

# **Ag<sub>2</sub>S nanocaps: template synthesis induced by asymmetric atomic structure of polar surface and their SERS activity**

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## **1. Experimental Section**

**1.1 Chemicals.** Potassium iodide (KBr, >99%), silver nitrate (AgNO<sub>3</sub>, 99%), ethylene glycol (EG, >99.5%), and sodium sulfide (Na<sub>2</sub>S, >98%), sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, >99.5%), selenium powder (Se, 99.5%) and sodium borohydride (NaBH<sub>4</sub>, 98%) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Poly(vinyl pyrrolidone) (PVP, K30) were supplied by Sinopharm Chemical Reagent Co., Ltd. All reagents were used directly without any further purification.

**1.2 Preparation of {111}-polar faceted AgBr nanoplates and subsequent transformation into Ag<sub>2</sub>S nanocaps.** The AgBr nanoplates as template were pre-fabricated via a simple precipitation route using PVP as capping agent, according to a previous report with minor modifications.<sup>1</sup> In a typical synthetic procedure, PVP (10 g) and KBr (0.27 g) were added to 60 mL of EG and vigorously stirred at 60 °C until completely dissolved. Then a solution of AgNO<sub>3</sub> (0.285 g) in EG (5 mL) was dropwise added into the above solution under stirring and was stirred for 30 min. The resulting yellow suspension was heated to 160 °C and aged for 2 h under stirring. After the reaction was finished, the brownish yellow AgBr powders were collected by centrifugation, repeatedly washed with distilled water and absolute ethanol to remove residue PVP, and dried at 60 °C in vacuum oven.

The transformation from AgBr nanoplates to Ag<sub>2</sub>S nanocaps was conducted via a

simple ion exchange route. In a typical process, the pre-fabricated AgBr nanoplates (20 mg) were ultrasonically dispersed in 9 mL of distilled water, and an aqueous solution of Na<sub>2</sub>S or Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.1 M, 1.00 mL) was added into the above suspension. The resulting suspension was heated to 90 °C and kept for 24 h. After reaction, the black products were collected by centrifugation, washed with distilled water and ethanol three times, and finally dried at 60 °C in vacuum oven. In our study, different concentrations (0.01 M, 0.006 M, and 0.002 M) of sulfide ions were realized by adding different volumes (1.0 mL, 0.6 mL, and 0.2 mL) of the 0.1 M Na<sub>2</sub>S solution into reaction solution, keeping the total volume of solution constant (10 mL).

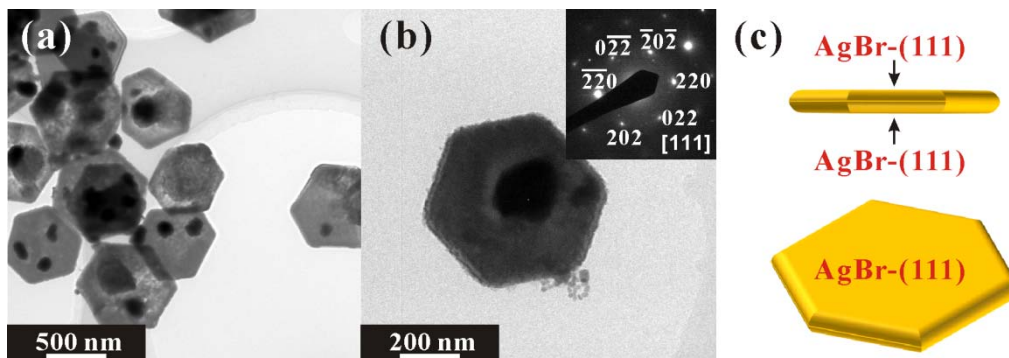
The conversion from AgBr nanoplates to Ag<sub>2</sub>Se nanocaps was conducted via a similar ion exchange process preceded at room temperature, in which the Na<sub>2</sub>S solution was replaced by a freshly prepared NaHSe solution. The synthetic procedure of the NaHSe solution was as follows. First, Se powder (10 mg) was dispersed in 50 mL of distilled water under stirring and bubbled with N<sub>2</sub> for 10 min to remove the dissolved oxygen. After that, NaBH<sub>4</sub> (100 mg) was added into the dispersion solution of Se under the N<sub>2</sub> flow. With vigorous foaming (H<sub>2</sub>), the Se powder was gradually consumed and the virtually colorless solution of NaHSe was finally formed.

