvent interface.

The oleylamine-stabilized AuNWs were synthesized¹³⁻¹⁴ and purified¹⁴ as previously reported. However, our standard encapsulation methods^{15,17-20} did not work as the ultrathin AuNWs were prone to aggregation in DMF solutions and they easily fused or dissolved away upon heating.²¹ As shown in Figure 3-2, it is clear that the AuNWs were easy to fuse or etch upon heating in DMF or THF and H₂O mixture. A room temperature method was thus developed: the as-synthesized AuNWs were mixed with PS₁₅₄-*b*-PAA₄₉ dissolved in a ternary solvent mixture, DMF/THF/H₂O (4:4:1, v/v/v), and then incubated for

24 hrs. THF was used to improve the solubility of the oleylamine-stabilized AuNWs and the large percentage of organic solvents was intended to swell the polymer and facilitate its assembly at room temperature. The sample was then diluted by water to de-swell the polymer shells, and centrifuged to remove the excess solvent and free PSPAA micelles.

Figure 3-2. A typical TEM image of the fused AuNW@PSPAA prepared by heating AuNWs with PSPAA in DMF/THF/H₂O = 4/4/1 solution at 60 °C.

Instead of random coils, however, the originally straight AuNWs (Figure 3-3a) were unexpectedly transformed into orderly structures (Figure 3-3b), with each polymer micelle containing one coil of 5~10 loops (AuNW@PSPAA)

(Figure 3-3c). The Au nanosprings appeared highly circular (94% yield) for the well-separated ones on a TEM grid. At crowded regions (e.g., Figure 3-4a), some nanosprings offered side views showing that the overall PSPAA shells had shapes of circular discs, and that the metal coils consisted of closely packed co-planar rings. Considering the radii of the nanosprings (52.1 ± 6.7 nm) (Figure 3-4b), the overall circumferences of the loops were in general agreement with the original length of the AuNWs (ca. 1-2 μm ;²¹ the AuNWs often break during TEM characterization, e.g., Figure 3-3a). Close inspection showed that the nanosprings often revealed two ends (Figure 3-4b, c) with arguably chiral structures, suggesting that they each originated from a single wire.

Figure 3-3. TEM images of (a) as-synthesized oleylamine stabilized AuNWs, (b) coiled nanosprings embedded in PS₁₅₄-*b*-PAA₄₉ micelles, (c) several typical Au nanosprings shown the each polymer micelle containing one coil of 5~10 loops. Some of the nanosprings in (b) probably formed racket-shape intermediates before fully coiled to give the circular shapes.

Figure 3-4. TEM images of (a) side view of Au nanosprings, (b, c) two typical Au nanosprings from different perspectives, with arrows indicating their ends. (d) TEM image and schematic illustration (e) of a typical Au nanospring that did not coil along its first loop but via a new loop formed by the folded double-wire. (f) Diameter distribution of the Au nanosprings.

A slightly different polymer, $\text{PS}_{144}\text{-}b\text{-PAA}_{22}$ could also be used to fabricate similar nanosprings. Furthermore, other block polymers, such as $\text{PS-}b\text{-PEO}$, triblock polymer P4VP-PS-P4VP also can be used for prepared Au nanosprings (Figure 3-5). These results showed the generality of block copolymer application.

Figure 3-5. TEM images of Au nanosprings prepared in DMF/THF/H₂O = 4/4/1 with (a) PS-*b*-PEO, (b) P4VP-PS-P4VP.

3.3.2 Mechanism study

Investigation of yield of nanorings: Before discussion on mechanism, yield of the nanorings was investigated.

Survey of Figure 3-3b and additional TEM images of the same sample showed that 94% of 592 particles were nanosprings. In Table 3-1, the rest of the 6% particles consisted of collapsed coils and fused product with PSPAA shell. There were only a few cases of uncoiled wires observed and those ones appeared to be partially fused multiple-wire aggregates (side-by-side aggregated).

Table 3-1. Determining the yields of Au nanosprings

	Nanosprings	Collapsed coils	^a Other products	Total
Number	556	23	13	592
Yield	94%	4%	2%	100%

^aOther products include uncoiled wires and those ones appeared to be partially fused multiple-wire aggregates (side-by-side aggregated).

Survey of Figure 3-7a, c, and additional TEM images of the same sample showed that 181 out of the 253 AuNW@PSPAA observed (72%) were single-wire core-shell structures. As shown in Table 3-2, the remaining 28% of the AuNW@PSPAA consisted of double-wire structures coated with polymer (17%;), and other products (11%).

Table 3-2. Determining the yields after the swelling of the nanosprings.

	^a Single-wire	^b Racket and Double-wire	^c Other prod- ucts	Total
Number	181	43	29	253
Yield	72%	17%	11%	100%

^aSince the straight AuNWs were ultrathin and very long, it was hard to see complete AuNWs with high enough magnification. Typically, those with only one short end in the TEM images (mostly single-wires, 17 cases in our survey) were not included in our statistics, as it was still possible that they have coiled.

^bIt is often difficult to tell whether these are folded single-wires or aggregates of two wires

^cOther products include random/collapsed coils, multi-wire aggregates encapsulated by PSPAA, and a small number of nanosprings.

For racket-shaped AuNW@PSPAA, only AuNW@PSPAA with clear racket shape was considered as shown in Figure 3-7b, d. Out of the 284 AuNW@PSPAA observed, 141 had racket shapes. The rest of the AuNW@PSPAA were double-wire@PSPAA (15%), single-wire AuNW@PSPAA (24%), and other products (11%).

Table 3-3. Determining the yields of racket shape AuNWs@PSPAA.

	Racket	^aDouble-wire @PSPAA	Single-wire @PSPAA	^bOther products	Total
Number	141	44	68	31	284
Yield	50%	15%	24%	11%	100%

^aDouble-wire@PSPAA may also be the tails of a racket.

^bOther products include random coils and multi-wire aggregates encapsulated by PSPAA, and nanosprings.

Mechanism study: Since the AuNWs cannot spontaneously coil up, the PSPAA must have played a critical role. To trap the coiling intermediates, amine-functionalized TEM grids (positively charged) were used to fix the negatively charged PSPAA micelles.²¹ Most of the AuNW@PSPAA directly trapped from the encapsulation solution (4/4/1 DMF/THF/H₂O, 11% water) were single wires with cylindrical shells of 20 nm (72% yield, Figure 3-7a, c), supporting our assertion that the nanosprings were single-wire coils. The shells were thicker than those on NPs in our previous reports,¹⁵ presumably because they were trapped and fixed to the substrate before the de-swelling with the addition of water. As we know that the free spherical micelles in this sample showed that the PSPAA cannot form cylindrical micelles²²⁻²⁴ by itself under the same conditions. Another strong evidence, as shows in Figure 3-6, large number of free spherical micelles were formed together with the cylindrical AuNWs@PSPAA. Importantly, this result indicated that the coiling of the

AuNWs must have occurred *after* the PSPAA attachment, and probably during the addition of water. In general, addition of water de-swells the PSPAA micelles, increasing the PS-solvent interfacial tension²²⁻²⁴ and decreasing the mobility of polymer.

Figure 3-6. TEM image of spherical micelles formation together with cylindrical AuNWs@PSPAA.

Figure 3-7. TEM images of AuNW@PSPAA trapped under the conditions of (a) 11% water, giving coaxial core/shell structures; (b) 23% water, giving racket-shape intermediates. (c) and (d) enlarged view of (a) and (b).

After addition of water (23% v/v) and incubation for 20 min, racket-shaped structures²⁵ were found with 50% yield among the trapped AuNW@PSPAA (Figure 3-7b, d). At 41% water, most of the AuNW@PSPAA turned into nanosprings, which is stable with further addition of water. The incubation in the low-water solvents allowed the AuNWs to equilibrate in the viscous polymer and improved the yield of nanosprings. After this step, the nanosprings can be re-dispersed in pure water, where they remained stable for weeks. Quick addition of large amount of water (> 99%) to the AuNW@PSPAA

in 4/4/1 DMF/THF/H₂O gave mostly random coils, but we were not able to trap intermediates from the redistribution of PSPAA.

Figure 3-8. Schematics showing the polymer-induced coiling of AuNWs.

From this information of intermediates, we proposed the mechanism of Au nanorings formation. The increase of PS-solvent interfacial tension likely led to the contraction of the polymer micelles, which initiated the coiling of AuNWs. We postulate that the PSPAA shell exerted compressive force on the AuNW, causing it to bend and then twist to form a first loop (Figure 3-8). The PSPAA shell on the metal coil maintained inward compression, counteracting the induced elastic tension. Some of the first loops after incubation at 23% water can be trapped as rackets²⁵ or folded single wires (Figure 3-7b, d). Once formed, the first loop could template the formation of the subsequent loops, possibly assisted by weak Van der Waals attraction among the loops. At the final state, the AuNW formed a circular ring to evenly distribute its internal stress. Apparently, some of the AuNWs did not coil along their first loops and the racket-shaped intermediates were further coiled via new loops of the folded

double-wires (Figure 3-4d, e). About 8% of the nanosprings were coiled through this pathway, as judged from the remaining racket heads (Figure 3-4b).

