The opposite photocurrent response to ultraviolet and visible light

Shengxue Yang, Jian Gong,* and Yulin Deng*

Experimental Section

Materials. All used chemicals were of analytical grade. Aniline (Beijing Chemical Co.) was distilled twice under vacuum before use. $K_2S_2O_8$ was purchased from Beijing chemical factory as the oxidant without further purification. $H_4SiW_{12}O_{40}$ (SiW_{12}) as the dopant was synthesized and characterized according to the literature.[s1] Methylene chloride ($CHCl_3$), zinc acetate dehy-drate [$Zn(CH_3COO)_2$•$2H_2O$], zinc nitrate $Zn(NO_3)_2$•$6H_2O$ and hexamethylenetetramine (HMTA) were purchased from Beijing chemical factory without further purification. ([$RuL_2(NCS)_2$]:2TBA) (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid, TBA = tetra-n-butylammonium) (N-719) dye was purchased from Sigma-Aldrich Corporation without further purification.

Characterization. FT-IR spectrum was measured on an Alpha-Centauri 650 spectrometer with a KBr pellet. The frequency range was 4000-400 cm^{-1}. The XRD was measured with a D/max 2200 PC spectrometer with a Cu Kα source. Scans were made from 3 to 90 ° (2θ) at the speed of 2° min^{-1}. Scanning electron microscopy (SEM) images were obtained by using a XL-30 ESEM FEG scanning electron microscope operated at 20 KV with gold sputtered on samples. Electrochemical experiments were all performed with a CHI800B electrochemical workstation in a conventional three-electrode electrochemical cell. Indium tin oxide (ITO) substrate (3 cm × 1 cm) as work interface was pretreated before used. It was sonicated in ethanol for 15 min, followed by rinsing with water, and ultrasonic agitation in concentrated NaOH in a 1:1 (v/v) water/ethanol bath for 15 min. The ITO substrate was then rinsed further with ethanol and twice distilled water for 15 min under sonication, respectively, and dried with nitrogen stream. Spinning coatings were all performed with a Chemat Technology

Spin-coater KW-4A. Electrochemical experiments were all performed in a conventional three-electrode electrochemical cell.

Synthesis of PANI nanowebs and ZnO nanorods. Typically the interfacial reaction was performed in a 50 mL glass bottle, and the preparation process was similar to that of Huang and co-workers[s2]. A mixture of 3.28 g of $K_2S_2O_8$ and 5 g of $H_4SiW_{12}O_{40}$ was dissolved in 20 mL of distilled water under magnetic stirring in ice bath (Mixture 1). Next, 0.2 mL of aniline was dissolved in 20 mL of organic solvents (methylene chloride) under gentle magnetic stirring in ice bath (Mixture 2). The obtained liquid mixture 1 was carefully transferred to mixture 2 to form an interfacial system. We observed the immediate formation of an interface between the two liquids when oxidant and organic solution were combined in equal volumes. The polymerization took place under static conditions for 24 h at required temperatures (ca.0-5 ^{o}C). Finally, the green precipitate was filtered and washed with distilled water and ethanol several times until the filtrate became colorless and then dried in a vacuum at 50 ^{o}C for 24 h.

Vertically aligned ZnO nanorods were grown on ITO substrates via a hydrothermal method[s3]. Firstly, 0.01 M of zinc acetate dehydrate [$Zn(CH_3COO)_2{\bullet}2H_2O$] in ethanol was dropped onto a clean ITO substrates and spin coated at 3000 rpm for 60 s. This coating step was repeated three times followed by annealing at 350 ^{o}C for 30 min to yield a thin ZnO seed layer. The coating and annealing procedures were carried out twice to obtain a uniform coverage of ZnO seeds. Finally, hydrothermal growth was carried out at 85 ^{o}C for 4 h in sealed bottles with the substrates suspended in an aqueous solution containing 20 mM of zinc nitrate $Zn(NO_3)_2{\bullet}6H_2O$ and 20 mM of hexamethylenetetramine (HMTA).

