

---

# Facile synthesis of cubical $\text{Co}_3\text{O}_4$ supported Au nanocomposites with highly activity for the reduction of 4-nitrophenol to 4-aminophenol

Yuwen Yang<sup>a\*</sup>, Yongyun Mao<sup>a</sup>, Bin Wang<sup>b</sup>, Xianwei Meng<sup>a</sup>, Jiao Han<sup>a</sup>, Chuan Wang<sup>a</sup> and Hongwei Yang<sup>a\*</sup>

<sup>a</sup>State Key Laboratory of Advanced Technologies for Comprehensive Utilization of Platinum Metals, Kunming Institute of Precious Metals, Kunming, 650106, China. <sup>b</sup>State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing Tech. University, Nanjing, 210009, China.

\*E-mail: yywen@hotmail.com (Y. W. Yang), yhw@ipm.com.cn (H. W. Yang).

## Supplementary data

### Experimental details

#### Chemicals:

Cobalt chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , Sinopharm Chemical Reagent Co., Ltd.,  $\geq 99\%$ ), Polyvinylpyrrolidone (PVP, K30, Sinopharm Chemical Reagent Co., Ltd.), Potassium hydroxide (KOH, Sinopharm Chemical Reagent Co., Ltd., 85%), Potassium chlorate ( $\text{KClO}_3$ , Sinopharm Chemical Reagent Co., Ltd., 99.55%), 4-Nitrophenol (4-NP, Tianjin Zhiyuan Chemical Reagent Co., Ltd, AR, 99%), sodium borohydride ( $\text{NaBH}_4$ , Sinopharm Chemical Reagent Co., Ltd., 96%), Gold(III) chloride trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , Aldrich,  $\geq 99\%$ ). All chemical reagents were used as received without further purification. Ultrapure water with the specific resistance of 18.2  $\text{M}\Omega \text{ cm}$  was obtained by reversed osmosis followed by ion exchange and filtration.

#### Synthesis of cubical $\text{Co}_3\text{O}_4$ nanocrystals.

10 mmol  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and 50 mmol PVP were dissolved in 30 mL of distilled water to form a red solution (solution 1). 20 mmol KOH and 10 mmol  $\text{KClO}_3$  dissolved in 20 mL distilled water was added to solution 1 to make a blue suspension. After 30 min of stirring at room temperature, the greenish-blue suspension was aged at 393 K for 18 h in a Teflon-lined autoclave. The  $\text{Co}(\text{OH})_2$  thus obtained were centrifuged, washed first with

---

distilled water and then with ethanol, dried at 333 K for 12 h, and were finally calcined in air at 573 K for 2 h by raising the temperature at a rate of 373 K/h to produce cubical  $\text{Co}_3\text{O}_4$ .

### **Synthesis of cubical $\text{Co}_3\text{O}_4$ supported Au NPs nanocomposites.**

The cubical  $\text{Co}_3\text{O}_4$  supported Au NPs nanocomposites were prepared by the conventional impregnation method. The cubical  $\text{Co}_3\text{O}_4$  (78.7 mg) was dissolved in 10 ml of distilled water, then 2 mL of an aqueous solution of  $\text{HAuCl}_4$  (0.01 mol/L) was added into above solution, while the mixed solution was stirred vigorously for 12 h at room temperature. Then,  $\text{NaBH}_4$  (10 mg) was added as reducing agent into the above solution with magnetic stirring at room temperature. The resulting black product was Au/ $\text{Co}_3\text{O}_4$  (5 wt% of Au) NCs. The product obtained was further washed with anhydrous ethanol and water three times and eventually obtained by drying in vacuum oven at 313 K overnight.

### **Catalytic reduction of 4-nitrophenol**

4-NP was reduced by the following procedure: 40 mL of 0.1 mmol/L 4-NP aqueous solution was stirred with freshly prepared  $\text{NaBH}_4$  solution (0.0146 mol/L) resulting in the formation of deep yellow solution. Then 0.15 mg of Au/ $\text{Co}_3\text{O}_4$  (5 wt.% of Au) NCs was added into the yellow solution. The initial molar ratio of 4-NP/ $\text{NaBH}_4$  is 1/146. As the reaction proceeded, the color of the solution changed gradually from yellow to colorless at room temperature. UV-Vis spectra were recorded at short intervals to monitor the progress of the reaction. The intensity of the absorption peak at 400 nm for 4-NP was monitored by UV-vis spectroscopy along with time. The catalyst was separated by centrifugation after monitoring the whole reduction process, washed several times with water and ethanol, respectively, and then reused.

