Electronic Supplementary Information (ESI) for:

## Facile synthesis of chain-like CoCu bimetallic nanomaterial and its catalytic property

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## **Experimental section**

**Reagents** Cobalt chloride, trisodium citrate dehydrate, cupric chloride were purchased from Beijing chemical reagent Ltd and used without further treatment. Sodium borohydride (NaBH<sub>4</sub>, 99%) was purchased from Aldrich. All chemicals were of analytical reagent grade and used as received. Water used for preparation of aqueous solutions was purified using a Millipore-Q water purification system.

Synthesis of chain-like CoCu hollow nanoparticles (CHNs) Briefly, 50 mL of double-distilled H<sub>2</sub>O contain CoCl<sub>2</sub>·6H<sub>2</sub>O (0.7 mM) and trisodium citrate dehydrate (7 mM) was purged with N<sub>2</sub> for 30 min, and the solution was kept at 30 °C by a water bath. A freshly prepared solution of NaBH<sub>4</sub> (20 mL, 13mM) was then added quickly under mechanical stirring. After all of the NaBH<sub>4</sub> has been added, CuCl<sub>2</sub>·2H<sub>2</sub>O (20 ml, 2 mM) was added immediately. To avoid the oxidation of CoCu nanoparticles in the presence of atmospheric oxygen, N<sub>2</sub> is bubbled through the solution during the whole procedure. After 30 min, the product was collected by centrifugation, washed for several times.

Synthesis of Citrate-Stabilized Cu nanoparticles (CNs) In a typical procedure, 50 mL of double-distilled H<sub>2</sub>O contain CuCl<sub>2</sub>·2H<sub>2</sub>O (2 mM) and trisodium citrate dehydrate (7 mM) was purged with  $N_2$  for 30 min. A freshly prepared solution of NaBH<sub>4</sub> (20 mL, 13mM) was then added quickly under stirring. After all of the NaBH<sub>4</sub> has been added, the stirring was continued for 30 min. To avoid the oxidation of Cu nanoparticles in the presence of atmospheric oxygen,  $N_2$  is bubbled through the solution during the whole procedure. The product was collected by centrifugation, washed for several times.

**Apparatus** UV-vis detection was carried out on a Cary 50 UV–vis spectrophotometer (Varian, USA). TEM and HRTEM images were obtained with a TECNAI G2 high-resolution transmission electron microscope operating at 200 kV. X-ray diffraction (XRD) analysis was carried out on a D/Max 2500 V/PC X-ray diffractometer using Cu (40 kV, 30 mA) radiation. X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALAB-MKII 250 photoelectron spectrometer (VG Co.) with Al Ka X-ray radiation as the X-ray source for excitation. The composition of chain-like CoCu bimetallic nanomaterial was determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, X Series 2, Thermo Scientific USA).

**Catalytic toward** *p***–nitrophenol** The aqueous solutions of *p*-nitrophenol (10 mM) and NaBH<sub>4</sub> (3 M) were freshly prepared. 2.5 mL of an aqueous solution containing 25  $\mu$ L CHNs was added into a quartz cuvette. Then, 25  $\mu$ L of the mixture containing 12.5  $\mu$ L *p*–nitrophenol solution and 12.5  $\mu$ L of NaBH<sub>4</sub> solution was injected into the cuvette to start the reaction, and the intensity of the absorption peak at 400 nm was monitored by UV-vis spectroscopy as a function of time. After each round of reaction,

another 25 µL of mixed aqueous solution was added to the reaction solution. This step

was repeated nine times to explore the stability of the catalysts.



Fig. S1 The typical TEM images of the as-prepared Co nanoparticles (A) and Cu nanoparticles (B).



Fig. S2 The  $C/C_0$  versus reaction time for the reduction of p-nitrophenol over CHNs after pre-treatment through initial introduction of NaBH<sub>4</sub>.



Fig. S3 The TEM image of the obtained sample after the first cycle for catalytic reduction of p-nitrophenol.



**Fig. S4** Photograph of aqueous dispersions of as-synthesized CHNs before (A) and after (B) under magnetic field.