Polydopamine-based strategy towards multifunctional heterogeneous nanostructures

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NANYANG
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**Polydopamine-Based Strategy towards
Multifunctional Heterogeneous Nanostructures**

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School of Chemical and Biomedical Engineering

2016

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List of Abbreviations

PDA	Polydopamine
0D	Zero dimensional
1D	One dimensional
2D	Two dimensional
MOF	Metal–organic framework
CTAB	Cetyltrimethylammonium bromide
MAPs	Mussel adhesive proteins
PEG	Poly(ethylene glycol)
TRIS	Tris(hydroxymethyl)aminomethane
DTBE	2,2'-dithiobis[1-(2-bromo-2-methylpropionyloxy)]ethane
rGO	Reduced graphene oxide
4-NPh	4-nitrophenol
4-APh	4-aminophenol
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
AuNP	Au nanoparticle
LSPR	Localized surface plasmon resonance
NC	Nanochain
CCK-8	Cell Counting Kit-8
PI	Propidium iodide
AuNP	Au nanoparticle
tNDA	Targeted deoxyribonucleic acid
sDNA	Scrambled deoxyribonucleic acid
MagNP	Polystyrene-trapped magnetic iron oxide nanoparticle
AuNS	Au nanostar
MSN	Mesoporous silica nanoparticle
PSN	Polystyrene nanoparticle

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Summary

Polydopamine-Based Strategy towards Multifunctional Heterogeneous Nanostructures

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Supervisor: Associate Professor Hongwei Duan

The work in this thesis takes advantage of mussel-inspired polydopamine (PDA) to develop heterogeneous nanostructures with complement and/or synergistic properties that are not available in individual building blocks. PDA, which is self-polymerized by dopamine under alkaline conditions, exhibits a unique set of physicochemical properties such as universal adhesion on virtually any solid organic and inorganic substructures, versatile chemical reactivity such as reducing activity and ready coupling with nucleophilic amine and thiol groups *via* Michael addition and/or Schiff base reactions, strong metal chelating capability, and highly crosslinked hydrogel structures. In three individual systems summarized in this thesis, I have demonstrated that these properties collectively offered new possibilities for preparing heterogeneous nanostructures with unique catalytic, optical, and structural properties arising from the structural integration of individual components. In particular, the universal adhesion allows PDA forming a conformal layer of coating on the nanostructures of interest, which opens the avenue for exploring the other

properties towards desired functionalization; the versatile chemical reactivity can be used for reducing metal precursors and introducing surface functionalities by spontaneous chemical conjugation of amine or thiol groups.

In the first system, I discovered the ability of polydopamine to direct the interfacial self-assembly of colloidal nanoparticles to form closely packed two-dimensional (2D) assembly. On the basis of this finding, recyclable heterogeneous catalysts of core-shell bimetallic nanocrystals were developed through PDA coating-directed one-step seeded growth, interfacial assembly, and substrate-immobilization of Au@Ag core-shell nanocrystals. In addition, the hydrogel structure provides excellent permeability for chemical substrate to access the coated nanocrystals for catalytic conversion. The Au@Ag@PDA nanocatalysts capitalize on a bimetallic synergistic effect, showing better catalytic activity than PDA-coated monometallic Au and Ag nanocrystals. This strategy provides new opportunities to design and optimize heterogeneous nanocatalysts with tailored size, morphology, chemical configuration, and supporting substrates for metal-catalyzed reactions.

In the second system, I employed PDA for fixing the nanochains of aligned magnetic nanoparticles in an external magnetic field, which led to a new type of multifunctional 1D magnetic nanochains. The key finding is that self-polymerization of PDA around magnetically aligned nanoparticles affords

robust rigid magnetic nanochains with versatile reactivity imparted by PDA. Loading of metal nanoparticles on the nanochains *via* localized reduction by PDA gave rise to magnetically recyclable, self-mixing nanocatalysts. Surface coupling of PDA with nucleophilic thiol and amine groups through Michael addition and/or Schiff base reactions, on the other hand, enabled easy bioconjugation of targeting ligands such as DNA aptamer for specific recognition of the nanochains to cancer cells, which led to magnetolysis of the cancer cells in a spinning magnetic field.

Finally, I used PDA for constructing single-nanoparticle@metal–organic framework (MOF) core–shell nanohybrids. In this case, the capability of polydopamine to form a robust conformal coating on colloidal substrates of any composition and to direct the heterogeneous nucleation and growth of MOFs provides new opportunities for customized structural integration of a broad range of inorganic/organic nanoparticles and functional MOFs. Furthermore, the redox activity of polydopamine adds additional possibilities to tailor the functionalities of the nanohybrids by sandwiching plasmonic/catalytic metal nanostructures between the core and shell *via* localized reduction. By combining different functional parts, I successfully obtained MagNP@PDA@Au@MOF nanohybrid, which can serve as a recyclable nanocatalyst with molecular sieving property.

In summary, this PDA-based strategy allows us to fabricate 0D, 1D, and 2D heterogeneous nanostructures easily via epitaxial growth or self-assembly. The obtained multifunctional heterogeneous nanostructures then have been explored for many applications, involving catalysis and biomedicine.

Chapter 1 Introduction

1.1 Background

1.1.1 Nanocrystals

Nanocrystals of metal and semiconductors have optical, electrical, and catalytic properties that are strongly dependent on the key structural parameters such as size, shape, chemical configuration, and surface facets.¹ Localized surface plasmon resonance (LSPR) of noble metal nanostructures and fluorescence of semiconductor quantum dots are the best known examples.²⁻³ The continuous efforts in the past two decades have led to reliable wet-chemical methods to synthesize high-quality nanocrystals with tailored structures and properties.⁴ Recently, there has been growing interest in developing heterogeneous nanocrystals containing more than one component, in which structural integration of different building blocks give rise to collective properties that are not available in individual components, and therefore find widespread uses in key fields such as biosensing, nanomedicine, and catalysis.⁵

Typically, there are three key components in the synthesis of colloidal nanocrystals, namely, nanocrystal precursors, reaction solvents, and capping ligands.⁶ In many cases, coordinating solvents can also act as capping ligands during the synthesis. The synthesis of nanocrystals would contain two steps,

namely, nucleation and growth. In a classical colloidal synthesis, when the reaction system is heated up to certain temperature, the precursors of the nanocrystals chemically decompose or react to produce a supersaturation of active atomic or molecular species, which is followed by a burst of nucleation. Subsequently, the nuclei will continue to grow into nanocrystals by incorporating the rest of active species in the reaction medium. After that, organic surfactants, or we can call ligands, will attach to the surface of these small-sized nanocrystals as a dynamic equilibria to keep them stable from aggregation. It is essential to control the kinetics of the two steps to achieve tailored nanocrystals synthesis.⁷

Kinetic size control

Because of the size-dependent properties of nanocrystals, it is of critical importance to produce nanocrystals with narrow size distribution.⁸⁻⁹ Aiming to achieve monodisperse nanocrystals, tremendous work has been paid to understand the detailed mechanism. From size-distribution focusing theory (Figure 1.1),¹⁰ we can know that nanocrystals under critical size would be unstable and dissociate due to their high fraction of active atoms on the surface. However, if the size is above the critical size, the larger nanocrystals would be stable and grow due to the relatively lower surface-to-volume ratio. At the critical size, the nanocrystals would neither grow nor dissociate. It is notable

that the critical size largely determined by the concentration of the precursor, with higher concentration preferring a smaller critical size.

Figure 1.1 Size-distribution focusing theory. Two different modes for the growth process of nanocrystals dependent on the concentration of the precursor in the reaction system. Copyright 2005 Nature Publishing Groups.

According to the size-distribution focusing theory, when the concentration of the precursor is high, the critical size of this system is relatively small. As a result, all the initial nanocrystals in the reaction are above this critical size. Since smaller nanocrystals grow faster than the larger ones, all the initial nanocrystals will grow simultaneously at different rate and reach a similar size finally. In contrast, if there is a low concentration of precursors, it favors a larger critical size, which may be even closed to average initial size of nanocrystals. In this case, some of smaller nanocrystals will shrink while larger ones grow, which can be called Ostwald ripening. Eventually, the size distribution will be broadened. This theory has now been clearly proved

experimentally, and nanocrystals with narrow size distribution can be achieved if the average size of nanocrystals is kept larger than the critical size.¹¹

Beside, in order to ensure monodisperse nanocrystals, nucleation usually must occur in a short time, which means increase the concentration of the precursor abruptly to transient supersaturation to result in a burst of nucleation. After the large consumption on the formation of nuclei, the concentration of the precursor will obviously decrease below the nucleation threshold. Subsequently, the residual precursors in solution will only be used to grow on existed nuclei. Sometimes, there is an overlap of time existed between the nucleation and growth, so the desired size of nanocrystals needs to be compromised for a better distribution.

Kinetic shape control

Even though there are faceted structures in one nanocrystal, they are relatively similar in energy level. For this reason, the preferred equilibrium shape of inorganic nanocrystals is spherical for a minimization of the total surface area. By contrast, there is a significant growth rate difference on the different facets, which depends on the surface energy exponentially. In other words, facets with high energy grow much faster than the ones with low energy (Figure 1.2a). This is one of the important guidelines to fabricate shaped nanocrystals.¹²⁻¹⁵

Meanwhile, ligand selective passivation has also been widely used to manipulate the kinetic shape of nanocrystals (Figure 1.2b). Based on the dynamic solvation theory, organic ligands always undergo exchange on the surface of nanocrystals during the growth, and the exchange rates on different facets are not the same. In other words, the ligand molecule would preferentially attach onto a certain facet. This selective attachment of ligands on a particular crystal facet would render it lower in surface energy, subsequently inducing a slower growth rate compared to other facets.¹⁶ For example, gold nanorods can be synthesized by using cetyltrimethylammonium bromide (CTAB) as surfactant molecules, which can selectively adhere to {100} facets of the nanocrystal, allowing the nanocrystal to grow along the [110] direction to form rod-shape as the side edges/faces become blocked.¹⁷⁻¹⁸

Figure 1.2 Scheme for shape control of colloidal nanocrystals. (a) Kinetic shape control at high growth rate. The facets processing higher energy grow faster than facets with lower energy in a kinetic regime. (b) Kinetic shape control through ligand selective adhesion on certain facets. (c) Intricate shapes result from sequential elimination of a high-energy facet. (d) Controlled branching of nanocrystals. Copyright 2005 Nature Publishing Groups.

More complex shapes can be constructed by other pathways (Figure 1.2c). For example, when a high-energy facet is sequentially eliminated by slower-growing facets, arrow-shaped nanocrystals can be formed eventually. In this growth process, the facet of higher-energy grows so fast that the second or even third layer of atoms begins to grow before the first layer has been completed. So a transient facet, which is intermediate in energy between the initial two different facets, may be created. Once such a facet appears, it will continue to grow and replace the high-energy facet eventually. As a result, the shape of nanocrystals will evolve into a complex structure during growth.^{15, 19}

Another interesting highly anisotropic shape is branched nanocrystals (Figure 1.2d).²⁰ Nowadays, researchers can prepare branched tetrapod nanocrystals with controllable branch length and diameter in a colloidal system.²¹⁻²² In the case of the CdSe nanocrystal, even though the cubic zincblende ABC stacking has higher energy than the hexagonal wurtzite ABAB stacking, it is preferred kinetically. At the beginning of the synthesis, the precursors of high concentration form nuclei of pyramidal shape in zincblende structure, dominated in (111) facet. With decrease of the precursors, the zincblende core turns to ABAB growth in the [1000] direction of the hexagonal phase, which gives rise to a rod-like CdSe. Then, a crystalline inorganic structure with four rods at the tetrahedral angle, termed as tetrapod, would be

obtained. This dendritic structure should be one of the most intricate structures in colloidal nanocrystal synthesis so far.²³

1.1.2 Heterogeneous Nanostructures

Heterogeneous nanostructures are heterostructured nanocrystals which are constructed by more than one inorganic component. Similar to nanocrystals, they are also protected by a layer of organic ligands on the surface. The novel structure of these complex materials always exhibit combined and/or extraordinary properties compared to their individual components, since every component in the system can be independently tuned and sometimes synergistic effect from this combination will appear to offer new properties.²⁴ Due to these merits, the hybrid heterogeneous nanomaterials have provided more opportunities for a wide range of applications, such as catalysis, optoelectronics, and biomedical applications.²⁵⁻²⁷

Generally, a heterogeneous nanostructure is constructed by at least two different components, which are connected by one or more interfaces. The composites of the different components which form the heterojunction are various (Figure 1.3). For example, heterogeneous nanostructures can be constructed from metals and metals (e.g., Au@Ag),²⁸ metals and semiconductors (e.g., Au@CdSe),²⁹ metals and insulators (e.g., Au@SiO₂),³⁰

metal alloy and metal oxides (e.g., FePt/Fe₃O₄),³¹ semiconductors and insulators (e.g., CdSe/ZnS@SiO₂),³² etc. Moreover, multicomponent heterogeneous nanostructures of more than two different components can be synthesized (e.g., Au@SiO₂@CdSe).³³

Figure 1.3 TEM images of various heterogeneous nanostructures. (a) Core-shell Au@Ag,²⁸ (b) core-shell Au@CdSe,²⁹ (c) core-shell Au@SiO₂,³⁰ (d) Janus FePt/Fe₃O₄,³¹ (e) core-shell CdSe@SiO₂,³² and (f) core-satellites Au@SiO₂@CdSe.³³ (a) Copyright 2010 American Chemical Society; (b) Copyright 2010 Nature Publishing Groups; (c) Copyright 2010 American Chemical Society; (d) Copyright 2004 American Chemical Society; (e) Copyright 2010 American Chemical Society; (f) Copyright 2006 American Chemical Society.