Preparation of ZnO nanorods loading of N719 dye. The ITO glass supported of aligned ZnO nanorods was immersed in a $3{\times}10^4$ mM of ethanol solution of N719 dye for 24 h in dark, resulting in the sufficient adsorption of the N719 dye onto the ZnO nanorods. A dye-sensitized ZnO electrode was obtained.

Fabrication processes for the photodetector. The green color PANI precipitate prepared by the interfacial reaction was dispersed into the ethanol, then dropped onto the surface of the ITO with ZnO nanorods and Dye/ZnO nanorods, respectively, and spin coated at 3000 rpm for 60 s. This spin coating step was repeated three times before the two pieces of ITO were oppositely put together, and then dried at room temperature.

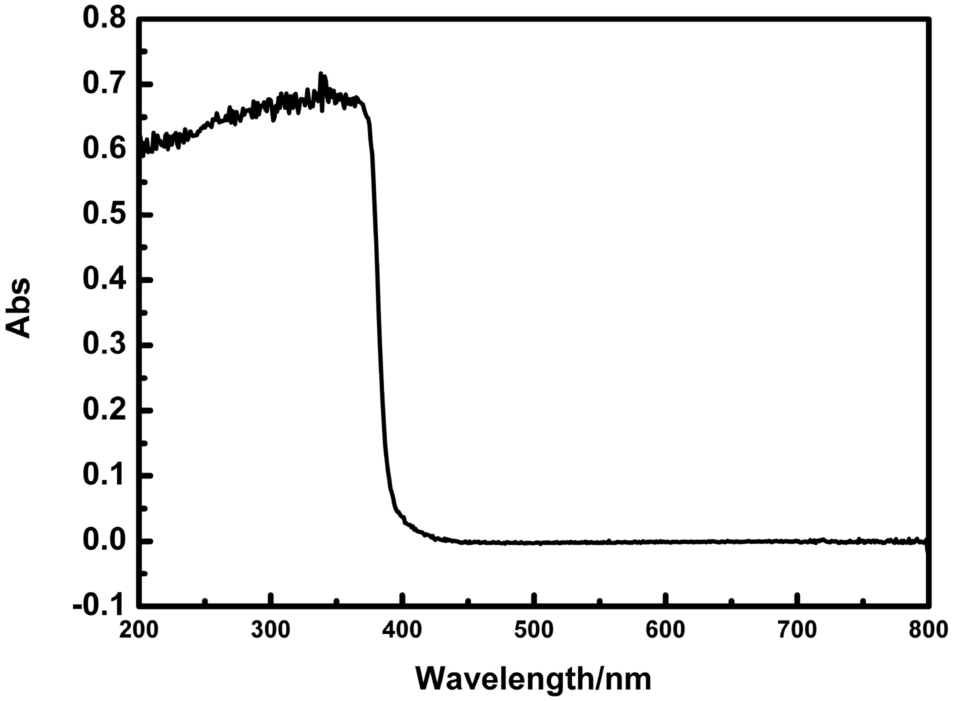


Figure S1 The UV-Vis light absorption spectrum of pure ZnO nanorods.

