Supporting Information

Ordered mesoporous silver superstructures with SERS hot spots

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MATERIALS AND METHODS

Chemicals: Hexacarbonyl tungsten ($W(CO)_6$, 97%) was purchased from Alfa Aesar. Silver nitrate ($AgNO_3$, 99%), oleylamine (OAm, 70%) and 1-octadecene (ODE, 90%) were purchased from Sigma Aldrich. Ethylene glycol (EG, 99%), toluene (99.5%), n-hexane (97.0%) and ethanol (99.7%) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. OAm and ODE were dried by heating at 170 °C under vacuum for 1.5 hours and then stored under an argon atmosphere prior to use. All other reagents were used as received.

Synthesis of 12.0 nm Ag NPs: 20 mg of $AgNO_3$ and 25 mg of $W(CO)_6$ were placed into a 100 mL three-necked round-bottom flask followed by the addition of 10 mL of ODE and 0.5 mL of OAm, and then the reaction system was degassed under vacuum at ambient temperature for 12 minutes. Next, the reaction flask was filled with argon gas and sealed. The reaction mixture was then heated at 240 °C using a heating block for 1 hour, forming a yellow-brown solution. After heating, the reaction flask was transferred to a cold water bath and cooled. 5 mL of n-hexane was added to dilute the solution, and then 30 mL of ethanol was added to precipitate Ag NPs, which were collected by centrifugation at 5000 rpm for 5 minutes. Size selection was performed to obtain uniform NPs. To do that, 15 ml of n-hexane was added to the as-obtained precipitate and dispersed by ultra-sonication, followed by centrifugation at 7000 rpm for 8 minutes. After that, the precipitate was dispersed in 5 mL of n-hexane, and the synthesized NPs were purified again by centrifugation at 5000 rpm for 5 minutes and the precipitation was discarded to get rid of the aggregates. Through this synthetic process, about 1.8 mg of monodisperse 12.0 nm spherical Ag NPs were obtained and kept in n-hexane for preservation and additional use.

Preparation of mesoporous Ag superstructures: (1) 3.0 mL of EG was added into a glass vial (Ø 25 mm). 0.25 mL of Ag NPs dispersed toluene solution with an initial NP concentration of 1.5×10^{-7} M was spread out on top of EG. Then, ① *NP assembly* and ② *core coalescence* successively occurred in the following process. ① The reaction solution was undisturbed for 4 hours at room temperature, allowing the toluene to slowly evaporate. After toluene evaporated, a thin film of Ag NP superlattice was formed on the soft substrate of EG. ② Then, the glass vial including both Ag NP superlattice film and liquid substrate of EG was carefully transferred into a heating block. The heating process was maintained at a controlled temperature of 110 ^{o}C for 10 minutes. After thermally induced desorption of ligands from the NPs, Ag cores irreversibly coalesced and formed ***ordered*** mesoporous Ag superstructures. After cooled to room temperature, the Ag superstructures were washed by dispersion in a n-hexane/ethanol mixture, centrifugation, and re-dispersion of sediments in ethanol. **(2)** For the control experiment, ***disordered*** mesoporous Ag superstructures were prepared by skipping the above step ①. Briefly, the glass vial including both Ag NP toluene solution and liquid substrate of EG was directly transferred into the heating block, and heated at 110 ^{o}C for 10 minutes. The following steps were kept the same.

Characterizations: Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) pattern were collected using a TEM Tecnai F30 (FEI) operated at an accelerating voltage of 300 kV. HAADF images and tomographic reconstruction were taken by an FEI Talos F200X at 200 kV controlled at a scanning TEM (STEM) mode; the 3D reconstruction of collected images was made using a FEI software package of Inspect3D and Avizo. UV/Vis extinction spectra were obtained using a Cary Model 5000i spectrophotometer for solution measurement. A Cs-corrected Environmental TEM (FEI Titan 80-300) was employed for electron energy-loss spectroscopy (EELS) at 300 kV. The EELS image and spectrum collected and controlled at a STEM monochromatic mode had a spatial resolution of 1.5 nm and an EELS zero-loss peak full-width at half maximum of 0.9-1.0 eV. For the characterization of SERS properties, Rhodamine 6G (R6G) was used as the probe molecule. SERS mapping and spectra were carried out using a confocal Raman spectrometer (WITec Alpha 300A) equipped with a 532 nm laser line. The mapping and spectra were collected using a ×50 L objective lens with a diffraction limited laser spot diameter of about 870 nm. The laser power and integration time (for each pixel) for SERS mapping were 14.8 µW and 0.05 s, respectively. And the laser power and integration time to obtain the SERS spectra were 14.3 µW and 30 s, respectively. Before each measurement, an aqueous solution of R6G of desired concentration (10^{-5} M for mapping and 10^{-6} M for spectra) was spread on the target substrate and incubated for 30 minutes at ambient conditions. The excess solution was then wiped away with a filter paper.

