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Self-Assembly of Shape-Controlled Nanoparticles into Tunable Two- Dimensional Metasurfaces at the Oil- Water Interface

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Abstract

This thesis includes my four-year researches on the fabrication of tunable two-dimensional (2D) metasurfaces by assembling shape-controlled nanoparticles at the oil-water interface. Our aim is to break the limited planar structure and achieve the high tunability of macroscopic superstructures. In Chapter 1, we summarize recent studies on the fabrication of 2D structures, self-assembly method, parameters influencing assembled structure and the application of plasmonic structure. In Chapter 2, we report a new chemical strategy of controlling surface distribution to achieve tunable metasurfaces with non-planar nanocube orientations, creating novel lattice-dependent field localization patterns. In Chapter 3, we further utilize solvent-tunable molecular-level polymer conformation changes to achieve ‘multiple metacrystals using one nanoparticle with one chemical functionality’. This method breaks the limitation of changing surface chemistry by replacing surface ligands. In Chapter 4, we study the shape-mediated structure transformation and establish a phase diagram of polyhedral particles to indicate the relationship between vertex truncation, surface functionalization, interfacial position and superstructure. In the above works, we study the interfacial behavior by understanding the interaction between particle surface and two liquid phase. In Chapter 5, we study the

particle-particle interaction to achieve the control over assembled structure by using two surface ligands with similar bulk wettability.

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1 Introduction

ABSTRACT. This chapter provides an introduction to the assembly of shape-controlled nanoparticles, particularly focusing on the fabrication of two-dimensional structures.

Following this, we introduce the thermodynamic mechanism of self-assembly at the liquid-liquid interface and summarize the past studies on the interfacial assembly. Next, we discuss the influence of different critical parameters, including particle size, morphology and surface property, on forming the assembled superstructures at the liquid-liquid interface.

Finally, we bridge the relationship between assembled structure and potential application.

We introduce the localized surface plasmon resonance of metallic nanoparticles and their coupling in the assembled structure. Assembly of metallic nanoparticles play critical role for the chemical and biological molecule sensing by performing as surface enhanced Raman scattering platform and exhibiting tunable optical properties.

1.1 FABRICATION OF TWO-DIMENSIONAL SUPERLATTICES

Nowadays, as the nanoscience and nanotechnology have been developing rapidly, the research focus in this field goes through a dramatic transformation from the synthesis of individual nanoparticle with accurate size and morphological control to the fabrication of the macroscopic two-dimensional (2D) superlattice structures via the lithography or assembly method¹⁻⁴. 2D structures, such as ordered nanostructure arrays⁵⁻⁷, surface-patterned nanostructures⁸⁻¹⁰ and free-standing patterned films^{11, 12}, have been drawing intensive attention due to the exhibition of unique pattern-dependent properties and applications. The 2D structures are promising in various technologically significant areas including electronics¹³⁻¹⁵, photonics^{13, 16, 17}, energy conversion^{18, 19}, and sensing²⁰⁻²². Accurate organization of nanoparticles on the surface or at interface is an essential step, since it facilitates the entire manufacturing process. In the following part, we will discuss several methods of nanoparticle self-assembly.

1.1.1 Top-down (lithography) method

As a typically applied physical strategy to fabricate nanoparticles in large array, lithographic arrangement of nanoparticles is also known as a top-down method²³. In general, such methods allow for the formation and precise control of particle positions to create well-

defined interparticle gaps. For instance, Alivisatos et al. exploited double electron-beam lithography in combination with a double lift-off procedure to fabricate planar, gold and palladium nanoantennas of specific shapes²⁴. The authors were able to tune the inter-particle gaps precisely from 10 nm to 90 nm to demonstrate the effect of inter-particle gap on resonance peak.

Lithography-based method is widely used to fabricate the well-packed nanoparticles on substrates. Many lithography-based methods could create the patterns by the way of pattern transfer or irradiation. First, the microcontact printing is taken as an example (Figure 1.1a)²⁵. Kumar and Whitesides were the pioneers to develop the microcontact printing technique²⁶. The colloid solution was used as ink, and then the target patterned platform with bas relief feature was printed as stamp. For the substrate, it should be good at attracting the colloids. The conformal contact between the target stamp and substrate should provide high fidelity when the ink was transferred to the substrate surface. In addition, photolithography is a well-developed approach (Figure 1.1b)²⁷. A layer of thiol-terminated polymer, which is sensitive to the light, is used to cover the substrate. Then, a mask lies on the top of the polymer layer and laser is utilized to irradiate the multilayer, resulting in the polymer layer melting. Then mask is removed. Finally, adding nanoparticles make them

attach with the thiol-terminated polymer. The photolithography could help us control the position as we design.

However, such top-down methods would require complex preparations, highly specific equipment, and are both expensive and time consuming. Moreover, it is also technically challenging to obtain single-crystalline nanoparticles from lithography, which further limits their applications.

Figure 1.1 Lithographic pattern structure fabrication. (a) Microcontact printing process. (b)

Photolithographic methods utilize a negative photoresist material and irradiation mask.

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1.1.2 Bottom-up (assembly) method

Assembling the as-prepared nanoparticles, which are normally obtained by chemically synthesis, is classified as a bottom-up approach. Nature shows various self-assembled structures, which are mimicked by using bottom-up approach for materials design and fabrication. Single-crystallinity, complex morphologies and relatively low cost are some advantages of using such an approach²⁹. Here we would like to discuss some strategies for the assembly, particularly focusing on solution-based colloidal aggregation, interfacial assembly and template arrangement. These various assembly methods discussed in Chapter 1 have different advantages and disadvantages in terms of ease of method, area of patterning, grain dimensions, ability to control interparticle spacing and arrangement (Table 1.1).

Table 1.1 Comparison of various assembly methods in terms of different parameters.

Assembly method	Ease of method	Patterning area	Ability to control interparticle spacing and arrangement
Solution based	Easy	Small area	Hard to control
Interfacial assembly	Easy	Large area	Well-controlled
Template based	Complex	Depend on template area	Hard to control

1.1.2.1 Solution-based self-assembly

Assembly can occur on the basis of colloidal solution, driven by the equilibrium of attractive and repulsive forces³⁰ and gives rise to various structures, including chains³¹⁻³³, vesicles^{34, 35}, sheets^{36, 37} and three-dimensional (3D) highly ordered crystals³⁸⁻⁴⁰. Attraction forces include covalent bonds, hydrogen bonding, depletion force, electrostatic attraction and dipole interaction. Repulsion forces involve steric repulsion and electrostatic repulsion force. Solution-based self-assembly is widely used for block copolymers, which have attracted vast attention for many decades due to its ability of generating a variety of complex structures by controlling the copolymer composition, solvent nature, and the additives (Figure 1.2)⁴¹.

Figure 1.2 Transmission electron microscopy (TEM) imaging and corresponding schemes of assembled structures composed of PS_m-b-PAA_n copolymers. Red color corresponds to hydrophobic PS and blue part means hydrophilic PAA. HHHs and LCMs are the

abbreviation of hexagonally packed hollow hoops and large compound micelles. Reprinted with permission from Chemical Society Reviews⁴¹.

By using the similar assembly strategy for block copolymer, site-specific interactions between chemically heterogeneous particles can also be utilized to achieve various superstructures. For instance, gold nanorod with hydrophilic cetyltrimethylammonium bromide (CTAB) and hydrophobic polystyrene on difference facets can be assembled into different structures with end-to-end and side-by-side configuration by varying the solvent quality⁴².

Figure 1.3 Self-assembled structure in selective solvents of gold nanorods with different polymer functionality at the end and sides. Reprinted with permission from Nature Materials⁴².

1.1.2.2 Interfacial assembly

Interfacial assembly of nanoparticle includes the assembly at liquid-air, liquid-solid and liquid-liquid interfaces. Based on the observation of Ramsden and Pickering, nanostructures

possess a large tendency to be trapped at interfaces, which hence leads to the stabilization of colloidal particles at the respective interface⁴³. Moreover, the reason that liquid interfaces can be stabilized by attachment of nanoparticles is the reduction of interfacial energy (Figure 1.4a-c, details in section 1.2).

Figure 1.4 (a) Schematic description of particle assembly at the interface. (b) Optical imaging of highly-oriented stripes of Ag nanoparticles. Scale bar, 100 μm . (c) Confocal fluorescence characterization of water-in-toluene emulsion with CdSe nanoparticles. Scale bar, 20 μm . TEM images of (d,e) different superlattice structures. Scale bars, 10 nm.

Reprinted with permission from Nature Nanotechnology⁴⁴.

Liquid interfacial assembly methods include Langmuir-Blodgett or Langmuir-Schaefer techniques⁴⁵⁻⁴⁷, and solvent evaporation or sedimentation driven assembly⁴⁸⁻⁵⁰. By utilizing Langmuir-Blodgett technique, the packing structure and packing density of nanoparticles in the 2D lattices and 1D arrays can be changed by varying the surface wetting of building blocks and the speed for withdrawing substrate, as well as the physical parameters of individual nanoparticles (Figure 1.4b)⁵¹. Solvent evaporation provides direct method to assemble highly ordered 3D structures on the solid platform, which can be mediated by van der Waals and electrostatic, dipole-dipole interactions⁵². Figure 1.4d,e exhibits the generation of different superlattices by adding oleic acid, dodecylamine or octylphosphine oxide to the particle solutions to tune their charge state⁴⁸.

1.1.2.3 Template assembly

Template is the active site that can attract nanoparticles to deposit on. Templates are divided into hard and soft templates. Hard templates include inorganic nanowires or carbon nanotubes. They provide well-defined structure for particle to assemble, but can hardly give control over the interparticle spacing and configuration. For instance, the deposition of anionic gold nanorods is on the surface of cationic carbon nanotubes⁵³⁻⁵⁵ (Figure 1.5a). Soft templates involve proteins⁵⁶, DNA⁵⁷⁻⁵⁹, polymers^{60, 61}, viruses⁶² and so on. They have

various chemical structures, which can be utilized to offer well-defined spatial distribution of specific reactive sites for the affinity of nanoparticles. This gives rise to well-controlled arrangement of the assembled particles and furthermore define the final hierarchical structures. For instance, gold nanoparticles with functionalization of DNA strands form diverse assembly structures with well-defined interparticle spacing⁵⁷. Electrostatic binding of cationic nanoparticles and anionic DNA double strand lead to the structure of linear chain, ribbons, which is composed of parallel chains, and branched 3D aggregates. (Figure 1.5b).

Figure 1.5 Template assembly of nanoparticles. (a) TEM characterization of self-assembling Au nanorods on carbon nanotube. Scale bar, 50 nm. (b-d) TEM imaging of assembling Au nanoparticles linear chain, ribbons, and branched 3D structure using DNA double strands template. Reprinted with permission from Angewandte Chemie International Edition⁵³ and Nature Materials⁵⁷.

1.2 LIQUID-LIQUID INTERFACES

The interface between oil and aqueous solution is generally termed as liquid-liquid interface, or oil/water interface. In recent years, oil/water interfaces have drawn intense attention due to its simple manipulation system for the assembly of nanoparticles. Oil/water interface is a highly-reproducible and defect-free platform for the self-assembly of various particles with different sizes, morphologies, and surface properties. These assembled structures give arise to a large amount of applications, involving catalysis, electronic, optics and molecule sensing.

1.2.1 Mechanism of liquid-liquid interfacial self-assembly

Self-assembly of nanoparticles at the liquid-liquid interface is opened up by Pickering⁶³ and has been intensively investigated for a century. The assembly of particles at curved interface forms emulsions, which are called Pickering emulsions. In the past years, planar liquid-liquid interfaces are widely utilized as ideal template for the fabrication of 2D superstructure with long-range orders widely⁶⁴⁻⁶⁷. For instance, Vanmaekelbergh et al. first observed the gold nanoparticle assembly⁶⁸. They utilized the addition of inducer to form monolayer film at the interface spontaneously. By adding ethanol, assembled layer at the

heptane-water interface exhibited the color change from pink to blue (Figure 1.6). They also reported the first transfer of interfacial layer to the solid substrate by evaporation of oil layer and horizontal or vertical lifting.

Figure 1.6 (a) Images showing the change from pink-color Au aqueous phase covered with heptane to the blue-color Au assembled layer at the heptane-water interface via the addition of ethanol. (b) TEM characterization of gold nanoparticle assembled 2D monolayer.

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Based on Pieranski's thermodynamics theory, the organization of nanoparticles at the planar liquid-liquid interface is driven by the lowering of interfacial tension, which is also the reduction of total free energy^{69, 70}. Before the addition of nanoparticles, total free energy is the oil/water interfacial energy. After dispersing particle solution at the interface, oil-water interface changes to particle-oil and particle-water interface, giving rise to the interfacial energy change (Figure 1.7). The variation of total free energy is contributed by three factors, particle-oil, particle-water and particle-particle interactions, arising from the interface changes. By combining Pieranski's thermodynamics model with Yong's equation, the change of total free energy is described as follows^{52, 69}:

$$\Delta E = -\pi R^2(\gamma_{OW} - (\gamma_{PW} - \gamma_{PO}))^2 \quad (1)$$

Figure 1.7 Interfacial tension variation at the oil/water interface due to the nanoparticle assembly. Reprinted with permission from Angewandte Chemie International Edition⁷¹

where γ_{OW} , γ_{PW} , and γ_{PO} correspond to the oil-water, particle-water and particle-oil interfacial tension respectively. And R represents the radius of spherical particles. Based on this equation, the total energy achieves negative change ΔE after adding the nanoparticle to the interface. Thereby the assembled structure at the oil/water interface is determined by a minimization of the total free energy, which is mainly affected by physical feature of nanoparticles and their surface chemistry.

1.2.2 Oil/water interfacial assembled structure

In recent years, researchers have done intensive studies to fabricate well-controlled oil-water interfacial assembled structure with excellent physical and chemical properties. Since Vanmaekelbergh group first achieved the observation of Au nanoparticle self-assembly at oil-water interface, Wang et al. made further remarkable achievements on the assembly of

hydrophilic-ligand-modified Au and Ag nanoparticles at the toluene/water interface⁷²⁻⁷⁷.

They demonstrated that the stability of nanoparticles at the interface was only achieved at the contact angle of 90°. Significantly, they first used the addition of ethanol as inducer and successfully fabricated a close-packed structure of freestanding Au nanoparticles (Figure 1.8a-c). Sun et al. also studied the self-assembly of Au, Pt, and SiO₂ nanoparticles at the toluene/water interface into ordered structure⁷⁸. Park's group reported a systematic study on the nanoparticle interfacial assembly⁷⁹⁻⁸¹. At the hexane/water interface, Au nanoparticles were assembled into 2D film. After the evaporation of hexane phase, the as-formed large-area film was packed until a mirror reflection was observed (Figure 1.8d). Multiple transferring processes resulted in the multilayer formation with well-defined layer thickness. They observed the blue reflection from the monolayer structure and increment of layer number lead to the increase of the film darkness (Figure 1.8e). Furthermore, highly-ordered assembled structure formed with an in-situ particle surface modification with a small amount of 1-dodecanethiol. The adsorption of 1-dodecanethiol onto particle surface changed the particle surface charge, leading to the reduction of electrostatic repulsive force between nanoparticles and thus favoring the formation of close-packed assembled structure. Higher amount of 1-dodecanethiol caused apparent aggregation of the nanoparticles (Figure 1.8f).

Figure 1.8 Recent studies on interfacial assembly. Optical image of assembled structure of free standing Au nanoparticles (a) at the toluene/water interface and (b) on the transferred film. (c) The corresponding TEM images. Optical images of assembled film with different layer thickness of Au nanoparticle (d) at hexane/water interface and (e) on ITO-coated glass slide. (f) Scanning electron microscope (SEM) images of eight-layer film. Reprinted with permission from Chemical Society Reviews⁸².

In these years, Yang and Xia group have developed many close-packed arrays and discussed the assembly work involving shape-controlled Ag nanoparticles as the example. They have generated close-packed monolayer and 3D structure of different polyhedral nanoparticles and 2D cluster of nanorods, nanospheres by tuning the size, morphology and material of building blocks^{23, 45, 47, 51}.

More recently, tunability of superstructures becomes the research focus in the self-assembly field. In Lee et al.'s work⁸³, surface chemistry was controlled by changing the surface alkylthiols or tuning the molecule distribution in the mixed monolayer. In this

strategy, surface chemistry was well-tuned from hydrophilicity to hydrophobicity (Figure 1.9a) and thus the interfacial behavior of nanoparticles was well-controlled in terms of interfacial configuration and position. Thus the assembled structure went through a structural transformation from planar hexagonal close-packed to standing square structure (Figure 1.9b,c). This work opened up the new approach to form the novel standing structure and achieve the continuous structural changes.

Figure 1.9 (a) Control over the wettability of particle surface by changing surface functionalization. (b-c) SEM and corresponding schematic description of corresponding assembled structure. Reprinted with permission from Nature Communications⁸³.

1.3 PARAMETER AFFECTING ASSEMBLED SUPERSTRUCTURE

1.3.1 Size of building blocks

Based on equation (1), ΔE is proportional to particle radius R . Hence particles at the interface are able to achieve larger ΔE and the assembly is more stable for larger size than for smaller size^{43, 52, 84, 85}. For the particles with large size, the decrease in the total energy

is much larger than the thermal energy, kBT , leading to the strong absorption of particles at the liquid-liquid interface. For particles with small size, thermal energy is higher than the energy reduction, resulting in the nanoparticle displacement from the interface. Thus particles are dynamically adsorbed to and desorbed from oil/water interfaces and the assembly of small-sized nanoparticles is dynamic. Therefore, this liquid-liquid interfacial self-assembly is significantly dependent on the size of building blocks. Russell et al. observed no droplet stabilization at curved liquid-liquid interface due to thermal fluctuation when the particles have diameter less than 1.6 nm⁵². In this study, CdSe nanoparticles are dispersed in toluene and then a water droplet with diameter of $\sim 20\text{ }\mu\text{m}$, was dispersed in toluene. Fluorescence image (Figure 1.10a) exhibited the segregation of nanoparticles to the toluene/water interface, as well as the formation of monolayer at the interface. By adjusting the water amount, they observed nanoparticle-coated water droplets with diameters from 10 to 100 μm (Figure 1.10b). They further introduced 4.6 nm CdSe particles (green, fluoresce at 610 nm) into water-in-toluene system stabilized with 2.8-nm particle (red, fluoresce at 525 nm, Figure 1.10c). Larger particles assembled on the surface of an existing water droplet in the toluene, displacing the smaller particles. However, smaller nanoparticles were unable to displace larger ones. This result demonstrated the size-dependent assembly at the oil/water interface.

Figure 1.10 Fluorescence confocal microscopy characterization of water-in-toluene emulsion with the encapsulation of CdSe nanoparticles with different sizes. Scale bar, (a,b) 20 nm; (c) 16 nm. Reprinted with permission from Chemical Society Reviews⁸².

1.3.2 Shape of building blocks

Non-spherical nanoparticles exhibit different shape-dependent self-assembled structures compared with spherical nanostructures⁸⁶. Particle orientation and interparticle configuration dependent self-assembly has been investigated for many years. Formation of various crystal, plastic crystalline and liquid-crystalline structures, including cylinder, nematic and smectic lattices, bundle and linear structures are achieved by utilizing rod and plate⁸⁷⁻⁹¹, wire and tube^{92, 93} shapes. Current synthetic technology for different anisotropic shapes provides the opportunity to proceed theoretical predictions and experimental investigation on the ordering of nanomaterials.

Gong et al utilized the combination of experimental and simulation studies for Au nanoparticles with the spherical, cubic, octahedral and rhombic dodecahedral morphology⁹⁴. They used the sedimentation and solvent evaporation method to study the transformation from disordered suspension to large-scale ordered self-assembled structures (Figure 1.11). They indicated the strong dependence of the ultimate coherence length of superstructure on nanoparticle morphology, as well as the factors that had the negative influence on the formation of high-quality superstructures. Recently Stam et al demonstrated that only a small vertex truncation is sufficient to influence the superstructure symmetry from hexagonal to tetragonal structure by experimental and theoretical investigation on the self-assembly of hexagonal bipyramid- and bipyramid ZnS nanoparticles⁹⁵. Their work highlighted the crucial role of nanoscale shape control to the symmetry of macroscopic structures.

Figure 1.11 Large-area assembled superstructures using gold nanoparticles with different morphologies, including rhombic dodecahedra, octahedra, cubes and spheres. Reprinted with permission from Nature Communications⁹⁴.

1.3.3 Surface chemistry of building blocks

Colloidal nanoparticles remain their stability in the dispersed status due to the dominant repulsive interparticle potential. Surface ligands (e.g., hydrocarbon surfactants, alkylthiols, polymers) on the nanoparticle surfaces achieve the steric stability, while the charged ligand provides the electrostatic stability. These two fundamental mechanisms of particle stabilization provide complementary approaches to disperse nanoparticles in different solvents.

The assembly of nanoparticle is induced by the change of effective interparticle interaction from repulsive to attractive. Complete freeze of nanoparticles into superlattice with interparticle separation at the interface is due to the balance between attraction forces between nanoparticle cores and repulsion between surface ligands. Thus apart from the physical feature of building block, their surface chemistry also plays great significance in their assembly.

Surface wettability is utilized to influence particle-liquid interaction due to the surface ligands⁸³ (Figure 1.9a). As the surface increased the hydrophobicity, the nanoparticle interaction with oil phase increased and hence the octahedral nanoparticle reduced the contact with oil phase forming standing configuration (Figure 1.9b). The effect of the surface charge on particle interfacial behavior was also studied⁹⁶. They observed the nanoparticle assembly at the interface and the particle detachment from the interface at low and high pH value respectively (Figure 1.12). This was due to the protonation and deprotonation of the carboxylic group on particle surface. This work demonstrated the influence of surface charge density, whose increase reduced particle interfacial interaction and enhanced the electrostatic repulsion between the neighboring charged particles.

Figure 1.12 Photographs of nanoparticle assembly and detachment at the oil/water interface at different pH values. Reprinted with permission from Physical Chemistry Chemical Physics⁹⁶.

1.4 APPLICATIONS OF PLASMONIC NANOPARTICLE METACRYSTAL

1.4.1 Localized surface plasmon resonance (LSPR) of metallic nanoparticles

Metallic nanoparticles exhibit excellent abilities to manipulate nanoscale light-matter interactions, which is due to the localized surface plasmon resonance (LSPR) from metallic nanoparticles^{97, 98}. Surface plasmon resonance (SPR) is defined as the oscillation of free electrons by the excitation of electromagnetic radiation (such as light) on the metal nanoparticle surfaces. For LSPR, light interacts with a metallic nanoparticle whose size is smaller than its incident wavelengths, so that the resulting oscillation of free electrons is confined to a limited volume surrounding the nanoparticles (Figure 1.13). Metallic nanoparticles supporting surface plasmon resonance are known as plasmonic nanoparticles, such as Ag and Au nanostructures. Due to the surface plasmon oscillations at the LSPR frequency, the electromagnetic fields are strongly concentrated and enhanced at the surfaces of nanoparticles. The regions with greatly localized and enhanced electromagnetic fields are known as “hot spots”.

Figure 1.13 Scheme description of localized surface plasmon resonance (LSPR). Reprinted with permission from Annual Review of Physical Chemistry⁹⁷.

Plasmonic nanoparticles supporting LSPR are of interest for various researches due to their potential applications. The application of LSPR properties can be traced back to the medieval times⁹⁹. Plasmon light scattering of embedded gold nanoparticles led to the brilliantly colored stained glass windows of Notre-Dame de Paris. However, this phenomenon remained largely unstudied until a century ago when German physicist Gustav Mie applied Maxwell's equations to illustrate the strong absorption of light by gold nanoparticles with subwavelength sizes¹⁰⁰. This discovery paved the way for scientists to pursue for in-depth understanding of the unique SPR phenomenon. Nowadays, with the ability to localize and convert light to energy, metallic nanostructures are widely utilized to improve the device performance, including tunable optical properties, biological and chemical sensing, two-photon luminescence, information storage and photodetector.

1.4.2 Molecule sensing and SERS platform

The assembly of nanoparticles makes them sufficiently close to each other, which leads to the coupling of the surface plasmons between the neighboring nanoparticles and the enhanced hot spots or electromagnetic field in the vicinity of the nanoparticles^{101, 102}. This

coupling is due to the electromagnetic energy transfer and confinement. For nanoparticles with strong interparticle interaction, researchers have used Mie theory to simply predict the absorption properties of nanoparticle assembly. Effective medium theories¹⁰³, modified versions of Mie theories¹⁰⁴ or numerical simulations (for example, the finite-difference time-domain method)^{105, 106} are widely utilized to more effectively describe the electromagnetic field enhancement of assembled structure. LSPR frequencies and electromagnetic field are sensitive to the changes in local dielectric environment, which is determined by the particle configuration in the assembled structure. Thereby the assembled structure can be used for sensing and the difference of particle configuration determines the sensitivity of biological- or chemical- molecule sensing.

Raman scattering from molecules which are placed near or absorbed on the plasmonic nanoparticles is reported to be proportional to the electromagnetic field intensity. The Raman scattering intensity enhancement of such molecules is well-known as surface-enhanced Raman scattering (SERS) enhancement^{107, 108}. The advantage of SERS for molecule sensing in comparison with other traditional sensing technology (such as mass spectroscopy, gas chromatography) is much higher sensitivity. Thus current research mainly focuses on the achievement of ultra-high sensitivity and convenient sensing large-scale platform. For instance, standing cube and octahedral nanoparticles exhibited higher

SERS enhancement factor, indicating more efficient sensing of absorbed molecule on the surfaces^{30, 105}. Close-packed monolayer of Au nanoprisms (Figure 1.14) was proved to give strong SERS signals owing to the generation of large numbers of hot spots in the tip-to-tip and edge-to-edge inter-prism gaps¹⁰⁹.

Figure 1.14 Molecule sensing by using the nanoprism monolayers deposited on different substrates. (a) Schematic description of (i) thermo-evaporated Au film, (ii) monolayer-over-dielectric, and (iii) monolayer-over-mirror. (b) SERS spectra by using different platform.

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1.4.3 Tunable optical properties

The Lycurgus cup exhibited the changing of different colors, which was an ancient application of plasmonic nanoparticles¹¹⁰. The cup showed green color which was observed from front view due to the scattering light, but it showed red color from behind view due to

the transmission. Analysis on the Lycurgus cup composition revealed the presence of 70-nm Ag-Au alloy nanoparticles. Thus different color appearance was owing to the enhanced far-field absorption and scattering at the LSPR frequencies of these nanoparticles.

The optical properties of the superstructures of anisotropic metallic nanoparticles depends on the control over the orientation and configuration of nanoparticles. This structure determines the spatial distribution of charge polarizations, which influences the splitting of plasmon bands. For example, the anisotropic nanorods assemble into side-by-side and end-to-end configuration. The side-by-side organization of nanorods leads to blue shift of longitudinal plasmon band and redshift of transverse plasmon band, while the plasmon coupling between end-to-end nanorods gives rise to redshift of the longitudinal plasmon band⁴². Collective optical properties of self-assembled structures of metal nanoparticles with different polyhedral morphologies have also been studied⁴⁷. Optical transmission and reflectance measurements demonstrated that different symmetries of nanoparticle assembly contributed to the interaction of light with the nanoparticle assembly monolayer. The difference of individual nanoparticle surface plasmon modes due to different shapes, as well as the configuration in which they are assembled, leads to their unique collective plasmonic properties in each assembled film.

1.5 MOTIVATION AND OBJECTIVES

In the nanoscience and nanotechnology, systematic fabrication of self-assembled functional metamaterials is a key field in leading future technology development. Various self-assembly techniques have been widely adopted for the systematic fabrication of functional nanomaterials and received an extensive research attention. In this chapter, we have introduced different self-assembly methods for the fabrication of two-dimensional superstructures, the parameters being used to control the particle orientation, interparticle configuration and assembled structures, as well as their properties and possible application.

Generally, one major limitation of past plasmonic metasurfaces of polyhedral nanoparticles is their planar configurations and the ability to create tailored local electromagnetic fields. Programming of the large-area assembly of one type of anisotropic particle have not been extensively investigated to generate tunable self-assembled superstructures, particularly in the fabrication of non-close-packed structures. Thereby it is significant to achieve large-area metasurfaces with non-planar building blocks to bridge the gap between nanomaterials and macroscopic applications, which enables the control over the periodic manipulation of light over macroscopic length scales.

Based on the current challenge in this field, our objective is to achieve the tunability of assembled two-dimensional metasurfaces by controlling the nanoscale surface chemistry

and building block morphology. Our studies focus on Ag polyhedral nanoparticles because Ag supports high strength of surface plasmon resonances without damping induced by interband transition in the visible range and the well-defined facets with facet-dependent properties. Moreover, SERS is the potential application and we use our assembled structure as novel SERS platform for the enhancement of sensing efficiency.

