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Immobilized Seed-Mediated Growth of Two-Dimensional Array of Metallic Nanocrystals with Asymmetric Shapes

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KEYWORDS: Two-dimensional arrays, self-assembly, metallic nanocrystals, seed-mediated growth, asymmetric nanoparticles, octahedrons, polyhedral nanocrystals
ABSTRACT: Bottom-up fabrication of such arrays with specific orientation of nanoparticles, still remains a challenge. In this article, we report an immobilized seed-mediated growth strategy for the fabrication of two-dimensional (2D) arrays of mono- and bi-metallic polyhedral nanocrystals with well-defined shapes and orientations on a substrate. This method relies on the controlled solution-phase deposition of metals (i.e., Au and Pd) on selectively exposed surface of self-assembled seed nanoparticles that are immobilized on a substrate through collapsed polymer brushes. By using this approach, we demonstrated the preparation of various 2D arrays of shaped Au nanocrystals and Au core/Pd shell nanocrystals with asymmetric geometry of two halves and controlled orientations with respect to the substrate. The shape evolution of seeds to final nanocrystals was systematically monitored and evaluated by electron microscopic imaging. Our study suggests that the shape and orientation of nanocrystals within arrays is determined by the preferential orientation of assembled seed nanoparticles on the substrate, and controllable deposition of metals on exposed crystal facets of immobilized seeds. The synthetic approach we developed presents an important addition to current tools for the fabrication of substrate-supported functional nanostructures.
Noble metal nanoparticles (NPs) (e.g., Au, Ag, and Pd) exhibit fascinating optical, electronic, and catalytic properties that are strongly dependent on their size, shape, and composition.\textsuperscript{1-2} Successful implementation of these NPs into functional devices usually requires effective control of their spatial arrangement and orientation on substrates.\textsuperscript{3-7} The organization of metallic NPs (MNPs) on substrates allows utilizing and modulating the collective optical and electronic properties of NP arrays, thus facilitating their applications in photovoltaic devices,\textsuperscript{8-9} data storage,\textsuperscript{10-11} catalysis,\textsuperscript{12-13} and biological and chemical sensors.\textsuperscript{14-16} As an example, one- or two-dimensional (1D or 2D) arrays of plasmonic nanostructures (e.g., Au nanorods) can be used to manipulate or concentrate light with wavelength below the diffraction limit.\textsuperscript{17-19} In this case, the energy transportation in the array is strongly dependent on the relatively position and orientation of plasmonic nanostructures. Although current research on MNP arrays has been largely centered on monometallic NPs, bimetallic NPs may show properties that surpass their monometallic counterparts, due to the combination or synergistic effect of the two metals.\textsuperscript{20-24} For instance, Au@Pd core-shell nanocrystals can be used as highly sensitive reusable hydrogen gas sensors in which the Pd shell absorbs hydrogen molecules, while the Au core serves as a plasmonic antenna to sense absorbed hydrogen.\textsuperscript{20}

Self-assembly of NPs has been widely studied for the fabrication of arrays of MNPs with different shapes (e.g., spheres, cubes, and rods) on substrates.\textsuperscript{25-29} One common strategy is to use interfaces (e.g., air/liquid, liquid/liquid, liquid/solid) to guide the spontaneous organization of MNPs into ordered structures directly or indirectly on substrates.\textsuperscript{26-32} Unlike top-down approaches (e.g., electron beam lithography\textsuperscript{33}), self-assembly methods are simple, scalable, and do not require special instrumentation in the production of MNP arrays. However, these bottom-up approaches usually offer limited control over the orientation of shaped MNPs with respect to
the substrate. One potential strategy to address this challenge is to grow arrays of oriented NPs directly from seeds immobilized on a substrate. Recently, Hajfathalian et al.\textsuperscript{34-35} reported the fabrication of 2D array of bimetallic core-shell nanostructures using seeds deposited by vapor phase assembly technique on substrates. In this work, the patterning of seed arrays requires the deposition of sacrificial layers and high temperature annealing (up to 1100 °C), which may limit the types of substrates and seed materials that can be used for the synthesis. Nevertheless, there is a need for a general approach to the fabrication of high quality substrate-supported arrays of shaped NPs.