This combination of different materials in the same heterogeneous nanostructure opens up new pathways to design multifunctional materials.³⁴ For example, magnetic nanocrystals with magnetic properties can be integrated with nanocrystals with optical functionalities to fabricate a new type of multifunctional heterogeneous nanostructure (e.g., Fe₂O₃@Au core/shell

nanostructure).³⁵⁻³⁶ Besides, nanocrystals can be incorporated with an inert material, such as SiO₂ to improve the stability of the nanocrystals, or modify surface properties, resulting in changes of the solubility without affecting its original optical or catalytic properties (e.g., CdSe/ZnS@SiO₂).³⁰

More interestingly, some additional properties or functions, which may be due to the interplay of different components in heterogeneous nanostructure, would appear.³⁷ For example, surface atoms on the nanocrystal have fewer surrounded atoms compared with their counterparts interior, as a result they suffer unsatisfied chemical bonds.³⁸ These surface defects with lower energy states are harmful for the photoluminescence quantum yield of the nanocrystals, since exciton will be trapped in localized surface states, thereby reducing the combination between the electron (e) and hole (h). This will result in nonradiative recombination, such as energy dissipation as heat instead of radiative recombination. To overcome this, control of the surface quality *via* eliminating dangling bonds is necessary. Interestingly, surface passivation by introducing a shell of semiconductor processing a wider band gap, which results in a heterogeneous nanocrystal, can help to resolve this problem well.³⁹

Besides, there are some other fantastic properties from the heterogeneous nanostructures. Among them, metal-enhanced fluorescence or fluorescence quenching, which occur in heterogeneous nanostructures fabricated by metal

and semiconductor, have attracted great interest in the past a few years.⁴⁰⁻⁴²

Plasmonic metal nanocrystals, such as Au and Ag nanocrystals, can localize and even significantly enhance the incident electromagnetic field once they are excited at their plasmon resonance. When plasmonic metal nanocrystal meets with semiconductor, the whole optical properties of the obtained metal-semiconductor heterogeneous nanostructures largely depend on the complex interactions involving the enhanced local excitation field and the change of radiative and nonradiative exciton decay rates. This result of interaction will result in either quenching or enhancement of the fluorescence. For example, a series of colloidal core-satellite Au-quantum dots (QDs) can be fabricated by using DNA. The interparticle distance of the Au and QDs can be turned through the DNA linker length to modulate optical properties, from photoluminescence quenching to photoluminescence enhancement (Figure 1.4).

Figure 1.4 (a) AuNP-QDs Core-Satellites nanostructure template by DNA (purple). (b) PL enhancement vs separation distance under excitation at 440 nm (square and black line) and 530 nm (dots and black line), respectively. Copyright 2015 American Chemical Society.

Aiming to achieve desirable properties, heterogeneous nanostructures of different composition, size and shape have been investigated intensively. Tremendous research has been done to understand the roles of organic surfactants and the interactions between different inorganic components during the synthesis of heterogeneous nanostructures. Currently, there are mainly two strategies to fabricate the heterogeneous nanostructures, namely, heteroepitaxial growth and self-assembly of nanocrystals.

1.1.3 Current Challenges in Synthesis of Heterogeneous Nanostructures

In the past decades, researchers have developed several methods for the synthesis of colloidal heterogeneous nanostructures. Moreover, many insightful mechanisms have been proposed to serve as useful guidelines for the design of heterogeneous nanostructures. Now, scientists continue to push this topic to a new high, where more sophisticated nanostructures with various compositions, sizes, and shapes, can be tailored.³⁴ However, some challenges which still existed must be addressed in order to realize this tailorable synthesis of complex multifunctional colloidal heterogeneous nanostructures.

The most challenging one should be the development of theories that allow the rational design and fabrication of diverse heterogeneous nanostructures. Even though, some knowledge has been concluded and applied to guide the synthesis of heterogeneous nanostructures, the understanding of some

fundamental questions is still quite fragmentary.⁴³⁻⁴⁴ So, when it comes to a new heterogeneous nanostructure system, researchers may need to seek for a new theory.

Besides the theoretical studies, we are still facing some practical challenges in the synthesis of heterogeneous nanostructures. Lattice mismatch at nanoheterojunctions is a crucial issue that affects the parameters of the heterogeneous nanostructures.⁴⁵⁻⁴⁶ It hinders the combination of two different materials which have a big lattice mismatch, which seriously limits the library of the heterogeneous nanostructures. If we can overcome the drawbacks of the lattice mismatch, a myriad of novel colloidal heterogeneous nanostructures with diverse functions will be designed and open up more opportunities for a wide range of applications.

1.2 Objectives

The overall objective of this thesis is to develop a broadly applicable strategy to fabricate multifunctional heterogeneous nanostructures, which can be applied in a wide range of applications, such as catalytic and biomedical applications.

For epitaxial growth, the design of the heterogeneous nanostructure usually needs to take the lattice match of each component into consideration, which significantly hinders the development of heterogeneous nanostructures. To resolve this problem, here we use an intermediate mussel-inspired polydopamine platform to bridge the lattice mismatch and allow two or more different functional components to integrate into one system. The resultant heterogeneous nanostructures then exhibit combined and/or improved performance compared to their individual counterparts.

To demonstrate that our strategy is versatile, we applied our strategy on a wide arrange of nanocrystal materials, both organic and inorganic. Due to the unique adhesive and chemical reactive properties of polydopamine, we coat a layer of polydopamine on various nanocrystals, and therefore use it as an intermediate to combine another type of functional nanocrystals regardless of the lattice mismatch between them. Moreover, the polydopamine layer can help nanocrystals undergo self-assembly into more hierarchical nanostructures, for

example, 1D or 2D nanostructures, which facilitates their functions in some fields.

Chapter 2 Review of the Literature

2.1 Polydopamine (PDA)

Recently, adhesives inspired by nature have attracted tremendous interest, and are now investigated intensively. For instance, mussels can adhere onto the surface of a wide variety of materials firmly under aqueous conditions due to the mussel adhesive proteins (MAPs), *Mytilus edulis* foot protein (Mefp). Researchers have found that Mefp-3 and Mefp-5 in adhesive proteins preferentially play a significant role in this adhesive interaction (Figure 2.1).⁴⁷⁻⁴⁸

Figure 2.1 (a) Photograph of a blue mussel adhering to Teflon surface. (b) Distribution of different proteins identified in the byssus of *Mytilus edulis*. (c) The amino acid sequences of Mefp-3 and Mefp-5. Copyright 2007 American Association for the Advancement of Science.

Further analysis of the MAPs shows there is a higher content of catecholic

amino acid in the structure, which is believed to contribute to the adhesive properties. In other words, dopamine and its analogues may offer the excellent adhesive properties to mussels.⁴⁹ Admittedly, dopamine is more likely to be known as a neurotransmitter previously.⁵⁰ Now inspired by this mussel adhesion, dopamine has come on stage to act as adhesive molecule, although the detailed adhesion mechanism is still unclear.

Figure 2.2 The synthesis of PDA involves two pathways: (a) formation of covalent bonding between DHI during the oxidative polymerization, and (b) formation of physical self-assembly containing dopamine and DHI. Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA.

In the last decade, polydopamine (PDA), which is self-polymerized from

dopamine under aerobic and basic aqueous environment, has been utilized as a universal coating strategy on a variety of substrates, such as metals, oxides, polymers, carbon materials, etc.⁵¹⁻⁵³ (Figure 2.2). Recent work even successfully coated PDA on different substrates in nanoscale. The obtained PDA coating is robust and chemically versatile, arousing much interest in many fields.

2.1.1 Adhesive properties

One of the most important properties of PDA is the strong adhesion on virtually any surface, regardless of the nature of the substrate. This unique property is proposed to originate from the catechol group in structure of PDA.⁵¹ So far, however, the exact adhesion mechanism of PDA is not fully understood, the interaction between catechol bonding with different surface has actually been investigated intensively to reveal the chemistry behind to some extent.

In brief, the complex adhesion interaction can be classified into two general interactions, namely, covalent binding and noncovalent binding. The surface processing amine or thiol groups can form robust covalent bonds with PDA *via* Michael addition and/or Schiff base reactions in alkaline environment.⁵⁴ Besides, PDA can form several types of noncovalent bindings with the substrate of different properties, such as metal chelating, π - π stacking,

and hydrogen bonding.⁵³ For example, when it comes to metal or metal oxide surfaces, catechol groups in PDA can chelate with the metal ions on the surface by replacing the hydroxyl group with deprotonated ligand. This mechanism has been widely accepted in the case of Fe_2O_3 , Al_2O_3 , etc.⁵⁵ However, in the case of TiO_2 , more than one mechanism has been proposed, which involves the coordination between catechol and one Ti atom, and bidentate chelating bonding.⁵⁶

Another striking aspect of the adhesive PDA is that it can adhere on organic or hydrophobic surfaces. For this unprecedented property, Lee et al. propose that the chemistry behind is relevant to the oxidation of catechols into quinones, which therefore give rise to covalent binding onto the organic surfaces through aryl–aryl interaction or Michael-type addition reactions.⁴⁸

Even though the comprehensive understanding of the binding mechanism for PDA is incomplete by far, a large number of works taking advantage of adhesive PDA have been reported extensively.⁵⁷

2.1.2 Versatile reactivity

From the view of chemical structure, catechols are benzene derivatives carrying two neighboring hydroxyl groups. This unique structure has already

indicated the physico-chemical versatility of catechols, for example, it should be able to serve as a weak acid or reducing agent, and the two vicinal hydroxyl groups on benzene group would allow this moiety to form bidentate coordination and hydrogen bonding. Intriguingly, PDA can play more roles.

Figure 2.3 Three typical chemical reactions of PDA. (a) Copyright 2010 American Chemical Society. (b) Copyright 2013 American Chemical Society. (c) Copyright 2010 American Chemical Society.

One of the highlighted chemical properties should be the reaction between PDA and the amine or thiol-containing molecules (Figure 2.3). In basic environment, the catechol groups in PDA undergoes oxidation to transform into

the quinone groups, which are ready to link with the nucleophilic amine groups through a Schiff base reaction or Michael-type addition reaction. Similarly, molecules containing thiol groups can react with PDA covalently through Michael addition reaction. These reactions between PDA and molecules with amine or thiol groups are quite easy, so that a simple mixing of these reactive molecules with PDA at room temperature in alkaline environment can afford to functionalize the PDA.⁵⁴

The existence of the imine and amine groups in the PDA structure also allows other chemical reactions. For example, carboxyl groups in poly(acrylic acid) can react with imine groups in PDA at 50 °C under vacuum.⁵⁸ Besides, it has been reported that the amine groups on PDA can react with 1,3,5-benzenetricarbonyl trichloride in Isopar.⁵⁹

PDA can also act as a reducing agent for metal salts. When the catechol in dopamine is oxidized into quinone, it will donate two free electrons to reduce metal ions or other metallic precursors into the corresponding metal nanocrystals, and subsequently anchor the resultant nanocrystals on PDA due to the metal chelating property of PDA.⁵¹ This unique redox activity of PDA has attracted great interest in the development of various organic–inorganic nanohybrids with unique properties for many applications.

2.1.3 Applications of Polydopamine

Energy Application

PDA has showed great contributions for the applications in energy fields. Most work in these fields take the advantages of striking properties of PDA, such as strong adhesion, high carbon yield and reducing potential.

Li-Ion Batteries. The robust wet-resistant adhesion of PDA can help to design the Li-ion batteries, in which each component is assembled together in a liquid environment. Inspired by the wet-resistant adhesive PDA, hydrophobic polyethylene (PE) separator, which suffers from the poor compatibility with liquid electrolytes, can be easily modified with a PDA layer. This process renders the separator more hydrophilic, and therefore improves the current capacity and cycle life of the obtained Li-ion battery.⁶⁰⁻⁶¹

Supercapacitors. Compared to batteries, supercapacitors have many superior properties such as higher power capacity, faster charging process, wider operational temperature, and longer cycle life.⁶²⁻⁶³ Currently, many PDA-derived hybrid materials have been developed for high-performance supercapacitors, in which PDA can transfer into carbon materials for an enhanced conductivity. For example, a new type of 1D manganese oxide/mesoporous carbon/manganese oxide hybrid nanowires has been

fabricated via PDA, exhibit improved capacitive performance with longer cycle life.⁶⁴

Catalysts

The oxygen reduction reaction (ORR) has a significant effect on the performance of many energy applications, for example fuel cells.⁶⁵⁻⁶⁷ However, commercial and efficient ORR electrocatalysts are based on Pt-based materials, which limit its application due to the high cost. Lu and co-workers developed a new type of N-doped carbon microspheres prepared from carbonized PDA microspheres, which exhibits higher current density and potential. By introduce the iron ions into the PDA matrix, the ORR performance has been further improved, even showing a superior catalytic performance compared to the commercial Pt/C catalyst.⁶⁸

Besides, PDA has been widely utilized for heterogeneous catalysts. While PDA itself has no catalytic activity, it could promote the photocatalytic activity of the catalysts with the $\pi-\pi^*$ electron transition existed in PDA matrix, or act as a platform to produce and mobilize catalytic nanocrystals. For example, a number of photocatalysts, such as Au and Ag nanoparticles, have been synthesized to degrade various organic dyes by taking advantage of the synergistic effect from PDA.⁶⁹⁻⁷⁰ On the other hand, PDA can be utilized to fabricate supported metal catalysts, which emerges as an effective pathway to

recover and recycle these tiny catalysts from the reaction solution. For example, a supported-metal catalyst, in which catalytic Ag nanoparticles were synthesized on PDA-coated substrate by electroless plating, has been designed for catalytic reduction by Demirel and co-workers. Thanks to the excellent redox capability and metal ion-chelating property from PDA, a dense layer of Ag nanoparticles can be formed on the PDA-coated substrate without obvious aggregation or detachment of catalytic nanocrystals.⁷¹

Figure 2.4 (a) Scheme of the preparation of $\text{Fe}_3\text{O}_4\text{@PDA@Au}$ as a recyclable nanocatalyst. (b) Photo of the catalytic conversion of nitrophenol by $\text{Fe}_3\text{O}_4\text{@PDA@Au}$. Copyright 2013 American Chemical Society.

Another ideal strategy to recycle the nanocatalysts is to combine the nanocatalysts with magnetic materials, so that the whole heterogeneous materials can be separated from the reaction solution by magnetic separation upon an external magnetic field. Inspired by this, PDA has been used as a platform to bridge magnetic part and noble metal catalysts to fabricate new heterogeneous catalyst. Several recent work have even report the synthesis of

magnetically recyclable nanocatalyst by the in situ growth of nanocatalysts (Figure 2.4).⁷²⁻⁷⁴

Biomedical applications

PDA-based materials have attracted great interest in the biomedical field due to its biocompatibility and hydrophilicity. More importantly, it offers opportunities to further functionalization with various polymers or biomolecules. As a result, a number of bio-functionalized platforms have been developed using PDA.⁵⁷ For example, Chien and co-workers modified micropatterns with PDA to facilitate the adhesion of cells. Interestingly, this system can be further modified with amine-terminated PEG, functionalized protein, and metal nanocrystals easily (Figure 2.5a).⁷⁵ Yeo and co-workers coated PDA on nanoparticles, then functionalized surfaces by simple incubation with desired ligands, such as a small molecule (folate), a peptide (Arg-Gly-Asp), and a polymer poly(carboxybetaine methacrylate) (Figure 2.5b). The obtained modified NPs showed the expected cellular interactions without cytotoxicity.⁷⁶

Figure 2.5 (a) Scheme of patterning by using PDA as the ink. (b) Schematic

illustration of PDA-assistant surface modification of nanoparticles with different biomolecules for application. (a) Copyright 2012 American Chemical Society. (b) Copyright 2014 American Chemical Society.

