## Synthesis of octahedral Cu<sub>2</sub>O/Au nanocomposites

 $Cu_2O/Au$  nanocomposites were prepared as a comparison experiment. 10 mg of  $Cu_2O$  octahedral was dispersed in 20mL of distilled water under ultrasonication for 10min. After that, 0.1g of Polyvinyl pyrrolidone (PVP) was dissolved in the suspension liquid under magnetic stirring. Soon after, different amounts of HAuCl<sub>4</sub> solution was added dropwise and stirred for 1 h. The final black products were washed with distilled water and absolute ethanol.



Figure S1 SEM images of the obtained Cu<sub>2</sub>O/Au nanocomposites under different counts of HAuCl<sub>4</sub> solution (24 mM): (a) 100μL, (b) 200μL, (c) 300μL, (d) 500μL, (e) 1 mL and (f) 1.5 mL. The bar is 500 nm.



Figure S2 SEM images of the obtained Ni-introduced CuAu nanocages under different counts of Ni<sup>2+</sup>: (a) 0.01 mmol, (b) 0.02 mmol, (c) 0.03 mmol and (d) 0.04 mmol. The bar is 500 nm.

The UV-vis spectra of the as-synthesized nanostructures were shown **Figure S3**. Pure octahedral Cu<sub>2</sub>O have multiple absorption bands at ~530 nm, ~600 nm and near-infrared regions ~750 nm, which is attributed to the absorption and light scattering of Cu<sub>2</sub>O nanocages, and the positions of these absorption band are in close agreement with the Cu<sub>2</sub>O polyhedron with large size in the previous reports<sup>1-2</sup>. After the AuCl<sub>4</sub>-

was added, the absorption bands appeared at ~575 nm and red shift at ~830 nm can be attributed to the plasmon resonance of the Au nanoparticles<sup>3-4</sup>. The UV-vis spectrum of as-obtained Ni-introduced CuAu nanocages was also shown, a new broad absorption band appeared at ~600 nm corresponding to the plasma resonance absorption of Cu nanoparticles<sup>5-6</sup>, and since the Cu and Ni nanoparticles were covered the Au nanoparticles, the absorption bands of Au became very weak. The whole UV-vis spectra also verify the formation process of products.



Figure S3 The UV-vis spectra of as-prepared products.

The SEM, EDS analysis and element mapping of Ni-introduced CuAu nanocages under minimum and maximum Ni<sup>2+</sup>/AuCl<sub>4</sub><sup>-</sup> were also shown. **Figure S4** depict the characterization of two products under different amount of Ni<sup>2+</sup> and AuCl<sub>4</sub><sup>-</sup> (0.01 mmol Ni<sup>2+</sup> and 500  $\mu$ L of AuCl<sub>4</sub><sup>-</sup>, 0.04 mmol of Ni<sup>2+</sup> and 100  $\mu$ L of AuCl<sub>4</sub><sup>-</sup>, respectively ). As shown, the octahedral morphology of two products were still retained, the EDS analysis and element mapping clearly confirm that the content of Ni<sup>2+</sup> and AuCl<sub>4</sub><sup>-</sup> is different. From EDS analysis, the atomic proportions of Ni vs Au are about 0.84:3.68 and 17.88:1.05, respectively. Thus, the metallic atomic proportions of products can be general adjusted easily by controlling mass of Ni<sup>2+</sup> and AuCl<sub>4</sub><sup>-</sup>.



Figure S4 The characterization of products under 0.01 mmol Ni<sup>2+</sup> and 500 μL of AuCl<sub>4</sub><sup>-</sup> (a) SEM, (b) EDS analysis and (c) element mapping. The characterization of products under 0.04 mmol of Ni<sup>2+</sup> and 100 μL of AuCl<sub>4</sub><sup>-</sup> (d) SEM, (e) EDS analysis and (f) element mapping.

The corresponding contrast experiments of the catalytic activity under different productswere are displayed in **Figure S5**. As shown, the initial octahedral Cu<sub>2</sub>O templates also have certain catalytic activity for the reduction of H<sub>2</sub>O<sub>2</sub>, but the catalytic activity of Cu<sub>2</sub>O/Au nanocomposites is superior than pure Cu<sub>2</sub>O templates, which can be attributed to the presence of Au. Compared with Cu<sub>2</sub>O/Au nanostructures, the catalytic activity of CuAu is better, which can be attributed to the formation of Cu. In addition, judge from the peak intensity at 652nm after 15 min, the catalytic activity of as prepared products without Ni<sup>2+</sup> is closely to Ni-introduced CuAu nanocages. Thus, in our opinion, Cu and Au in products act as main active sites for the reduction of H<sub>2</sub>O<sub>2</sub>, and Ni element in products mainly provides magnetism for the cyclic utilization of catalyst.



Figure S5 (a) UV-Vis absorption spectra of the octahedral Cu<sub>2</sub>O templates-H<sub>2</sub>O<sub>2</sub>-TMB system at various reaction times. (b) UV-Vis absorption spectra of the CuAu-H<sub>2</sub>O<sub>2</sub>-TMB system at various reaction times. (c) Performance comparison of different reaction systems at various reaction times. (d) Histogram of the peak intensity at 652 nm of different reaction systems after 15 min.

## Reference

1. C. H. Kuo, C. H. Chen and M. H. Huang, Adv. Funct. Mater., 2007, 17, 3773-3780.

2. X. W. Liu, RSC Adv., 2011, 1, 1119–1125.

3. M. Pang, Q. Wang and H. C. Zeng, Chem. - Eur. J., 2012, 18, 14605-14609.

4. H. Zhu, M. L. Du, D. L. Yu, Y. Wang, M. L. Zou, C. S. Xu and Y. Q. Fu, *Dalton Trans.*, 2012, **41**, 13795-13799.

5. Y. Zhao, J. J. Zhu, J. M. Hong, N. Bian and H. Y. Chen, Eur. J. Inorg. Chem., 2004, 4072-4080.

6. S. H.Wu and D. H. Chen, J. Colloid Interface Sci., 2004, 273, 165-169.