

## Supporting Information

# Site-specific Ag coating on concave Au nanoarrows by controlling surfactant concentration

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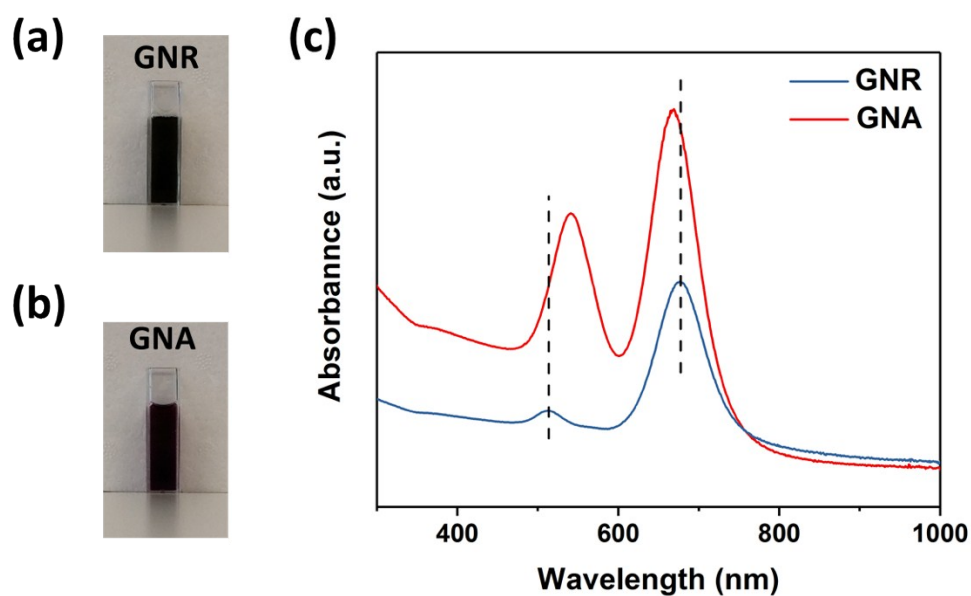
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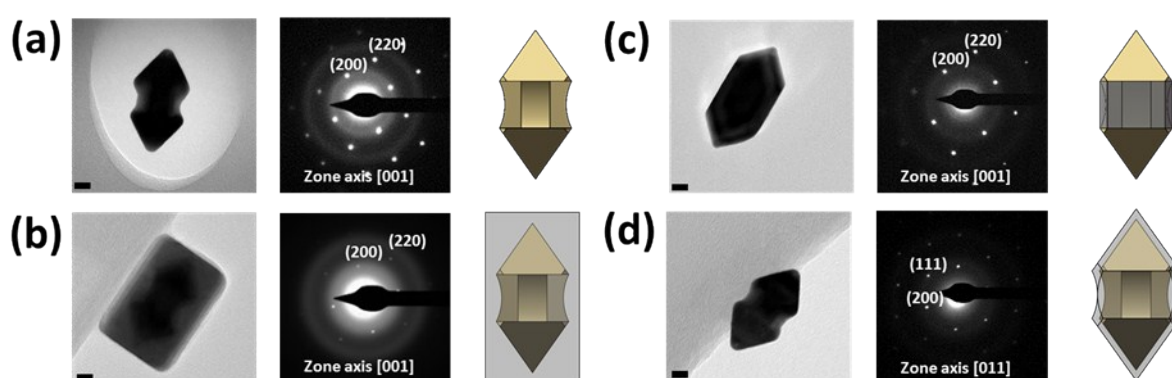
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## 1. Characterisation of gold nanorod and gold nanoarrow