Herein, we report an immobilized seed-mediated growth method to fabricate 2D periodical arrays of mono- or bi-metallic polyhedral nanocrystals with defined shapes and crystal orientations with respect to substrates. This method involves the self-assembly of polystyrene (PS)-grafted shaped Au NPs into 2D arrays on a substrate, oxygen plasma etching of polymer ligands to selectively expose the top surface of Au seeds, and subsequent deposition of a second metal onto the exposed Au surfaces through seed-mediated growth (Figure 1). By using this synthetic method, we demonstrated the preparation of various 2D arrays of shaped Au nanocrystals and \textit{Au core/Pd shell (Au@Pd)} nanocrystals with controlled orientation (\textit{i.e.,} \textlangle 110 \rangle, \textlangle 100 \rangle and \textlangle 111 \rangle orientation) with respect to the substrate. The individual mono- and bi-metallic polyhedral nanocrystals within the arrays exhibit asymmetric geometry, that is, different shapes of the top half and bottom half of the nanocrystals. Because of the presence of collapsed PS chains at the bottom surface of immobilized seeds, there is slower metal deposition rate on the bottom half of MNPs seeds. The shape evolution of seed MNPs to final nanocrystals was systematically monitored and evaluated by electron microscopic imaging. Our study suggests that the shape and orientation of nanocrystals within arrays are determined by the preferential
orientation of assembled MNP seeds on the substrate and controllable deposition of metals on
exposed crystal facets of immobilized seeds. The synthetic approach we developed presents an
important addition to current tools for the fabrication of substrate-supported functional
nanostructures.

RESULTS AND DISCUSSION

2D Array of Asymmetric Au Polyhedral Nanocrystals. Au truncated octahedrons with <110>
orientation (with respect to the substrate) were obtained using 2D monolayer arrays of Au seeds
with cuboctahedral shape (Figure 2). The seed arrays were prepared by drop casting a dispersion
of PS-grafted Au cuboctahedrons in THF onto a Si wafer (Figure 2a, S1 and S2). The
interparticle distance between seed NPs can be approximately controlled between ~10-40 nm by
varying the molecular weight (Mw) of grafted PS chains from 5 to 50 kDa (Figure S3, S4). After
plasma etching to expose Au surface, the seed arrays were incubated in a growth solution
containing Au precursors for metal deposition. It was found that the optimal exposure time of
plasma etching was dependent on the Mw of grafted polymers. For system with shorter
polymers, the etching time should be reduced to avoid the complete removal of polymers and
hence damage of 2D arrays. PS with Mw of 50 kDa was used throughout the study unless
otherwise specified. After completion of the reaction, the nanocrystals in the arrays transformed
into monodispersed Au truncated octahedrons (Figure 2b,c). With the successful shape
transformation, the average diagonal length of nanocrystals increased from 73.8 ± 3.9 nm to 92.1
± 4.2 nm, while the average spacing between NPs decreased from 21.8 ± 5.0 nm to 16.7 ± 4.0 nm
(Figure S5). The hexagonal packing of nanocrystals was maintained after the metal deposition,
which suggests that the seeds were immobilized on the substrate, owing to the residual
hydrophobic PS collapsed on the bottom surface of nanocrystals.\textsuperscript{36}
The uniform transformation of cuboctahedrons to truncated octahedrons can be attributed to the defined crystal facets and orientation of the Au cuboctahedral seeds on the substrate. Au cuboctahedrons had a preferential \(<110>\) orientation with respect to the substrate, as shown in the histogram analysis of crystal orientation in Figure 2d. Au cuboctahedrons are composed of eight triangular facets and six square facets.\(^{37}\) During solvent evaporation, the square \(\{100\}\) crystal facet of cuboctahedrons aligned face-to-face to achieve more dense and efficient packing.\(^{38-39}\) The face-to-face contact and hence \(<110>\) orientation of hexagonally packed cuboctahedrons maximizes the entropy state of nanocrystal arrays.\(^{40-41}\) At this orientation, four crystal facets (i.e., two \(\{111\}\) and two \(\{100\}\)) at the top surface of nanocrystals were exposed directly to oxygen plasma treatment, leading to the selective removal of PS ligands on the top surface of nanocrystals. The efficient deposition of fresh Au on these four exposed crystal facets led to the transformation of Au cuboctahedral seeds into truncated octahedrons with \(<110>\) orientation. Three dimensional (3D) models in Figure 2c illustrate the top-view shape transformations of Au cuboctahedral seeds with different orientations (i.e., \(<110>\), \(<110>\), and \(<111>\) orientation) on the substrate. Quantitative analysis of nanocrystal orientation after growth indicates that 81% of the seeds transformed into truncated octahedrons, of which 63%, 7.6 %, and 10.4 % of the truncated octahedrons displays \(<110>\), \(<100>\), \(<111>\) orientation, respectively (Figure 2e). NPs with irregular shape represented 19% of total NPs within the array, which can be attributed to seed defects. The strong correlation between the orientation of seeds and resulting nanoparticles in the histograms indicates the important role of preferential orientation of assembled seeds in the production of high-quality arrays with defined orientation. The formation of nanocrystals with defined shapes did not occur using 15 nm seed NPs without defined crystal facets (Figure S6). Furthermore, when the top crystal facets of Au cuboctahedron...
seed arrays are covered with PS (i.e., in absence of oxygen plasma treatment), there is no uniform shape transformation (Figure S7).

