

Polyamine-assisted hydrothermal synthesis of bimetallic Pd₁Cu₃ multipods and their high catalytic ability in 4-nitrophenol reduction

Xiaoyu Qiu,[‡] Ruopeng Zhao,[‡] Yanan Li, Yawen Tang,^{*} Dongmei Sun, Shaohua Wei,^{*} and Tianhong Lu

Jiangsu Key Laboratory of New Power Batteries, Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, China

[‡] *Both authors contributed equally to this work*

Experimental Details

Reagents and chemicals: Polyallylamine hydrochloride (PAH, weight-average molecular weight 15 0000) was supplied from Nitto Boseki Co., Ltd. (Tokyo, Japan). Palladium chloride (PdCl_2), cupric chloride (CuCl_2), formaldehyde solution (HCHO, 40%), 4-nitrophenol (4-NP), and sodium borohydride (NaBH_4) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Commercial Pd black was purchased from Johnson Matthey Corporation. Other reagents were of analytical reagent grade and used without further purification.

Synthesis of Pd_1Cu_3 -MNCs: In a typical synthesis, 0.33 mL of 50 mM PdCl_2 , 1.0 mL of 50 mM CuCl_2 , and 1.74 mL of 0.43 M PAH (molarity of PAH given with respect to the repeating unit) aqueous solutions were added to 6.0 mL water with continued stirring. After adjusting solution pH to 10.0, 0.5 mL of HCHO solution (40%) was added into the mixture solution and mechanically stirred for 10 min. Then, the mixture solution was transferred to a 20-mL Teflon-lined stainless-steel autoclave, and was then heated at 120 °C for 4 h. After being cooled to room temperature, the obtained Pd_1Cu_3 -MNCs were separated by centrifugation at 15000 rpm for 15 min, washed several times with water, and then dried at 60 °C for 5 h in a vacuum dryer.

Electrochemical measurement: All electrochemical experiments were performed on a CHI 660 C electrochemical analyzer (CH Instruments, Shanghai, Chenghua Co., Ltd.) at 30 ± 1 °C. A standard three-electrode system was used, which consisted of a platinum wire as the auxiliary electrode, a saturated calomel reference electrode (SCE), and a glassy carbon electrode as the working electrode.

Catalytic reduction of 4-nitrophenol (4-NP): Typically, 1.0 mL of 0.1 M NaBH_4 and 2 mL of 1.0×10^{-5} M 4-NP solutions were first put in a quartz cuvette having 1-cm path length. Then, 40 μL of Pd_1Cu_3 -MNCs aqueous solution (1.0 g L^{-1}) was added into the mixture solution. The reduction progress of 4-NP was then monitored by recording the time-dependent absorption UV-vis spectra of the reaction solution at a regular time interval of 3 min. For comparison, commercial Pd black was also used as heterogeneous catalyst for the reduction of 4-NP under same experimental conditions

(40 μL of 1.0 g L^{-1} Pd black aqueous solution).

Physical characterization: Transmission electron microscopy (TEM) measurements were made on a JEOL JEM-2100F transmission electron microscopy operated at an accelerating voltage of 200 kV. The composition of products was determined using the energy dispersive spectrum (EDX) techniques. X-ray diffraction (XRD) patterns of nanocrystals were obtained with Model D/max-rC X-ray diffractometer using Cu Ka radiation source ($\lambda=1.5406 \text{ \AA}$) and operating at 40 kV and 100 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo VG Scientific ESCALAB 250 spectrometer with a monochromatic Al Ka X-ray source (1486.6 eV photons). The binding energy was calibrated by means of the C1s peak energy of 284.6 eV. Ultraviolet-visible spectroscopy (UV-vis) measurements were performed on a Shimadzu UV3600 spectrophotometer at room temperature.