The coiled nanosprings were co-planar and the circular disc, and considered that except the PSPAA contraction, the interaction force between the circles also affected the formation of nanosprings. When hydrophilic surfactants (PAA, or mercaptoacetic acid) were used, the obtained AuNWs@PSPAA was mostly with random coils (Figure 3-9b, c). These results suggested that the surface molecule of AuNWs play an important role during the formation of Au nanosprings. But it is hard to prove the interaction force between the circles is a dominant factor.

Figure 3-9. TEM images AuNWs@PSPAA with different ligand; (a) PS-SH; (b) MAA; and (c) PAA.

In our system, the AuNWs were stabilized by oleylamine. When PS-SH (thiol terminated polystyrene) was used to exchange the oleylamine, the similar nanospring were obtained (Figure 3-9a). Unfortunately, the polystyrene played two roles: it acted as a spacer between the neighboring NWs affecting (probably lowering) the inter-loop attraction but it also swelled the PSPAA micelles²⁶

making it potentially responsible for the formation of the observed spherical and saddle-shaped coils. It is not trivial to fine-tune the attractive interactions among the loops.

The PSPAA micelles exert compressive force on the AuNWs, which depends on the solvent ratio. After the PSPAA is removed, the dominant forces are (a) elastic energy favoring uncoiling; and (b) Van der Waals potential energy maintaining the coils. It is likely that these two forces do not strongly depend on the solvent ratio (the solubilization energy is unlikely a significant factor). Hence, the un-coiling of AuNWs after removal of PSPAA in our experiments have shown that the elastic energy is likely the dominant factor and, thus, change of solvent ratio will unlikely affect this process. We have also shown in our experiments (Figure 3-3b) that the nanosprings could uncoil even in the presence of PSPAA shells, which should have provided additional binding energy maintaining the nanospring structure. Our preliminary results have indicated that the structure of the nanosprings may not be thermodynamically controlled. That is, the coiling of the AuNWs may have been limited by the friction among the loops and thus, the momentum of the coiling/uncoiling AuNWs may be critical in determining the ring sizes. If so, we do not think we will be able to enlarge the nanosprings slowly by controlling the swelling of PSPAA shells. Once the nanosprings start to uncoil, the attractive force among the loops will only decrease owing to the decreased overlapping regions (the elastic force will also decrease). In addition, a swelled micelle will exert less compressive force. Hence, the uncoiling may accelerate and the focused kinetic energy may lead to the kinks that we observed.

In our system, the mechanical force arisen from the surface tension between the hydrophobic PS and solvent. The PS nanodroplet prefers to increase its surface/volume ratio (by aggregation) but this is balanced by the strong charge and steric repulsion among the PAA chains. Hence, shorter PAA chains will induce stronger interfacial tension. At the limiting conditions, if we assume a PS nano-droplet could maintain its structure with zero PAA units on its surface, the theoretical maximum force could be calculated by the Laplace's law for a spherical liquid drop:

$$P_{\text{PS}} - P_{\text{w}} = 2\gamma/r$$

Where γ is the surface tension of PS, and r is the radii of PS nanodroplet (assumed as a sphere), P_{w} is the external pressure of 1 atm. Generally, the surface tension of PS is 33-35 dyne/cm.²⁷ So the pressure difference between the inside and outside of a PS sphere of 50 nm radius is:

$$2 \times (35 \times 10^{-3} \text{ N/m}) / (50 \times 10^{-9} \text{ m}) = 1.4 \times 10^6 \text{ Pa} = 13.9 \text{ atm}$$

This value is the up-limit of the internal pressure, since the coronal PAA chains obviously have a strong effect on the size and surface tension of the polystyrene nanodroplet. The charge interactions among the PAA chains at nanometer range is a significant, if not dominant, force. They should be highly dependent on the ionic strength and solvent ratio. The surface tension is expected to be significantly smaller between swelled polystyrene nanodroplet and DMF/water mixture solvent. To our best knowledge, there has been no established method for calculating the internal pressure of swelled amphiphilic nanoscale polymer micelles in a mixture solvent. Pressure arises from the Brow-

nian motions of molecules. Hence, at nanoscale, the forces exerted onto the AuNWs may not be static and strictly proportional to the calculated pressure.

Figure 3-10. TEM image of hydrophobic ligand modified Pd NWs within PSPAA shells. Noted they were straight after encapsulating.

Actually, this method only applied to ultrathin NWs. For those NWs with diameters around 20 nm, the interfacial force is too small to coil the thick NWs. As shows in Figure 3-10, the ligand 1 functionalized Pd NWs could not be coiled into nanorings. Only the straight Pd NWs encapsulated by PSPAA observed.

For one loop of circular nanospring at equilibrium state, the inward pressure exerted by the polymer shell presumably equals to the outward elastic

forces from the stressed AuNWs. However, the interfacial tension between Au and the swelled polymer shells is a significant but unknown value. Moreover, the Young's modulus of the ultrathin AuNWs is expected to be very different from bulk Au and should be dependent on the number of surface defects (assuming no internal defects owing to the nanoscale size) and density of surface ligands. Adding to these unknowns is the inter-loop interactions, which is dependent on the polarity and surface density of the ligands. In our experiments, changing the ligand from oleylamine to a thiol-ended polystyrene has brought about significant changes in the structure of resulting nanosprings.

3.3.3 Mechanical properties of Au nanosprings

In the literature, the coiled nanofilaments from direct synthesis¹⁻⁸ were probably at thermodynamic minima (not global minima), and the spontaneous coiling of CNTs⁹⁻¹¹ was likely driven by the attraction among the loops. As such, it remains challenging to exploit the un-coiling of these nanostructures.⁵ In contrast, the coiling of AuNWs here was driven by the energy-minimization of the combined AuNW-polymer system. As a PSPAA micelle lowered its surface energy by contraction, the strain energy in the AuNW increased as its outer surface stretched in tension while the inner surface compressed. Thus, the AuNW stabilized as a circular coil when its outward elastic tension reached a balance with the isotropic inward compression from the ellipsoidal PSPAA shell (Figure 3-4).

To probe the tension in the AuNWs, the polymer shell on the nanosprings were swelled in DMF/THF/H₂O (4/4/1) in the presence of excess PSPAA (Fig-

ure 3-11a, c) or dissolved away by pure THF (Figure 3-11b, d). As a result, the coiled AuNWs spontaneously sprang back to give nearly straight wires, releasing the internal stress. Apparently, the elastic potential energy stored in the nanosprings was larger than the attractive interactions among the loops. However, a significant number of kinks were observed in the uncoiled AuNWs. Since the addition of organic solvent affected both the surface tension and the liquidity/mobility of the polymer shells, it is conceivable that the swelling may not have occurred uniformly within the shells as the AuNWs uncoiled. This would focus the released mechanical energy onto a few spots and cause inelastic deformations of the AuNWs.

Figure 3-11. TEM images of Au nanospring (a) after swelling the nanosprings using 4:4:1 DMF/THF/H₂O; and (b) after dissolving the nanosprings in THF. (c) and (d) is enlarged view of (a) and (b). (e) Schematic showing the spontaneous uncoiling of AuNWs. Several kinks were labelled with red circles in (b).

3.4 Conclusions

In summary, we report the first example of storing and releasing mechanical energy at nanoscale by a simple solution-phase process. The self-assembled polymer shells served as a unique tool to manipulate the entire population of

colloidal gold nanowires. This simple methodology could be potentially applied to other systems involving different nanofilaments, such as nanowires or nanotubes,²⁸⁻³² and different polymer shells such as polystyrene or conductive polymers.³³⁻³⁵ We believe the environment-responsive transformation of AuNWs and the control of their mechanical energy could be applied to fields such as biology, nanofabrication, and nanoengineering.

3.5 Bibliograph

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Chapter 4 Oil Induced Interfacial Coiling of Au Nanowires towards Nanorings

4.1 Introduction

One of the significant goals for future nanoscience is to fabricate advanced nanodevices. Rational design and synthesis with as less steps as possible of complex nanostructures with fine control are most important for this purpose.¹⁻⁴ Such synthesis development demands fundamental understanding of the underlying processes. During the past several decades, the growth of various NPs with different morphologies in chemical solution phase has attracted extensively attention.⁵⁻⁷ With the rapid development of nanoscience and nanotechnology, complex nanostructures, instead of simple NPs are highly desired. Thus current goal of nano research is gradually shifting to precise control of complex nanostructures. However, fine tuning shape of complex nanostructures is still a great challenge.^{8-16, 17-19} To this end, something has to interact with and exert anisotropic force to nanostructures.

Recently, the fabrication of nanoring structure has attracted more interest than that of other nanostructures. The closed ring structures are so unique that they have distinctive formation mechanisms and properties, as well as broad applications.²⁰⁻²³ Various nanorings, such as Ni-Co,²⁴ Co,²⁵ Ag,²⁶ Au,²⁷

ZnO,²⁰ CuO,²⁸ TiO₂,²⁹ SnO₂,³⁰ Fe₂O₃,³¹⁻³² Cd(OH)₂,³³ CdS,³⁴ CdSe,³⁵ and Ag₂V₄O₁₁,³⁶ are successfully synthesized through different routes.

