Electronic Supplementary Material (ESI) for CrystEngComm.

Experimental section

All reagents and chemicals are bought from Shanghai Aladdin Bio-Chem Technology Co., Ltd., and used without further purification.

Synthesis of Ag, Au seed solution

The Ag seed solution was prepared based on a convenient method[1].And Au seed solutionwas also prepared through a modified Turkevich method[2].

Synthesis of Ag nanoechinus

8.5 mg of $AgNO_3$ was dissolved in 200 mL of distilled water under magnetic stirring. And the solution was heated at 40℃ for 20 min. Subsequently, 50μL of Ag seed solution was added and followed by magnetic stirring for another 10min. After that, 200 μL of 37% HCHO and 400 μL of 25% $NH_3{\cdot}H_2O$ were dropped into the reaction system step by step. After 20 s, the PVP aqueous solution (1g/20mL) was dumped into the mixed solution rapidly. The final products were collected and washed with ethanolseveral times, and then re-dispersed in 3mL of absolute ethanol.

Synthesis of urchin-like Au nanocages

Typically, 0.1 g of PVP was dispersed in 20 mL of distilled water under magnetic stirring, and the solution was heated to 80℃ under reflux condition. 1mL as-prepared Ag nanoechinus/ethanol suspensionwas

added into the mixture solution, subsequently. After 10 min, 150 μL of 24 mM $HAuCl_4$ solution was added dropwise. And the whole mixture system was kept for another 3h. The black products were collected and washed with saturated NaCl solution to remove the generated AgCl during the reaction process, then washed with distilled water and absolute ethanol respectively.

Synthesis of octahedral Cu_2O and octahedral Au nanocages

The octahedral Cu_2O nanoparticles were prepared based on previous reports[3], and the octahedral Au nanocages were prepared mainly based on the synthetic procedure of urchin-like Au nanocages. The end products were washed with ammonia solution and distilled water.

Characterization

XRD patterns were obtained by employing a Shimadzu XRD-6000 X-ray diffractometer equipped with Cu Kα radiation (λ = 0.154060 nm).Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) images were obtained using Zeiss ultra-plus scanning electron microscope at 15 kV-20 kV.High resolution transmission electron microscopy (HR/TEM) and selected area electron diffraction (SAED) images of the samples were carried out on a HITACHI H-8100 electron microscope (Hitachi, Tokyo, Japan) with an accelerating applied potential of 200 kV. The Raman experiments were done on a Renishaw

Invia Reflex system equipped with Peltier-cooled charge-coupled device (CCD) detectors and a Leica microscope. Samples were excited with a He-Ne laser (785 nm) with a spot size of approximately 2 mm and the laser power was 0.06 mW.

The morphologies of the obtained Ag nanoechinus were displayed by SEM technologies. As shown in **Figure S1a**, Ag nanoechinus was successfully prepared using a modified Ag seed-mediated growth method. A close-up view of Ag nanoechinus in **Figure S1b** shows lots of rod-like tips were grown radially with 200~300 nm in length, and the surface of per branch is relatively smooth. Particularly, the length of Ag branch could be also adjusted by introducing various amounts of Ag seeds. As demonstrated in **Figure S2**, the length of Ag branch decreased with the volume of Ag seeds increasing obviously. It laid a foundation for preparing Au nanocages with different sizes.

The SERS analytical enhancement factors (AEF) for NBA on the urchin-like Au nanocages can be calculated by using the equation as follows[4-5].

$$AEF = \frac{ISERS/NSERS}{IRaman/NRaman}$$

Here, I_{SERS} and I_{Raman} represent the intensity of SERS spectrum and Raman spectrum in turn. N_{SERS} and N_{Raman} is the number of molecules probed in SERS substrate and bulk sample respectively. The illumination

focus of the 785 nm laser beam has a diameter of ~1 μm and the penetration depth ~3 mm. The estimated value of N_{Raman} (10^{-3} M of NBA) is ~1.42 $\times 10^{9}$, and the I_{Raman} is ~174. The SERS intensity for the concentrations of 10^{-3} M of NBA is very closely to that for 10^{-4} M, thus it can be presumed that the surface of Au nanocages have been fully adsorbed with NBA molecules (10^{-3} M) under the laser spot area. We assumed that NBA molecules were absorbed as a monolayer on the surface of urchin-like Au nanocages. The estimated value for N_{SERS} is ~7.85 $\times 10^{5}$. In this study, the AEF value is calculated about 1.4×10^{6} for the urchin-like Au nanocages as substrate.