Close inspection of the side and bottom view of resulting truncated octahedron with <110> orientations indicates an asymmetric polyhedral geometry with respects to the shape of the top half (Figure 3).42 While the top half of the nanocrystals transformed into truncated octahedron shape, the bottom half retained their original cuboctahedral shape with a slight elongation of the two {111} crystal facets. The nanocrystals exhibit different appearances depending on the rotation angle of the NPs (see 3D models of nanocrystals viewed at different angles). As mentioned above, the presence of relatively low-density PS at the bottom surface of seeds helped to immobilize individual nanocrystals and kept them fixed at their original position on the substrate throughout the metal deposition process. Moreover, the residual PS at the bottom surface (and the physical blocking by the substrate) slowed down the deposition of metals at the bottom, while not affecting the growth from the top crystal facets, thus resulting in the formation of nanocrystals with asymmetric shape.

The immobilized seed-mediated growth method offers us a simple way to systematically analyze the time-dependent shape evolution of nanocrystals on the substrate. By imaging the nanocrystal arrays at different points in time of Au deposition, we witnessed the shape transformations of cuboctahedral seed arrays (Figure 4). Within ~2 hours of incubation, the Au cuboctahedral seeds preserved their original shape. After ~3-4 hours, the seeds transformed into truncated octahedrons in which the top {111} crystal facets increased in size while the {100} crystal facets decreased (Figure S8). With the extension of growth time, the {111} crystal facets continuously increased to dominate the top surface of nanocrystals, while the size of {100} crystal facets kept reducing until they almost completely disappeared after ~8 hours of
incubation (Figure S9, S10). The controllable shape transformation was further confirmed by the gradual increase in the diagonal length of nanocrystals. The diagonal length of Au cuboctahedral seeds increased from $73.8 \pm 3.9$ nm, to $83.7 \pm 5.6$ nm, and eventually to $92.1 \pm 4.2$ nm at the aforementioned time points, respectively (Figure S5).

*Au cuboctahedrons and Au octahedrons with <100> orientation* were synthesized by taking advantage of the <100> preferential orientation of truncated Au cubes seeds along the substrate (Figure 5). The preferential <100> orientation of cubes within the arrays was resulted from the face-to-face alignment of the {100} crystal facets of cubes to produce densely packed arrays (Figure 5d and S11). With this orientation, the crystal facets on the top part of the cubic seeds were exposed to plasma treatment caused the exposure of one {100} and four {111} crystal facets on the top half of the seeds (Figure 5a). The subsequent Au deposition selectively on the exposed crystal facets led to the formation of truncated octahedrons (Figure 5b). About three quarters of all the resulting truncated octahedrons exhibited <100> orientation in the arrays (Figure 5e). The rest existed either in other orientation modes (*i.e.*, 8.7 % in <110> orientation and 10.5 % in <111> orientation) or presented as defects originated from the irregular shape of seeds. The average space between nanocrystals decreased from $26.5 \pm 4.3$ nm to $20.1 \pm 7.6$ nm after Au deposition when truncated cubes transformed into truncated octahedrons.