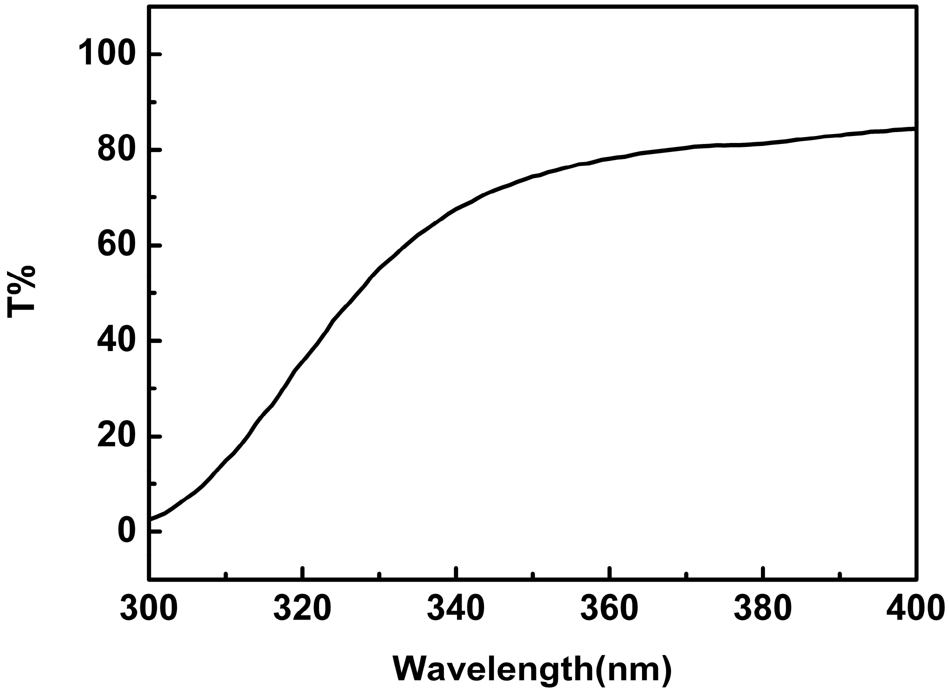


Figure S2 Transmittance of ITO glass under 365 nm UV light.

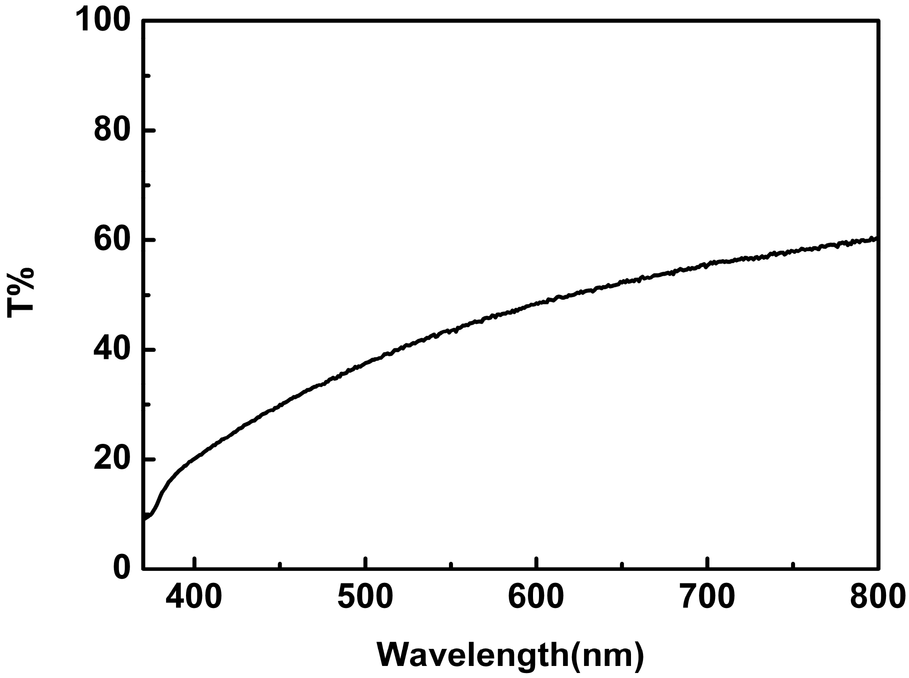
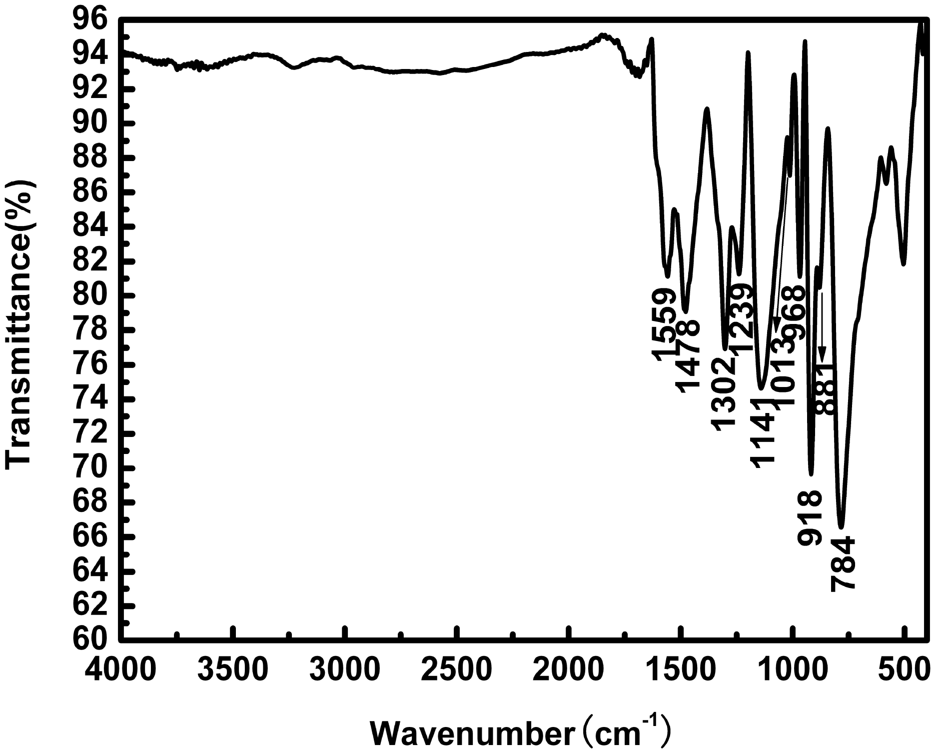


