Nanoscale surface chemistry directs the tunable assembly of silver octahedra into three two-dimensional plasmonic superlattices

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A major challenge in nanoparticle self-assembly is programming the large-area organization of a single type of anisotropic nanoparticle into distinct superlattices with tunable packing efficiencies. Here we utilize nanoscale surface chemistry to direct the self-assembly of silver octahedra into three distinct two-dimensional plasmonic superlattices at a liquid/liquid interface. Systematically tuning the surface wettability of silver octahedra leads to a continuous superlattice structural evolution, from close-packed to progressively open structures. Notably, silver octahedra standing on vertices arranged in a square lattice is observed using hydrophobic particles. Simulations reveal that this structural evolution arises from competing interfacial forces between the particles and both liquid phases. Structure-to-function characterizations reveal that the standing octahedra array generates plasmonic ‘hotstrips’, leading to nearly 10-fold more efficient surface-enhanced Raman scattering compared with the other more densely packed configurations. The ability to assemble these superlattices on the wafer scale over various platforms further widens their potential applications.
Controlled organization of nanoparticles into scalable superlattices with tunable crystal structure and spacing is a grand challenge in nanotechnology. Nanoparticle superlattices exhibit unique crystal structure-dependent physicochemical functionalities, playing a pivotal role in the design of next-generation devices. Several methods are commonly used to form superlattices, including varying interparticle forces among spherical particles, using anisotropic nanoparticles with various morphologies, and forming localized chemical patchiness on anisotropic nanoparticles. However, it remains difficult to assemble multiple superlattices over large areas using just one nanoparticle morphology. Overcoming this limitation will enhance superlattice diversity, enable direct investigations of structure-to-function variations arising solely from superlattice structural changes and allow more specific customization of superlattices for targeted applications. In particular, anisotropic nanoparticles possessing well-defined facets are appealing because these facets can interact with each other in various ways to create distinct superlattices. However, such interactions among one type of particle morphology have not yet been extensively explored to achieve tunable self-assembled nanoparticle superlattices, particularly in the formation of non-close-packed superlattices.

Here we demonstrate the concept of ‘one anisotropic particle, multiple superlattices’ using octahedral silver (Ag) nanoparticles. We are able to tailor the surface chemistry of Ag octahedra to assemble three wafer-scale two-dimensional (2D) plasmonic superlattices at the oil/water interface, one of which is a square superlattice with Ag octahedra standing on their vertices. Through molecular dynamics (MD) simulations, we find that these bespoke superlattices arise from a competition of interactions between the nanoparticles and both liquid phases. Despite having the lowest-packing density, the square superlattice is the most efficient surface-enhanced Raman scattering (SERS) superlattice. This finding demonstrates the importance of nanoscale superlattice design, where more nanoparticles do not always generate stronger scattering signals, contrary to the rule of thumb in SERS research.

Results

Assembly of three plasmonic superlattices with one particle. We employ a chemical approach to tune the surface hydrophobicity of Ag octahedra building blocks. As-synthesized Ag octahedra (edge lengths $\approx 350 \pm 10$ nm) are stabilized with the hydrophilic polyvinylpyrrolidone (PVP). The hydrophobicities of these particles are homogeneously increased via ligand exchange with alkylthiols of increasing chain lengths, including C1-propanethiol (C3SH) and 1-hexadecanethiol (C16SH). These Ag octahedra are then assembled at the oil/water interface and subsequently immobilized using the gel-trapping technique. Once trapped at the interface, the superlattices can be transferred to various solid platforms.

A hexagonal close-packed (HCP) 2D superlattice forms at the oil/water interface using PVP-functionalized Ag octahedra (PVP octahedra, bulk water contact angle (CA) measured on Ag film functionalized with PVP $\approx (39 \pm 5)^\circ$; Fig. 1b,c). neighbouring Ag octahedra contact via a face-to-face configuration (Fig. 1d; Supplementary Fig. 2). This superlattice is planar, with one facet of the octahedra in direct contact with the substrate (Fig. 1d). Long-range order of this superlattice is evident from the regularly oscillating curves in its corresponding radial distribution function (Fig. 1e) and honeycomb network of Voronoi cells (Supplementary Fig. 3a); the nearest neighbour distance is estimated to be 188 nm (Fig. 1e). The packing efficiency of this close-packed array is 88.9% (Supplementary Fig. 4).

The HCP superlattice changes to an open hexagonal (OH) array using CSH-functionalized Ag octahedra for the self-assembly (C3-octahedra, CA = $(83 \pm 3)^\circ$; Fig. 1f,g). A comparison of this monolayer (Fig. 1h) with the HCP array (Fig. 1d) clearly illustrates the change from a face-to-face contact to an edge-to-edge alignment. Order is also evident from the radial distribution function and Voronoi cells of this 2D array (Fig. 1i; Supplementary Fig. 3b), with the nearest neighbour distance increased to 313 nm. The packing efficiency of this monolayer decreases to 66.7% (Supplementary Fig. 5).