Experiment details for the fabrication of ordered mesoporous Ag superstructures:

In the process of assembly, Ag NPs were dissolved in toluene and carefully dropped onto a soft substrate in a glass vial at room temperature. Toluene was chosen as the solvent because it has a slow evaporation rate that helps to assemble the NPs into a thermodynamically stable superlattice film. For the soft substrate, diethylene glycol (DEG) and EG were tested. When DEG was used, its low affinity to toluene due to the polarity difference resulted in disordered NP superlattices attached on the wall of the vial. In contrast, on the surface of EG, toluene spread out evenly and directed NPs into a flat superlattice film. The superlattice film used to fabricate ordered mesoporous Ag superstructures should be thin. If a thick film is used, the NPs in the upper layers cannot reach the reaction temperature in the following heating step, causing problems in ligands desorption and NP coalescence. To obtain superlattice film with proper thickness (about 4-5 NP monolayers), the NP concentration and solution volume were adjusted to optimize the thickness and also the quality of the superlattice film. We found that too large or too small amount of NP solution (too low or too high NP concentration) would cause long assembly time or some defects in the superstructures, respectively. After a series of experimental conditions were tested, 0.25 mL of NP toluene solution with a concentration of 1.5×10^{-7} M was used and assembled on 3.0 mL of EG to form a perfect Ag NP superlattice film upon complete evaporation of toluene solvent. The whole assembly process took about 4 hours.

The assembled Ag NP superlattice film in the glass vial on the EG surface was then treated with heat which induced ligands desorption and Ag NPs coalescence. The heating temperature is critical for the formation of ordered mesoporous Ag superstructures. Too low or too high temperature either leads to failure in ligands desorption or generation of large aggregates (Figures S1A-B), respectively. Heating time also affects the morphology of the Ag superstructures. Short heating time causes partial desorption of ligands and incomplete NP cores coalescence, while long heating time results in excessive heating and the appearance of large aggregates (Figures S1C-D). After attempting a range of heating temperature and time, we found that heating at 110 ^{o}C for 10 minutes could keep the optimum balance between ligands desorption and NP cores coalescence, and produced ordered mesoporous Ag superstructures with nearly 100 % yield.

