

Supporting Information

For

Facile synthesis of graphene-wrapped ZnO nanospheres directly from cyanobacterial cells

Jiao He, Liang Jiang, Yongjuan Chen, Zhifang Luo, Zhiying Yan and Jiaqiang Wang*

School of Chemical Sciences & Technology, National Center for International

Research on Photoelectric and Energy Materials, Yunnan Provincial

Collaborative Innovation Center of Green Chemistry for Lignite Energy, Yunnan

Province Engineering Research Center of Photocatalytic Treatment of Industrial

Wastewater, The Universities' Center for Photocatalytic Treatment of Pollutants

in Yunnan Province, Yunnan University, Kunming 650091, China

Tel.: +86 871 65031567, Fax: +86 871 65031567

E-mail: jqwang@ynu.edu.cn (J. Wang)

Materials

The cyanobacteria (*Microcystis* sp.) cells were collected from Dianchi Lake (Kunming, Yunnan province) by filtering the water when algal grow vigorously. They were then washed with distilled water by centrifugation and immersed in 4% glutaraldehyde solution for storage at 4 °C. All chemicals were analytical pure and used without further purification.

Synthesis

Cya/ZnO: After washing by distilled water, about 15g of the cyanobacteria cells were transferred in a round bottom flask. Purified water dissolved with 1.0g of anhydrous zinc acetate and 5 mL triethanolamine were then added. The pH of the slurry was adjusted to 9.0 by aqua ammonia and the final volume is about 100 mL. The mixture was then refluxed at 90 °C for 3 hours, natural cooling and aged overnight ^[1]. The precipitates were thoroughly washed with purified water and ethanol for several times to remove unreacted reagents and dried in an oven at 90 °C.

Cya-ZnO: To remove the cyanobacterial cells in *Cya/ZnO* composites, *Cya/ZnO* was calcined in the air at 500 °C for 4 hours. The rate of rise in temperature is 1 °C/min.

Cya-G/ZnO: To carbonize the biomass from cyanobacterial cells in *Cya/ZnO* composites, a hydrothermal process was carried out in a 100 mL stainless steel vessel with Teflon liner. 80 mL of purified water was added and the vessel was treated at

180 °C with spontaneous pressure for 12 hours. After that, the product was collected and washed by water and dried in an oven at 90 °C. For synthesis of Cya-G/ZnO(10%) and Cya-G/ZnO(3%), all the processes were the same except the dosage of cyanobacteria cells used were reduced to 10% and 3% of 15g (1.5g and 0.45g, respectively).

Characterizations

Wide angle X-ray powder diffraction (XRD) experiments were conducted on a Rigaku TTRAX III spectrometer with Cu K α radiation from 10° to 80°. Optical microscopy images were taken on an Olympus IX73 inverted fluorescence microscope. Scanning electron microscopy (SEM) images were taken on a FEIQuanta200FEG microscope. Transmission electron microscopy (TEM) and HR-TEM micrographs were obtained using a JEM-2100 microscope. X-ray photoelectron spectroscopy (XPS) was recorded using a Thermo Fisher Scientific K-Alpha⁺ XPS system with Al K α radiation. UV-Vis diffuse reflectance spectra were measured on a Shimadzu UV-2600 photometer from 200 nm to 800 nm. FT-IR spectra of the samples were obtained on a Thermo Nicolet 8700 instrument. KBr pellets containing 0.5% of the samples were used and 32 scans were accumulated at a spectral resolution of 4 cm⁻¹. N₂ adsorption/desorption measurements were carried out on a Micromeritics Tristar II 3020 Analyzer. The samples were degassed at 90 °C for at least 3 hours prior to measurement. The measurements of zeta potential and size distribution were carried out on a Zetasizer Nano ZS analyser. The analysis

wavelength is 633nm.

