

## Electronic Supplementary Material

### **A novel deposition mechanism of Au on Ag nanostructures involving galvanic replacement and reduction reactions**

*Juan Xu,<sup>a</sup> Qinru Yun,<sup>a</sup> Han Zhang,<sup>c</sup> Yanzhen Guo,<sup>c</sup> Shanlin Ke,<sup>a</sup> Jianfang Wang,<sup>c</sup> Xingzhong Zhu<sup>\*a</sup> and Caixia Kan<sup>\*a</sup>*

<sup>a</sup>College of Science, Nanjing University of Aeronautics and Astronautics, Nanjing 211106, China

<sup>b</sup>Key Laboratory of Aerospace Information Materials and Physics (NUAA), MIIT, Nanjing 211106, China

<sup>c</sup>Department of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong SAR, China

## Experimental Section

### Chemicals

HAuCl<sub>4</sub>·3H<sub>2</sub>O (99%), NaBH<sub>4</sub> (98%), trisodium citrate (99%), ascorbic acid (99%) and AgNO<sub>3</sub> (99%) were purchased from Sigma-Aldrich. Cetyltrimethylammonium bromide (CTAB, 98%) were obtained from Alfa Aesar. H<sub>2</sub>O<sub>2</sub> solution (30 wt% in water), cetyltrimethylammonium chloride (CTAC, 97%), NaOH (96%), NH<sub>3</sub>·H<sub>2</sub>O solution (25 wt% in water) and HCl solution (37 wt% in water) were purchased from Aladdin Reagent. Deionized water with a resistivity of 18.2 MΩ cm produced by a Direct-Q 5 ultraviolet water purification system was used in all experiments.

### Synthesis of the Au NBPs

The Au NBP samples were prepared through seed-mediated method. Firstly, the HAuCl<sub>4</sub> (0.125 mL, 0.01 M), trisodium citrate (0.25 mL, 0.01 M) and water (9.625 mL) were mixed at room temperature. Next, a freshly prepared, ice-cold NaBH<sub>4</sub> solution (0.15 mL, 0.01 M) was injected quickly under vigorous stirring for 2 min. The resultant seed solution was kept at room temperature for 2 h before use. For the growth solution, CTAB (40 mL, 0.1 M), HAuCl<sub>4</sub> (2 mL, 0.01 M), AgNO<sub>3</sub> (0.4 mL, 0.01 M), HCl (0.8 mL, 1 M) and ascorbic acid (0.32 mL, 0.1 M) were mixed together, followed by the injection of seed solution (0.4 mL) with gentle inversion mixing for 10 s. The reaction solution was left undisturbed overnight at room temperature. The longitudinal dipolar plasmon wavelength of the obtained Au NBP sample was 794 nm. The purification of the as-prepared Au NBPs was conducted using a depletion-induced separation method. The number percentage of the purified Au NBPs was found from TEM imaging to be 99%.

### Synthesis of the Au NBP@Ag nanorods

In a standard synthesis, the purified Au NBPs (10 mL, the longitudinal dipolar plasmon peak extinction value is  $\sim 1$  when measured with a 0.5-cm cuvette) were collected by centrifugation at 7000 rpm for 10 min. The precipitate was redispersed into a cetyltrimethylammonium chloride (CTAC) solution (10 mL, 0.08 M), followed by the addition of  $\text{AgNO}_3$  (250  $\mu\text{L}$ , 0.01 M) and ascorbic acid (125  $\mu\text{L}$ , 0.1 M) under gentle shaking. The mixture solution was placed in an air-bath shaker (65 °C, 100 revolutions per minute) and kept for 4.5 h. The resultant sample was centrifuged twice at 6000 rpm for 10 min. The precipitate was redispersed into a CTAB solution (4 mL, 0.05 M) for further use.