Besides, Park and co-workers prepared an injectable hydrogel by covalently cross-linking catechol-grafted hyaluronic acid and a thiol-capped Pluronic polymer. Cross-linking was assumed to take place via Michael addition of the thiol groups to oxidized catechol (i.e. o-quinone) moieties. The hydrogels showed longer-lasting stability and improved adhesion to biological tissues.⁵⁷

2.2 Fabrication of Heterogeneous Nanostructures

In past decades, heterogeneous nanostructures of different composition, size and morphology have been investigated intensively. By far, there are two general ways to fabricate heterogeneous nanostructures. One is heteroepitaxial growth, and another is self-assembly.

2.2.1 Heteroepitaxial Growth

As we discussed above, nanocrystals are typically synthesized by mixing precursors with organic surfactants in a solvent at a proper temperature, and the formation of nanocrystals involves the nucleation and the growth. Interestingly, sometimes when there is pre-existed nanocrystal in the reaction system, the addition of the second precursor can result in colloidal heterogeneous nanocrystal.²⁵

The mechanism of heteroepitaxial growth of heterogeneous nanostructures is similar to that of homoepitaxial growth of nanocrystals discussed previously. However, control over the parameters of heterogeneous nanostructures is much more difficult, since the lattice mismatch at the heterointerface imposes more limitations on the design of heterogeneous nanostructures. As a result, the formation of heterogeneous nanostructure is largely dependent on the nature of

the seed (size, shape, crystal structure, surface defects, etc.) and the characteristics of the growing component.³⁴ Even though it lacks a full understanding of the formation of heterogeneous nanostructure, it has revealed that the mismatch strain at the junction interface is critical. Besides, other issues, such as solid-state atomic diffusion and/or exchange, phase separation, redox processes, and oriented attachment, have also been believed to affect the heteroepitaxial growth process.

Interfacial strain originating from lattice mismatch at the heterointerface is a critical issue in heterogeneous nanostructures synthesized by heteroepitaxial growth. The evolution of growth can be determined by the interfacial strain that results from the interface free energy and the lattice mismatch. Judging from lattice difference, three different heteroepitaxial growth modes can be classified, namely, Frank van der Merwe (FM) mode, Stranski–Krastanov (SK) mode, and Volmer-Weber (VW) mode, as demonstrated in Figure 2.6.⁷⁷⁻⁷⁸

Figure 2.6 Thermodynamical classification of epitaxial growth modes.

In the case of the FM mode, due to the similar lattice structure of two materials, the interfacial strain is almost negligible. Consequently, the thickness of the growing layer is unlimited in theory. By contrast, in the case of VW mode (larger mismatches higher than 10%), the growing material will deposit as small islands in order to lower the interfacial strain. In the case of SK mode (small mismatches, i.e., 10%), a thin layer can be formed heteroepitaxially. However, if the thickness of the growth material increases, the strain will also increase. Therefore, when the thickness reaches a critical value, the growth layer will undergo self-reorganization into islands to decrease the strain. This critical thickness dependent on the interfacial strain energy is usually a few monolayers of atoms. For instance, the critical thickness for the growth of InAs on GaAs, which has 7% lattice mismatch, is 2 monolayers.⁷⁹

2.2.2 Self-Assembly

Another useful strategy to fabricate heterogeneous nanostructures, which is different from the heterogeneous growth, is self-assembly. Self-assembly is a process in which nanocrystals or other discrete components spontaneously organize into one ordered system either by direct interactions (e.g., interparticle forces), or indirectly using a template or an external field.⁸⁰ Recently, researchers have paid a lot of efforts to synthesize nanocrystals with specific physical properties to fabricate assemblies. Typically, the self-assembly is accompanied with thermodynamic equilibrium, which has a lowest free energy as the whole system.

Figure 2.7 Heterogeneous nanostructures fabricated from different self-assembly strategies. (a) core-satellites Au-Pt induced by opposite charges,⁸¹ (b) assembly of Au nanoparticles templated by small molecule,⁸² (c) assembly of Au and Fe₂O₃ by crosslinked different surface ligands,⁸³ (d) assembly of Au and carbon nanotube,⁸⁴ (e) CdSe patterns directed by block polymer,⁸⁵ (f) assembly Fe₃O₄-CdSe/ZnS directed by block polymers,⁸⁶ (g) Au core-satellites template by DNA,⁸⁷ and (h) Fe₃O₄@SiO₂ nanochain directed by external magnetic field.⁸⁸ (a) Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA. (b) Copyright 2009 American Chemical Society. (c) Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA. (d) Copyright 2006 Royal Chemical Society. (e) Copyright 2009 Nature Publishing Groups. (f) Copyright 2007 American Chemical Society. (g) Copyright 2013 Royal Chemical Society. (h) Copyright 2013 Wiley-VCH Verlag GmbH & Co. KGaA.

Templated Self-Assembly

The template in the self-assembly can be any object that acts as a platform to guided different nanocrystals to be organized into a similar morphology to

that of the template. With this conception, a number of objects can serve as templates, such as small molecules, polymers, and even another nanostructure.

80, 89

The templates can be classified into two types, namely, hard templates and soft templates. The hard templates can define the final architecture of assemblies as its structure is fixed at the very beginning. Usually, hard templates can offer some extra novel functions when integrated with assembled nanocrystals. For example, a sensing platform has been designed by taking advantage of the fluorescence resonance energy transfer (FRET) from QDs to graphene when assembled closely.⁹⁰⁻⁹¹ However, hard templates can hardly control the periodicity within the assembly. By contrast, soft templates can process a designed distribution of specific binding sites, which can link to certain nanocrystals exclusively. It will give rise to a controlled periodicity of the assembled nanocrystals in the assembly. Currently, there are many soft templates, such as small molecules, copolymers, and biomolecules (e.g., DNA).^{89, 92}

Template-Free Self-Assembly

In this template-free self-assembly strategy, the capping molecules on the surface of the nanocrystals not only help to stabilize the colloid stability, but also direct the assembly process when an external stimulus is applied without

additional templates. Additionally, the distribution of surface capping ligands is also very important, which may result in an ordered assembly of the nanocrystal building blocks, for example, Au nanorods.²⁶

There are many ways to direct template-free self-assembly. One of the simple ways is to mix oppositely charged different nanocrystals to form colloidal crystals.⁹³ Besides, external stimuli, such as temperature, light, solvent polarity, and even ion concentration, can provide more opportunities to modulate the interparticle forces, such as hydrophobic interactions, hydrogen bonding, π - π stacking, or molecular dipole interactions under equilibrium or non-equilibrium conditions.⁹⁴ However, one notable thing is that the self-assembly of heterogeneous patchy colloids, such as Janus particles, in 100 nm range remains challenging.⁹⁵

External Directed Self-Assembly

Recently, external directed fields have been widely used as tools to facilitate the assembly of nanocrystals. For example, electric or magnetic fields, flow fields, and even electromagnetic fields hold great promise for the fabrication of novel functional heterogeneous nanostructures.

Electric and Magnetic Fields. Generally, most nanoparticles will undergo polarization in electric fields due to the different dielectric properties compared with the surrounding environment. The assembly of nanoparticles in electric

fields results from the induced interactions. In this process, the induced field surrounding a polarized nanoparticle gives rise to a strong, anisotropic dipole-dipole interaction among nanoparticles.⁹⁶⁻⁹⁷ Once this interaction becomes strong enough to surpass Brownian motion, nanocrystals of building blocks will initially organize into assemblies.

Obviously, one key parameter of the field-induced assembly of nanocrystals is the magnitude of the dipolar interaction compared to thermal forces. The dipole strength, which indicates the dipole-dipole interaction between particles relative to thermal energy, is

$$\lambda = \frac{\pi \epsilon_0 \epsilon_s |C|^2 a^3 E^2}{kT}$$

where C is the complex dipole coefficient, a is the particle radius, E is the field amplitude, and ϵ_s and ϵ_0 are the solvent dielectric constant and permittivity of free space, respectively. Therefore, according to this equation, the dipole-dipole interaction decreases dramatically as the size of particles become smaller. Nonetheless, some assemblies from nanoparticles have been successfully fabricated using external electric fields.⁹⁸⁻¹⁰⁰

Flow Fields. Macroscopic viscous flows have been proved to direct the assembly of a suspension of disordered nanoparticles into ordered assembly. Particularly, large amplitude oscillatory shear (LAOS) acts as a reliable tool to organize the particles with size down to 100 nm into assembly.¹⁰¹⁻¹⁰² However,

one drawback of this strategy is that a high flow strength is usually required. As a result, once the strength is diminished, the crystal assembly will dissociate into disordered components. Besides, traditional techniques, for instance spin coating, can also provide opportunities to construct ordered assemblies.¹⁰³

Self-Assembly at Liquid Interfaces. Liquid-liquid interfaces are another kind of convenient tool to direct nanoparticle assembly. The reduction in interfacial energy is the dominating driving force to allow the assembly of the nanocrystals at the interface.¹⁰⁴ Moreover, this assembly can be further manipulated through lateral interface-mediated capillary forces. Interestingly, when the nanocrystals are non-spherical, Janus-like, or surface-modified with some specific ligands, this strategy is also applicable, providing a facile tool to direct the assembly.¹⁰⁵⁻¹⁰⁶

Chapter 3 Interfacial Assembly of Au@Ag@PDA

Core–Shell Nanoparticles for Recyclable

Nanocatalysts

3.1 Introduction

Metal nanocrystals with structure-defined optical, electronic, and catalytic properties hold great promise in a wide spectrum of biomedical, chemical, and environmental applications.¹⁰⁷⁻¹⁰⁹ Recent advances in wet-chemical synthesis open new possibilities to systematically tailor the structural parameters (size, morphology, chemical configuration, and exposed facets) of metal nanocrystals, and have stimulated considerable interest in optimizing metal nanocatalysts for specific chemical reactions.¹¹⁰⁻¹¹⁶ The large surface areas and abundant exposed low coordination sites of metal nanostructures are critical for their prominent catalytic activities.¹¹⁵ However, the associated high surface energy tends to drive the aggregation of colloidal metal nanocrystals, leading to reduced activity. Although surface functionalization with small molecular or polymeric ligands can improve the colloidal stability of nanocrystals, the strong binding of the surface capping ligands often results in “poisoning” and deactivation of the nanocatalysts.¹¹⁷⁻¹¹⁸ Effective post-reaction separation and recycling of the tiny nanocatalysts is also a significant technological challenge to be addressed. In response to these challenges, a variety of colloidal or solid scaffolds based on polymers, carbon materials, silica, metal organic frameworks, and metal oxides

have been used to support metal nanocrystals for heterogeneous catalysis.¹¹⁹⁻¹²⁵ Significant advances have been made in engineering the local environment of immobilized metal nanocrystals for efficient catalysis.^{118, 126} Nevertheless, existing efforts primarily focus on in-situ synthesis of metal nanocatalysts on the scaffolds, in which one typically lacks the degree of control over nanocrystal growth as achieved in solution-based synthesis.¹²⁷⁻¹²⁸

Here we report a polydopamine (PDA)-based approach to developing efficient and recyclable heterogeneous catalysts of core-shell bimetallic nanocrystals. As illustrated in Figure 3.1, our strategy involves one-step seeded growth, interfacial assembly, and loading of the densely packed bimetallic nanocrystals on solid substrates. Bimetallic nanocrystals with core-shell configuration are under intense research for heterogeneous catalysis because the preformed core can guide epitaxial growth of the shell toward optimized catalytic activity, which is not available for single-component nanocrystals.^{109, 129-130} We have found that a redox couple between dopamine and Ag^+ in solution can induce the seeded growth of an Ag shell of tunable thickness on Au nanocrystals, culminating in the formation of a layer of PDA coating on the core-shell Au@Ag nanocrystals. The PDA coating has many advantageous attributes for the development of recyclable heterogeneous catalysts with dense loading of Au@Ag nanocrystals. First, a key finding of the current study is that Au@Ag@PDA nanoparticles can self-assemble at the chloroform-water

interface to form a closely packed monolayer. Second, the mussel-inspired self-polymerized PDA exhibits strong adhesion on virtually any organic and inorganic substrates,^{51, 57, 131-133} facilitating robust binding of the interfacial assembly of metal nanocatalysts on solid substrates, such as glass and free-standing reduced graphene oxide (rGO) paper, assembled from individual rGO nanosheets in layer-by-layer fashion, used in this study. Interfacial self-assembly of colloidal particles, driven by the decrease of total free energy in biphasic systems, has emerged as a versatile approach toward the fabrication of large areas of densely packed nanoparticle arrays.¹³⁴⁻¹³⁸ Surface chemistry and nanoparticle size are the major factors determining their thermodynamic tendency to assemble at oil-water interfaces. The ability of PDA coating to drive the interfacial assembly of nanoparticles, in conjugation with its adhesive property, gives rise to a general approach toward heterogeneous catalysts with densely loaded functional nanoparticles. Third, a large number of hydrophilic groups endows the crosslinked PDA coating with porous hydrogel-like structure, which allows for free access of water-soluble reactants to nanocatalyst surfaces.¹³⁹ Of equal importance is that the PDA coating is bound to the nanocrystal surface through weak non-covalent interactions, minimizing passivation of the biometallic nanocatalyst. Combining these attributes, the substrate-immobilized Au@Ag@PDA core-shell nanocatalysts showed excellent catalytic activity in a model reaction involving catalytic reduction of 4-nitrophenol (4-NPh) to 4-aminophenol (4-APh) by NaBH₄ (Figure 3.1). In

particular, the nanocatalyst-loaded rGO paper represents a new class of flexible heterogeneous catalysts that combine the excellent mechanical stability of free-standing rGO paper with the high catalytic performance of Au@Ag@PDA nanocatalysts.

Figure 3.1 Schematic illustration of the synthesis and interfacial assembly of core-shell Au@Ag@PDA nanoparticles and the preparation of recyclable nanocatalysts.