Assembly of nanorings in emulsion system has received wide attention.³⁷⁻³⁹ An emulsion is a suspension of liquid droplets in another immiscible liquid. The interfacial force between the emulsified droplet and immiscible is often utilized as anisotropic force to induce self-assembly of NPs. Also, another important quality of emulsion is that it can be readily prepared in large scale. Therefore, the interface of the two liquids offers a promising chance to manipulate a large number of colloidal nanostructures. In fact, in order to confine the particle assembly process, oil droplets have been widely used. The hollow superstructure which is called colloidosomes was formed after the particles are confined at the droplet-solution interface.⁴⁰⁻⁴³ At the same time, close-packed globular clusters could be obtained while particles confined inside the droplets.³⁷⁻³⁹ These literatures reported that most of the emulsion droplets served as a static role utilizing their body or surface as a structural soft template. Whether people can exploit the confining effects of the droplets to manipulate nanostructures is a fascinating question following. An example is how to induce conformational changes in nanofilaments.

Previously, our group developed a new method using polymer shells to encapsulate nanofilaments. Polymer shells on the surface of nanofilaments were found to act like liquid droplets to compress these embedded nanofilaments into rings.¹⁷⁻¹⁸ It is clear that the plain emulsion droplets could provide main force to convert bundles of CNTs into nanorings. As shown in some papers, crumpled balls could be formed by the compression of these dissolved graphene through the rapid evaporation of aerosol droplets.¹⁹ It is clear to commend that the na-

nostructures were obtained by confining the droplets when the shape or volume of the droplets changed greatly. Besides, using sonication cavities to generate shock waves in a similar system was also reported, and it is upon collapsing. A proposal about the shock waves is the exerting force to bend CNT into nanorings.⁴⁴

Herein, we demonstrate that plain oil droplets in water can compress AuNWs into rings under suitable conditions, and that the method can be extended to a variety of oils. The goal of this project is to transfer the new method into simpler systems rather than the preformed polymer shells to understand the underlying interactions. Besides the wide-spread use of emulsions, it is critical to know the mechanism for explaining and studying droplet-nanostructure interactions.

4.2 Experimental section

4.2.1 Materials and characterization

All chemical reagents were used as purchased without further purification. Hydrogen tetrachloroaurate (III) hydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), 99.9% (metal basis Au 49%) was purchased from Alfa Aesar; Triisopropylsilane (TIPS) was obtained from Sinopharm; and all other chemicals were purchase from Aldrich. Deionized water (resistance $> 18.2 \text{ M}/\text{cm}$) was used in all reactions. Copper specimen grids (300 mesh) with formvar/carbon support film (referred to as TEM grids in the text) were purchased from Beijing XXBR Technology Co.

TEM images were collected from a JEM-1400 Transmission Electron Microscopy (JEOL) operated at 120 kV. UV-VIS-NIR spectra were collected from Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer.

4.2.2 Preparation of Au nanorings

Synthesis and purification of AuNWs are the same procedure with that of Au nanospring. After AuNWs separation, 200 μL separated AuNWs was purified and dissolved in 200 μL THF. Then 60 μL 1% oleylamine THF solution was added as oil template. Finally, 1 mL SDS (8 mM) solution was quickly injected under vertex. The resulting mixture was heated at 60 $^{\circ}\text{C}$ for 2 hrs to evaporate THF.

4.2.3 Preparation of Au@Ag@Ppy nanorings

1 mL Au nanorings solution centrifuged and dispersed in 250 μL H_2O . Then 150 μL 10 mM pyrrole and 40 μL 40 mM SDS solution added. Finally, 60 μL 50 mM AgNO_3 solution was introduced, and deep yellow solution obtained. This mixture was incubated at room temperature overnight.

4.2.4 Preparation of Ppy functionalized Au nanorings

1 mL Au nanorings solution was centrifuged and dispersed in 300 μL H_2O . Then 150 μL 10 mM pyrrole and 40 μL 40 mM SDS solution were added. Finally, 5 μL H_2O_2 was added. This mixture was heated at 70 $^{\circ}\text{C}$ over night.

The obtained products (Au nanoring@Ppy) were centrifuged for further experiment.

4.2.5 Preparation of Au nanoring@Ppy freestanding films

5 mL Au nanoring@Ppy solution was centrifuged and dispersed in 4 mL H₂O. Then 1 mL pentanol was poured into the Au nanorings aqueous solution to form a water/oil interface. Subsequently, 0.25 mL EtOH was introduced to mixture to induce the Au nanoring self-assembly at water/oil interface. After the monolayer of film forming, the pentanol layer was removed carefully. Then obtained mixture was heated at 50 °C for 4 hrs. To demonstrate the as-prepared film freestanding, the film was fished out on a hollow copper TEM grid and dried at room temperature.

4.3 Results and discussions

4.3.1 Au nanorings from solvent-shifting method

To prepare oil-in-water emulsion with Au nanorings, the “solvent-shifting” well-known method could be used successfully,⁴⁵ and AuNWs with length around several micrometers were separated and dispersed in THF which will lead to the red-brown transparent suspension. During the whole process the AuNWs were well dispersed in THF which has been confirmed by TEM (Figure 4-1). Following this step, a limited oleylamine/THF (60 µL 1%) solution was then dissolved in this THF solution in order to study the assembly process. The system color changed to lightly turbid after the quick addition of 1 mL SDS

(8 mM) solution, which indicates that the oil droplets have formed through emulsification. THF is miscible with water but oleylamine is not. Oleylamine to be excluded from the solution forming fine droplets⁴⁶ because of the shifting of the solvent (THF) from nonpolar (oleylamine) to polar (H₂O). Finally, the nanorings were isolated by centrifugation during THF evaporation. As shown in Figure 4-2, the as-product contained mostly ring-like structures. Evidently, probably due to the strong hydrophobic interaction among the AuNWs, these Au rings did not uncoil after the removal of oleylamine droplets. (Detailed discussion in next chapter).

Figure 4-1. TEM image of straight AuNWs dissolved in THF.

Figure 4-2. TEM image of as-prepared Au nanorings.

4.3.2 Effects of oil templates

The amount of oleylamine is critical to determine the nanoring structures. Firstly, oleylamine could be seemed as oil droplet (soft template) to compress the straight AuNWs coiling. As shown in Figure 4-3a, the AuNWs also were able to be coiled into rings without addition of extra oleylamine. This may be due to the residual oleylamine which was introduced during AuNWs synthesis and served as templates. However, since the residual oleylamine is not enough to provide sufficient oil droplets as templates, the yield of ring is quite low. The AuNWs could not form nanorings after purification twice with EtOH, which gets rid of such residual oleylamine. Meanwhile, some etching and fusion took place because the lack of oleylamine results in the instability of AuNWs (Figure

4-3b). However, when additional oleylamine was added into those EtOH purified AuNWs, ring structures still formed in usual size (Figure 4-3c). On the other hand, a large amount of oleylamine was important in forming irregular rings. When a large amount of oleylamine was used, the excess of oleylamine could swell the droplets, and break the hydrophobic interaction among AuNWs resulting in loose ring shape (Figure 4-3d). These results mean that the formation of sufficient fine oleylamine droplets was essential.

Figure 4-3. TEM images of Au nanorings prepared (a) without addition of extra oleylamine, (b) using EtOH purified AuNWs, (c) using EtOH purified

AuNWs with additional oleylamine and (d) with high concentration of oleylamine (1%, 100 μ L).

It is clear that oleylamine was not unique in this process. Other types of oil which is immiscible with water, such as hexane, toluene and cyclohexane, can also be used. As shown in Figure 4-4, the Au nanorings could be obtained. However, due to the different solubility of these oil in SDS, ring formation was induced by the slight aggregation. A usual model is that the oil must be non-polar and interact well with the hydrophobic AuNWs. Additionally, the oil should be first dissolution and then, the oil-carrying solvent should be miscible with water. Thus, upon mixing emulsion can be generated.

Figure 4-4. TEM images of Au nanorings prepared using different solvents as oil templates: (a) cyclohexane, (b) toluene, (c) hexane and (d) chloroform.

4.3.3 Morphological variety of nanorings

Many new kinds of rings in different shapes have been observed besides regular ring shapes in this new emulsion system. There are many new structures in the new emulsion compared with previous ring that prepared using polymer shells.¹⁸ According to Figure 4-5, there are many kinds of different structures such as simple regular circle-shaped rings (type **1**), racket-shaped (type **2**), Yin-Yang-shaped (type **3**) and 8-shaped (type **4**) ring structures. As discussed in our previous papers,⁴⁷ **1** was formed by coiling a straight AuNW bundle; **2**

was formed by bending a bundle followed by parallel packing of its two ends; and **3** was formed by coiling **2**. We are not sure whether the formation of **2** involves oil droplets. But two stages must be involved during the formation of **4**: Firstly, a large simple ring must be formed before it was compressed further to **4** although the twisting process is not clear. However, besides these known structures, there were B-shaped compressed rings and complex structures consisting of a twisted 8-shaped ring inside a circular ring (type **5**). It is clear that the complex but regular structures cannot be formed by random coiling/folding of AuNWs. The complex structures were probably formed by bending and compressing **4** after close inspection of these structures. In order to achieve smaller structure of type **5**, a 3rd-stage compression was necessary.⁴⁸

Figure 4-5. TEM images of different shapes of rings and their corresponded schemes. Circle-ring shaped (type **1**), racket-shaped (type **2**), Yin-Yang-shaped (type **3**), 8-shaped (type **4**) and B-shaped (type **5**).