### **Synthesis of the Ag nanorod@AuAg nanoframes**

The Ag nanorod@AuAg nanoframes with different shapes were produced following the same procedure. Firstly, the Ag nanorod solution (4 mL) were mixed with ascorbic acid (1 mL, 0.1 M) and aqueous HCl (1 mL, 0.1 M) or NaOH (1 mL, 0/0.1/0.2/1 M) under gentle shaking. Afterwards, aqueous  $\text{HAuCl}_4$  (1.3 mL, 0.1 mM) was titrated into the solution using a syringe pump at a rate of 20  $\mu\text{L}/\text{min}$  at room temperature. The reaction was left for another 20 min once the titration was completed. The product was centrifuged twice at 6000 rpm for 10 min and then redispersed into 4 mL of water, followed by the addition of CTAB (0.08 mL, 0.1 M),  $\text{H}_2\text{O}_2$  (4 mL, 6 wt%) and  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (0.2 mL, 28 wt%). The resultant sample was left at room temperature for 1.5 h and then centrifuged at 4000 rpm for 10 min. The precipitate was redispersed into water (3 mL) for further characterization. In order to explore the shape evolution of the samples, experiments were carried out with different volume of  $\text{HAuCl}_4$  (0.1 mM) while keeping the other parameter same.

### **Synthesis of the Ag nanocubes**

The Ag nanocubes were synthesized using polyol method. In the typical synthesis, 5 mL EG solution was heated in the oil bath at 150 °C under magnetic stirring, followed by the introduction of NaHS (0.06 mL, 3 mM in EG). After stirring for 2 min, HCl (0.5 mL, 3 mM in EG) and PVP-55 (1.25 mL, 20 mg/mL in EG) were introduced subsequently, followed by injecting CF<sub>3</sub>COOAg (0.4 mL, 282 mM in EG) after stirring for another 2 min. The mixture was stirred continuously until the extinction peak shifted to 434 nm. The Ag nanocubes were obtained after washed with actone and water by centrifugation at 9000 rpm for 10 min, and the precipitate was redispersed into water (1.5 mL) for further use.

### **Synthesis of the Ag cuboctahedras**

The Ag cuboctahedras were produced through overgrowth of Ag atoms on Ag nanocubes. In a typical synthesis, Ag nanocube solution (200 µL) was mixed with PVP-55 (5 mL, 2 mg/mL), sodium citrate (50 µL, 20 mM), ascorbic acid (100 µL, 0.1 M) under gentle shaking. Afterwards, aqueous AgNO<sub>3</sub> (3 mL, 1 mM) was titrated into the solution using a syringe pump at a rate of 5 mL/h at room temperature. The product was obtained through centrifugation at 1500 rpm for 10 min to remove the impurity of large particles, followed by washed with water and ethanol repeatedly by centrifugation at 9000 rpm for 10 min. The precipitate was redispersed into water (0.1 mL) for further use.

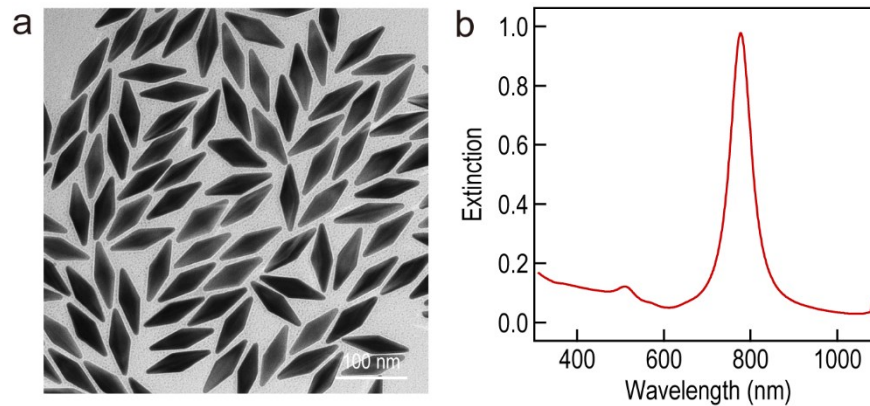
### **Synthesis of the Ag cuboctahedra@AuAg nanoframes**