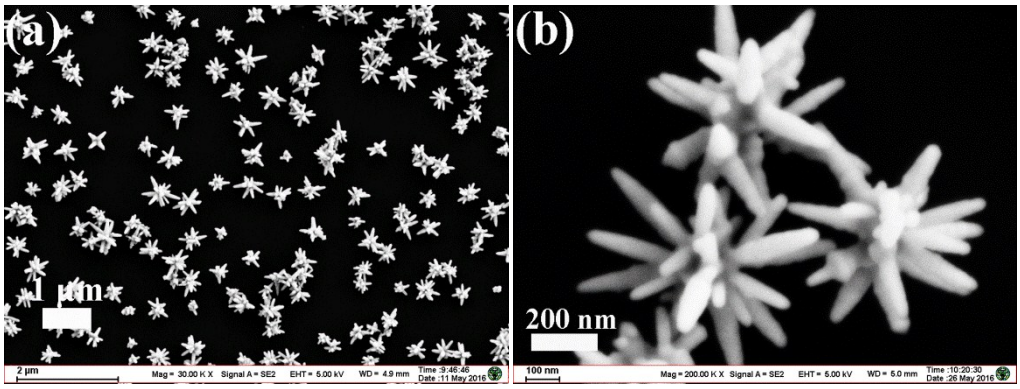

Figure S1 SEM images of as-preparedAg nanoechinus.