An entirely different square superlattice is formed by assembling hydrophobic C16SH-functionalized Ag octahedra (C16-octahedra, CA = $(110 \pm 2)^\circ$; Fig. 1j,k). Partial submersion of edge-to-edge aligned Ag octahedra within the poly(dimethylsiloxane) (PDMS) mold gives a pyramidal appearance (Fig. 1j; inset). Cross-sectional scanning electron microscopy (SEM) images of these superlattices transferred to a Si substrate (Supplementary Fig. 3a) show only a single vertex of the octahedra contacting the substrate (Fig. 1i). This superlattice of standing octahedra has the lowest-packing efficiency among the three arrays at 33.3% (Supplementary Fig. 6). Superlattice crystallinity is evident from the radial distribution function (Fig. 1m) and the square Voronoi cells (Supplementary Fig. 3c), with the nearest neighbour distance estimated to be 362 nm. Notably, the three different superlattices observed heretofore arise solely from variations of Ag octahedra surface wettability.

Interfacial behaviour of Ag octahedra. MD simulations show that Ag octahedra move spontaneously to the interface to attain thermodynamic equilibrium (Supplementary Notes 1 and 2; Supplementary Movies 1–3; Supplementary Fig. 7). PVP octahedra migrate from a tilted configuration in the aqueous phase to become planar on breaching the oil/water interface (Fig. 2a). For C3-octahedron, the particle rotates from a nearly upright configuration to attain a stable planar equilibrium configuration. In contrast, C16-octahedron adopts an upright configuration from the beginning and this configuration is maintained at equilibrium. Notably, the interfacial configurations of these Ag octahedra match well with the experimental topological characterization using atomic force microscopy (AFM; Fig. 2e). The experimental height percentages of the particle in contact with the oil phase are 11%, 18% and 57% for PVP, C3- and C16-octahedra, respectively (Fig. 2f; Supplementary Fig. 8; Supplementary Table 1). These values are different from those observed in the simulations (Supplementary Fig. 9), likely arising from different magnitudes of capillary forces due to the smaller particle sizes used in the simulations.

The interfacial behaviour of Ag octahedra is dictated by the competition between the particle–water and particle–oil interactions, defined as the hydrophobic/hydrophilic potential energy ratio. This ratio increases from 0.3 to 6, and to 52 as the ligands change from PVP to C3SH, and to C16SH, respectively (Fig. 2d; Supplementary Fig. 10). Particle–oil interaction becomes increasingly favourable with increasing hydrophobicity of the ligands. Consequently, PVP octahedron remains in contact with the aqueous phase due to a favourable ligand–water interaction, forming the HCP superlattice. C3-octahedron moves further into the oil phase with a stronger particle–oil interaction, suggesting that an OH lattice is desirable to achieve an optimal interaction with both phases. In contrast, dominant particle–oil interaction for C16-octahedron drives it into a standing configuration to minimize contact with the aqueous phase, giving rise to a square superlattice of standing octahedra aligned edge to edge.
Tuning superlattice structure using surface hydrophobicity. By systematically using Ag octahedra functionalized with different alkythiols (to impart different hydrophobicity to the particles) for self-assembly (Fig. 3a), we show that the superlattice structures observed are related to each other (Fig. 3b; Supplementary Fig. 11). The hydrophobicity of the alkythiols we use increases in the order of PVP<sub>12</sub>-mercaptododecanoic acid (MDA) < C<sub>3</sub>-SH < 1-hexanethiol (C<sub>6</sub>SH) < 1-dodecanethiol (C<sub>12</sub>SH) < C<sub>16</sub>SH (Fig. 3a). The HCP superlattice quickly loses its crystallinity as the PVP octahedra is changed to the slightly more hydrophobic MDA-octahedra (CA = (69 ± 5)°). Changing MDA-octahedra to C<sub>3</sub>-octahedra leads to the formation of the OH array; a mixture of planar and standing octahedra clusters forms when C<sub>3</sub>-octahedra is replaced by C<sub>6</sub>-octahedra (CA = (95 ± 3)°). The population of the standing octahedra increases markedly with the use of C<sub>12</sub>-octahedra (CA = (101 ± 4)°). A schematic illustrating the relationship between the superlattices is shown in Fig. 3c. While the oil/water interface is quintessential for the formation of the
standing octahedra superlattice (Supplementary Figs 12,13), the formation of the standing octahedra superlattice is insensitive to the locations at which the C16-octahedra are added in the presence of both phases (Supplementary Fig. 14). Our self-assembly protocol enables versatile superlattice transfer onto various polymeric platforms (Supplementary Fig. 15), Si substrates (Supplementary Fig. 16), and scaling up to \( 50 \text{ cm}^2 \) (Fig. 4a).