Figures

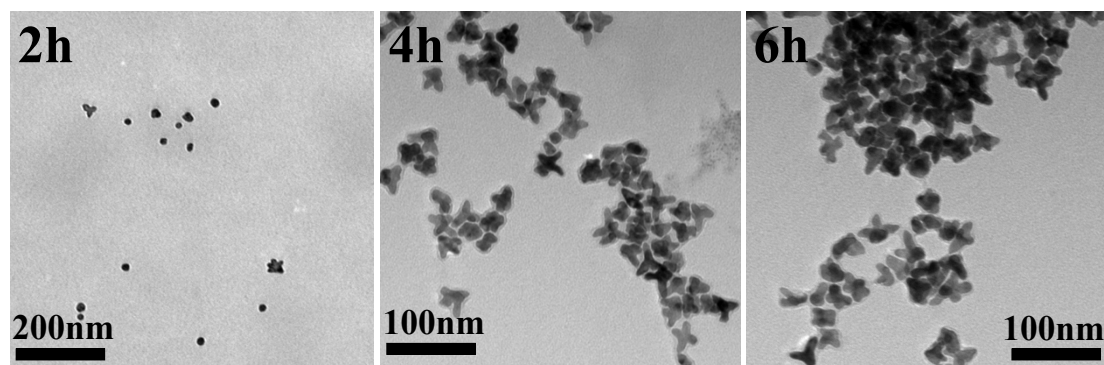


Fig. S1. TEM images of the Pd₁Cu₃-MNCs samples collected at 2, 4 and 6 h. TEM images show like-spheres Pd₁Cu₃ nanocrystals evolve into Pd₁Cu₃-MNCs at 4 h. And, the shape of Pd₁Cu₃-MNCs remains unchanged after 4 h.

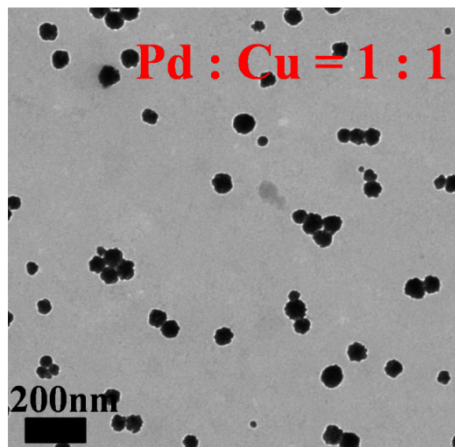


Fig. S2. TEM image of the Pd₁Cu₁ nanoflowers.

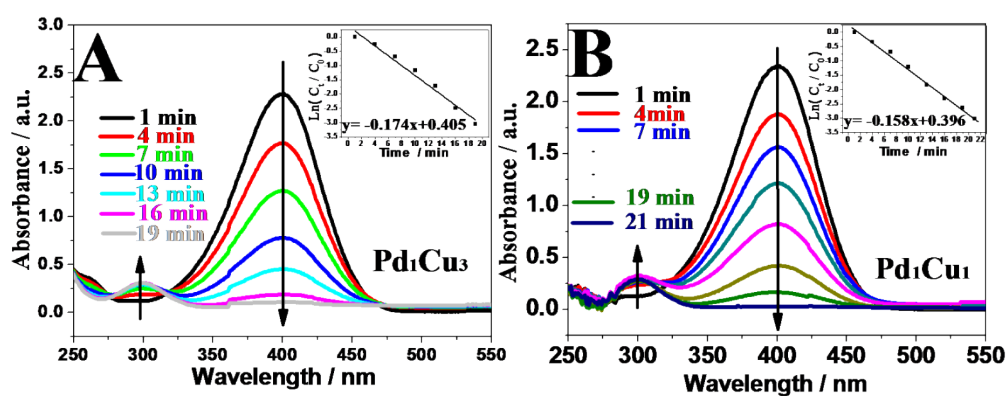


Fig. S3. UV-vis spectra for successive reduction of 4-NP with NaBH_4 using (A) Pd_1Cu_3 -MNCs and (B) Pd_1Cu_1 nanoflowers as catalysts at 3 min intervals. Inserts in A-B: the relationship between $\ln(C_t/C_0)$ and reaction time (t), where in the ratio of the 4-NP concentration (C_t at time t) to its initial value C_0 were directly given by the relative intensity of the respective absorbance A_t/A_0 .