Because only water, THF and oleylamine were involved in the emulsion system, the multi-stage compression of the Au rings is counterintuitive. There is no obvious mechanism to explain how the bundle could be repeatedly compressed. To explain the multi-stage compression of **5**, a hypothesis, that the process involved continued shrinking of the droplets because of the loss of residual THF from the oil domains during the heating, was found.

Then, control experiments were designed to confirm this hypothesis. After addition of SDS to AuNWs THF solution, the samples were dropped on TEM grid immediately. As shown in Figure 4-6a, the main products were bundle of AuNWs, and some large rings with relate irregular morphologies. However, regular rings were generated after the above mixture incubated at room temperature for 2 hrs. This suggested that THF was excluded from oil droplets leading to the compression of AuNW bundle coiling. Additionally, the ring yield is still low due to that residual THF still swells oil droplets.

Obviously, the heating process could induce the evaporation of residual THF, which continue compression of oil droplets. Similar results were obtained when THF was removed by evaporation under N₂ flow (Figure 4-7).

Figure 4-6. TEM images of Au nanorings prepared by (a) directly dropped on TEM grid upon SDS addition, (b) incubation at room temperature for 2 hrs after addition of SDS.

Figure 4-7. TEM image of Au nanorings prepared when THF was removed by evaporation under N₂ flow.

Large amounts of Au nanorings were obtained after THF was totally evaporated. The following experiments were designed to evaluate the effect of THF content on ring formation, because the evaporation process is difficult to quantify directly. We used closed vial to make sure the THF content constant. When THF content was higher than 400 μL , the droplets were so large that the AuNWs cannot establish sufficient overlap to form stable rings (Figure 4-8a). By decreasing THF content, the yields of ring increase (Figure 4-8). But, on the other hand, when the amount of THF was reduced to 50 μL or fewer, the average size of oleylamine/THF droplets was too small to coil the AuNW bundles (Figure 4-8d).

Figure 4-8. TEM images of Au nanorings prepared with closed vial, which the content of THF is (a) 400 μL , (b) 200 μL , (c) 100 μL and (d) 50 μL , respectively.

Whether it is favorable for the AuNWs to bend and coil in order to fit inside the smaller oil droplets is the critical issue. Except occurring at the nanoscale under strain energy the process is in essence equivalent to the phase-transfer of AuNWs from water to oil⁴⁹. An AuNW bundle has different solvation energy in water (E_{water}) with that in oleylamine (E_{oil}). If their difference is larger than the induced strain (E_{strain}), the bundle would bend in order to

enter the oil droplet. But if the droplet is too small, bending by high curvatures is unfavorable. Once the first loop is formed, the hydrophobic interaction among the loops (E_{stacking}) becomes nonzero, and the subsequent coiling is more favorable. It is rational that thermodynamically must be more favorable for the AuNW bundle to enter and coil inside an oil droplet if not considering the complex kinetics. In fact, the truth is that they cannot be coiled into rings using this method if similar AuNWs were hydrophilic.⁴⁸

4.3.4 Mechanism study

Here is the formation mechanism of nanoring. As shown in Figure 4-9, the mixing of SDS aqueous solution and the AuNW THF solution separates the THF domains into small pockets. And then THF can be continuously removed via the interface with water. Thus, it is possible to trap not only oleylamine but also AuNWs inside such solution pockets, giving oil droplets. A ring was formed by the assembly of AuNW bundle when a droplet reaches a critical size. However, the AuNW ring cannot be coiled tighter because of the friction among the loops even though further loss of THF further decreases the droplet size. As a result, the ring is forced to flatten and bend in order to fit inside the reduced volume. This process can be continuous until the total removal of THF, or when the induced strain exceeds the driving force.

Figure 4-9. Schematic illustration of nanoring formation.

SDS was used as surfactant for stabilizing oil droplets and resulting rings during the process of coiling. The oil droplets tend to aggregate without THF in the solution because of unstable emulsion, and the resulting products were aggregated forming nanorings. Other surfactants, such as PVP, polymers, PAA, Tween 80, Co-520 (structures were shown in Figure 4-10), were used instead of SDS for stabilizing oil droplets and forming rings to avoid aggregation. As shown in Figure 4-11, all of these molecules could be used to stabilize oil droplets, which is critical to form the final rings. However, the rings were different slightly due to the different solubility of oleylamine in these surfactant solutions. For example, amphiphilic polymer Tween 80 and Co-520, can form micelles with oleylamine absorption inside. Thus the low yields of nanorings are caused by the decrease of oil-droplet concentration. However, the yields of nanorings are high, because PAA and PVP are so less amphiphilic that oleylamine droplets induced most of AuNWs coiled into rings. Anyway, less amphiphilicity of these

two surfactants led to the relatively high concentration of oleylamine, and caused incompact loops.

Tween 80

Co-520

Figure 4-10. Structures of Tween 80 and Co-520.

Figure 4-11. TEM images of Au nanorings prepared with same concentration (8 mM) of surfactant of (a) Tween 80, (b) Co-520, (c) PAA and (d) PVP.

Figure 4-12. TEM images of Au nanorings prepared with SDS concentration of (a) 0.4 mM, (b) 4 mM, (c) 16 mM and (d) 40 mM.

Besides stabilizer, SDS concentration determined the distance among AuNW loops, which is crucial for the following fusion process, and will be discussed in details in next chapter. As shown in Figure 4-12, when the SDS concentration was low (0.4 mM) (Figure 4-12a), the AuNW bundle rings were

quite loose. The distance among AuNW loops is decreased while increasing the SDS concentration, and rings become tight and regular. As discussed above, SDS is amphiphilic molecule, and can form micelles in solution when its concentration exceeds CMC. Also it was known that CMC for SDS in water is 8 mM. So the SDS could form micelles when using high concentration of SDS. These micelles absorbed oleylamine inside, given the tightly packed AuNW loops.

A main difference of this work from previous work is that the AuNW-containing droplets were made in the environment of THF and oleylamine, whereas in previous works the “droplets” were composed of (a) polymer, DMF, and oleylamine;¹⁷ or (b) polymer, DMF, and DCB.¹⁸ The polymer shells swollen by organic solvents acted like liquid droplets,⁵⁰⁻⁵¹ while more oil was used in our current experiments to get the liquid droplets. It would be hard to distinguish the contributions from the individual components because the mixture of polymer, DMF, and oil was essentially a unified droplet. There are many kinds of solvents combinations available in this system, and it is reported that toluene is a mimic to the polystyrene shell formation. In this extent, there is no difference between the polymer droplets and the other kinds of droplets.

New insights during the formation of AuNW rings have been provided by the simpler system according to our investigation: (a) the serious competition between the strain energy and the attaching energy of AuNWs to oil; (b) the indispensability between the confinement of polymer shells and the shape change from cylinders to spheres; (c) the importance of oil droplets shrinking in the process of multi-stage compression; and (d) the assembly of super ring struc-

tures which is formed by a ring twisting and bending to survive in a smaller oil domain.

4.4 Applications of Au nanorings

Since ring is unique, it may be potential used as unique building block for further constructing complex structures. To prove the concept, we developed a simple method for growth of Ag rings@Ppy (polymer pyrrole) based on Au ring template. Previously, (Au@Ag)@Ppy was prepared via a one-step synthesis from Au NP seeds, whereby Ag layers was deposited simultaneously from the redox reaction between pyrrole and AgNO_3 .⁵² Based on this method, Ag nanorings@Ppy was synthesized. Here, the Au nanorings were used as templates, where the Ag deposited on. Ag was grown from the redox reaction between pyrrole and AgNO_3 (Figure 4-13). As shown in Figure 4-14a,b, the obtained Au@Ag@Ppy rings are very close to Au nanorings in size. The Ppy layer is thin and uniform. However, the Ag layer is relative rough. As shown in Figure 4-14b, the Ag NPs were attached on Au ring surface, forming necklace like structure. The possible reason is that the hydrophilic Ag^+ is difficult to nucleate on hydrophobic AuNWs surface. It was proposed that the Ag only nucleated at where the Ppy replaced oleylamine on ring surface, resulting in multi-nucleation of Ag. From the enlarged image, it is clear that the Ag grew on the AuNW surface, and the thickness of Ag layer could be roughly tuned by varying AgNO_3 concentration. As shown in Figure 4-14c, d, when high concentration of Ag precursor was used, the obtained Au@Ag@Ppy rings were thicker than those prepared with low concentration of AgNO_3 .

Figure 4-13. Schematic showing the growth of Au@Ag@Ppy nanoring.

Figure 4-14. TEM images of Au@Ag@Ppy rings. (a) AgNO₃ concentration is 0.25 mM, (b) enlarged view of (a). (c) AgNO₃ concentration is 1.25 mM, and (d) enlarged view of (c).