**1.4 Structural characterization and SERS measurement of samples.** The morphologies of the products were examined on a scanning electron microscopy (SEM, JEOL 6700F) at an accelerating voltage of 5 kV, and transmission electron microscopy (TEM, JEOL 2010F) at an accelerating voltage of 200 kV. The composition of the products was determined by powder X-ray diffraction (XRD, Philips PW-1830) with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ).

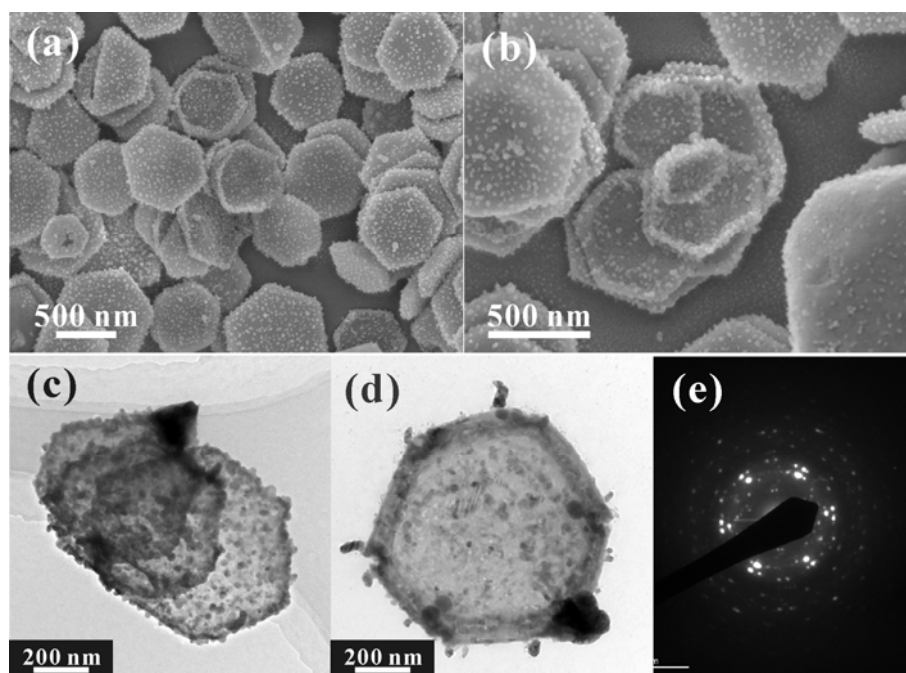
Ag<sub>2</sub>S modified substrates for SERS measurement were obtained by dropping the dispersion of Ag<sub>2</sub>S nanoparticles onto silicon substrates, and then Rhodamine 6G (R6G) of different concentrations (10<sup>-3</sup>, 10<sup>-4</sup>, 10<sup>-5</sup> and 10<sup>-6</sup> M) were dropped onto the substrates by using a pipette. After dried, the substrates were immersed in distilled water to remove the residual unbound R6G. To illustrate the role of Ag<sub>2</sub>S nanoparticles, a Si substrate loaded with R6G (10<sup>-3</sup> M) was simultaneously measured as the blank sample. SERS measurements were carried out on a Renishaw 2000 laser

Raman microscope equipped with a 514.5 nm 20 mW argon ion laser of 2 mm spot size for excitation. During measurements, the laser power was reduced to 1%, and the signal collection time was 10 s.