We studied the shape evolution of nanocrystals from cubic seeds to cuboctahedrons, truncated octahedrons and finally octahedrons, throughout the course of Au deposition (Figure 6). Au cuboctahedrons were obtained after incubating the seeds in the growth solution at 40 °C for 2 hours (Figure S12). At a 5-hour incubation time, the prolonged metal deposition produced truncated octahedrons (Figure S13). When the metal deposition occurred in growth solution with doubled concentration of gold precursor at 60 °C for 8 hours, Au octahedrons were obtained.
With the evolution of the nanocrystals, the \{100\} center crystal facet of cube seeds gradually decreased and eventually disappeared, while the four \{111\} triangular crystal facets at the top corners elongated and merged at the time point when the \{100\} crystal facet disappeared. With the transformation of nanocrystals from cubes, to cuboctahedrons, and finally to octahedrons, the diagonal length of nanocrystals increased from $71.5 \pm 3.7$ nm, to $77.8 \pm 5.7$ nm and eventually to $83.5 \pm 5.0$ nm (Figure S14). 

As a result of the different metal deposition rate on the top and bottom halves of the seed NPs, the final nanocrystals were asymmetric in shape with respect to their top and bottom halves (Figure 7, S15). Such shape difference between the top and bottom halves can be seen from the side view SEM images and 3D models of the asymmetric Au cuboctahedrons and octahedrons. Furthermore, an examination of the bottom part of the Au cuboctahedrons and octahedrons indicates that the \{100\} square facets located at the bottom of the Au cuboctahedrons and octahedrons still remained. The average diagonal lengths of the bottom \{100\} crystal facets of the Au cuboctahedrons and octahedrons were $59.8 \pm 6.7$ nm and $49.0 \pm 4.7$ nm, respectively (Figure S15).

\textit{Au octahedrons with <111> orientation} were obtained using 2D arrays of Au octahedrons as seeds (Figure 8). Au octahedrons are composed of eight triangular \{111\} crystal facets. When PS-tethered Au octahedrons assembled into 2D arrays, they acquired <111> orientation on the substrate, as a result of the entropy-driven face-to-face contact between the \{111\} crystal facets (Figure 8a, d and S16). With the <111> orientation, the top view of seed NPs looks like that of Au triangles, as only one \{111\} triangular crystal facet of the Au octahedral seeds can be observed in the SEM images. After treating the seed arrays with oxygen plasma and depositing Au at 40 °C for 5 hours, the top view triangular \{111\} crystal facets were preserved and
increased in size (Figure 8b and S17). An analysis of crystal orientations shows that 80.9% of the nanocrystal exhibited triangle-like geometry due to the <111> orientation of seeds (Figure 8e and S17). Surface growth defects such as merged particles or irregular shapes counted 17.3 %, while 1.9 % of the octahedrons adopted <110> orientation. There were no Au octahedrons with <100> orientation.

Figure 9 illustrates the evolution of the top {111} triangular crystal facet of the Au octahedrons. When the 2D array was incubated in the Au growth solution at 40 °C for 5 hours, the top crystal facet increased in size and became more truncated. By doubling the concentration of Au and incubating for 10 hours, the truncation decreased and the top {111} crystal facet of the Au octahedrons increased in size (Figure S18). The length between one triangular vertex to the opposite side edge increased from 46.6 ± 4.9 nm to 58.8 ± 4.7 nm (see 2D models in Figure S19).

Octahedrons, cuboctahedrons, and cubes can be produced generally based on the relative growth rates of {100} or {111} crystal facets. In our case, the immobilized seed NPs preferred to adopt octahedron shape, in order to minimize the total interface free energy of the system by maximizing the expression of the {111} crystal facet following the Wulff’s theorem, although CTAB is known to passivate {100} crystal facet to obtain cubes. In absence of CTAB, low-quality truncated octahedrons were produced (Figure S20). Interestingly, when cetyltrimethylammonium chloride (CTAC) was used, the Au deposition produced low-quality trisoctahedron-like NPs rather than cubes. Nevertheless, the exact mechanism for the formation of thermodynamically favored octahedrons in the immobilized seed-mediated growth is still unclear. We presume that this might be attributed to the slow reduction of Au precursor due to the surface-limited diffusion of chemicals toward seeds and the low concentration of reducing
agent AA.