Owing to their perfect ring structure, the organization macroscopic free-standing films from nanorings is particularly interested toward applications on catalysis and separation. A convenient and cost-effective approach to fabricate free standing films composed of high closed packed Au nanoring@Ppy at water/oil interfaces was further described in this part. The method is modified from the report of fabrication of macroscopic freestanding films of metallic NP monolayers by interfacial self-assembly.⁵³ As shown in Figure 4-15, as-synthesized Au nanoring@Ppy, stabilized with SDS and thus negatively charged, were dissolved in pure water and contacted with pentanol. The rings were quickly self-assembled spontaneously into a monolayer film at pentanol/water interface after the adding of EtOH. The possible mechanism is that surface charge density of rings was decreased by the absorbed pentanol on nanoring surface, causing self-assembly of rings at oil/water interface.⁵⁴⁻⁵⁵ After moving the pentanol, the as-obtained mixture was heated at 50 °C for 4 hrs. A large film, which composed of close packed monolayer of Au rings, was generated on the water phase. The resulting film was fished from the surface of the aqueous phase using a hollow copper grid and dried at room temperature for several hours. According to the TEM image (Figure 4-16c), obviously, the resulting film was close-packed monolayer of Au nanorings with low packing density, which is typical for NP monolayers derived from interfacial self-assembly.⁵⁴⁻⁵⁵ The optical image indicated the film uniformity and free-standing. However, the resulting freestanding film is not strong enough (Figure 4-16a, b), thus a tiny shrinkage of film and server hollows were observed.

Figure 4-15. Schematic illustration of the fabrication of freestanding monolayer films of Au nanoring@Ppy by means of self-assembly at the pentanol/water interface.

Figure 4-16. (a) Optical image of a freestanding film of monolayer of Au nanoring@Ppy. (b) Optical image of the dried film obtained by transferring the film onto hollow carbon TEM grid. (c) TEM image of the resulting films.

4.5 Conclusions

Finally, a very important efficient system for the fabrication of AuNW nanorings has been exploited in our research. It is important to know the effects of mechanical forces during the formation of droplets, and often unsuspected to evaluate their roles when coexist with NWs, or nanosheets (e.g., graphene). Emulsions are efficient tools to the fabrication of ring structures although ring structures are difficult to obtain using other methods. It is possible to produce scalable rings using this emulsion system, and it could also make a breakthrough in other designs and applications. For example, silver rings have been obtained through this emulsion method, which means that such gold rings were used as soft templates during the silver growth. Another example is the synthesis of freestanding films. The freestanding films, which are composed by close-packed single layer Au rings, have been observed using oil/water interfacial system.

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Chapter 5 Zipper Mechanism: Preservation of Lattice Orientation in Coalescing Pre-aligned Au Nanowires

5.1 Introduction

Long-range order is a common feature in our daily devices and their components. Top-down methods can easily create long-ranged repeating features in screws, gears, and propellers,¹⁻³ but such a “simple” task is still a great challenge for bottom-up processes. In nanocrystals, the regular shapes and facets are a manifestation of the underlying lattice order.⁴⁻¹³ Bridged by such an internal order, it would be feasible, at least in theory, to grow distant crystal domains with spatial alignment.

Here, we report the synthesis of solid Au rings in a colloidal solution by fusing rings of Au nanowires (NWs). Surprisingly, after the coalescence, the axial lattice orientation of the original Au NWs is roughly maintained. We are able to grow spatially-aligned Ag blocks from the rings, proving the preservation of Au lattice. Thus, this system provides a unique platform for studying the theory of oriented attachment (OA), with single-crystalline Au NWs pre-aligned for their coalescence.

Lattice order in nanocrystals can arise from the growth of single-crystals during direct deposition or Ostwald ripening, or from the OA of primary nanocrystals. The former theories have been well established.¹⁴⁻¹⁵ Notably, the latter is also gaining popularity because of an increasing body of evidences.^{6,16-30}

It is tempting to propose that the attachment of two nanocrystals may occur *after* the surface ligands are completely lost from the two colliding faces. But in the literature, typically ligands were present in the solution. It takes about 175 ligands to fully cover a $5 \times 5 \text{ nm}^2$ area of Au(111) facet.³¹ Given the large junction area during the typical assembly of nanocrystals, it is statistically improbable for all ligands to be cleared before a successful collision event. The dissociation of surface ligands must be sequential. With ligands present, lattice alignment is difficult; whereas premature coalescence may lock in the ligands and freeze the crystals in a wrong alignment. Thus, the critical issue in the theory of OA is to propose logical steps that can account for the interlocking of three major events: ligand loss, lattice alignment, and coalescence.

The key literature evidences supporting OA can be roughly categorized into two groups: The first group of papers studied both the primary nanocrystals and the ending unified supercrystals.^{22,24} The critical starting state, *i.e.*, the exact configuration of two colloidal nanocrystals at the instant of successful collision, cannot be known. The second group of papers studied the *in situ* coalescence of nanocrystals during TEM characterization.^{14,29,32-34} Typically, the studied nanocrystals are case-specific, with nearly rounded shape and small facets. Under high-energy electron irradiation, the coalescing nanocrystals were rotating and moving, making it difficult to tell the original lattice orientation.

In comparison to these literature systems, pre-aligning single-crystalline Au NWs in a colloidal solution provides an ideal platform for revealing the detailed steps of OA.

5.2 Experimental section

5.2.1 Materials and characterization

All chemical reagents were used as purchased without further purification. Hydrogen tetrachloroaurate(III) hydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), 99.9% (metal basis Au 49%) was purchased from Alfa Aesar; Triisopropylsilane (TIPS) was obtained from Sinopharm; oleylamine (C_{18} -content 80-90%) was purchased from Acros organics; all other chemicals were purchased from Aldrich. 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 (referred to as TEM grids in the text) were purchased from Beijing XXBR Technology Co.

TEM images were collected from a JEM-1400 Transmission Electron Microscopy (JEOL) operated at 120 kV. HRTEM images were collected from JEM-2100 Transmission Electron Microscopy (JEOL) operated at 200 kV.

5.2.2 Coalescence of Au nanorings

AuNWs synthesis:

Synthesis and concentration of ultrathin AuNWs is the same as that in chapter 3.

Au nanoring synthesis:

The Au nanorings synthesis is the same as that in chapter 4.

Coalescence of as-synthesized Au nanorings:

1 mL of the as-synthesized Au nanoring solution was concentrated to 20 μL by centrifugation at 6000 rpm (2900 g) for 10 min. Then, the concentrated Au nanorings were dissolved in 0.5 mL SDS solution (4 mM). After that, 5 μL of H_2O_2 was introduced. This mixture were heated at 100 $^\circ\text{C}$ for 2 hrs and then cooled down to room temperature. To trap coalescing intermediates, the heating time was reduced to 30 min, 45 min and 90 min, respectively. Other control experiments were conducted instead of H_2O_2 with other additive.

The obtained products were purified, and then directly characterized by TEM.

5.2.3 Growth of perpendicular Ag blocks on coalesced nanorings

The purified nanorings were separated by centrifugation, and then dispersed in a mixture of 245 μL of pure water, 400 μL of THF, 100 μL of PVP (20 mg/mL), 40 μL of 2-mercaptopyridine (10 mM of EtOH solution) and 25 μL of AgNO_3 (50 mM) under vortex. Finally, 30 μL of scorbic acid (100 mM) was injected into the above suspension under vortex. The color of the solution changed immediately from deep brown to gray, indicating the formation of Ag blocks.

5.2.4 Calculation of diameter of nanorings

The diameter of nanoring was measured by using Nano Measurer software.

The average diameter of as-synthesized Au nanorings was directly calculated using original measured diameters.

For the shapes of coalesced rings were not circular, their average diameter was calculated using following equation:

$$D = 2r = \frac{C_{\text{ellipse}}}{\pi} = \frac{\pi \sqrt{2a^2 + 2b^2}}{\pi}$$

where D is diameter of the coalesced ring; a, b are the measured length of the semi-major axis and semi-minor axis of the ellipse, respectively.

Standard deviation of averaged thickness of bundles is relatively high, because the rings were composed of different number of AuNWs. However, for each ring, the thickness was quite uniform.

5.2.5 Calculation of ligands on $5 \times 5 \text{ nm}^2$ area of (111) facet

Scheme 5-1. The idealized aliphatic ligand packing on Au (111) surface. One ligand is coordinated to every three Au atoms.

Here, we use Au(111) facet to give a very rough estimate of the ligands on a $5 \times 5 \text{ nm}^2$ area of Au surface. Assuming that one ligand binds to every three Au atoms (Scheme 5-1).³¹ This value was previously obtained from aliphatic ligands and the situation may be similar for oleylamine. So the average surface area of one ligand binding site on Au (111) surface:

$$3\sqrt{3}a \times 3a \div 6 = \frac{3}{2}\sqrt{3} \times 0.235^2 = 0.1435 \text{ nm}^2$$

Therefore, ligands on a $5 \times 5 \text{ nm}^2$ area are:

$$5 \times 5 \div 0.1435 = 175$$

Assuming that the ligand coordination is independent of each other, and that each site has $\frac{1}{2}$ probability of having a ligand, the probability for all ligands to be lost simultaneously is:

$$(1/2)^{175} = 2.08 \times 10^{-53}$$

This probability is extremely small ($10^{53} \text{ s} = 3 \times 10^{45} \text{ year} = 2 \times 10^{35}$ times the age of our universe). In real experiments, the area of the colliding facets are larger and the probability of having a bound ligand is much smaller than $\frac{1}{2}$. Therefore, simultaneous dissociation of all ligands is close to impossible.