3.2 Experimental Section

3.2.1 Materials and Characterization

Gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), 4-nitrophenol (4-NPh), sodium borohydride (NaBH_4), and sodium citrate were purchased from Sigma Aldrich. Silver nitrate (AgNO_3) was received from Strem Chemicals. Dopamine and ascorbic acid were purchased from Alfa Aesar. Tris(hydroxymethyl)aminomethane (TRIS) was obtained from J. T. Baker. Methoxy-poly(ethylene glycol)-thiol (PEG-SH, 2 kDa) was purchased from Laysan Bio, Inc. 2,2'-dithiobis [1-(2-bromo-2-methylpropionyloxy)] ethane (DTBE) was prepared according to our previous report. Ultrapure water (18.2 $\text{M}\Omega \cdot \text{cm}$) was purified using a Sartorius AG arium system and used in all experiments. Scanning electron microscopy (SEM) images were acquired on a FESEM (JSM-6700F, Japan). Transmission electron microscopy (TEM) observations were conducted on a Jeol JEM 2010 electron microscope at an acceleration voltage of 300 kV. UV-vis spectra were recorded using a Shimadzu UV2501 spectrophotometer. FT-IR spectra was recorded using Nicolet 5700.

3.2.2 Synthesis of Au Nanoparticles

Au nanoparticles of 14 nm were prepared by citrate reduction of HAuCl_4 in aqueous phase. Typically, a sodium citrate (102 mg) DI-water solution (2 mL)

was rapidly injected into a boiling aqueous HAuCl_4 (30 mg in 200 mL of water) solution under vigorous stirring. After boiling for 15 min, the solution was cooled to room temperature.

3.2.3 Synthesis of Ag Nanoparticles

Ag NPs of 14 nm diameter were prepared by reducing AgNO_3 (0.1 M) by NaBH_4 . In brief, 0.45 mL of freshly prepared AgNO_3 was added into 180 mL deionized filtered water, which was precooled to 4 °C. Afterwards, 1.00 mL of 50 mM sodium citrate solution and 0.80 mL of 0.6 M NaBH_4 were added to the reaction mixture under vigorous stirring in an ice bath. The reaction mixture developed a clear yellow color. The reaction mixture was kept at 4 °C overnight, and eventually turned dark yellow.

3.2.4 Synthesis of Au@Ag@PDA , Au@Au@PDA, and Ag@Ag@PDA

Nanoparticles

PEGylated Au nanoparticles were first obtained via ligand exchange with methoxy-PEG-thiol overnight. To synthesize Au@Ag@PDA, PEGylated Au nanoparticles (4 mM with respect to the Au precursor concentration) were dispersed in 3 mL 10mM TRIS buffer (pH 8.5) under stirring. Dopamine (2 mg/mL) was added into the solution, followed by slow addition of AgNO_3 solution (2.5 mM). The reaction was maintained under stirring for 8 hr.

Yellowish-brown Au@Ag@PDA nanoparticles were obtained by centrifugation (8000 rcf, 15 min) and redispersed in ultrapure water. In the case of Au@Au@PDA or Ag@Ag@PDA nanoparticles, similar procedures were adopted with the metal seeds or metal precursors changed accordingly.

3.2.5 Synthesis of Au@Ag Nanoparticles

Au@Ag nanoparticles were synthesized using a seed mediated approach. Briefly, 10 ml Au nanoparticles of 14 nm were added into 50 ml H₂O containing 100 mg sodium citrate, followed by 1 mg/ml ascorbic acid. Afterwards, 2.5 mM AgNO₃ was added into the mixture solution to reduce the precursor to form an Ag layer of desired thickness surrounding the Au seed.

3.2.6 Preparation of Au@Ag@PDA Film on Substrates

Glass slides were cleaned in a boiling piranha solution (H₂SO₄/H₂O₂=1:4, v/v) for 0.5 hr and washed with ultrapure water subsequently. rGO paper and 2D-assembly of nanoparticles were prepared according to our recent work.¹³⁶ To drive the self-assembly, 40 μ L of nanoparticles is added into 960 μ L H₂O. Then, 0.5 mL chloroform was added. With the assistance of gentle shaking for better mixing, a thin layer in brown color was formed at the interface of two phases. The 2D-assembly was transferred on the substrates by dip coating, and was dried at room temperature for further characterizations.

3.2.7 Catalytic Study

The rate of catalytic reaction was determined using UV–vis spectroscopy. For this purpose, 4-nitrophenol (1.5 mL, 0.2 mM) was mixed with fresh NaBH₄ solution (1.5 mL, 15 mM). The catalysts coated on rGO paper or glass slide was placed in the reaction mixture at room temperature. The absorbance change was recorded in the spectral range of 280 nm to 550 nm. All of the experiments were carried out under the same condition.

3.3 Results and Discussion

3.3.1 Synthesis of Au Nanoparticles

Au nanocrystals of 14 nm were prepared by citrate reduction of HAuCl_4 in aqueous phase. The Au nanocrystal dispersion initially exhibits the distinct red color, resulting from localized surface plasmon resonance (LSPR) at 522 nm (Figure 3.2).

Figure 3.2 UV-vis spectra (a) and TEM images (b) of Au nanocrystal seeds.

3.3.2 Synthesis of Au@Ag@PDA

The Au@Ag@PDA core-shell nanoparticles were synthesized by seeded growth on 14 nm Au nanocrystals coated with PEG-SH ($M_n = 2$ kDa). We observed that addition of dopamine into the Au nanoparticle dispersion in pH 8.5 TRIS buffer containing Ag precursor induced a quick color change from red to yellow within 1 min. UV-vis spectra (Figure 3.3a) show that the LSPR peak

(440 nm) blue-shifted toward the characteristic LSPR peaks of spherical Ag (400 nm), indicating the growth of Ag shell on Au cores. Increasing the ratio of the Ag precursor to the Au seed did not have a major impact on the spectroscopic signature, but led to stronger absorption, suggestive of an increase in the size of the metal nanocrystals. FT-IR and EXD results confirm the formation of PDA and Au-Ag bimetallic nanoparticles. We found that it was necessary to graft the original citrate-stabilized Au nanocrystals with PEG chains prior to the shell growth because the nanocrystals without PEG coating have poor stability in the growth medium and immediately form macroscopic precipitates out of the dispersion. TEM observation reveals well-dispersed nanoparticles with a triple-layer structure, which corresponds to a dark Au core, an Ag shell with lower contrast, and a layer PDA coating of 4 nm in thickness surrounding the core-shell nanocrystal (Figure 3.3).

Figure 3.3 (a) UV-vis spectra of Au@Ag@PDA with increasing Ag precursors. (b) FT-IR spectrum of Au@Ag@PDA nanoparticles. (c) EXD result of

Au@Ag@PDA nanoparticles. TEM images (d-f) of Au@Ag@PDA with increasing Ag precursors.

3.3.3 Synthesis of Au@Au@PDA and Ag@Ag@PDA

Similarly, Au and Ag shells can be generated on nanocrystal seeds of the same chemical identity to form monometallic Au@Au@PDA and Ag@Ag@PDA nanoparticles (Figure 3.4), respectively.

Figure 3.4 TEM images of Au@Au@PDA (a) and Ag@Ag@PDA (b).

3.3.4 Synthesis of rGO paper

Free-standing rGO paper is fabricated by assembling individual rGO nanosheets in layer-by-layer fashion. From Figure 3.5, we found that a multi-layer rGO paper has been synthesized with a smooth surface. The obtained rGO paper exhibit an excellent mechanical stability (tensile strength of 102.5 MPa and ultimate tensile stain of 7.97%) (Figure 3.6)

Figure 3.5 SEM images of top view (a) and cross-sectional view (b) of rGO paper. Inset in Figure S1a: photograph of the foldable rGO paper.

Figure 3.6 Mechanical property of rGO paper.

3.3.5 Self-Assembled Au@Ag@PDA

Au@Ag@PDA core-shell nanoparticles are highly stable in aqueous medium. Upon addition of chloroform into water dispersion of Au@Ag@PDA, and with the aid of gentle shaking, the nanoparticles accumulated to form a brownish layer at the oil-water interface. Theoretical analysis and experimental results both confirm that surface coating of nanoparticles, which affects the

contact angle of nanoparticles at interfaces, nanoparticle sizes, and surface tension of the biphasic system play dominant roles in driving the interfacial assembly.^{135, 140-142} The interfacial self-assembly of PDA coated nanoparticles has not been discovered before. LSPR (Figure 3.7a) of the assembled Au@Ag nanocrystals showed a red-shift of 40 nm and became broader due to the strong interparticle coupling of neighboring nanocrystals. A uniform and transparent coating was observed when the interfacial assembly was transferred to glass substrates (Figure 3.7a). SEM images (Figure 3.7b,c) display a large area of closely packed nanocrystal arrays with few defects. The formation of a monolayer of densely arranged nanoparticles without long-range order is a typical observation in interfacial assembly of nanoparticles. Interestingly, the core-shell structure of Au@Ag@PDA is visible once anchored on conductive rGO paper (Figure 3.7d).

Figure 3.7 UV–vis spectra (a) of assembled Au@Ag nanocrystals. SEM images (b,c) of closely packed nanocrystal arrays on a glass substrate. SEM images (d) of closely packed nanocrystal arrays on rGO paper.

3.3.6 Self-Assembled Au@Au@PDA and Ag@Ag@PDA

Moreover, PDA-coated monometallic nanoparticles exhibited similar behavior in interfacial assembly and substrate immobilization (Figure 3.8).

Figure 3.8 SEM images of interfacial assembly of Au@Au@PDA nanoparticles (a) and Ag@Ag@PDA (b) loaded on rGO paper.

3.3.7 Catalytic Study

Immobilizing a homogeneous monolayer of non-aggregated nanocatalysts on substrates in high density can maximize the active surface areas exposed to reaction media, which is beneficial for catalysis. The PDA coating on the metal nanocatalysts imparts strong adhesion to the monolayer assembly on both hydrophilic glass substrate and hydrophobic rGO paper. Soaking the catalyst-loaded substrates in various aqueous and organic media did not lead to any evident detachment of the coating layer from the substrates, which is highly important for the consistent catalytic performance.

Figure 3.9 (a) Time-dependent UV–vis spectra of the reaction mixture of catalytic reduction of 4-NPh. (b) The dependence of $\ln(C_t/C_0)$ on reaction time for the reactions catalyzed by different catalysts. (c) Absorbance of the reaction mixture at 400 nm during the catalytic reaction in presence of the nanocatalyst and with an intermittence of 20 min without the nanocatalyst. (d) Conversion efficiency of 4-NPh in 2 hr reaction in 6 consecutive reaction cycles.

Catalytic activity of the 2D assembly of Au@Ag@PDA coated on rGO paper was tested through NaBH_4 -catalyzed reduction of 4-NPh to 4-APh, which does not occur in absence of metal catalysts.^{121, 143} The absorption of 4-APh at 295 nm and 4-NPh at 400 nm, which forms 4-nitrophenolate anions in alkaline reaction media, allows for real-time monitoring of the reaction by UV–vis spectroscopy. Immersing the nanocatalyst-loaded substrate into the reaction mixture is quickly accompanied by an increase of absorption of 4-APh at 295 nm and a decrease of the peak at 400 nm (Figure 3.9a), which otherwise does

not occur over several hours. Here, it is possible to analyze the reaction using pseudo-first-order kinetics based on 4-NPh, because the concentration of NaBH_4 , which is in large excess relative to that of 4-NPh, can be assumed unchanged throughout the reaction. We compared the catalytic performance of Au@Ag core-shell nanocrystals with monometallic Au and Ag nanocrystals by using the same number of particles (0.75 pmol) of similar sizes (20 nm). The linear dependence of $\ln(C_t/C_0)$ observed further verifies the pseudo-first-order kinetics. The rate constants (Figure 3.9b) (0.050 min^{-1}) of Au@Ag core-shell nanocrystals is more than 2 times of those of monometallic Au (0.020 min^{-1}) and Ag (0.023 min^{-1}) nanocrystals, indicative of a synergistic effect in the Au@Ag core-shell structures to promote their catalytic activity, as demonstrated in several studies previously.^{121, 124} Also, in clear contrast was that the interfacial assembly derived from Au@Ag nanocrystals coated with small molecule ligand, i. e., DTBE,¹³⁵ completely lost their activity due to the poisoning effect by forming strong Ag-S bond (Figure 3.10). This result underscores the importance of PDA coating for the catalytic reaction, in addition to its contribution to interfacial assembly and substrate immobilization.

Figure 3.10 4-NPh catalytic reduction catalyzed by Au@Ag@PDA (black line) and Au@Ag@DTBE (red line).

The substrate-immobilized nanocatalysts can be easily recovered and recycled. As demonstrated in Figure 3.9c, the reaction immediately stopped once the catalyst was removed, and resumed again with similar kinetics after reintroduction of the catalyst. Performance stability of the nanocatalysts was further examined by repeated uses of the same catalyst. Between each cycle, the supported catalyst was removed from the reaction, rinsed with distilled water, and air dried at room temperature. Our results (Figure 3.9d) show that almost identical activities were measured in six successive cycles. The nanocatalyst layer survived many catalytic cycles without showing signs of detachment, which is consistent with the strong adhesive properties of the PDA coating.

3.4 Conclusion

In summary, we have developed a new class of highly active, easily recyclable nanocatalysts by taking advantage of the ability of dopamine to direct the seeded growth of bimetallic core–shell nanocrystals and to form PDA coating on the nanocrystals. The strongly adhesive PDA coating drives the interfacial assembly of the nanocrystals, leading to 2D assembly of densely packed nanocatalysts that can be stably anchored on a diverse range of solid substrates with varied physiochemical and surface properties. The modular nature of our approach and the performance stability of the nanocatalysts provide new opportunities to develop and optimize heterogeneous nanocatalysts with tailored sizes, morphologies, chemical configuration, and supporting substrates for metal-catalyzed reactions.

3.5 Declaration

This work presented in this chapter has been published in Advanced Materials.

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Chapter 4 Multifunctional Magnetic Nanochains:

Exploiting Self-Polymerization and Versatile

Reactivity of Mussel-Inspired PDA

4.1 Introduction

There is growing fundamental and practical interest in developing ordered ensembles of metal, semiconductor, and magnetic nanostructures, in which tailored interactions of surface plasmons, excitons, or magnetic moments of the nanostructures give rise to emerging collective properties distinctively different from those of individual building blocks.¹⁴⁴⁻¹⁴⁵ Among a wide spectrum of well-defined ensembles, 1D chain-like structures with directional electronic, optical, or magnetic properties, imparted by linear arrangement of the functional units, hold great promise in fast-developing fields such as optoelectronics and nanomedicine.¹⁴⁶⁻¹⁴⁷ Great research efforts have been made to prepare nanochains of functional nanostructures by organizing them along 1D templates such as carbon nanotubes¹⁴⁸⁻¹⁵⁰ or taking advantage of their directional self-assembly,¹⁵¹ which usually originates from anisotropic surface chemistry introduced by region-selective surface modification. Alternatively, for nanoparticles with intrinsic properties responsive to external magnetic and electrical fields, the interparticle dipole-dipole interaction can drive the nanoparticles to align in the field, providing a straightforward approach to producing 1D nanochain ensembles.¹⁵² Nevertheless, nanochains generated in

external fields mostly suffer from transient stability, and often quickly fall apart once the field is removed.¹⁵³ To address this challenge, silica^{88, 98} and various types of polymers¹⁵⁴⁻¹⁵⁷ were previously used to covalently link the closely spaced nanoparticles and fix the nanochains in presence of the field.