The 2D NP arrays grown on the substrate show tunable interparticle spacing, defined crystal orientation and shape asymmetry, thus facilitating their property discovery and application development. As a demonstration, we evaluated the surface plasmon resonance (SPR) property of truncated octahedron arrays with <100> orientation (growth from cubic seeds) and with <111> orientation (grown from octahedral seeds) on glass slides. The UV-vis spectra of the 2D arrays were obtained using incident light of different irradiation angles (Figure S21). One relatively narrow SPR peak located at ~550 nm was observed for cubic seeds in solution, while 2D array of the seeds showed a very broad peak at ~560 nm, regardless the tested angles of incident light. The red-shift in SPR band upon 2D assembly can be explained by the plasmonic coupling between neighboring NPs in the arrays. After the deposition of Au on cubic seeds, the resulting truncated octahedrons arrays with <100> orientation exhibited two SPR peaks located at ~530 nm and ~480 nm that are corresponding to the plasmonic band along the direction parallel and perpendicular to the substrate, respectively (Figure S22). The appearance of a new peak at the short wavelength and the narrowing of peak at the long wavelength can be attributed to the elongation of the NPs from the substrate. More studies on the optical response of 2D arrays are needed for better understanding the underlying mechanism. Similar phenomenon was also observed for truncated octahedrons arrays with <111> orientation transformed from octahedral seeds. Moreover, we further demonstrated the utilization of such 2D arrays of nanocrystals with defined orientation as substrates for surface-enhanced Raman scattering (SERS) detection (Figure S23). Arrays of cubic seeds and resulting cuboctahedrons and truncated octahedrons after Au deposition (all with <100> orientation) were used as substrates for analyzing Raman probe 4-mercaptobenzoic acid. The SERS signals were highly uniform cross the samples due to
the ordering of the NPs. Interestingly, the SERS enhancement factor (EF) for the 1590 cm$^{-1}$ associated with the aromatic ring vibrations was found to decrease from 1.3 x 10$^7$, to 8.3 x 10$^6$, and to 3.5 x 10$^6$ with the transformation of cubes, to cuboctahedrons and to truncated octahedrons upon Au deposition. This could be due to the decrease in the sharpness of nanocrystal corners and edges during the shape transformation of nanocrystals.

2D array of Asymmetric Au@Pd core-shell Polyhedrons. Asymmetric nanocrystals with shaped Au core and Pd cubic shell (Au@Pd) were produced by depositing Pd on monolayer seed arrays of either Au cuboctahedrons or cubes (Figure 10, S24). The deposition of Pd on either of the two types of seeds led to the formation of Au core and Pd cubic shell bimetallic nanocrystals. Similar to the case of monometallic nanocrystals, the shape of resulting Au@Pd core-shell nanocrystals was dependent on the orientation of the seeds. The majority (~64.0%) of the Au@Pd nanocrystals showed a <110> orientation in the array, while the population of <100> and <111> orientation were 7.3% and 11.5%, respectively (Figure 10f). Defected nanocrystals counted for another 17.2%. The Au@Pd nanocrystals were also asymmetric, as indicated by the bottom view SEM image of the nanocrystals and the side view TEM image of a single nanocrystal (Figure 10c, d). The asymmetric distribution of Pd on Au NP surface was further confirmed by the energy dispersive X-ray spectrometry (EDS) line scan along different positions of the nanocrystal (Figure S25).

We further studied the evolution of the Au@Pd nanocrystals by adjusting the incubation time and concentration of Pd and AA (Figure 11). In 8h incubation, at a relatively low concentration of Pd precursor, Pd deposition occurred on the {111} crystal facet of the Au cuboctahedrons. In general, the deposition of atoms favors surface cites with high surface energies such as vertices, edges and uncapped facets.\textsuperscript{46} We presume that the selective passivation of {100} facets of Au
cuboctahedrons by CTAB reduced the surface energy of \{100\} facets and made \{111\} crystal facets to be the facets with the highest surface energy. When more Pd was deposited on the \{111\} crystal facets, Pd surrounded the \{100\} crystal facets of Au cuboctahedrons, leading to the formation of Au@Pd cubic frames (i.e., Au cuboctahedron enclosed within Pd cubic frame) (Figure S26). The formation of Pd shell led to an increase in the diagonal length of nanocrystals from 73.8 ± 3.9 nm to 82.0 ± 3.0 nm. The complete engulfment of Au seeds in a Pd cubic shell was achieved with the further increase in the concentration of Pd. This was accompanied with an increase in the diagonal length of nanocrystal to 95.3 ± 6.3 nm (Figure S27).