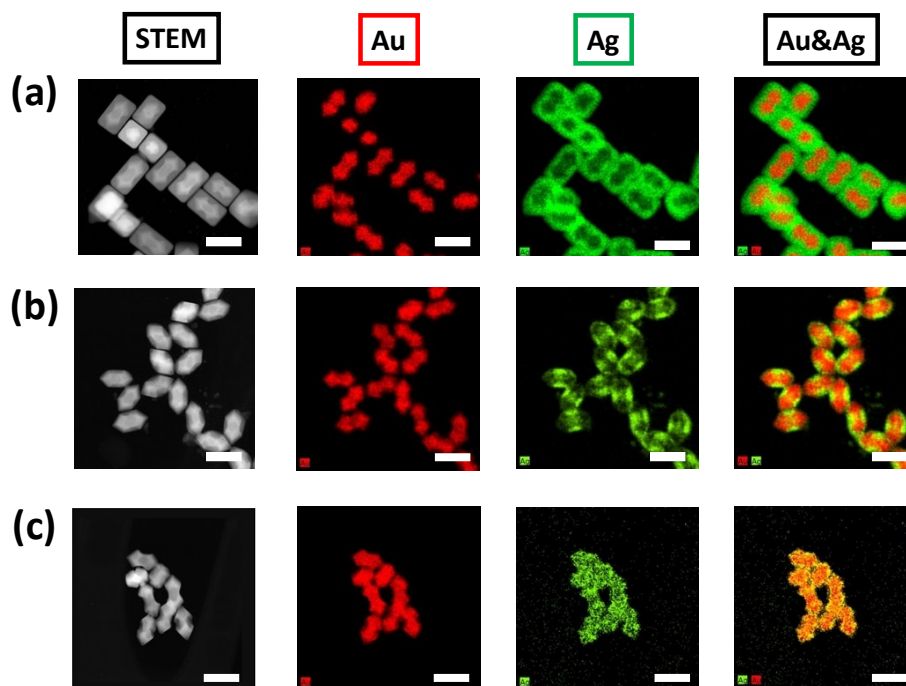
**Figure S1.** Photo of as-synthesized gold nanorod (GNR) (a), gold nanoarrow (GNA) (b) and its corresponding UV-visible spectra (c).

## 2. Electron diffraction pattern of obtained particles



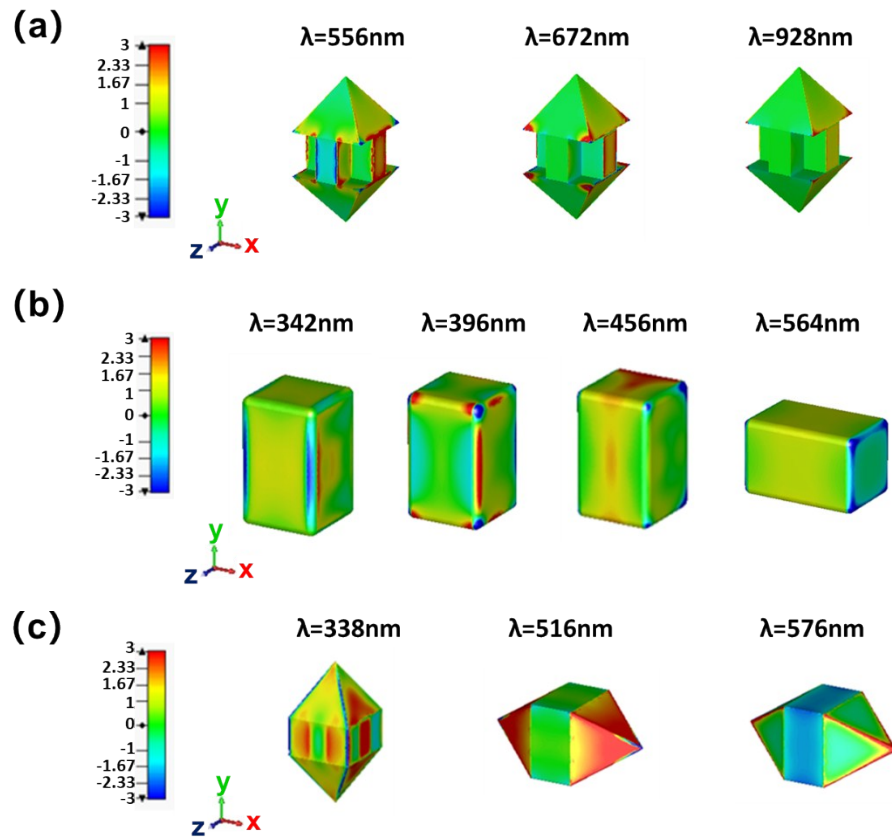
**Figure S2.** High magnification TEM images (left) and its corresponded SAED pattern (middle). (a) Gold nanoarrows. (b)-(d) Ag overgrowth on gold nanoarrows under 80mM, 378mM, 600mM CTAC. Scale bar is 10 nm for TEM images.