In this thesis, we firstly utilize the mixed monolayer formation of hydrophilic/hydrophobic molecules with well-controlled ratio on Ag nanocube surfaces to manipulate nanocube configuration at the oil-water interface. This work opens up an innovative strategy for the fabrication of open superstructures composed of non-planar nanocubes (Chapter 2). Secondly, we further utilize the solvent-tunable molecular-level polymer conformation changes in the mixed monolayer to continuously modulate the particle interfacial behavior without changing the surface functionality group. Thereby this provides a novel method to achieve unprecedented tunability of metasurface structure (Chapter 3). Thirdly, we furthermore the effect of surface chemistry on different particle morphologies. Thus we report on the shape-dependent two-dimensional assembly transformation by changing surface chemistry, and establish phase diagram for Ag polyhedral nanoparticles. The establishment of phase diagram of polyhedral nanoparticles provides the possibility for the development of a framework that allows the design and

fabrication of tailored superstructures. Finally, we study the nanoscale effect of surface polymer with similar bulk property on the particle interfacial behavior and macroscopic structure. by controlling the nanoscale surface structure, we achieve the control over macroscopic structure. This fundamental study provides new possibility for control over macroscopic structures.

1.6 REFERENCES

1. Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annul. Rev. Mater. Sci.* **2000**, *30*, 545-610.
2. Boles, M. A.; Engel, M.; Talapin, D. V. *Chem. Rev.* **2016**, *116*, 11220-11289.
3. C. P. Collier; T. Vossmeier, a.; Heath, J. R. *Annu. Rev. Phys. Chem.* **1998**, *49*, 371-404.
4. Min, Y.; Akbulut, M.; Kristiansen, K.; Golan, Y.; Israelachvili, J. *Nat. Mater.* **2008**, *7*, 527-538.
5. Brune, H.; Giovannini, M.; Bromann, K.; Kern, K. *Nature* **1998**, *394*, 451-453.
6. Choi, H. K.; Kim, M. H.; Im, S. H.; Park, O. O. *Adv. Funct. Mater.* **2009**, *19*, 1594-1600.
7. Wei, X.; Chen, X.; Jiang, K. *Nanoscale Res Lett* **2010**, *6*, 25.
8. Wang, H.; Wang, Z.; Huang, L.; Mitra, A.; Yan, Y. *Langmuir* **2001**, *17*, 2572-2574.

9. Kubicova, I.; Pudis, D.; Skriniarova, J.; Kovac, J.; Jaroslav, K.; Jakabovic, J.; Suslik, L.; Novak, J.; Kuzma, A. *Appl. Surf. Sci.* **2013**, *269*, 116-119.
10. Koh, J. K.; Jeon, Y.; Cho, Y. I.; Kim, J. H.; Shul, Y.-G. *J. Phys. Chem. A* **2014**, *2*, 8652-8659.
11. Greco, F.; Zucca, A.; Taccola, S.; Mazzolai, B.; Mattoli, V. *ACS Appl. Mater. Inter.* **2013**, *5*, 9461-9469.
12. Buck, M. E.; Lynn, D. M. *Langmuir* **2010**, *26*, 16134-16140.
13. Ozbay, E. *Science* **2006**, *311*, 189-193.
14. Murray, R. W. *Chem. Rev.* **2008**, *108*, 2688-2720.
15. Turk, M. E.; Vora, P. M.; Fafarman, A. T.; Diroll, B. T.; Murray, C. B.; Kagan, C. R.; Kikkawa, J. M. *ACS Nano* **2015**, *9*, 1440-1447.
16. Lin, Q.-Y.; Li, Z.; Brown, K. A.; O'Brien, M. N.; Ross, M. B.; Zhou, Y.; Butun, S.; Chen, P.-C.; Schatz, G. C.; Dravid, V. P.; Aydin, K.; Mirkin, C. A. *Nano Lett.* **2015**, *15*, 4699-4703.
17. Konstantatos, G.; Sargent, E. H. *Nat. Nanotechnol.* **2010**, *5*, 391-400.
18. Lan, X.; Voznyy, O.; García de Arquer, F. P.; Liu, M.; Xu, J.; Proppe, A. H.; Walters, G.; Fan, F.; Tan, H.; Liu, M.; Yang, Z.; Hoogland, S.; Sargent, E. H. *Nano Lett.* **2016**, *16*, 4630-4634.

19. Rowland, C. E.; Fedin, I.; Zhang, H.; Gray, S. K.; Govorov, A. O.; Talapin, D. V.; Schaller, R. D. *Nat. Mater.* **2015**, *14*, 484-489.
20. Lee, J.; Hernandez, P.; Lee, J.; Govorov, A. O.; Kotov, N. A. *Nat. Mater.* **2007**, *6*, 291-295.
21. Chang, Y.; Tang, N.; Qu, H.; Liu, J.; Zhang, D.; Zhang, H.; Pang, W.; Duan, X. *Nat. Nanotech.* **2016**, *6*, 23970.
22. Cecchini, M. P.; Turek, V. A.; Demetriadou, A.; Britovsek, G.; Welton, T.; Kornyshev, A. A.; Wilton-Ely, J. D. E. T.; Edel, J. B. *Adv. Optical Mater.* **2014**, *2*, 966-977.
23. Rycenga, M.; Cobley, C. M.; Zeng, J.; Li, W.; Moran, C. H.; Zhang, Q.; Qin, D.; Xia, Y. *Chem. Rev.* **2011**, *111*, 3669-3712.
24. Liu, N.; Tang, M. L.; Hentschel, M.; Giessen, H.; Alivisatos, A. P. *Nat. Mater.* **2011**, *10*, 631-636.
25. Nie, Z.; Kumacheva, E. *Nat. Mater.* **2008**, *7*, 277-290.
26. Kumar, A.; Whitesides, G. M. *Appl. Phys. Lett.* **1993**, *63*, 2002-2004.
27. Acikgoz, C.; Hempenius, M. A.; Huskens, J.; Vancso, G. J. *Eur. Polym. J.* **2011**, *47*, 2033-2052.
28. Kaufmann, T.; Ravoo, B. J. *Polym. Chem.* **2010**, *1*, 371-387.
29. Boles, M. A.; Engel, M.; Talapin, D. V. *Chem. Rev.* **2016**, *116*, 11220-11289.

30. Bishop, K. J. M.; Wilmer, C. E.; Soh, S.; Grzybowski, B. A. *Small* **2009**, *5*, 1600-1630.
31. DeVries, G. A.; Brunnbauer, M.; Hu, Y.; Jackson, A. M.; Long, B.; Neltner, B. T.; Uzun, O.; Wunsch, B. H.; Stellacci, F. *Science* **2007**, *315*, 358-361.
32. Kang, Y.; Erickson, K. J.; Taton, T. A. *J. Am. Chem. Soc.* **2005**, *127*, 13800-13801.
33. Caswell, K. K.; Wilson, J. N.; Bunz, U. H. F.; Murphy, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 13914-13915.
34. Park, S.; Lim, J.-H.; Chung, S.-W.; Mirkin, C. A. *Science* **2004**, *303*, 348-351.
35. Nikolic, M. S.; Olsson, C.; Salcher, A.; Kornowski, A.; Rank, A.; Schubert, R.; Frömsdorf, A.; Weller, H.; Förster, S. *Angew. Chem. Int. Ed.* **2009**, *48*, 2752-2754.
36. Tang, Z.; Zhang, Z.; Wang, Y.; Glotzer, S. C.; Kotov, N. A. *Science* **2006**, *314*, 274-278.
37. Zhao, N.; Liu, K.; Greener, J.; Nie, Z.; Kumacheva, E. *Nano Lett.* **2009**, *9*, 3077-3081.
38. Kalsin, A. M.; Fialkowski, M.; Paszewski, M.; Smoukov, S. K.; Bishop, K. J. M.; Grzybowski, B. A. *Science* **2006**, *312*, 420-424.
39. Iacovella, C. R.; Glotzer, S. C. *Nano Lett.* **2009**, *9*, 1206-1211.
40. Park, S. Y.; Lytton-Jean, A. K. R.; Lee, B.; Weigand, S.; Schatz, G. C.; Mirkin, C. A. *Nature* **2008**, *451*, 553-556.
41. Mai, Y.; Eisenberg, A. *Chem. Soc. Rev.* **2012**, *41*, 5969-5985.

42. Nie, Z.; Fava, D.; Kumacheva, E.; Zou, S.; Walker, G. C.; Rubinstein, M. *Nat. Mater.* **2007**, *6*, 609-614.
43. Boker, A.; He, J.; Emrick, T.; Russell, T. P. *Soft Matt.* **2007**, *3*, 1231-1248.
44. Nie, Z.; Petukhova, A.; Kumacheva, E. *Nat. Nanotechnol.* **2010**, *5*, 15-25.
45. Tao, A. R.; Huang, J.; Yang, P. *Acc. Chem. Res.* **2008**, *41*, 1662-1673.
46. Collier, C. P.; Saykally, R. J.; Shiang, J. J.; Henrichs, S. E.; Heath, J. R. *Science* **1997**, *277*, 1978-1981.
47. Tao, A.; Sinsermsuksakul, P.; Yang, P. *Nat. Nanotechnol.* **2007**, *2*, 435-440.
48. Shevchenko, E. V.; Talapin, D. V.; Kotov, N. A.; O'Brien, S.; Murray, C. B. *Nature* **2006**, *439*, 55-59.
49. Courty, A.; Mermet, A.; Albouy, P. A.; Duval, E.; Pileni, M. P. *Nat. Mater.* **2005**, *4*, 395-398.
50. Cheng, W.; Campolongo, M. J.; Cha, J. J.; Tan, S. J.; Umbach, C. C.; Muller, D. A.; Luo, D. *Nat. Mater.* **2009**, *8*, 519-525.
51. Huang, J.; Kim, F.; Tao, A. R.; Connor, S.; Yang, P. *Nat. Mater.* **2005**, *4*, 896-900.
52. Lin, Y.; Skaff, H.; Emrick, T.; Dinsmore, A. D.; Russell, T. P. *Science* **2003**, *299*, 226-229.

53. Correa-Duarte, M. A.; Pérez-Juste, J.; Sánchez-Iglesias, A.; Giersig, M.; Liz-Marzán, L. M. *Angew. Chem. Int. Ed.* **2005**, *44*, 4375-4378.
54. Georgakilas, V.; Gournis, D.; Tzitzios, V.; Pasquato, L.; Guldi, D. M.; Prato, M. *J. Mater. Chem.* **2007**, *17*, 2679-2694.
55. Engtrakul, C.; Kim, Y.-H.; Nedeljković, J. M.; Ahrenkiel, S. P.; Gilbert, K. E. H.; Alleman, J. L.; Zhang, S. B.; Mičić, O. I.; Nozik, A. J.; Heben, M. J. *J. Phys. Chem. B* **2006**, *110*, 25153-25157.
56. Ryadnov, M. G.; Woolfson, D. N. *J. Am. Chem. Soc.* **2004**, *126*, 7454-7455.
57. Warner, M. G.; Hutchison, J. E. *Nat. Mater.* **2003**, *2*, 272-277.
58. Seeman, N. C. *Nature* **2003**, *421*, 427-431.
59. Aldaye, F. A.; Palmer, A. L.; Sleiman, H. F. *Science* **2008**, *321*, 1795-1799.
60. Wang, H.; Lin, W.; Fritz, K. P.; Scholes, G. D.; Winnik, M. A.; Manners, I. *J. Am. Chem. Soc.* **2007**, *129*, 12924-12925.
61. Zhang, Q.; Gupta, S.; Emrick, T.; Russell, T. P. *J. Am. Chem. Soc.* **2006**, *128*, 3898-3899.
62. Dujardin, E.; Peet, C.; Stubbs, G.; Culver, J. N.; Mann, S. *Nano Lett.* **2003**, *3*, 413-417.
63. Pickering, S. U. *J. Chem. Soc., Trans.* **1907**, *91*, 2001-2021.

64. Dinsmore, A. D.; Hsu, M. F.; Nikolaides, M. G.; Marquez, M.; Bausch, A. R.; Weitz, D. A. *Science* **2002**, *298*, 1006-1009.
65. Velez, O. D.; Furusawa, K.; Nagayama, K. *Langmuir* **1996**, *12*, 2374-2384.
66. Aveyard, R.; Binks, B. P.; Clint, J. H. *Adv. Colloid Interface Sci.* **2003**, *100*, 503-546.
67. Booth, S. G.; Dryfe, R. A. W. *J. Phys. Chem. C* **2015**, *119*, 23295-23309.
68. Reincke, F.; Hickey, S. G.; Kegel, W. K.; Vanmaekelbergh, D. *Angew. Chem. Int. Ed.* **2004**, *43*, 458-462.
69. Pieranski, P. *Phys. Rev. Lett.* **1980**, *45*, 569-572.
70. Binks, B. P.; Clint, J. H. *Langmuir* **2002**, *18*, 1270-1273.
71. Binder, W. H. *Angew. Chem. Int. Ed.* **2005**, *44*, 5172-5175.
72. Wang, D.; Mohwald, H. *J. Mater. Chem.* **2004**, *14*, 459-468.
73. Duan, H.; Wang, D.; Kurth, D. G.; Möhwald, H. *Angew. Chem. Int. Ed.* **2004**, *43*, 5639-5642.
74. Wang, J.; Wang, D.; Sobal, N. S.; Giersig, M.; Jiang, M.; Möhwald, H. *Angew. Chem. Int. Ed.* **2006**, *45*, 7963-7966.
75. Xia, H.; Wang, D. *Adv. Mater.* **2008**, *20*, 4253-4256.
76. Wang, D.; Duan, H.; Mohwald, H. *Soft Matter* **2005**, *1*, 412-416.
77. Mao, Z.; Xu, H.; Wang, D. *Adv. Func. Mater.* **2010**, *20*, 1053-1074.

78. Li, Y.-J.; Huang, W.-J.; Sun, S.-G. *Angew. Chem. Int. Ed.* **2006**, *45*, 2537-2539.
79. Park, Y.-K.; Yoo, S.-H.; Park, S. *Langmuir* **2007**, *23*, 10505-10510.
80. Park, Y.-K.; Park, S. *Chem. Mater.* **2008**, *20*, 2388-2393.
81. Park, Y.-K.; Yoo, S.-H.; Park, S. *Langmuir* **2008**, *24*, 4370-4375.
82. Hu, L.; Chen, M.; Fang, X.; Wu, L. *Chem. Soc. Rev.* **2012**, *41*, 1350-1362.
83. Lee, Y. H.; Shi, W.; Lee, H. K.; Jiang, R.; Phang, I. Y.; Cui, Y.; Isa, L.; Yang, Y.; Wang, J.; Li, S.; Ling, X. Y. *Nat. Commun.* **2015**, *6*, 6990.
84. Lin, Y.; Skaff, H.; Böker, A.; Dinsmore, A. D.; Emrick, T.; Russell, T. P. *J. Am. Chem. Soc.* **2003**, *125*, 12690-12691.
85. Lin, Y.; Böker, A.; Skaff, H.; Cookson, D.; Dinsmore, A. D.; Emrick, T.; Russell, T. P. *Langmuir* **2005**, *21*, 191-194.
86. Jana, N. R. *Angew. Chem. Int. Ed.* **2004**, *43*, 1536-1540.
87. Livolant, F.; Levelut, A. M.; Doucet, J.; Benoit, J. P. *Nature* **1989**, *339*, 724-726.
88. Buining, P. A.; Philipse, A. P.; Lekkerkerker, H. N. W. *Langmuir* **1994**, *10*, 2106-2114.
89. Dogic, Z.; Fraden, S. *Phys. Rev. Lett.* **1997**, *78*, 2417-2420.
90. Li, L.-s.; Walda, J.; Manna, L.; Alivisatos, A. P. *Nano Lett.* **2002**, *2*, 557-560.
91. van der Kooij, F. M.; Kassapidou, K.; Lekkerkerker, H. N. W. *Nature* **2000**, *406*, 868-871.

92. Vigolo, B.; Pénicaud, A.; Coulon, C.; Sauder, C.; Pailler, R.; Journet, C.; Bernier, P.; Poulin, P. *Science* **2000**, *290*, 1331-1334.
93. Yu, S.-H.; Antonietti, M.; Cölfen, H.; Hartmann, J. *Nano Lett.* **2003**, *3*, 379-382.
94. Gong, J.; Newman, R. S.; Engel, M.; Zhao, M.; Bian, F.; Glotzer, S. C.; Tang, Z. *Angew. Chem. Int. Ed.* **2017**, *8*, 14038.
95. Van der Stam, W.; Gantapara, A. P.; Akkerman, Q. A.; Soligno, G.; Meeldijk, J. D.; van Roij, R.; Dijkstra, M.; de Mello Donega, C. *Nano Lett.* **2014**, *14*, 1032-1037.
96. Reincke, F.; Kegel, W. K.; Zhang, H.; Nolte, M.; Wang, D.; Vanmaekelbergh, D.; Mohwald, H. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3828-3835.
97. Willems, K. A.; Duyne, R. P. V. *Annu. Rev. Phys. Chem.* **2007**, *58*, 267-297.
98. Novotny, L.; van Hulst, N. *Nat. Photon.* **2011**, *5*, 83-90.
99. Feynman, R. P. *Polym. Eng. Sci.* **1960**, *23*, 22-36.
100. Mie, G. *Annalen der Physik* **1908**, *330*, 377-445.
101. von Cube, F.; Irsen, S.; Diehl, R.; Niegemann, J.; Busch, K.; Linden, S. *Nano Lett.* **2013**, *13*, 703-708.
102. Guo, L.; Ferhan, A. R.; Chen, H.; Li, C.; Chen, G.; Hong, S.; Kim, D.-H. *Small* **2013**, *9*, 234-240.
103. Zhang, X.; Wu, Y. *Angew. Chem. Int. Ed.* **2015**, *5*, 7892.

104. Doicu, A.; Ebert, F.; Schabel, S. *Part. Part. Syst. Char.* **1996**, *13*, 79-88.
105. Yang, Y.; Lee, Y. H.; Phang, I. Y.; Jiang, R.; Sim, H. Y. F.; Wang, J.; Ling, X. Y. *Nano Lett.* **2016**, *16*, 3872-3878.
106. Jiang, R.; Qin, F.; Liu, Y.; Ling, X. Y.; Guo, J.; Tang, M.; Cheng, S.; Wang, J. *Adv. Mater.* **2016**, *28*, 6322-6331.
107. Braun, G.; Lee, S. J.; Dante, M.; Nguyen, T.-Q.; Moskovits, M.; Reich, N. *J. Am. Chem. Soc.* **2007**, *129*, 6378-6379.
108. Zhang, X.-Y.; Hu, A.; Zhang, T.; Lei, W.; Xue, X.-J.; Zhou, Y.; Duley, W. W. *ACS Nano* **2011**, *5*, 9082-9092.
109. Lee, Y. H.; Lee, C. K.; Tan, B.; Rui Tan, J. M.; Phang, I. Y.; Ling, X. Y. *Nanoscale* **2013**, *5*, 6404-6412.
110. Montelongo, Y.; Tenorio-Pearl, J. O.; Williams, C.; Zhang, S.; Milne, W. I.; Wilkinson, T. D. P. *Natl. Acad. Sci.* **2014**, *111*, 12679-12683.

2 A Chemical Approach to Break the Planar Configuration of Ag Nanocubes into Tunable Two-dimensional Metasurfaces**

ABSTRACT. Current plasmonic metasurfaces of nanocubes are limited to planar configurations, restricting the ability to create tailored local electromagnetic fields. Here, we report a new chemical strategy to achieve tunable metasurfaces with non-planar nanocube orientations, creating novel lattice-dependent field localization patterns. We manipulate the interfacial behaviors of Ag nanocubes by controlling the ratio of hydrophilic/hydrophobic molecules added in a binary thiol mixture during the surface functionalization step. The nanocube orientation at an oil/water interface can consequently be continuously tuned from planar to tilted and standing configurations, leading to the organization of Ag nanocubes into three unique large-area metacrystals, including square close-packed, linear, and hexagonal lattices. In particular, the linear and hexagonal metacrystals are unusual open lattices comprising non-planar nanocubes, creating unique local electromagnetic field distribution patterns. Large-area ‘hot hexagons’ with significant delocalization of hot spots forms in the hexagonal metacrystal. With a lowest packing density of 24 %, the hexagonal metacrystal generates nearly 350-fold stronger surface-

enhanced Raman scattering as compared to the other denser-packing metacrystals, demonstrating the importance of achieving control over the geometrical and spatial orientation of the nanocubes in the metacrystals.

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2.1 INTRODUCTION

Cubic nanoparticles belong to a class of unique shape-controlled nanoparticles known as Platonic solids¹. Despite their high symmetry (point group O_h), nanocubes exhibit distinct anisotropic properties along different crystallographic directions, such as preferred magnetization axes^{2,3}, higher catalytic activities on (100) facets⁴. Nanocubes have also been organized into various clusters⁵⁻¹⁰, exhibiting collective optical¹¹⁻¹⁴, electronic¹⁵⁻¹⁷, and magnetic¹⁸⁻²¹ properties distinct from bulk materials and their building blocks. In plasmonics, individual nanocubes support various complex high-order surface plasmon resonance modes arising from the anisotropic charge polarization and distribution across the nanocube surfaces²²⁻²⁴. Due to nonspherical morphology, nanocubes show polarization dependence along tips and edges, which can be used for SERS. The large radii of curvatures along the tips and edges of nanocubes also give rise to deep subwavelength confinement of electromagnetic fields, creating intense hot spots for ultrasensitive trace detection²³⁻²⁶. Plasmonic nanocubes are also shown to assemble into two-dimensional (2D) planar metasurfaces with unique nanoscale light-matter interactions²⁷⁻²⁹, which can direct the flow of light to create electromagnetic behaviors not found in naturally occurring materials²⁷. These ultrathin metasurfaces are emerging platforms with demonstrated applications in all-

absorptive surfaces³⁰, superresolution imaging^{31, 32}, smart transformation optical devices³³, and terahertz compressive imaging³⁴.

Among the various plasmonic nanocube metasurfaces fabricated to date, nanocubes are predominantly oriented in the planar configuration, with limited ability to tune the lattice structures. Current methods utilized to form nanocube metasurfaces include Langmuir-Blodgett deposition technique¹³, tuning polymer-solvent interactions followed by subsequent spin-casting³⁵, and simple sample drop-casting^{28, 36}. These techniques impart limited control over interparticle separation in the face-to-face configuration, and certainly lack control over the metasurface crystal structure formed. Since the orientation and configuration of nanocubes in the metasurfaces significantly impact nanoscale light-matter interactions, it is essential to achieve finer control over the assembled nanocube lattices within the metasurfaces. Quasi-one-dimensional strings of nanocubes have shown that edge-to-edge and face-to-face interparticle junctions between planar cubes can lead to different field localization effects³⁷. Consequently, the ability to tune and break the planar configuration of nanocubes is expected to enrich the nanoscale optical behaviors of these metasurfaces. Furthermore, it is critical to achieve large-area crystalline metasurfaces to bridge the gap between nanomaterials and macroscopic applications, thereby enabling better control over the periodic manipulation of light over macroscopic length scales.

Here, we demonstrate the large-scale tunable self-assembly of Ag nanocubes into three distinct 2D metacrystals with square close-packed, linear, and hexagonal lattices. By tuning the interfacial behaviors of the nanocubes during the self-assembly, we gain control over their spatial and geometrical alignment at the oil/water interface. Our strategy involves a judicious manipulation of the Ag nanocube surface chemistry using a binary mixture of hydrophobic and hydrophilic thiol molecules. By controlling the ratio of thiol molecules in the feedstock, we are able to direct the formation of nanocube metacrystals in which the nanocube facets, edges, or tips are selectively in contact with the substrate. The unique lattice structures of these metacrystals create distinct packing densities and nanoscale electromagnetic field confinement patterns. Despite its lowest packing density, the hexagonal metacrystal with Ag nanocubes with tips contacting the substrate generates large-area ‘hot hexagons’ with significant electromagnetic field delocalization away from the individual nanocubes. We further highlight how this particle-efficient metacrystal exhibits significantly stronger surface-enhanced Raman scattering as compared with the other two denser-packing metacrystals.

2.2 RESULTS AND DISCUSSION

To create the various plasmonic metacrystals, we tailor the surface chemistry of the Ag nanocubes (average edge length (107 ± 3) nm, Figure 2.1) from hydrophilic to hydrophobic, and subsequently assemble them at the oil/water interface. Utilizing a binary mixture of thiol molecules, we choose a hydrophilic thiol-terminated poly (ethylene glycol) (PEG, $M_w=1000$) in conjunction with a hydrophobic 1-hexadecanethiol (C16) to systematically modulate the surface functionality of the Ag nanocubes (Figure 2.2a). During the ligand exchange reaction, the total number of ligands added in the feedstock (C16 + PEG) is kept constant, and the molar percentage of C16 (abbreviated as x -C16 %; defined as an x percentage of C16 (%) = $[C16]/([C16] + [PEG])$) is tuned from 0 to 100 %. After assembling the functionalized Ag nanocubes at the oil/water interface, the metacrystals are immobilized using the gel-trapping technique³⁸ (Figure 2.2b). The assembled metacrystals are stably trapped at the interface upon aqueous phase gelling. By decanting the oil phase, the assembled metacrystals can subsequently be lifted-off onto a poly(dimethylsiloxane) (PDMS) platform by curing the polymer premix over the aqueous gel.

Figure 2.1 SEM characterization of Ag nanocubes, showing the high yield and edge length of (107 ± 3) nm. Scale bar, 100 nm.

Figure 2.2 Formation of mixed monolayer and interfacial assembly of nanocubes.

Schematic of (a) Ag cubes functionalized with a binary mixture of thiol molecules, forming a mixed monolayer on cube surface and (b) the process of self-assembly at the oil/water interface.

Three metasurfaces with Ag nanocubes in planar, tilting, and standing configurations are observed when assembling Ag nanocubes with different surface wettabilities at the oil/water interface (Figure 2.3a,b,c). A square close-packed (SCP) metacrystal forms when using Ag nanocubes homogeneously functionalized with PEG (bulk water contact angle (CA) = 35°) for the self-assembly (Figure 1.3a,d,e). Nanocubes in this planar metacrystal adopt a face-to-face configuration, with the nanocube facets in contact with the solid substrate. For every nanocube, the area of contact with neighboring nanocubes is 2/3 of a cube surface area. This metacrystal structure has a packing density of 100 % (Figure 2.4a).

At 67-C16 % (CA = 82°), the Ag nanocubes form a linear metacrystal (Figure 2.3b,f,g). Ag nanocubes align in a tilted configuration, with the cube edges in contact with the solid substrate. In this metacrystal, individual nanocubes are aligned in a face-to-face configuration to form linear lattice structure, with nanocubes between neighboring strings aligned edge-to-edge. The contacting area between face-to-face contacting cubes along the one-dimensional string is 1/3 of a cube surface area, with a decrease in corresponding packing density to 50 % (Figure 2.4b).

A further increase of C16 % to 95 % (CA = 102°) leads to the formation of a hexagonal metacrystal (Figure 2.3c,h,i). Nanocubes change to a standing configuration, with only the nanocube tips contacting the substrate. The standing nanocubes align edge-to-edge in the

hexagonal metacrystal with <1% contact between neighboring nanocubes, leading to the lowest packing density of just 24 % (Figure 2.4c).

Figure 2.3 Tunable assembly Ag nanocubes into three metacrystals. SEM images of the metasurfaces of Ag nanocubes functionalized with a mixture of C16-SH and PEG-SH, with C16% of (a) 0%, (b) 67%, and (c) 95% respectively. Insets are close-up views. (a,b,c) Scale bars, 1 μm ; (a,b,c) inset scale bars, 200 nm. (a) For 0-C16%, a square close-packed metacrystal forms, with nanocubes adopting (d,e) a planar configuration. (b) At 67-C16%, the linear metacrystal is formed with tilted nanocubes, where the cubes align (f,g) face-to-face within the string, and edge-to-edge between neighboring strings. (c) At 95-C16%, the hexagonal metacrystal forms, where the standing nanocubes are aligned (h,i) edge to edge. (e,g,i) Tilted SEM characterization of the various Ag nanocube metacrystals and (j,l,n) corresponding fast-Fourier transform analyses (FFT). (k,m,o) Unique color appearance of three metacrystals. (e,g,i) Scale bars, 1 μm .

Figure 2.4. Scheme of packing efficiency of metacrystals of (a) planar Ag cubes, (b) tilting cubes, (c) standing cubes. (d) Changes in packing efficiency with variations in metacrystal structures.

Calculation of packing density.

The squares in (a) show the repeat unit of the planar Ag cubes, which is filled with one cube, with no remaining space filled with holes. The rectangles in (b) show the simplest repeat unit of tilting structure, which is filled with one cube, with the remaining space filled with

two tetrahedral holes. The simplest repeat unit of the standing structure is shown by the rectangles in the figure above. The repeat unit is filled with one cube, with the remaining space filled with two tetrahedral holes.

The edge length of a single cube is l , interparticle distance is b for (a,b) and a for (c).

In the square in (a)

Length of cube = l ($a = b = c = l$)

Volume of repeat unit = $l \times l \times l = l^3$, volume of one cube = l^3

Packing efficiency of planar cubes = $\frac{l^3}{l^3} = \underline{100\%}$

In the rectangle in (b),

$a = l$, $b = \frac{\sqrt{2}}{2}l$, $c = \frac{\sqrt{2}}{2}l$

Volume of repeat unit = $a \times b \times c = \sqrt{2}l \times l \times \sqrt{2}l = 2l^3$, volume of one cube = l^3

Packing efficiency of tilting cubes = $\frac{l^3}{2l^3} = \underline{50\%}$

In the rectangle in (c),

$a = \sqrt{3}l$, $b = \sqrt{2}l$, $c = \sqrt{3}l$

Volume of repeat unit = $a \times b \times c = \sqrt{3}l \times \sqrt{2}l \times \sqrt{3}l = 3\sqrt{2}l^3$, volume of one cube = l^3

Packing efficiency of standing cubes = $\frac{l^3}{3\sqrt{2}l^3} = \underline{24\%}$

Among these three metacrystals, the linear structure of tilting cubes and hexagonal structure of standing cubes have not been reported hitherto. Our approach here opens up a new pathway to achieve metacrystal tunability, and enable deeper understanding of nanoscale light-matter interactions. Moreover, the metacrystal assembly is entirely scalable, with typical assembled metacrystal area on the order of 5 cm^2 (Figure 2.5).