The Ag cuboctahedra@AuAg nanoframe with different shapes were produced following the same procedure. Firstly, the Ag cuboctahedra solution (0.1 mL) were mixed with ascorbic acid (1 mL, 0.1 M), CTAB (2 mL, 0.05 M) and aqueous HCl (1 mL, 0.1 M) or NaOH (1 mL, 0.2 M) under gentle shaking. Afterwards, aqueous HAuCl<sub>4</sub> (0.6 mL, 0.1 mM) was titrated into the solution using

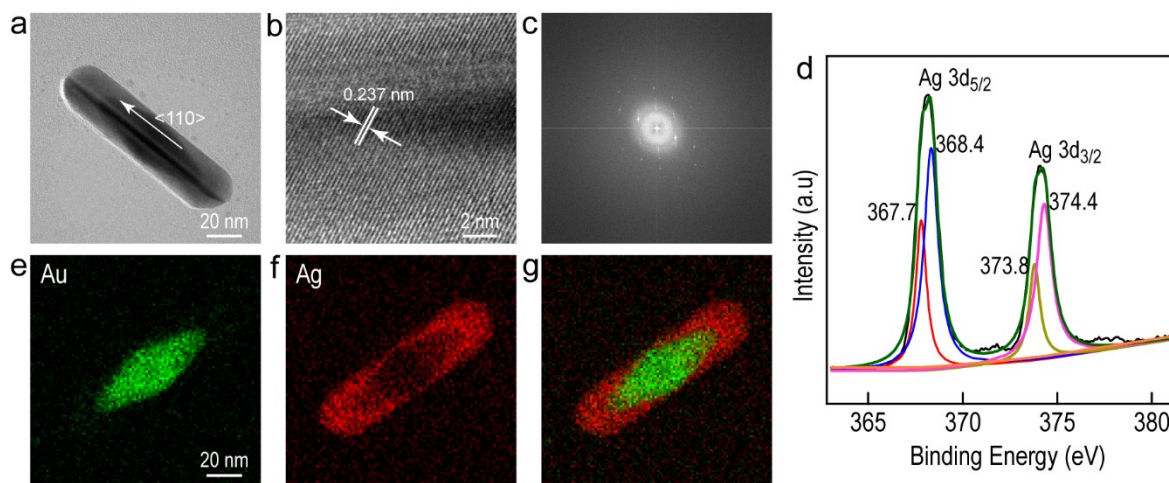
a syringe pump at a rate of 20  $\mu\text{L}/\text{min}$  at room temperature. The reaction was left for another 20 min once the titration was completed. The product was centrifuged twice at 9000 rpm for 10 min and then redispersed into 0.5 mL of water, followed by the addition of CTAB (25  $\mu\text{L}$ , 0.1 M),  $\text{H}_2\text{O}_2$  (0.3 mL, 6 wt%) and  $\text{NH}_3\cdot\text{H}_2\text{O}$  (16  $\mu\text{L}$ , 28 wt%). The resultant sample was left at room temperature for 1.5 h and then centrifuged at 9000 rpm for 10 min. The precipitate was redispersed into water (0.2 mL) for further characterization.