### 3. Elemental mapping of synthesized particles



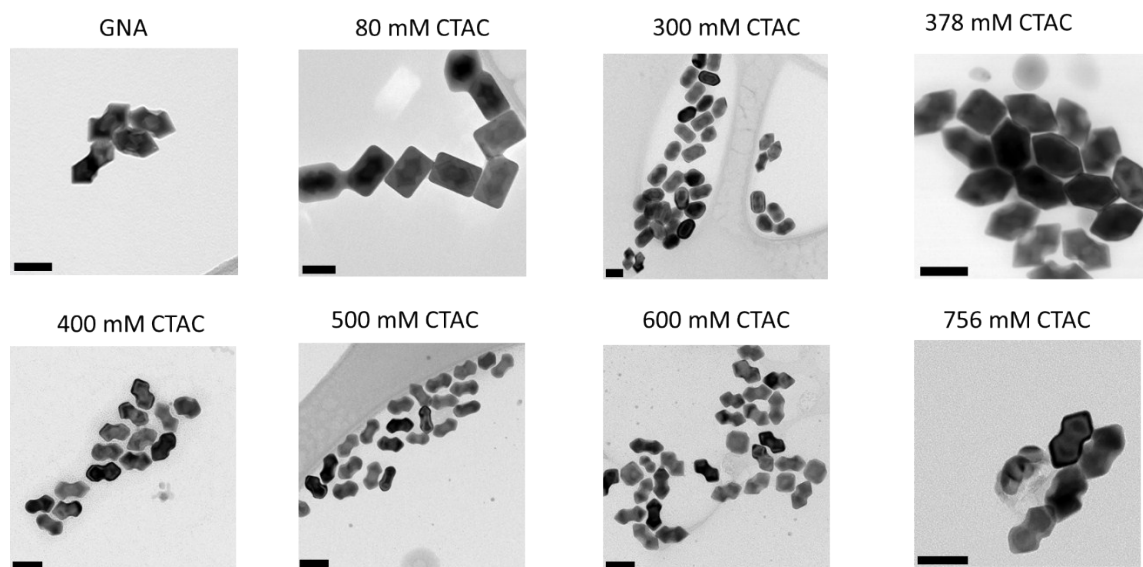
**Figure S3.** HRTEM images and elemental maps of correspond Ag coated nanoarrows obtained from different CTAC concentration condition. (a) 80 mM CTAC. (b) 378 mM CTAC. (c) 600 mM CTAC. Scale bar is 70 nm.

#### 4. Simulated Electric-field distribution



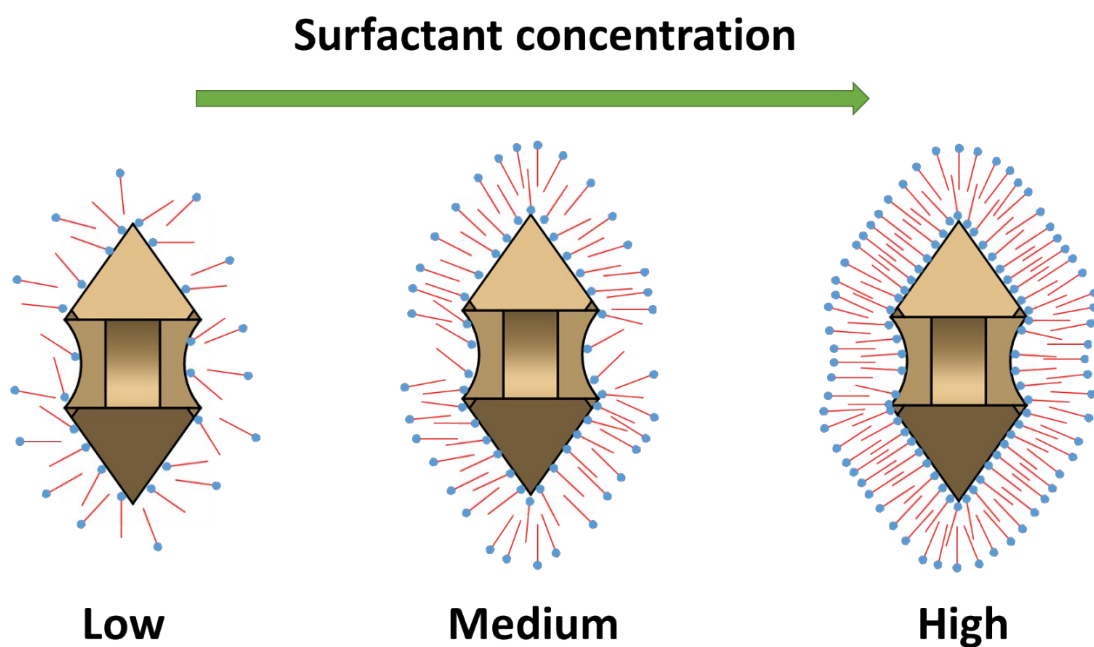
**Figure S4.** Electric-field distribution for (a) GNA, (b) ac-GNA, and (c) cc-GNA, depicting different modes from low to high energy (right to left). To make simulations less computationally expensive, the sample geometry models were built based on a few simplifying assumptions and possess symmetry.