Figure 2.5. Typical assembled metacrystal area at $\sim 5\text{ cm}^2$.

The crystallinity and long-range order of these three metacrystals are clearly evident from the fast-Fourier transform analyses, with square, linear, and hexagonal patterns observed for the SCP, linear, and hexagonal metacrystals respectively (Figure 2.3j,l,n). In addition, long-range order of these three metacrystals is also evident from the regularly oscillating features in the radial distribution function analyses (Figure 2.6). Radial distribution function describes how density varies as a function of distance from a reference particle and is usually determined by calculating the distance between all particle pairs and binning them into a histogram. The nearest neighbor distance increases from 110 nm to 137

nm and to 162 nm as the metacrystal changes from the SCP to the linear and hexagonal lattices respectively. This finding corroborates well with the decrease in packing density across the three metacrystals, indicating the formation of increasingly open meta-structures as the lattices change.

Figure 2.6. Radial distribution function of superstructures with (a) planar cubes, (b) tilting cubes, (c) standing cubes.

Furthermore, the decreased packing density of both the linear and hexagonal metacrystals also gives rise to different colored appearance as compared to the SCP metacrystal (Figure 2.3k, m, o), arising from the different Ag nanocube configurations. The SCP metacrystal behaves like a silver mirror due to its planarity and high packing density. In contrast, both the linear and hexagonal metacrystals are yellowish-gold, likely arising from different Bragg's reflections off the nanocube edges and tips on these non-planar surfaces. UV/Vis spectra are obtained to characterize the optical extinction spectra of three metasurfaces on PDMS substrate (Figure 2.7). The extinctions of nanocubes in different

configurations show broad peaks, whose similarity has also been observed and reported before for different nanocube configurations³⁷.

Figure 2.7. Extinction spectra of metasurfaces of Ag nanocubes in planar, tilting and standing configuration above PDMS substrate.

A judicious control over the mixed monolayer feedstock ratio enables us to observe a systematic lattice transformation of the metacrystal structure at the oil/water interface (Figure 2.8). By varying the mixed monolayer feedstock ratio, we achieve a continuous and precise control of the nanocube hydrophobicity, which increases with increasing C16 % (Figure 2.8a). To track the metacrystal evolution more quantitatively, we also tabulate the population of nanocubes in each orientation (planar, tilted, or standing) over assembled areas of $100 \mu\text{m}^2$ (Figure 2.8b). To gain more insights on the interfacial behavior of the variously functionalized Ag nanocubes, we perform atomic-force microscopy (AFM)

measurements on selected samples to characterize the topological height of nanocube protrusion from the flat PDMS surface. This height corresponds to the amount of nanocube that is in contact with the aqueous phase. From this height, we can derive a height percentage of nanocube in contact with the oil phase (% cube_{oil}, Figure 2.9, Table 2.1). This information can be in turn correlated with the surface hydrophobicity of the variously functionalized Ag nanocubes.

Figure 2.8. Creating continuous metacrystal transformation by systematically tuning the molecule ratio in the feedstock. (a) Increase in the bulk water contact angles of Ag film functionalized with increasing C16%. Error bars are s.d. of five measurements for each functionalization. (b) Histogram charting the relative population Ag nanocubes in the planar, tilted, and standing configurations for every feedstock ratio shown. (c-k) Changing C16% in the feedstock gives rise to a continuous metacrystal evolution, with the particle

orientation changing into planar, tilting, standing and finally back into the planar cubes. All scale bars, 200 nm. Insets show the schematic depicting the assembled meta-structures.

$$\% \text{ of cube}_{oil} = (1 - \text{height}_{AFM} / \text{size}_{orientation}) * 100\%$$

Figure 2.9. Scheme of the calculation of cube percentage in contact with oil phase.

Table 2.1 AFM measurements of Ag nanocubes in different configurations functionalized with two thiol molecules.

C16%	AFM Height (in aqueous phase) / nm	Height in oil phase / nm	% Immersed in aqueous phase (%)	% Immersed in oil phase (%)
0-C16%	85 ± 9	22 ± 9	80 ± 8	20 ± 8
50-C16%	72 ± 8	35 ± 8	67 ± 7	33 ± 7
67-C16%	77 ± 17	74 ± 17	51 ± 16	49 ± 16
95-C16%	32 ± 10	153 ± 10	17 ± 9	83 ± 9
100-C16%	8 ± 3	99 ± 3	7 ± 3	93 ± 3

For feedstock < 40-C16 % (CA ranging from 36°- 62°), the nanocube surfaces remain relatively hydrophilic (Figure 2.8a). At 0-C16 %, the height of nanocube protrusion from AFM measurements is (85 ± 9) nm for the planar nanocubes (Figure 2.8a), with a

corresponding % cube_{oil} of $(20 \pm 8) \%$ (Figure 2.10a,d,e). Consequently, the dominant metacrystal is the SCP lattice within this range of C16 %, with $\sim 100 \%$ of the nanocubes adopting the planar configuration (Figure 2.8b, c, 2.11a-c). Increasing C16 % drives the nanocubes further into the oil phase. At 50-C16 %, the height of planar nanocube protrusion from AFM measurements decreases to $(72 \pm 8) \text{ nm}$, and the corresponding % cube_{oil} increases to $(32 \pm 7) \%$ (Figure 2.12a,c). Linear structures with tilted nanocubes also begin to form. As the C16 % changes from $\sim 40\%$ to $\sim 70\%$ -C16 % (CA ranging from 66° to 82°), we observe a gradual increase in the population of tilted Ag nanocubes assembling into the linear metacrystal (Figure 2.8d-f, 2.11d). At $\sim 70\%$ -C16 %, the population of planar nanocubes decreases to just 0.2% , accompanied by a corresponding increase in tilted nanocube percentage from 10% to 83% (Figure 2.8b). At the same time, the interfacial position of nanocubes also changes: the height of tilted nanocube protrusion becomes $(77 \pm 19) \text{ nm}$ (Figure 2.10b) and the corresponding % cube_{oil} increases to $(49 \pm 16) \%$ (Figure 2.10d,e). A further increase to 95-C16 % (CA increases from 82° to 102°) causes the linear metacrystal to transform into the hexagonal metacrystal (Figure 2.8g-j, 2.11e,f). The population of the tilted nanocube population decreases from 83% to 20% , and the corresponding population of standing nanocubes increases from 17% to 80% (Figure 2.8b). The height of nanocube protrusion decreases to $(32 \pm 10) \text{ nm}$ for the standing cubes (Figure

2.10c), with a corresponding % cube_{oil} of (83 ± 9) % (Figure 2.10d,e). At 100-C16 % (CA = 115°), Ag nanocubes are almost fully immersed in oil phase, and the SCP nanocube metacrystal is again observed (Figure 2.8k). The height of nanocube protrusion is (8 ± 3) nm, with a corresponding % cube_{oil} of (93 ± 3) % (Figure 2.12b,c).

Figure 2.10. Interfacial behavior of variously functionalized Ag nanocubes. (a-c) AFM

topological characterization of the variously functionalized Ag nanocubes on PDMS. All

scale bars, 100 nm. (d) Schematic depicting the interfacial configuration and position

changes of the Ag nanocubes. (e) From AFM measurements, the height of the Ag nanocubes

in contact with the oil phase can be derived. Increasing the surface hydrophobicity of

nanocubes increases the height percentage in contact with the oil phase.

Figure 2.11. Metacrystals of Ag nanocubes with different C16 %, (a) 16.7%, (b) 25%, (c) 33.3%, (d) 50%, (e) 75%, (f) 80%. All scale bars, 200 nm.

Figure 2.12. AFM topological characterization of the variously functionalized Ag nanocubes with (a) 50-C16% and (b) 100-C16%. (a,b) Scale bar, 100 nm. (c) Diagram shows the percentage of Ag nanocubes in contact with oil phase.

The interfacial behaviors of Ag nanocubes are primarily governed by the particle-oil and particle-water interactions³⁹. With increasing C16 %, the observed increase in the extent of nanocubes in contact with the oil phase points to an increased dominance of particle-oil interactions over particle-water interactions in stabilizing the Ag nanocubes at the oil/water interface. At low C16%, the small proportion of hydrophobic C16 on the nanocube surfaces leads to a planar configuration, enabling the nanocubes to remain mostly immersed within the aqueous phase to maximize particle-water interactions. As the population of hydrophobic C16 increases, the Ag nanocubes begin to tilt as they assemble into the linear metacrystal, enabling an optimal balance between particle-oil and particle-water interactions. When the Ag nanocubes are predominantly hydrophobic at high C16%, the hexagonal metacrystal of standing nanocubes forms at the oil/water interface to minimize particle-water interactions and maximize particle-oil interactions.

Notably, both the linear and hexagonal metacrystals are only achievable using our mixed monolayer strategy in combination with self-assembly at the oil/water interface. To demonstrate this, we assemble Ag nanocubes functionalized with single thiol molecules having similar bulk CAs as those in the mixed monolayer system. 1-butanethiol (C4) and 1-octanethiol (C8) are used to achieve identical bulk CAs for 67- and 95- C16 % respectively (Figure 2.13). Both C4- and C8-functionalized Ag nanocubes give rise to

predominantly random structures (Figure 2.13c,d) rather than the well-defined linear and hexagonal metacrystals. The corresponding population of tilted and standing nanocubes is also in the minority, amounting to 13 % and 45 % respectively (Figure 2.13e).

Figure 2.13. (a-d) Different assembled metacrystals of Ag nanocubes are observed with (a,b) mixed monolayer and (c,d) homogeneous surface functionalization at the same bulk wettability. (a-d) Scale bars, 1 μm ; inset scale bars, 200 nm. (e) Percentage of planar, tilting, and standing cubes in (a-d). This disparity suggests a likely phase-separation of the mixed thiol monolayer on the nanocube surfaces.

Furthermore, systematically changing the surface functionality within the single monolayer system also does not give rise to the same metacrystal transformation as observed in the mixed monolayer system (Figure 2.14). The main metacrystal observed in the single monolayer system is the SCP array. Consequently, our mixed monolayer approach is a more dynamic strategy, which enables a fine control over the formation of

various metacrystals that is otherwise unachievable by single monolayer-functionalized nanoparticle system.

Figure 2.14. SEM images of assembled Ag nanocubes functionalized with pure monolayer with (a) PVP, (b) C3, (c) C4, (d) C5, (e) C6, (f) C8, (g) C12, (h) C16. (a-h) Scale bar, 1 μm; inset scale bar, 200 nm. (i) Bulk contact angle of Ag film functionalized with different pure thiol monolayer.

The difference in assembled metacrystals observed between the single and mixed monolayer systems leads us to hypothesize that phase separation of the thiol molecules⁴⁰⁻⁴² may have occurred in the mixed monolayer system during the ligand exchange reaction. In the single monolayer system, the thiol molecules should be homogeneously distributed on the nanocube surfaces. On the other hand, thiols in the mixed monolayer system can either be distributed homogeneously or be phase-separated into anisotropic patches on the nanocube surfaces^{43, 44}. Consequently, a homogeneous distribution of mixed thiols would

have given rise to the same metacrystal as the single monolayer system at the same bulk CA. Since different assembled structures are observed, it is therefore more likely that the thiols phase-separate into domains. For 67-C16 %, a Janus-like distribution could be probable, leading to the nanocubes tilting and straddling halfway across the oil/water interface. In this way, both particle-oil and particle-water interactions are optimized to stabilize the nanocubes in the linear metacrystal. For 95-C16 %, the small population of hydrophilic PEG component could be localized to near a specific tip/edge region of the nanocubes, driving the cubes into a standing configuration in which the PEG -dominant side of the nanocube is in contact with the aqueous phase. The presence of patchy ligand distribution on particles functionalized with binary mixtures of ligands has also been reported earlier, with their distribution driven by the lowering of the system enthalpy^{44, 45}.

The distinct meta-atom configurations in the three metacrystals also give rise to unique electromagnetic field distribution⁴⁶. We simulate the field distribution of our metacrystals in PDMS mold using the finite-difference time-domain (FDTD) method at an incident wavelength of 532 nm. Thin strips of plasmonic hot spots are observed from both the SCP and linear metacrystals, localized within regions of contacting facets (Figure 2.15a, b). The close proximity of the nanocubes in these two metacrystals creates intense field localization, with maximum field intensity ($|E|/|E_0|^2$) of 18 and 180 for the SCP and linear metacrystals

respectively. While the maximum $|E|/|E_0|^2$ of 4 is weaker in the hexagonal metacrystal, the total $|E|/|E_0|^2$ along the line profile shown in Figure 2.16 shows 0.2-fold and 26-fold higher total $|E|/|E_0|^2$ for the hexagonal metacrystal (794) as compared to the linear (667) and SCP metacrystals (29) respectively. In addition, every hot spot area within the hexagonal metacrystal is 9-fold and 81-fold larger than that of the linear and SCP metacrystals respectively ($\sim 13640 \text{ nm}^2$ versus $\sim 1335 \text{ nm}^2$ and $\sim 165 \text{ nm}^2$). Large hexagonal hot spots form in the hexagonal metacrystal, with the field localization spreading from the edges of the nanocubes to the interstitial regions between nanocubes (Figure 2.15c). The larger hot spot regions in this metacrystal generates an overall larger total $|E|/|E_0|^2$ as compared to the other two metacrystals (Figure 2.16). Our findings here evidently demonstrate the importance of gaining control over the geometrical and spatial orientation of the Ag nanocubes to achieve large-area field delocalization using the metacrystal with the lowest packing density.

Figure 2.15. Controllable metacrystal structures provide tunable light-matter interactions. Localized electromagnetic field distributions of the three metasurfaces with (a) planar, (b) tilting, (c) standing configurations at an incident wavelength of 532 nm. All scale bars, 100 nm. The 3D and cross-sectional schematic descriptions are shown on the top for corresponding metacrystals. (d) SERS spectra and (e) EFs of 4-MBT from three metasurfaces. Error bars in (e) are s.d. of 10 measurements (area of each measurement is 40 x 3 μm^2).

Figure 2.16. Intensity ($|E/E_0|^2$) of three metasurfaces with (a) planar, (b) tilting, (c) standing configuration on PDMS substrate at $\lambda = 532$ nm.

The significantly larger areas of electromagnetic field concentration in the hexagonal metacrystal gives rise to stronger surface-enhanced Raman scattering (SERS) enhancement compared to the other two metacrystals. We use 4-methylbenzenethiol (4-MBT) as the probe molecule at a laser excitation wavelength of 532 nm in our SERS experiments. Characteristic vibrational modes of 4-MBT at 1080 and 1600 cm^{-1} are observed in the SERS spectra (Figure 2.15d). The SCP metacrystal exhibits the lowest SERS signals of (42 ± 20) counts, followed by the linear metacrystal at (224 ± 27) counts, and the hexagonal metacrystal with the highest SERS signals of (285 ± 50) counts. The corresponding SERS enhancement factors calculated based on the 1080 cm^{-1} vibration are 4.3×10^3 , 4.1×10^4 and 1.5×10^6 respectively (Figure 2.14e). The enhancement factors of the hexagonal metacrystal are 36-fold and 348-fold higher than the linear and SCP metacrystals respectively. Notably, our findings create a particle-efficient approach to create efficient SERS substrates. The highest SERS enhancement and the largest hotspot areas are observed from the lowest-packing density hexagonal metacrystal with the lowest number of particles per unit area. This is brought about by the significant electromagnetic field delocalization

in the hexagonal metacrystal, with more molecules exposed to stronger field enhancements than the other two metacrystals.

Calculation of SERS Enhancement Factors

$$\text{SERS EF} = \frac{I_{\text{SERS}}}{N_{\text{SERS}}} \div \frac{I_{\text{ref}}}{N_{\text{ref}}}$$

$$I_{\text{surface}} (\text{planar}) = 8.29 \text{ counts per second}$$

$$I_{\text{surface}} (\text{tilting}) = 44.72 \text{ counts per second}$$

$$I_{\text{surface}} (\text{standing}) = 57.05 \text{ counts per second}$$

$$I_{\text{solution}} = 0.973 \text{ counts per second (1 M 4-MBT in ethanol)}$$

In solution

$$N_{\text{solution}} = V_{\text{solution}} \cdot C_{4\text{-MBT}} \cdot \text{Avogadro's number} = \pi \times \frac{x}{2} \times \frac{y}{2} \times z \times c \times \text{Avogadro's number}$$

$$N_{\text{solution}} = 1.26 \cdot 10^9 \text{ for 1 M 4-MBT in ethanol}$$

Laser resolution in ethanol

$$x = 910 \text{ nm}$$

$$y = 680 \text{ nm}$$

$$z = 4320 \text{ nm}$$

Laser resolution in air:

$$x = 520 \text{ nm}$$

$$y = 380 \text{ nm}$$

$$z = 810 \text{ nm}$$

$$\text{Area of laser spot in air} = \pi \times \frac{x}{2} \times \frac{y}{2} = 1.552 \times 10^5 \text{ nm}^2 = 1.552 \times 10^{-1} \mu\text{m}^2$$

Cube density estimated from counting the number of cubes over areas of $320 \mu\text{m}^2$ for each

array:

$$D (\text{SCP}) = 89.00 \text{ cubes}/\mu\text{m}^2$$

$$D (\text{wire-like}) = 62.94 \text{ cubes}/\mu\text{m}^2$$

$$D (\text{hexagonal}) = 51.38 \text{ cubes}/\mu\text{m}^2$$

Number of Ag nanocubes within the laser spot:

$$N (\text{SCP}) = 13.813$$

$$N (\text{wire-like}) = 9.768$$

$$N (\text{hexagonal}) = 7.965$$

Exposed surface area of one Ag nanocube in three arrays:

$$S (\text{SCP}) = 3.984 \times 10^4 \text{ nm}^2$$

$$S (\text{wire-like}) = 3.202 \times 10^4 \text{ nm}^2$$

$$S (\text{hexagonal}) = 1.366 \times 10^3 \text{ nm}^2$$

Exposed surface area of Ag nanocube within the laser spot:

$$S (\text{SCP}) = 5.503 \times 10^5 \text{ nm}^2$$

$$S \text{ (wire-like)} = 3.128 \times 10^5 \text{ nm}^2$$

$$S \text{ (hexagonal)} = 1.088 \times 10^4 \text{ nm}^2$$

Taking 4.5×10^{14} molecules/cm² for a monolayer of 4-MBT on silver , number of 4-MBT molecules adsorbed on the particles surface within the laser spot:

$$N \text{ (SCP)} = 4.5 \text{ molecules/nm}^2 \times 5.503 \cdot 10^5 \text{ nm}^2 = 2.476 \times 10^6$$

$$N \text{ (wire-like)} = 4.5 \text{ molecules/nm}^2 \times 3.128 \cdot 10^5 \text{ nm}^2 = 1.408 \times 10^6$$

$$N \text{ (hexagonal)} = 4.5 \text{ molecules /nm}^2 \times 1.088 \cdot 10^4 \text{ nm}^2 = 4.896 \times 10^4$$

$$\text{SERS EF} = \frac{I_{\text{SERS}}}{N_{\text{SERS}}} \div \frac{I_{\text{ref}}}{N_{\text{ref}}}$$

$$\begin{aligned} \text{EF (SCP)} &= \frac{8.29}{2.476 \times 10^6} \div \frac{0.973}{1.26 \times 10^9} \\ &= \underline{4.34 \times 10^3} \end{aligned}$$

$$\begin{aligned} \text{EF (wire-like)} &= \frac{44.72}{1.408 \times 10^6} \div \frac{0.973}{1.26 \times 10^9} \\ &= \underline{4.11 \times 10^4} \end{aligned}$$

$$\begin{aligned} \text{EF (hexagonal)} &= \frac{57.05}{4.896 \times 10^4} \div \frac{0.973}{1.26 \times 10^9} \\ &= \underline{1.51 \times 10^6} \end{aligned}$$

2.3 CONCLUSIONS

We successfully utilize surface chemistry to direct the organization of Ag nanocubes into three unique metacrystals at the oil/water interface. This work breaks the current limitation in plasmonic metasurfaces of nanocubes, where nanocubes are restricted to planar face-to-face configurations. By using a binary combination of hydrophilic and hydrophobic thiol molecules to design target surface functionality, we achieve control over the geometrical and spatial orientation of Ag nanocubes in the assembled metacrystals. Ag nanocubes can be directed into planar, tilted, or standing configurations, assembling into square close-packed, linear, and hexagonal metacrystals respectively. The metacrystals demonstrated in this current work break the current limitation of nanocube metasurfaces with predominantly planar configurations. In addition, we highlight the importance of the non-planar nanocube configuration in the hexagonal metacrystal, in which large-area electromagnetic field delocalization gives rise to the strongest SERS enhancement factors among the three metacrystals. The SERS enhancement factor of this low packing density metacrystal is 1.5×10^6 , nearly 350-fold stronger than the much denser-packing planar square close-packed lattice. Coupled with large-area intense electromagnetic fields, this high enhancement factor indicates the possibility of using the hexagonal metacrystal as efficient single-molecule detection platforms.

2.4 MATERIALS AND METHODS

Materials. Silver nitrate ($\geq 99\%$), 1,5-pentanediol (PD, $\geq 97\%$), poly(vinylpyrrolidone) (PVP, average MW = 55 000 g/mol), poly(ethylene glycol) methyl ether thiol (PEG, average m.w. = 1000 g/mol), 1-propanethiol (C3), 1-hexanethiol (C6), 1-octanethiol (C8), 1-dodecanethiol (C12), 1-hexadecanethiol (C16), decane ($\geq 99\%$), and isopropyl alcohol (IPA) were purchased from Sigma Aldrich; copper(II) chloride ($\geq 98\%$) was from Alfa Aesar. Ethanol (ACS, ISO, Reag. Ph Eur) was obtained from EMSURE. Silicon elastomer curing agent and silicone elastomer base were purchased from Dow Corning. Gellan Gum (KELKOGEL) was kindly sponsored by CP Kelco (USA). All chemicals were used without further purification. Milli-Q water ($>18.0 \text{ M}\Omega\cdot\text{cm}$) was purified with a Sartorius Arium 611 UV ultrapure water system.

Ag nanocube synthesis. The synthesis of Ag nanocubes was carried out using the polyol reduction method⁴⁷. Briefly, 8 mg CuCl_2 , 20 mg poly(vinylpyrrolidone) (PVP) and 20 mg AgNO_3 were dissolved in 10 mL 1,5-pentanediol (PD) separately, using repeated sonication and vortex. After the complete dissolution of these precursors, 35 μL CuCl_2 solution was added to AgNO_3 solution. Then in a round bottomed flask, 20 mL PD was heated at 190°C for 10 min. 250 μL PVP solution was dropwise injected into 20 mL PD, followed by quick

injection of 500 μL AgNO_3 solution. Subsequently, AgNO_3 precursor was injected quickly every min and PVP precursor was dropwise injected every 30 s until nanocubes were formed. The heating was then stopped and the whole reaction system was cooled down to room temperature. For the purification of Ag nanocubes, PD was first removed by using acetone, ethanol over multiple centrifugation rounds, followed by redispersing in 20 ml ethanol. The Ag nanocube dispersion was then vacuum filtered using polyvinylidene difluoride filter membranes (Durapore) with pore sizes ranging from 5,000, 650, 450 to 220 nm.

Mixed monolayer formation. The purified Ag nanocube dispersion was allowed to sediment for several days. 0.5 μL of the sediment was dispersed in ethanol and centrifuged once before re-dispersing in 1.5 ml of ethanol/isopropyl alcohol (IPA) (1:1). A mixture of 1 mM PEG and C16 solution was then added dropwise to this dispersion under stirring. The total volume of ligands added was kept constant of 10 μL and molar ratio of C16 was tuned from 0 to 100%. Functionalization took place for 4 h, followed by centrifugation to remove excess molecules. Then the sediment was redispersed in 1.5 mL of ethanol/IPA (1:1) and 10 mL fresh thiol solution with same ratio was added under stirring. The functionalization was allowed to continue for another 3 h, followed by three rounds of centrifugation and washing with IPA/water (1:1).

Interfacial Self-assembly. The assembly process was described in Fig. S1. Gellan gum solution (2 wt%, 6 mL) was used as aqueous phase and n-decane was added on top of the aqueous polymeric phase as the oil phase. The gel-trapping experiments were slightly modified from the procedure reported by Paunov and co-workers⁴⁸. The gellan gum solution was prepared under ~80 °C in oil bath and under stirring at 1400 rpm until the gel was completely hydrated. Subsequently, pre-heated n-decane was added to the top of the gel solution to create the oil phase. Ag nanocubes, which were dispersed in 0.5 μ l IPA/H₂O, were injected onto the interface. The whole system was left at 80 °C for ~15 min before cooling down to room temperature to ensure that the cubes at the oil/water interface had sufficient time to spread out and achieve thermodynamic equilibrium. After the gelling of gellan gum, n-decane was decanted gently and premixed PDMS precursor mixture (5:1; elastomer:curing agent) was deposited onto the arrays of Ag nanocubes. After the curing of PDMS, the monolayer of Ag nanoparticles was peeled off and washed in hot water.

Scanning electron microscopy (SEM). SEM imaging was performed using scanning electron microscopy (JEOL-JSM-7600F) at an accelerating voltage of 5 kV. Assembled monolayer of Ag nanoparticles on PDMS was imaged by using SEM directly and analyzed using Image J software.

UV-vis spectroscopy. UV-vis spectra were recorded using a Cary 60. For each metasurface, five areas were measured and averaged to derive the extinction spectra.

Contact angle measurements. PEG/C16 solution was used to functionalize Ag film (114 nm thickness) to form a mixed monolayer. Contact angles of the functionalized 114-nm-thick Ag films were measured on a Theta Lite tensiometer equipped with a Firewire digital camera. Static contact angle was measured with a 4- μ l ultrapure sessile water droplet. Each contact angle data was achieved by the average of five readings taken on the Ag film with different C16% functionalization.

Atomic force microscopy (AFM) measurements. AFM was used to study the topological changes in the metasurfaces of Ag nanocubes on the PDMS molds using a Bruker Dimension ICON with NanoScope V controller from Bruker. Tapping mode (non-contact mode) image was acquired using silicon probes (Tap300Al-G with 30-nm aluminium reflex coating) from BudgetSensor. Data analysis was carried out using WSxM Scanning Probe Microscopy Software, a free program from Nanotec Electrónica S.L36.

Surface-enhanced Raman scattering (SERS) characterization. 4-methylbenzenethiol (4-MBT) was used as probe molecule and metasurfaces on PDMS were immersed in 10 mM 4-MBT solution for ligand exchange. SERS measurements were performed via x-y imaging mode of the Laser Raman Microscope RAMANtouch system with an excitation

wavelength of 532 nm (power = 3 μ W). A 100 $\times$ (numerical aperture 0.9) objective lens with 5 s accumulation time was used for data collection between 200 to 1,800 cm^{-1} . X-y imaging measurements were collected from 10 different spots with the area of each spot spanning $40 \times 3 \mu\text{m}^2$. The SERS measurement was verified by using uRaman module from Technospex mounted on Nikon Ci-S microscope.

Finite-difference time-domain (FDTD) simulation. 2D metasurface FDTD simulations were performed using the commercial software (FDTD Solution 7.5, Lumerical Solutions, Inc.). The nanocube arrays were simulated under periodic boundary conditions. An electromagnetic pulse, whose wavelength is 532 nm, was launched to simulate a propagating plane wave interacting with the arrays. The unit cells of arrays and its surrounding medium were divided into meshes of 0.5 nm in size. All arrays were built on the basis of the experimental parameters. The refractive index of PDMS and air were set to be 1.4 and 1 respectively⁴⁹. The dielectric function of Ag was taken according to previously reported values⁵⁰. The electric field intensity at wavelength of 532 nm was monitored at the surface of PDMS.

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2.6 REFERENCES

1. Torquato, S.; Jiao, Y. *Nature* **2009**, *460*, 876-879.
2. Kronast, F.; Friedenberger, N.; Ollefs, K.; Gliga, S.; Tati-Bismaths, L.; Thies, R.; Ney, A.; Weber, R.; Hassel, C.; Römer, F. M.; Trunova, A. V.; Wirtz, C.; Hertel, R.; Dürr, H. A.; Farle, M. *Nano Lett.* **2011**, *11*, 1710-1715.
3. Donaldson, J. G.; Kantorovich, S. S. *Nanoscale* **2015**, *7*, 3217-3228.
4. Deori, K.; Gupta, D.; Saha, B.; Deka, S. *ACS Catal.* **2014**, *4*, 3169-3179.
5. Singh, G.; Chan, H.; Baskin, A.; Gelman, E.; Repnin, N.; Král, P.; Klajn, R. *Science* **2014**, *345*, 1149-1153.
6. Lee, S. Y.; Hung, L.; Lang, G. S.; Cornett, J. E.; Mayergoyz, I. D.; Rabin, O. *ACS Nano* **2010**, *4*, 5763-5772.
7. Xiong, Y.; Ye, J.; Gu, X.; Chen, Q.-W. *J. Phys. Chem. C* **2007**, *111*, 6998-7003.
8. Ken-ichi, M.; Kazumi, K.; Hiroaki, I.; Satoshi, W.; Hajime, H.; Makoto, K. *Jpn. J. Appl. Phys.* **2012**, *51*, 09LC03.