Figure S3 The transmittance of Vis light passed through the ZnO/PANI composite film measured by UV-Vis spectra.

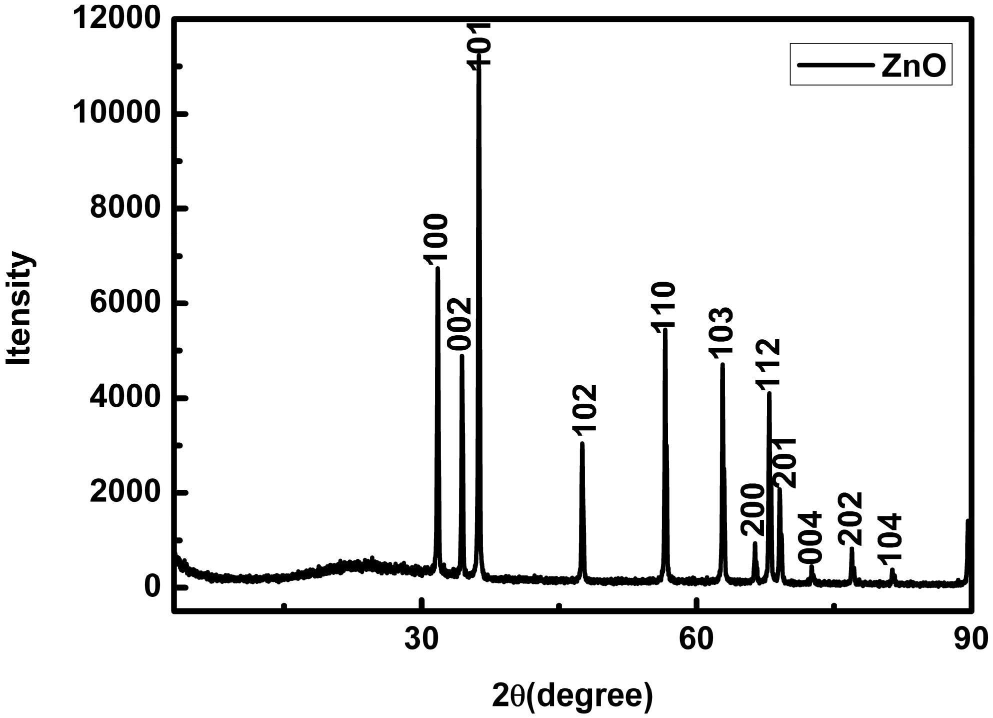
FT-IR spectra of the PANI.