## 5. TEM images of particles from different CTAC concentration



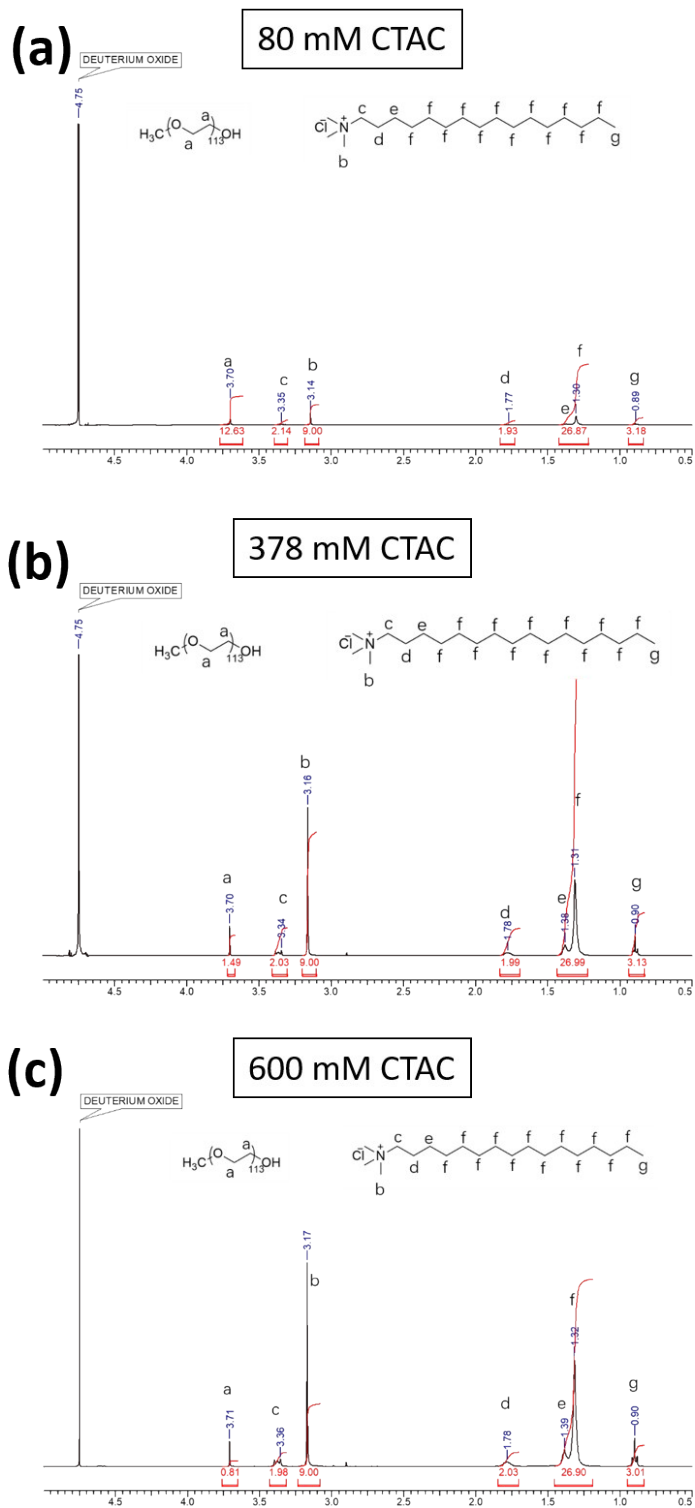
**Figure S5.** Ag coating onto GNA in different CTAC concentration. Scale bar is 50 nm.

