## **Supporting Information**

# Ligand-Manipulated Selective Transformations of Au–Ni Bimetallic Heteronanostructures in an Organic Medium

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## Part I. Experimental details

## Materials:

All purchased chemical reagents, including HAuCl<sub>4</sub>·4H<sub>2</sub>O, AuCl<sub>3</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, ODA (octadecylamine), OA (oleylamine), DDAB (didodecyldimethylammonium bromide), tetrabutylammonium borohydride (TBAB), ethanol, toluene and cyclohexane were of analytical grade and were used without further purification. HAuCl<sub>4</sub>.4H<sub>2</sub>O was purchased from Sinopharm chemical reagent Co., Ltd.; OA was obtained from Acros Organics Ltd.; TBAB, DDAB and AuCl<sub>3</sub> were purchased from Aladdine Reagent Inc. All other chemicals were purchased from the Beijing Chemical Factory.

**Preparation of Au-Ni spindly colloids**<sup>1</sup>: In a typical synthesis, 0.05 g of AuCl<sub>3</sub> and 0.25 g of Ni(NO<sub>3</sub>)<sub>2</sub>· $6H_2O$  were added into 10 ml of ODA at 120 °C and the solution turned to red within 1 min. Then, the system was heated to 220 °C and the color began to turn black. The solution was kept for 10 min with stirring at 220 °C. After twice centrifugation and washing with ethanol, the Au-Ni spindly nanoparticles were obtained. Finally, the

Au-Ninanoparticles were evenly dispersed in 50 ml cyclohexane under ultrasonication.

Preparation of OA-containing Au<sup>3+</sup> precursor: 41 mg of HAuCl<sub>4</sub>·4H<sub>2</sub>O was dissolved in 10 ml of OA solution

(100 mM, in toluene) under ultrasonic.

Preparation of DDAB-containing Au<sup>3+</sup> precursor: 41 mg of HAuCl<sub>4</sub>·4H<sub>2</sub>O was dissolved in 10 ml of DDAB

solution (100 mM, in toluene) under ultrasonic.

**Transformation reaction of Au-Ni nanostructures in OA-containing Au<sup>3+</sup> system:** 200  $\mu$ Lof Au-Ni colloids were mixed with 100, 150, 200 and 300 $\mu$ L of OA-containing Au<sup>3+</sup> precursor, respectively. All solutions were sealed and placed in oven for 180 min at 70 °C.

**Transformation reaction of Au-Ni nanostructures in DDAB-containing Au<sup>3+</sup> system:** 200  $\mu$ L of Au-Ni colloids solution were mixed with 25, 50, 100 and 125 $\mu$ L of DDAB-containing respectively. All solutions were sealed and placed in oven for 3 min at 70 °C.

The transformation reaction conditions were schemed in Table 1.

Volume of Au-Ni colloids	200 μL				Reaction condition
Volume of OA-containing HAuCl <sub>4</sub> .4H <sub>2</sub> O solution (10mM; Au: OA = 1:10)	100 µL	150 µL	200 µL	300 µL	70 °C, 180 min
Volume of DDAB-containing HAuCl <sub>4</sub> .4H <sub>2</sub> O solution (10mM; Au: DDAB = 1:10)	25 μL	50 µL	100 µL	125 µL	70 °C, 3 min

Table 1: Scheme of detailed transformation reaction conditions

**Preparation of Au colloids<sup>2</sup>:** 10 mg of HAuCl<sub>4</sub>·4H<sub>2</sub>O and 43mg of decanoic acid were dissolved in 2.5 mL of DDAB solution (100 mM, DDAB in toluene). Then 1ml TBAB solution (25 mg of TBAB dissolved in 1 ml DDAB) was injected during vigorous stirring. The solution color changed to deep red within one minute, indicating particle formation. The as-obtained Au nanoparticles were stable and could be kept for more than 24 hours. The purification of Au nanoparticles was carried out by precipitation with ethanol followed by redispersion in 12 ml cyclohexane. Approximately,  $[Au^0] = 2.03$  mM was estimated.