### **Catalyst characterization**

The powder X-ray diffraction (XRD) was performed on a Rigaku RINT-22005 X-ray diffractometer with a Cu  $K\alpha$  source (40 kV, 20 mA). Transmission electron microscope (TEM, G2 TF30) for the detailed microstructure and composition analyses, and the amorphous carbon coated copper grids were used as the sample support. The atomic structures of samples were examined using an FEI TITAN Cs-corrected ChemiSTEM, operating at 80-200 kV. This instrument incorporates the functions of spherical aberration corrector and ChemiSTEM technology. A probe-corrector aids in achieving a resolution up to 0.08 nm for the HAADF-STEM image. The chemical compositions with atomic resolution were determined by ChemiSTEM EDX technology. The Au content in Au/ $\text{Co}_3\text{O}_4$  NCs is

---

measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALABMKLL X-ray photoelectron spectrometer with Al K $\alpha$  radiation. Hydrogen temperature programmed reduction (H<sub>2</sub>-TPR) experiments were carried out on a Micromeritics AutoChem II 2920 automated catalyst characterization system. The UV–vis absorption spectra were recorded by UV-vis spectrophotometer (UV-vis, TU-1901) from the scale range of 250–550 nm.

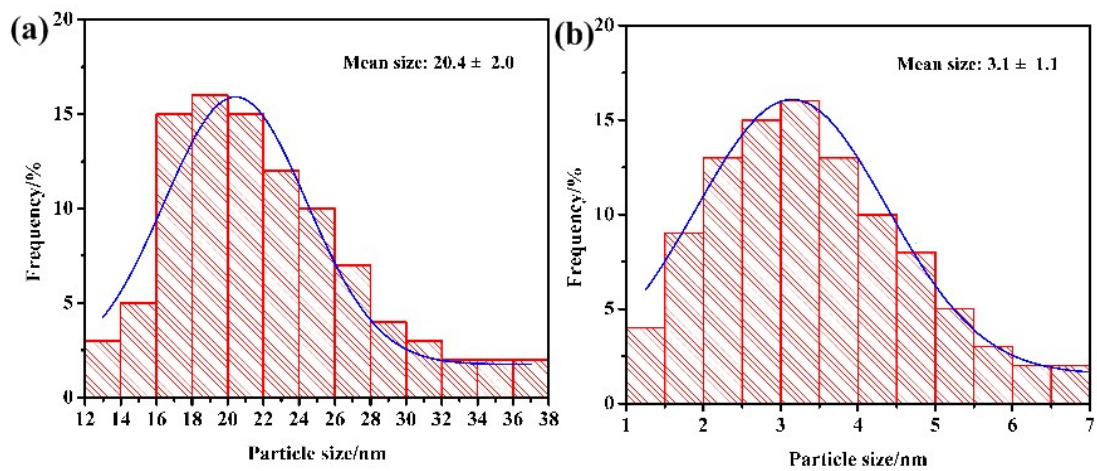


Fig. S1. Particle size distribution for the (a)  $\text{Co}_3\text{O}_4$  and (b)  $\text{Au}/\text{Co}_3\text{O}_4$ .

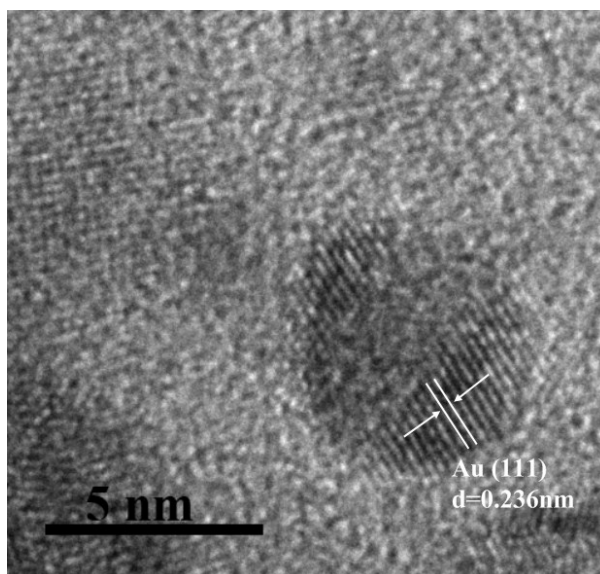
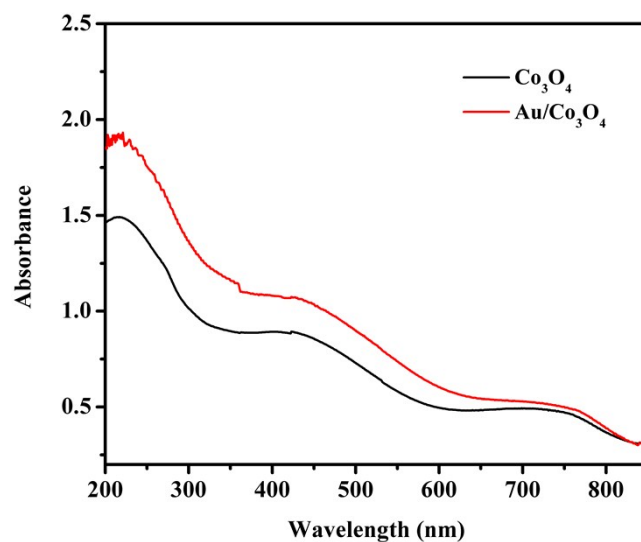
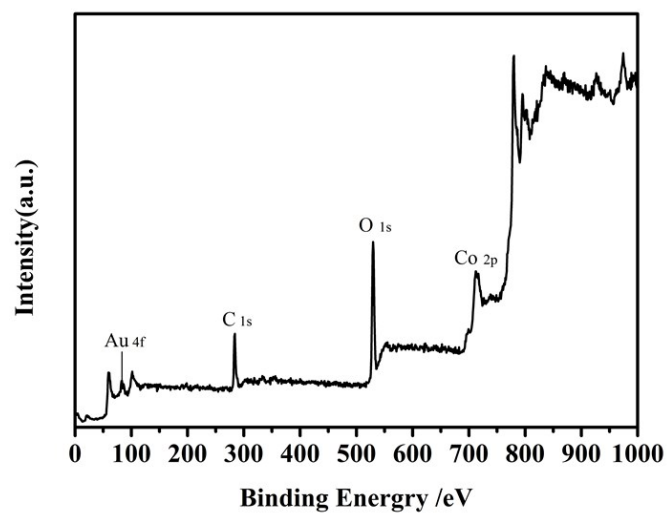