9. Quan, Z.; Xu, H.; Wang, C.; Wen, X.; Wang, Y.; Zhu, J.; Li, R.; Sheehan, C. J.; Wang, Z.; Smilgies, D.-M.; Luo, Z.; Fang, J. *J. Am. Chem. Soc.* **2014**, *136*, 1352-1359.
10. Quan, Z.; Siu Loc, W.; Lin, C.; Luo, Z.; Yang, K.; Wang, Y.; Wang, H.; Wang, Z.; Fang, J. *Nano Lett.* **2012**, *12*, 4409-4413.
11. Camargo, P. H. C.; Au, L.; Rycenga, M.; Li, W.; Xia, Y. *Chem. Phys. Lett.* **2010**, *484*, 304-308.
12. Lee, H. K.; Lee, Y. H.; Phang, I. Y.; Wei, J.; Miao, Y.-E.; Liu, T.; Ling, X. Y. *Angew. Chem. Int. Ed.* **2014**, *53*, 5054-5058.
13. Tao, A.; Sinsermsuksakul, P.; Yang, P. *Nat. Nanotechnol.* **2007**, *2*, 435-440.
14. Black, C. T.; Murray, C. B.; Sandstrom, R. L.; Sun, S. *Science* **2000**, *290*, 1131-1134.
15. Zhang, X.; Zhang, Z.; Glotzer, S. C. *J. Phys. Chem. C* **2007**, *111*, 4132-4137.
16. Koh, W.-k.; Saudari, S. R.; Fafarman, A. T.; Kagan, C. R.; Murray, C. B. *Nano Lett.* **2011**, *11*, 4764-4767.
17. Sun, S.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. *Science* **2000**, *287*, 1989-1992.
18. Tlusty, T.; Safran, S. A. *Science* **2000**, *290*, 1328-1331.
19. Klokkenburg, M.; Vonk, C.; Claesson, E. M.; Meeldijk, J. D.; Ern, B. H.; Philipse, A. *J. Am. Chem. Soc.* **2004**, *126*, 16706-16707.
20. Chen, M.; Kim, J.; Liu, J. P.; Fan, H.; Sun, S. *J. Am. Chem. Soc.* **2006**, *128*, 7132-7133.

21. Nie, Z.; Petukhova, A.; Kumacheva, E. *Nat. Nanotechnol.* **2010**, *5*, 15-25.
22. Choi, H.; Park, J. S.; Jeong, E.; Kim, G. H.; Lee, B. R.; Kim, S. O.; Song, M. H.; Woo, H. Y.; Kim, J. Y. *Adv. Mater.* **2011**, *23*, 2759-2763.
23. Sherry, L. J.; Chang, S.-H.; Schatz, G. C.; Van Duyne, R. P.; Wiley, B. J.; Xia, Y. *Nano Lett.* **2005**, *5*, 2034-2038.
24. Cobley, C.M.; Skrabalak, S.E.; Campbell, D.J.; Xia, Y. *Plasmonics* **2009**, *4*, 171-179.
25. Lee, H. K.; Lee, Y. H.; Zhang, Q.; Phang, I. Y.; Tan, J. M. R.; Cui, Y.; Ling, X. Y. *ACS Appl. Mater. Interfaces* **2013**, *5*, 11409-11418.
26. Tan, J. M. R.; Ruan, J. J.; Lee, H. K.; Phang, I. Y.; Ling, X. Y. *Phys. Chem. Chem. Phys.* **2014**, *16*, 26983-26990.
27. Meinzer, N.; Barnes, W. L.; Hooper, I. R. *Nat. Photon.* **2014**, *8*, 889-898.
28. Moreau, A.; Ciraci, C.; Mock, J. J.; Hill, R. T.; Wang, Q.; Wiley, B. J.; Chilkoti, A.; Smith, D. R. *Nature* **2012**, *492*, 86-89.
29. Rozin, M. J.; Rosen, D. A.; Dill, T. J.; Tao, A. R. *Nat. Commun.* **2015**, *6*, 7325.
30. Hao, J.; Wang, J.; Liu, X.; Padilla, W. J.; Zhou, L.; Qiu, M. *Appl. Phys. Lett.* **2010**, *96*, 251104.
31. Zhang, S.; Fan, W.; Panoiu, N. C.; Malloy, K. J.; Osgood, R. M.; Brueck, S. R. J. *Phys. Rev. Lett.* **2005**, *95*, 137404.

32. Hentschel, M.; Saliba, M.; Vogelgesang, R.; Giessen, H.; Alivisatos, A. P.; Liu, N. *Nano Lett.* **2010**, *10*, 2721-2726.
33. Shin, D.; Urzhumov, Y.; Lim, D.; Kim, K.; Smith, D. R. *Sci. Rep.* **2014**, *4*, 4084.
34. Watts, C. M.; Shrekenhamer, D.; Montoya, J.; Lipworth, G.; Hunt, J.; Sleasman, T.; Krishna, S.; Smith, D. R.; Padilla, W. J. *Nat. Photon.* **2014**, *8*, 605-609.
35. Gurunatha, K. L.; Marvi, S.; Arya, G.; Tao, A. R. *Nano Lett.* **2015**, *15*, 7377-7382.
36. Hoang, T. B.; Akselrod, G. M.; Argyropoulos, C.; Huang, J.; Smith, D. R.; Mikkelsen, M. H. *Nat. Commun.* **2015**, *6*, 7788.
37. Gao, B.; Arya, G.; Tao, A. R. *Nat. Nanotechnol.* **2012**, *7*, 433-437.
38. Cayre, O. J.; Paunov, V. N. *J. Mater. Chem.* **2004**, *14*, 3300-3302.
39. Lee, Y. H.; Shi, W.; Lee, H. K.; Jiang, R.; Phang, I. Y.; Cui, Y.; Isa, L.; Yang, Y.; Wang, J.; Li, S.; Ling, X. Y. *Nat. Commun.* **2015**, *6*, 6990.
40. Centrone, A.; Hu, Y.; Jackson, A. M.; Zerbi, G.; Stellacci, F. *Small* **2007**, *3*, 814-817.
41. Lee, H.-Y.; Shin, S. H. R.; Drews, A. M.; Chirsan, A. M.; Lewis, S. A.; Bishop, K. J. M. *ACS Nano* **2014**, *8*, 9979-9987.
42. Stranick, S. J.; Parikh, A. N.; Tao, Y. T.; Allara, D. L.; Weiss, P. S. *J. Phys. Chem.* **1994**, *98*, 7636-7646.

43. Ong, Q. K.; Reguera, J.; Silva, P. J.; Moglianetti, M.; Harkness, K.; Longobardi, M.; Mali, K. S.; Renner, C.; De Feyter, S.; Stellacci, F. *ACS Nano* **2013**, 7, 8529-8539.
44. Liu, X.; Yu, M.; Kim, H.; Mameli, M.; Stellacci, F. *Nat. Commun.* **2012**, 3, 1182.
45. Singh, C.; Ghorai, P. K.; Horsch, M. A.; Jackson, A. M.; Larson, R. G.; Stellacci, F.; Glotzer, S. C. *Phys. Rev. Lett.* **2007**, 99, 226106.
46. Shi, Q.; Si, K. J.; Sikdar, D.; Yap, L. W.; Premaratne, M.; Cheng, W. *ACS Nano* **2016**, 10, 967-976.
47. Tao, A.; Sinsermsuksakul, P.; Yang, P. *Angew. Chem. Int. Ed.* **2006**, 45, 4597-4601.
48. Arnaudov, L. N.; Cayre, O. J.; Cohen Stuart, M. A.; Stoyanov, S. D.; Paunov, V. N. *Phys. Chem. Chem. Phys.* **2010**, 12, 328-331.
49. Mark, J. E. *Oxford Univ. Press* **1999**.
50. Palik, E. D. *Academic Press* **1985**.

3 Tuning Molecular-level Polymer Conformations Enables Dynamic Control Over Both the Interfacial Behaviors of Ag nanocubes and Their Assembled Metacrystals **

ABSTRACT. In surface chemistry-directed nanoparticle self-assembly, it remains challenging to continuously modulate nanoparticle behavior at the oil/water interface without replacing surface functionality or particle morphology. Here, we utilize solvent-tunable molecular-level polymer conformation changes to achieve ‘multiple metacrystals using one nanoparticle with one chemical functionality’. We use Ag nanocubes functionalized with a mixed monolayer of thiol-terminated poly(ethylene glycol) (PEG) and hexadecanethiol (C16). We continuously modulate PEG conformation from swollen to coiled states by decreasing solvent polarity, whereas C16 promotes nanocube dispersion in organic carrier solvents. Such PEG conformation changes drive Ag nanocubes to adopt tilted, standing, and planar configurations at the oil/water interface, with their interfacial positions changing from halfway across the interface to almost immersed within the oil phase. We also identify four specific polarities which enable Ag nanocubes to assemble into large-area metacrystals with linear, hexagonal, and square close-packed lattices. Our work

establishes an innovative strategy to achieve robust tunability of nanoparticle interfacial behavior and unprecedented modulation of metacrystal structure.

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3.1 INTRODUCTION

Nanoscale surface chemistry plays a critical role in dictating the chemical behaviors of nanoparticles,¹⁻⁴ imparting specific functionalities which can be effectively utilized to direct their organization into ordered structures.⁵⁻¹⁰ Diverse approaches have been introduced to modulate the surface chemistry of nanoparticles, including the use of DNA,¹¹⁻¹⁴ polymers,¹⁵⁻¹⁷ alkylthiols,^{18, 19} mixed monolayers,²⁰⁻²² charged ligands,²³⁻²⁵ and photo-switchable ligands.^{26, 27} By using different nanoparticle morphologies and judiciously tuning their interparticle spacing, chemical patchiness, and particle orientation during self-assembly, a comprehensive library of self-assembled nanoparticle superstructures comprising chains,^{21, 28, 29} rings,³⁰⁻³² bundles,^{33, 34} hexagonal film^{18, 35, 36} and free-standing arrays^{37, 38} has been demonstrated. Among various self-assembly techniques, the oil/water interface presents a versatile platform to assemble nanoparticles.³⁹⁻⁴³ Tailoring the chemical interactions between nanoparticles and both liquid phases changes the interfacial behaviors of the nanoparticles, in turn giving rise to configurational changes in the particle-assembled structures.^{22, 44, 45} However, the main drawback here is that variations of nanoparticle interfacial behavior is currently achieved through a continuous replacement of surface ligands prior to self-assembly at the interface, thereby reducing its versatility. Hence, an alternative method which allows tuning of molecular-level changes on nanoparticle surfaces

without changing surface ligands will enable a more systematic control over the interfacial behaviors of these nanoparticles, thus enhancing the flexibility in crystal design and structural diversity achievable at the oil/water interface.

Here, we use solvent-tunable molecular-level changes in polymer conformation to demonstrate the concept of ‘multiple metacrystals using one nanoparticle with one chemical functionality’. Using Ag nanocubes functionalized with a mixed monolayer of thiol-terminated hydrophilic poly(ethylene glycol) (PEG) chain and hydrophobic hexadecanethiol (C16), we achieve a continuous solvent-dependent tuning of nanocube configuration at the oil/water interface without changing its surface functionality. By controlling carrier solvent polarity, we systematically modulate the molecular conformation of PEG from swollen to coiled states on the nanocube surfaces while C16 promotes nanocube dispersion in organic carrier solvents. PEG conformational changes provide unprecedented tuning of the nanocube interfacial interaction with the two liquid phases, leading to the continuous changes of nanocubes from planar to tilted, tilted to standing, and then back to planar configuration at the oil/water interface. In conjunction with the nanocube configurational variations, we also achieve refined control over its interfacial position from being straddled halfway across the interface to nearly fully immersed in the oil phase. Such tunability of interfacial behavior is superior to Ag nanocubes functionalized

with a homogeneous monolayer, in which only planar configurations are observed. Furthermore, we establish four solvent polarities which enable us to assemble the nanocubes into large-area metacrystals with linear, hexagonal and square close-packed lattices without changing particle morphology or surface functionality. By modulating molecular-level conformational changes, our work demonstrates a continuous tunability of nanocube interfacial behavior at the single particle level and subsequently, their macroscopic assembled metacrystals.

3.2 RESULTS AND DISCUSSION

Our approach in this work focuses on tuning the molecular conformations of capping ligands on the Ag nanocube surfaces to impact their interfacial behaviors at the oil/water interface, which can further direct their macroscopic crystal structures formed during self-assembly. We graft a mixed monolayer comprising a hydrophilic thiol-terminated poly(ethylene glycol) (PEG, $M_n=1000$) and hydrophobic 1-hexadecanethiol (C16, Figure 3.1a) in a molar ratio of 1:2 (67-C16%) onto the Ag nanocube surfaces. A mixed monolayer surface functionalization enables interactions with both aqueous and organic phases at the oil/water interface, and allows the nanocubes to be stably dispersed in carrier solvents with a greater range of polarities as compared to single monolayer-functionalized nanoparticles.

Furthermore, we have previously demonstrated that 67-C16% gives rise to unprecedented large-area linear structures, with nanocubes straddling halfway across the oil/water interface. Consequently, this ratio enables us to investigate the possibility of tuning nanocube interfacial behaviors without changing nanocube surface composition.

Figure 3.1 Tuning molecular conformation changes of PEG on Ag nanocube surfaces.

(a) Schematic depiction of solvent polarity-dependent polymer conformation changes on Ag nanocubes functionalized with a mixed monolayer of PEG and C16. (b) Hydrodynamic diameter of mixed monolayer-functionalized Ag nanocubes decreases with decreasing carrier solvent polarity. (c) Hydrodynamic diameter changes of single monolayer-functionalized Ag nanocubes in different carrier solvents.

Modulating Polymer Conformation on Ag Nanocube Surfaces

We first investigate how changes in solvent polarity impact the molecular conformation of the ligands on Ag nanocube surfaces through dynamic light scattering (DLS)

measurements (Figure 3.1a,b). Ag nanocubes have estimated effective diameters⁴⁶ of ~147 nm due to their non-spherical morphologies and numerous orientations arising from Brownian motions in solution (Figure 3.2). The functionalized Ag nanocubes are dispersed in various binary carrier solvents to systematically control carrier solvent polarity. We use polarity index (PI) to standardize the polarity of various binary carrier solvents used experimentally, with PI ranging from 0.85 (most polar, 1:1 IPA/water) to 0.33 (least polar, 1:1 hexane/ethanol, Table 3.1 for full list and calculation of binary solvent PI)^{47, 48}. PI values outside this range are not used, because $PI > 0.85$ does not allow the particles to be trapped at the oil/water interface while the particles cannot be stably dispersed in solvents with $PI < 0.33$.

Figure 3.2 (a) SEM characterization of Ag nanocubes after the synthesis and purification.

Scale bar, 200 nm. (b) Scheme of the calculation of effective diameter of nanocubes.

$$a = l, b = l \cdot \sqrt{2}, c = l \cdot \sqrt{3}$$

l is the edge length of nanocubes

$$\text{effective diameter} = (a + b + c)/3 = (1 + \sqrt{2} + \sqrt{3}) * 106/3 = 147 \text{ nm}$$

Table 3.1 Polarity index of binary solvent mixture with different compositions.

Solvent composition	Volume ratio	Polarity Index (PI)
H ₂ O	NA	1.00
Ethanol	NA	0.65
1-Hexanol	NA	0.56
IPA	NA	0.55
Chloroform	NA	0.27
THF	NA	0.21
Toluene	NA	0.10
Hexane	NA	0.01
IPA/H ₂ O	V _{IPA} % =33%	0.85
IPA/H ₂ O	V _{IPA} %=40%	0.82
IPA/H ₂ O	V _{IPA} %=50%	0.77
1-Hexanol/ethanol	V _{1-hexanol} %=50%	0.61
Chloroform/ethanol	V _{chloroform} %=33%	0.52
Chloroform/ethanol	V _{chloroform} %=40%	0.50

Chloroform/ethanol	$V_{\text{chloroform}}\% = 46\%$	0.47
Chloroform/ethanol	$V_{\text{chloroform}}\% = 50\%$	0.46
THF/ethanol	$V_{\text{THF}}\% = 50\%$	0.43
Toluene/ethanol	$V_{\text{toluene}}\% = 46\%$	0.40
Toluene/ethanol	$V_{\text{toluene}}\% = 50\%$	0.38
Hexane/ethanol	$V_{\text{hexane}}\% = 47\%$	0.35
Hexane/ethanol	$V_{\text{hexane}}\% = 50\%$	0.33

$$P_M = P_A * V_A\% + P_B * V_B\%$$

P_M : Polarity index of the mixture of binary solvents

P_A : Polarity index of solvent A

$V_A\%$: Volume ratio of solvent A

P_B : Polarity index of solvent B

$V_B\%$: Volume ratio of solvent B

For instance,

Calculation of IPA and water (volume are both 250 μL):

$$P_M = P_A * V_A\% + P_B * V_B\% = 0.546 * 0.5 + 1 * 0.5 = 0.77$$

DLS experiments show that decreasing PI (decreasing solvent polarity) leads to a concomitant decrease in the hydrodynamic diameters of Ag nanocubes functionalized with

a mixed monolayer of PEG and C16 (Figure 3.1b). The hydrodynamic diameters of the functionalized Ag nanocubes gradually decrease from (208 ± 6) nm to (198 ± 8) nm, to (157 ± 8) nm, and to (137 ± 12) nm as the carrier solvent PI decreases from 0.85, to 0.77, to 0.47, and to 0.33 respectively (Figure 3.1b). The theoretical chain lengths of PEG and C16 are ~ 10.4 nm and ~ 2.5 nm respectively, based on the number of carbon/oxygen atoms in their corresponding skeletal structures. Consequently, PEG plays a more dominant role than C16 in controlling the observed hydrodynamic diameter changes. This is further evident in the comparison of hydrodynamic diameter variations with single monolayer functionalized nanocubes at different PI values (Figure 3.1c). Nanocubes functionalized with only PEG ligands show similar decreasing trends with decreasing PI as those functionalized with a mixed monolayer, with a comparable size range of 130 – 215 nm. On the other hand, C16-functionalized nanocubes exhibit smaller hydrodynamic diameter range of 139 – 178 nm (see Table 3.2 for the comparison).

Table 3.2 Comparison of hydrodynamic diameter of Ag nanocubes with functionalization of PEG, C16 and binary molecules.

Surface group	67-C16%	PEG	C16
Highest hydrodynamic diameter	208	215	178

Lowest hydrodynamic diameter	137	130	139
Swelling size	71	85	39

X-C16% is defined as the molar percentage of C16 in the feedstock of PEG and C16 mixture which is used for particle functionalization. It is calculated by the equation, $x\text{-C16 \%} = \frac{[C16]}{[C16] + [PEG]}$. 67-C16% means 67% molar percentage of C16 in the feedstock of PEG and C16 mixture.

DLS measurements collectively establish our ability to use carrier solvent polarity to modulate the molecular conformation of the polymer chains on the functionalized Ag nanocubes. PEG chains exhibit superior water binding properties; individual chain segments adsorb water molecules efficiently, leading to an increase in polymer shell volume. Polymer chains become fully stretched on the Ag nanocube surfaces, thus increasing the hydrodynamic diameter of the functionalized Ag nanocubes. As PI decreases with the increased use of non-polar solvents, PEG chains gradually coil up to minimize polymer-solvent interactions and lead to a corresponding decrease in hydrodynamic diameters. In water-based solvents (PI=0.85), we observe a maximum PEG chain swelling of ~36 nm. As a comparison, the hydrodynamic diameters of spherical Au nanoparticles of comparable physical diameter shows that PEG chains on the spherical surfaces swell up to ~18 nm

(Figure 3.3). It is noteworthy that in addition to the solvation-related polymer swelling on the nanocube surfaces, the use of non-spherical nanocube morphology during DLS measurements can also contribute to the observed swelling size difference between the spherical and cubic nanoparticles.

Figure 3.3 (a) SEM images of Au nanospheres, showing the size of (149 ± 4) nm. (b) Hydrodynamic diameter of Au nanosphere functionalized with 67-C16%. Scale bar, 100 nm.

Interfacial behavior of nanocubes at the oil/water interface

Next, we investigate how the various solvent polarity-dependent molecular conformations can influence the interfacial behavior of the Ag nanocubes at the oil/water interface. A dilute dispersion of Ag nanocubes in various carrier solvents is added and subsequently immobilized at the oil/water interface using the gel-trapping technique. This technique allows subsequent transfer of the nanocubes to a hardened poly(dimethylsiloxane) (PDMS) surface (Figure 3.4). The exposed part of the nanocubes on the PDMS surface

corresponds to the amount in contact with the aqueous phase. We then use atomic force microscopy (AFM) to characterize the nanocube configuration and position at the oil/water interface. The height percentage of nanocubes in contact with the oil phase (%cube_{oil}) can be further derived using the equation $\%cube_{oil} = (1 - H_{AFM}/H_{orientation}) * 100\%$ (Figure 3.5). H_{AFM} is the measured height of nanocubes above PDMS substrate and $H_{orientation}$ is the full nanocube height at planar, tilted, and standing orientations.

Figure 3.4 Using carrier solvent polarity to modulate interfacial behavior of Ag nanocubes. (a) Schematic illustration of using gel-trapping to immobilize Ag nanocubes at the oil/water interface. (b) Schematic depiction of solvent polarity-dependent Ag nanocube interfacial behavior. (c) Using AFM to characterize the interfacial position and configuration of Ag nanocubes at the oil/water interface. (d) Corresponding height profiles

of Ag nanocubes extracted along the red line in (c). AFM measurements enable the derivation of the percentage of Ag nanocubes in contact with the oil phase. Percentage of Ag nanocubes in contact with oil phase for (e) mixed monolayer functionalization and (f) single monolayer functionalization. Scale bars in (c), 200 nm.

Figure 3.5 Scheme of the calculation of cube percentage in contact with oil phase.

% of cube_{oil} is the height ratio of cubes in contact with oil phase, H_{AFM} is the height of nanocubes above PDMS substrate, H_{orientation} is the height of nanocubes with different orientation.

The calculation process is as follows.

l is defined as the edge length of cubes.

For planar cubes,

$$H_{orientation} = H_{planar} = l$$

$$\% \text{ of cube}_{oil} = 1 - H_{AFM}/H_{planar} = 1 - H_{AFM}/106$$

For tilting cubes,

$$H_{orientation} = H_{tilting} = l * \sqrt{2}$$

$$\% \text{ of cube}_{\text{oil}} = 1 - H_{\text{AFM}}/H_{\text{tilting}} = 1 - H_{\text{AFM}}/(106*\sqrt{2})$$

For standing cubes,

$$H_{\text{orientation}} = H_{\text{standing}} = l*\sqrt{3}$$

$$\% \text{ of cube}_{\text{oil}} = 1 - H_{\text{AFM}}/H_{\text{standing}} = 1 - H_{\text{AFM}}/(106*\sqrt{3})$$

Changing PI leads to a continuous modulation of both the interfacial configuration and position of the Ag nanocubes (Figure 3.4b-e, Table 3.3). Specifically, decreasing PI pushes the Ag nanocubes further into the oil phase, with $\% \text{cube}_{\text{oil}}$ increasing from $\sim 40\%$ to $\sim 95\%$. In addition, with decreasing PI, the orientation of Ag nanocubes also varies from planar to tilted, tilted to standing, and back to the planar configuration as the nanocube's position move into the oil phase (Figure 3.4b). At $\text{PI}=0.85$, Ag nanocubes are primarily planar at the oil/water interface, with a $\% \text{cube}_{\text{oil}}$ of $(40 \pm 4)\%$ (Figure 3.4ci, di). As PI decreases to 0.77, Ag nanocubes become tilted at the interface, with $\% \text{cube}_{\text{oil}}$ increasing to $(49 \pm 5)\%$ (Figure 3.4cii, dii). Ag nanocubes then adopt a standing orientation at $\text{PI}=0.47$, with the corresponding $\% \text{cube}_{\text{oil}}$ further increasing to $(71 \pm 2)\%$ (Figure 3.4ciii, diii). At $\text{PI}=0.38$, the nanocubes maintain a standing configuration, but $\% \text{cube}_{\text{oil}}$ increases to $(83 \pm 4)\%$ (Figure 3.4civ, div). At the lowest experimental PI of 0.33, the nanocubes revert to a planar orientation, and attains the highest $\% \text{cube}_{\text{oil}}$ of $(95 \pm 2)\%$ (Figure 3.4cv, dv).

Table 3.3 AFM measurements of Ag nanocubes with 67-C16% functionalization dispersed in different solvents and oriented in different configurations.

Polarity index (PI)	AFM Height (in aqueous phase) / nm	Height in oil phase / nm	% Immersed in aqueous phase (%)	% Immersed in oil phase (%)
0.85	64 ± 10	42 ± 10	60 ± 4	40 ± 4
0.82	89 ± 11	65 ± 11	54 ± 4	46 ± 4
0.77	76 ± 8	74 ± 8	51 ± 5	49 ± 5
0.61	62 ± 3	121 ± 20	37 ± 2	63 ± 2
0.50	53 ± 8	113 ± 11	31 ± 7	69 ± 7
0.47	46 ± 12	119 ± 19	29 ± 2	71 ± 2
0.42	43 ± 5	131 ± 15	25 ± 6	75 ± 6
0.38	23 ± 10	108 ± 12	17 ± 4	83 ± 4
0.35	19 ± 7	129 ± 19	9 ± 4	91 ± 4
0.33	5 ± 3	101 ± 3	5 ± 2	95 ± 2

In addition, we also observe mixed configurations at the interface at PI=0.82, 0.61, 0.50, 0.42 and 0.35, comprising planar, tilted and standing orientations instead of a homogeneous one. These varied configurations can be observed from large-area AFM topographic images

(Figure 3.6). At $PI=0.82, 0.61, 0.50, 0.42$, and 0.35 , the corresponding $\%cube_{oil}$ based on the average configuration of 50 nanocubes gradually increases to $(46 \pm 4)\%$, $(53 \pm 6)\%$, $(68 \pm 4)\%$, $(75 \pm 2)\%$, and $(91 \pm 4)\%$ respectively (Figure 3.7). Notably, this ability to continuously tune the interfacial configuration of Ag nanocubes without changing surface functionality has not been demonstrated to date. We achieve a large dynamic tunable range of $\sim 55\%$ for $\%cube_{oil}$ which is accompanied by a systematic change in nanocube configuration from planar to tilted and standing configurations.

Figure 3.6 Large-area AFM topographical images of Ag nanocube in the solvent of (a) $PI=0.82$, (b) $PI=0.61$, (c) $PI=0.42$, which has various configuration at the oil-water interface.

Figure 3.7 AFM measurements of Ag nanocubes in the solvent of PI : (a) 0.82 , (b) 0.61 , (c) 0.50 , (d) 0.42 , (e) 0.35 . Scale bar, 100 nm .

We further demonstrate that our mixed monolayer approach enables a significantly more dynamic interfacial modulation of Ag nanocubes' configuration and position as compared to a single monolayer approach. Firstly, the predominant interfacial configuration is planar across various PI values for both variants of single monolayer functionalized nanocubes (Figure 3.8). Secondly, the tunable range of the interfacial position of the single monolayer functionalized Ag nanocubes is significantly smaller as compared to the mixed monolayer functionalized ones. Mixed monolayer functionalization enables a dynamic tunable range of $\sim 55\%$ for $\%cube_{oil}$, whereas PEG alone only allows a maximum tunable range of $\sim 35\%$ ($\%cube_{oil}$ from 20% to 57%) and that for C16 is merely 5% ($\%cube_{oil}$ from 93% to 98%). Since the assembled structure is affected by particle interfacial behavior, a higher tunability enabled by the mixed monolayer functionalization should create a greater structural tunability of metacrystal structure at the oil/water interface.

Figure 3.8 (a) AFM topographic images and (b) the corresponding height profile along the highlighted line. Scale bar, 150 nm.

The changes in interfacial configuration and position of Ag nanocubes at different PIs can be correlated with the molecular behaviors of the PEG chains on the nanocube surfaces.

We estimate the relative chain collapse percentage based on the hydrodynamic diameter variations at different PIs. PEG chains are assumed to be fully stretched at PI=1.00 with a hydrodynamic diameter of (232 ± 11) nm and fully collapsed at PI=0.33, corresponding to a chain collapse percentage of 0 % and 100 % respectively (see Table 3.4 for the calculation and full list). To quantify the behavior of PEG chains in various carrier solvents, we use the polymer-solvent interaction parameter χ (absolute value)⁴⁹. In general, good solvents have small χ values below 0.5, and polymer chains swell due to its favorable interaction with the solvent, whereas poor solvents have high χ values above 0.5, leading to the coiling and collapse of polymer chains.

Table 3.4 Collapsing percentage of PEG on Ag nanocubes with 67-C16% functionalization dispersed in different solvents.

