The preparation of decahedral Au NPs

A method developed by Song's group was used to prepare Au decahedron NPs.[1] In a typical preparation, 5 g PVP was dissolved in 25 mL DEG and the solution was heated to boiling. 2 mL another DEG containing 20 mg $HAuCl_4$ was injected quickly to the boiling solution. Immediately, the solution changed from colourless to red. After 10 min refluxing, it was cooled down to room temperature and a similar purifying process to above octahedral NPs was employed to remove excess PVP and DEG.

Electrochemical Measurements

A method developed by Xiong's group was used to carry out electrochemical measurements.[2] All measurements were performed at room temperature. To remove excess polymer and other byproducts, nanoparticles should be washed with ethanol three times and water four times. Then 10 μL of an aqueous suspension of the nanoparticles (about 118 μg/mL) was dropped onto a glassy carbon electrode with 3 mm diameter. After drying for 3 h at 50 °C, the electrode was cleaned with plasma asher (EMITECH K1050X) at a power level of 50Wfor 30 min to remove surface organics. An aqueous solution containing 3 μL Nafion (wt 0.025%) was then dropped on nanoparticles surface. The cathode was dried for another 3 h at 50 °C and used as working cathode. An Ag/AgCl electrode and a platinum foil were used as the reference and counter electrode respectively. A CHI 760D electrochemical station (Shanghai Chenhua, China) was used for recording potential-current evolution. In order to measure the concentration of Au decahedra and Au/Ag decahedra, they were dissolved with aqua regia (The volume ratio of HCl and HNO_3 is 3:1. **Cautious: aqua regia is very dangerous and should be handled with extreme caution**), and then were measured with a varian inductively coupled plasma mass spectrometry (ICP-MS). Based on the ICP-MS results, all samples were diluted to the concentration of 118 μg/mL.

References

1. D. Seo, C. Yoo, I. Chung, S. Park, S. Ryu and H. Song, *J. Phys. Chem. C,* 2008, **112**, 2469.
2. L. Ma, C. Wang, M. Gong, L. Liao, R. Long, J. Wang, D. Wu, W. Zhong, M. J. Kim, Y. Chen, Y. Xie and Y. Xiong, *ACS Nano,* 2012, **6**, 9797.

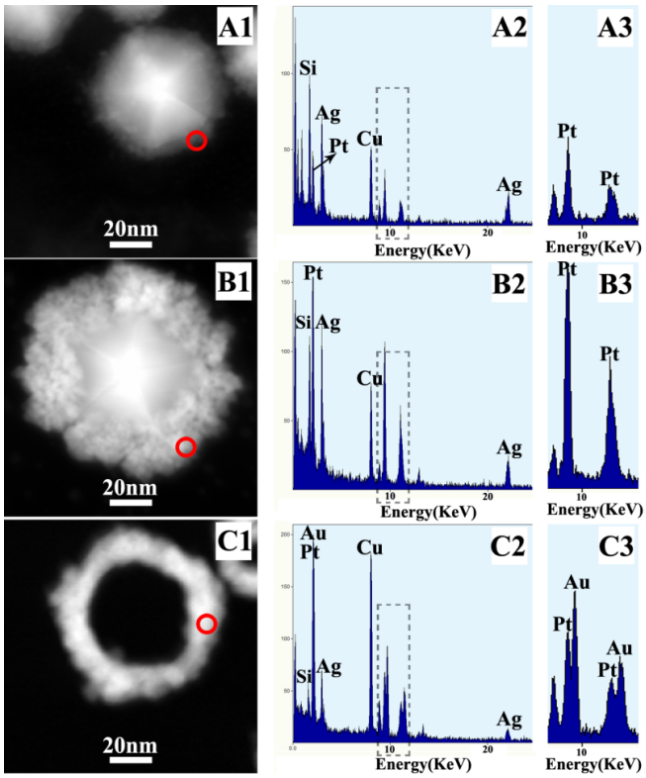

Fig. S1 HAADF images and STEM-EDS analyses of products prepared using a standard synthesis of trimetallic nanorings after the reaction had proceeded for different times: (A1-A2) 30 min; (B1-B2) 60 min; (C1-C2) 120 min. A3, B3 and C3 are the enlarged images of areas marked by the dotted box in **Fig. S1A2**, **Fig. S1B2** and **Fig. S1C2** respectively.

