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2017

Yang, Y., Lee, Y. H., Lay, C. L., & Ling, X. Y. (2017). Tuning molecular-level polymer conformations enables dynamic control over both the interfacial behaviors of Ag nanocubes and their assembled metacrystals. *Chemistry of Materials*, 29(14), 6137-6144.
doi:10.1021/acs.chemmater.7b02211

<https://hdl.handle.net/10356/143424>

<https://doi.org/10.1021/acs.chemmater.7b02211>

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

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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.

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 arrays³⁷⁻³⁸ 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.

EXPERIMENTAL SECTION

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[®]) 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 method.⁴⁶ 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 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-workers.⁴⁷ The gellan gum solution was prepared under $\sim 80^\circ\text{C}$ 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 °C. All the particle suspensions were diluted with the solvent and transferred into quartz sample cell for the measurement.

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 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 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.²² Consequently, this ratio enables us investigate the possibility of tuning nanocube interfacial behaviors without changing the nanocube surface composition.

Figure 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 1a,b). Ag nanocubes have estimated effective diameters⁴⁸ of ~147 nm due to their non-spherical morphologies and numerous orientations arising from Brownian motions in solution (Figure S1, S2). 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, see S3 for the calculation of binary solvent PI, Table S1 for full list).⁴⁹⁻
⁵⁰ 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 $PI < 0.33$.

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 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 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 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 S2 for the comparison).

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 S4). 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.

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 2a). 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 S5). 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 2. 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.

Changing PI leads to a continuous modulation of both the interfacial configuration and position of the Ag nanocubes (Figure 2b-e, Table S3). Specifically, decreasing PI pushes the Ag nanocubes further into the oil phase, with %cube_{oil} increasing from ~40 % to ~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 2b). At PI=0.85, Ag nanocubes are primarily planar at the oil/water interface, with a %cube_{oil} of $(40 \pm 4) \%$ (Figure 2ci, di). As PI decreases to 0.77, Ag nanocubes become tilted at the interface, with %cube_{oil} increasing to $(49 \pm 5) \%$ (Figure 2cii, dii). Ag nanocubes then adopt a standing orientation at PI=0.47, with the corresponding %cube_{oil} further increasing to $(71 \pm 2) \%$ (Figure 2ciii, diii). At PI=0.38, the nanocubes maintain a standing configuration, but %cube_{oil} increases to $(83 \pm 4) \%$ (Figure 2civ, div). At the lowest experimental PI of 0.33, the nanocubes revert to a planar orientation, and attains the highest %cube_{oil} of $(95 \pm 2) \%$ (Figure 2cv, dv).

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 S6). 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 S7). 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 ~55 % for %cube_{oil} which is accompanied by a systematic change in nanocube configuration from planar to tilted and standing configurations.

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 S8). 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 ~55 % for %cube_{oil}, whereas PEG alone only allows a maximum tunable range of ~35 % (%cube_{oil} from 20% to 57%) and that for C16 is merely 5 % (%cube_{oil} from 93% to 98%). The limited interfacial tunability of Ag nanocubes functionalized with only C16 suggests that

the role of C16 in the mixed monolayer system is to primarily facilitate interactions between Ag nanocubes and the oil phase. 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.

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 S4 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).⁵¹ 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.

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 respectively,⁵¹ 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 1ai). Consequently, we observe a planar nanocube configuration with a %cube_{oil} of (40 ± 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 ± 6) nm to (173 ± 8) 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 surfaces.⁵² 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} $(71 \pm 2)\%$ and $(83 \pm 4)\%$ 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 $(95 \pm 2)\%$. 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 2a).

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, see Table S5 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 3a-d). Nanocubes are tilted in this metacrystal. Fast Fourier transform (FFT) analysis exhibits the linear structure (Figure 3a) and radial distribution function analysis shows an interparticle separation of ~142 nm (Figure 3e). The packing efficiency of this metacrystal is 50 % (Figure S9). A hexagonal plasmonic metacrystal forms at the oil/water interface for PI=0.47 (Figure 3f-i). Nanocubes organize in a standing configuration with edge-to-edge contact in this metacrystal. FFT shows a hexagonal structure (Figure 3f). The interparticle distance increases to ~162 nm (Figure 3j), and leads to a decrease in packing efficiency to 24 % (Figure S9). This hexagonal metacrystal structure is also observed at PI=0.38. A square close-packed metacrystal forms at PI=0.33 (Figure 3k-n). The nanocubes are planar, and contact each other via their facets. The square lattice is evident from FFT analysis (Figure 3k). The interparticle distance is the smallest at ~110 nm (Figure 3o) and this metacrystal has 100% packing efficiency (Figure S9). AFM measurement shows that the heights of assembled structures are similar with that of the single particle height at the oil/water interface (Figure 3b,d,g,i,l,n).

Figure 3. 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), $1\ \mu\text{m}$; scale bars in (b,g,l) and (c,h,m), $200\ \text{nm}$. (e,j,o) Radial distribution function analyses of tilted, standing, and planar nanocubes in the (a) linear, (f) hexagonal and (k) square lattices.

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 $\sim 49\%$. 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 $\sim 71\%$ and $\sim 83\%$ 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 4a). 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 4b,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 S10a, S11). 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 4c,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 4d,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 S10b,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 S11). At PI=0.47, 80 % of the nanocubes adopt standing configurations and assemble into the hexagonal metacrystal (Figure 4e,i). As PI further reduces to 0.46 and 0.40, intermediate structures comprising various orientations are formed (Figure S10d,e, 4f) and the standing nanocube population slightly decreases to 65% and 62% respectively (Figure 4i, S11). 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 4g,i). Intermediate disordered structures are again observed at PI=0.35 (Figure S10f) before the square close-packed structure forms at PI=0.33 (Figure 4h). At PI=0.35, the intermediate structure is composed of 68% planar, 3% tilted and 29% standing nanocubes

(Figure S11). At $PI=0.33$, planar nanocubes increase to 93% and form the square structure (Figure 4i). 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 4. 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.

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 S12). 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 S13). 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 S14). 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.

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.

ASSOCIATED CONTENT

Supporting Information.

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Author Contributions

Y.J.Y, Y.H.L., X.Y.L designed research; Y.J.Y and C.L.L performed research; Y.J.Y, Y.H.L and X.Y.L analyzed data and wrote the manuscript. All authors read and commented on the manuscript.

ACKNOWLEDGEMENTS

X.Y.L. thanks the financial support from National Research Foundation, Singapore (NRF-NRFF2012-04), Singapore Ministry of Education, Tier 1 (RG21/16) and Tier 2 (MOE2016-T2-1-043) grants, and Nanyang Technological University. C.L.L. acknowledges support from an A*STAR Graduate Scholarship, Singapore.

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