Electronic Supplementary Information for

Folded-Up Thin Carbon Nanosheets Grown on Cu₂O Cubes for Improving Photocatalytic Activity

Denghui Jiang, *^{,a,b} Yuegang Zhang,^cand Xinheng Li*^{,a}

^aThe State Key Laboratory for Oxo Synthesis and Selective Oxidation, Suzhou

Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese

Academy of Sciences, Lanzhou 730000, China

^b Centre for Mineral Materials, School of Minerals Processing and Bioengineering,

Central South University, Changsha 410083, China

^c i-Lab, Suzhou Institute of Nano-tech and Nano-bionics, Chinese Academy of

Sciences, Suzhou 215123, China

Corresponding Author

*E-mail: xinhengli@licp.cas.cn; dhjiang@csu.edu.cn

MATERIALS AND METHODS

Synthesis of Cu₂O crystals

In this work, all of the chemical reagents used in this experiment were of analytical grade and used without further purification. Cu₂O cubes were prepared according to a previously reported method.¹ In a typical procedure, 10 mL of 2.0 M NaOH aqueous solution was added dropwisely to 100 mL of 0.01 M CuCl₂ aqueous solution at 55 °C. After stirring for 0.5 h, 10 mL of 0.6 M ascorbic acid aqueous solution was added dropwisely to the above solution. The mixture was kept at 55 °C with adequate stirring for 5 h, and the mixed solution had gradually become brick-red, indicating the formation of Cu₂O. After that, the brick-red products were collected by centrifugation, washed with distilled water and absolute ethanol several times each, and dried in a vacuum furnace at 60 °C for 6 h.

Synthesis of Au/C/Cu₂O

Typical Au/C/Cu₂O sample was synthesized as follows. A 43.3 mg sample of Cu₂O cubes were dispersed in to 30ml glucose aqueous solution (2.5mM) by sonication. Then, suspension was sealed into a PTFE vessel, and heated at 180 °C for 5 h. After the reaction, the products were collected, went through several rinse-centrifugation cycles with DI water and absolute ethanol separately, and then dried in a vacuum oven at 60°C for 5 h for further use. After that, 20 mg the products modified by carbon (C/Cu₂O) were dispersed into 3 mL distilled water by sonication. Then the suspension was irradiated with a 300 W Xe lamp (PLS-SXE300). Under continuous stirring, 2.0 mL of 0.125 g/L (0.25mg) HAuCl₄ solution were added to the above suspension, and the suspension was further irradiated for 1 h. After that, the products were collected by centrifugation, washed with distilled water and absolute ethanol several times each. The final products are denoted as Au/C/Cu₂O.

Synthesis of C/Au/Cu₂O

Typical C/Au/Cu₂O sample was synthesized as follows. A quantity of 43.3 mg of Au(0.25)/Cu₂O HCs were separately dispersed into 30 ml of 10mM glucose aqueous solution by sonication. Then, suspension was sealed into a PTFE vessel, and heated at 180 $^{\circ}$ C for 5 h. After the reaction, the products were collected, went through several rinse-centrifugation cycles with DI water and absolute ethanol separately, and then dried in a vacuum oven.

The Au(0.25)/Cu₂O were prepared according to our previously reported method.²

Characterizations

The X-ray diffraction(XRD) patterns of the products were measured by using a BRUKER D8 Discover diffractometer with Cu-K_{α} radiation (λ =0.15406 nm), and at a scanning rate of 0.02 deg/s in a 2 θ range from 20° to 80°. Scanning electron microscopy (SEM) images were obtained using a Hitachi S4800 SEM. Transmission electron microscopy (TEM) images were recorded on a FEI Tecnai G2 F20 S-TWIN microscope operating at 200 kV. Elemental analysis of the sample was conducted using an energy-dispersive X-ray analysis system attached to the TEM. An ultraviolet–visible light (UV–vis) spectrophotometer (PE Lambda 650s, Perkin-Elmer, USA) was used to perform optical measurements of the product.

Photocatalytic activity test

Photocatalytic studies were carried out as follows: 15 mg of catalyst sample was dispersed into a 50 mL of 2×10^{-5} M MO aqueous solution. The suspended solution was magnetically stirred in the darkness for 0.5 h to reach its adsorption/desorption equilibrium, and then it was irradiated with magnetic stirring in a water bath kept at 25 °C under a 300 W Xe lamp (PLS-SXE300, 150 mw/cm²) equipped with UV filter (cutoff wavelength of ~420 nm) from a distance of 15 cm. At a given time interval, 1 ml of dispersion was sampled, and centrifuged to separate the catalyst. Then the concentration of MO was tested by absorption spectra on a spectrophotometer (PE Lambda 650s).

Photoelectrochemical measurements

Photoelectrochemical measurements were conducted in a conventional three electrode cell by a computer-controlled electrochemical work station (Autolab PGSTAT204). 10 mg of the asobtained samples were mixed with 0.5 mL of 1% Nafion aqueous solution and ultrasonicated for 15 min. The obtained solution (0.1 ml) was dipped onto ITO glass (1 cm \times 2 cm) and dried in air. i-t curves were collected at 1.0 V vs SCE

Supplementary Figures:



Fig. S1 XRD pattern (A) of the C/Au/Cu₂O after 600° C heat treatment, and size distribution histograms (B) of carbon nanosheets of the as-obtained Au/C/Cu₂O.



Fig. S2 Energy dispersive spectra (EDS) of the as-obtained Au/C/Cu₂O, demonstrating the existence of Au on Cu₂O cubes.



Fig. S3 SEM images of $Au/C/Cu_2O$ prepared using different concentration of glucose: 1.25 mM (A) and 10 mM (B).



Fig. S4 SEM images of C/Cu₂O after being etched by NaCl solution under light irradiation (A) and pristine Cu₂O (B) as a contrast. Note: the concentration of Cl⁻ is the same as that of HAuCl₄.



Fig. S5 TEM images of C/Cu₂O (A), and TEM images with higher magnification (B) and (C) showing very thin carbon film and flaws such as cracks. Note that fragile part refers to those areas possibly damaged during sample processing.



Fig. S6 SEM images and size distribution histograms of Au nanoparticles of Au/Cu₂O (A and C) and C/Au/Cu₂O (B and D) after 600° C heat treatment.



Fig. S7 Photocatalytic cycling test of the obtained Au/C/Cu₂O (A), and SEM image of Au/C/Cu₂O after three cycles of photodegradation test (B).



Fig. S8 Photocatalytic degradation of MO (A) by Au/C/Cu₂O obtained by different concentration of glucose, and specific reaction rates (B) of sample C/Au/Cu₂O against cycle numbers.



Fig. S9 Long time dark adsorption tests of Cu₂O, Au/Cu₂O, Au/C/Cu₂O, and C/Au/Cu₂O.

	k	R ²	Standard Error
Au/Cu ₂ O	0.0226	0.9180	0.0036
C/Cu ₂ O/Cu ₂ O	0.0088	0.7822	0.0022
Au/C/Cu ₂ O	0.0605	0.9810	0.0042

Table S1 Data fitting using a Langmuir-Hinshelwood model and reaction rate constants for photodegradation of MO of different composites

References:

- D.-F. Zhang, H. Zhang, L. Guo, K. Zheng, X.-D. Han and Z. Zhang, J. Mater. Chem., 2009, 19, 5220-5225.
- D. Jiang, W. Zhou, X. Zhong, Y. Zhang and X. Li, ACS Appl. Mat. Interfaces, 2014, 6, 10958-10962.