SUPPORTING FIGURES

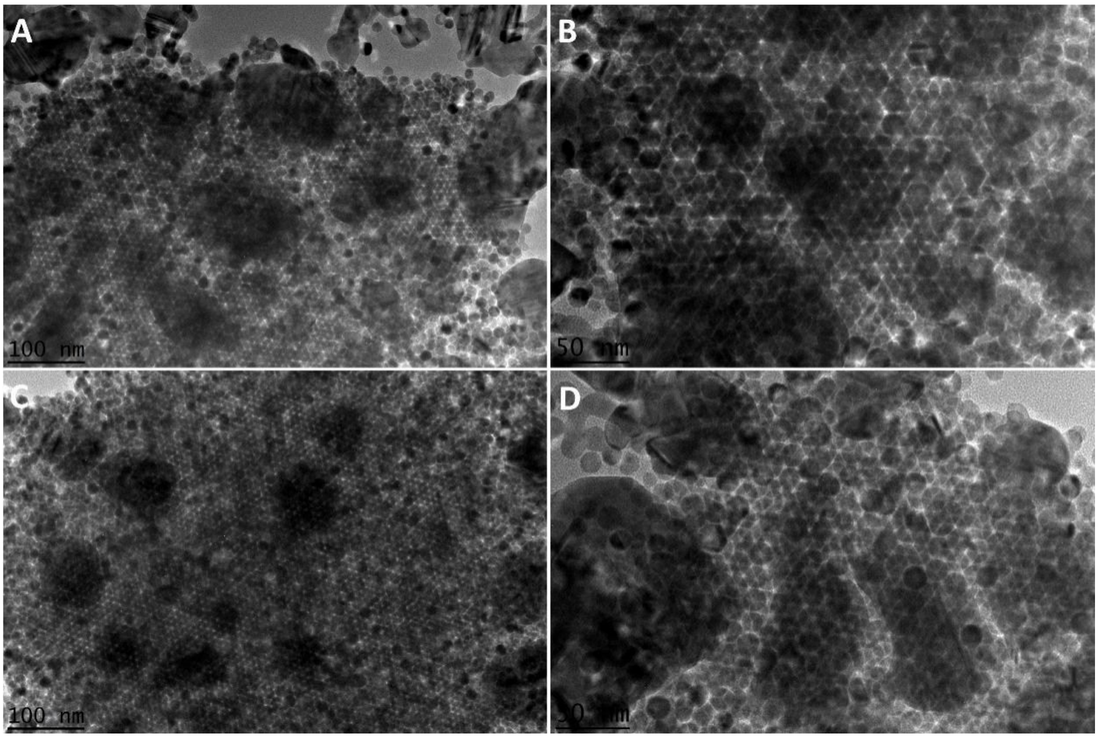

Figure S1. TEM images of ordered mesoporous Ag superstructures obtained at (A, B) 120 ^{o}C for 10 minutes and at (C, D) 110 ^{o}C for 15 minutes.