CONCLUSION

In summary, we developed an immobilized seed-mediated growth method for the fabrication of 2D arrays of asymmetric Au and Au@Pd nanocrystals with defined shapes and specific orientations on substrates. This method relies on the selective position of a second metal on the exposed surface of seed NPs immobilized on substrates. In the monometallic system, Au seeds with cuboctahedral, cubic, and octahedral shapes transformed into Au truncated octahedrons preferentially oriented in the \(<110>\), \(<100>\) and \(<111>\) mode, respectively. In the bimetallic system, the deposition of Pd on to Au cuboctahedral and Au cubic seeds led to the formation of 2D arrays of asymmetrical Au@Pd core-cubic shell nanocrystals with \(<110>\) and \(<100>\) orientation, respectively. The locally collapsed polymer at the bottom surface of the seeds fix the seed arrays on the substrate, and simultaneously confine the metal deposition on the top crystal facets of the seeds to produce asymmetric polyhedral nanocrystals, which distinguishes our method from existing methodologies for the fabrication of shaped MNP arrays. Furthermore, our method provides a simple technique to acquire arrays of polyhedral nanocrystals with specific orientation by selecting shaped seeds with predominant orientation. We expect that the
immobilized seed-mediate growth can be scaled up for fabricating much larger-area monolayers of oriented nanocrystals with the assist of such as Langmuir–Blodgett technique. Our synthetic method has the following important features: i) it can be extended to seed NPs with other shapes and compositions; ii) it is inexpensive and does not require any lithography steps; iii) it is applicable to substrates made from various materials (e.g., low-melting point materials); and iv) it allows for easy monitoring the growth kinetics of NP arrays. We expect that the library of substrate-supported NP arrays will find a broad range of applications in sensing, catalysis, optical and electronic devices.

METHODS

**Synthesis of Au Cuboctahedral, Cubic, and Octahedral Seeds.** One-pot synthetic method was used to synthesize Au cuboctahedral, cubic and octahedral nanocrystals. In a 20 mL vial, a 19.75 mL of 10 mM CTAB was prepared in water, and placed in a water bath at 42 °C. When the temperature of CTAB solution stabilized, 250 µL of 10 mM HAuCl₄ was added and stirred at 550 rpm for 30 seconds to obtain a transparent-yellow solution. Subsequently, 100 µL of 100 mM AA were added under stirring for 30 seconds to form a colorless solution. The (Au-CTAB)-AA solution was kept steady (i.e., incubated at constant temperature and without stirring) for 0-5 minutes. Then, 100 µL of 100 mM NaOH aqueous solution was quickly added under stirring at 550 rpm, for 2 minutes. The solution turned fuchsia in color in approximately 20-30 seconds, indicating the nucleation and formation of Au cuboctahedrons. Au cuboctahedrons were obtained by incubating the reaction in a water bath at 42 °C without stirring for 2 hours. The production of Au cubes and octahedrons was achieved by controlling incubation time of (Au-CTAB)-AA solution and the reaction temperature. Specifically, Au cubes were obtained by incubating the (Au-CTAB)-AA solution at 42 °C, for 10-15 minutes before the addition of NaOH, while all other experimental conditions were the same as described above. Au octahedrons were
synthesized by elevating the reaction temperature to 50 °C, while all other experimental conditions were the same as the synthesis of Au cuboctahedrons. After the formation of desired Au nanocrystals, the solution was centrifuged to remove excess precursors and hence stop the further proceeding of the reaction.

**Surface Modification of Shaped Au Seeds.** Using ligand exchange method,\textsuperscript{49-51} thiol-terminated polystyrene (PS-SH, Mn= 50,000) was grafted onto the surface of shaped Au nanocrystals. As-prepared shaped Au nanocrystals were centrifuged twice at 2,500 - 3,000 rpm (1.5 mL centrifuge tubes are highly recommended). After the first and second centrifugation cycle, the nanocrystals were redispersed and concentrated in 3 mL and in 200 µL of water, respectively. Then, 200 µL of shaped Au nanocrystals were added dropwise into 10 mL of 0.75 mg/mL PS-SH solution in DMF under stirring. Subsequently, the solution was sonicated for 10 minutes and incubated for another 10 min at room temperature. The PS-grafted Au nanocrystals solutions were centrifuged for ~3-4 cycles to remove excess PS. After each centrifugation cycle, the supernatant was discarded and PS-grafted NPs at the bottom were redispersed in 1.0 mL of THF. After the last centrifugation cycle, PS-grafted Au shaped nanocrystals were dispersed in 200 µL THF and stored at 4 °C for further use.