### **Instrumentation**

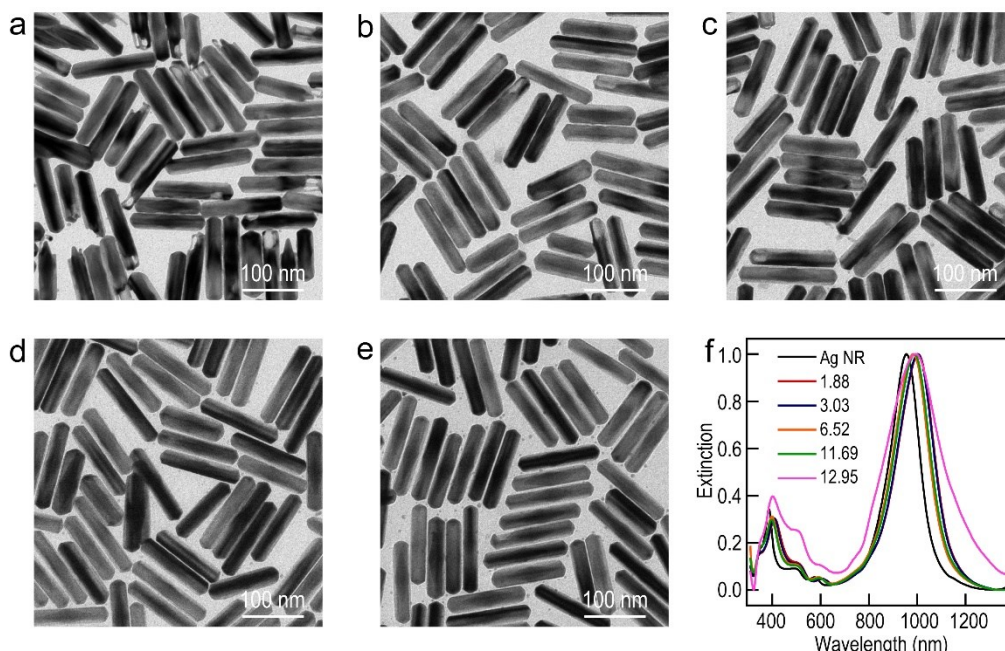
Extinction spectra were measured on a Shimadzu UV-3600 Plus ultraviolet/visible/near-infrared spectrophotometer with plastic cuvettes of 0.5-cm optical path length. TEM imaging was carried out on a FEI Tecnai 12 microscope operated at 120 kV. HRTEM imaging, HAADF-STEM characterization and elemental mapping were performed on a FEI Tecnai F20 microscope operated at 200 kV and equipped with an Oxford energy-dispersive X-ray (EDX) analysis system. ICP-OES measurements were performed on an Agilent ICP-MS 7500a system.



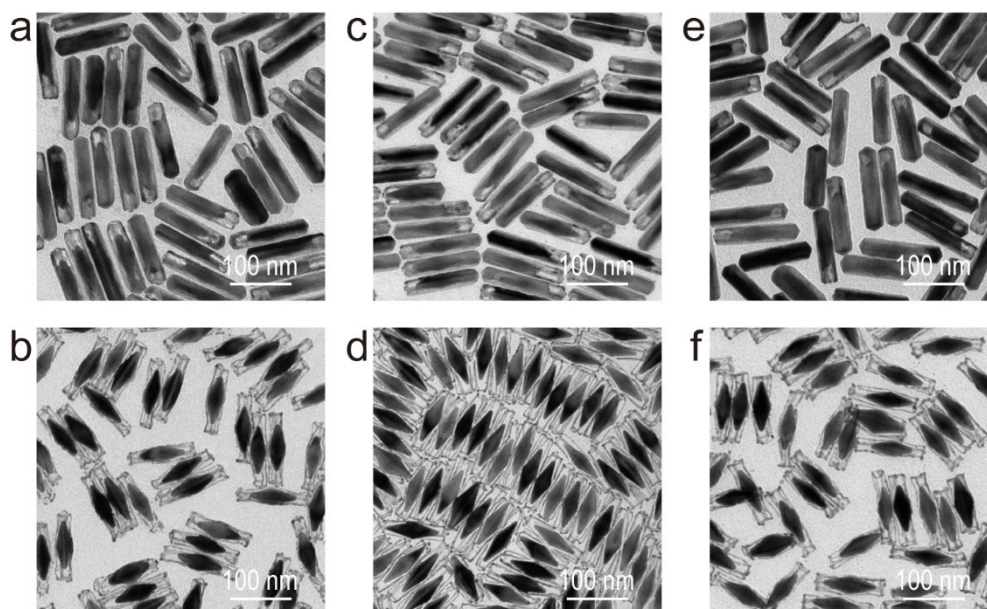
**Fig. S1** Characterization of Au NBPs. (a) TEM image of Au NBPs with average waist width of  $28 \pm 1$  nm and length of  $98 \pm 3$  nm. (b) Extinction spectrum of Au NBPs.



**Fig. S2** Characterization of Ag nanorod. (a) TEM and (b) HRTEM image of a single Ag nanorod. (c) The fast Fourier transform spectra of area shown in b. (d) XPS spectra of Ag 3d of Ag nanorods. (e–g) Elemental mapping images of a single Ag nanorod.