## 6. Concentration-dependent distribution of CTAC on GNA



**Figure S6.** Scheme of CTAC distribution on GNA surface at difference concentration.

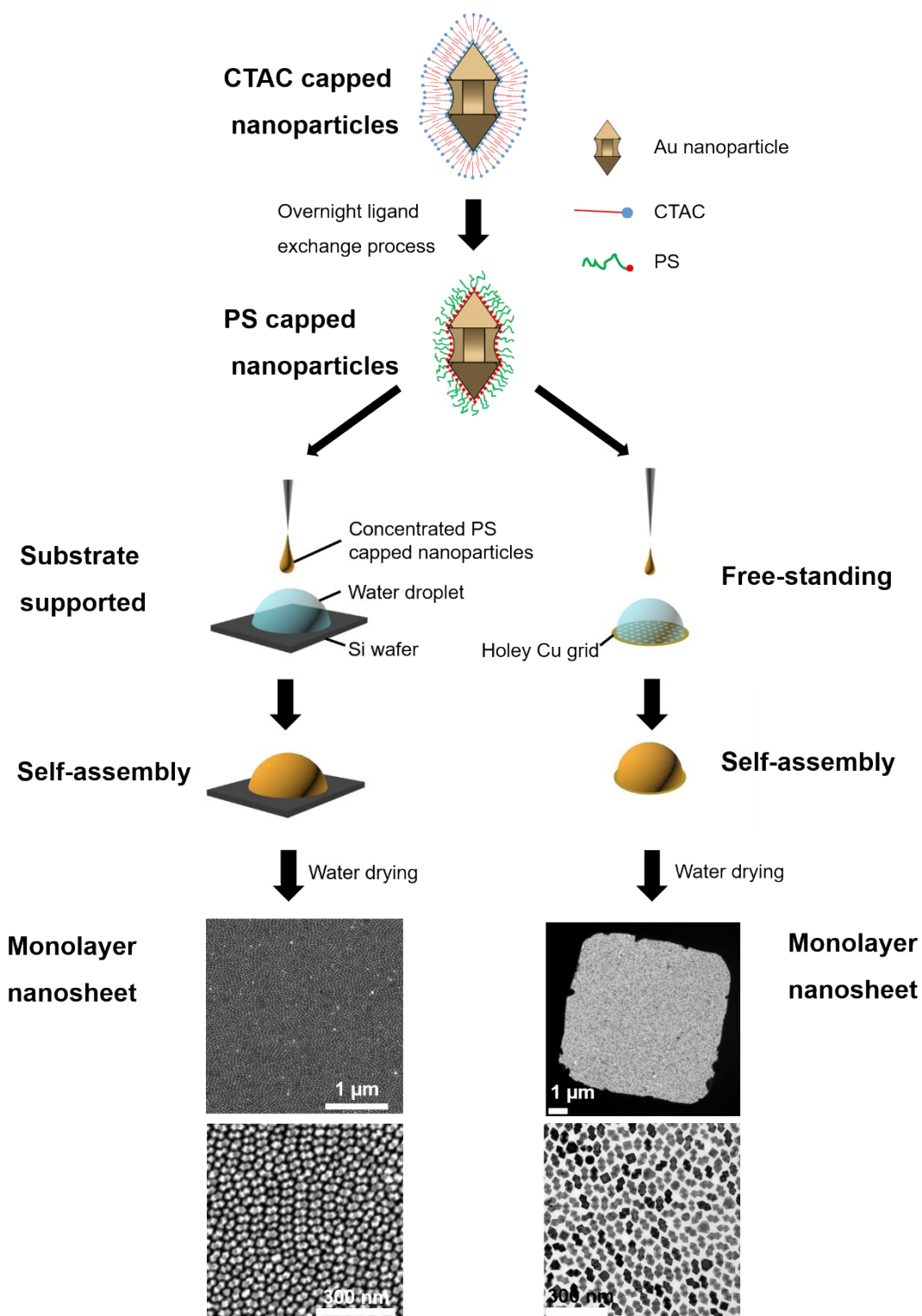
To further verify the proposed uneven distribution of CTAC, we carried out NMR test to trace the differences of CTAC presented on freeze-dried GNA surfaces. Here, we first took three tubes of 10 ml GNA solutions and each tube was re-dispersed with 10 ml CTAC solution, of which the concentrations are 80 mM, 378mM and 600 mM respectively. Then, the solution were transferred into glass vials under constant stirring with a 60 °C water bath for 1 hr. Next, the solutions were centrifuged down @ 7800 rpm for 20 min to ensure firm precipitation. The supernatants were immediately removed. The three residues were then freeze-dried and dissolved in 1.0 ml D<sub>2</sub>O solution (Cambridge Isotope Laboratories, Inc.) with 1 mg/mL of poly(ethylene glycol) methyl ether (Sigma-Aldrich, Mn = 5000 g/mol) separately. <sup>1</sup>H NMR was then taken on Varian 400 MHz NMR system. The concentration of CTAC was calculated by comparing the integration of PEG with CTAC peaks. As shown in Figure S7, the mass of CTAC were found to be 2.02 mg, 19.52 mg, and 35.84 mg for 80 mM, 378 mM, and 600 mM CTAC respectively. Although the NMR experiment couldn't reveal the exact mass of CTAC attached onto GNA in aqueous state, it still reflected the differences of CTAC.