5.2.6 Calculation of lattice mismatch between parallel-stacked adjacent AuNWs

Average diameter of Au nanorings is 476 nm, thus the radius of a single ring is 238 nm.

The thickness of AuNWs is about 3 nm. For two parallel-stacked adjacent AuNWs, the distance between outer and inner atom is set as 8 nm.

The lattice mismatch is calculated as follow:

Assume the difference between the outer and inner arc is 0.23 nm (spacing between (111) planes) over an angle of θ , then θ could be expressed as following,

$$\frac{\theta}{360} \times 2\pi (238 + 8) - \frac{\theta}{360} \times 2\pi \times 238 = 0.23$$

$$\theta = 1.65$$

$$n = \frac{\frac{\theta}{360} \times 2\pi (238 + 3)}{0.23} = 30.12$$

Therefore, the lattice mismatch increases 0.23 nm (1 extra (111) plane) over roughly 30 (111) planes.

5.3 Results and discussions

5.3.1 Au nanorings consisting of parallel aligned Au nanowires

In our system, the single-crystalline AuNWs were coiled into rings by emulsion droplets; this method was modified from our recent report.³⁵ The initial AuNWs were synthesized using oleylamine as the ligand (Figure 5-1a).³⁶⁻³⁷ After purification, they were dispersed in a mixture of 250 μ L of THF and 0.3 μ L of oleylamine. Then, 1 mL of aqueous SDS solution (8 mM) was added to induce emulsification, where the “solvent-shifting” method caused the dissolved oleylamine in THF to be excluded as fine droplets. The

sample was then heated at 60 °C for 2 h. With the removal of the residue THF, the oil phase contracted further, causing the embedded AuNW bundles to coil into rings.³⁵ Most of the product was circular rings, which can be easily isolated by centrifugation (96% in purity, Figure 5-1b). These rings have an average diameter of 476 ± 85 nm and bundle width of 27 ± 8 nm.

Closer inspection showed that the rings were composed of close-packed AuNWs with roughly parallel alignment (Figure 5-1c). Figure 5-1d shows the HRTEM image of a typical ring section. The NWs were all single-crystalline with the Au(111) planes perpendicular to the wire axis, as was previously known in the initial syntheses.³⁷⁻⁴² Thus, the crystallinity of the AuNWs was not significantly affected after the coiling process. The inter-wire separation was overall quite uniform within the bundles (Figure 5-1c), indicating the presence of surface ligands.

Figure 5-1. TEM images of (a) as-synthesized AuNWs dissolved in THF, (b) as synthesized Au nanorings, (c) a typical Au nanorings composed of close-packed AuNWs and (d) HRTEM image of a typical ring section, showing the aligned $\langle 111 \rangle$ axial direction.

As shown in Figure 5-2, several rings presenting in other shape suggested that the rings were not obtained from a single coiled wire. Thus, it was further confirmed that the ring was close-packed AuNWs with roughly parallel alignment. The bundle provided accumulated hydrophobic interaction which is sufficient to stabilize rings undergoing consequence fusion treatment.

Figure 5-2. TEM images of (a) other shapes of as-synthesized rings and (b) typical Ying-yang shaped ring.

5.3.2 Coalescence of nanorings with preserved lattice orientation

After purification, the rings with parallel AuNWs were coalesced into solid rings. Briefly, the Au rings were dispersed in 500 μL of aqueous SDS solution (4 mM), followed by addition of 5 μL of H_2O_2 (35% w/w). After heating the mixture at 100 $^\circ\text{C}$ for 2 h, solid rings were obtained. As shown in Figure 5-3, the coalesced rings often deviated from smooth circles, probably because the hardening Au wires forced some local sections to straighten. In addition, the rings have slightly wavy outline and obvious kinks. Their average diameter remained roughly unchanged at 474 ± 93 nm, but the average width of the solid rim decreased to 15 ± 4 nm.

Figure 5-3. TEM images of (a) large view of fused Au nanorings, which prepared by heating at 100 °C together with H₂O₂ and (b) enlarged view of typical fused Au nanorings.

To our great interest, HRTEM analysis of the coalesced rings showed that most of the non-kinked sections were single-crystalline (*e.g.*, Figure 5-4d, e), with Au (111) planes perpendicular to the wire axis. In other words, it appeared that the lattice orientation of the original AuNWs was preserved. Given the size of the rings, the coalescence was unprecedented in terms of structural preservation (the ring shape) and the total coalesced volume. The AuNWs cannot move away or rotate outward because they were restricted in the bundles. Most importantly, the facile solution process allowed us to trap intermediates for mechanistic study.

The coalescence results cannot be explained by ripening or Au deposition: After purifying the rings, the residue Au ions in the solution were negligible.

On the other hand, it is impossible for a newly formed Au domain to have a ring shape. Partial ripening is expected to cause thick wires to grow thicker and thin ones even thinner. But thinned NWs or broken sections were not observed in our experiments. In particular, the highly uniform width of the coalesced rings was a strong indication that the coalescence did not occur at the cost of a few AuNWs or certain ring sections.

At the initial state before coalescence (Figure 5-1b, c), by geometric requirement the outmost NWs in the rings must have longer perimeters than the innermost NWs. Though all NWs were roughly aligned in the $\langle 111 \rangle$ directions, the alignment cannot be perfect. Considering the random twisting of different NWs and the multiple loops in a bundle, it is highly improbable that the neighboring NWs can always align in the x and y directions. Thus, a great amount of structural reorganization will be needed in order to align the nanocrystals and remove the imperfections.

After the coalescence, there were occasional dislocation defects near the outer rim of the fused wires (Figure 5-4g), consistent with their longer outer periphery. In addition, stacking faults can often be observed, particularly near the kinks. Given the near circular shape of the rings, the sharp turning angles at the kink sites probably resulted from the squeezing of nearby straightened sections. At such sites, usually the (111) planes on the two sides were misaligned and grain boundaries can be identified (Figure 5-4b, Figure 5-5).

Figure 5-4. HRTEM images of (a) a typical coalesced Au ring; and (b-h) the magnified sections as illustrated. Scale bar for HRTEM were all 2 nm.

Figure 5-5. HRTEM images of crystal defects existing on fused nanorings. (a) small angle grain boundary, and (b) twin boundary.

To study the crystallinity in a large number of rings, we tried to grow Ag blocks on them: The fused rings were first mixed with the reductant ascorbic acid and the ligand 2-mercaptopyridine in THF/H₂O mixture ($v/v = 1:1$). Then, AgNO₃ was added and the sample was incubated at room temperature for 20 min. Due to the strong ligand, the Ag growth was not uniform, forming blocks (Figure 5-6a, b). HRTEM confirmed that the Ag blocks were epitaxially aligned with the underlying Au lattice (Figure 5-6c, d). Regardless of their position, the Ag blocks were *always* aligned perpendicular to the wire axis. This pattern of consistent alignment was highly unusual. There is no reason for a Ag block to “feel” the alignment of a distant Ag block, except that all of them must have

aligned with the orderly Au lattice over the entire ring. This is an unambiguous evidence for the preservation of lattice orientation in all of the fused rings.

Figure 5-6. (a), (b) TEM images of perpendicular growth of Ag nanorods on Au nanorings; (c) and (d) HRTEM images showing the epitaxial relationship in the junctions between a Au ring and two perpendicular Ag blocks thereon.

5.3.3 Mechanism study

To trap the coalescing intermediates, we reduced the heating step with H_2O_2

from 2 h to 30, 45, and 90 min (Figure 4). At $t = 30$ min, coalescence between neighboring AuNW sections can be observed. The fused NWs became thicker, but the rings did not deviate obviously from the overall smooth circular shape. At $t = 45$ and 90 min, the rings were no longer smooth. Most of the AuNWs were fused together, but large gaps were frequently observed between thick strands. It appeared that the initial coalescence occurred rapidly, whereas the removal of twisted sections and bulges took longer time. Selected images were shown in Figure 5-7b,c to illustrate the “squeezed” ring sections: In a number of cases, a few strands of AuNW were forced to bulge out from the main strands, probably a result of their different initial perimeters. The extra length of the strands near the outer rim can no longer be accommodated in the coalesced wire. Though this length difference was distributed in the initial ring, the sequential coalescence of the AuNWs can accumulate the difference onto a few spots, causing significant bulges.

Figure 5-7. TEM images of coalescence intermediates isolated after heating with H_2O_2 for (a) 30 min, (b) 45 min, and (c) 90 mins. (d-f) Magnified ring sections as illustrated.

In Figure 5-7e,f, a bulged section was found to have a twisted configuration. Such a high-energy strain cannot be explained by crystal growth or

simple OA.^{37,41-42} Apparently, the coalescing AuNWs from both sides of this bulge has accumulated sufficient twist in the “squeezed” section. Should such a section eventually coalesce into a solid block, it is conceivable that defects (*e.g.*, grain boundary) will be generated. The small gap shown in Figure 5-7f was narrower than the gaps in Figure 5-1d and thus, most of the ligands at its inner surface should have dissociated by this time.