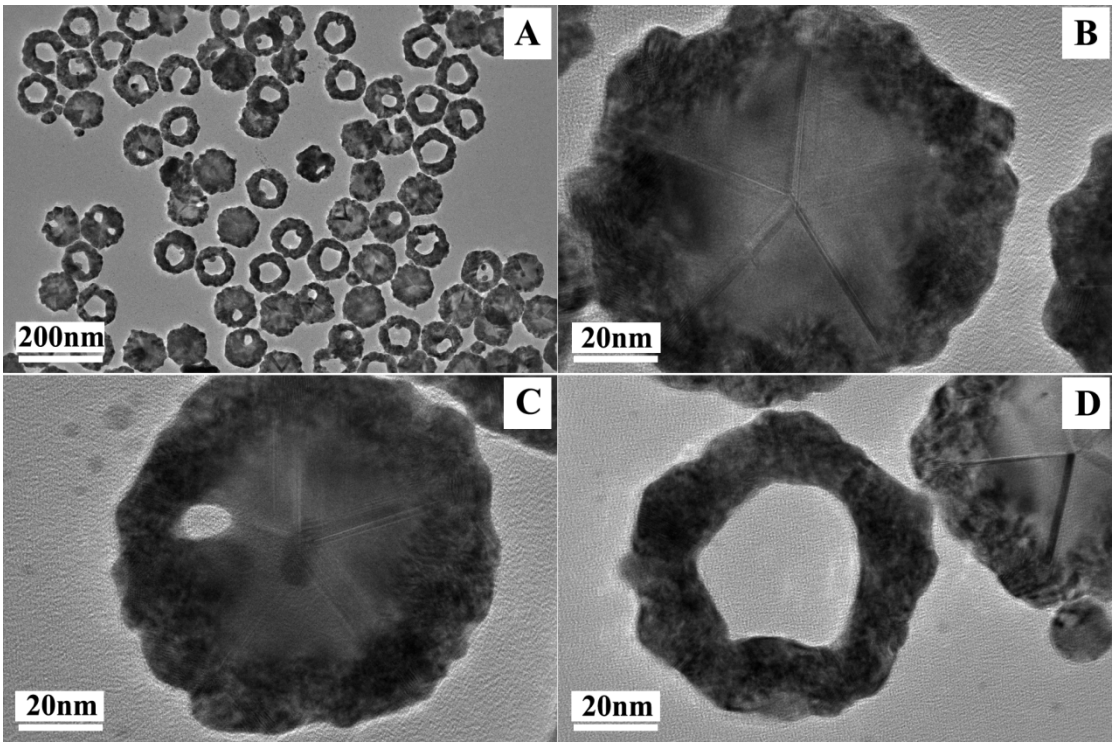

Fig. S2 (A-D) TEM images of products prepared using a standard procedure of trimetallic nanorings except that the reaction time was 90 min. This demonstrates that the etching on each decahedron is not uniform.

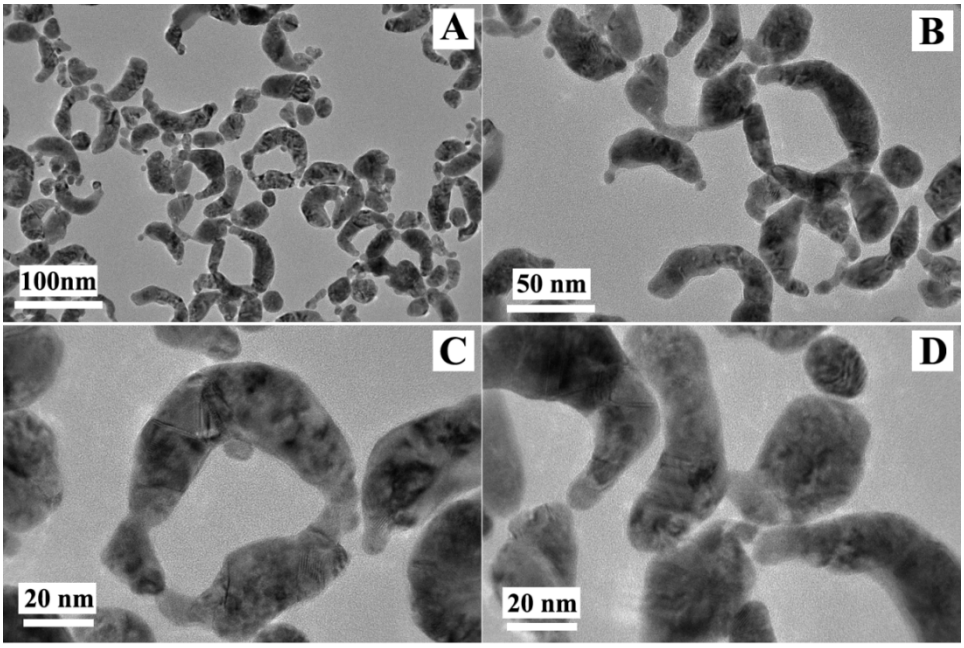

Fig. S3 (A-D) TEM and HRTEM images of products using a standard procedure of trimetallic nanorings except that the reaction time was 150 min.