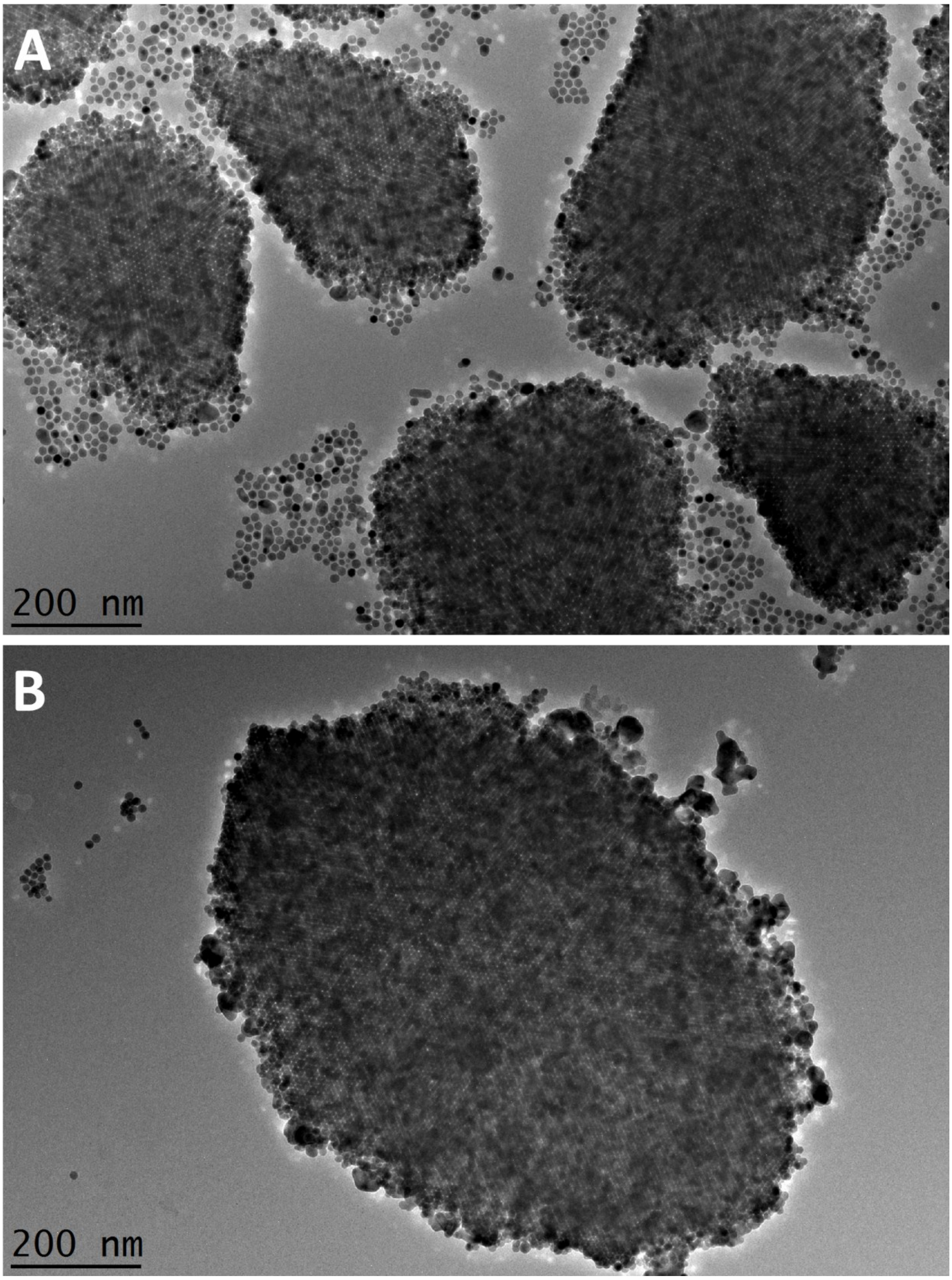

Figure S2. Low magnification TEM images of ordered mesoporous Ag superstructures.