## 2. Experimental Results

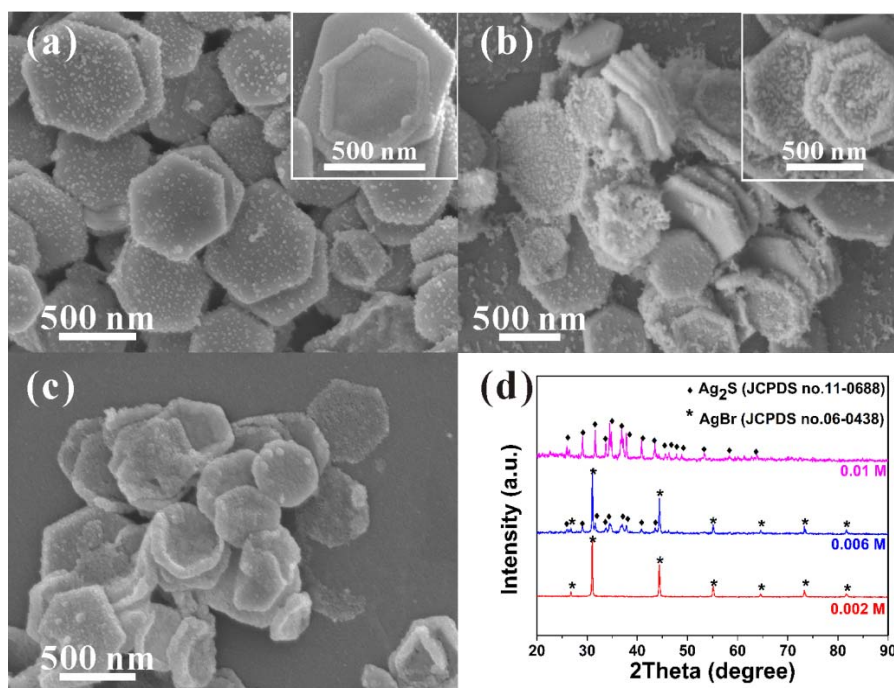


**Fig. S1** (a) Low-magnification TEM image, (b) high-magnification TEM image and SAED pattern (inset) of the prefabricated AgBr hexagonal nanoplates used for the template and precursor. (c) Schematic illustration of polar  $\{111\}$  faceted AgBr hexagonal nanoplates. (**Note:** Particles with darker contrast on the hexagonal nanoplates are Ag nanoparticles produced by the decomposition of AgBr upon irradiation of the electron beam).

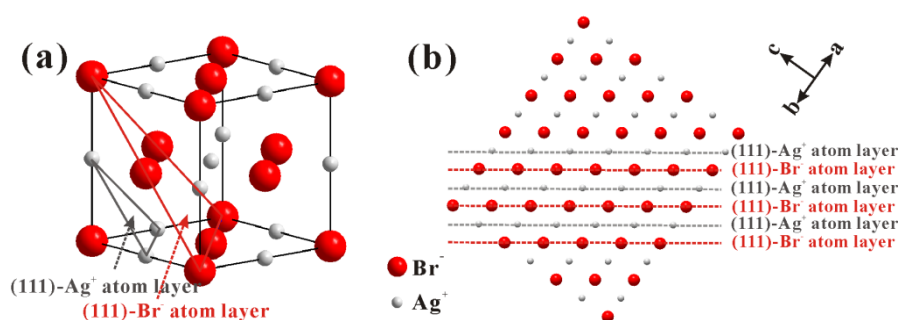


**Fig. S2** (a,b) SEM and (c) TEM images of the Ag<sub>2</sub>S nanocaps obtained via the ion exchange process in 0.01 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution at 90 °C for 24 h. (d) TEM image and (e) SAED pattern of the Ag<sub>2</sub>S nanocaps.

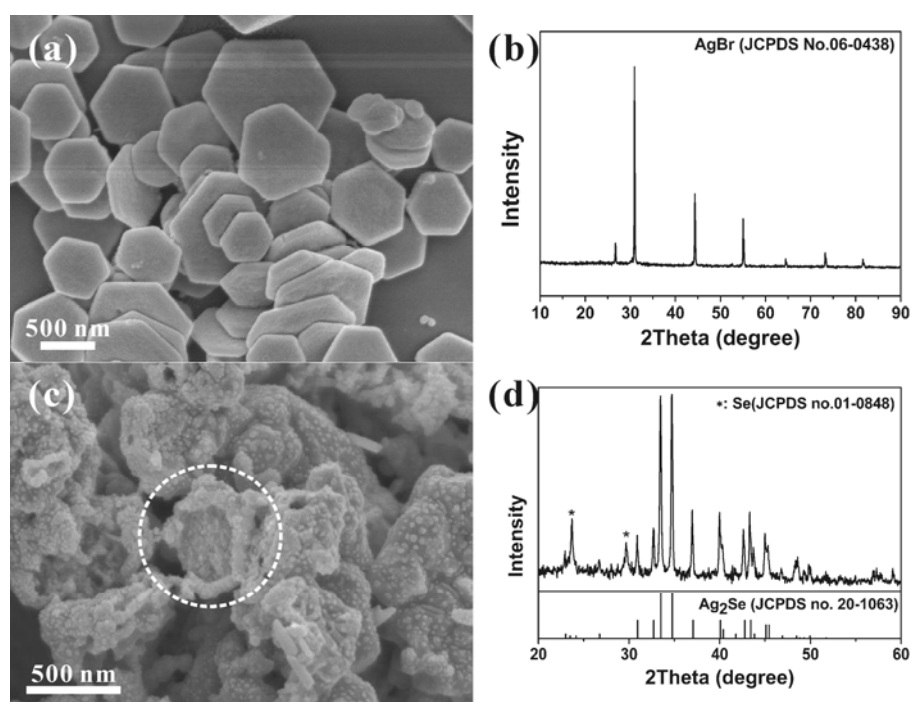
(e) corresponding SAED pattern of an individual hexagonal  $\text{Ag}_2\text{S}$  nanop. cap.