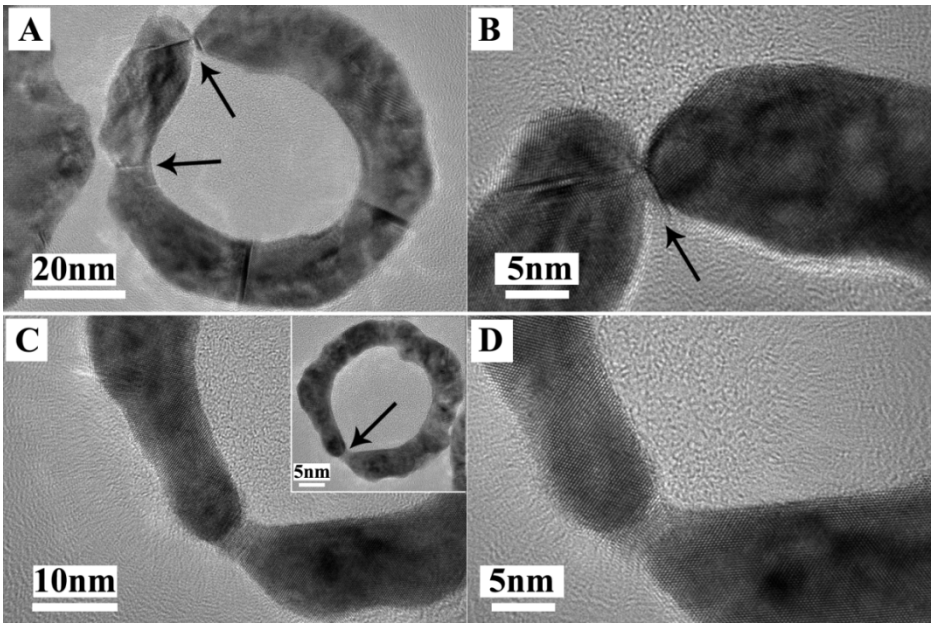

Fig. S4 (A-D) HRTEM images of products shown in **Fig. S3**.