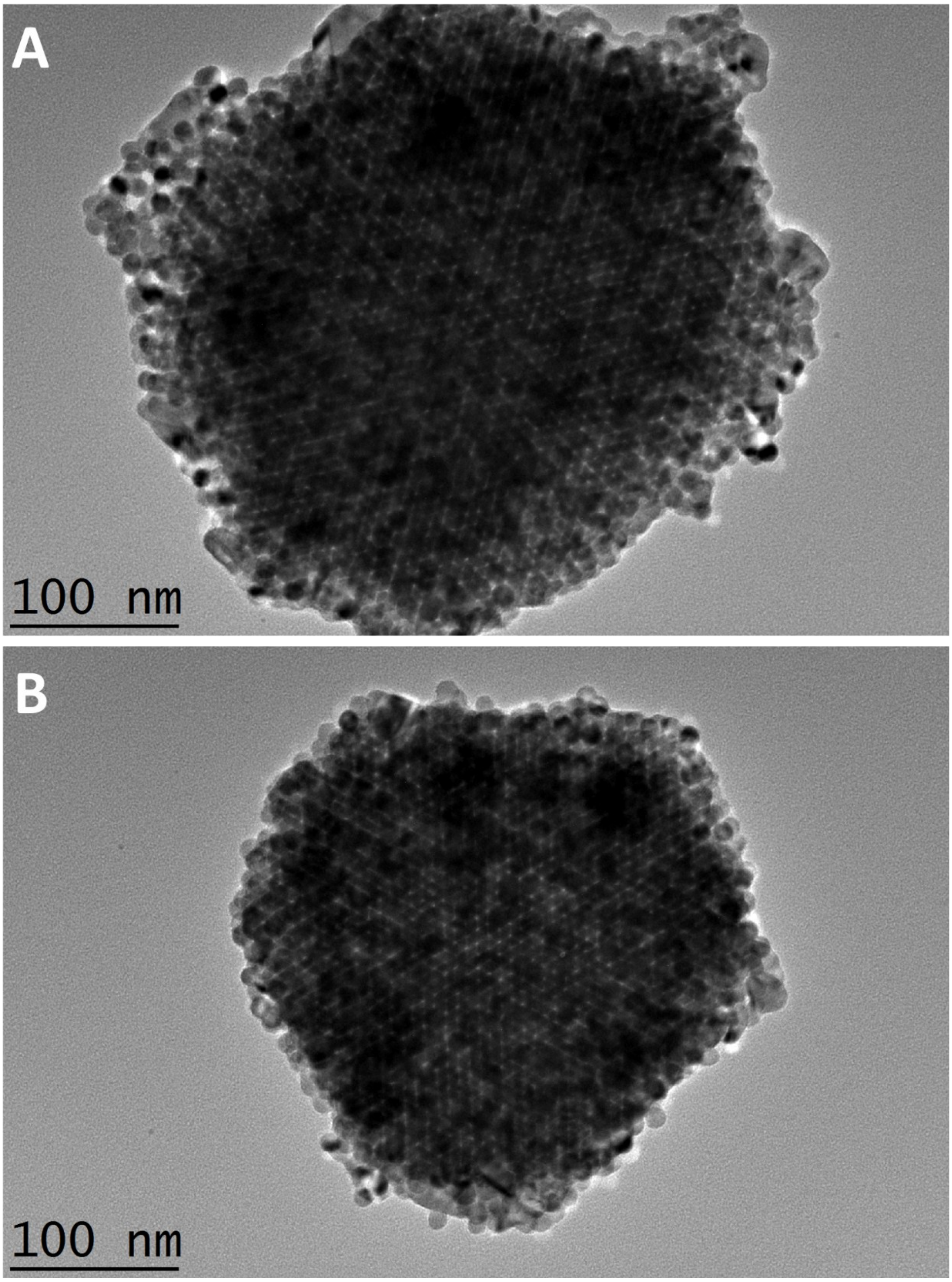

Figure S3. High magnification TEM images of ordered mesoporous Ag superstructures.

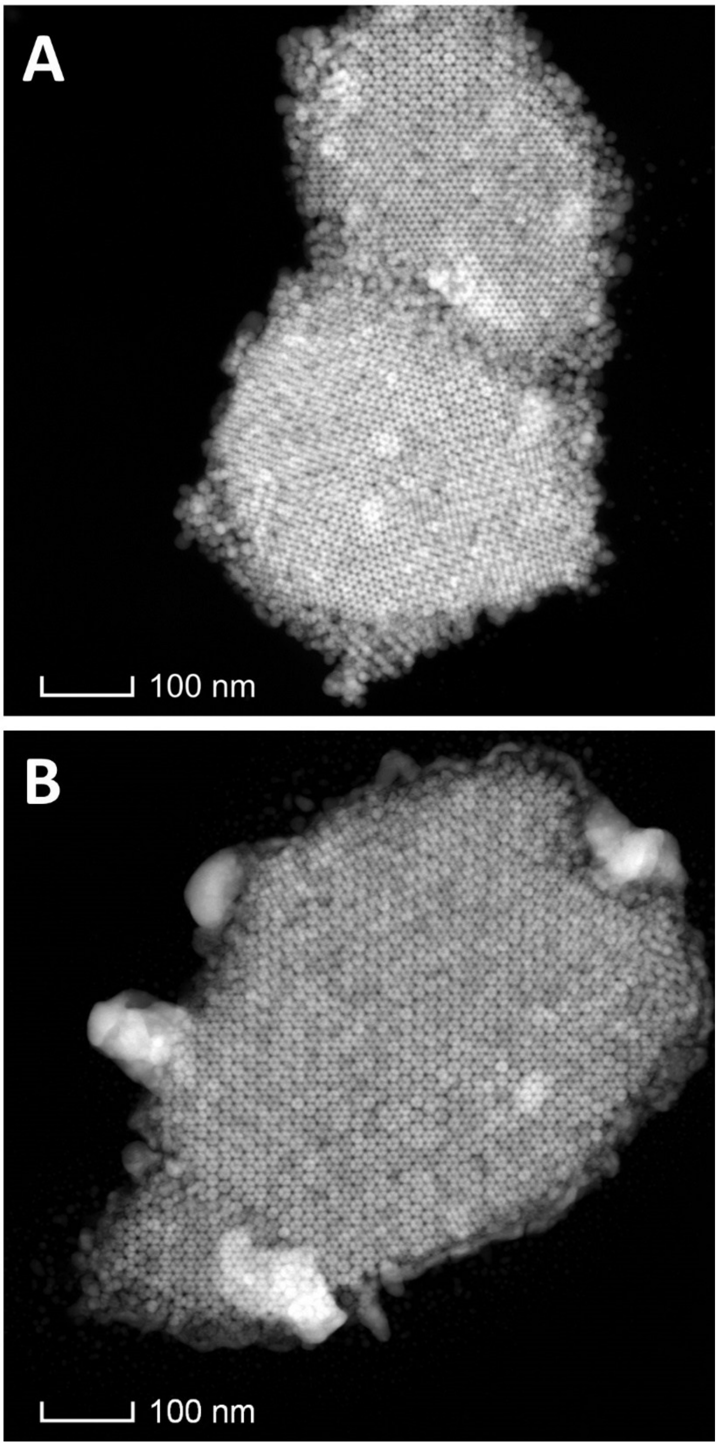

Figure S4. STEM images of ordered mesoporous Ag superstructures.