Here we report a new approach, built upon the use of mussel-inspired PDA, to prepare robust multifunctional nanochains of magnetic nanoparticles with readily tailorable surface chemistry for applications in different environments. Dopamine undergoes self-polymerization at basic conditions via successive oxidation of catechol into dopaminequinone and intermolecular cyclization, followed by oxidative oligomerization and self-assembly to form highly crosslinked, rigid PDA that can strongly adhere on virtually any solid substrates.^{51, 57, 158-159} Furthermore, PDA exhibits versatile chemical reactivity that enables a variety of surface functionalization strategies: namely, the reducing activity offered by the abundant catechol groups^{54, 76} and the readily coupling of quinone groups with nucleophilic groups such as thiol and amino via Michael addition and/or Schiff base reactions. As schematically illustrated in Figure 4.1, our synthesis starts with aligning magnetic nanoparticles in a magnetic field, and dopamine is subsequently introduced to initiate the self-polymerization of PDA. The adhesive property of PDA leads to the deposition of a conformal layer of PDA on the linearly arranged nanoparticles to permanently lock the nanochains. We have found that the resulting rigid

magnetic nanochains undertake localized rotation when placed in a spinning magnetic field, making it possible for the nanochains to serve as nanomotors and nanoscale stir bars to promote molecular transport and mixing in extremely small spaces, which is highly desirable for applications in microreactors and ultrasmall sensing devices.

Figure 4.1 Illustration of the stepwise preparation of multifunctional magnetic nanochains via magnetic alignment of magnetic nanoparticles, depositing self-polymerized, adhesive PDA for crosslinking the nanochain, and subsequent functionalization by taking advantage of the multifaceted reactivity of PDA.

4.2 Experimental Section

4.2.1 Materials and Characterization

Dopamine, Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) Iron(II) chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ammonium hydroxide, oleic acid, sodium dodecyl sulfate (SDS), styrene, tetradecane, potassium peroxydisulfate (KPS), propidium iodide (PI), 4-nitrophenol (4-NPh), and sodium borohydride (NaBH_4) were purchased from Sigma Aldrich.. Hydrogen tetrachloroaurate(III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was from Alfa Aesar. Tris(hydroxymethyl)aminomethane (TRIS) was obtained from J. T. Baker. Methoxy-poly(ethylene glycol)-thiol (PEG-SH, 2 kDa) was purchased from Laysan Bio, Inc. SH-MUC1 aptamer sequence: 5'SH-TTTTTTTTTTGCAGTTGATCCTTTGGATACCCTGG-3' (35bp) and control DNA sequence: 5'SH-TTTTTTTTTTTATACCTGGGGGAGTATATAAT-3'(31bp) were purchased from Shanghai Sangon Biotechnology Incorporation (Shanghai, China). Ultrapure water ($18.2 \text{ M}\Omega \cdot \text{cm}$) was purified using a Sartorius AG arium system and used in all experiments.

Scanning electron microscopy (SEM) images were acquired on a FESEM (JSM-6700F, Japan). Transmission electron microscopy (TEM) observations were conducted on a Jeol JEM 2010 electron microscope at an acceleration voltage of 300 kV. UV-vis spectra were recorded using a Shimadzu UV2501

spectrophotometer. Surface potential were measured using a BIC PALS ZetaSizer. The room-temperature magnetization curves were obtained by using a MPMS-VSM. Dark-field imaging of live cells were carried out in an Olympus71 inverted microscope with an oil-immersion dark-field condenser at 40 magnification, and fluorescence images were collected using Photometrics CoolSNAP-cf cooled CCD camera. Live cells were immobilized on a polylysine-modified glass coverslip for the imaging experiments.

4.2.2 Synthesis of Magnetic Nanoparticles

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.4 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.982 g) were dissolved in 10 mL DI water under N_2 gas with vigorous stirring at 80 °C. Then, 5 mL of ammonium hydroxide was added rapidly into the solution. The color of solution turned to black immediately. After 30 min, 3 mL of oleic acid was added and the suspension was kept at 80 °C for 1.5 h. The obtained magnetite nanoparticles were washed with water and methanol until pH became neutral. Magnetite nanoparticles (0.5 g) were added into 12 mL water containing 10 mg SDS, and the mixture in ice-water bath was treated with ultrasound for 10 min to obtain miniemulsion of magnetite nanoparticles. A styrene emulsion was prepared using 5 mL styrene, 50 mg SDS, 40 mL water, and 0.033 mL tetradecane. Miniemulsion of magnetite nanoparticle and 5 mg KPS were added to a three-neck flask and stirred for 30 min at 500-600 rpm in N_2 atmosphere. Afterwards, 10 mL of styrene emulsion was added into the mixture, and the

flask was placed in 80 °C water bath and maintained for 20 h to obtain magnetic nanoparticles. The as-fabricated magnetic nanoparticles were collected with a magnet and redispersed in H₂O, and the collection-redispersion cycle was repeated three times before dispersing the magnetic nanoparticles in 10 mL H₂O for further usage.

4.2.3 PDA-Coated Magnetic Nanoparticles

0.2 mL of magnetic nanoparticles was dispersed in 40 mL TRIS buffer (pH 8.5), followed by adding 10 mg dopamine. The reaction solution was kept stirring for 4 h. The dark brown product was purified by centrifugation and magnetic separation.

4.2.4 Synthesis of Magnetic Nanochains

0.05 mL of magnetic nanoparticles was dispersed in 10 mL TRIS buffer (pH 8.5), followed by adding 2.5 mg dopamine. The reaction solution was placed next to a magnet for 4 min, then incubated without disturbing for 4 h. The brown nanochains were purified by magnetic separation and dispersed in 1 mL H₂O. The different length of nanochains can be obtained when the reaction solution was sonicated before it was left undisturbed for PDA coating. Larger interparticle distance can be achieved when the reaction solution was incubated with dopamine for 1 h before put being placed next to a magnet.

4.2.5 Au Nanoparticles-Loaded Nanochains

0.2 mL IO@PDA nanochains solution was injected into 50 mL H₂O at 85 °C under vigorous stirring. After 2 min, 4 mL 0.1 wt.% of HAuCl₄ was injected into the solution. The reaction solution was kept stirring for 15 min at 85 °C. The color of solution turned dark brown first, then finally became red finally. After purified by a magnet, the obtained Au nanoparticles-loaded nanochains nanochains was stored in 2 mL H₂O.

4.2.6 Catalytic Study

The rate of catalytic reaction was determined using UV–vis spectroscopy. For this purpose, 4-nitrophenol (22.5 µL, 0.2 mM) was mixed with fresh NaBH₄ solution (22.5 µL, 15 mM). 5 µL of Au nanoparticles-loaded nanochains was added into the reaction mixture at room temperature. To induce the stirring, the reaction solution was placed on a magnetic stir plate (400 rpm). The absorbance change was recorded in the spectral range of 280 nm to 550 nm.

4.2.7 Bioconjugation of Nanochains

Typically, 20 µL of nanochains was dispersed in 2 mL of TRIS buffer in a clean glass bottle under vigorous stirring, and then appropriate amount 50 µL of targeted DNA (SH-MUC1 aptamer sequence) was carefully added into the solution, followed by PEG-SH. NaCl solution (1M) was added dropwise into

solution and the salt concentration was adjusted to 80 mM. After overnight incubation, aptamer-conjugated nanochains (Aptamer-NC) were purified by magnetic separation and stored in 4 °C for further use. For the scramble DNA or PEG-SH (2 kDa) modified nanochains, the procedure is similar with the method above.

4.2.8 Cell Culture

Human MCF-7 breast cancer cells were cultured in Dulbecco's modified Eagle's medium (DMEM) medium mixed with 1.5 g/L sodium bicarbonate, 10% fetal bovine serum (FBS) and 1% streptomycin, with 5 % CO₂ at 37 °C.

4.2.9 Dark Field Imaging

Cells were planted and grown on poly-L-lysine modified glass coverslips and incubated for one day. Aptamer-NC in 1 mL DMEM medium with the concentration of 40 µg/mL were incubated with cells for 60 min. Then, cells were washed three times with PBS to remove free Aptamer-NC. After washing, cell slides were observed using dark field microscopy.

4.2.10 Fluorescence Imaging

Cells were planted and grown in 24-well plate and incubated for one day. Aptamer-NC in 400 µL DMEM with the concentration of 40 µg/mL were

incubated with cells for 60 min. Then, cells were washed three times with PBS to remove free Aptamer-NC. After washing process, 400 μ L DMEM with 20 μ g/mL propidium iodide (PI) was added to each well and the well was placed on magnetic mixer for 60 min, followed by another washing process. 400 μ L PBS was added to each well and the plate was observed using fluorescence microscopy.

4.2.11 Cytotoxicity Analysis

A standard Cell Counting Kit-8 (CCK-8) was utilized to analyze the cytotoxicity of Aptamer-NC following a general protocol. Briefly, MCF-7 cells were seeded in a 96-well plate with the concentration of 50000 cells/well. After a 24 h incubation in the incubator at 37 °C, Aptamer-NC with different final concentration were incubated with cells for 60 min. Then, each well was washed three times with PBS to remove the free Aptamer-NC, followed by stirring for 30 min and 60 min respectively. After the stirring, 10 μ L of CCK-8 solution was added to each well of the 96-well plate to incubate for another 4 h. The amount of an orange formazan dye, produced by the reduction of WST-8 (active gradient in CCK-8) by dehydrogenases in living cells, is directly proportional to quantity of living cells in the well. Therefore, by measuring the absorbance of each well at 450 nm using a microplate reader, cell viability could be determined with the calculation of the ratio of absorbance of experimental wells to that of the cell control wells. All experiments were

triplicated and results were averaged.

4.3 Results and Discussion

4.3.1 Synthesis of Magnetic Nanoparticles

Magnetic nanoparticles with a cluster of Fe_3O_4 nanocrystals embedded in a polystyrene matrix (Figure 4.2a) were synthesized by miniemulsion polymerization, and were used as building blocks of the nanochain. Magnetic measurement (Figure 4.2b) shows that the nanoparticles of 90 nm in sizes are superparamagnetic with a saturation magnetization of 34 emu/g at 300 K.

Figure 4.2 TEM images of magnetic nanoparticles (a), and PDA coated magnetic nanoparticle Magnetization curves at 300 K of as-synthesized magnetic nanoparticles (b).

4.3.2 Synthesis of Nanochains

TEM images (Figure 4.3a), dispersing the nanoparticles in a dopamine solution (0.15 mg/mL) in Tris buffer (pH 8.5, 10 mM) and stirring for 4 h led to the deposition of a conformal layer of PDA on the nanoparticles. To prepare the

nanochain, the reaction mixture was first exposed to a magnetic field for 15 min and then left undisturbed for 4 h during PDA formation. Separation of the product by magnetic field became much more efficient than the nanoparticles, suggestive of forming larger nanoparticle ensembles. TEM observation (Figure 4.3b) indeed reveals nanochains of interconnected nanoparticles rather than individual nanoparticles. Apparently, exposure to the magnetic field aligned the superparamagnetic nanoparticles and deposition of PDA eventually crosslinked them to afford the nanochains. The nanochains have a uniform diameter of 105 nm.

Figure 4.3 TEM images of PDA-coated magnetic nanoparticle (a), magnetic nanochains (b).

4.3.3 Synthesis of Nanochains with Different Parameters

The nanochains have a uniform diameter of 105 nm (Figure 4.3b) and an average length of 20 μm , as shown in SEM images (Figure 4.4a). Notably, if we

sonicated the reaction mixture 3 or 10 sec before it was left undisturbed for PDA deposition, the average length of the nanochains decreased to 2.7 and 1.0 μm , respectively (Figure 4.4b,c). Most likely, the ultrasonication reduced the length of the aligned array of magnetic nanoparticles before its structure was fixed by PDA. Controlling the time sequence of PDA deposition and magnetic alignment allowed for tailoring interparticle distance in the nanochain. For example, if the nanoparticle and dopamine solution was mixed first to initiate the PDA growth and the magnetic field was applied after an interval of 1 h, the interparticle distance increased from 3 to 25 nm (Figure 4.4d,e).

Figure 4.4 SEM images of magnetic nanochains with an average length of 20 μm (a), 2.7 μm (b) and 1 μm (c). TEM images of representative nanochains with 3 nm (d) and 25 nm (e) interparticle distances.

Figure 4.5 SEM image of magnetic nanochains with different PDA thickness.

Furthermore, purified nanochains can be subjected to repeated PDA deposition. In general, each cycle led to an increase of approximately 20 nm in the PDA thickness, providing a means to control the width of the nanochains (Figure 4.5). Collectively, key structural parameters such as length, aspect ratio, and interparticle distance all can be systematically changed in our PDA-based synthesis.

4.3.4 Magnetic Response of the Nanochains

We next examined magnetic response of the nanochains. When a drop of the nanochain dispersion was dried naturally, randomly distributed nanochains were observed in SEM image (Figure 4.6a). In contrast, all of the nanochains became well-aligned along the magnetic field in presence of a magnet (Figure 4.6b). The nanochains exhibit strong light scattering under dark-field microscope, making it possible to track the magnetic response of individual nanochains in real time. Figure 4.6c shows that the nanochains were randomly arranged initially, and were immediately aligned when a magnetic field was applied and turned around in response to changes of the field direction. More interestingly, close observation at higher magnification revealed that the nanochains evidently underwent concerted, localized rotation in place with the rotating magnetic field, making them highly suitable for serving as nanomotors.

We have also found that, in a spinning magnetic field, the nanochain dispersion blinks synchronously, which was not seen with the magnetic nanoparticles (Figure 4.6d). Unlike the isotropic spherical nanoparticles, light scattering efficiency of the anisotropic nanochains is largely different in transverse and longitudinal directions. Thus, the blinking should result from periodic changes of the nanochain orientation in the spinning magnetic field. It is noteworthy that the nanochains remained stably stirring without any sign of

aggregation and precipitation for at least 4 h, implying the robustness of the nanochains from both structural and colloidal perspective.

Figure 4.6 SEM images of the magnetic nanochains dried in absence (a) and presence (b) of a magnetic field. (c) Dark-field microscopy images of randomly distributed nanochains (1) and the ones that align along a magnetic field (2–4). (d) Extracted still frames of a video showing water dispersion of the magnetic nanoparticles (left), PDA coated magnetic nanoparticles (middle), and the nanochains (right) under a spinning magnetic field.