Polarity index (PI)	Hydrodynamic diameter (nm)	Collapsing percentage (%)
1.00	230 ± 11	0

0.85	208 ± 6	24
0.82	206 ± 5	26
0.77	198 ± 4	34
0.61	173 ± 8	61
0.50	161 ± 11	74
0.47	157 ± 8	78
0.42	151 ± 9	85
0.38	142 ± 8	95
0.35	139 ± 10	98
0.33	137 ± 9	100

Calculation of collapsing percentage

The collapsed percentage at PI=1.00 and 0.33 is assumed to be 0% and 100% respectively.

The hydrodynamic diameter at PI=1.00 and 0.33 is assumed to be 230 nm and 137 nm respectively.

So collapsing percentage = $(230 - \text{hydrodynamic diameter}) / (230 - 137) * 100\%$

For instance,

Calculation of collapsing percentage at PI=0.77:

Collapsing percentage = $(230 - 198) / (230 - 137) * 100\% = 34\%$

Decreasing PI from 0.85 to 0.77 causes the nanocubes to switch from a planar to a tilted configuration. In this PI range, we vary the volume percentage of isopropyl alcohol (IPA) in the IPA/water binary mixture to tune the PI. The individual χ values of PEG in water and IPA are 0.43 and 0.47 respectively⁴⁹, indicating that IPA is a comparatively poorer solvent for PEG than water. At a relatively higher PI of 0.85, PEG adopts a swollen conformation (24 % collapse) due to favorable interactions between PEG and water (Figure 3.1ai). Consequently, we observe a planar nanocube configuration with a %cube_{oil} of $(40 \pm 4) \%$, in which PEG chains on the nanocubes maximizes its contact with the aqueous phase while simultaneously avoiding contact with the oil phase at the bulk interface. Increasing IPA content from PI=0.85 to 0.77 reduces the hydrodynamic diameters of Ag nanocubes from $(208 \pm 6) \text{ nm}$ to $(173 \pm 8) \text{ nm}$. PEG chains coil up slightly, with a collapse percentage of 14% on the nanocube surface. The corresponding increase of %cube_{oil} to $(49 \pm 5) \%$ also points to a slightly more favorable interaction with the oil phase with the coiling of PEG chains.

In addition, we observe the standing nanocube configurations at PI=0.47 and 0.38, as well as the planar configuration at PI=0.33. At these PI values, ethanol ($\chi=0.70$) is the main solvent, and the co-solvents change from chloroform ($\chi=0.55$, ~1:1 v/v, PI=0.47) to toluene ($\chi=0.26$, 1:1 v/v, PI=0.38) and hexane ($\chi=1.7$, 1:1 v/v, PI=0.33). These solvents are

generally poor for PEG, leading to progressive coiling of PEG chains on the nanocube surfaces⁵⁰. The corresponding collapse percentage increases to 78%, 95% and 100% at PI=0.47, 0.38 and 0.33 respectively. Such conformational changes are consistent with the continual decrease in the hydrodynamic diameters of Ag nanocubes, which decreases from (157 ± 8) nm at PI=0.47 to (142 ± 8) nm at PI=0.38 and further to (137 ± 9) nm at PI=0.33. Increasing PEG collapse percentage enhances interaction with the oil phase, as the hydrophilic components coil within the polymer chains to expose the more hydrophobic segments of the PEG chains. This in turn leads to the formation of uniform standing nanocube configuration to reduce the interaction with aqueous phase with %cube_{oil} (71 ± 2)% and (83 ± 4)% at PI=0.47 and 0.38 respectively. With 100 % coiling at PI=0.33, PEG essentially becomes hydrophobic and this leads to a planar nanocube configuration with a %cube_{oil} of (95 ± 2)%. This behavior is similar with nanocubes functionalized with only C16. In these three instances, contact with the oil phase is optimized while that with the aqueous phase is minimized. At intermediate PI values, nanocube configurations at the oil/water interface are somewhat randomized. This observation suggests that the PEG chains on the nanocube surfaces likely comprise a mixture of conformations. Our findings here successfully demonstrate the ability to modulate polymer chain conformations on the nanocube surfaces to achieve a dynamic tuning of the nanocube interfacial behavior.

Multiple metacrystals using one nanoparticle with one chemical functionality

Having established how changes in molecular conformations on the nanocube surfaces can impact the interfacial configuration of the Ag nanocubes, we further investigate the types of assembled structures formed at the oil/water interface at various PIs. Ag nanocubes are dispersed in different carrier solvent and are then assembled at the oil-water interface. The assembled plasmonic metacrystals are subsequently immobilized using the gel-trapping technique (Figure 3.4a).

Four large-area plasmonic metacrystals with three distinct structures can be formed at the oil/water interface when the carrier solvent PI changes from 0.77 to 0.47, 0.38 and to 0.33 (Figure 3.9, see Table 3.1 for the solvent composition at these four specific PIs).

Ag nanocubes first assemble into linear metacrystal with face-to-face configuration within the wire and edge-to-edge configuration between neighboring strings at $PI=0.77$ (Figure 3.9a-d). Nanocubes are tilted in this metacrystal. Fast Fourier transform (FFT) analysis exhibits the linear structure (Figure 3.9a) and radial distribution function analysis shows an interparticle separation of ~ 142 nm (Figure 3.9e). The packing efficiency of this metacrystal is 50 % (Figure 3.10). A hexagonal plasmonic metacrystal forms at the oil/water interface for $PI=0.47$ (Figure 3.9f-i). Nanocubes organize in a standing configuration with edge-to-edge contact in this metacrystal. FFT shows a hexagonal structure (Figure 3.9f).

The interparticle distance increases to ~ 162 nm (Figure 3j), and leads to a decrease in packing efficiency to 24 % (Figure 3.10). This hexagonal metacrystal structure is also observed at $PI=0.38$. A square close-packed metacrystal forms at $PI=0.33$ (Figure 3.9k-n). The nanocubes are planar, and contact each other via their facets. The square lattice is evident from FFT analysis (Figure 3.9k). The interparticle distance is the smallest at ~ 110 nm (Figure 3.9o) and this metacrystal has 100% packing efficiency (Figure 3.10). AFM measurement shows that the heights of assembled structures are similar with that of the single particle height at the oil/water interface (Figure 3.9b,d,g,i,l,n).

Figure 3.9 Multiple metacrystals using one nanoparticle with one chemical functionality. (a,f,k) Assembled metacrystals of tilted, standing and planar nanocubes at

PI=0.77, 0.47, and 0.33 respectively. Insets are the corresponding fast Fourier transform (FFT) analysis. (a-e) At PI=0.77, tilted nanocubes form linear structures, align face-to-face within the wire, and edge-to-edge between neighboring wires. (f-j) Decreasing the solvent polarity to PI=0.47 drives the formation of a hexagonal structure with the standing nanocubes aligned edge to edge. (k-o) At PI=0.33, a square close-packed structure forms with nanocubes adopting a planar configuration. (b,d,g,i,l,n) AFM characterization of assembled nanocube interfacial behavior. Scale bars in (a,f,k), 1 μm ; scale bars in (b,g,l) and (c,h,m), 200 nm. (e,j,o) Radial distribution function analyses of tilted, standing, and planar nanocubes in the (a) linear, (f) hexagonal and (k) square lattices.

Figure 3.10 Scheme of packing efficiency of metacrystals of (a) planar Ag cubes, (b) tilting cubes, (c) standing cubes. (d) Changes in packing efficiency with variations in metacrystal structures.

The squares in (a) show the repeat unit of the planar Ag cubes, which is filled with one cube, with no remaining space filled with holes. The rectangles in (b) show the simplest repeat unit of tilting structure, which is filled with one cube, with the remaining space filled with two tetrahedral holes. The simplest repeat unit of the standing structure is shown by the rectangles in the figure above. The repeat unit is filled with one cube, with the remaining space filled with two tetrahedral holes.

The edge length of a single cube is l

In the square in (a)

Length of cube = l ($a = b = c = l$)

Volume of repeat unit = $l \times l \times l = l^3$

Volume of one cube = l^3

Packing efficiency of planar cubes = $\frac{l^3}{l^3} = \underline{100\%}$

In the rectangle in (b),

$$a = l, b = \frac{\sqrt{2}}{2}l, c = \frac{\sqrt{2}}{2}l$$

Volume of repeat unit = $a \times b \times c = \sqrt{2}l \times l \times \sqrt{2}l = 2l^3$

Volume of one cube = $l^3 = \underline{50\%}$

In the rectangle in (c),

$$a = \sqrt{3}l, b = \sqrt{2}l, c = \sqrt{3}l$$

$$\text{Volume of repeat unit} = a \times b \times c = \sqrt{3}l \times \sqrt{2}l \times \sqrt{3}l = 3\sqrt{2}l^3$$

$$\text{Volume of one cube} = l^3$$

$$\text{Packing efficiency of standing cubes} = \frac{l^3}{3\sqrt{2}l^3} = \underline{24\%}$$

We note that four PI values give rise to ordered metacrystal formation, namely PI=0.77, 0.47, 0.38 and 0.33. At PI=0.77, swollen PEG chains on nanocube surfaces result in a tilted orientation at the oil/water interface, with a %cube_{oil} of ~ 49 %. This tilted configuration maximizes the contact between PEG-grafted surfaces with aqueous phase, thus leading to the formation of linear structures. At PI=0.47 and 0.38, PEG chains coil up on the nanocube surfaces. To enhance interaction with the oil phase, nanocubes form standing configurations and organize into a hexagonal metacrystal with estimated %cube_{oil} of ~ 71 % and ~83% respectively. At PI=0.33, PEG chains are completely coiled up. To minimize interactions with the aqueous phase, nanocubes form square close-packed structures with planar configuration and a %cube_{oil} of ~95 %.

Systematic metacrystal structural transformation

In addition to these four metacrystals with three distinct structures, we unravel a systematic metacrystal structural transformation by simply changing the carrier solvent PI (Figure 3.11). Reducing solvent PI changes the dominant population of the nanocube

configuration at the oil/water interface. At $PI=0.85$, the planar orientation with face-to-face configuration dominates the self-assembly, with 76 % of the nanocubes organized in this configuration (Figure 3.11b,i). Slight reduction of PI to 0.82 leads to an intermediate disordered structure, with an accompanying decrease of planar nanocubes to 51 %, and increase in tilted and standing nanocubes (Figure 3.12a, 3.13). At $PI=0.77$, the tilted nanocube population increases from 17 % to 83 %, resulting in the formation of ordered linear structures of tilted cubes (Figure 3.11c,i). At $PI=0.61$, the intermediate disordered structure is formed, with a decrease of tilted cubes to 35% and an increase of planar and standing nanocube population (Figure 3.11d,i). Further decreasing the carrier solvent PI leads to decreased planar and increased standing configurations. This intermediate structure persists over PI values of 0.52 and 0.50 (Figure 3.12b,c). At $PI=0.52$ and 0.50, the population of planar nanocubes gradually decreases from 63% to 23%, while the population of standing cubes increases from 19% to 51% (Figure 3.13). At $PI=0.47$, 80 % of the nanocubes adopt standing configurations and assemble into the hexagonal metacrystal (Figure 3.11e,i). As PI further reduces to 0.46 and 0.40, intermediate structures comprising various orientations are formed (Figure 3.11f, 3.12d,e) and the standing nanocube population slightly decreases to 65% and 62% respectively (Figure 3.11i, 3.13). In this range, the standing cubes are still the dominant orientation. At $PI=0.38$, the nanocubes

assemble into the hexagonal metacrystal with increased 91% standing nanocube configurations (Figure 3.11g,i). Intermediate disordered structures are again observed at $PI=0.35$ (Figure 3.12f) before the square close-packed structure forms at $PI=0.33$ (Figure 3.11h). At $PI=0.35$, the intermediate structure is composed of 68% planar, 3% tilted and 29% standing nanocubes (Figure 3.13). At $PI=0.33$, planar nanocubes increase to 93% and form the square structure (Figure 3.11i). Notably, the formation of the above intermediate assembled structures also coincides with the mixed configurations observed during the single-particle AFM measurements, likely arising from the co-existence of different polymer conformations on the nanocube surfaces.

Figure 3.11 Achieving continuous transformation of assembled structures by simply tuning carrier solvent polarity. By tuning the carrier solvent polarity, the structural transformation of Ag nanocube assembly can be observed from (a) schematic description

and corresponding (b-h) SEM images. (i) Population of Ag nanocubes adopting planar, tilted, standing orientations in the assembled structures under different carrier solvent polarity. (b-h) Scale bar, 500 nm.

Figure 3.12 SEM images of assembled structure at other solvent polarity. Scale bar, 1 μm .

Figure 3.13 Population diagram of planar, tilted and standing nanocubes in the assembled structures which are shown in Figure 3.12.

We further emphasize the advantages of our mixed monolayer system by comparing with the assembled nanocube structures formed using pure monolayers. With a predominant planar configuration, the only metacrystal formed using Ag nanocubes functionalized with a single monolayer is the square close-packed structure (Figure 3.14). Moreover, we

demonstrate that mixed monolayer with 95-C16% can also enable structural tunability.

Similar conformational changes of PEG on the nanocube surfaces are observed from hydrodynamic diameter measurement (Figure 3.15). These molecular-level changes in turn lead to structural transformation of nanocube organization, including hexagonal lattice of standing nanocubes, linear structure of tilted cubes, and the square metacrystal of planar cubes (Figure 3.16). Our findings also highlight the advantage of mixed monolayer functionalization over single monolayer functionalization to achieve solvent-tunable nanocube assembly. Ligand-solvent interaction thus plays a vital role in predicting nanoparticle interfacial behavior as well as provides a simpler and more accurate control on the assembled metacrystal structure.

Figure 3.14 Assembly of (a) pure PEG- and (b) C16-functionalized nanocubes in different solvent can hardly achieve the tunability of superstructure, showing only one structure.

Scale bar, 1 μm .

Figure 3.15 Hydrodynamic diameter of 95-C16%-functionalized nanocubes in different solvents.

Figure 3.16 Gradual change of assembled structure of Ag nanocube with 95-C16% functionalization in different solvent. Scale bar, 1 μm .

3.3 CONCLUSION

In this work, we demonstrate the concept of ‘multiple metacrystals using one nanoparticle with one chemical functionality’ by utilizing molecular-level solvent-dependent polymer conformation changes. Ag nanocubes functionalized with a mixed monolayer of PEG and alkylthiol is used as our model system. By gradually manipulating the solvent-dependent PEG conformation of PEG from swollen to coiled states, we achieve a continuous tuning of nanocube configuration at the oil/water interface. We find four solvent polarities ($PI=0.77, 0.47, 0.38, 0.33$) at which single nanocubes undergo a transformation from tilted to standing, and standing to planar configurations. The nanocube position at the interface also exhibits high tunability with polarity variations, changing from being straddled across the oil/water interface to being nearly fully immersed in the oil phase. Nanocubes also organize into large-area linear, hexagonal and square close-packed metacrystals at these four specific polarities. In addition, we demonstrate the advantage of our mixed monolayer approach over a homogeneous ligand functionalization in terms of metacrystal tunability, where homogeneously functionalized nanocubes can only form planar structures at the oil/water interface. Our work demonstrates an innovative and simple approach to utilize carrier solvent to achieve excellent tunability of particle interfacial behavior. Such continuous modulation of the assembled metacrystals without changing surface functionality can potentially be applied to other shape-controlled building blocks as

well. This fundamental study bridges solvent-dependent molecular level changes to macroscopic structure and provides a promising approach to fabricate metacrystals with tunable properties.

3.4 MATERIALS AND METHODS

Materials. Silver nitrate ($\geq 99\%$), 1,5-pentanediol (PD, $\geq 97\%$), poly(vinylpyrrolidone) (PVP, average MW = 55 000 g/mol), poly(ethylene glycol) methyl ether thiol (PEG, average m.w. = 1000 g/mol), 1-hexadecanethiol (C16), isopropyl alcohol (IPA), 1-hexanol, chloroform, Tetrahydrofuran (THF), toluene, hexane, decane ($\geq 99\%$), and were purchased from Sigma Aldrich; copper(II) chloride ($\geq 98\%$) was from Alfa Aesar. Ethanol (ACS, ISO, Reag. Ph Eur) was obtained from EMSURE. Silicon elastomer curing agent and silicone elastomer base were purchased from Dow Corning. Gellan Gum (KELKOGEL K) was kindly sponsored by CP Kelco (USA). All chemicals were used without further purification. Milli-Q water ($>18.0 \text{ M}\Omega\cdot\text{cm}$) was purified with a Sartorius Arium 611 UV ultrapure water system.

Ag nanocube synthesis. The synthesis of Ag nanocubes was carried out using the polyol reduction method⁵¹. Briefly, 8 mg CuCl_2 , 20 mg poly(vinylpyrrolidone) (PVP) and 20 mg AgNO_3 were dissolved in 10 mL 1,5-pentanediol (PD) separately, using repeated sonication

and vortex. After the complete dissolution of these precursors, 35 μL CuCl_2 solution was added to AgNO_3 solution. Then in a round bottomed flask, 20 mL PD was heated at 190 $^\circ\text{C}$ for 10 min. 250 μL PVP solution was dropwise injected into 20 mL PD, followed by quick injection of 500 μL AgNO_3 solution. Subsequently, AgNO_3 precursor was injected quickly every min and PVP precursor was dropwise injected every 30 s until nanocubes were formed. The heating was then stopped and the whole reaction system was cooled down to room temperature. For the purification of Ag nanocubes, PD was first removed by using acetone, ethanol over multiple centrifugation rounds, followed by redispersing in 20 ml ethanol. The Ag nanocube dispersion was then vacuum filtered using polyvinylidene difluoride filter membranes (Durapore) with pore sizes ranging from 5,000, 650, 450 to 220 nm.

Mixed monolayer formation. The purified Ag nanocube dispersion was allowed to sediment for several days. 0.5 μL of the sediment was dispersed in ethanol and centrifuged once before re-dispersing in 1.5 ml of ethanol/isopropyl alcohol (IPA) (1:1). A mixture of 1 mM PEG and C16 solution was then added dropwise to this dispersion under stirring. A 10 μL mixture of 1 mM PEG and C16 solution was then added dropwise to this dispersion under stirring. The molar percentage of C16 in the feedstock was 67% (defined as 67-C16%, $\text{C16\%} = [\text{C16}]/([\text{C16}] + [\text{PEG}])$). Functionalization took place for 4 h, followed by

centrifugation to remove excess molecules. Then the sediment was redispersed in 1.5 mL of ethanol/IPA (1:1) and 10 mL fresh thiol solution with same ratio was added under stirring. The functionalization was allowed to continue for another 3 h, followed by three rounds of centrifugation and washing with IPA/water (1:1).

Interfacial Self-assembly. The assembly process was described in Figure 2a. Gellan gum solution (2 wt%, 6 mL) was used as aqueous phase and n-decane was added on top of the aqueous polymeric phase as the oil phase. The gel-trapping experiments were slightly modified from the procedure reported by Paunov and co-workers⁵². The gellan gum solution was prepared under ~80 °C in oil bath and under stirring at 1400 rpm until the gel was completely hydrated. Subsequently, pre-heated n-decane was added to the top of the gel solution to create the oil phase. Ag nanocubes were dispersed in 0.5 µl binary solvents, whose component is shown in Table S1. The range of solvent component is from water (PI=1) to hexane (PI=0.01). Particle dispersion was then injected at the interface. The whole system was left at 80 °C for ~15 min before cooling down to room temperature to ensure that the cubes at the oil/water interface had sufficient time to spread out and achieve thermodynamic equilibrium. After the gelling of gellan gum, n-decane was decanted gently and premixed PDMS precursor mixture (5:1; elastomer: curing agent) was deposited onto

the arrays of Ag nanocubes. After the curing of PDMS, the monolayer of Ag nanoparticles was peeled off and washed in hot water.

Scanning electron microscopy (SEM) characterization. SEM imaging was performed using scanning electron microscopy (JEOL-JSM-7600F) at an accelerating voltage of 5 kV. Assembled monolayer of Ag nanoparticles on PDMS was imaged by using SEM directly and analyzed using Image J software.

Atomic force microscopy (AFM) measurement. AFM was used to study the topological changes in the metasurfaces of Ag nanocubes on the PDMS molds using a Bruker Dimension ICON with NanoScope V controller from Bruker. Tapping mode (non- contact mode) image was acquired using silicon probes (Tap300Al-G with 30-nm aluminium reflex coating) from BudgetSensor. Data analysis was carried out using WSxM Scanning Probe Microscopy Software, a free program from Nanotec Electrónica S.L36.

Dynamic light scattering (DLS) characterization. DLS measurements were performed by using Malvern Instruments Zetasizer Nano series instrument equipped with a 22 mW He-Ne laser operating at $\lambda = 633$ nm at 25 0C. All the particle suspensions were diluted with the solvent and transferred into quartz sample cell for the measurement.

3.5 REFERENCES

1. Bent, S. F.; Kachian, J. S.; Rodríguez-Reyes, J. C. F.; Teplyakov, A. V. *Proc. Natl. Acad. Sci.* **2011**, *108*, 956-960.
2. Jiang, Y.; Huo, S.; Mizuhara, T.; Das, R.; Lee, Y.-W.; Hou, S.; Moyano, D. F.; Duncan, B.; Liang, X.-J.; Rotello, V. M. *ACS Nano* **2015**, *9*, 9986-9993.
3. Azcárate, J. C.; Corthey, G.; Pensa, E.; Vericat, C.; Fonticelli, M. H.; Salvarezza, R. C.; Carro, P. J. *Phys. Chem. Lett.* **2013**, *4*, 3127-3138.
4. Nasir, I.; Lundqvist, M.; Cabaleiro-Lago, C. *Nanoscale* **2015**, *7*, 17504-17515.
5. Grubbs, R. B. *Nat. Mater.* **2007**, *6*, 553-555.
6. Whitesides, G. M.; Grzybowski, B. *Science* **2002**, *295*, 2418-2421.
7. Nie, Z.; Petukhova, A.; Kumacheva, E. *Nat. Nanotechnol.* **2010**, *5*, 15-25.
8. Xu, L.; Han, G.; Hu, J.; He, Y.; Pan, J.; Li, Y.; Xiang, J. *Phys. Chem. Chem. Phys.* **2009**, *11*, 6490-6497.
9. Boles, M. A.; Engel, M.; Talapin, D. V. *Chem. Rev.* **2016**, *116*, 11220-11289.
10. Choi, J. J.; Bealing, C. R.; Bian, K.; Hughes, K. J.; Zhang, W.; Smilgies, D.-M.; Hennig, R. G.; Engstrom, J. R.; Hanrath, T. *J. Am. Chem. Soc.* **2011**, *133*, 3131-3138.
11. Auyeung, E.; Li, T. I. N. G.; Senesi, A. J.; Schmucker, A. L.; Pals, B. C.; de la Cruz, M. O.; Mirkin, C. A. *Nature* **2014**, *505*, 73-77.

12. Zhang, Y.; Lu, F.; Yager, K. G.; van der Lelie, D.; Gang, O. *Nat. Nanotechnol.* **2013**, *8*, 865-872.
13. Sapsford, K. E.; Park, D.; Goldman, E. R.; Foos, E. E.; Trammell, S. A.; Lowy, D. A.; Ancona, M. G. *Langmuir* **2008**, *24*, 10245-10252.
14. Fischler, M.; Homberger, M.; Simon, U., DNA-Mediated Assembly of Metal Nanoparticles: Fabrication, Structural Features, and Electrical Properties. In *Nanobioelectronics - for Electronics, Biology, and Medicine*, Offenhäusser, A.; Rinaldi, R., Eds. Springer New York: New York, NY, 2009; pp 11-41.
15. Ye, X.; Zhu, C.; Ercius, P.; Raja, S. N.; He, B.; Jones, M. R.; Hauwiller, M. R.; Liu, Y.; Xu, T.; Alivisatos, A. P. *Nat. Commun.* **2015**, *6*, 10052.
16. Gao, B.; Arya, G.; Tao, A. R. *Nat. Nanotechnol.* **2012**, *7*, 433-437.
17. Shi, Q.; Si, K. J.; Sikdar, D.; Yap, L. W.; Premaratne, M.; Cheng, W. *ACS Nano* **2016**, *10*, 967-976.
18. Lee, Y. H.; Shi, W.; Lee, H. K.; Jiang, R.; Phang, I. Y.; Cui, Y.; Isa, L.; Yang, Y.; Wang, J.; Li, S.; Ling, X. Y. *Nat. Commun.* **2015**, *6*, 6990.
19. Comeau, K. D.; Meli, M. V. *Langmuir* **2012**, *28*, 377-381.
20. Walker, D. A.; Leitsch, E. K.; Nap, R. J.; Szleifer, I.; Grzybowski, B. A. *Nat. Nanotechnol.* **2013**, *8*, 676-681.

21. Lee, H.-Y.; Shin, S. H. R.; Drews, A. M.; Chirsan, A. M.; Lewis, S. A.; Bishop, K. J. M. *ACS Nano* **2014**, *8*, 9979-9987.
22. Yang, Y.; Lee, Y. H.; Phang, I. Y.; Jiang, R.; Sim, H. Y.; Wang, J.; Ling, X. Y. *Nano Lett.* **2016**, *16*, 3872-3878.
23. Gao, P.; Yi, Z.; Xing, X.; Ngai, T.; Jin, F. *Langmuir* **2016**, *32*, 4909-4916.
24. Bianchi, E.; Likos, C. N.; Kahl, G. *Nano Lett.* **2014**, *14*, 3412-3418.
25. Pillai, P. P.; Kowalczyk, B.; Grzybowski, B. A. *Nanoscale* **2016**, *8*, 157-161.
26. Jha, P. K.; Kuzovkov, V.; Grzybowski, B. A.; Olvera de la Cruz, M. *Soft Matter* **2012**, *8*, 227-234.
27. Zhao, H.; Sen, S.; UdayabhaskararaoT; Sawczyk, M.; Kučanda, K.; Manna, D.; Kundu, P. K.; Lee, J.-W.; Král, P.; Klajn, R. *Nat. Nanotechnol.* **2016**, *11*, 82-88.
28. Fang, W. X.; He, Z. H.; Xu, X. Q.; Mao, Z. Q.; Shen, H. *EPL* **2007**, *77*, 68004.
29. Nithiyanantham, U.; Ede, S. R.; Anantharaj, S.; Kundu, S. *Cryst. Growth Des.* **2015**, *15*, 673-686.
30. Wei, A.; Kasama, T.; Dunin-Borkowski, R. E. *J. Mater. Chem.* **2011**, *21*, 16686-16693.
31. Lin, G.; Zhu, X.; Anand, U.; Liu, Q.; Lu, J.; Aabdin, Z.; Su, H.; Mirsaidov, U. *Nano Lett.* **2016**, *16*, 1092-1096.

32. Roller, E.-M.; Khorashad, L. K.; Fedoruk, M.; Schreiber, R.; Govorov, A. O.; Liedl, T. *Nano Lett.* **2015**, *15*, 1368-1373.
33. Nie, Z.; Fava, D.; Kumacheva, E.; Zou, S.; Walker, G. C.; Rubinstein, M. *Nat. Mater.* **2007**, *6*, 609-614.
34. Reiser, B.; Gerstner, D.; Gonzalez-Garcia, L.; Maurer, J. H. M.; Kanelidis, I.; Kraus, T. *Phys. Chem. Chem. Phys.* **2016**, *18*, 27165-27169.
35. Wang, Y.-W.; Kao, K.-C.; Wang, J.-K.; Mou, C.-Y. *J. Phys. Chem. C* **2016**, *120*, 24382-24388.
36. Chou, L. Y. T.; Zagorovsky, K.; Chan, W. C. W. *Nat. Nanotechnol.* **2014**, *9*, 148-155.
37. Ng, K. C.; Udagedara, I. B.; Rukhlenko, I. D.; Chen, Y.; Tang, Y.; Premaratne, M.; Cheng, W. *ACS Nano* **2012**, *6*, 925-934.
38. Kim, K.; Han, H. S.; Choi, I.; Lee, C.; Hong, S.; Suh, S.-H.; Lee, L. P.; Kang, T. *Nat. Commun.* **2013**, *4*, 2182.
39. Duan, H.; Wang, D.; Kurth, D. G.; Mohwald, H. *Angew. Chem. Int. Ed.* **2004**, *43*, 5639-5642.
40. Booth, S. G.; Dryfe, R. A. W. *J. Phys. Chem. C* **2015**, *119*, 23295-23309.
41. Hu, L.; Chen, M.; Fang, X.; Wu, L. *Chem. Soc. Rev.* **2012**, *41*, 1350-1362.