**Figure S7.**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ) spectrum of (a) GNA from 80 mM CTAC solution. (b) GNA from 378 mM CTAC solution. (c) GNA from 600 mM CTAC solution. The internal standard was 1 mg/ml PEG.



## 7. Fabrication of ac-GNA, mc-GNA and cc-GNA superlattice nanosheets.



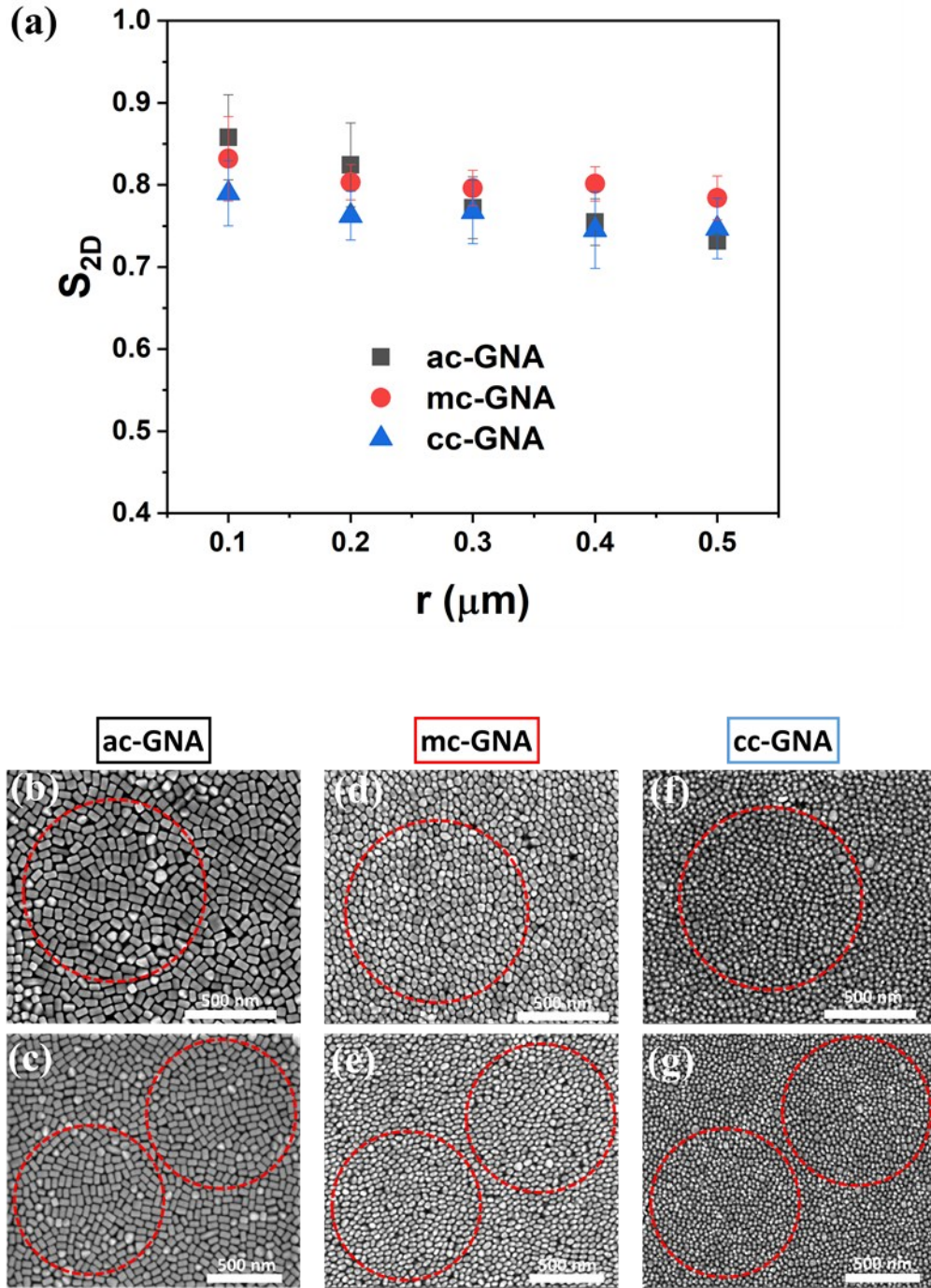
**Figure S8.** Schematic drawing of GNA based monolayer superlattice nanosheet fabrication. By using holey copper grid as substrate, free-standing monolayer nanosheet could be obtained. The bottom row are the SEM and TEM images of GNA based nanosheet. The scale bars are 1 μm and 300 nm (magnified ones), respectively.

## 8. Calculation of orientational ordering

The orientational order of the Ag coated GNA were calculated by using Hore's Method<sup>1</sup> using equation below:

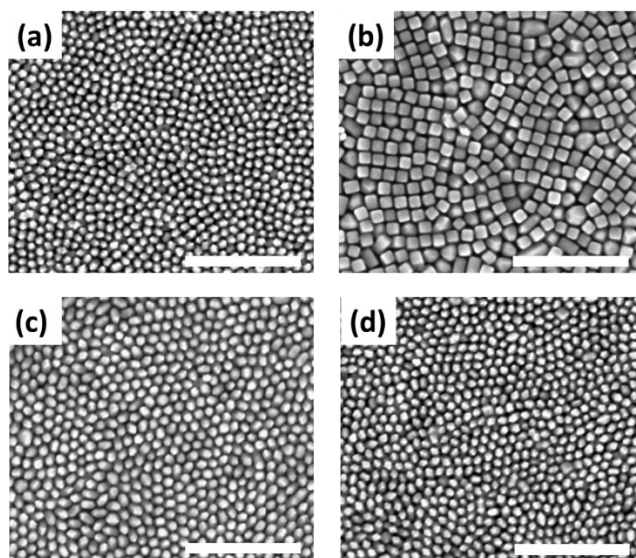
$$S_{2D} = \frac{1}{N_{Ag\ coated\ GNA}} \sum_{i=1}^{N_{Ag\ coated\ GNA}} \cos 2\vartheta_i$$

where  $S_{2D}$  is the 2D orientational order parameter,  $\vartheta_i$  is the angle between the Ag coated GNA  $i$  and the average orientation in the region of the radius  $r$ , and  $N_{Ag\ coated\ GNA}$  is the number of the Ag coated GNA in that region. When the value of  $S_{2D}$  equals to 1 means the perfect alignment of nanoparticles within the assembled structure. Figure S7 gives the calculated orientational order parameter for horizontal aligned ac-GNA, mc-GNA and cc-GNA superlattices.