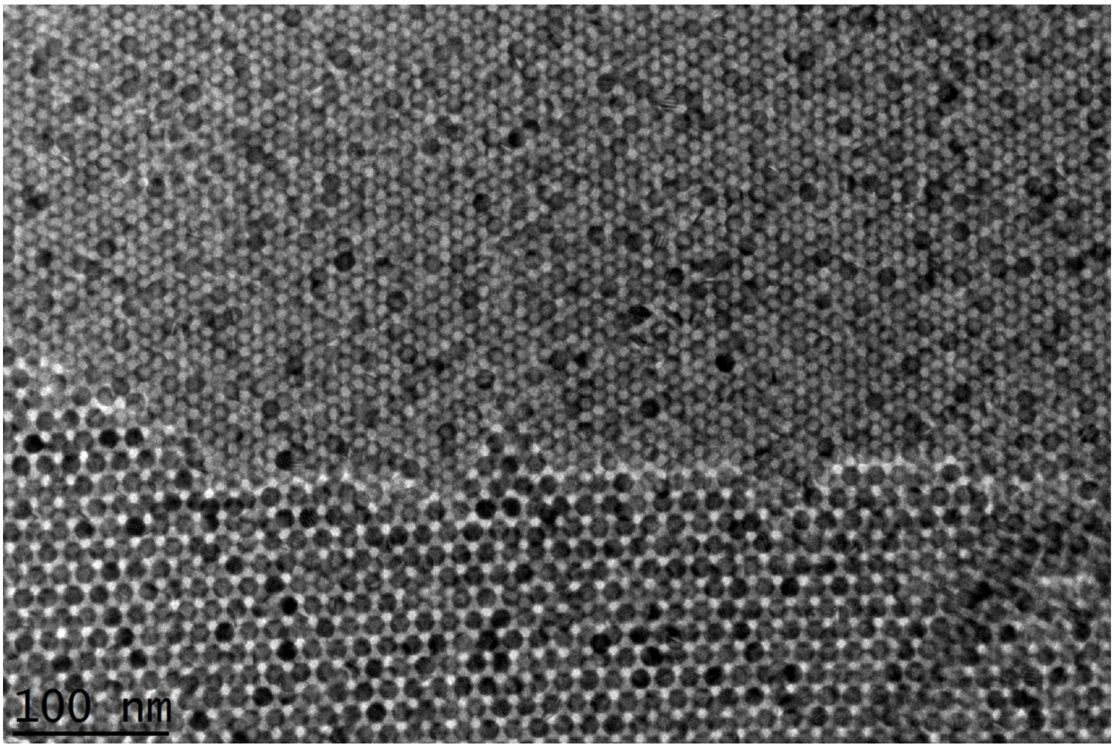

Figure S5. TEM image of Ag NP superlattice film showing the transition from two to three layers of constituent NPs.