42. Lee, Y. H.; Lee, H. K.; Ho, J. Y. C.; Yang, Y.; Ling, X. Y. *Analyst* **2016**, *141*, 5107-5112.
43. Guo, P.; Sikdar, D.; Huang, X.; Si, K. J.; Su, B.; Chen, Y.; Xiong, W.; Yap, L. W.; Premaratne, M.; Cheng, W. *J. Phys. Chem. C* **2014**, *118*, 26816-26824.
44. Biswal, N. R.; Rangera, N.; Singh, J. K. *J. Phys. Chem. B* **2016**, *120*, 7265-7274.
45. Patra, D.; Sanyal, A.; Rotello, V. M. *Chem. Asian J.* **2010**, *5*, 2442-2453.
46. Henzie, J.; Grünwald, M.; Widmer-Cooper, A.; Geissler, P. L.; Yang, P. *Nat. Mater.* **2012**, *11*, 131-137.
47. Reichardt, C., *Solvents and Solvent Effects in Organic Chemistry*. Wiley-VCH Publishers: 2003.
48. Cazes, J., *Encyclopedia of Chromatography, Second Edition*. Taylor & Francis Group: 2005; Vol. 1.
49. Orwoll, R. A.; Arnold, P. A., Polymer–Solvent Interaction Parameter χ . In *Physical Properties of Polymers Handbook*, Mark, J. E., Ed. Springer New York: New York, NY, 2007; pp 233-257.
50. Nalam, P. C.; Daikhin, L.; Espinosa-Marzal, R. M.; Clasohm, J.; Urbakh, M.; Spencer, N. D. *J. Phys. Chem. C* **2013**, *117*, 4533-4543.
51. Tao, A.; Sinsermsuksakul, P.; Yang, P. *Angew. Chem. Int. Ed.* **2006**, *45*, 4597-4601.

52. Arnaudov, L. N.; Cayre, O. J.; Cohen Stuart, M. A.; Stoyanov, S. D.; Paunov, V. N.

Phys. Chem. Chem. Phys. **2010**, *12*, 328-331.

4 Phase transition of polyhedral Ag nanoparticles by combining the control over shape and surface chemistry

ABSTRACT. In two-dimensional self-assembly, the relationship between shape, surface functionality and self-assembled superstructure remains challenging to be systematically investigated in detail. Here, we report on the shape-dependent two-dimensional phase transition by combining the control over shape and surface chemistry, and establish the assembly guideline by using phase diagram. We utilize Ag polyhedral nanoparticles in the family of cubes and interfacial assembly method to fabricate two-dimensional superstructures. By using the same surface chemistry, we firstly observe the variation of interfacial behavior and phase transition gradually from hexagonal to square packing structure when the particle morphology changes from cubes gradually to octahedra. Then we further enlarge the surface to other ligand functionalization and observe structural transformation. Hence a phase diagram of polyhedral particles with different surface functionalization is established to provide the assembly guideline and indicate the relationship between vertex truncation, surface functionalization, interfacial position and metacrystal structure. This work provides the development of a framework that allows the design and fabrication of tailored superstructures.

4.1 INTRODUCTION

Shape is widely utilized to drive the phase behavior of nanoparticles. Organization of anisotropic morphologies into complex crystals, liquid crystals, and even quasicrystals is achieved by utilizing nanoplates¹⁻³, truncated cubes, octahedra⁴⁻⁶, or bipyramid⁷⁻⁹ and bifrustum shape¹⁰. In recent years, many simulational techniques have also been developed, achieving more understanding on the relationship between particle morphology and packing structure¹¹⁻¹⁵. Two-dimensional superstructures of polyhedral particles are attracting increasing research interest, due to the requirement for fabricating ultrathin functional membranes and films¹⁶⁻¹⁸. Surface functionality also plays critical part in directing nanoparticle behavior and tune 2D superstructures of polyhedral nanoparticle due to the control over the particle-liquid interaction^{19, 20}. Current research on the control over 2D polyhedral particle assembly is mostly focusing on changing coating polymer²¹⁻²³, DNA chain length²⁴⁻²⁷, alkylthiol^{5, 28}, as well as using mixed monolayer^{19, 29}. Although these studies provided valuable insight in the self-assembly behavior of different polyhedral nanoparticles, the relationship between the shape, surface functionality and the structure of self-assembled metacrystal has not yet been systematically investigated in detail. The combination of shape-controlled nanoparticles and their surface chemistry can generate novel metacrystals which have not been predicted by theoretical simulation. Hence it is an

attractive approach. But there are a lot of unknown things about this combination, such as phase behavior and role of morphology versus surface functionality.

Phase diagram is widely utilized to provide guidelines for predicting the phase behavior from the nanoparticle shape³⁰⁻³². Previous studies on phase diagram of polyhedral nanoparticles mainly focus on the three-dimensional packing by adjusting building block morphologies. Nevertheless, the guideline and phase diagram for 2D superstructures is still lack of study due to the challenge of fabricating novel and tunable metacrystals by combining the control over different parameters including particle morphology, size, material and surface chemistry. Mapping the phase diagram for the 2D assembly of the family of cubes is imperative, not only from a fundamental viewpoint, but also as a guideline for future experimental 2D self-assembly to develop framework for design and generation of tunable 2D functional devices.

In this work, we report on the two-dimensional assembly by combining the control over particle morphology and surface chemistry, and provide assembly guideline by establishing the phase diagram for Ag polyhedra. We use polyol reduction method to synthesize different Ag polyhedral nanoparticles in the family of cubes which interpolates between cubes and octahedra via cuboctahedra. Then we functionalize these polyhedral nanoparticles with different surface ligands, followed by the self-assembly at the oil-water

interface to fabricate metacrystals. By using the same surface functionalization, the change of particle shape from cube to octahedron leads to the variation of interfacial configuration from standing to planar and standing. In addition, metacrystal structure also exhibits phase transition from hexagonal to square packing structure. Cubes with truncation (t) = 0 form standing configuration and hexagonal assembled metacrystals. Truncated cubes ($t=0.2$) and cuboctahedra ($t=0.5$) adopt planar configuration and pack into square metacrystal. Further increase of truncation (truncated octahedra, $t=0.7$; octahedra, $t=1.0$) results in the standing configuration and square metacrystal. We further enlarge the range to different surface functionalization ligands, showing various surface wettability. Truncated octahedron is chosen as the model morphology due to its performance of forming ordered crystal structure and similar surface area of different facets. This morphology exhibits structural transformation from hexagonal packing of planar particles gradually to square metacrystal of standing particles. Then by combining the control over polyhedral morphology and surface functionalization, phase diagram of metacrystal structure is established to indicate the relationship between vertex truncation, surface functionalization, interfacial position and metacrystal structure. When particles are halfway at the oil-water interface, they form square metacrystal by adopting (100) facet orientation. When particles have high contact with oil or aqueous phase, they form hexagonal metacrystal via (111) facet orientation. This

work highlights the significance of precise shape and surface property control in the fabrication of functional metacrystal. The establishment of polyhedral nanoparticle phase diagram provides the ability for the development of guidelines that instruct the design and fabrication of well-defined metacrystals.

4.2 RESULTS AND DISCUSSION

Polyhedral nanoparticles and their self-assembly process

We study five shapes from the family of cubes with increasing level of vertex truncation. In geometry, truncation is the operation that cuts vertices of cubes, creating a new polytope at the cube vertex. Thus the vertex truncation is defined by using the original uncutted cube and cutted edge length. Vertex truncation (t) is the edge length ratio of cutted polytope vertex to uncutted cube (t , calculation process is described in Figure 4.1).

Figure 4.1 (a,b) Schematic description of truncation (t) and (c) corresponding SEM images.

Calculation for particle truncation

Truncation (t) is defined with the ratio of truncated edge length to the original cube edge length.

L_1 and L_2 are the edge length of different facets.

a is the edge length of original cube edge length. b is the edge length of truncated polyhedra.

For nanocubes, $t = 0.0$; for octahedra, $t = 1.0$; for other morphologies, $t = \frac{b}{a}$

For truncated cubes, $l_1 = 110$ nm, $l_2 = 35$ nm.

$$a = l_1 + l_2/\sqrt{2}, b = l_2/\sqrt{2}, t = \frac{b}{a} = \frac{l_2/\sqrt{2}}{l_1 + l_2/\sqrt{2}} = 0.3$$

For cuboctahedra, $l = l_1 = l_2$.

$$a = 2 * l/\sqrt{2}, b = l/\sqrt{2}, t = \frac{b}{a} = 0.5$$

For truncated octahedra, $l_1 = 303$ nm, $l_2 = 114$ nm.

$$a = 2 * l_1/\sqrt{2} + l_2 * \sqrt{2} = \sqrt{2} * (l_1 + l_2), b = a/2 + l_2/\sqrt{2} = l_1/\sqrt{2} + l_2 * \sqrt{2}$$

$$t = \frac{b}{a} = \frac{l_1/\sqrt{2} + l_2 * \sqrt{2}}{\sqrt{2} * (l_1 + l_2)} = 0.7$$

Specifically, we study perfect cube (size (s) = 106 nm, $t = 0$), truncated cube (s = 135 nm, $t = 0.3$), cuboctahedron (s = 200 nm, $t = 0.5$), truncated octahedron (s = 303 nm, $t = 0.7$) and octahedron (s = 350 nm, $t = 1$, Figure 4.2a, 4.3, Table 4.1).

Figure 4.2 (a) Scheme of polyhedral nanoparticles morphological transformation from nanocubes to truncated cubes, cuboctahedra, truncated octahedra and octahedra. (b-f) SEM images of different morphologies. (g) Schematic description of self-assembly process at the oil-water interface followed by gel-trapping immobilization. (b-f) Scale bar, 200 nm.

Figure 4.3 SEM and TEM characterization and size distribution of five polyhedral nanoparticles. Scale bar, (b-f) 200 nm; (g-j) 100 nm. Particle size is highlighted in black lines.

Table 4.1 Edge length and truncation of different polyhedral nanoparticles.

Particle morphology	Size (nm)	Truncation
Nanocubes	106±3	0.0
Truncated cubes	135±4	0.2
Cuboctahedra	200±3	0.5
Truncated octahedra	303±4	0.7
Octahedra	350±8	1.0

Ag polyhedral nanoparticles are synthesized by using polyol chemical method. Nanocubes are firstly achieved and then with increasing reaction time, [111] grows faster at vertices to eventually become truncated cubes, cuboctahedra, truncated octahedra, and octahedra (Figure 4.2b-f). Then we use ligand exchange method to control the surface chemistry of polyhedral nanoparticles to different thiol-terminated ligands, including thiol-terminated polyethylene glycol (PEG), 11-mercaptoundecanoic acid (MUA), 1-propanethiol (C3), 1-hexanethiol (C6), (C8), 1-decanethiol (C12), 1-hexadecanethiol (C16). We further assemble

Ag polyhedra into large-area metacrystal at the oil-water interface, subsequently immobilized by using gel-trapping technique (Figure 4.2g). The gelling of the aqueous phase allows the transfer of metacrystals to the hardened PDMS solid platform.

Shape-dependent change from hexagonal to square crystal of the assembled metacrystal

We first utilize 1-dodecanethiol (C12) surface functionalization as a model to study the shape-dependent phenomenon of particle interfacial behavior and self-assembled structure. C12 functionality is utilized since it is reported to provide high possibility to achieve ordered structure. Firstly, we use scanning electron microscopy (SEM) to characterize the assembled structure on PDMS substrate. Different-shaped nanoparticles can have two types of orientations, planar and standing. Planar orientation means larger-area facet in contact with oil/water interface while standing orientation presents nanoparticles use their facet with smaller area contacting with the interface (Figure 4.4).

Figure 4.4 Schematic description of particle orientation

For nanocubes ($t = 0$), a hexagonal structure forms at the oil/water interface, consisting of standing nanocubes (Figure 4.5ai-ii). Neighboring nanocubes are in the edge-to-edge configuration. Fast Fourier transform (FFT) pattern exhibits the hexagonal packing structure (Figure 4.5aiii). When t increases to 0.3, the particle morphology changes to truncated cubes, leading to the change of assembled structure to square ordering (Figure 4.5bi-ii). The square structure is composed with planar truncated cubes in face-to-face configuration. FFT analysis shows the square structure (Figure 4.5biii). At $t = 0.5$, particle morphology is varied to cuboctahedra. Particles form multiple orientations and configurations at the oil/water interface and assemble into the hexagonal plastic crystal structure (Figure 4.5ci-ii). FFT analysis exhibits the circular pattern, indicating the non-ordered structure (Figure 4.5ciii). At $t = 0.7$ and 1.0, the particle morphology changes to truncated octahedra and octahedra, which still assembled to square metacrystals (Figure 4.5di-ii, ei-ii). However, the particle changes to standing orientation. Truncated octahedra assemble in the face-to-face configuration using their smaller area facet. Octahedra assembly changes to the edge-to-edge configuration. The square pattern in FFT analysis also presents the square packing (Figure 4.5diii, eiii).

Figure 4.5 Shape-dependent assembly of nanoparticles by using C12 surface functionalization. Shape, (a) nanocubes, (b) truncated cubes, (c) cuboctahedra, (d) truncated octahedra, (e) octahedra. (i) SEM images of C12-functionalized nanoparticle assembly at the oil/water interface. (ii) They adopt different configuration at the interface. (iii) Fast Fourier transform (FFT) analysis of assembled structure. (iv) AFM topographical images of single particle at the interface and corresponding height profile along the red line. (v) Radial distribution function analysis of assembled structure, showing the changes of interparticle spacing. (f) Changes of particle interfacial position as the particle truncation

varies. (i) Scale bar, 1 μm ; inset, 200 nm. (iv) Scale bar, 200 nm.

As the truncation increases, packing density of assembled metacrystals increases from 23% (nanocubes, Figure 4.6) to 95% (truncated cubes, Figure 4.7), and then decreases from 95% to 50% and 33% (Figure 4.8, 4.9).

Figure 4.6 Scheme of packing efficiency of standing nanocubes.

$$a = \sqrt{3}l, b = \sqrt{2}l, c = \sqrt{3}l$$

$$\text{Volume of repeat unit} = a \times b \times c = \sqrt{3}l \times \sqrt{2}l \times \sqrt{3}l = 3\sqrt{2}l^3$$

$$\text{Volume of one cube} = l^3$$

$$\text{Packing efficiency of standing cubes} = \frac{l^3}{3\sqrt{2}l^3} = 24 \%$$

Figure 4.7 Scheme of packing efficiency of planar truncated cubes.

$$x = y = z = (a + \sqrt{2}b)$$

$$\text{Volume of repeat unit} = (a + \sqrt{2}b)^3 - \frac{4}{3} \times \frac{\sqrt{2}}{2} b^3$$

$$\text{Volume of one cube} = (a + \sqrt{2}b)^3$$

Packing efficiency of standing cubes = 95%

Figure 4.8 Schematics of the standing truncated octahedra square superlattice.

$$x = y = z = 2\sqrt{2}a$$

$$\text{Volume of repeat unit} = x \times y \times z = (2\sqrt{2}a)^3 = 16\sqrt{2}a^3$$

$$\text{Volume of one truncated octahedra} = 8\sqrt{2}(a)^3$$

$$\text{Packing efficiency} = 8\sqrt{2}a^3 \div 16\sqrt{2}a^3 = \frac{1}{2} = 50 \%$$

Figure 4.9 Schematics of the standing octahedra square superlattice.

$$x = y = l, z = \sqrt{2}l$$

$$\text{Volume of repeat unit} = x \times y \times z = l \times l \times \sqrt{2}l = \sqrt{2}l^3$$

$$\text{Volume of one octahedra} = \frac{\sqrt{2}}{3}l^3$$

$$\text{Packing efficiency} = \frac{\sqrt{2}}{3}l^3 \div \sqrt{2}l^3 = \frac{1}{3} \approx 33 \%$$

Meanwhile, by analyzing radial distribution function, interparticle spacing in the assembled structure exhibits variation. By comparing the absolute interparticle distance (d) with particle size (s), we calculate the difference value (D-value = s - d, Table 4.2). As the truncation increases, D-value decreases from 44 nm (nanocubes, Figure 4.5av) to 6 nm (truncated cubes, Figure 4.5bv), 11 nm (cuboctahedra, Figure 4.5cv), and then increases to 53 nm (truncated octahedra, Figure 4.5dv) and 35 nm (octahedra, Figure 4.5ev).

Table 4.2 Comparison of particle size and interparticle distance.

Particle morphology	Particle size (nm)	Interparticle distance (nm)	Difference value (nm)
Nanocubes	106	150	44
Truncated cubes	135	141	6
Cuboctahedra	200	211	11
Truncated octahedra	303	356	53
Octahedra	350	385	35

We further utilize atomic force microscopy (AFM) to study the topographic feature of nanoparticles at the oil/water interface. %Particle_{oil} is the height percentage of individual

nanoparticle in contact with oil phase, which is derived from their height above PDMS platform (Figure 4.10).

Figure 4.10. Schematic description of %Particle_{oil} calculation

As the particle shape changes from cubes to octahedra with increased truncation, the interfacial position changes with the variation of interfacial configuration (Figure 4.5a-iv,f). C12-functionalized nanocubes form standing orientation at the oil/water interface, achieving (24 ± 8) nm height above the solid platform and (87 ± 4) % in contact with oil phase (%Particle_{oil}, Figure 4.5aiv,f). As the truncation increases to 0.3, truncated cubes are planar on their octagonal facets. The height of individual truncated cube on the PDMS substrate increases to (54 ± 11) nm and %Particle_{oil} decreases to (71 ± 5) %, indicating the decrease of interaction between nanoparticle and oil phase (Figure 4.5biv,f). At $t = 0.5$, individual cuboctahedron form various configuration at the interface and the height above solid platform is (102 ± 17) nm, based on the average calculation of the heights of different cuboctahedra configurations. %Particle_{oil} decreases to (64 ± 6) %, indicating less particle-oil interaction and more particle-water interaction (Figure 4.5civ,f). For truncated octahedra ($t = 0.7$) and octahedra ($t = 1.0$), the particle size increases with the morphological changes.

As the interfacial orientation changes to standing, the interfacial position also varies to $(59 \pm 3) \%$ and $(53 \pm 4) \%$ for $\%Particle_{oil}$ of truncated octahedra and octahedra (Figure 4.5div,eiv,f).

Due to the size difference of these five morphologies, even as the absolute height above substrate increases, $\%Particle_{oil}$ decreases. Particle size give arise to the gravity of nanoparticles at the oil/water interface. Larger size leads to greater gravity and thus lower interfacial position with smaller $\%Particle_{oil}$. In comparison, smaller size leads to smaller gravity and thus higher position with larger $\%Particle_{oil}$. However, here particle morphology plays a more significant role in controlling particle interfacial behavior since it achieves the control over both the interfacial position and interfacial configuration. Interfacial position and configuration demonstrates different interaction between particle and oil/water phase. This is due to the variation of facet area for different polyhedral morphologies. We calculate the (111) facet area ratio of the total surface area of all facets, which is 0, 0.1, 0.4, 0.8 and 1.0 for cube, truncated cube, cuboctahedra, truncated octahedra, and octahedra respectively (Figure 4.11).

Figure 4.11. Schemes of (a) cube depicting 8 (111) vertex facets, (b) truncated cube

depicting 8 triangular (111) facets, (c) cuboctahedron depicting 8 triangular (111) facets, (d) truncated octahedron depicting 8 hexagonal (111) facets, and (e) an octahedron depicting 8 triangular (111) facets.

Calculations for the surface area ratio of (111) facets of the various polyhedral shapes

For a cube with size, s ,

$$(111) \text{ facet ratio} = 0/s^2 = 0$$

For a truncated cube with size, s ,

$$(111) \text{ facet ratio} = 8\left(\frac{\sqrt{3}}{4}35^2\right) / [8\left(\frac{\sqrt{3}}{4}35^2\right) + 6((S + \frac{\sqrt{2}}{2} \times 35 \times 2)^2 - 4 \times \frac{1}{2}(\frac{\sqrt{2}}{2} \times 35)^2)] = 0.1$$

For a cuboctahedron with size, s ,

$$(111) \text{ facet ratio} = 8\left(\frac{\sqrt{3}}{4}s^2\right) / (8\left(\frac{\sqrt{3}}{4}s^2\right) + 6(s^2)) = 0.4$$

For a truncated octahedron with size, s ,

$$(111) \text{ facet ratio} = 8\left(\frac{3\sqrt{3}}{2}s^2\right) / (6(s^2) + 8\left(\frac{3\sqrt{3}}{2}s^2\right)) = 0.8$$

For an octahedron with size, s ,

$$(111) \text{ facet ratio} = 8\left(\frac{\sqrt{3}}{4}s^2\right) / 8\left(\frac{\sqrt{3}}{4}s^2\right) = 1$$

The (111) facet area ratio influences the C12 ligand amount ratio on the (111) facet of the total ligand amount on the particle surface. Hence this ratio shows C12 difference on

different facets, which affects the interaction with oil and water phase. Smaller difference leads to similar interaction with oil and water phase by using different orientations, providing less selectivity of particle orientation at the interface. In comparison, larger difference gives rise to greater selectivity. For cubes and octahedra, great difference between (111) and (100) facet ratio leads to predominant distinction of C12 amount on different facets, providing more selectivity in the orientation. For truncated cubes and truncated octahedra, 0.1 and 0.8 (111) facet ratio means the smaller but still obvious difference between (111) and (100) facet. Hence these two morphologies can still form ordered crystal structure with high selectivity in the orientation. For cuboctahedra, the (111) facet area ratio is much closer to 0.5. The difference between (111) and (100) facet area is less significant, leading to similar amount of C12 on (111) triangular and (100) square facets. Cuboctahedra exhibit a lower selectivity in their orientations and form hexagonal plastic crystal structure.

Increased hydrophobicity leads to hexagonal-to-square metacrystal transformation

To study the effect of surface chemistry on the metacrystal structure, we further change the surface functionalization from C12 to other ligands. Surface functionality of nanoparticles with different morphologies involves poly(ethylene glycol) methyl ether thiol

(PEG, average m.w. = 1000 g/mol), 11-mercaptopundecanoic acid (MUA), 1-propanethiol (C3), 1-hexanethiol (C6), (C8), 1-decanethiol (C12), and 1-hexadecanethiol (C16). These surface groups are reported to provide the change of surface wettability, which could give rise to different particle-liquid interaction and thus affecting particle assembly. Surface wettability can be observed from the contact angle measurement of bulk Ag film (Figure 4.12a). The most hydrophilic surface utilizes the polymer PEG, whose bulk contact angle is $(32 \pm 5)^\circ$, and the most hydrophobic molecule is C16, achieve the highest bulk contact angle of $(115 \pm 1)^\circ$.

Figure 4.12. Difference in packing structures of truncated octahedra self-assembled by using different surface functionalization to different packing density. (a) Wettability demonstration of particle surface with different surface functionality by using contactangle

measurement. SEM images and schematic description of assembled structure of truncated cuboctahedra with (b) PEG, (c) MUA, (d) C3, (e) C6, (f) C8, (g) C12 and (h) C16 surface functionalization. (b-h) Scale bar, 1 μm ; inset, 200 nm.

Here we use truncated octahedra ($t = 0.7$) as an example to demonstrate the effect of surface wettability. Truncated cubes, cuboctahedra and truncated octahedra have lower difference of (111) and (100) facets, which provides lower orientation selectivity and possibly leads to the disordered assembly. In comparison, C12-functionalized truncated octahedra exhibit novel assembled structure with standing orientation. Hence we choose this morphology as model study.

When the particles are functionalized with PEG (contact angle (CA) = $(32 \pm 5)^\circ$), MUA (CA = $(41 \pm 4)^\circ$) and C3 (CA = $(74 \pm 1)^\circ$), truncated octahedra achieve hydrophilic surface. Thus at the oil/water interface, hexagonal metacrystals form. Particles are planar on their (111) hexagonal facet and form hexagonal-to-hexagonal face configuration (Figure 4.12bi-ii,ci-ii,di-dii, 4.13). FFT analysis exhibits the hexagonal structure (Figure 4.12biii,ciii,diii).

Figure S10. Schematics of the planar truncated octahedra superlattice.

Assuming $l = 3a$ for a perfect truncated octahedra, where l is the edge length of an octahedra and a is the edge length of the truncated octahedra.

$$x = \frac{3}{4}l, \quad y = \frac{\sqrt{3}}{2}l, \quad z = \frac{\sqrt{6}}{3}l$$

$$\text{Volume of repeat unit} = x \times y \times z = \frac{3}{4}l \times \frac{\sqrt{3}}{2}l \times \frac{\sqrt{6}}{3}l = \frac{3\sqrt{2}}{8}(3a)^3$$

$$\text{Volume of one truncated octahedra} = 8\sqrt{2}a^3$$

$$\text{Packing efficiency} = 8\sqrt{2}a^3 \div \frac{3\sqrt{2}}{8}(3a)^3 = \frac{64}{81} \approx 79 \%$$

As surface functionality is changed to C6 (CA = $(96 \pm 1)^\circ$), the nanoparticles form various orientation at the interface including (100) square and (111) hexagonal facets facing up. Thus the assembled structure becomes disordered (Figure 4.12ei,ii). FFT analysis exhibits the quasi-circular pattern corresponding to the disordered structure (Figure 4.12eiii).

When the surface become more hydrophobic with C8 functionality (CA = $(104 \pm 1)^\circ$), the truncated octahedra adopt tilted orientation by using the edges in contact with solid platform.

A plastic structure forms at the oil/water interface with various interparticle configuration (Figure 4.12fi,ii). FFT analysis exhibits the irregular pattern, corresponding to the plastic crystal structure (Figure 4.12fiii). By using the most hydrophobic surface functionalization

C12 (CA = $(112 \pm 1)^\circ$) and C16 (CA = $(115 \pm 1)^\circ$), truncated octahedra varies to standing orientation, forming square metacrystal structure at the interface with square-to-square facet

configuration. The square facets with smaller area are in contact with the PDMS substrate (Figure 4.12gi-ii,hi-ii). FFT analysis exhibits the square structure (Figure 4.12giii,hiii). From the radial distribution function analysis, interparticle distance increases from ~312 nm (PEG, MUA, C3) to ~337 nm (C12, C16, Figure 4.14). This interparticle distance change also shows the transformation of assembled structure by tuning surface chemistry.

Figure 4.14. Radial distribution function analysis of (a) PEG- (b) MUA-, (c) C3-, (d) C6-, (e) C8- and (f) C16- functionalized truncated octahedra assembly.

The influence of surface chemistry is due to the interfacial behavior of differently functionalized truncated octahedra. At the oil-water interface, by increasing surface hydrophobicity, truncated octahedra change the interfacial configuration from planar (PEG, MUA and C3) to tilted (C8) and standing (C12, C16, Figure 4.15a).

Figure 4.15. (a) AFM topographic images of (i) PEG-, (ii) MUA-, (iii) C3-, (iv) C6-, (v) C8-, (vi) C16- functionalized truncated octahedra. Scale bar, 200 nm. (b) Height percentage variation of particle in contact with oil phase when the surface chemistry changes.

The interfacial position of truncated octahedra also varies. %Particle_{oil} increases from (20 ± 5) % with most hydrophilic ligand PEG to (61 ± 5) % with most hydrophobic ligand C16 (Figure 4.15b). The variation of interfacial behavior is due to the surface wettability. As the surface functionality increase the hydrophobicity, particle-water interaction decreases and particle-oil interaction become stronger. Thus the particle adopts different configuration to achieve lowest interfacial energy and particle interfacial position varies to increase the contact with oil phase. With hydrophilic ligand functionalization, higher percentage of truncated octahedra is in the aqueous phase and particle adopt planar configuration to increase the interaction with aqueous phase. With hydrophobic ligand

functionalization, truncated octahedra are nearly half-way at the oil-water interface. They form standing configuration to reduce the contact with aqueous phase in order to achieve stronger particle-oil interaction.

Phase diagram provides guideline for the assembly of polyhedral nanoparticles.

However, the influence of surface chemistry on metacrystal structure is shape-mediated (Figure 4.16-4.19).

Figure 4.16 Different surface functionalization affects the assembled structure for nanocubes. Scale bar, 1 μm ; inset, 200nm.

Figure 4.17 Different surface functionalization affects the assembled structure for truncated cubes. Scale bar, 1 μm ; inset, 200nm.

Figure 4.18 Different surface functionalization affects the assembled structure for cuboctahedra. Scale bar, 1 μm ; inset, 200nm.

Figure 4.19 Different surface functionalization affects the assembled structure for octahedra. Scale bar, 1 μm ; inset, 200nm.

Hence we summarize the phase diagram to indicate the relationship between truncation, surface wettability, particle interfacial behavior and assembled packing density. First we establish $\% \text{Particle}_{\text{oil}}$ - contact angle phase diagram to study the relationship between particle shape, surface wettability, and interfacial behavior and indicate the shape-dependent interfacial position transformation (Figure 4.20a).

Figure. 4.20 Phase diagram of family of polyhedral nanoparticles. (a) Phase diagram by analyzing relationship of % Particle_{oil}, packing fraction and surface functionalization of nanoparticles, which is demonstrated by contact angle. (b) Phase diagram by analyzing % Particle_{oil} and truncation, leading to different metacrystal structure.

We use interfacial position defined by %Particle_{oil} as y axis to demonstrate the individual particle interfacial behavior. Contact angle demonstrates particle surface wettability and is used as y axis. As a function of surface wettability, %Particle_{oil} of single particle exhibits the gradual increment for all the polyhedral morphologies. As the particle surface hydrophobicity increases, %Particle_{oil} also exhibits the increment. However, for

different morphologies, the range of %Particle_{oil} is diverse. For truncation of 0.0, nanocubes, the range of % Particle_{oil} is from $(49 \pm 6) \%$ to $(95 \pm 1) \%$. When truncation increases to 0.3, %Particle_{oil} of truncated cubes decreases the range to $(45 \pm 4) \%$ to $(80 \pm 3) \%$. Further increment of truncation to 0.5 leads to the decrease of cuboctahedra %Particle_{oil} range from $(41 \pm 7) \%$ to $(69 \pm 3) \%$. When lowest truncation of 0.8 and 1.0 is used, truncated octahedra and octahedra at the interface further increase their contact with aqueous phase and the range of %Particle_{oil} decreases to $(20 \pm 5) \%$ to $(61 \pm 5) \%$ and $(15 \pm 3) \%$ to $(56 \pm 2) \%$ (Figure 4.21, Table 4.3).