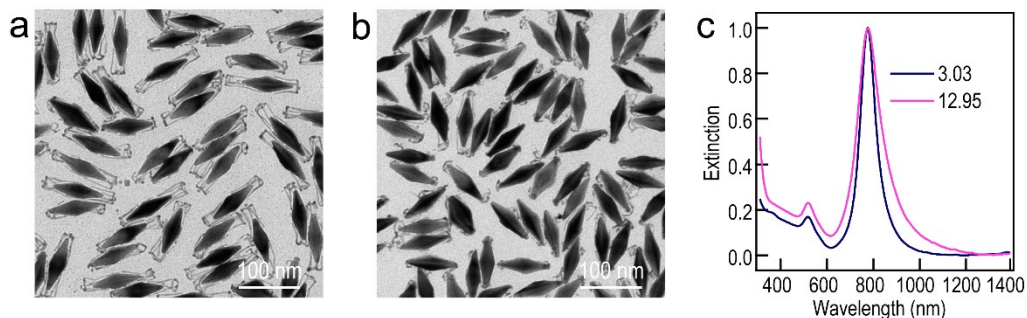


**Fig. S3** Shape evolution of Ag nanorod@AuAg nanoframes at different pH values. (a–e) TEM images of the Ag nanorod@AuAg nanoframe samples at pH of 1.88, 3.03, 6.52, 11.69, and 12.95, respectively. (f) Extinction spectra of the Ag nanorod sample and the Ag nanorod@AuAg nanoframe samples produced with HAuCl<sub>4</sub> (1.3 mL, 0.1 mM) at different pH values.

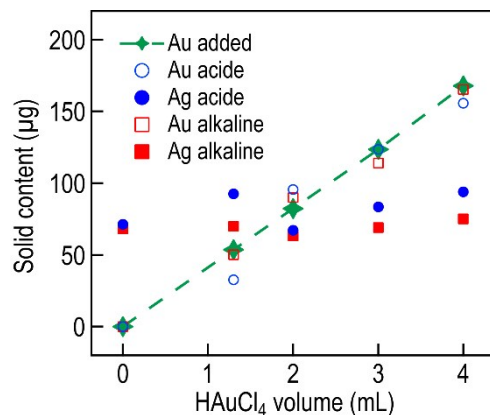


**Fig. S4** Shape evolution of Ag nanorod@AuAg nanoframes and the corresponding Au NBP@AuAg nanoframes in the absence of ascorbic acid at different pH values. (a,c,e) TEM images of Ag nanorod@AuAg nanoframe samples at pH of 1.88, 3.03 and 11.69, respectively.

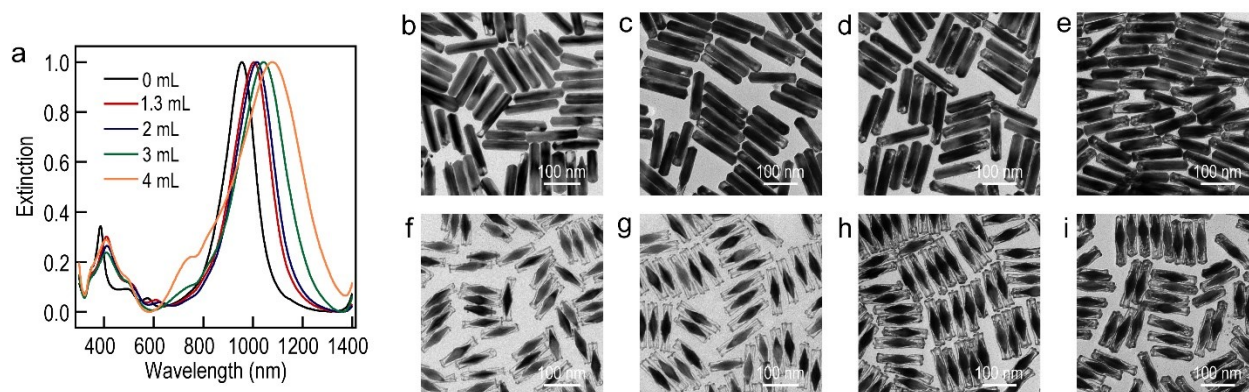
(b,d,f) TEM images of the corresponding Au NBP@AuAg nanoframe samples, respectively.