Photoelectric performance test: Photocurrent response vs. time profiles of the samples were recorded using a CHI660E electrochemical workstation under 300W xenon lamp irradiations. Pt plate was used as counter electrode and standard calomel electrode was used as reference electrode. The electrolyte was a 0.2 M Na₂SO₄ solution. The working electrode was prepared on ITO conductive glass by dipping the sample slurry on it, and the exposed area of the electrode was 0.25 cm².

Reference:

[1] H. Zhou, T. Fan, D. Zhang, *Micropor. Mesopor. Mater.*, 2007, **100**, 322.

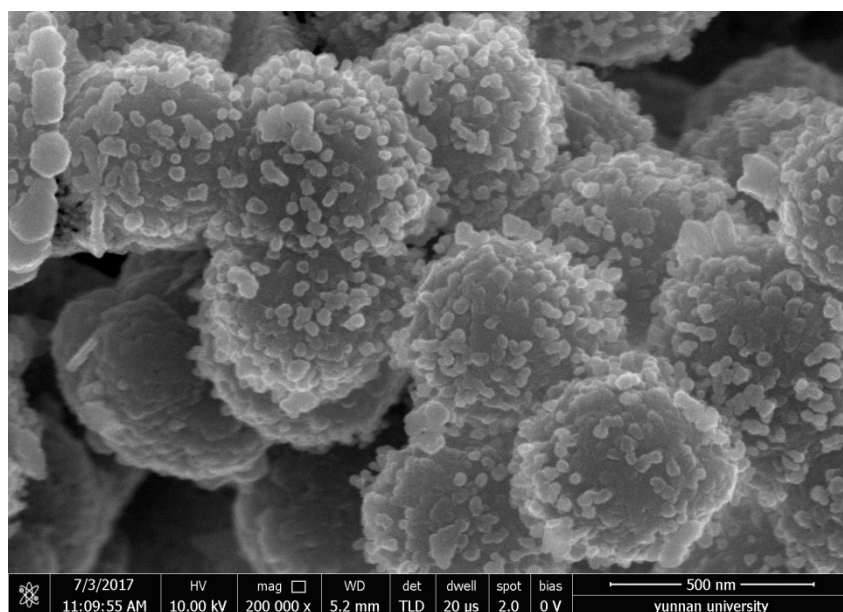


Fig. S1 SEM image of cyanobacteria templated ZnO (Cya-ZnO).

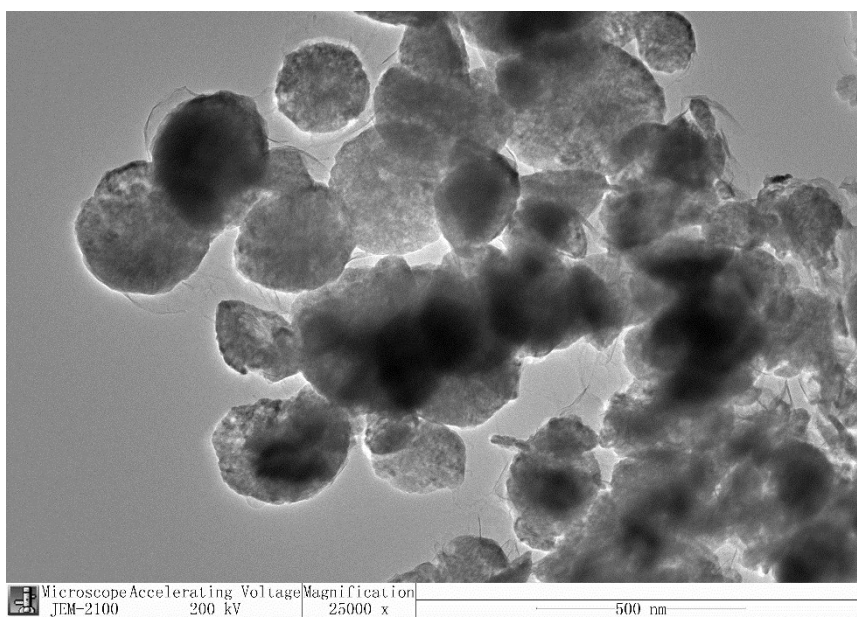


Fig. S2 TEM image of graphene wrapped ZnO nanospheres (Cya-G/ZnO).