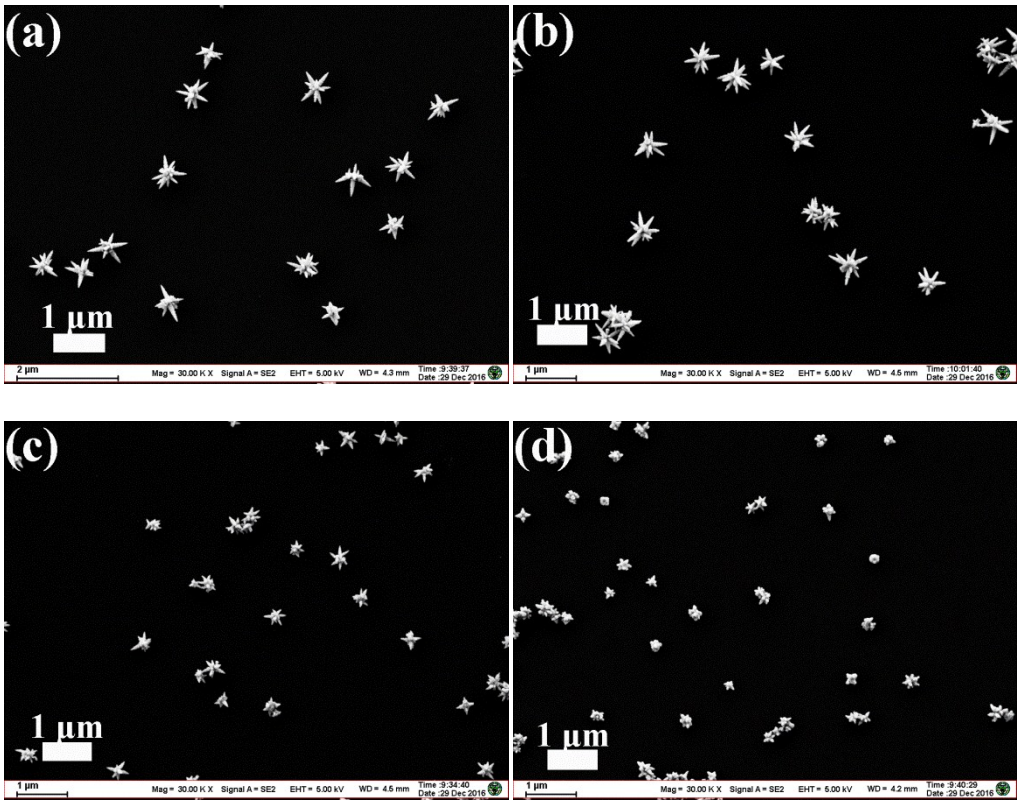

Figure S2 SEM images of as-prepared Ag nanoechinus by using different volumes of Ag seed solution: (a) 20 µL, (b) 40 µL, (c) 60 µL and (d) 100 µL.

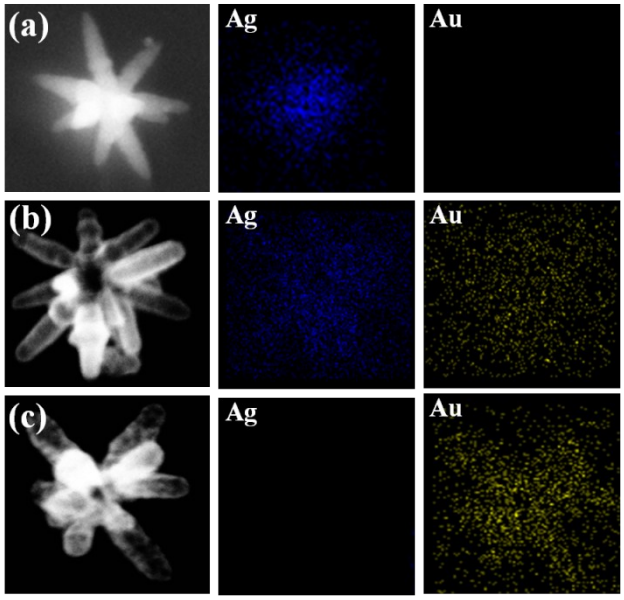

Figure S3 Elemental mapping images of as-prepared (a) Ag nanoechinus, (b) Au-Ag alloy(adding 50μL $HAuCl_4$), (c) urchin-like Au nanocage.

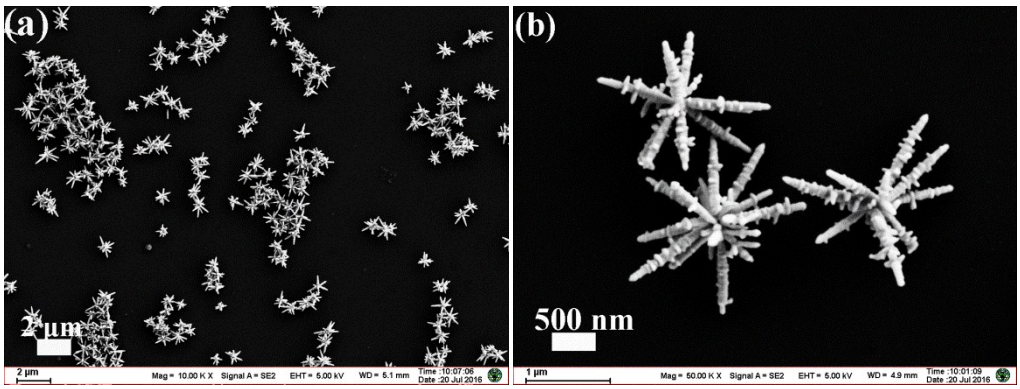

Figure S4 SEM images of as-obtained Ag nanoechinus by employing 50μL of Au seed solution.