Figure 4.21 Different surface functionalization affects the interfacial behavior. Scale bar, 200 nm.

Table 4.3 %Particle_{oil} for different morphologies with various surface functionalizations.

Morphology	Ligand	Height above PDMS (nm)	%Particle _{oil}
Nanocube	PEG	54±13	49±6

	MUA	50±9	53±4
	C3	41±11	61±5
	C6	36±15	66±6
	C8	40±10	78±4
	C12	54±8	87±4
	C16	5±3	95±1
Truncated cubes	PEG	101±9	45±4
	MUA	98±7	49±3
	C3	78±8	58±4
	C6	89±4	61±2
	C8	59±5	68±3
	C12	54±11	71±5
	C16	37±5	80±3
Cuboctahedra	PEG	168±20	41±7
	MUA	159±19	45±7

	C3	137±14	52±5
	C6	132±10	55±4
	C8	117±13	59±5
	C12	102±17	64±6
	C16	82±9	69±3
Octahedra	PEG	230±12	15±3
	MUA	202±17	23±4
	C3	189±17	30±4
	C6	164±10	35±3
	C8	140±7	43±1
	C12	225±15	53±4
	C16	210±10	56±2

From the above, surface chemistry determines the gradual variation of particle interfacial behavior. Particle morphology determines the variation range. Particle morphology influence particle interfacial behavior from two factors. One is the variation of facet area ratio. Particle position at the oil-water interface is not only determined by the

interaction with oil and water phase, but also influenced by the contact area between particle and oil, water phase. Due to the facet area of different polyhedral morphologies, with similar functionality, particles achieve similar contact area with two liquid phase but different height percentage. The other factor is particle size. The size difference of different polyhedral nanoparticles leads to the variation of gravity effect at the oil-water interface. Hence larger octahedra (size = 350 nm) exhibit more contact with aqueous phase compared with smaller cubes (size = 350 nm).

We further establish the % Particle_{oil} – truncation phase diagram to find out the relationship between % Particle_{oil} and metacrystal structure for different particle morphologies (Figure 4.20b). Particle morphology is defined by truncation, which serves as x axis. And % Particle_{oil} is used as y axis and defines particle interfacial behavior, which exhibits the different values for square and hexagonal metacrystals. When %Particle_{oil} is 41 % - 61 %, particles are almost halfway at the oil/water interface and we observe the formation of square assembled structure. For $s \leq 0.5$, particles form planar configuration and for $s > 0.5$, particles form standing configuration. However, regardless of the planar or standing configuration, the particles with different morphologies use their (100) facets in contact with solid substrate. For hexagonal metacrystal, %Particle_{oil} is less than 41 % or higher than 61 % due to different truncations. At $s < 0.5$, hexagonal metacrystal is composed

with standing configuration. At $s > 0.5$, the hexagonal metacrystal consists of planar configuration. Thus when higher ratio of particle position in the oil or aqueous phase, (111) facets are in contact with solid platform. Apart from two types of ordered metacrystal, the intermediate % Particle_{oil} 58 % - 87 % for $s < 0.5$ and 30 % - 59 % for $s > 0.5$ result in the plastic and disordered metacrystal structure. From the above analysis, we further propose the guidelines for Ag polyhedral interfacial assembly. To fabricate the square metacrystals, particles need to be nearly half-way at the oil-water interface. Thus particles have similar interaction with oil and water phase and orient by (100) facet. In addition, to fabricate hexagonal metacrystals, particles need to be have high percentage in oil or aqueous phase. Hence particles have higher interaction with either liquid phase and orient by (111) facet.

4.3 CONCLUSION

In this work, we demonstrate the shape-dependent two-dimensional assembly by controlling both particle morphology and surface chemistry, and establish new assembly guideline for Ag polyhedral via phase diagram. We utilize different Ag polyhedral nanoparticles in the family of cubes, followed by surface wettability modification and self-assembly method at the oil-water interface. Different polyhedral particles with the same surface functionality exhibit the variation of interfacial position and configuration between

standing and planar. Thus we observe phase transition from hexagonal to square packing structure. This shape dependence is highly affected by the surface area ratio of (111) facets. In addition surface wettability also exhibits structural transformation from hexagonal packing of planar particles gradually to square structure of standing particles. Surface wettability influence is mainly due to the particle-oil and particle-water interaction, proved by the interfacial position. Then we establish %Particle_{oil}-contact angle and %Particle_{oil}-truncation phase diagram to provide the 2D assembly guideline. Half-way interfacial position gives rise to the orientation by using (100) facet on platform and square metacrystals, while high position in liquid phase leads to the orientation by (111) facet and hexagonal. This work thus provides a versatile design and fabrication route for tailored 2D metacrystals of anisotropic nanoparticles. The pivotal role of combined shape and surface chemistry control in the fabrication of functional metacrystals give access to a wide range of interesting, scalable nanostructured materials, as well as the flexibility and control of structure-dependent property.

4.4 MATERIALS AND METHODS

Materials. Silver nitrate, poly(vinylpyrrolidone) (PVP, average m.w. = 55000 g/mol), poly(ethylene glycol) methyl ether thiol (PEG, average m.w. = 1000 g/mol), 11-

mercaptoundecanoic acid (MUA), 1-propanethiol (C3), 1-hexanethiol (C6), (C8), 1-decanethiol (C12), 1-hexadecanethiol (C16), isopropyl alcohol (IPA), decane and 1,5-pentanediol (PD) were purchased from Sigma Aldrich; copper(II) chloride and ethanol were obtained from Alfa Aesar and EMSURE. Silicon elastomer curing agent and silicone elastomer base were from Dow Corning. Gellan Gum (KELKOGEL®) was sponsored by CP Kelco (USA). All chemicals were used without further purification. Milli-Q water ($>18.0 \text{ M}\Omega\cdot\text{cm}$) was purified with a Sartorius Arium 611 UV ultrapure water system.

Ag polyhedral nanoparticle synthesis. The synthesis of Ag nanocubes was carried out by polyol reduction method. Briefly, 8 mg CuCl_2 , 20 mg PVP and 20 mg AgNO_3 were dissolved in 10 mL PD separately via repeated sonication and vortex. 35 μL CuCl_2 solution was then added to AgNO_3 solution. In a round bottomed flask, 20 mL PD was heated at 190°C for 10 min. 250 μL PVP solution was dropwise injected, followed by quick injection of 500 μL AgNO_3 solution. Subsequently, AgNO_3 precursor was injected quickly every minute and PVP precursor was injected dropwise every 30 s until nanocubes were formed. The heating was then stopped and the reaction system was cooled down to room temperature. For the synthesis of other polyhedral, 40 mg AgNO_3 was dissolved in 10 mL PD and 40 μL CuCl_2 solution was added to AgNO_3 solution instead. Ag nanocubes solution in round bottomed flask was heated at 190°C for 10 min. Similarly, 235 μL PVP precursor was

injected dropwise to the flask every 30 s while 500 μL AgNO_3 precursor was quickly added every minute. The shape of nanoparticles is dependent on the stopping time of the addition. For the purification, PD was removed by using acetone, ethanol over multiple centrifugation rounds, followed by redispersing in 20 ml ethanol. The solution was then vacuum filtered using polyvinylidene difluoride filter membranes (Durapore) with pore sizes ranging from 5,000, 650, to 450 (nanocubes, to 220 nm).

Ligand exchange. Particle solution was allowed to sediment for several days. 0.5 μL of the sediment was dispersed in ethanol and centrifuged before redispersing in 1.5 ml of ethanol/IPA. Ligand solution was then added under stirring. The concentration of ligands was kept 1mM for cubes, truncated cubes and 10mM for cuboctahedra, truncated octahedra and octahedra. The ligand volume was 10, 50, 10, 80, and 100 μL for cubes, truncated cubes, cuboctahedra, truncated octahedra and octahedra respectively. Functionalization took place for 4 h, followed by centrifugation to remove excess molecules and redispersing in 1.5 mL of ethanol/IPA. 10 mL ligand solution was subsequently added under stirring. The functionalization continues for 3 h, followed by centrifugation and washing with IPA/water.

Interfacial Self-assembly. Gellan gum solution (2 wt%, 6 mL) was used as aqueous phase and decane was added on top of aqueous polymeric phase as oil phase. Gel-trapping experiment was modified from the procedure reported by Paunov and co-workers³³. The

gellan gum solution was prepared under $\sim 80\text{ }^{\circ}\text{C}$ and stirring at 1400 rpm until the gel was completely hydrated. Subsequently, pre-heated decane was added to the top of gel solution. Particles dispersed in $0.5\text{ }\mu\text{l}$ IPA/water were then injected to the interface. The whole system was left at $80\text{ }^{\circ}\text{C}$ for $\sim 15\text{ min}$ for thermodynamic equilibrium and then cooled down to room temperature. After the gelling of gellan gum, decane was decanted and premixed PDMS precursor mixture was deposited onto the arrays. After the curing of PDMS, the monolayer of Ag nanoparticles was peeled off and washed in hot water.

Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM).

SEM and TEM characterization were performed using SEM (JEOL-JSM-7600F) and TEM (JEOL-JEM-1400) at voltage of 5 kV and 100 kV. The images are then analyzed using Image J software.

Atomic force microscopy (AFM) measurement. AFM was used to study the topological changes in the particles on PDMS platform using a Bruker Dimension ICON with NanoScope V controller from Bruker. ScanAsyst mode image was acquired using silicon probes (Tap300Al-G with 30-nm Al reflex coating) from BudgetSensor.

4.5 REFERENCES

1. Zhang, X.-Y.; Hu, A.; Zhang, T.; Lei, W.; Xue, X.-J.; Zhou, Y.; Duley, W. W. *ACS Nano* **2011**, *5*, 9082-9092.

2. Heo, J.; Lee, Y. W.; Kim, M.; Yun, W. S.; Han, S. W. *Chem. Comm.* **2009**, 1981-1983.
3. Giri, A. K.; Saha, A.; Mondal, A.; Chandra Ghosh, S.; Kundu, S.; Panda, A. B. *RSC Adv.* **2015**, *5*, 102134-102142.
4. Tao, A.; Sinsermsuksakul, P.; Yang, P. *Angew. Chem. Int. Ed.* **2006**, *45*, 4597-4601.
5. Lee, Y. H.; Shi, W.; Lee, H. K.; Jiang, R.; Phang, I. Y.; Cui, Y.; Isa, L.; Yang, Y.; Wang, J.; Li, S.; Ling, X. Y. *Nat. Commun.* **2015**, *6*, 6990.
6. Henzie, J.; Grünwald, M.; Widmer-Cooper, A.; Geissler, P. L.; Yang, P. *Nat. Mater.* **2012**, *11*, 131-137.
7. Haji-Akbari, A.; Chen, E. R.; Engel, M.; Glotzer, S. C. *Phys. Rev. E* **2013**, *88*, 012127.
8. Zhang, S.; Kou, X.; Yang, Z.; Shi, Q.; Stucky, G. D.; Sun, L.; Wang, J.; Yan, C. *Chem. Comm.* **2007**, 1816-1818.
9. Eom, J.-H.; Gong, J.; Kwon, S.; Jeon, A.; Jeong, R.; Driver, R. W.; Lee, H.-S. *Angew. Chem. Int. Ed.* **2015**, *54*, 13204-13207.
10. Van der Stam, W.; Gantapara, A. P.; Akkerman, Q. A.; Soligno, G.; Meeldijk, J. D.; van Roij, R.; Dijkstra, M.; de Mello Donega, C. *Nano Lett.* **2014**, *14*, 1032-1037.
11. Ye, X.; Chen, J.; Engel, M.; Millan, J. A.; Li, W.; Qi, L.; Xing, G.; Collins, J. E.; Kagan, C. R.; Li, J.; Glotzer, S. C.; Murray, C. B. *Nat. Chem.* **2013**, *5*, 466-473.

12. Jana, N. R. *Angew. Chem. Int. Ed.* **2004**, *43*, 1536-1540.
13. Gong, J.; Newman, R. S.; Engel, M.; Zhao, M.; Bian, F.; Glotzer, S. C.; Tang, Z. **2017**, *8*, 14038.
14. Gao, W.; Jiao, Y.; Dai, L. L. *J. Nanopart. Res.* **2016**, *18*, 91.
15. Yockell-Lelièvre, H.; Lussier, F.; Masson, J. F. *J. Phys. Chem. C* **2015**, *119*, 28577-28585.
16. Pieranski, P. *Phys. Rev. Lett.* **1980**, *45*, 569-572.
17. Lin, Y.; Skaff, H.; Emrick, T.; Dinsmore, A. D.; Russell, T. P. *Science* **2003**, *299*, 226-229.
18. Xia, H.; Wang, D. *Adv. Mater.* **2008**, *20*, 4253-4256.
19. Yang, Y.; Lee, Y. H.; Phang, I. Y.; Jiang, R.; Sim, H. Y. F.; Wang, J.; Ling, X. Y. *Nano Lett.* **2016**, *16*, 3872-3878.
20. Boles, M. A.; Engel, M.; Talapin, D. V. *Chem. Rev.* **2016**, *116*, 11220-11289.
21. Yu, S.-H.; Antonietti, M.; Cölfen, H.; Hartmann, J. *Nano Lett.* **2003**, *3*, 379-382.
22. Nie, Z.; Fava, D.; Kumacheva, E.; Zou, S.; Walker, G. C.; Rubinstein, M. *Nat. Mater.* **2007**, *6*, 609-614.
23. Park, S.; Lim, J.-H.; Chung, S.-W.; Mirkin, C. A. *Science* **2004**, *303*, 348-351.
24. Park, S. Y.; Lytton-Jean, A. K. R.; Lee, B.; Weigand, S.; Schatz, G. C.; Mirkin, C. A.

Nature **2008**, *451*, 553-556.

25. Aldaye, F. A.; Palmer, A. L.; Sleiman, H. F. *Science* **2008**, *321*, 1795-1799.

26. Lin, Q.-Y.; Li, Z.; Brown, K. A.; O'Brien, M. N.; Ross, M. B.; Zhou, Y.; Butun, S.; Chen, P.-C.; Schatz, G. C.; Dravid, V. P.; Aydin, K.; Mirkin, C. A. *Nano Lett.* **2015**, *15*, 4699-4703.

27. Cheng, W.; Campolongo, M. J.; Cha, J. J.; Tan, S. J.; Umbach, C. C.; Muller, D. A.; Luo, D. *Nat. Mater.* **2009**, *8*, 519-525.

28. Comeau, K. D.; Meli, M. V. *Langmuir* **2012**, *28*, 377-381.

29. Lee, H.-Y.; Shin, S. H. R.; Drews, A. M.; Chirsan, A. M.; Lewis, S. A.; Bishop, K. J. M. *ACS Nano* **2014**, *8*, 9979-9987.

30. van der Kooij, F. M.; Kassapidou, K.; Lekkerkerker, H. N. W. *Nature* **2000**, *406*, 868-871.

31. Damasceno, P. F.; Engel, M.; Glotzer, S. C. *ACS Nano* **2012**, *6*, 609-614.

32. Gantapara, A. P.; de Graaf, J.; van Roij, R.; Dijkstra, M. *Phys. Rev. Lett.* **2013**, *111*, 015501.

33. Arnaudov, L. N.; Cayre, O. J.; Cohen Stuart, M. A.; Stoyanov, S. D.; Paunov, V. N. *Phys. Chem. Chem. Phys.* **2010**, *12*, 328-331.

5 Surface Functionalization and Superstructures: Polymer Nature Directed Interparticle Interaction.

ABSTRACT. Surface chemistry is widely utilized in the control over particle-liquid interaction for the interfacial self-assembly. However, it also influences the interaction between neighboring particles, which is also a critical factor for the fabrication of assembled structure. In this chapter, we utilize PVP and PEG as model system to study the effect of polymer chemical nature on interparticle interaction and assembled structure. PVP and PEG are two similar polymers with similar surface wettability and lead to similar interfacial position of nanoparticle at the interface. Hence the particle-oil and particle-water interaction exhibit few difference for PVP- and PEG- functionalized nanoparticle. The variation of assembled superstructure of PVP- and PEG- functionalized nanoparticle is proved to be due to the nanoscale structure of PVP and PEG. Coiled PVP provides greater steric repulsion and leads to the formation of plastic structures with larger interparticle spacing. In comparison, linear PEG gives arise to smaller steric repulsion which allows for enhanced particle-particle interaction. This work demonstrates the significance of surface nanoscale structure and hence particle-particle interaction in the design and fabrication of macroscopic structures.

5.1 INTRODUCTION

Ordering of nanoparticle into large scale two-dimensional (2D) material is a crucial prerequisite for the functional application and device integration of nanomaterials in areas ranging from sustainable energy to pollutant detection or information storage¹⁻⁵. A widely-used method to fabricate defect-free nanoparticle arrays is the interfacial self-assembly of surface-functionalized nanoparticles⁶⁻⁸. Surface chemistry is widely exploited to drive the formation of distinct superstructures by affecting the particle interaction at the nanoscale⁹⁻¹¹. Polymer chains on particle surface via coordinative or covalent interactions^{12, 13}, stand for an interesting type of nanomaterials. The conformational flexibility and functional versatility make polymer chains an attractive platform for particle synthesis, assembly tunability and practical applications. The interaction between particle surface and surrounding liquid phase exhibits significance to the nanoparticle assembly¹⁴⁻¹⁷. Different bulk surface wettability gives arise to the variation of interactions with oil and water phase at the interface, which leads to distinct assembled structures^{8, 18-20}. Polymer distribution and solvent-tunable polymer conformation also affect assembled structure since it also achieves the controls over surface hydrophobicity^{21, 22}. However, current studies mostly focus on the particle-liquid interaction for controlling 2D interfacial assembly. Besides the interaction between particle-liquid interaction, surface ligands also play critical role in tuning

interparticle interaction. There are many types of molecular interactions (hydrophobic, electrostatic, H-bonding, π - π stacking, etc.) between the particle surfaces²³⁻²⁷. Among a few studies on interparticle interaction, the interparticle spacing and interparticle orientation in the assembled arrays is known to be a function of ligand molecular weight and the corresponding polymer configuration^{22, 28-30}. However, there are few studies focusing on the effect of chemical nature of polymer on interparticle interaction. Chemical nature of polymer has direct influence on the interparticle interaction due to the intramolecular and intermolecular interaction of surface polymers. Hence, a research gap has existed in the polymer-nanoparticle community. Even though polymer chains grafted on nanoparticle surface have similar bulk property and similar interaction with liquid phase, particles may also assemble into distinct structures. The study on the significance of surface polymer chemical nature on affecting interparticle interaction and thus tuning assembled macroscopic structures will enhance the structural diversity and flexibility at the oil-water interface.

In this work, we study the effect of chemical nature of surface polymer with similar bulk property on the formation of different assembled structure at the oil-water interface by influencing the interparticle interaction. We use thiol-terminated poly(vinylpyrrolidone) (PVP) and thiol-terminated poly(ethylene glycol) (PEG) to do the surface modification as

the model to demonstrate the nanoscale effect of surface polymers. From the perspective of bulk properties, PVP and PEG have similar surface wettability. This leads to similar interfacial position at the oil-water interface, indicating the similar particle-oil and particle-water interaction by using two different functionalization. We utilize cuboctahedra behavior as the model study due to the similar square and triangular facet area, which makes it difficult to achieve different particle configuration. Due to the difference of chemical nature, we observe distinct nanoscale structure of two polymers on cuboctahedra based on the hydrodynamic size. This is due to different intermolecular and intramolecular interaction of PVP and PEG. We further study cuboctahedra assembly. By functionalizing with PVP and PEG, cuboctahedra assemble into plastic lattice structure with differently oriented particles and square ordered structure with planar configuration on square faces. With PVP functionalization, cuboctahedra show stronger steric repulsion, reducing the interaction between neighboring cuboctahedra and increasing the interparticle distance. With PEG functionalization, cuboctahedra exhibit attraction that exceeds the steric repulsion between polymers, stabilizing square-to-square face configuration. We also utilize the variation of polymer chain length to tune the interparticle interaction and assembled structure. Longer chain length of PEG provides stronger steric repulsion, leading to disordered assembly. Then we extend the model study of cuboctahedra to other morphologies including

nanocubes and truncated cubes, which also exhibit difference of assembled structure for PVP and PEG functionalization. Chemical nature of surface polymers provides a versatile approach for controlling the particle-particle interaction and hence enhance the structural diversity for shape-controlled nanoparticles.

5.2 RESULTS AND DISCUSSION

Similar bulk surface wettability

We use thiol-terminated polyvinylpyrrolidone (PVP, m.w. = 1700) and thiol-terminated polyethylene glycol (PEG, m.w. = 2000) functionalization as the model study due to the polymers' similarity of bulk property and difference in chemical nature. Due to the usage of water and decane as the liquid phase for the latter interfacial assembly process (Figure 5.1a), we measure the contact angle of water and decane droplet on two functionalized Ag films (Figure 5.1b, 5.2). PVP functionalized Ag bulk surface exhibits hydrophilicity and lipophilicity with water and decane contact angle of $(40 \pm 1)^\circ$ and $(26 \pm 2)^\circ$ respectively. PEG functionalization on Ag bulk films give rise to similar effect. Similar water and decane contact angle is observed of $(39 \pm 2)^\circ$ and $(28 \pm 2)^\circ$ respectively. This similar bulk wettability between PVP and PEG leads to the similar interfacial position of PVP- and PEG- functionalized nanoparticles (Figure 5.1c).

Figure 5.1 Comparison between two surface functionality. (a) Schematic description of assembling Ag cuboctahedra with PVP (m.w.=1700) and PEG (m.w.=2000) functionalization at the oil-water interface. (b) Bulk properties of two surface functionalization, which is demonstrated by water contact angle of PVP- and PEG-modified Ag films. (c) Height percentage of cuboctahedra in contact with oil phase. AFM micrographs and cross-sectional height profiles of (d) PVP- and (e) PEG-functionalized cuboctahedra. (d,e) Scale bar, 200 nm.

Figure 5.2 Imaging of water contact angle on PVP- and PEG- functionalized bulk Ag film.

Ag cuboctahedron is first utilized as a model system to study the nanoscale effect of surface polymers chemical nature on the assembled structure. Cuboctahedron is chosen due

to its similar facet area, leading to the limitation of tuning assembled structure. We employ the polyol method to synthesize Ag cuboctahedra with effective diameter of (228 ± 3) nm (Figure 5.3). Ag cuboctahedra are then homogeneously stabilized with the hydrophilic polymer PVP and PEG via ligand exchange. With PVP or PEG surface functionalization, Ag cuboctahedra are then assembled at the oil-water interface and subsequently immobilized using the gel-trapping technique. During the gelling of the aqueous phase, the particles are stably trapped at the interface and thus the assembled structure can be transferred to the PDMS platform (Figure 5.1a).

Figure 5.3 Schematic description, SEM and TEM images of Ag cuboctahedra. Scale bar, 100 nm.

Calculation of effective diameter

l is the edge length of cuboctahedra (highlighted with black line)

$$l = 161 \text{ nm}$$

$$d = l \cdot \sqrt{2} = 228 \text{ nm}$$

We further do AFM measurement of PVP- and PEG- functionalized cuboctahedra on PDMS platform. AFM measurements show the interfacial position of cuboctahedra. Above

the solid substrate, the height of cuboctahedra is (187 ± 7) nm and (161 ± 3) nm for PVP and PEG functionalization (Figure 5.1d,e). % Particle_{oil} is used to calculate the height percentage of cuboctahedra in contact with oil phase (Figure 5.4), which is (42 ± 2) % and (43 ± 1) % for PVP- and PEG-functionalized cuboctahedra (Table 5.1). The similarity of interfacial position of PVP- and PEG- functionalized cuboctahedra indicates the similar particle-oil and particle-liquid interaction.

Figure 5.4. Schematic description of %Particle_{oil} calculation

H_{AFM} is the height of cuboctahedra above PDMS.

H_{particle} is the height of cuboctahedra in the assembled structure.

%Particle_{oil} is the height percentage of cuboctahedra in contact with oil phase.

Table 5.1 Height of cuboctahedra above PDMS substrate and corresponding %Particle_{oil}.

	Height above PDMS	%Particle _{oil}
PVP functionalization	(187 ± 7) nm	(42 ± 2) %
PEG functionalization	(161 ± 3) nm	(43 ± 1) %

Polymer chemical nature affects its nanoscale structure and macroscopic assembled structure.

Despite of similar bulk property of two polymer functionalized surfaces, two polymers vary in their chemical nature and nanoscale structure (Figure 5.5a). By utilizing hydrodynamic light scattering (DLS) measurement, hydrodynamic size exhibits the variation of polymer sizes on nanoparticle surfaces in the aqueous solvent. The hydrodynamic diameter of PVP-functionalized cuboctahedra ((208 ± 11) nm) is obviously higher than that of PEG-functionalized cuboctahedra ((222 ± 9) nm, Figure 5.5b).

This difference of hydrodynamic size indicates dissimilar molecular-level structures of PVP and PEG. Polyvinylpyrrolidone is reported to adsorb on Ag particles via its N and O atoms with charge transferring from PVP to Ag³¹. Hence thiol-terminated PVP interact with Ag via N, O and S atoms. In comparison, PEG interact with Ag surface only via Ag-S bond. Thus PEG form linear structure away from Ag surface, while PVP more coiled structure on the Ag surfaces (Figure 5.5a)³². This is also why PVP-functionalized cuboctahedra exhibits smaller hydrodynamic size than PEG-functionalized cuboctahedra.

Figure 5.5 Polymer nanoscale structure on particle surface and its influence on the superstructures of cuboctahedra. (a) Schematic description of PVP and PEG on the cuboctahedral surface. (b) Hydrodynamic size of PVP- and PEG- functionalized cuboctahedra in the aqueous environment. (i) SEM images of assembled structure of (c) PVP and (d) PEG functionalization and corresponding (ii) close-up view and (v) lateral view at the angle of 45°. Schematic description of the view from (iii) up and (vi) side of interfacial assembly of PVP- and PEG- functionalized cuboctahedra. (iv) FFT patterns from the ordered assembly of PVP- and PEG- functionalized cuboctahedra. (vii) The radial distribution function as a function of distance for the assembly of PVP- and PEG- functionalized cuboctahedra. Scale bar, (i) 1 μm , (ii,v) 200 nm.

When PVP-functionalized cuboctahedra are used for the interfacial assembly, the monolayer forms a plastic crystal at the oil-water interface, consist of different orientations

(Figure 5.5ci-v). Plastic rotator means the structure with translational order but no orientational order. 56% of the cuboctahedra adopt their square facet and 40% of the cuboctahedra use their triangular facets in contact with the solid substrate (Figure 5.6). Fast Fourier Transform exhibits the hexagonal structure (Figure 5.5cvi). Using PEG-functionalized nanoparticles for the self-assembly, the superstructure forms a square crystal lattice structure with a face-to-face configuration (Figure 5.5di-v). Crystal structure has both the translational and orientational order. Neighboring particles is in contact with their square facets. Fast Fourier Transform exhibits the square structure (Figure 5.5div). Square facet of cuboctahedra is in contact with PDMS substrate. The radial distribution function analysis exhibits the long-range order and the nearest neighbor distance is estimated to be 245 nm and 211 nm for PVP and PEG functionalization respectively (Figure 5.5cvii,dvii).

Figure 5.6 Population of different orientation in the assembled structure with PVP- and PEG-functionalized cuboctahedra.

Larger neighboring distance arises from weak intermolecular interaction and stronger steric repulsion between coiled PVP ligands on neighboring cuboctahedra surfaces. And due to stronger intermolecular interaction between PEG chains on the neighboring cuboctahedra surface, the neighboring distance become smaller. Difference of intermolecular interaction for PVP and PEG chains on the cuboctahedra surfaces leads to the variation of their assembled structure from plastic to the highly ordered crystal structure. Weaker intermolecular interaction between PVP polymer corresponds to the weak interparticle interaction and thus the cuboctahedra have various orientation at the oil/water interface, leading to the plastic structure. In contrast, the cuboctahedra with PEG functionalization allows for significantly more favorable polymer-polymer interaction. Thus the particles adopt uniform configuration and assemble into ordered crystal structure. Cuboctahedra orient planarly on their square facets due to the hydrophilic surfaces and interaction with liquid phase.

Chain length influence

Chain length of surface polymers is also one of the reasons affecting the interparticle interaction³³ and assembled structure due to the nanoscale polymer conformation resulted from the polymer chemical nature. Thus we study the effect of PEG with different chain lengths.

Thiol-terminated PEG with molecular weight of 1000, 2000, 5000, 10000 g/mol is used to functionalize the cuboctahedra. As PEG chain length become longer, water contact angle of PEG functionalized bulk Ag films gradually increases due to the larger ratio of hydrophobic C-C to hydrophilic C-O bond (Figure 5.7a). And hydrodynamic size of these PEG functionalized cuboctahedra exhibits slight increment due to the increase of polymer size on particle surfaces (Figure 5.7b). For PEG functionalization with molecular weights of 1000, 2000, 5000 g/mol, the particles assemble into similar crystal structure with face-to-face configuration (Figure 5.5d, 5.7c,d). By systematically changing the molecular weight of surface molecules, no obvious difference is observed, which proves that the changes in the range about from 1000 g/mol to 5000 g/mol for PEG will not result in the transformation of the assembled structure. When the chain length of PEG changes to 10000 g/mol, the superlattice structure varies to hexagonal plastic crystal (Figure 5.7e). Based on the observation of SEM imaging of above assembled structure, we further calculate the population of cuboctahedra on planar facets and the cluster size in the assembled structure.