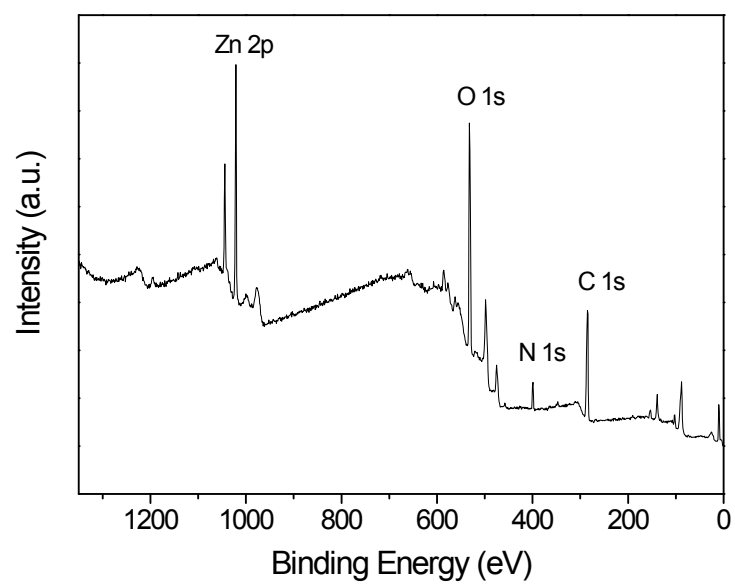


Fig. S3 Survey XPS spectrum of Cya/ZnO composite.

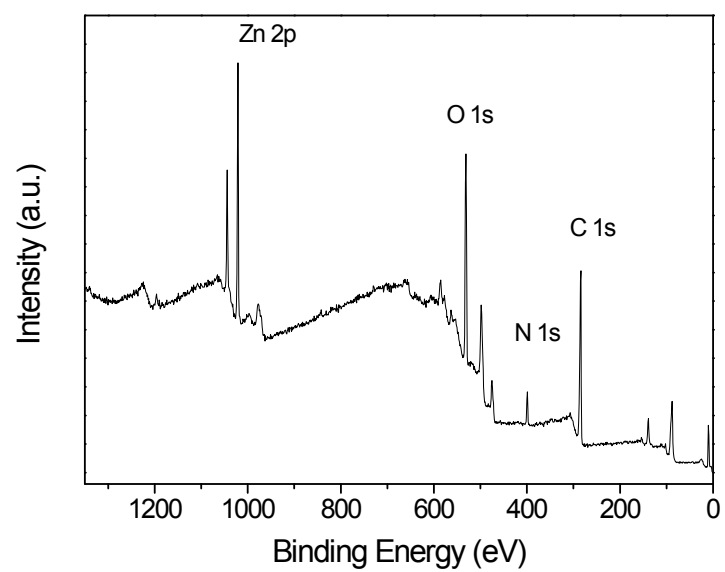


Fig. S4 Survey XPS spectrum of Cya-G/ZnO.