**Self-assembly of Polystyrene-Grafted Au Nanocrystals into 2D arrays.** 2D array of polystyrene-grafted Au nanocrystals were directly assembled on Si wafer substrates. Square pieces of Si wafers (~1.5 cm$^2$ in size) were cleaned thoroughly with piranha solution, a mixture of 3:1 H$_2$SO$_4$ and 30% H$_2$O$_2$ (*CAUTION: The mixing procedure is an exothermic reaction, which creates a highly CORROSIVE mixture. Refer to reliable SOP for piranha solution handling, and disposal procedures*). The Si wafers were rinsed with copious amount of water
and stored in water to avoid contamination from air. Si wafers were dried under Ar or N\textsubscript{2} gas and immediately used for self-assembly.

Monolayer arrays of Au nanocrystals were fabricated by the self-assembly of PS-grafted Au nanocrystals using method reported previously with appropriate modification\textsuperscript{52-53}. Briefly, clean Si wafers were placed on top of HPLC caps in a glass petri dish containing THF solvent (Figure S1). A 2 µL of PS-grafted Au shaped nanocrystals solution in THF was quickly dropped on the surface of Si wafer. The petri dish was immediately covered with lid to create a close system saturated with THF vapor. The solution of PS-grafted Au seeds spread over the surface of the Si wafer. Upon the slow evaporation of THF solvent in the nanocrystal solution, the PS-grafted Au nanocrystals nucleated and self-organized into monolayer arrays with hexagonally packed NPs on the substrate.

Selective Removal of Polystyrene from the Top Surface of Au Nanocrystals via Oxygen Plasma Treatment. The polystyrene on the top surface of Au nanocrystals with arrays was removed with oxygen plasma etching. Prior oxygen plasma treatment, Si wafers with assembled nanocrystal arrays were rinsed with deionized water and dried by blowing air to remove contaminants. Afterwards, the arrays of shaped seeds were treated with oxygen plasma for three minutes under medium Radio Frequency power (RF) using Harrick Plasma Cleaner PDC-32 G (115V). The exposure time was adjusted according to the size of the Au nanocrystals. PS-grafted Au cubes were etched between 3.5-4 minutes since their surface area was larger than cuboctahedrons surface area. The substrates with nanocrystal arrays were immediately rinsed with deionized water and stored in water for future use.

Au Deposition on Exposed Surface of Au Nanocrystal Arrays. The growth solution was first prepared as follows. In a 20 mL vial, specific quantity of 10 mM HAuCl\textsubscript{4} aqueous solution
was added into a 19 ml of 10 mM CTAB solution. The solution was swirled for thorough mixing. L-Ascorbic acid was then added (1:1 Au to AA mole ratio) and mixed well until the color of solution turned from yellow to clear. Subsequently, the plasma-treated seed arrays on Si wafers were immersed in the Au growth solution and incubated in a water bath at different temperatures and specific periods of time. After the completion of metal deposition, the samples were removed from the growth solution and rinsed with deionized water. The detailed reaction conditions (e.g., temperature and quantities of HAuCl₄ and AA) are given in Table SI 1-3.

**Pd Deposition on exposed Surface of Au Nanocrystal Arrays.** The Pd growth solutions were prepared in 20 mL vials containing 19 ml of 10 mM CTAB solution. The CTAB solution was placed in a water bath at 30 °C. After the temperature was stabilized, specific quantities of 10mM H₂PdCl₄ (H₂PdCl₄ was prepared in the lab using PdCl₂ and HCl) and 100mM AA were added to the CTAB solution. Subsequently, the plasma-treated seed arrays on Si wafers were immersed into the Pd growth and incubated for 8-12 hours. After the completion of metal deposition, the samples were removed from the growth solution and rinsed with deionized water. The detailed reaction conditions are given in Table SI 4. Similarly, Au cubic core @ Pd cubic shell were synthesized by incubating the substrates of Au cubic arrays in Pd growth solution in a water bath at 30 °C for 12 h. The Pd growth solution contained 19 ml of 10 mM CTAB solution 500 µL of 10mM H₂PdCl₄ and 250 µL of 100mM AA.