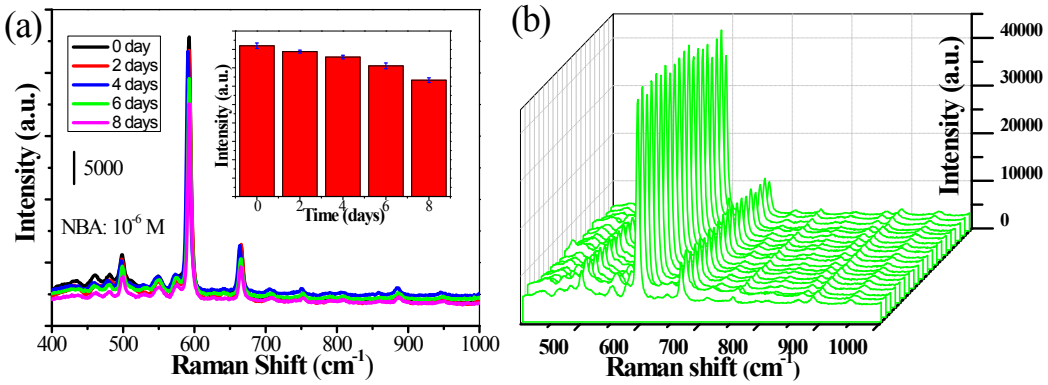

Figure S5 (a) SERS spectra of following Au nanocages substrate storage at room temperature. Inset depicts the histogram of storage time and SERS intensity at 592 cm^{-1}. (b) SERS spectra of NBA at 20 random points from differentarea of substrate.

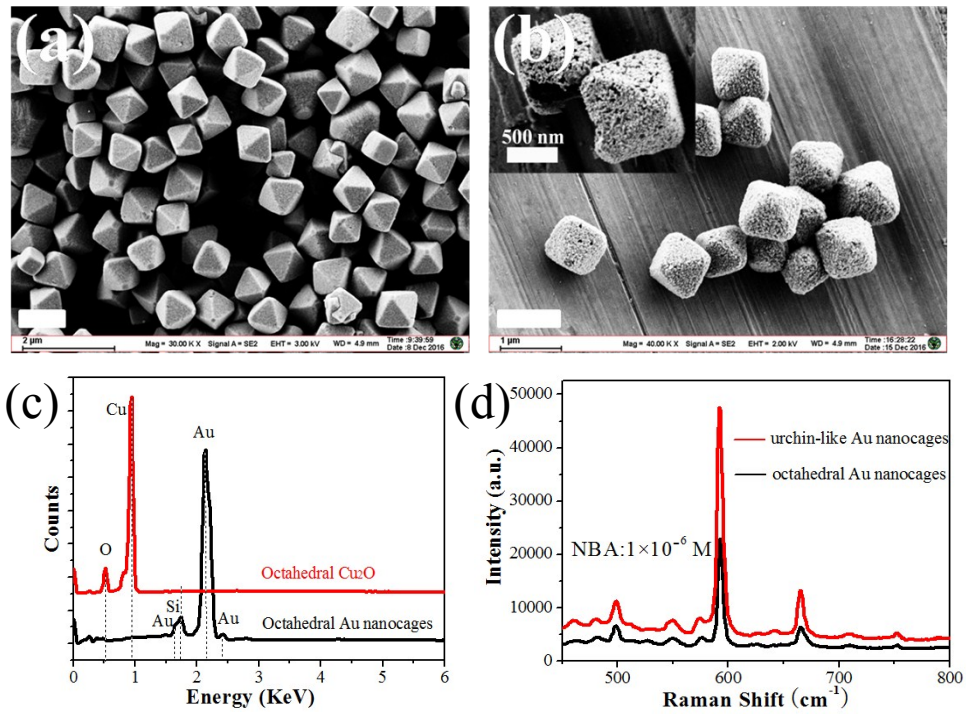

Figure S6 SEM images of as-obtained (a) octahedral Cu_2O, (b) octahedral Au nanocages. The bar is 1 μm. (c) EDS analysis of the obtained octahedral Cu_2O and Au nanocages. (d) A comparison in SERS activity of urchin-like Au nanocages and octahedral Au nanocages for the detection of NBA.

Reference

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