**Fig. S5** Shape evolution of the Au NBP@AuAg nanoframes at different pH values. (a, b) TEM images of the Au NBP@AuAg nanoframe samples at pH of 3.03 and 12.95, respectively. (c) Extinction spectra of the Au NBP@AuAg nanoframe samples.



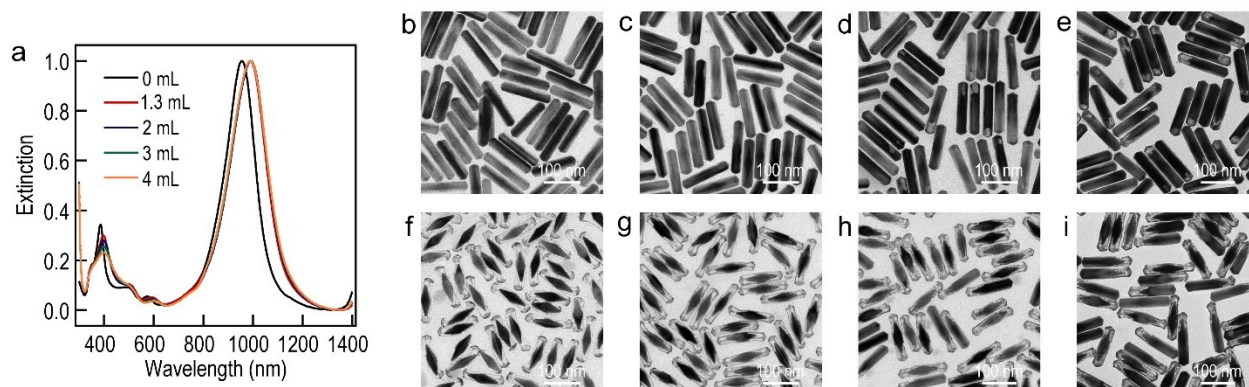
**Fig. S6** The Au and Ag contents in solid as a function of HAuCl<sub>4</sub> volume. The data points marked as “Au added” represent the amount of the added Au precursor.



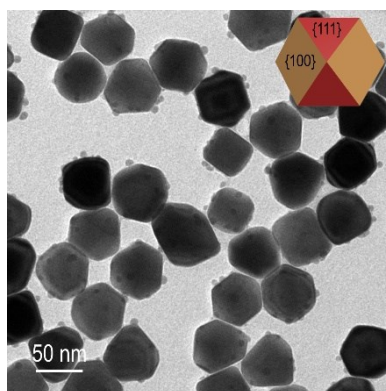
**Fig. S7** Extinction spectra and TEM images of Ag nanorod@AuAg nanoframes and the corresponding Au NBP@AuAg nanoframes at pH of 1.88. (a) Extinction spectra of the Ag nanorod



sample and the Ag nanorod@AuAg nanoframe samples produced with 1.3, 2, 3, and 4 mL of H<sub>2</sub>AuCl<sub>4</sub> (0.1 mM), respectively. (b–i) TEM images of the Ag nanorod@AuAg nanoframe samples and the corresponding Au NBP@AuAg nanoframe samples, respectively.



**Fig. S8** Extinction spectra and TEM images of Ag nanorod@AuAg nanoframes and the corresponding Au NBP@AuAg nanoframes at pH of 11.69. (a) Extinction spectra of the Ag nanorod sample and the Ag nanorod@AuAg nanoframe samples produced with 1.3, 2, 3, and 4 mL of H<sub>2</sub>AuCl<sub>4</sub> (0.1 mM), respectively. (b–i) TEM images of the Ag nanorod@AuAg nanoframe samples and the corresponding Au NBP@AuAg nanoframe samples, respectively.



**Fig. S9** TEM images of the Ag cubooctahedra samples. The inset shows the model in the appropriate orientation.