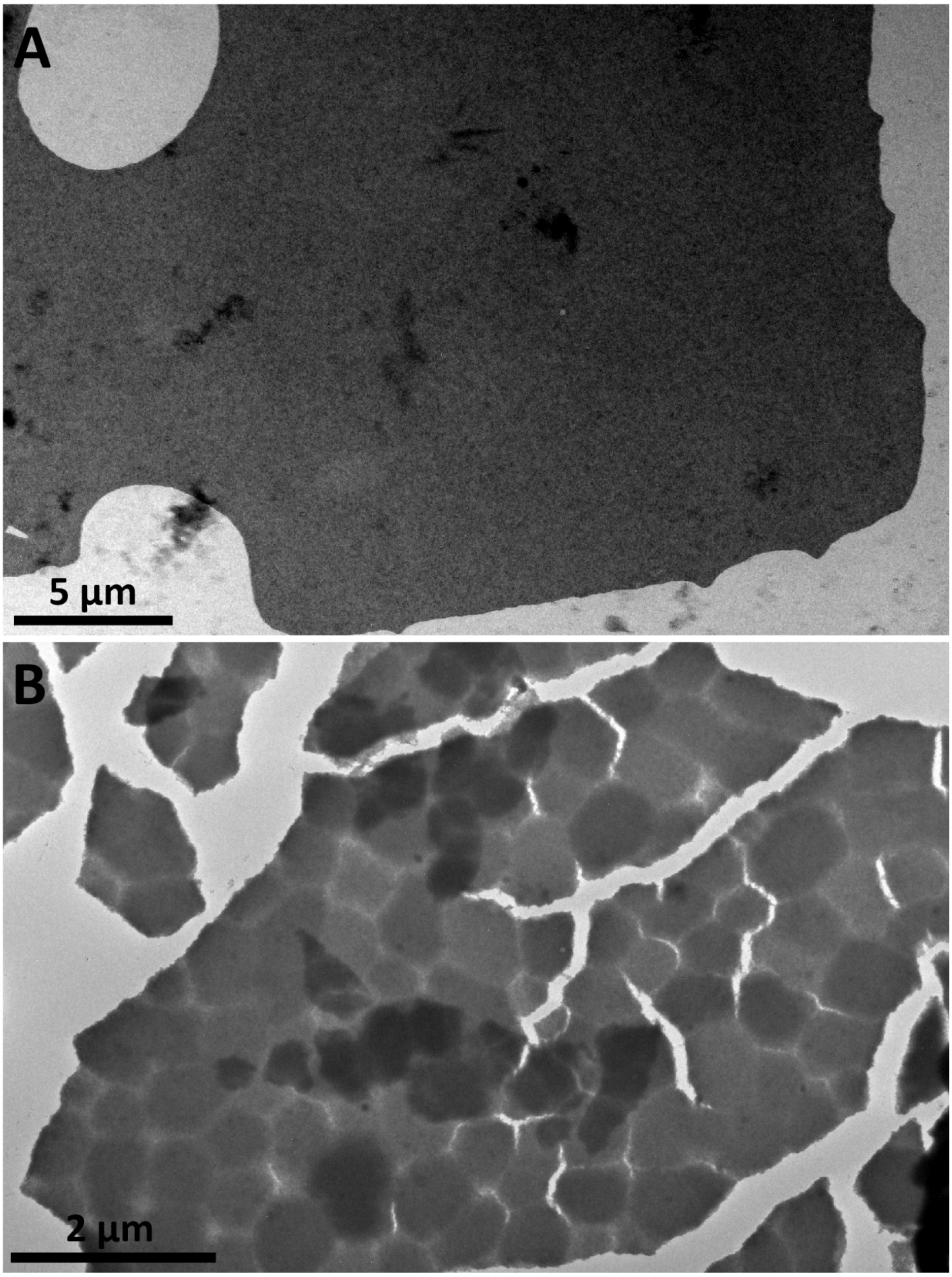

Figure S6. Low magnification TEM images of Ag NP superlattice film before (A) and after (B) thermal treatment at 110 ^{o}C for 10 minutes.