4.3.5 Au Nanoparticles-Loaded Nanochains for Heterogeneous

Nanocatalyst

Metal nanostructures with a large surface-to-volume ratio are actively explored as new types of catalysts for a broad range of chemical reactions. However, their tiny sizes make the post-reaction recovery exceedingly difficult and time-consuming, creating a significant barrier for their practical uses.¹⁶⁰ A unique combination of rapid separation and self-mixing capability, offered by the magnetic nanochains, makes them ideal colloidal carriers for metal nanocatalysts to address this challenge. Of equal importance is that self-polymerized PDA carries abundant catechol groups, which are highly reactive reducing agents at mild basic condition, offering the possibility to grow metal nanoparticles on the nanochains via localized reduction. Our results (Figure 4.7a–c) have shown that heating a mixture of the nanochains and HAuCl_4 in water at 85 °C for 20 min gave rise to a high density of Au nanoparticles (AuNPs) of approximate 15 nm anchored on the nanochains. UV–vis spectra (Figure 4.7d) reveal that PDA coating in the nanochain caused strong absorption across the entire spectral range of 400–900 nm. And a new peak centering at 550 nm emerged after AuNPs were loaded. LSPR peak of individual AuNPs of 15 nm is typically around 520 nm. It is evident that the closely arranged AuNPs are strongly coupled, which led to a significant redshift in the LSPR and the associated characteristic purple color (Inset of Figure

4.7d).¹⁶¹

Figure 4.7 TEM images (a–c) of a magnetic nanochain of 125 nm in width (a) and AuNPs-loaded magnetic nanochains at high (b) and low (c) magnifications. (d) UV–vis spectra and a photograph (inset: from left to right) of magnetic nanoparticles, magnetic nanochains, and AuNPs-loaded nanochains.

Due to the magnetic property nanochain, separation of the AuNPs-loaded nanochains can be easily completed by a magnet, leaving behind a colorless supernatant containing no free AuNPs, further supportive of the localized reduction by PDA (Figure 4.8).

Figure 4.8 Photography of AuNPs-loaded nanochains before (a) and (b) after magnetic separation.

We further tested the catalytic activity of the nanocatalyst-loaded nanochains using a model reaction, i.e., reduction of 4-nitrophenol into 4-aminophenol, which can be followed up by the disappearance of the absorption of 4-nitrophenol at 400 nm.¹⁶² A droplet (50 μL) of the reaction mixture containing the nanochains was continuously monitored. The nanochains of 20 μm long and 125 nm wide were chosen to provide sufficient mixing. As shown in Figure 3e, the presence of a spinning magnetic field led to a 57% increase in the reaction rate from 0.132 min^{-1} to 0.208 min^{-1} . Obviously, constant rotation of the magnetic nanochains promoted efficient mixing and mass transfer to speed up the reaction,¹⁶³⁻¹⁶⁵ suggesting the enormous potential

of the nanochains as magnetically recyclable, self-mixing nanocatalysts for microreactor applications, in which the use of macroscopic magnetic stirrers is limited by the size mismatch.

Figure 4.9 The time-dependent conversion of 4-nitrophenol into 4-aminophenol catalyzed by AuNPs-loaded nanochains with or without stirring. Inset: the dependence of $\ln(C_t/C_0)$ on reaction time.

4.3.6 Bioconjugated Nanochains for Magnetolytic Therapy

Biomolecules such as proteins and oligonucleotides containing nucleophilic amino and thiol groups can be attached on the PDA-coated nanochains to modulate their interaction with biological systems.

To check the facile bioconjugation of PDA, thiolated PEG was introduced into a dispersion of nanochains at pH 8.5. As we know that PDA is a highly

polar, which endows the nanochains with excellent dispersibility in polar solvents such as water, alcohols, and *N,N*-dimethylformamide (DMF), but not in less polar solvents like chloroform (CF). After 24h incubation, the obtained PEGylated magnetic nanochains can disperse well in CF, indicating a successful surface modification of PEG *via* Michael addition reaction (Figure 4.10).

Figure 4.10 Photography of PEGylated magnetic nanochains dispersed in different solvents.

Our results (Figure 4.11) have further shown that conjugating PEG and DNA molecules on the nanochains have greatly improved their stability in buffers and cell culture medium, in contrast to the as-prepared nanochains, which form aggregates and precipitate out within 2 h. PEGylation reduced the surface charges of the nanochains, and changed their zeta potential from -10.8 to -1.5 mV. And introducing negatively charged DNA aptamer gave rise to nanochains with a zeta potential of -40.2 mV.

Figure 4.11 (a,b) Photography of as-prepared nanochains (left) and PEGylated nanochains (right) at 0 (a) and 2 h (b) in 180 mM PBS.

More importantly, we have found that modifying the nanochains with a DNA aptamer of MUC-1 protein, which is overexpressed on breast cancer cell line MCF-7,¹⁶⁶ led to specific recognition of the nanochains to the cancer cells. Fluorescence and dark field imaging can locate the green fluorescent protein-labeled MCF-7 cells and the nanochain, respectively. The overlaid images (Figure 4.12a,b) clearly demonstrate that the targeted aptamer-labeled nanochains (Aptamer-NC) showed better binding with the MCF-7 cells than the non-targeted nanochains carrying scrambled DNA (sDNA-NC) of the similar length. The average amount of Aptamer-NCs on each cell is estimated to be 16 by the intensity of the light scattering (Figure 4.12c,d).

Figure 4.12 Overlaid dark-field and fluorescence images of MCF-7 cells after incubated with sDNA-NC (a) and Aptamer-NC (b). (c) Scattering spectra of cells incubated with different bioconjugated nanochains. (d) The average amount of different bioconjugated nanochains binding with each MCF-7 cell.

Then, we apply these targeted nanochains to serve as an agent for magnetolytic therapy. Magnetolytic therapy is a novel cancer therapy in which magnetic field induces the magnetolytic agent to apply mechanical force on cell membrane to cause the cell death. (Figure 4.13).

Figure 4.13 The scheme of the magnetolytic therapy.

After exposed to a low frequency (150 rpm) spinning magnetic field for 1 h, the nanochains labeled cells are stained by membrane impermeant fluorescence dye, PI (Figure 4.14a,b). The result shows that a large fraction of the cells became stained by PI when the cells are incubated with Aptamer-NC. We reason that in a spinning magnetic field, the nanochains bound to the cells are expected to exert mechanical forces on the cell membrane, imposing mechanical force to compromise integrity of the cell membrane and lead to magnetolysis of the cells.¹⁶⁷⁻¹⁶⁹

Quantitative analysis (Figure 4.14c) revealed that the cells maintained more than 80% viability when treated with the spinning magnetic field or the

nanochains alone, confirming biocompatibility of the nanochains. In contrast, the combination of Aptamer-NC and magnetic field caused 63% and 76% cell death after a treatment of 0.5 and 1.0 h respectively, while the PEGylated nanochain and sDNA-NC led to much less (< 40%) cell death. The magnetolytic therapy of the targeted Aptamer-NC showed dosage dependence, indicated by the gradually increased cell death from 7 to 75% in concert with an increase of nanochain concentration from 10 to 80 $\mu\text{g/mL}$ (Figure 4.14d).

Figure 4.14 Fluorescence images of the MCF-7 cells treated with sDNA-NC (a) and Aptamer-NC (b) after the magnetolytic therapy. Dead cells were stained with PI (red). (c) Viability of MCF-7 cells after treated with different bioconjugated NCs at different conditions. (d) Viability of MCF-7 cells after treated with Aptamer-NCs of different concentrations in presence or absence of a spinning magnetic field.

Magnetic nanostructures have found widespread uses for diagnostic and therapeutic applications,¹⁷⁰ including serving as contrast agents for magnetic resonance imaging,¹⁷¹⁻¹⁷² mediating magnetic hyperthermia,¹⁷³ and magnetic separation. Interfacing cells with magnetic nanostructures provides a remote-controlled and non-invasive means to manipulate cellular behavior.¹⁷⁴ Delicate optimization of the nanochain structure and magnetic field is necessitated for broader applications such as mechanotransduction in addition to magnetolytic therapy that we presented here.

4.4 Conclusion

In summary, we have demonstrated that self-polymerization of PDA around aligned magnetic nanoparticles is able to “polymerize” the nanoparticles into nanochains. The highly cross-linked PDA shell not only imparts structural robustness to the nanochains, its versatile reactivity also enables easy loading of metal nanocatalysts and tailoring surface functionalities. The magnetic nanochain is a multifunctional platform that allows flexible post-synthesis functionalization, and can serve as magnetically recyclable, self-mixing nanocatalysts to speed up chemical reactions in small volumes and for targeted magnetolytic therapy of cancer cells. Recent advances in colloidal synthesis of heterogeneous magnetic nanocrystals have provided new building blocks to construct multifunctional magnetic nanochains. Similarly, introduction of a range of biomolecules such as enzymes offers new possibilities for applications such as biocatalysis and medical diagnostics.

4.5 Declaration

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Chapter 5 Versatile Core–Shell

Nanoparticle@Metal–Organic Framework

Nanohybrids: Exploiting Mussel-Inspired PDA for Tailored Structural Integration

5.1 Introduction

In this chapter, we report a generally applicable strategy that allows for constructing heterogeneous core–shell nanostructures with a customized selection of functional nanoparticle core and metal–organic frameworks (MOFs) shell. The ability to control structural integration of functional materials at nanometer scale opens the access to heterogeneous nanohybrids with collective properties that are not available in individual building blocks.^{109, 175-176} Emerging properties of the heterogeneous nanohybrids hold great promise in catalysis, theranostics, and combination therapy, in which the synergistic action of multiple components is necessitated for optimal performance.^{33, 177-181} The structure-dependant optical, electrical, magnetic, and catalytic properties of metal, semiconductor, and metal oxide nanoparticles have stimulated intense research and developments in chemistry, materials sciences, biology and medicine.¹⁸² MOFs are an intriguing class of microporous crystalline materials built upon coordinated metal ions and organic ligands.¹⁸³ The readily tunable microporous structures and functionalities of MOFs, deriving from a diverse

collection of available building blocks, underpin their applications in molecular storage and separation, chemical sensing, and catalysis.¹⁸⁴⁻¹⁹⁰ There is growing interest in developing nanoparticle@MOF (NP@MOF) core-shell nanohybrids to complement nanoparticle functionality with the molecular sieving effect of MOFs, imparted by their defined pore apertures.¹⁹¹⁻¹⁹² Although considerable progress has been made, the majority of existing methods, by means of either in-situ synthesis of nanoparticles inside MOFs¹⁹³⁻¹⁹⁶ or depositing MOF coatings on preformed nanoparticles,¹⁹⁷⁻²⁰¹ mainly give rise to hybrid materials with many nanoparticles dispersed in the MOF matrix rather than well-defined core-shell nanostructures with a layer of MOF sealing off a single nanoparticle core. More recently, several groups have reported that selective nanoparticle capping ligands such as polyvinylpyrrolidone (PVP) can mediate the deposition of a MOF shell on metal nanoparticles to form core-shell nanohybrids.²⁰²⁻²⁰⁷

Figure 5.1 Illustration of the stepwise synthesis of nanoparticle@PDA, nanoparticle@PDA@MOF, and metal nanoparticle@PDA@MOF core-shell hybrid nanostructures.

Here we show that the use of an intermediate mussel-inspired PDA coating opens new possibilities for tailored synthesis of core-shell nanoparticle@MOF nanohybrids. Self-polymerization of dopamine in the presence of virtually any solid substrate leads to a stable and conformal PDA coating that is bound to the substrate through covalent and/or non-covalent interactions.^{51, 57, 132, 150, 208-210} A unique combination of physicochemical characteristics of PDA plays critical roles in the success of our strategy, as illustrated in Figure 5.1 First, the adhesive nature and controllable growth kinetics of PDA makes it possible to form a conformal layer of PDA with controlled thickness on a wide spectrum of nanoparticles of different chemical identities and functionalities. Second, metal-chelating activity of the catechol groups^{133, 211-212} in PDA can drive the

heterogeneous nucleation and growth of MOFs on PDA coated nanoparticles, affording exclusively the core-shell nanohybrids. Importantly, the PDA coating endows the nanoparticle cores with excellent colloidal stability, which prevents nanoparticles from aggregating in MOF growth solution. Third, the redox reactivity of PDA^{158, 213-214} enables localized reduction of metal precursors, which leaves metal nanostructures sandwiched between the nanoparticle core and MOF shell, providing unique opportunities for constructing multifunctional nanohybrids. We have demonstrated that our strategy allows controlled growth of classical MOFs on a broad range of inorganic and organic nanostructures, offering unprecedented chemical flexibility in developing core-shell nanohybrids. A prototypical example illustrated here involves loading catalytic Au nanoparticles in MOF-coated magnetic nanoparticles by taking advantage of the redox activity of PDA. Complementary properties of the multiple components of the nanohybrids give rise to magnetically recyclable nanocatalysts with molecular size selectivity.

5.2 Experimental Section

5.2.1 Materials and Characterization

Materials. Dopamine, sodium citrate, hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$), hexadecyl trimethyl ammonium bromide (CTAB), sodium hydroxide (NaOH), tetraethyl orthosilicate (TEOS), p-styrenesulfonic acid sodium salt (NaSS), iron(III) chloride hexahydrate ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$) iron(II) chloride ($\text{FeCl}_2\cdot 4\text{H}_2\text{O}$), ammonium hydroxide, oleic acid, sodium dodecyl sulfate (SDS), styrene, tetradecane, potassium peroxydisulfate (KPS), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2$), 2-methylimidazole, zirconium(IV) chloride (ZrCl_4), terephthalic acid (H_2BDC), acetic acid, 4-nitrophenol (4-NPh), methylene blue (MB) and sodium borohydride (NaBH_4) were purchased from Sigma Aldrich. Methanol (MeOH), ethanol (EtOH) and *N,N*-Dimethylmethanamide (DMF) were obtained from Fisher Chemical. Hydrogen chloride (HCl) was obtained from Schedelco. Silver nitrate (AgNO_3) was acquired from strem chemicals. L-ascorbic acid (LAA) was obtained from Tokyo Chemical Industry. Hydrogen tetrachloroaurate(III) trihydrate ($\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$) was supplied by Alfa Aesar. Tris(hydroxymethyl)aminomethane (TRIS) was obtained from J. T. Baker. Ultrapure water ($18.2\text{ M}\Omega\cdot\text{cm}$) was purified using a Sartorius AG arium system and used in all experiments.