Given the extensive coalescence in our system, it is obvious that the ligand loss, lattice alignment, and coalescence must have all occurred in a progressive manner. On the basis of our observations, we propose a “zipper” mechanism to resolve the inter-dependence of these events: coalescence should initiate at a small active site with no ligand, forming a junction; in the small junction, the lattices can align by tilting and rotating the NWs; such an active site can then zip along the NWs causing sequential loss of ligands; with a number of zipping active sites, the NWs in a bundle can be eventually fused together.

We hypothesize that the reduction of surface Au ions may promote ligand dissociation. This can initiate the active sites via two possible scenarios: (a) The reduced Au atoms may preferentially nucleate at a random ligand-deficient site, forming a fresh island (without ligand). Considering the Brownian motions of the NWs, such an island can exert steric influence on the ligands of a neighboring AuNW, facilitating their dissociation and thus causing a coalesced junction to form. (It would be less probable for two ligand-deficient sections at neighboring NWs to occur right opposite to each other.) (b) The NWs may collide with each

other, ejecting the surface ligands on the contact point. Directly coalescing two NWs without an island is potentially problematic because the ligands surrounding the active site would demand a gap in between. But since the AuNWs in our systems were ultrathin and highly flexible, we are actually more inclined to scenario b.

Once a coalesced junction is formed, matching its lattice with the neighboring NWs can lower its energy. This may be assisted by local wire vibration that tilts or rotates the NWs. In the literature, it is known that small junctions ($d < 5$ nm) or thin NWs¹⁰ ($d = 2$ nm) can rotate and reorganize. The wedge space near the coalesced junction (*e.g.*, Figure 5-7f) should be strained and this may promote ligand dissociation. Filling the high-curvature tip of a wedge is more favorable than depositing Au atoms on a surface facet. Such selective deposition or coalescence pushes the wedge along the NWs and causes the “zipping” of the active site.

As the coalesced wires grow thicker, they become mechanically stronger and harder to bend. Confined by the overall circular shape, the inability to curve a crystalline wire induces strain, which can be occasionally relaxed by the insertion of dislocations near the outer rim (Figure 5-4g). As the coalescing sites zippering around the ring, the accumulated twist or strain can eventually become too large to be reconciled, particularly when a section is being squeezed from both sides. As a consequence, strands are forced to twist or bulge out (Figure 5-7). Eventually, with prolonged coalescence, most of the AuNWs/strands are coalesced

together, except a few rings with bulged sections.

Figure 5-8. Schematics illustrating the coalescence of AuNWs by the “zipper” mechanism.

At the initial state, the ligand-deficient ultrathin Au NWs have a high surface energy. The zipping process is driven by the reduction in the overall surface to volume ratio of the Au domains (*i.e.*, reduction of the Au-solvent interfacial energy). Zipping provides a low-energy pathway to minimize the extent of atomic reorganization by tilting and twisting the NWs. Because the initial AuNWs were already aligned in the $\langle 111 \rangle$ directions, their inability to rotate out of the ring plane caused their axial lattice orientation to be preserved.

In our method, H_2O_2 was not the unique reagent for Au nanoring fusion. We used same batch of Au nanorings to test whether other additives other than H_2O_2 could work or not. When no any additive agent was used, as shown in Figure 5-9a, only a few etched Au nanorings were observed after heating at 100 °C for 2 hrs. When H_2O_2 was replaced by formaldehyde, fused Au nanorings with the same morphologies as those in Figure 5-3 were also obtained. (Figure 5-9b) When AA

was used, the obtained products were partially fused with many hollow structures observed on the rings. (Figure 5-9c) Considering the formaldehyde and AA were both general reductants, we estimated that the fusion may be promoted by weak reduction. To confirm this hypothesis, the strong oxidant APS ($[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ = 0.9 mM and $[\text{HCl}] = 4.5$ mM) solution was used. As shown in Figure 5-9d, no fused ring was observed, and only a few etched AuNWs appeared. This result confirmed our proposal.

Figure 5-9. TEM images of fused nanorings obtained by heating together with (a) no additive agent, (b) 10 μ L formaldehyde, (c) 10 μ L 0.1 M AA and (d) APS ($[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 0.9 \text{ mM}$ and $[\text{HCl}] = 4.5 \text{ mM}$) solution.

However, the detailed mechanism for the reductant induced fusion was still not clear in our system. One possibility was that the reductant could react with oleylamine, which enabled preferential removal of capping ligand from AuNWs surface and promoted fusion. As reported in literatures, amines bond very weakly with gold surface^{43–44} associated with physisorption.⁴¹ Also, it has been reported AA can react with oleylamine resulting in dissociation of the surface ligand on Au NPs.⁴¹ Considering a similar reaction condition in our system, the reductant might play same role to react with oleylamine.

Another possibility was that reductants could react with residual Au^+ on AuNWs surface resulting in merging of AuNWs. Previous literatures reported that cooperative interaction between the Au^{3+} and the oleylamine leads to a mesostructure formation followed by slow in situ reduction.⁴⁰ Based on their experimental results, it was proposed that the mesostructures of the Au^+ -oleylamine complex served as growth template and governed the anisotropic growth in nanoscale. After AuNWs forming, there was still a little bit Au^+ -oleylamine left on the AuNWs surface. Therefore, under reductive environment, the residual Au^+ would be reduced to Au and gave fused nanoring. To prove this hypothesis, X-ray photoelectron spectroscopy (XPS) was used to address valency evolution of the gold species at different fusion stages. The XPS spectrums revealed Au exist in the system. We further addressed the relative

ratio of different Au valance states (Au, Au⁺, and Au³⁺) in these samples. As show in Figure 5-10, 5-11 and Table 5-1, obviously, the ratio of Au⁺ and Au³⁺ decreased, while the Au content increased. Therefore, the fusion was probably promoted by the Au⁺ and Au³⁺ reducing.

Figure 5-10. XPS spectrum of Au nanorings (top) before and (bottom) after fusion.

Figure 5-11. XPS spectra for Au species (top) before and (bottom) after fusion.

Table 5-1 Summary of the Au Species before and after fusion

Stages	Relative ratio of XPS Au 4f peak		
	Au	Au ⁺	Au ³⁺
Before fusion	77.9	15.5	6.6
After fusion	90.7	6.2	3.1

The distance between two adjacent AuNWs was a crucial factor determining the fusion. When we used PVP instead of SDS for nanoring synthesis, the obtained rings had looser wall. As discussed in chapter 4, PVP was not an amphiphilic molecule, it could not form micelles to absorb extra oleylamine in the system. Therefore, the relatively high oleylamine concentration between adjacent AuNWs weakened wire-wire interaction. Thus there was no sufficient force to squeeze AuNWs to form highly ordered close-packed bundles. When PVP prepared nanorings were used, no fused product could be observed. (Figure 5-12a, b) Similarly, when we used rings synthesized from 1 mM SDS, no fused product was observed either. Instead, only irregular AuNWs aggregation occurred. These results indicated that fusion could not occur if the highly ordered close-packed AuNW bundles were not achieved (As shown in Figure 5-12c, d).

Figure 5-12. TEM images of as-synthesized Au nanoring, (a) and (b) before and after fusion using 4 mM PVP as surfactant; (c) and (d) before and after fusion using 0.4 M SDS as surfactant.

We varied the reaction temperature as an alternative approach to tune the rate of fusion. When the fusion experiment was conducted at 40 °C for 2 hrs, no obvious fused nanoring observed. Even heating was extended to 24 hrs at 40 °C, fused nanorings could not be obtained either. (Figure 5-13a) When reaction temperature was set to be 60 °C, partially fused nanoring observed after 2 hrs,(Figure 5-13b) and completely fused rings obtained after 24 hrs (Figure

5-13c). It seemed that the fusion took place at high reaction temperature. This could be understood that probably high reaction temperature facilitated desorption of surface oleylamine of AuNWs and resulted in fast fusion rate. However, heating Au nanorings without addition of reductant could not induce wire-wire fusion. Figure 5-13d showed that the products obtained by heating Au nanorings at 100 °C for 2 hrs without addition any reductant were etched Au nanorings. Also, the Au nanorings remained un-fused if only reductant was added without heating. This result suggested that fusion rate was determined by both heating and reductant.

Figure 5-13. TEM images of products obtained by heating at (a) 40 °C for 24 hrs (b) 60 °C for 2 hrs, (c) 60 °C for 24 hrs and (d) 100 °C for 2 hrs without addition of H₂O₂.

5.3.4 Growth of Ag nanorods on coalesced Au nanorings

Since the perpendicular growth of Ag nanorods on Au nanorings was quite novel, application of this new method for fabricating complex metallic nanostructures would be likely in the foreseeable future. To start with a simple preliminary investigation, we found that the as-synthesized Au nanorings could also be used as template for perpendicular growth of Ag nanorods. The obtained nanostructures (Figure 5-14) were similar with those using fused nanorings (Figure 5-4). This suggested that the growth of Ag nanorods was not related to the diameter of AuNWs. The perpendicular growth confirmed its epitaxial growth from AuNWs, and the lattice orientation of AuNWs was extremely important.

Figure 5-14. TEM images of perpendicular growth of Ag nanorods on as-synthesized nanorings. (b) enlarged view of (a).

