Supplementary Information for:

Volume Shrinkage Induced Formation of Porous Ag Sub-microcubes via Solid-liquid Reaction for SERS

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Experimental details.

Synthesis of Ag_3PO_4 sub-microcubes. A simple and straightforward strategy is developed to synthesized Ag_3PO_4 sub-microcubes. In a typical process, 0.045g of silver trifluoroacetate (CF_3COOAg) was dissolved in 150 mL of H_2O, then 8 mL Na_2HPO_4 (0.15M) aqueous solution was added by drops into the above solution under vigorous magnetic stirring. After the addition of Na_2HPO_4 (0.15M) aqueous solution, the yellow precipitate was formed. After stirring for another 2 hours, the Ag_3PO_4 sub-microcubes were collected by centrifugation at 6000 rpm for 5 min. The supernatant was decanted and the golden yellow precipitate was dispersed in 4 mL of distilled water, followed by centrifugation again at 6000 rpm for 5 min. This process was repeated for several times to remove ions like CF_3COO^- and Na^+ and HPO_4^{2-}. After washed by water, the Ag_3PO_4 sub-microcubes were characterized by scanning electron microscope and X-ray diffraction and then stored in water for further use.

Synthesis of porous Ag sub-microcubes. Ag sub-microcubes were prepared with a chemical reduction method: the half portion of the as-prepared Ag_3PO_4 sub-microcubes was solved in aqueous solution and dispersed in 50 mL of water by ultrasonicating for 10 min. Then 1mL $NaBH_4$ (0.025M) aqueous solution was added within one second under vigorous stirring, while the color of solution changed from golden yellow to black immediately. The black precipitate was collected by centrifugation and washed by water for several times. The porous Ag sub-microcubes have been synthesized.

Characterization methods. The X-ray diffraction (XRD) patterns were obtained with a BRUKER D8 ADVANCE X-ray diffractometer with a Cu KR X-ray source. Scanning electron microscope (SEM) images were taken on a JEOL JSM-7000F instrument. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were taken on a JEOL JEM-3010 instrument

SERS measurement. SERS measurements were carried out on a confocal microprobe Raman spectrometer (LabRAM HR800, HORIBA JOBIN YVON) with the 633 nm He–Ne laser line at room temperature. The probe

area was 1 μm in diameter with a x100 objective lens and the signal collection time was 5 s. The incident power of the laser at the samples was 0.055 mW after it was decreased by a D2 attenuation piece. The products transferred onto a cleaned quartz plate were used for SERS sample preparation. Samples for SERS were prepared by drop casting 10μL of 1×10^{-6}, 1×10^{-7} and 1×10^{-8} M rhodamine 6G (R6G) aqueous solution on the quartz plate and allowing the solvent to evaporate.

Volume Calculation. The density of Ag is 10.5g cm^{-3}, while the density of Ag_3PO_4 is 6.73 g cm^{-3}. The mass of 1 mole Ag_3PO_4 is 418.58g, equal to $V1=\frac{418.58g}{6.73g\cdot cm^{-3}}=62.2cm^3$. If 1 mole of Ag_3PO_4 was reduced into Ag completely, it will produce 3 mole of Ag. The mass of 3 mole Ag is 323.7 g, equal to $V2=\frac{323.7g}{10.5g\cdot cm^{-3}}=30.8cm^3$. As a result, the volume of Ag obtained by reduction is only 49.5% of the volume of Ag_3PO_4. The average size of Ag_3PO_4 was 765 nm. If the after-reaction Ag was solid, the average size of Ag should be $V3=\sqrt[3]{(765\text{nm})^3\times0.495}=605nm$. But the experimental result shows that the average size of Ag sub-microcubes is 706 nm, smaller than the calculation result 605nm. Therefore, we suppose that the voids should compensate the volume which made the as-synthesized Ag had a much large size. As a result, the as-synthesized Ag sub-mircocubes were made up by Ag and voids.

Additional Figures

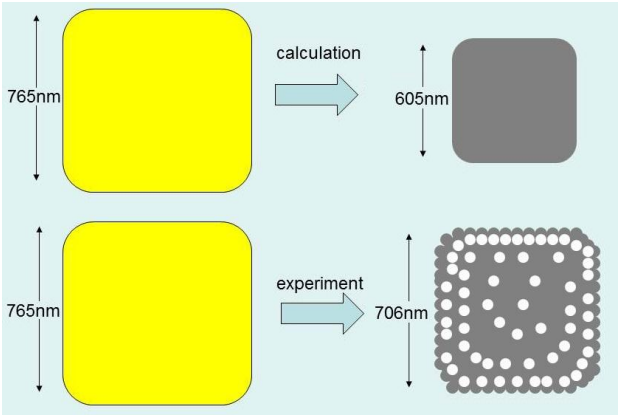

Fig. S1 Schematic illustration of the volume shrinkage of during the solid-liquid reduction reaction.