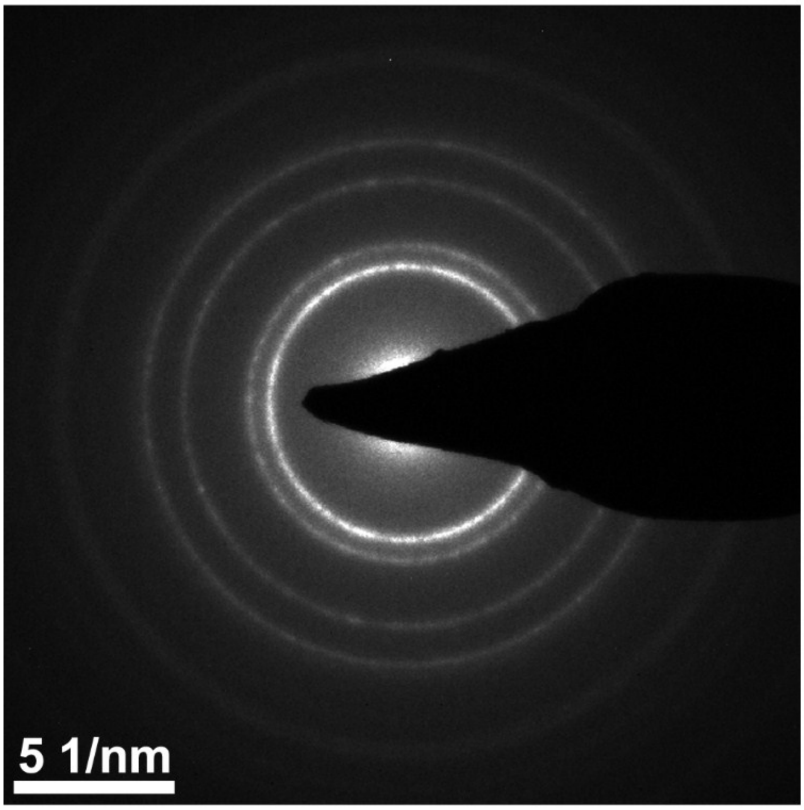

Figure S7. SAED pattern of the ordered mesoporous Ag superstructure.

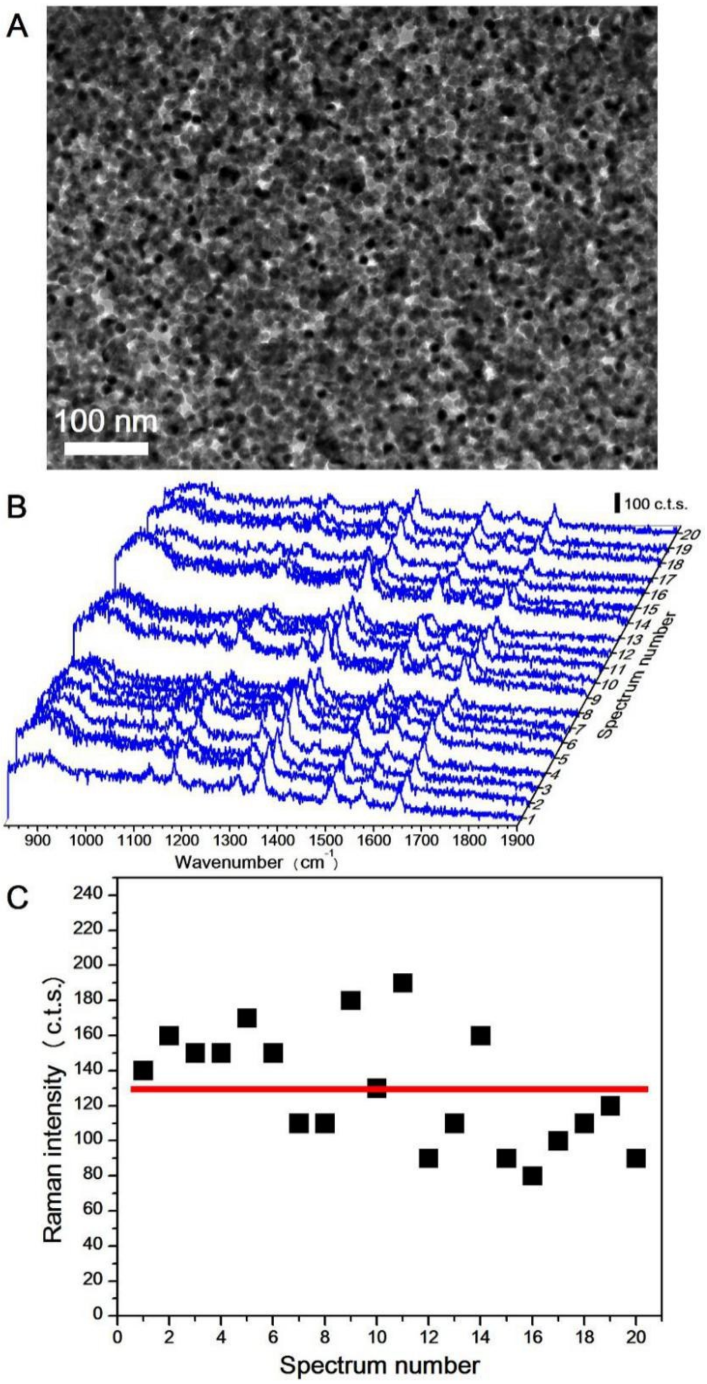

Figure S8. (A) TEM image of disordered mesoporous Ag superstructures. (B) SERS spectra of 10^{-6} M R6G molecules with the concentration of at 20 different positions on the disordered mesoporous Ag substrate. (C) Spot-to-spot intensity variation of the characteristic peak at 1359 cm^{-1} in (B). Note: the red line represents the average intensity of 20 spectra.