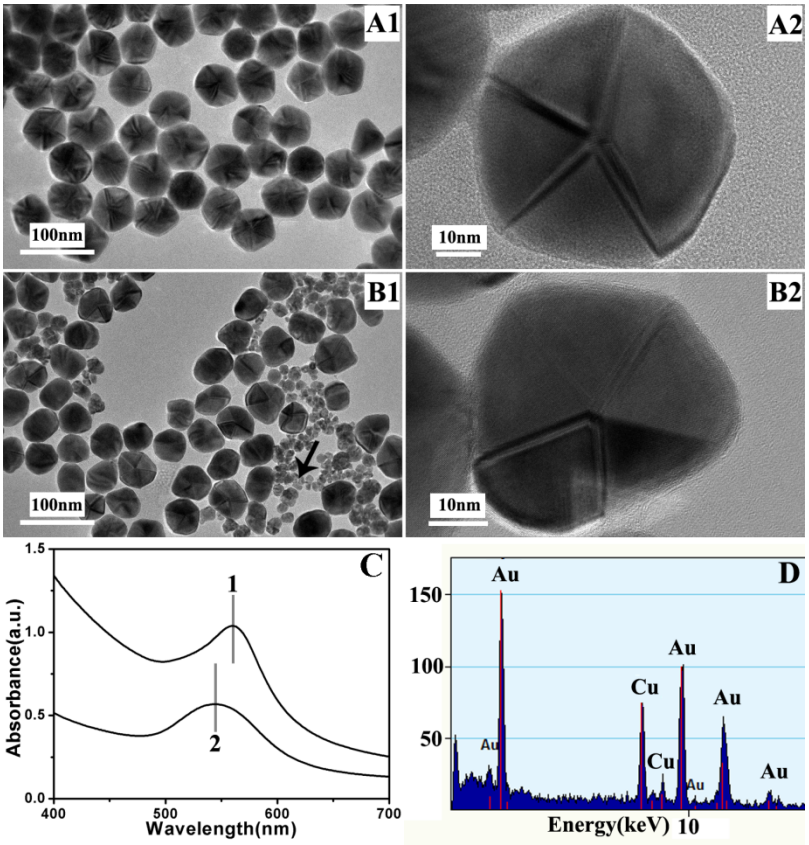

Fig. S5 TEM images of Au/Ag decahedra (A1-A2). (B1-B2) TEM images of products prepared using Au/Ag decahedra as seeds in a standard synthesis of trimetallic nanorings except that no H_2PtCl_6 was added. (C) UV-Vis spectra of Au/Ag decahedra shown in **Fig. S5A** (Curve 1) and colloid shown in **Fig. S5B** (Curve 2). (D) EDS pattern of nanoparticles marked by the arrow in **Fig. S5 B1**.

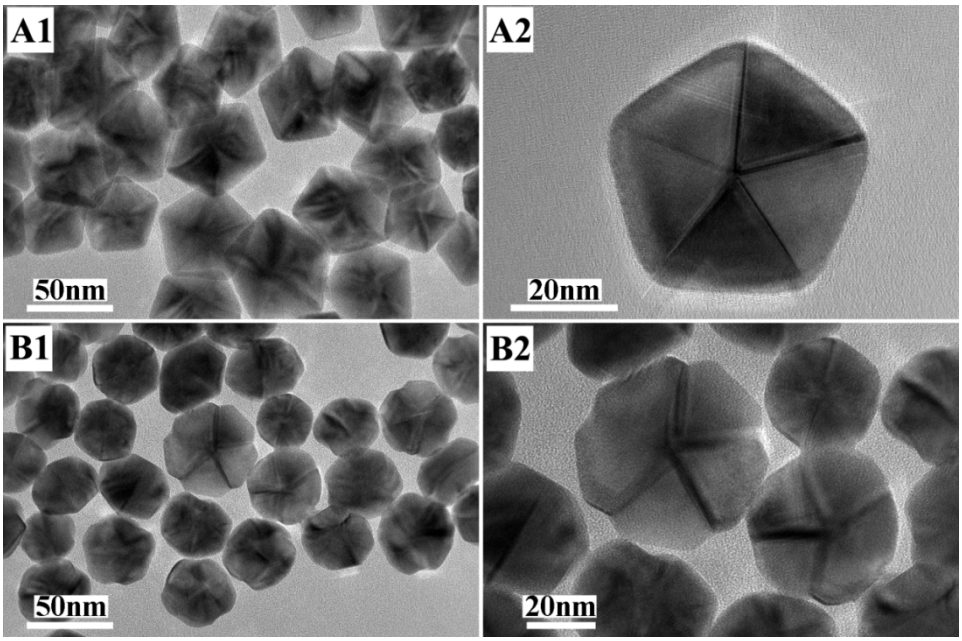

Fig. S6 TEM images of Au/Ag decahedra colloid and corresponding products prepared using a standard synthesis of trimetallic nanorings except that no AA and H_2PtCl_6 were added (Reaction time was 12 h).

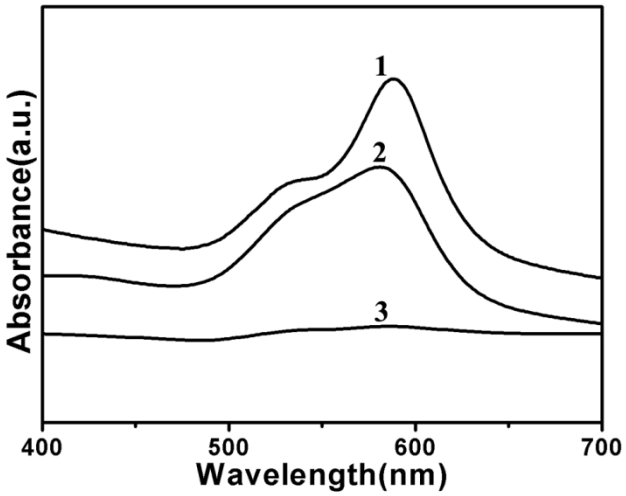

Fig. S7 UV-Vis spectra of Au/Ag decahedra colloid (Curve 1), colloid etched for 12 h in solution containing PVP as protecting agents (Curve 2), colloid etched for 150 min in solution containing PVP as protecting agents and 0.001 M H_2SO_4 (Curve 3).