Characterization. SEM images were acquired on a FESEM (JSM-6700F, Japan). TEM observations were conducted on a Jeol JEM 2010 electron microscope at an acceleration voltage of 300 kV. UV–vis spectra were recorded using a Shimadzu UV1800 spectrophotometer. Powder X-ray diffraction (XRD) patterns were obtained on a Bruker AXS D2 Advanced X-ray diffractometer with monochromatized Cu K α radiation (λ = 1.54056 Å, 40 kV and 20 mA). BET surface area was measured by N₂ adsorption and desorption at 77 K using a Micromeritics ASAP 2020 apparatus.

5.2.2 Synthesis of 50 nm Au Nanoparticles

Au nanoparticles. 50 nm AuNPs were prepared using a seeded-growth method. Typically, seed AuNPs with a diameter of 14 nm were prepared firstly. 5 mL of 12 mg/mL sodium citrate solution were injected into a 50 mL boiling water solution containing 5 mg HAuCl₄ under vigorous stirring. A color change from colorless to red was observed in 5 min. Heat the solution for another 20 min and then allows the solution cool to room temperature before further use. Then, this seed AuNP solution was used to synthesize 50 nm AuNPs. Briefly, 50 mL water was added into a 100 mL round-bottom flask. 2 mL of seed AuNP solution and 200 μ L of 0.2 M NH₂OH·HCl were added into this flask consecutively. Afterwards, 3 mL of 0.1 wt% HAuCl₄ was added dropwise into the solution under vigorous stirring followed by 30 min reaction at room temperature. A gradual color change from light red to dark red was observed.

Finally, adjust the concentration of sodium citrate to 1 mM. After reacting for another 2 h, nanoparticle dispersion was stored at 4 °C for further use.

5.2.3 Synthesis of Au Nanostars.

To synthesize Au nanostars, 0.2 mL 25 mM HAuCl_4 was added into 15 mL H_2O , followed by 20 μL 1 M HCl and 0.145 mL 14 nm AuNP seeds. The solution was kept stirring for 2 min. Then, 40 μL 10 mM AgNO_3 was injected into the reaction. After 2-3 min, 100 μL LAA (100 mM) was added rapidly. The solution turned green immediately once LAA was added. After another 2 min, 1 mL CTAB (10 mM) was introduced into the mixture to stabilize the Au nanostars.

5.2.4 Synthesis of Mesoporous Silica Nanoparticles (MSNs)

MSN was prepared by co-condensation method. CTAB (500 mg) was dissolved in DI water (240 mL) followed by the addition of NaOH aqueous solution (1.50 mL, 2 M). The mixture was heated up to 80 °C under N_2 in 500 mL round bottomed flask with vigorous stirring. When the temperature became stable, TEOS (2.5 mL) was slowly added into the mixture solution via syringe. The solution became turbid after adding TEOS, and was then stirred at 80 °C for another 2 h. Afterwards, nanoparticles were collected by centrifugation at 6000 rcf for 10 min. The product was washed with MeOH, water and MeOH thoroughly. Surfactant (CTAB) was removed by suspending the nanoparticles in

MeOH (150 mL) containing HCl (3 mL, 37%). The mixture was refluxed at 80 °C for 24 h. The product mesoSiO₂ NPs were collected by centrifugation at 6000 rcf for 10 min and thoroughly washed by MeOH, water and MeOH.

5.2.5 Synthesis of Polystyrene Nanoparticles (PSNs)

The polystyrene nanoparticles were prepared by soap-free polymerization in the present of NaSS. Distilled 10 g styrene, 0.0831 g KPS, 90 mL water, and NaSS were charged into the reactor and then deoxygenated with N₂ for 1 h. The reactant mixture was reacted at 70 °C for 24 h under N₂ atmosphere. The obtained PSNs were dialyzed against water before further use.

5.2.6 Synthesis of MagNPs

FeCl₃·6H₂O (2.4 g) and FeCl₂·4H₂O (0.982 g) were dissolved in 10 mL DI water under N₂ gas with vigorous stirring at 80 °C. Then, 5 mL of ammonium hydroxide was added rapidly into the solution. The color of solution turned to black immediately. After 30 min, 3 mL of oleic acid was added and the suspension was kept at 80 °C for 1.5 h. The obtained magnetite nanoparticles were washed with water and MeOH until pH became neutral. Magnetite nanoparticles (0.5 g) were added into 12 mL water containing 10 mg SDS, and the mixture in ice-water bath was treated with ultrasound for 10 min to obtain miniemulsion of magnetite nanoparticles. A styrene emulsion was prepared using 5 mL styrene, 50 mg SDS 40 mL water, and 0.033 mL tetradecane.

Miniemulsion of magnetite nanoparticle and 5 mg KPS were added to a three-neck flask and stirred for 30 min at 500-600 rpm in N₂ atmosphere. Afterwards, 10 mL of styrene emulsion was added into the mixture, and the flask was placed in 80 °C water bath and maintained for 20 h to obtain MagNPs. This as-fabricated MagNPs was collected with a magnet and redispersed in H₂O, and the collection-redispersion cycle was repeated three times before dispersing the MagNPs in 10 mL H₂O for further usage.

5.2.7 Nanoparticle@PDA Core–Shell Nanoparticles

Typically, 50 mL of as-synthesized 50 nm Au nanoparticles were centrifuged at 900 rcf for 15 min. Then, the pellets were redispersed in 2 mL H₂O. 600 µL of the concentrated AuNPs was dispersed in 16 mL TRIS buffer (pH 8.5), followed by adding 10 mg dopamine. The reaction solution was stirred for 18 h and the purple product was purified by centrifugation. Similar procedure was applied to deposit PDA on other nanoparticles.

5.2.8 Synthesis of MagNP@PDA@AuNPs

MagNP@PDA solution was injected into 50 mL H₂O at 85 °C under vigorous stirring. After 2 min, 4 mL 0.1 wt.% of HAuCl₄ was injected into the solution. The reaction solution was stirred kept stirring for 15 min at 85 °C. The color of dispersion turned into dark brown first, and then became red finally. After purified by centrifugation, the obtained MagNP@PDA@AuNPs were

stored in DMF.

5.2.9 Synthesis of ZIF-8 Nanoparticles

Nanosized ZIF-8 particles were prepared by mixing 5 mL MeOH solution of $\text{Zn}(\text{NO}_3)_2$ (12.5 mM) with 5 mL MeOH solution of 2-methylimidazole (25 mM). The mixture was shaken for 10 s, and then allowed to react at room temperature for 12 h. The product was collected by centrifugation, washed several times with MeOH, and dried under vacuum overnight.

5.2.10 Synthesis of UiO-66 Nanoparticles

Nanosized UiO-66 particles were prepared by dissolving 4 mM ZrCl_4 and 4 mM H_2BDC in a mixture of DMF and EtOH containing acetic acid. The reaction vial was capped and placed into an oven preheated at 100 °C for 12 h. The product was collected by centrifugation and then washed three times with DMF. The product was suspended in MeOH, and maintained at 60 °C for three days. MeOH was renewed every 24 h to remove DMF. Finally, the product was washed 3 times with MeOH.

5.2.11 Synthesis of NP@PDA@ZIF-8 Nanoparticles

Typically, a predetermined amount of AuNP@PDA in MeOH was added into 3 mL MeOH solution of $\text{Zn}(\text{NO}_3)_2$ (12.5 mM), followed by 3 mL MeOH

solution of 2-methylimidazole (25 mM). The mixture was shaken for 10 s, and then allowed to react at room temperature for 12 hours. The pink product was collected by centrifugation and washed 3 times with MeOH before dried under vacuum overnight. Similar procedure and conditions were used to coat ZIF-8 on other nanoparticles.

5.2.12 Synthesis of NP@PDA@UiO-66 Nanoparticles

Typically, a predetermined amount of AuNP@PDA in DMF was added into a mixture of 4 mM ZrCl_4 and 4 mM H_2BDC in a DMF-EtOH (v/v= 5:3) mixture. Afterwards, the solution was treated by ultrasonication for 10 min. Subsequently, the vial was capped and placed into an oven preheated at 100 °C for 12 h. The pink product was collected by centrifugation and then washed three times with DMF. The product was soaked in MeOH at 60 °C for three days, and MeOH was renewed every 24 h to remove DMF. Finally, the product was washed 3 times with MeOH.

5.2.13 Catalytic Study on 4-Nitrophenol

The rate of catalytic reaction was determined using UV–vis spectroscopy. For this purpose, 4-nitrophenol (1.5 mL, 0.2 mM) was mixed with fresh NaBH_4 solution (1.5 mL, 15 mM). 50 μL of different catalysts were added into the reaction mixture at room temperature. The absorbance spectra was recorded in the range of 350 nm to 800 nm.

5.2.14 Catalytic Study on Methylene Blue

The rate of catalytic reaction was determined using UV–vis spectroscopy. For this purpose, methylene (1.5 mL, 8 mg/L) was mixed with fresh NaBH₄ solution (1.5 mL, 15 mM). 50 µL of different catalysts were added into the reaction mixture at room temperature. The absorbance spectra was recorded in the range of 400 nm to 750 nm.

5.3 Results and Discussion

5.3.1 Synthesis of AuNP@PDA

Au nanoparticles with LSPR highly sensitive to the change of their surrounding dielectric environment and aggregation status are excellent model core materials that can provide real-time colorimetric feedback on the successful loading of shell coatings.^{161, 215} Here the deposition of PDA on Au nanoparticles of 50 nm was conducted in freshly prepared dopamine solution in Tris buffer (10 mM, pH 8.5). Afterwards, the nanoparticles can be separated by centrifugation and redispersed in NaCl solution (0.15 M) and methanol, indicating a considerable change in surface properties (Figure 5.2).

Figure 5.2 UV-vis spectra of (a) AuNP and (b) AuNP@PDA dispersed in water and methanol, respectively. Inset of photographs show color change of solution.

Figure 5.3 (a) UV-vis spectra of AuNP@PDA with different thickness. TEM images of 50 nm AuNP (b) and AuNP@PDA with different thickness (c,d).

After the PDA coating, from UV-vis spectra (Figure 5.3a), we can find that there is a red shift of LSPR on AuNP@PDA due to the higher refractive index of PDA. This also indicates the successful coating of PDA. In TEM images (Figure 5.3b-d), a PDA coating of lower contrast surrounding the Au nanoparticles can be easily identified. We have found that the thickness of PDA shell is highly dependent on the dopamine concentration. While 0.25 mg/mL dopamine led to a uniform PDA coating of 6 nm after reacting with Au nanoparticles (0.2 nM) for 18 h, increasing the concentration to 0.5 mg/mL

gave rise to a thickness of 25 nm, as observed in Figure 5.3c,d.

5.3.2 Synthesis of AuNP@PDA@ZIF-8

We next examined the growth of a representative zeolitic imidazole framework material (ZIF-8) on PDA coated Au nanoparticles (AuNP@PDA). ZIF-8 precursors, $\text{Zn}(\text{NO}_3)_2$ (12.5 mM) and 2-methylimidazole (25 mM) in methanol, are mixing at room temperature together to synthesize ZIF-8. From Figure 5.4, we can see that nanosized ZIF-8 nanoparticles have been obtained.

Figure 5.4 SEM (a) and TEM (b) images of ZIF-8 at different magnifications.

After this, ZIF-8 precursors were mixed with the AuNP@PDA dispersion in methanol for the synthesis of AuNP@PDA@ZIF-8, and the resultant product was collected after 12 h.

Figure 5.5 (a) UV-vis spectra of Au nanoparticle, AuNP@PDA, and AuNP@PDA@ZIF-8. (b) TEM image of AuNP@PDA@ZIF-8. (c) XRD patterns of different samples. (d) Nitrogen-sorption isotherms for different samples at 77 K up to 1 bar. The solid and open symbols represent adsorption and desorption, respectively.

Figure 5.5a shows that the LSPR peak of 50 nm Au nanoparticles red-shifted from 535 to 560 nm in AuNP@PDA, and further moved to 580 nm after the ZIF-8 shell was deposited to form the core-shell nanohybrids, because of the higher refractive index of PDA and ZIF-8 than that of water. TEM image (Figure 5.5b) of the pink-red products clearly shows a homogeneous layer (90 nm) of ZIF-8 crystal on top of the AuNP@PDA nanoparticles. X-ray diffraction (XRD) patterns of both AuNP@PDA@ZIF-8 core-shell nanohybrids display the characteristic peaks of face-centered-cubic phase of Au and ZIF-8 crystals,

confirming the high loading of nanocrystals in the core-shell configuration (Figure 5.5c). The type I N_2 isotherm revealed in nitrogen-sorption measurements is suggestive of the microporosity of the core-shell nanohybrids. In comparison with the pure nanosized ZIF-8, which show gravimetric Brunauer-Emmett-Teller (BET) surface areas of $1541 \text{ m}^2\text{g}^{-1}$, the core-shell AuNP@PDA@ZIF-8 nanohybrids exhibit smaller surface areas of $1082 \text{ m}^2\text{g}^{-1}$, resulting from the introduction of non-porous Au core in the hybrids (Figure 5.5d).

Figure 5.6 UV-vis spectra of the AuNP@PDA@ZIF-8 reaction solution recorded in the initial 30 min.

Time-dependent UV-vis spectroscopy measurements reveal that the LSPR redshifts primarily occurred in the first 3 min of ZIF-8 growth (Figure 5.6), which indicates the rapid nucleation and growth of the ZIF-8 on PDA layer.

Figure 5.7 TEM images of AuNP@PDA with 6 nm PDA encapsulated by ZIF-8 layer of 40 nm (a) and 90 nm (b). (c) TEM images of AuNP@PDA with a 25 nm PDA layer and corresponding AuNP@PDA@ZIF-8. (d) SEM image of AuNP@PDA@ZIF-8.

Additionally, the parameters of the AuNP@PDA@ZIF can be tuned easily. For example, the thickness of ZIF-8 layer can be down to 40 nm (Figure 5.7a), when we just use the half of precursor concentration for a layer of 90 nm (Figure 5.7b). Notably, if the AuNP@PDA nanoparticles with 25 nm PDA coating were used, two concentric layers around the Au nanoparticle cores (Figure 5.7c) were evidently observed after the ZIF-8 growth, suggesting that ZIF-8 nucleated rapidly on the surface of PDA coating and subsequently grew

into larger nanocrystals. The strong chelating power of residual catechol groups in PDA and the hydrophobic interaction between aromatic groups of PDA and the organic ligands both are expected to facilitate rapid nucleation, leading to high yield of the well-defined core-shell nanohybrids. SEM observation (Figure 5.7d) further confirmed its homogeneous size distribution across a large population.