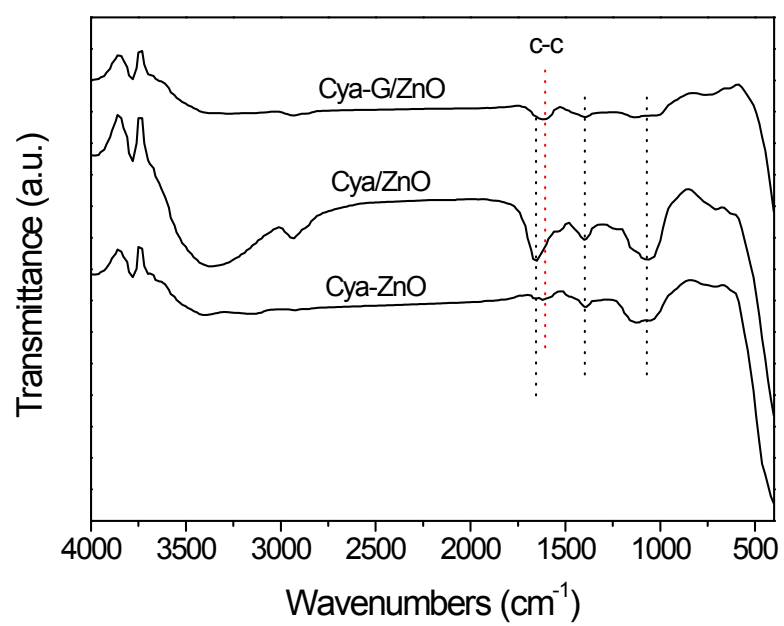


Fig. S5 FT-IR spectra of Cya-ZnO, Cya/ZnO and Cya-G/ZnO.

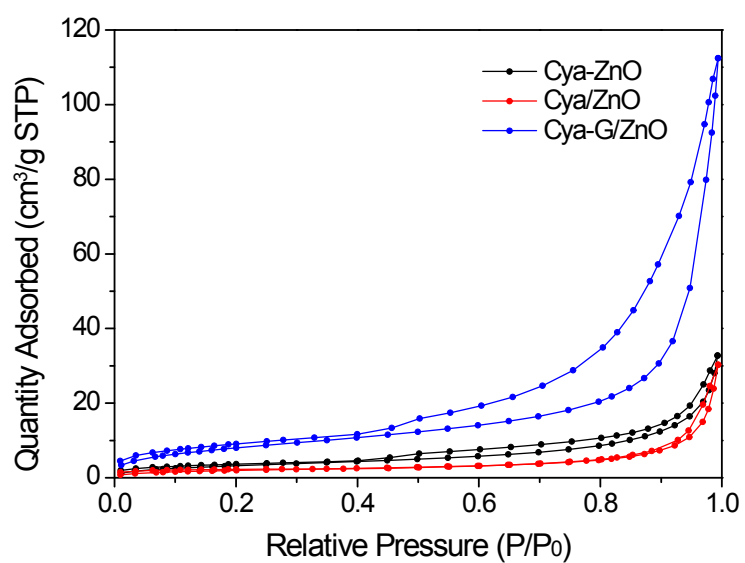


Fig. S6 N₂ adsorption/desorption isotherms of Cya-ZnO, Cya/ZnO and Cya-G/ZnO.

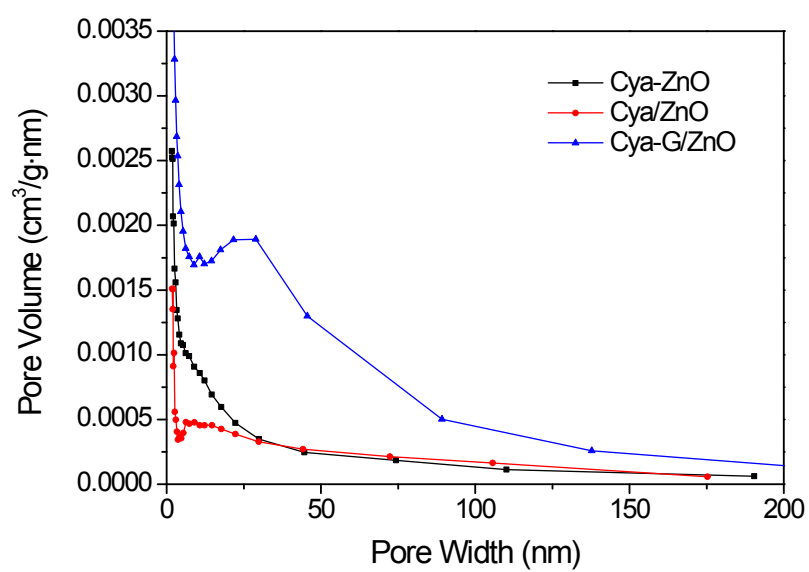


Fig. S7 BJH pore size distributions of Cya-ZnO, Cya/ZnO and Cya-G/ZnO.