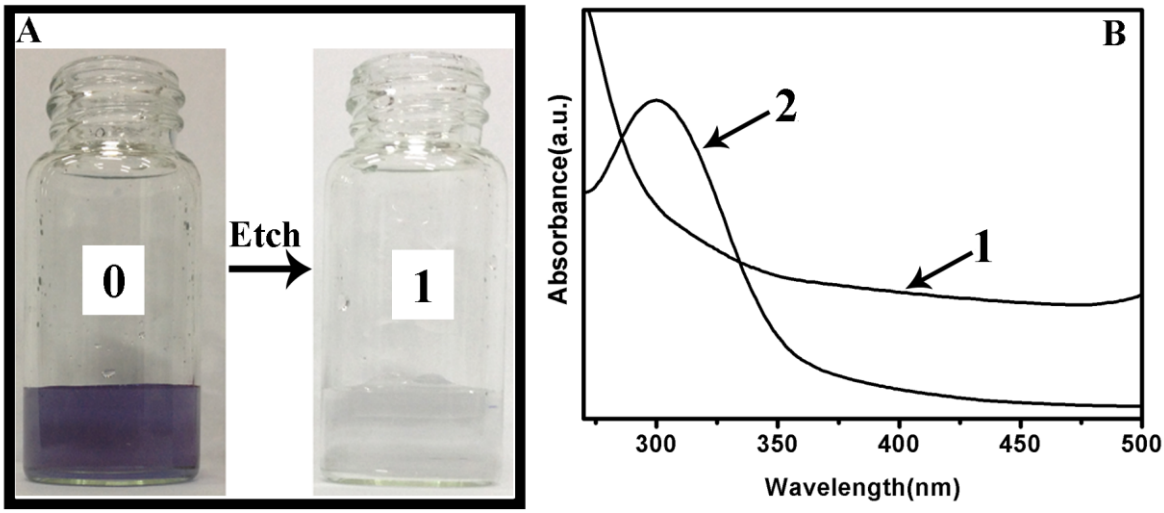

Fig. S8 The optical color of (A0) Au/Ag decahedra colloid and (A1) corresponding solution after complete etching; The UV-Vis spectra of $HAuCl_4$ (Curve 2 in **Fig. 8B**) and solution 1 in **Fig. S8 A1** (Curve 1 in **Fig. 8B**).

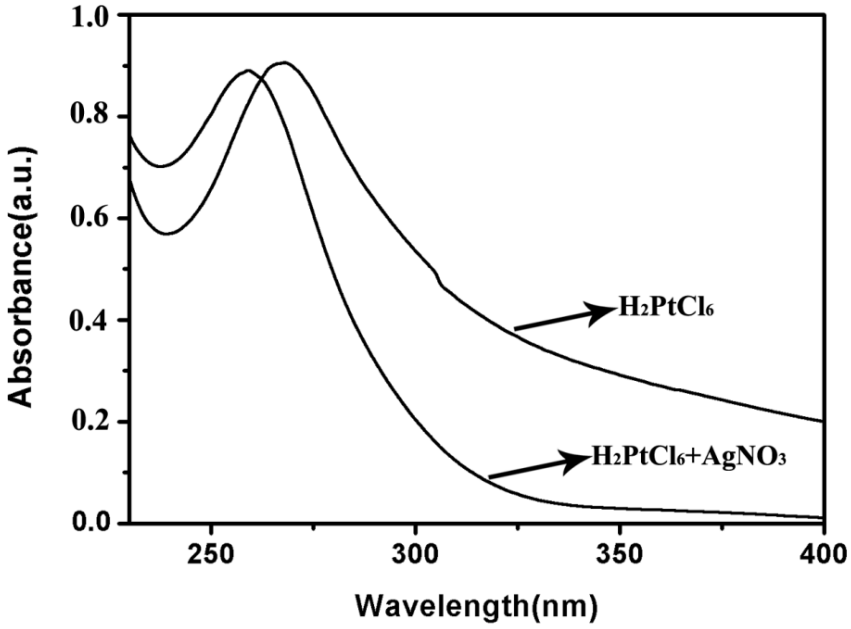

Fig. S9 UV-Vis spectra of H_2PtCl_6 aqueous solution and mixture (H_2PtCl_6 and $AgNO_3$).