Bending this large mold leads to distinct color changes (Fig. 4b), likely arising from the angle-dependent Bragg reflection of incident light off the periodic pyramidal superlattice.

SERS behaviours of the plasmonic superlattices. A structure-to-function characterization of the SERS capabilities of these three superlattices highlights the superior performance of the square superlattice over the hexagonally tiled ones. Constructing different superlattices without changing nanoparticle morphology allows us to single out the influence of superlattice structure on the corresponding SERS performance. Using 4-methylbenzenethiol as the probe molecule, fingerprint vibrational modes at 1,080 and 1,600 cm\(^{-1}\) are observed (Fig. 4c; Supplementary Table 2). The SERS enhancement factor for the 1,080 cm\(^{-1}\) mode of the standing array is estimated to be \( 9.9 \times 10^4 \), 7.5-fold higher than both the hexagonal arrays (Fig. 4d; Supplementary Note 3).

This difference in SERS enhancement factors of the three superlattices arises from the stark contrast in their plasmonic hot spot distribution. The local electromagnetic field distribution for the Ag octahedra superlattices along the surface of the PDMS...
molds is simulated using finite-difference time-domain (FDTD) method. At the incident laser excitation wavelength of 532 nm, plasmonic hot spots are highly localized in both hexagonal superlattices to regions of contacting points between neighbouring Ag octahedra (Fig. 4e). On the other hand, strips of plasmonic hot spots are formed in the standing array: hot spots spread over the entire edge length of the exposed Ag octahedra and are almost continuous along the entire array across neighbouring Ag octahedra. An estimate of the hot spot areas in these arrays indicates that a single hot spot is almost 130-fold larger in the standing array compared with the hexagonal lattices (\( B^{22,650} \) versus \( B^{360} \) nm\(^2\)). Furthermore, the pyramidal structure of the standing octahedra array enables efficient scattering of SERS signals\(^3^4\). These factors collectively lead to much stronger SERS enhancement in the square standing superlattice. Notably, this SERS study indicates that 'more is not always better' for SERS, since the lowest-packing density superlattice is the most efficient SERS substrate. Our finding shows that structural design on the nanoscale can significantly impact the resulting macroscopic optical behaviours, owing to the nanoscale unique and structure-specific light–matter interactions. We believe this finding will inspire future work to factor in the relevance of nanoscale organization in designing functional and efficient materials.

**Discussion**

In this work, we demonstrate the ability to assemble three bespoke 2D plasmonic superlattices by tailoring the surface chemistries of Ag octahedra. By controlling the hydrophobic/hydrophilic interactions of the octahedral particles at the oil/water interface, we demonstrate the relationship between the three superlattices. The homogeneity of surface functionalities also enables the superlattices to be assembled on the wafer scale, bridging the gap between nanoscopic materials and macroscopic applications. To this end, we further highlight the importance of superlattice design in tailoring nanoscale light–matter interactions for efficient macroscopic sensing applications.

**Methods**

**Nanocrystal synthesis.** The preparation of Ag octahedra was carried out using the polyol reduction method\(^3^5\), starting first with the synthesis of Ag nanocubes. In a typical nanocube synthesis, 10 ml of CuCl\(_2\) (8 mg ml\(^{-1}\)), PVP (20 mg ml\(^{-1}\)) and AgNO\(_3\) (20 mg ml\(^{-1}\)) were separately dissolved in 1,5-pentanediol (PD). 35 \( \mu \)l
CuCl2 solution was added to the AgNO3 solution. 20 ml PD was then heated to 190 °C for 10 min. 250 µl PVP precursor was added to a round-bottom flask, dropped 39 s. The 500 µl AgNO3 precursor was then injected into the flask every minute in one go. The reaction was allowed to proceed for ~20 min following which, the injection was continued using 30 ml of PVP (20 mg ml−1) and AgNO3 (40 mg ml−1 with 120 µl CuCl2). Both precursors were separately prepared in PD.

The reaction was allowed to proceed until the precursors were used up. The Ag octahedra solution was dispersed in 20 ml ethanol after removing the PD via multiple centrifugation rounds, and diluted, then vacuum filtered multiple times using polyvinylidene difluoride filter membranes (Durapore) with pore sizes ranging from 5,000, 650, 450 to 20 nm to remove impurities before finally dispersing in ethanol. Following purification, the PVP-functionalized Ag octahedra were subjected to ligand exchange reactions to tailor their surface chemistry for subsequent self-assembly experiments.