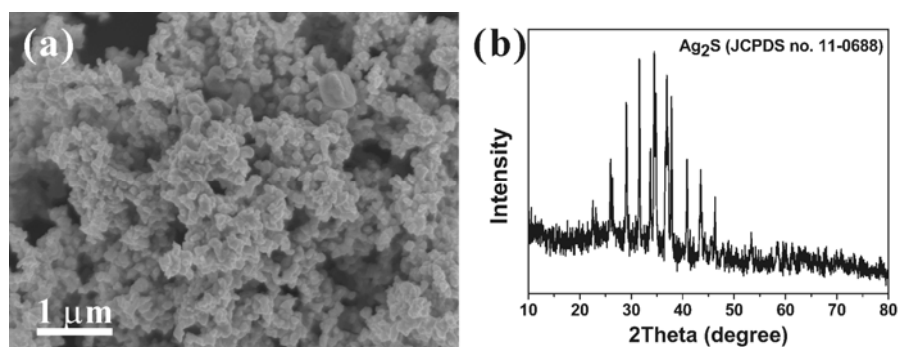
**Fig. S3** SEM images of the products prepared by immersing  $\text{AgBr}$  hexagonal nanoplates in the  $\text{Na}_2\text{S}$  solutions of (a) 0.002 M, (b) 0.006 M, and (c) 0.01 M. Reaction temperature is  $90^\circ\text{C}$ , and reaction time is 24 h. (d) XRD patterns of the products.



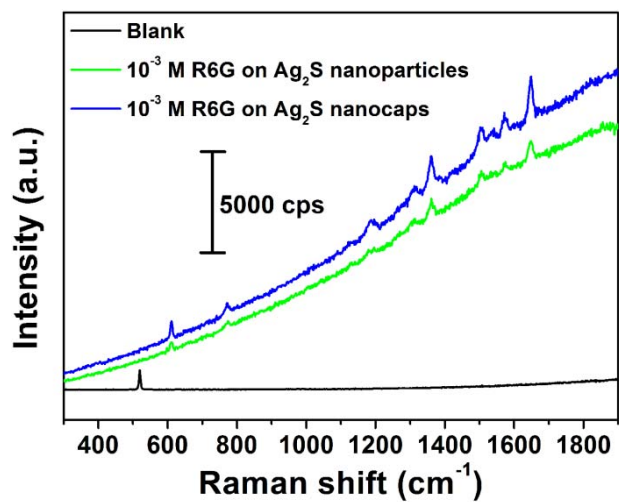
**Fig. S4** Schematic models of (a) a rocksalt-type  $\text{AgBr}$  unit cell and (b) atomic arrangement projected from the [110] direction, where the  $\text{Ag}^+$ - and  $\text{Br}^-$ -(111) polar planes are indicated by the grey and red lines, respectively.



**Fig. S5** (a) SEM image and (b) XRD pattern of the products prepared by immersing AgBr hexagonal nanoplates in the  $\text{Na}_3\text{PO}_4$  solutions of 0.01 M, while keeping other conditions unchanged. (c) SEM image and (d) XRD pattern of the products prepared by immersing AgBr hexagonal nanoplates in the freshly prepared NaHSe solution at room temperature, while keeping other conditions unchanged.



**Fig. S6** (a) SEM image and (b) XRD pattern of  $\text{Ag}_2\text{S}$  nanoparticles obtained by reaction of AgBr nanoplates in 0.05 M  $\text{Na}_2\text{S}$  solution at 90 °C for 24 h.



**Fig. S7** Raman spectra of R6G ( $10^{-3}$  M) adsorbed on Ag<sub>2</sub>S nanocaps and Ag<sub>2</sub>S nanoparticles. The excitation line of laser is 514 nm and the laser power 20 mW, 1%; integration time: 10 s.

#### Reference

- [1] H. Wang, J. Gao, T. Q. Guo, R. M. Wang, L. Guo, Y. Liu and J. H. Li, *Chem. Commun.*, 2012, **48**, 275-277.