**Characterizations.** The morphologies of polyhedral nanocrystals were imaged using a Hitachi SU-70 Schottky Field Emission Gun Scanning Electron Microscope (FEG-SEM) and JEOL JEM 2100 Field-Emission Gun Transmission Electron Microscope (JEM 2100 FEG). Elemental analysis was performed on JEM 2100 FEG Transmission Electron Microscope (FEG-TEM)
using the scanning transmission electron microscopy mode. Information about sample preparation can be found in SI.

ASSOCIATED CONTENT

The Supporting Information

Sample preparation for imaging; supplementary tables for metal deposition; schematic illustrations and length measurements of nanocrystals; additional SEM images of arrays; UV-vis analysis of arrays; EDS line scan; SERS measurement (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

Z.N., J.H., and M.P-C. designed the research project. M.P-C., S.L., M.M. and C.K. carried out major experiments. Z.N., M.P-C., J.H. and C.K. wrote the manuscript. All authors have given approval to the final version of the manuscript.

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REFERENCES


**Figure Captions**

**Figure 1.** Schematic illustration of immobilized seed-mediated growth of 2D array of asymmetric Au and Au@Pd polyhedral nanocrystals. The process involves the self-assembly of polymer-grafted Au NPs into 2D monolayer arrays on the substrate, selective removal of polymer ligands from the top surface of NPs by oxygen plasma treatment, and deposition of a second metal selectively on the exposed surface of seed NP arrays.

**Figure 2.** Top view SEM images of 2D array of (a) Au cuboctahedral seeds with <110> orientation with respect to the substrate (before Au deposition) and (b) Au truncated octahedrons with <110> orientation (after Au deposition). c) 3D models illustrating the shape transformation of Au cuboctahedral seeds with the <110>, <100>, <111> orientation. d,e) Histogram analysis of the orientation of (d) Au cuboctahedral seeds and (e) resulting truncated octahedrons within the 2D array.
**Figure 3.** (a,c) Side view and (b,d) bottom view SEM images and their corresponding 3D models of (a,b) cuboctahedral seeds (before Au deposition) and (c,d) resulting asymmetrical truncated octahedron (after Au deposition).

**Figure 4.** Top view SEM images, 3D, and 2D models illustrating the time-dependent shape evolution of Au cuboctahedral seeds along the <110> orientation.

**Figure 5.** Top view SEM images of 2D array of (a) Au truncated cubic seeds with <100> orientation with respect to the substrate (before metal deposition) and (b) Au truncated octahedrons with <100> orientation (after metal deposition). c) 3D models illustrating the shape transformation of Au truncated cubic seeds with <110>, <100>, <111> orientation. d,e) Histogram analysis of the orientation of (d) Au truncated cubic seeds and (e) resulting truncated octahedrons within the 2D array.

**Figure 6.** Top view SEM images, 3D, and 2D models illustrating the time-dependent shape evolution of Au truncated cubic seeds along the <100> orientation.

**Figure 7.** (a, c) Side view and (b, d) bottom view SEM images and 3D models of (a, b) asymmetric Au cuboctahedrons and (c, d) asymmetric Au octahedron obtained after the metal deposition on Au cubic seeds.

**Figure 8.** Top view SEM images of 2D array of (a) Au octahedron seeds (before Au deposition) and (b) Au truncated octahedrons (after Au deposition). c) 3D models showing the shape transformation of Au octahedral seeds with <110> and <111> orientation. d) Histogram analysis of the orientation of resulting Au truncated octahedrons within the 2D array.
**Figure 9.** Top view SEM images, 3D, and 2D models illustrating the time-dependent shape evolution of Au octahedral seeds along the <111> orientation.

**Figure 10.** (a-c) Top view (a), side view (b) and bottom view (c) SEM images of 2D array of asymmetrical Au cuboctahedral core@Pd cubic shell nanocrystals. d) Side view TEM image of a single nanocrystal released from the substrate. The red dashed line indicates the boundary between the top and bottom half of the resulting nanocrystals. e) 3D models showing the shape transformation of Au cuboctahedral seeds with <110> <100> <111> orientation with the deposition of Pd. f) Histogram analysis of the orientation of resulting Au cuboctahedral core@Pd cubic shell in the 2D array.

**Figure 11.** Top view SEM images, 3D, and 2D models illustrating the shape transformation of Au cuboctahedral seeds into Au@Pd core-cubic shell with <110> orientation.
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100x78mm (300 x 300 DPI)
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85x69mm (300 x 300 DPI)
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