Ligand exchange reactions. The purified Ag octahedra dispersion was generally allowed to sediment. Sediment (0.5 µl) was dispersed in ethanol and centrifuged once more before dispersing in 1.5 ml of ethanol/isopropanol alcohol (1:1). 100 µl of 10 mM thiol solution (MDA, C3SH, C6SH, C12SH and C16SH) was then added dropwise to this dispersion under stirring. Ligand exchange was allowed to take place for 4 h, followed by two rounds of centrifugation, redispersion in 1.5 ml of ethanol/isopropanol alcohol (1:1) and addition of fresh thiol solution under stirring. This step was allowed to continue for another 3 h, followed by three rounds of centrifugation and washing with isopropanol alcohol/water (1:1). Subjecting Ag octahedra to two rounds of ligand exchange removed the replaced PVP and facilitated subsequent ligand exchange. For ligand exchange reactions, the AgNO3 precursor was injected into the flask in a 10 mM thiol solution for at least 12 h to allow the self-assembled monolayers to form before rinsing with ethanol to remove the excess unbound thiols.

Interfacial self-assembly and gel-trapping experiments. The gel-trapping experiments are illustrated in Fig. 1a. Gellan gum aqueous solution (2 wt%) was used as the water phase and n-decane was used as the oil phase instead. The gel-trapping experiments were slightly modified from the procedure reported by Paunov and co-workers32. The gellan gum solution was first heated to 94 °C for 10 min. 250 µl CuCl2 was then added to the flask to simulate the nanostructure arrays. During the simulations, an electromagnetic pulse in the wavelength range 300–1,200 nm was launched to simulate a propagating plane wave interacting with the nanostructure. The unit cells of nanocrystals and its surrounding medium were divided into meshes of 0.5 nm in size. All nanostructure arrays were built according to the experimental parameters. The refractive index of PDMS was taken to be 1.4 (ref. 39) and the refractive index of air was set to be 1. The dielectric function of silver was taken from previously reported values40. The electric field intensity at wavelength of 532 nm was monitored at the surface of PDMS.

AFM experiments. AFM was used to investigate the topological changes in the self-assembled Ag octahedra superlattices 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 (Tapp300AI-G with 30-nm aluminum reflection coating) from BudgetSensor. Data analysis was carried out using WSxM Scanning Probe Microscopy Software, a free program from Nanotec Electronica S.L.35.

Quantitative image analyses. Long-range order of the various 2D octahedra arrays was characterized using the freeware ImageJ. The radial distribution function profiles were analysed by converting the SEM images into a binary format, followed by the automatic identification of the centres of the Ag octahedra. Voronoi–Delauzay cells were constructed using custom-written IDL (Exels) algorithms. The centre of each particle (or each facet for the hexagonal superlattices) was found by locating local intensity maxima after filtering the SEM images with a band-pass filter, followed by constructing the Voronoi–Delauzay cells.

MD simulations. All MD simulations were conducted on single Ag octahedron placed at the oil/water interface using the GROMACS 4.07 simulation package37 and GROMOS996 force fields38. See Supplementary Fig. 17, Supplementary Table 1 and Supplementary Tables 3–5 for detailed discussion.

SERS experiments. SERS measurements were performed using the x–y imaging mode of the Laser Raman Microscope RamanTouch system with an excitation wavelength of 532 nm (power = 3 mW). A × 100 (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 60 × 60 µm2. The probe molecule used was 4-methylbenzenethiol and was placed exchange onto the superlattices.

FDTD calculations. FDTD simulations were performed using FDTD Solution 7.5, which was developed by Numerical Solutions, Inc. The periodic boundary was used to simulate the nanostructure arrays. During the simulations, an electromagnetic pulse in the wavelength range 300–1,200 nm was launched to simulate a propagating plane wave interacting with the nanostructure. The unit cells of nanocrystals and its surrounding medium were divided into meshes of 0.5 nm in size. All nanostructure arrays were built according to the experimental parameters. The refractive index of PDMS was taken to be 1.4 (ref. 39) and the refractive index of air was set to be 1. The dielectric function of silver was taken from previously reported values40. The electric field intensity at wavelength of 532 nm was monitored at the surface of PDMS.

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Author contributions
Y.H.L. and X.Y.L. designed research; H.K.L., I.Y.P., Y.C. and Y.Y.J. performed research; W.X.S. and S.Z.L. performed MD simulations; R.B.J. and J.F.W. performed FDTD simulations; L.I. performed image analyses; Y.H.L., W.X.S., S.Z.L. and X.Y.L. wrote the manuscript. All authors read and commented on the manuscript.

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