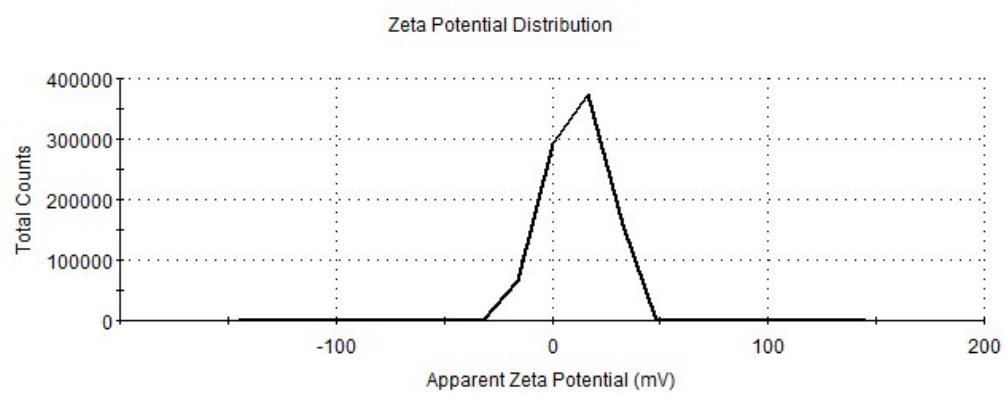


Fig. S8 Zeta potential distribution of Cya-G/ZnO.

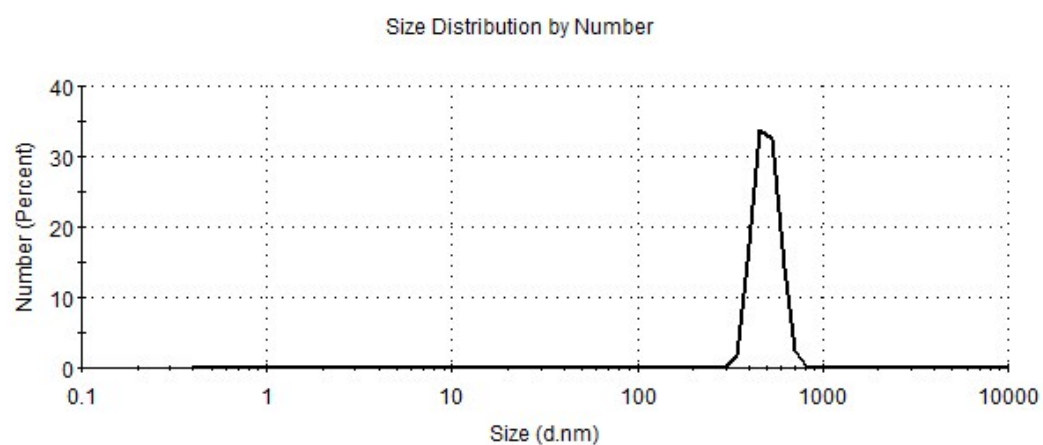


Fig. S9 Size distribution by number of Cya-G/ZnO.

Table S1. Surface area and pore structural properties of the samples.

	S_{BET} (m²/g)	Pore Volume (cm³/g)	Pore Size (nm)
Cya-ZnO	12.46	0.05	13.1
Cya/ZnO	7.57	0.05	27.67
Cya-G/ZnO	30.71	0.17	14.2