**Reaction between Au colloids and OA-containing Au<sup>3+</sup> precursor:** 200  $\mu$ L of Au colloids were mixed with of 25, 50 and 100  $\mu$ Lof OA-containing Au<sup>3+</sup> precursor, respectively. All solutions were sealed and placed in oven for 180 min at 70 °C.

**Reaction between Au colloids and DDAB-containing Au<sup>3+</sup> precursor:** 200  $\mu$ L of Au colloids were mixed with 10, 15 and 25  $\mu$ L of DDAB-containing Au<sup>3+</sup> precursor, respectively. All solutions were sealed and placed in oven for 3 min at 70 °C.

**Reaction between Au colloids and DDAB solution:** 200  $\mu$ L of Au colloids were mixed with 25, 50 and 100  $\mu$ L of DDAB solution (100 mM, dissolved in toluene), respectively. All solutions were sealed and placed in oven for 3 min at 70 °C.

The products of the above three reactions were dissolved in equal volume of cyclohexane to characterize UV-Vis spectroscopy.

## Stoichiochemistry Investigation on Conproportionation Reaction betweenAu<sup>3+</sup> and Au<sup>0</sup>

We assumed that all the Au<sup>3+</sup>precursors (10 mg HAuCl<sub>4</sub>·4H<sub>2</sub>O) were reduced when fabricating Au colloids and  $[Au^{0}] = 2.03$  mM was estimated. When 15 µL of DDAB-Au<sup>3+</sup> was added to titrate Au<sup>0</sup>, the Au colloids was almost bleached while25 µL of DDAB-Au<sup>3+</sup> made the solution totally bleached. So the maximum and minimum dosage of DDAB-Au<sup>3+</sup> were used to estimate a proper range of the Au<sup>3+</sup>: Au<sup>0</sup> and 1±0.3: 2 could be obtained, which coincide with the stoichiometric ratio of Au<sup>3+</sup>:Au<sup>0</sup> in the conproportionation reaction.

## Proof of Dissolving NiO in OA-containing HAuCl<sub>4</sub> Solution

NiO colloids were prepared following a reported work<sup>3</sup>. In a typical synthesis, 1 g of Ni  $(NO_3)_2 \cdot 6H_2O$  was added to 10 mL octadecylamine at 180 °C. After 10 min of magnetic stirring, the NiO nanocrystals were collected and washed with ethanol. The sediments were evenly redispersed in 120 mL cyclohexane under ultrasonication.

Dissolve of NiO colloids in OA-containing HAuCl<sub>4</sub> solution: 200  $\mu$ L of brown NiO colloids ([Ni]=28.6 mM) were suspended in 1 mL of OA-containing HAuCl<sub>4</sub> ([Au<sup>3+</sup>]=10 mM) precursor. The solutions were sealed and placed in oven for 180 min at 70 °C. After added equal volume of ethanol, the suspension was centrifuged to remove the nanoparticles, and the green supernatant liquor was characterized by UV-Vis spectroscopy (Figure S9).

## **Characterization:**

**UV-Vis Spectroscopy:** UV-Vis characterization was performed in transmission mode on a UV-2501PC Shimadzu UV-Vis-NIR spectrometer over the range 800 to 300 nm. Measurements were typically performed on the fractions in a 2 mm path length quartz cuvette.

**Transmission electron microscopy:** A transmission electron microscope, (Hitachi H-800, operated at 200 kV), was used for characterization of particle size and shape evaluation. Samples were directly dried on carbon film supported on copper grids for TEM characterization. High-resolution transmission electron microscopy images were taken on a JEOL JEM-3010 microscope operated at 300 kV.EDS were also measured with a JEOL JEM-3010 microscope operated at 300 kV.EDS were measured with a FEI Titan 80–300 instrument operating at 300 kV.

Part II. Supplementary Figures



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100 nm HV=200.0kV Direct Mag: 100000x

Figure S1: TEM images of original Au-Ni spindly nanostructure.