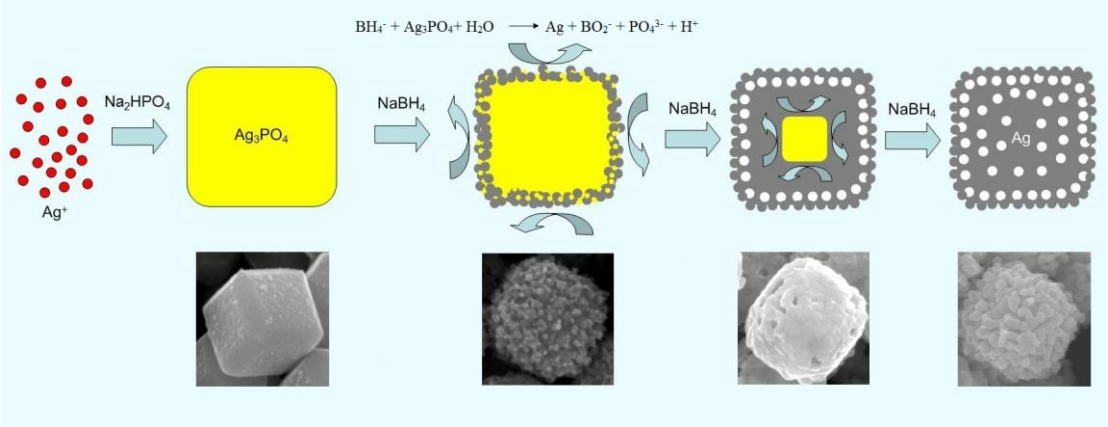

Fig. S2 Schematic illustration of the synthesis process of the Ag_3PO_4 sub-microcubes and porous Ag sub-microcubes and the reaction procedure.

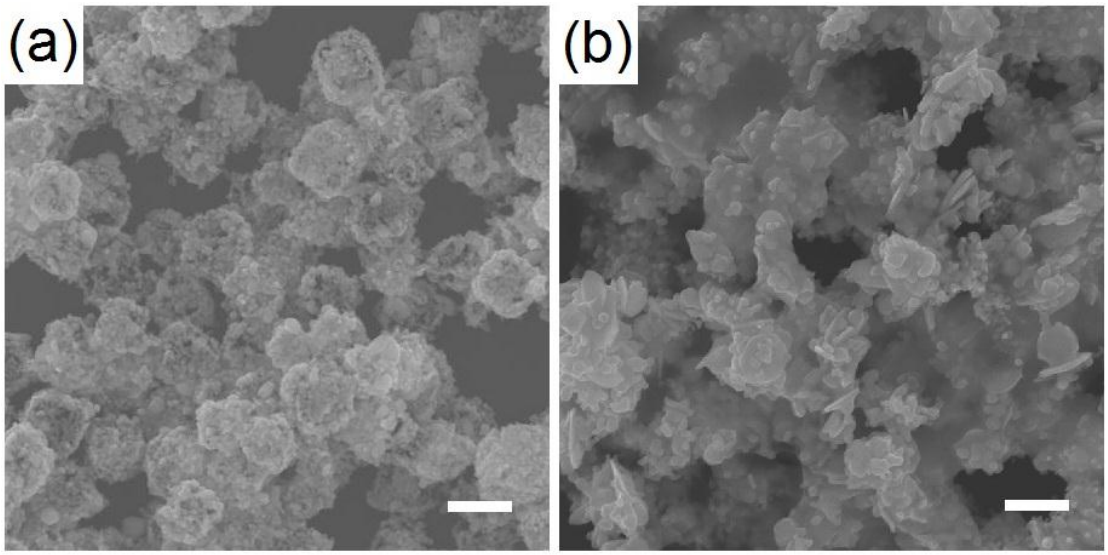

Fig. S3 The SEM images of the Ag crystals obtained by using (a) ascorbic acid and (b) hydrazine hydrate as reducing agent. The scale bars are 0.5 μm.