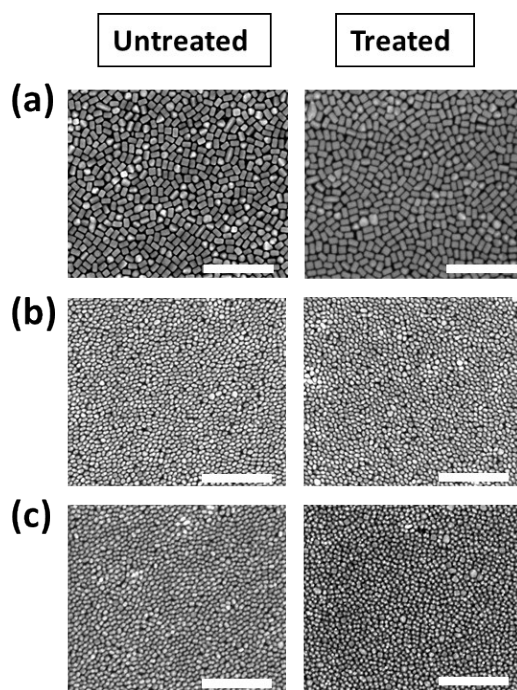
**Figure S9.** (a) Plots of 2D orientational order parameter ( $S_{2D}$ ) for horizontal aligned ac-,mc- and cc-GNA superlattice nanosheets. The measured positions (Red dash circle, radius of 0.5  $\mu\text{m}$ ) on SEM images were shown for ac-GNA nanosheet (b-c), mc-GNA nanosheet (d-e), and cc-GNA nanosheet (f-g). The Scale bars in (b-g) are 500nm.

## 9. SEM images of fabricated nanosheet with vertical aligned building blocks.



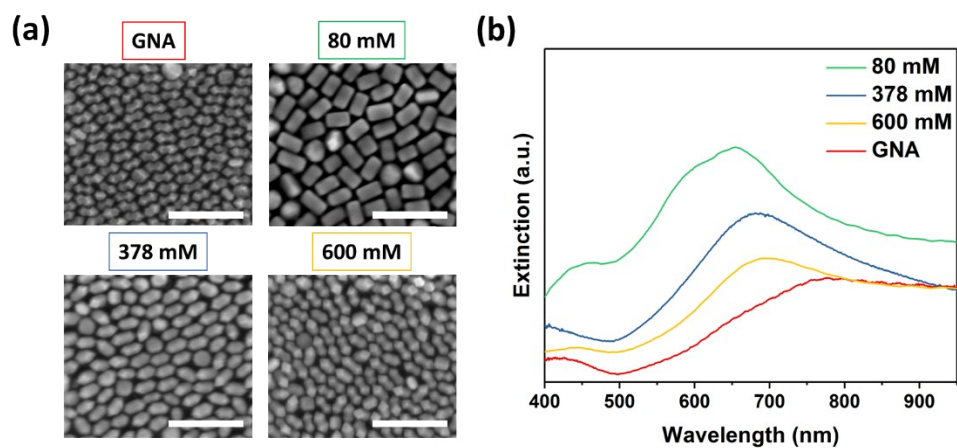
**Figure S10.** The SEM images of superlattice nanosheet with vertical orientation. The building blocks are (a) gold nanoarrows and Ag-coated gold nanoarrows obtained from (b) 80 mM CTAC. (c) 378 mM CTAC. and (d) 600 mM CTAC. Scale bar is 400 nm.

## 10. UV-Ozone treatment effect on nanosheet



**Figure S11.** The SEM images of superlattice nanosheet before and after UV Ozone treatment. The building blocks are Ag-coated gold nanoarrows obtained from (a) 80 mM CTAC. (b) 378 mM CTAC. and (c) 600 mM CTAC, respectively. Scale bar is 500 nm.

## 11. Extinction spectra of the self-assembled nanosheet



**Figure S12.** (a) High magnification SEM images of superlattice nanosheets. Scale bar is 200 nm. (b) Extinction spectra collected from nanosheet on top of ITO glass.

## 12. Reference

1. M. J. Hore and R. J. Composto, *ACS nano*, 2010, **4**, 6941-6949.