Figure S2: Large area TEM images of samples after (A) 100, (B) 150, (C) 200 and (D) 300 µL of OA-containing

HAuCl<sub>4</sub>.4H<sub>2</sub>O solution added to 200 µL of Au-Ni colloids



Figure S3: Large area TEM images of samples after (A) 25, (B) 50, (C) 100 and (D) 125  $\mu$ L of DDAB-containing HAuCl<sub>4</sub>.4H<sub>2</sub>O solution added to 200  $\mu$ L of Au-Ni colloids.



Figure S4: A) HRTEM image of Au-Ni spindly nanostructure after reaction with OA-containing HAuCl<sub>4</sub>.4H<sub>2</sub>O

solution. B-C) Enlarged images of corresponding areas in A).



Figure S5: A) HRTEM image of Au-Ni spindly nanostructure after reaction with 25 µL of DDAB-containing HAuCl<sub>4</sub>.4H<sub>2</sub>O solution. B-C) Energy dispersive X-ray spectroscopy (EDS) of regions marked in (A).



Figure S6: A) HRTEM image of Au-Ni spindly nanostructure after reaction with 50 µL of DDAB-containing HAuCl<sub>4</sub>.4H<sub>2</sub>O solution. B) Enlarged images of corresponding areas in A). C) Energy dispersive X-ray spectroscopy (EDS).



Figure S7: A) HRTEM image of Au-Ni spindly nanostructure after reaction with 100 μL of DDAB-containing HAuCl<sub>4</sub>.4H<sub>2</sub>O solution. B-C) Energy dispersive X-ray spectroscopy (EDS) of regions marked in (E).



Figure S8: A) HRTEM image of Au-Ni spindly nanostructure after reaction with 125 µL of DDAB-containing HAuCl<sub>4</sub>.4H<sub>2</sub>O solution. B) Enlarged images of corresponding areas in A). C) Larger area HRTEM image. E) Energy dispersive X-ray spectroscopy (EDS).



Figure S9: UV–Vis absorption spectra (inset: digital photo) of supernatant liquor NiO colloid after reaction with 1 mL of OA-containing HAuCl<sub>4</sub>.4H<sub>2</sub>O precursor solution.



Figure S10: A) UV–visible absorption spectra (the inset: shows digital photos) of colloidal Au solution after reaction with 25, 50 and 100  $\mu$ L of OA-containing HAuCl<sub>4</sub>.4H<sub>2</sub>O solution. B) UV–visible absorption spectra (the inset shows digital photos) of colloidal Au solution after reaction with 10, 15 and 25  $\mu$ L of DDAB-containing HAuCl<sub>4</sub>.4H<sub>2</sub>O solution.



Figure S11. UV-Vis spectroscopy of HAuCl<sub>4</sub> dispersed in DDAB, OA and water



Figure S12: A) TEM image and B) corresponding selected area electron diffraction (SAED) of Au colloid after reaction with 25 µL of DDAB-containing HAuCl<sub>4</sub>.4H<sub>2</sub>O solution. C) Selected area electron diffraction (SAED) pattern and corresponding lattice plane of tetragonal AuBr crystal



Figure S13: UV-Vis absorption spectra (inset: digital photo) of Au colloid before and after reaction with 15, 25 and

50 µL of DDAB solution.



Figure S14: UV–visible absorption spectra of Au–Ni nanostructures after reaction with A) 100, 150, 200 and 300  $\mu$ L of OA-containing HAuCl<sub>4</sub>.4H<sub>2</sub>O solution and B) 25, 50, 100 and 125  $\mu$ L of DDAB-containing HAuCl<sub>4</sub>.4H<sub>2</sub>O solution.

#### Reference

- 1. D. S. Wang and Y. D. Li, J. Am. Chem. Soc., 2010, **132**, 6280–6281.
- 2. N. R. Jana and X. G. Peng, J. Am. Chem. Soc., 2003, **125**, 14280-14281.
- 3. D. S. Wang, T. Xie, Q. Peng, S. Y. Zhang, J. Chen and Y. D. Li\*, *Chem. Eur. J.*, 2008, **14**, 2507 2513.