The presence of ligand, MPY, was essential for Ag nanorods growth on Au nanorings. Without addition of this ligand, self-nucleation of Ag occurred resulting in irregular Ag NPs instead of Ag nanorods growth on Au nanoring. (Figure 5-15) Here, MPY might serve as active molecule to facilitate Ag nucleation on Au surface. As we know, AuNWs were packed by a high density of oleylamine. Ag could not penetrate oleylamine layer to attach on Au surface. MPY was a thiol ligand that has strong affinity with Au. Oleylamine was replaced by MPY leading to low ligand density on surface. We found some other ligand could also be used instead of MPY.

Figure 5-15. TEM image of growth of Ag without addition of ligand 2-MPY.

When using high concentration of MPY, the uniform growth of Ag thin layer other than Ag nanorods on AuNWs surface was observed. As shown in Figure 5-16a, b, the AuNWs were clearly coated by Ag layer. A similar Ag layer was also observed when fused Au nanoring used. (Figure 5-16c, d) It seemed that the concentration of ligand greatly influenced the morphologies of growing Ag@Au nanostructures. Since the Ag nucleated only at the site where the oleylamine was exchanged by MPY, it was reasonable to deduce that oleylamine on AuNWs surface were completely replaced by MPY. When MPY concentration was low, oleylamine could be partially replaced. Thus the Ag nucleated at active sites where the MPY functionalized. The obtained Ag nanorods were relatively long and the gaps between adjacent Ag nanorods were larger than those obtained from MPY with 13 times higher concentration. (Figure 5-17)

Figure 5-16. TEM images of growth Ag with high concentration of MPY (2.5 mM), using (a), (b) as-synthesized Au nanorings, and (c), (d) fused nanorings. (a) and (c) low magnification; (b) and (d) high magnification.

Figure 5-17. TEM images of growth of Ag with low concentration of MPY (0.125 mM) (a) low magnification and (b) high magnification.

5.4 Conclusions

In summary, we presented a case study on the oriented attachment of nanocrystals: single-crystalline Au nanowires were used; they were pre-arranged in parallel for their coalescence; the reaction was carried out in solution, so that the key intermediates were trapped and characterized; and finally, the preserved lattice orientation was proved in a large number of rings. Our model system provides a rare window for probing the fundamental processes of crystal coalescence. We proposed the “zipper” mechanism to reconcile the interlocked events of ligand loss, lattice alignment and coalescence. To this end, the proposal is provided with details that are logical and consistent with our experimental observations.

Oriented attachment is an important process in the synthesis of nanocrystals. Understanding it is a first step towards rational synthetic designs. As shown in this work, the ability to control lattice alignment is essential for creating aligned crystal blocks at the nanoscale and via facile self-assembly.

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Chapter 6 Summary and Outlook

6.1 Summary

It was just the simple synthesis of nanostructures in the early stage of nanoscience and nanotechnology study. During the past few decades, it has been developed into a new stage-towards widely application areas, and constructing functional device made of complex nanostructures. In this thesis, the main goal of my research is trying to explore a new methodology for preparation of complex nanostructures for future advanced nanodevice.

There are two strategies in this design: 1) block copolymer assisted self-assembly and; 2) oil/water interface assembly, which were used for demonstrating concept. Based on these strategies, we successful developed 1) core-shell system, which utilized amphiphilic block copolymers as shells and wide range of inorganic NPs as core materials; 2) emulsion system, which utilized emulsified oil droplets as soft templates for constructing complex structures.

The core-shell system is based on well-established method that amphiphilic block copolymers could self-assemble and form uniform shells on gold NPs (5 nm) in selective mixture of organic solvent/H₂O. We further extend the core materials to other types of inorganic NPs, including metal, metal oxide and semiconductor NPs. Regardless of the difference of size, morphologies and hy-

drophobicity, all of these NPs could be encapsulated by uniform polymer shells. Further study demonstrated that one block of the polymer was extremely hydrophobic and that the other was extremely hydrophilic. And the polymer formed micelles which include hydrophobically functionalized NPs. The micelles are covered by long ionic PAA chains in extended conformation, which introduce charge and steric repulsion against aggregation. After encapsulation, we further demonstrated that the presence of polymer shells maintained the structural integrity of nanoclusters and allowed them to be isolated, enriched and then characterized. Therefore, polymer encapsulation provided a promising tool for controlling the aggregation of NPs. We further found that the competitive binding of hydrophobic and hydrophilic ligands on NPs surface led to selective attachment of polymer on one side of the NPs. In addition to concentric core-shell structures, anisotropic polymer coating was also achieved for both hydrophobic and hydrophilic NPs using this strategy. Triblock copolymer P4VP-PS-P4VP encapsulation also achieved, and it demonstrated the generality of our polymer encapsulation method.

Core-shell system showed great potential for manipulating nano-objects in nanoscale to achieve novel complex nanostructures. We described the synthesis of Au nanosprings by coiling of prefabricated AuNWs. The oleylamine-stabilized straight ultrathin AuNWs were synthesized by a simple reduction method. The sizes were 3 nm in diameter and about several μm in length. After purification via centrifugation, AuNWs were dispersed into THF/DMF/water mixtures ($v/v/v = 4:4:1$) and coated by a layer of PSPAA shell. In this high content organic solvents solution, the polymer shells were highly swelled exhibiting low polymer/solvent interfacial tension. A large amount of

water was added into the solution to remove the THF and DMF from the polymer shells and de-swell them. This led to a significant increase of polymer/solvent interfacial tension and the contraction of the polymer nano-droplet. Thus, as the cylindrical polymer shells transformed to a spherical droplet, the incorporated AuNWs were forced to coil into rings. The obtained Au nanosprings uncoiled when the polymer shells were removed or swelled by organic solvent. Obviously, these results suggested the elastic potential energy of the nanosprings was converted back to kinetic energy. This was a first demonstration of energy storage in colloidal NPs.

Emulsion system was also utilized for assembly of complex nanostructures. Here, the emulsion droplets did not serve as static templates. We demonstrated that the oil droplets could exert sufficient force to straight bundles of AuNWs, and compress them into perfect nanorings. Simple addition of SDS aqueous solution into a mixture of oleylamine, THF and AuNWs induced emulsification and shrinking of oil droplets, and consecutive compressing of the confined AuNW bundles in ring structure. Further studies revealed that the oil droplets could be other kinds of solvents, showing generality of our method. Also, systematical studies showed the concentration of oil (oleylamine), solvent-shifting process, and surfactant greatly influenced the morphologies of final rings. As a proof of concept, we successfully achieved Au@Ag@Ppy nanorings by using as-synthesized Au nanorings as templates. Another possible application of Au nanorings was free-standing films, which Ppy modified Au nanorings self-assembled at water/oil interface to form close-packed monolayer films.

Finally, we demonstrated that the as-synthesized Au nanorings could be fused into coherent Au nanorings. The method is very simple, just heating

as-synthesized Au nanorings together with reductant in SDS aqueous solution for a short time to get fused rings. Importantly, we found that fused nanorings were single-crystalline dominant structure, and that a few crystal defects presented within small range. Further studies revealed that single crystal parts of nanoring were same lattice orientation with as-synthesized Au nanorings. Zippering aligned AuNWs together was proposed for explanation of lattice orientation preserved fusion. Besides HRTEM characterization, perpendicular growth of Ag nanorods on fused nanorings also confirmed our proposal. The obtained Ag nanorods were single crystal, and showed same lattice fringe direction with fused Au nanorings suggesting epitaxial growth.

In all, this work has exploited rationale control assembly of complex nanostructures in solution phase. Core-shell structures, nanosprings and nanorings were successfully achieved, and the formation mechanisms were well studied. Importantly, this investigation opened new insight on complex nanostructures control. It would be helpful to both the fundamental investigation of constructing complex nanostructures and applications of those nanostructures in advanced nanodevices.

6.2 Outlook

The study on preparation of complex nanostructures in solution phase is one of the popular fields among other topic in nanoscience/nanotechnology. Considering the developed methodology in this thesis, the following directs are proposed in the future work.

Core-shell nanostructure offers a promising tool for application of NPs in biological areas. The carboxylic acid moieties of our PSPAA shells are suitable for attaching biomolecules, such as peptides, proteins, antibodies, and nucleic acids, to the NPs complexes through standard bioconjugation techniques. However, to utilize these core-shell nanostructures for really application, there is still a long way to go. Therefore, one of the future directions is to address this issue.

Polymer-assisted self-assembly is a very novel system. Since the core filaments are independent from the assembly process, it is expected to be wide range of nano-filaments. In fact, our group has already prepared CNT nanosprings using similar method. On the other hand, there are plenty of studies on ultrathin nanofilaments synthesis. Therefore, to broaden our scopes, preparation nanosprings with other materials is a reasonable direction. Furthermore, this method also could be used for manipulating 2D ultrathin nanosheets.

There is a lot of work can be done based on the ring structures. Ring synthesis and fusion are well established. And the scale-up method is also demonstrated. Large amount of high quality nanorings will be provided as building block for constructing future advanced nanodevice. Metal nanorings may be potentially used as novel optical device. Semiconductor nanorings also could be used for future optical device. Also, hetero-nanorings, which were prepared by coiling two or mutli-types of NWs together, will be prepared. They may be used as mutli-functional components towards future nanodevice.

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