The well-resolved peaks at about 1560 cm^{-1} and 1480 cm^{-1} correspond to the C=C stretching vibration of quinoid rings and benzene rings, respectively.[s4] The peak around 1300 cm^{-1} relates to the C–N stretching vibration with aromatic conjugation. The peak around 1140 cm^{-1} assigned to the characteristic of Q=NH^{+}–B absorption peaks (where Q and B denote quinoid ring and benzene ring, respectively) is also observed.[s5] Four characteristic peaks of $H_4SiW_{12}O_{40}$ (about 788 cm^{-1} ascribed to W–Oc–W, about 881 cm^{-1} ascribed to W–Ob–W, about 919 cm^{-1} ascribed to Si–Oa, and about 969 cm^{-1} ascribed to W=Od) attest to the presence of $H_4SiW_{12}O_{40}$ in the PANI. The appearance of these peaks indicates that PANI doped with $H_4SiW_{12}O_{40}$ has been synthesized.[s6]

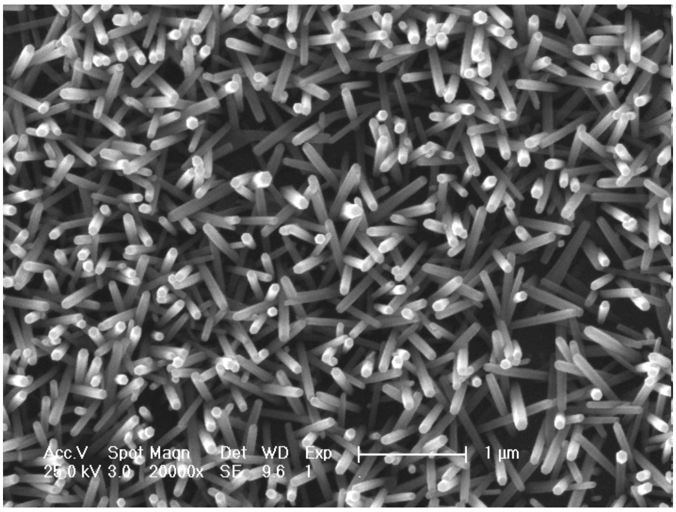


XRD patterns of the ZnO nanorods.

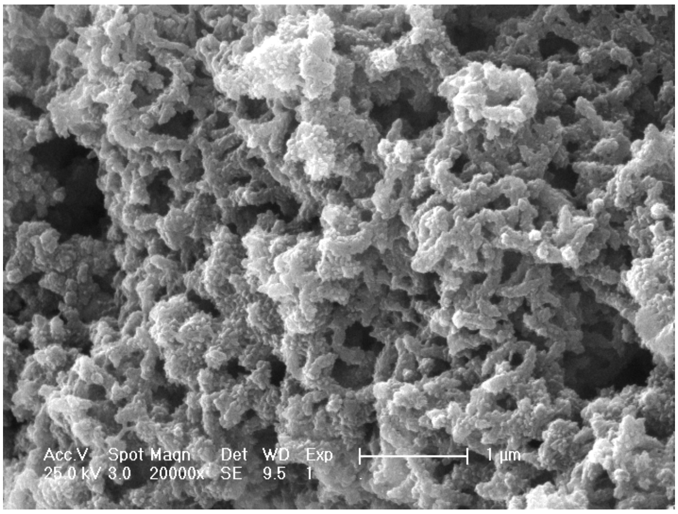
Notably, all the strong sharp diffraction peaks can be indexed as ZnO with cell constants a=3.249 Å, b=3.249 Å, c=5.205 Å, which are consistent with the values in the literature (JCPDS Card, No. 89-0510).



SEM Image of ZnO nanorods



SEM image of PANI nanowebs



References

s1. T. Andrea, G. Hervea, R. G. Finke and D. K. Lyon, *Inorg. Synth.,* 1990, **27**, 85-95.

s2. J. X. Huang and R. B. Kaner, *J. Am. Chem. Soc.* 2004, **126,** 851.

s3 L. E. Greene, M. Law, P. H. Tan, M. Montano, J. Goldberger, G. Somorjai, P. D. Yang, *Nano Lett,* 2005, **5**, 1231.

s4. Z. M. Zhang, Z. X. Wei, and M. X. Wan, *Macromolecules*, 2002, **35**, 5937.

s5. Z. Zhang, M. Wan, and Y. Wei, *Adv. Funct. Mater.*, 2006, **16**, 1100.

s6. B. Ding, J. Gong, J. H. Kim, and S. M. Shiratori, *Nanotechnology*, 2005, **16**, 785.