5.3.3 Synthesis of AuNP@PDA@UiO-66

ZIF-8 represents an easily synthesized MOF material that is formed rapidly under ambient condition. To check the potential of our PDA strategy for other types of MOFs, we further use UiO-66, which is solvothermally prepared using 1,4-benzenedicarboxylic acid (H_2BDC) as organic linkers and zirconium(IV) as metal cores, to confirm its versatility. We first prepare pure nanosized UiO-66 nanocrystal without the incorporation of the AuNP@PDA (Figure 5.8).

Figure 5.8 SEM (a) and TEM (b) images of UiO-66 at different magnifications.

Figure 5.9 (a) UV-vis spectra of Au nanoparticle, AuNP@PDA, and AuNP@PDA@UiO-66. (b) TEM image of AuNP@PDA@ZIF-8. (c) XRD patterns of different samples. (d) Nitrogen-sorption isotherms for different samples at 77 K up to 1 bar. The solid and open symbols represent adsorption and desorption, respectively.

Figure 5.9a shows that the LSPR peak of 50 nm Au nanoparticles red-shifted from 535 to 560 nm in AuNP@PDA, and further moved to 582 nm

after the UiO-66 shell was deposited, which is similar to the result of AuNP@PDA@ZIF-8 core-shell nanohybrids. However, the baseline of the absorbance has been increased a lot, indicating the larger size of the nanoparticles. TEM image (Figure 5.9b) of the products clearly shows a homogeneous layer (200 nm) of UiO-66 crystal encapsulate AuNP@PDA nanoparticles. XRD patterns of both AuNP@PDA@UiO-66 core-shell nanohybrids display the characteristic peaks of face-centered-cubic phase of Au and UiO-66 crystals, confirming the high loading of nanocrystals in the core-shell configuration (Figure 5.9c). The type I N₂ isotherm revealed in nitrogen-sorption measurements reveals the microporosity of the core-shell nanohybrids. In comparison with the pure nanosized UiO-66, which shows gravimetric BET surface areas of 1496 m²g⁻¹, the core-shell AuNP@PDA@UiO-66 nanohybrids exhibit smaller surface areas of 1353 m²g⁻¹, resulting from the introduction of non-porous Au core in the hybrids (Figure 5.9d).

In conclusion, we can synthesize different AuNP@PDA@MOFs using our PDA-based strategy, indicative of the compatibility of the strategy with other synthesis conditions and a diverse range of functional groups found in MOF building blocks.

5.3.4 Synthesis of Anisotropic AuNS@PDA@ZIF-8

To examine the compatibility of the PDA-based method with nanoparticle cores of different morphologies, anisotropic Au were used for preparing the core-shell nanohybrids. Au nanostars with sharp tips were prepared by a seeded-growth method on 14 nm Au nanoparticles (Figure 5.10a).²¹⁶ Regardless of the anisotropic structure and different surface property of Au nanostars compared to Au nanoparticles, a PDA layer can also be coated on Au nanostars (Figure 5.10b). TEM image shows that ZIF-8 crystal was readily grown on PDA coated Au nanostars of 80 nm (Figure 5.10c), forming core-shell structures with the nanostars completely trapped inside the ZIF-8 shell. Similar to that of the spherical Au nanoparticles, the broad LSPR peak of Au nanostars at 826 nm red-shifted to 897 and 913 nm after PDA and ZIF-8 layers were introduced (Figure 5.10d).

Figure 5.10 TEM images of (a) Au nanostars (AuNSs), (b) AuNS@PDA, (c) AuNS@PDA@ZIF-8. (d) UV-vis spectra of different materials.

5.3.5 Synthesis of NP@PDA@ZIF-8 with Core Composition

This strategy is also valid for cores of different chemical composition. Mesoporous silica nanoparticles (MSNs)²¹⁷ and polystyrene nanoparticles (PSNs)²¹⁸ were selected as representative inorganic oxide and organic nanomaterials, which are also under intense research for a broad spectrum of applications.¹⁸⁰ Following the similar protocol developed for Au-based nanomaterials, we were able to successfully coat ZIF-8 of a controlled layer thickness on both MSNs and PSNs.

Figure 5.11 TEM images of (a) MSN, (b) MSN@PDA, (c) MSN@PDA@ZIF-8, (d) PSN, (e) PSN@PDA, (f) PSN@PDA@ZIF-8.

TEM observation (Figure 5.11) confirmed that the successive coating of PDA and MOF layers can also be done on MSNs and PSNs, leading to

well-defined core-shell structures. Taken together, the generation of a robust PDA coating by self-polymerization of dopamine is not dependent on the nature of the underlining substrates, and the PDA-enabled strategy allows customized structural integration of functional nanostructures and MOFs.

5.3.6 Synthesis of NP@PDA@ZIF-8 with Functional Core

The general applicability of this strategy opens the access to diverse core-shell nanoparticles with the functionality of the core nanoparticles complementing molecular size selectivity of the MOF shell. Polystyrene-trapped magnetic iron oxide nanoparticles (MagNPs) were prepared by emulsion polymerization.²¹⁹⁻²²⁰ A core of magnetic iron oxide nanoparticles is clearly visible within the polystyrene nanobead (Figure 5.12a). The growth of PDA and ZIF-8 shell gave rise to obvious size increase, forming core-shell nanoparticles with their MagNP core and ZIF-8 shell easily identified in TEM images (Figure 5.12b,c). Due to the addition of non-magnetic PDA and MOF components, the resulting MagNP@PDA@ZIF-8 core-shell nanoparticle has a decreased magnetization saturation value of 3.1 emu/g in comparison with that of MagNP (33.2 emu/g) and MagNP@PDA (12.7 emu/g) (Figure 5.12d).²²¹

Figure 5.12 TEM images of (a) MagNP, (b) MagNP@PDA, (c) MagNP@PDA@ZIF-8. (d) Magnetization curves at 300 K of different materials.

5.3.7 Synthesis of MagNP@PDA@AuNPs@MOF Nanohybrids as

Nanocatalysts

Self-polymerization of dopamine proceeds *via* oxidation of catechol into dopaminequinone followed by intramolecular cyclization, further oxidative oligomerization and self-assembly, leaving behind abundant redox-active catechol groups in PDA.

Figure 5.13 TEM images of (a) MagNP@PDA@AuNPs, and MagNP@PDA@AuNPs coated with (b) ZIF-8 and (c) UiO-66. (d) UV-vis spectra of different materials.

Figure 5.13a shows that PDA coating on MagNPs is able to induce localized reduction of Au precursor, giving rise to a number of uniform Au nanoparticles of 15 nm in size loaded on PDA coating. It appears that the Au nanoparticles reside on the surface of PDA instead of trapped inside the PDA network. Furthermore, ZIF-8 and UiO-66 shells (Figure 5.13b,c) both can be coated on MagNPs carrying Au nanoparticles (MagNP@PDA@AuNPs), implying that the loading of Au nanoparticles did not affect the ability of PDA to mediate MOF growth. In UV-vis spectra (Figure 5.13d), the characteristic

LSPR peak of AuNPs emerged after the localized reduction on PDA coated MagNPs, and remained in the MOF coated nanoparticles. The three-component MagNP@PDA@AuNPs@MOF nanohybrids can be easily recovered by a magnetic field (inset of Figure 5.13d)

We next explored the application of the nanoparticle–MOF core–shell nanohybrids with complement properties. Metal nanoparticles with large surface areas have emerged as a new class of catalysts that are receiving increasing attention. The MagNP@PDA@AuNPs@MOF nanohybrids have built-in magnetic property from the MagNP core, catalytic activity from the loaded Au nanocatalysts, and molecular sieving effect from the MOF shell, which are collective characteristics necessitated for magnetically recyclable nanocatalysts with molecular size selectivity. The metal-catalyzed reduction of 4-nitrophenol (4-NPh) to 4-aminophenol (4-APh) and methylene blue (MB) to leuco MB (LMB) by NaBH₄ were selected as the model reactions to examine this potential of the core–shell nanohybrids. 4-NPh has strong absorption at 400 nm which disappears upon conversion into 4-APh, making it possible to follow the reaction using UV–vis spectroscopy.²⁰⁸ In control experiments, ZIF-8 and UiO-66 themselves did not show any catalytic activity (Figure 5.14) for both reactions. As demonstrated in Figure 5.14a, while MagNP@PDA@AuNPs without MOF shell led to rapid conversion of 4-NPh into 4-APh, the reaction was completely inhibited when a layer of ZIF-8 was coated on the nanoparticles.

Apparently, the small aperture size of ZIF-8 (3.4 Å) prevented the diffusion of 4-NPh (~4.8 Å) through the MOF shell to access the Au nanocatalysts. In line with this analysis, the use of UiO-66 MOF shell with a larger aperture size (6.0 Å) did not affect the reaction significantly. The slight reduction of reaction rate possibly resulted from the limited diffusion of 4-NPh through the MOF shell.²²² Recycling nanoscale catalysts has been a significant challenge in the field. Our results demonstrate that the magnetically recycled nanohybrids maintained excellent colloidal stability and catalytic activity (Figure 5.15) in repeated uses. For the reduction of MB (Figure 5.14b), which has a molecular size of ~7.6 Å, it is apparent that even UiO-66 coated nanoparticles did not show any reaction activity due to diffusion inhibition caused by molecular selectivity of the MOF layer.

Figure 5.14 Reaction kinetics of the conversion of (a) 4-NPh and (b) MB catalyzed by various materials.

Figure 5.15 UV-vis spectra of the reduction of 4-NP catalyzed by MagNP@PDA@AuNPs@UiO-66 in two consecutive cycles (a) and (b). Inset of Figure 5.14a: photograph shows the magnetic separation of MagNP@PDA@AuNPs@UiO-66.

5.4 Conclusion

In summary, we have presented a versatile, PDA-enabled strategy for developing well-defined nanohybrids consisting of a nanoparticle core and a MOF shell. The ability of PDA to adhere to colloidal substrates of any chemical composition and to bind with a wide spectrum of MOF building blocks forms the fundamental basis of our strategy, and its unique redox activity adds an additional dimension to customize the functionalities of the resultant core-shell nanohybrids. The general applicability of this new approach was highlighted with varieties of nanohybrids consisting of different nanoparticle and MOF pairs. In particular, nanohybrids with catalytic Au nanoparticles sandwiched between the magnetic core and MOF shell through localized reduction by PDA, as magnetically recyclable nanocatalysts with molecular size selectivity, have demonstrated the potential of our strategy for flexible, rational functionality integration. The full potential of this strategy in emerging fields such as nanomedicine and photocatalysis is to be realized by the introduction of new building blocks, fueled by recent advances in tailored synthesis of nanocrystals and functional MOFs. The core-shell nanohybrids with a molecular sieving effect added onto the intrinsic properties of the nanoparticle core are of considerable interest for controlled drug release and improved selectivity in sensing and catalysis applications.

5.5 Declaration

This work presented in this chapter has been published in ACS Nano.

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Chapter 6 Conclusions and Future Research

6.1 Conclusions

In this thesis, we successfully develop a PDA-based strategy to fabricate a series of heterogeneous nanostructures regardless of the nature of the individual component. PDA here exhibits many important properties in the synthesis of the heterogeneous nanostructures, involving the adhesive property, redox property, metal-ion chelating, amphiphilic property, and other chemical reactivity which allow for designing the heterogeneous nanostructure more flexibly. The obtained multifunctional heterogeneous nanostructures then have been used for several applications.

First, we fabricated a novel type of 2D recyclable heterogeneous catalysts of core-shell bimetallic nanocrystals through PDA coating-directed epitaxial growth, interfacial assembly, and substrate-immobilization of Au@Ag core-shell nanocrystals. The Au@Ag@PDA nanocatalysts possess a bimetallic synergistic effect, showing better catalytic activity than PDA-coated monometallic Au and Ag nanocrystals.

Second, we put forward a strategy to design multifunctional 1D nanochains of magnetic nanoparticles. Self-polymerized PDA can help to fix the magnet field-aligned nanoparticles, which results in robust magnetic

nanochains with versatile reactivity inherited from PDA. We have shown that loading of metal nanoparticles on the nanochains *via* localized reduction by PDA gave rise to magnetically recyclable, self-mixing nanocatalysts. On the other hand, bioconjugated nanochains can be used for specific recognition of the nanochains to cancer cells, which then induces magnetolysis.

Finally, we report a versatile strategy based on the use of multifunctional PDA to constructing well-defined core-shell NP@PDA@MOF nanohybrids of various nanoparticle cores and MOF shells. By introducing magnetic and catalytic parts into this system, a novel heterogeneous nanocatalyst with molecule size selectivity can be achieved.

6.2 Future Research

Our strategy here has been proved to be a versatile and facile method to fabricate a diversity of multifunctional heterogeneous nanostructures. It will provide more opportunities for us to synthesize various heterogeneous nanostructures for a broader range of applications.

The future work will be proposed in the following aspects:

- 1) Currently, we can incorporate up to three different types of components into the heterogeneous nanostructure. Actually, due to the unique properties of

the PDA, more than three components can be integrated to serve as a single multifunctional assembly, which not only significantly expands the library of heterogeneous nanostructures, but also offers more combined and/or improved properties. For example, Ag can be introduced into the MagNP@PDA@Au@MOF system to achieve selective recyclable nanocatalyst with higher catalytic activity.

- 2) In previous work, most of the applications focus on the catalysis. However, heterogeneous nanostructures can do more than that. Heterogeneous nanostructures can be further applied for various applications, such as biomedicine, energy, sensing, etc. For example, a new targeted theranostic drug delivery system can be developed by a combination of plasmonic AuNP (for plasmonic imaging), magnetic iron oxides (for MRI imaging and targeting), porous MOF (for drug loading), and biocompatible PDA (for bioconjugating and targeting). Nanochains can be applied to promote the mixing efficiency in microfluidics, which suffer from intricate structures requiring a series of laborious fabrication processes. By using this, we can design a biomedical diagnostic testing platform. Furthermore, we can develop magneto-plasmonic heterogeneous nanostructure to have both enrichment and SERS properties to improve the detection limit.
- 3) As we discussed above, there are two general pathways to fabricate heterogeneous nanostructures, heteroexpitail growth and self-assembly. Amazingly, PDA can facilitate both of them. This indicates that we can

direct the PDA-mediated heterogeneous nanocrystals to self-assemble, or heteroexptially grow another material on assembly which is driven by PDA. In other words, heteroexpitial growth and self-assembly can be combined rationally to acquire advanced nanostructures with multiple synergistic functions.

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1. **Jiajing Zhou**, Peng Wang, Chenxu Wang, Yi Ting Goh, Zheng Fang, Phillip B. Messersmith, and Hongwei Duan. *ACS Nano*, **2015**, 9, 6951–6960.
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