Fig. S2. HRTEM image of  $\text{Au}/\text{Co}_3\text{O}_4$ .

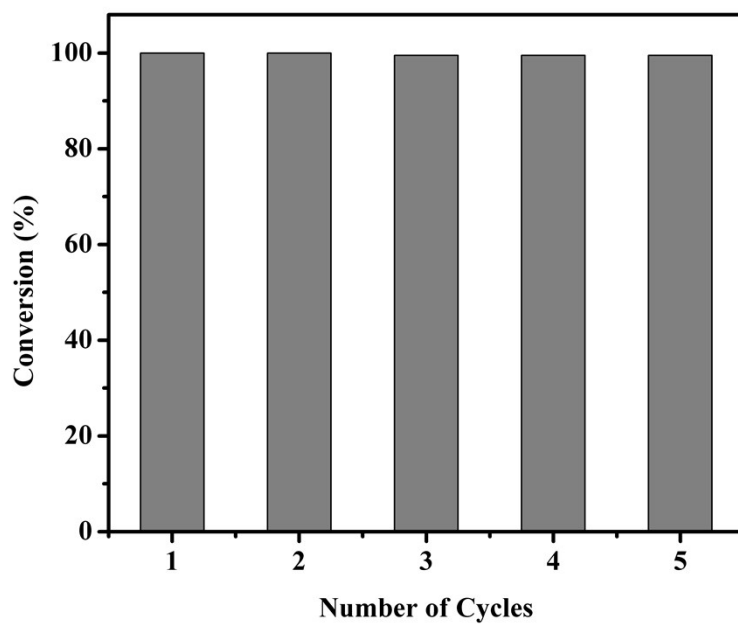


**Fig. S3.** UV-vis spectra of  $\text{Co}_3\text{O}_4$  and  $\text{Au/Co}_3\text{O}_4$ .

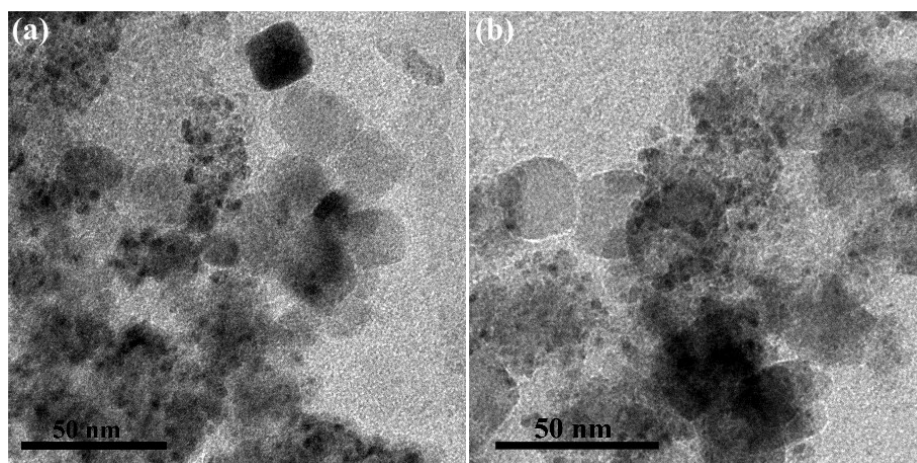
The optical absorption behaviors of  $\text{Co}_3\text{O}_4$  and  $\text{Au/Co}_3\text{O}_4$  are characterized by UV-vis spectra (Fig. S3), there is no obvious change between  $\text{Co}_3\text{O}_4$  and  $\text{Au/Co}_3\text{O}_4$ .



**Fig. S4.** X-ray photoelectron (XPS) spectrum survey scan of  $\text{Au/Co}_3\text{O}_4$  NCs.



**Fig. S5.** The reusability of Au/Co<sub>3</sub>O<sub>4</sub> NCs as a catalyst for the reduction of 4-NP.



**Fig. S6.** (a-b) TEM images of Au/Co<sub>3</sub>O<sub>4</sub> before and after 5 runs.