As surface PEG chain length gradually increases from 1000 to 2000, 5000, 10000 g/mol, the population of cuboctahedra planar on square facets gradually decreases from 98% to 95%, 87%, 79% respectively and the corresponding cluster size sharply reduces from 249 to 145, 60, 31 (Figure 5.7f). The variation of assembled structure arises from the changes

of polymer conformation on the cuboctahedra surfaces. Longer chain length is reported to provide higher steric repulsion to interparticle interaction (Figure 5.7g). When the polymers grafted to the cuboctahedra are long, the steric repulsion between these longer polymer chains exceeds the attraction, reducing the interparticle interaction. Hence cuboctahedra adopt various orientation and form plastic structure.

Figure 5.7 Comparison of superstructures for cuboctahedra with surface ligands of variable chain length. (a) Bulk contact angle characterization of PEG surfaces with different chain lengths. Molecular weight of PEG1000, PEG2000, PEG 5000, PEG10000 corresponds to 1000, 2000, 5000, 10000 g/mol. (b) Hydrodynamic diameter of PEG-

functionalized cuboctahedra with different chain lengths. (c-d) Corresponding assembled structures. When chain length increases, the assembled structure varies gradually from square ordered structure to hexagonal plastic structure. (f) Population analysis and domain cluster size calculation in c-d. (g) Schematic description of surface interaction between neighboring cuboctahedra due to the change of chain length. Scale bar, (c,d,e) 1 μm ; inset, 200 nm.

Influence of surface polymer on other morphologies

We enlarge the range of cuboctahedra model study to other morphologies including cubes and truncated cubes (Figure 5.8). For different shapes, PVP and PEG functionalization still give rise to similar interfacial position, indicating the similar particle-oil and particle-water interaction. For nanocubes, the height of PVP- and PEG-functionalized cubes above PDMS is similar, (57 ± 3) nm and (53 ± 4) nm respectively. Hence %Particle oil shows similar interfacial position to be (49 ± 2) % and (50 ± 4) % for PVP and PEG functionalization (Figure 5.9a,c, Table 5.2). For truncated cubes, the similar height is (83 ± 7) nm for PVP and (77 ± 6) nm for PEG functionalization, and the corresponding %Particle oil are (47 ± 5) % and (44 ± 4) % (Figure 5.9b,c, Table 5.2).

Figure 5.8 Characterization of nanocubes and truncated cubes. Scale bar, 100 nm.

Figure 5.9 AFM topographic images of (i) PVP- and (ii) PEG- functionalized (a) nanocubes and (b) truncated cubes. (c) Corresponding %Particle_{oil}. Scale bar, 200 nm.

Table 5.2. Height and corresponding %Particle_{oil} of nanocubes and truncated cubes.

	Height (nm)	%Particle _{oil} (%)
PVP-functionalized nanocubes	57 ± 3	49 ± 2
PEG-functionalized nanocubes	53 ± 4	50 ± 4
PVP-functionalized truncated cubes	83 ± 7	47 ± 5
PEG-functionalized truncated cubes	77 ± 6	44 ± 4

For different shapes, different polymer chemical natures also lead to the similar assembly change between plastic and crystal structure. For nanocubes, PVP-

functionalization leads to the formation of plastic macroscopic structure (Figure 5.10ai,ii), consist of 67% planar and 33% nonplanar cubes. FFT exhibits the circular pattern, indicating the plastic structure (Figure 5.10iii). Radial distribution function shows 135 nm neighbor distance (Figure 5.10aiv). PEG-functionalized nanocubes assemble into highly-ordered crystal structure, consist mostly of planar cubes (Figure 5.10bi,ii). FFT also exhibits the square structure (Figure 5.10biii). Neighboring cubes adopt face-to-face configuration, with the square facet in contact with PDMS substrate and from radial distribution function the nearest neighboring distance is 116 nm (Figure 5.10biv). For truncated cubes, with PVP functionalization, the particles adopt different orientations and the assembled superlattices form plastic rotator (Figure 5.10ci,ii). Different facets are in contact with PDMS platform. FFT analysis exhibits the quasi-circular pattern, indicating the plastic structure (Figure 5.10ciii). PEG-functionalized truncated cubes assemble into square crystal superstructure with planar particle orientation (Figure 5.10di,ii). Truncated cubes adopt face-to-face configuration via octagonal faces. Their octagonal facets of truncated cubes contact with PDMS substrate. FFT analysis exhibits the square structure (Figure 5.10diii). From the radial distribution function, the nearest neighboring distance for PVP-functionalized truncated cubes is 165 nm, larger than that for PEG-functionalized truncated cubes, 156 nm (Figure 5.10civ,div). The difference of assembled structure by using different polymer

functionalization for nanocubes and truncated cubes demonstrates universality of the influence of polymer chemical nature on assembled structure.

Figure 5.10 Comparison of superstructures for other morphologies with surface ligands of PVP and PEG. Assembled structure of (a,c) PVP- and (b,d) PEG- functionalized nanocubes and truncated cubes. (i) SEM characterization and corresponding (ii) schematic illustration, (iii) FFT analysis and (iv) radial distribution function. Scale bar, (i) 1 μm , inset, 200 nm.

In addition, the above study of nanoscale surface influence on assembled structure is not affected by the transferred platform. We also assemble the particles at the hexane-water interface and utilize lift-up transferring technique. The macroscopic structure on Si substrate exhibits the similar difference by using PVP and PEG functionalization (Figure 5.11). Air-water interface also shows difference for the assembly of PVP- and PEG- functionalized cuboctahedra (Figure 5.12). This difference further support that the influence of surface polymer chemical nature on the macroscopic assembled structure is due to the

interparticle interaction. The difference of assembled structure at the oil/water and air/water interface arise from the variation of interfacial tension.

Figure 5.11 Assembled structure transferred onto silicon substrate. Scale bar, 1 μm .

Figure 5.12 Assembled structure of PVP- and PEG- functionalized (a,b) nanocubes, (c,d)

truncated cubes, (e,f) cuboctahedra. Scale bar, 1 μm ; inset, 200 nm.

5.3 CONCLUSION

In this work we use PVP and PEG surface functionalized cuboctahedra as model system to demonstrate the nanoscale chemical effect of surface polymer on the particle macroscopic structure. From the perspective of bulk properties, PVP and PEG are two similar polymers, both providing similar hydrophilicity and leading to similar interfacial behavior of cuboctahedra. However, their nanoscale size and chemical nature are different. By DLS measurement, PVP functionalization on the cuboctahedra leads to smaller hydrodynamic size than PEG functionalization. By the assembly study, we demonstrate the polymers with similar bulk property but different chemical nature provides the ability to switch from a liquid crystalline phase with differently oriented particles (PVP) to a crystalline lattice with uniform planar configuration on square faces (PEG). PVP functionalization show stronger steric repulsion between neighboring surface, decreasing the neighboring cuboctahedra interaction and increasing the interparticle distance, resulting in various orientation. With PEG functionalization, cuboctahedra exhibit attraction that exceeds weak steric repulsion between surface polymers, stabilizing the planar orientation on square facets and square-to-square face configuration. Surface chain length also affects cuboctahedra assembly. This is also due to the chemical nature. Longer chain provides larger steric repulsion, decreasing interparticle interaction and leading to plastic assembled structure. The similar phenomenon for PVP and PEG functionalization, observed at the

hexane-water, air-water and using other morphologies, proves the universality of our demonstration. Thereby our work demonstrates the significance of chemical nature of surface polymers, which could provide better control over the macroscopic structure. By controlling the nanoscale surface structure, we achieve the control over macroscopic structure. This fundamental study provides new possibility for control over macroscopic property and generation of novel devices.

5.4 MATERIALS AND METHODS

Materials. Silver nitrate, 1,5-pentanediol (PD), poly(ethylene glycol) methyl ether thiol (average m.w. = 1000 g/mol, PEG1000), poly(vinylpyrrolidone) (average m.w. = 55000 g/mol, PVP55k), isopropyl alcohol (IPA) and decane were purchased from Sigma Aldrich. Ethanol and hexane were obtained from EMSURE and RCI Labscan. Milli-Q water (>18.0 M Ω ·cm) was purified with a Sartorius Arium 611 UV ultrapure water system. Thiol-terminated poly(vinylpyrrolidone) (average m.w. = 1700, PVP or PVP1700), poly(ethylene glycol) methyl ether thiol (average m.w. = 2000, 5000, 10000 g/mol, PEG or PEG2000, PEG5000, PEG10000) were obtained from Polymer Science. Silicone elastomer base and curing agent were purchased from Dow Corning. Gellan Gum (KELKOGEL[®]) was sponsored by CP Kelco. All chemicals were used without further purification.

Synthesis of Ag nanoparticles. The synthesis of Ag nanocubes, truncated cubes, cuboctahedra, is achieved via chemical polyol reduction method. Briefly, 8 mg CuCl_2 , 20 mg PVP and 20 mg AgNO_3 were dissolved in 10 mL PD separately followed by repeated sonication and vortex. After these chemicals were completely dissolved, 35 μL CuCl_2 solution was added to AgNO_3 solution. Then in round bottomed flask, 20 mL PD was heated at 190 °C for 10 min. 235 μL PVP solution was dropwise added into 20 mL PD, followed by quick injection of 500 μL AgNO_3 solution. Then AgNO_3 precursor was injected quickly every min while PVP precursor was dropwise injected every 30 s. When observing tea-like color, we stopped heating and cooled down the whole system to room temperature. For the synthesis of other morphologies, firstly 40 mg AgNO_3 was dissolved in 10 mL PD and 40 μL CuCl_2 solution was added to AgNO_3 solution. The solution of Ag nanocubes in the round bottomed flask was heated at 190° C for 10 min. Similarly, 235 μL PVP precursor was injected dropwise to the flask every 30 s while 500 μL AgNO_3 precursor was quickly added every min. The shape of nanoparticles is dependent on the stopping time of the addition. We chose different time to stop to achieve truncated cubes ad cuboctahedra.. For the purification of Ag nanoparticles, PD was removed by washing with acetone and ethanol, followed by redispersing of sediment in 10 mL ethanol and in aqueous PVP solution (0.2 g/L). The vacuum filtration was done by using PVDF filter membranes with every pore size,

500, 650, 450 and 220 nm.

Ligand exchange. Particle solution was allowed to sediment for several days. 0.5 μL of the sediment was dispersed in ethanol and centrifuged before redispersing in 1.5 ml of ethanol/IPA. Ligand solution was then added under stirring. The concentration of ligands was kept 1mM for cubes, truncated cubes and 10mM for cuboctahedra, truncated octahedra and octahedra. The ligand volume was 10, 50, 10, 80, and 100 μL for cubes, truncated cubes, cuboctahedra, truncated octahedra and octahedra respectively. Functionalization took place for 4 h, followed by centrifugation to remove excess molecules and redispersing in 1.5 mL of ethanol/IPA. 10 mL ligand solution was subsequently added under stirring. The functionalization continues for 3 h, followed by centrifugation and washing with IPA/water.

Interfacial Self-assembly. Gellan gum solution (2 wt%, 6 mL) was used as aqueous phase and decane was added on top of aqueous polymeric phase as oil phase. Gel-trapping experiment was modified from the procedure reported by Paunov and co-workers³³. The gellan gum solution was prepared under $\sim 80^\circ\text{C}$ and stirring at 1400 rpm until the gel was completely hydrated. Subsequently, pre-heated decane was added to the top of gel solution. Particles dispersed in 0.5 μl IPA/water were then injected to the interface. The whole system was left at 80°C for ~ 15 min for thermodynamic equilibrium and then cooled down to room temperature. After the gelling of gellan gum, decane was decanted and premixed PDMS

precursor mixture was deposited onto the arrays. After the curing of PDMS, the monolayer of Ag nanoparticles was peeled off and washed in hot water.

Assembly at hexane-water interface and transfer to silicon substrate. This step utilized the machine of Langmuir-Blodgett to control the assembly. Firstly, 10 ml water and 15 ml hexane were added to the 25 ml beaker to produce the interface. After that, the silicon substrate with O₂ plasma was placed a bit below the hexane-water interface. Ag nanoparticle was then dissolved in 0.5 ml IPA/H₂O and the suspension was injected onto the interface and kept stable for 15 min. Substrate was subsequently lifted up 1.0 mm/min. Until the substrate was above the surface of hexane and was dried enough, SEM imaging can be performed to analyze the arrays on the silicon substrate.

Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) characterization. SEM and TEM imaging were performed using SEM (JEOL-JSM-7600F) and TEM (JEOL-JEM-1400). Assembled monolayer of Ag nanoparticles on PDMS was also imaged by using SEM directly and analyzed using Image J software.

Dynamic light scattering (DLS) measurement. Dynamic light scattering (DLS) measurements were performed using an HPPS (high-performance particle sizer) 5001 autosizer (Malvern Instrument, UK) at 25 °C. The cumulant method was chosen to measure the z-average hydrodynamic diameter and size polydispersity. All the particle suspensions

were diluted with the deionized water and ethanaol and transferred into quartz sample cell for the measurement.

Contact angle measurements. Contact angle measurements were performed on Theta Lite tensiometer equipped with Firewire digital camera. The measurement of static contact angle was done with 4 μ L ultrapure water and decane droplet. Each contact angle data was achieved by the average of at least five times measurement across each substrate.

5.5 REFERENCE

1. Yu, X.; Prévot, M. S.; Guijarro, N.; Sivula, K. *Nat. Commun.* **2015**, *6*, 7596.
2. Abb, S.; Harnau, L.; Gutzler, R.; Rauschenbach, S.; Kern, K. *Nat. Commun.* **2016**, *7*, 10335.
3. Li, H.; Carter, J. D.; LaBean, T. H. *Mater. Tod.* **2009**, *12*, 24-32.
4. Zhou, B.; Li, X.; Tang, X.; Li, P.; Yang, L.; Liu, J. *ACS Appl. Mater. Inter.* **2017**, *9*, 7772-7779.
5. Tang, S.; Li, Y.; Huang, H.; Li, P.; Guo, Z.; Luo, Q.; Wang, Z.; Chu, P. K.; Li, J.; Yu, X.-F. *ACS Appl. Mater. Inter.* **2017**, *9*, 7472-7480.
6. Xia, H.; Wang, D. *Adv. Mater.* **2008**, *20*, 4253-4256.
7. Iacovella, C. R.; Glotzer, S. C. *Nano Lett.* **2009**, *9*, 1206-1211.

8. Li, Y.-J.; Huang, W.-J.; Sun, S.-G. *Angew. Chem. Inter. Ed.* **2006**, *45*, 2537-2539.
9. Reincke, F.; Kegel, W. K.; Zhang, H.; Nolte, M.; Wang, D.; Vanmaekelbergh, D.; Mohwald, H. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3828-3835.
10. Lee, H.-Y.; Shin, S. H. R.; Drews, A. M.; Chirsan, A. M.; Lewis, S. A.; Bishop, K. J. M. *ACS Nano* **2014**, *8*, 9979-9987.
11. Lee, Y. H.; Shi, W.; Lee, H. K.; Jiang, R.; Phang, I. Y.; Cui, Y.; Isa, L.; Yang, Y.; Wang, J.; Li, S.; Ling, X. Y. *Nat. Commun.* **2015**, *6*, 6990.
12. Zhang, Q.; Gupta, S.; Emrick, T.; Russell, T. P. *J. Am. Chem. Soc.* **2006**, *128*, 3898-3899.
13. Nie, Z.; Kumacheva, E. *Nat. Mater.* **2008**, *7*, 277-290.
14. Wang, J.; Wang, D.; Sobal, N. S.; Giersig, M.; Jiang, M.; Möhwald, H. *Angew. Chem. Inter. Ed.* **2006**, *45*, 7963-7966.
15. Wang, D.; Duan, H.; Mohwald, H. *Soft Matt.* **2005**, *1*, 412-416.
16. Oettel, M.; Dietrich, S. *Langmuir* **2008**, *24*, 1425-1441.
17. Kralchevsky, P. A.; Nagayama, K. *Adv. Colloid Interface Sci.* **2000**, *85*, 145-192.
18. Lee, Y. H.; Lee, C. K.; Tan, B.; Rui Tan, J. M.; Phang, I. Y.; Ling, X. Y. *Nanoscale* **2013**, *5*, 6404-6412.

19. Tang, Z.; Zhang, Z.; Wang, Y.; Glotzer, S. C.; Kotov, N. A. *Science* **2006**, *314*, 274-278.
20. Sahai, N.; Kaddour, H.; Dalai, P.; Wang, Z.; Bass, G.; Gao, M. *Nat. Commun.* **2017**, *7*, 43418.
21. Yang, Y.; Lee, Y. H.; Phang, I. Y.; Jiang, R.; Sim, H. Y. F.; Wang, J.; Ling, X. Y. *Nano Lett.* **2016**, *16*, 3872-3878.
22. Yang, Y.; Lee, Y. H.; Lay, C. L.; Ling, X. Y. *Chemistry of Materials* **2017**.
23. Kalsin, A. M.; Fialkowski, M.; Paszewski, M.; Smoukov, S. K.; Bishop, K. J. M.; Grzybowski, B. A. *Science* **2006**, *312*, 420-424.
24. Yue, M.; Li, Y.; Hou, Y.; Cao, W.; Zhu, J.; Han, J.; Lu, Z.; Yang, M. *ACS Nano* **2015**, *9*, 5807-5817.
25. Kato, T.; Fréchet, J. M. J. *Macromolecular Symposia* **1995**, *98*, 311-326.
26. Sánchez-Iglesias, A.; Grzelczak, M.; Altantzis, T.; Goris, B.; Pérez-Juste, J.; Bals, S.; Van Tendeloo, G.; Donaldson, S. H.; Chmelka, B. F.; Israelachvili, J. N.; Liz-Marzán, L. M. *ACS Nano* **2012**, *6*, 11059-11065.
27. Lin, Y.; Böker, A.; Skaff, H.; Cookson, D.; Dinsmore, A. D.; Emrick, T.; Russell, T. P. *Langmuir* **2005**, *21*, 191-194.

28. Akcora, P.; Liu, H.; Kumar, S. K.; Moll, J.; Li, Y.; Benicewicz, B. C.; Schadler, L. S.; Acehan, D.; Panagiotopoulos, A. Z.; Pryamitsyn, V.; Ganesan, V.; Ilavsky, J.; Thiyagarajan, P.; Colby, R. H.; Douglas, J. F. *Nat. Mater.* **2009**, *8*, 354-359.
29. Maillard, D.; Kumar, S. K.; Rungta, A.; Benicewicz, B. C.; Prud'homme, R. E. *Nano Lett.* **2011**, *11*, 4569-4573.
30. Moffitt, M. G. *J. Phys. Chem. Lett.* **2013**, *4*, 3654-3666.
31. Ren, M.; Jin, Y.; Chen, W.; Huang, W. *J. Phys. Chem. C* **2015**, *119*, 27588-27593.
32. Kyrychenko, A.; Korsun, O. M.; Gubin, I. I.; Kovalenko, S. M.; Kalugin, O. N. *J. Phys. Chem. C* **2015**, *119*, 7888-7899.
33. Gao, B.; Arya, G.; Tao, A. R. *Nat. Nanotechnol.* **2012**, *7*, 433-437.

6 SUMMARY AND OUTLOOK

6.1 SUMMARY

In this thesis, we break the current limitation of planar structure for shape-controlled nanoparticles and achieve the high tunability of two-dimensional (2D) metasurfaces by assembling shape-controlled nanoparticles at the oil-water interface.

First we report a new chemical strategy of controlling surface distribution to achieve tunable metasurfaces with non-planar nanocube orientations. We tune the hydrophilic/hydrophobic molecule ratio for surface functionalization and thus manipulate the metasurface structure of Ag nanocubes. Nanocube orientation at the oil/water interface is continuously tuned from planar to tilted and standing configuration. Ag nanocubes are assembled into three unique metacrystals, including square close-packed, linear, and hexagonal crystal structures. Notably, the linear and hexagonal metacrystals achieve unusual open lattices, creating novel electromagnetic field distribution patterns. Hexagonal metacrystal generates large-area ‘hot hexagons’ with significant delocalization. Hence this metacrystal generates stronger SERS signal and provides much higher efficiency as compared to denser-packing square close-packed and linear metacrystals.

Secondly, we further utilize solvent-tunable molecular-level polymer conformation changes to achieve the tunability of interfacial behavior and assembled metacrystal. This method breaks the limitation of changing surface chemistry by replacing surface ligands. Ag nanocubes functionalized with a mixed monolayer of PEG and alkylthiol is used as our model system. By gradually manipulating solvent-dependent PEG conformation from swollen to coiled states, we achieve a high tunability of nanocube interfacial configuration from tilted to standing, and standing to planar and position from being straddled across the oil/water interface to being nearly fully immersed in the oil phase. Nanocubes also organize into large-area linear, hexagonal and square close-packed metacrystals. Our mixed monolayer approach exhibits advantage over a homogeneous ligand functionalization in terms of metacrystal tunability, where homogeneously functionalized nanocubes can only form planar structures.

In Chapter 4, we study the shape-mediated structure transformation and establish a complete phase diagram of polyhedral particles to indicate the relationship between different parameters. We utilize different Ag polyhedral nanoparticles in the family of truncated cubes which interpolates smoothly between cubes and octahedra via cuboctahedra. By using the same surface functionalization, the morphologies change from cube to octahedra leads to the variation of interfacial configuration between standing and planar and

structural transformation from hexagonal to square packing structure. Interfacial behavior of building blocks and the selectivity of different facets achieve the shape-dependent packing structure. We further study the effect of surface functionalization ligands, showing various surface wettability. Truncated octahedra exhibit structural transformation from hexagonal packing of planar particles gradually to square structure of standing particles. Then a complete phase diagram of assembled structure by using polyhedral particles with different surface functionalization is established to indicate the relationship between vertex truncation, surface functionalization, interfacial position and superstructure. The combination of surface chemistry and particle morphology determines particle interfacial behavior. Packing fraction is thus achieved by packing crystallographic symmetry and particle morphology.

Finally, in Chapter 5, we study the particle-particle interaction to achieve the control over assembled structure by utilizing nanoscale structure of surface polymer. In the previous works, we study the interfacial behavior by controlling surface chemistry to tune the interaction between particle surface and two liquid phase. Surface chemistry is also critical to influence the interaction between neighboring particles. We utilize PVP and PEG with similar chain length as a model study since they have similar bulk wettability and thus lead to similar particle interfacial behavior. Due to nanoscale structural difference, large

repulsion from PVP leads to plastic superstructure and larger interparticle spacing, while smaller repulsion from PEG results in ordered crystal structure and smaller interparticle gap size. This thesis summarizes our fundamental study, which bridges molecular level changes to nanoparticle behavior, macroscopic structure and provides a approach to fabricate metacrystals with tunable field localization.

6.2 OUTLOOK

The fundamental studies in this thesis break the current limitation of planar structure for shape-controlled nanoparticles, bridge molecular level changes to macroscopic structure, and provide a promising approach to fabricate metacrystals with tunable properties.

We demonstrate the control over the interfacial behavior of cubic building blocks and the fabrication of tunable 2D platform for nanocubes by utilizing surface functionality distribution and polymer conformation in the mixed monolayer system in Chapter 2 and 3. The variation of surface hydrophobicity has been reported to change interfacial behavior and assembled superstructures for Ag nanooctahedra¹. Surface functionality and polymer conformation also affect assembled structure since it also the controls over surface hydrophobicity. However, this has not been utilized before for shape-controlled nanoparticles. We aim to break the current limitation and achieve better control over

nanoparticle assembly. Hence in this thesis, we utilize Ag nanocubes as a model system to do the study. However, shapes and sizes are also critical on the particle interfacial behaviors and assembled structure^{2, 3}. We have observed the phase transition of different polyhedral nanoparticles by tuning their surface hydrophobicity directly (Chapter 4). We believe that our mixed monolayer method should be broadly applicable to Ag nanocubes with other sizes and other shape-controlled nanoparticles since they all can interact differently and adopt different configurations at the interface for different surface distribution and solvent PI. But for other particle sizes and shapes, we do not have the direct experimental proof to indicate the universality. Hence based on the current observation, we will first establish the interfacial behaviors at different C16%, followed by tuning solvent PI to elucidate the impact of these experimental parameters on the nanoparticles' interfacial behaviors and their assembled structures. Moreover, in Chapter 4, we utilize thiol molecules to tune the surface hydrophobicity and change the assembled structure for different morphologies. However, for truncated cubes and cuboctahedra, different alkylthiol molecules provide low tunability and standing orientation is not observed in their phase transition. Mixed monolayer provides more accurate control over the surface hydrophobicity by changing molecular ratio and polymer conformation. We aim to utilize mixed monolayer system to achieve higher tunability for these two morphologies.

The applications of noble metals, such as Au, Ag, are usually determined by their plasmonic properties. At the surface plasmon resonance (SPR) frequency, the free electrons are excited and collectively oscillating in the metal, giving rise to the locally electromagnetic fields⁴. Individual nanoparticle indeed has excellent plasmonic properties, but assembling them into larger area of structures could allow us to manipulate the collective properties. The gap between nanostructures can concentrate light and then lead to large near-field enhancements⁵. This enhancement can provide unique optical properties, which are important for potential applications, such as enhanced light absorption and transmission⁶, surface-enhanced Raman scattering⁷. Optical properties can be manipulated by tuning the size, shape, position, orientation and configuration of nanoparticles. Joel Henzie et.al assembled silver polyhedral particles with uniform interparticle space into different arrangements⁸. The size of interparticle gap was controlled by the thickness of surfactant and determined the optical properties. Our work in Chapter 2 presented that two-dimensional arrays of nanocubes can serve as ideal SERS substrate and the standing structure provides high sensitivity and efficiency. In this work, we also observed the color difference of PDMS film with different assembled structures. To characterize the optical extinction spectra of different configurations, UV/Vis spectra were obtained for the metasurfaces on PDMS substrate. However, this spectra exhibit broad peak instead of clear

absorption response, which can be utilized to understand the color difference. To explore the in-depth nanoscale optical responses of the metacrystals on PDMS substrate, we intend to perform more nanoscale optical characterization in the future, by utilizing techniques including cathodoluminescence microscopy (CL) and electron energy loss spectroscopy (EELS), with nanometer-scale spatial and spectral resolution.

6.3 REFERENCE

1. Lee, Y. H.; Shi, W.; Lee, H. K.; Jiang, R.; Phang, I. Y.; Cui, Y.; Isa, L.; Yang, Y.; Wang, J.; Li, S.; Ling, X. Y. *Nat. Commun.* **2015**, *6*, 6990.
2. Jana, N. R. *Angew. Chem. Int. Ed.* **2004**, *43*, 1536-1540.
3. Gao, W.; Jiao, Y.; Dai, L. L. *J. Nanopart. Res.* **2016**, *18*, 91.
4. Lu, X.; Rycenga, M.; Skrabalak, S. E.; Wiley, B.; Xia, Y. *Annu. Rev. Phys. Chem.* **2009**, *60*, 167-192.
5. Brongersma, M. L.; Shalaev, V. M. *Science* **2010**, *328*, 440-441.
6. Fang, Z.; Zhu, X. *Adv. Mater.* **2013**, *25*, 3840-3856.
7. Willets, K. A.; Duyn, R. P. V. *Annu. Rev. Phys. Chem.* **2007**, *58*, 267-297.
8. Henzie, J.; Andrews, S. C.; Ling, X. Y.; Li, Z.; Yang, P. P. *Natl. Acad. Sci.* **2013**, *110*, 6640-6645.

7 LIST OF PUBLICATION

- **Yijie Yang**, Yih Hong Lee*, Chee Leng Lay, Xing Yi Ling*; Tuning molecular-level polymer conformations enables dynamic control over both the interfacial behaviors of Ag nanocubes and their assembled metacrystals, *Chem. Mater.*, **2017**, 29 (14), 6137–6144.
- **Yijie Yang**, Yih Hong Lee*, In Yee Phang, Ruibin Jiang, Howard Yi Fan Sim, Jianfang Wang, Xing Yi Ling*; A Chemical Approach To Break the Planar Configuration of Ag Nanocubes into Tunable Two-Dimensional Metasurfaces, *Nano Lett.*, **2016**, 16 (6), 3872-3878.
- Yih Hong Lee, Hiang Kwee Lee, Jonathan Yong Chew Ho, **Yijie Yang**, Xing Yi Ling*; Assembling Substrate-less Plasmonic Metacrystals at the Oil/Water Interface for Multiplex Ultratrace Analyte Detection, *Analyst*, **2016**, 141, 5107-5112.
- Yih Hong Lee, Wenxiong Shi, Hiang Kwee Lee, Ruibin Jiang, In Yee Phang, Yan Cui, Lucio Isa, **Yijie Yang**, Jianfang Wang, Shuzhou Li, Xing Yi Ling*; Chemically Directed Tunable Assembly of Three Distinct Plasmonic Superlattices from Silver Octahedra, *Nat. Commun.*, **2015**, 6, 6990.