A sandwich-structured ultraviolet photodetector driven only by opposite heterojunctions

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Experimental Section

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. Polystyrene sulfate (PSS) and poly(diallyldimethylammonium chloride) (polyDADMAC) were purchased from Sigma-Aldrich Corporation without further purification. TiO_2 nanoparticles were purchased from Beijing chemical factory.

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. 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 coating was performed with a Chemat Technology Spin-coater KW-4A. Electrochemical experiments were all performed in a conventional three-electrode electrochemical cell. Two ITO glasses (3 cm×1 cm) grown with ZnO were adopted as an electrode, respectively.

Typically the interfacial reaction was performed to synthesize PANI nanowires 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 $K_2S_2O_8$, 5 g of SiW_{12} 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 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 zinc acetate dehy-drate [$Zn(CH_3COO)_2 \bullet 2H_2O$] 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 zinc nitrate $Zn(NO_3)_2 \bullet 6H_2O$ and 20 mM hexamethylenetetramine (HMTA).

The PANI green precipitate dispersed into the ethanol was dropped onto the surface of the ITO with ZnO nanorods and spin coated at 3000 rpm for 60 s. This spin coating step was repeated three times and then dried at room temperature.

A layer-by-layer (LBL) self-assembly method was used for functionalizing polystyrene sulfate onto the ZnO. Since the functional PSS used for UV sensing was negatively charged, a positively charged polymer, poly(diallyldimethylammonium chloride) (polyDADMAC) was chosen to assist the electrostatic assembly of the negatively charged polymer. Experimentally, positively charged polyDADMAC was first adsorbed onto negatively charged ZnO surface by immersing ZnO into polyDADMAC solution. After washed several times using distilled water, the ZnO was immersed in an anionically charged PSS solution. The prepared ITO grown with ZnO was repeatedly washed with distilled water and then dried under vacuum for 24 h at 40 ^{o}C.

The white TiO_2 precipitate dispersed into the ethanol was dropped onto the surface of the ITO and spin coated at 3000 rpm for 60 s and dried at room temperature. Then, the PANI green precipitate dispersed into the ethanol was dropped onto the surface of the ITO with TiO_2 and spin coated at 3000 rpm for 60 s. After drying in a vacuum at

50 ^{o}C for 24 h, a TiO_2/PANI/TiO_2 sandwich-structured device was obtained.

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**, 851-855.

s3 L. E. Greene, M. Law, P. H. Tan, M. Montano, J. Goldberger, G. Somorjai, P. D. Yang, *Nano Lett.,* 2005, **5**, 1231-1236.

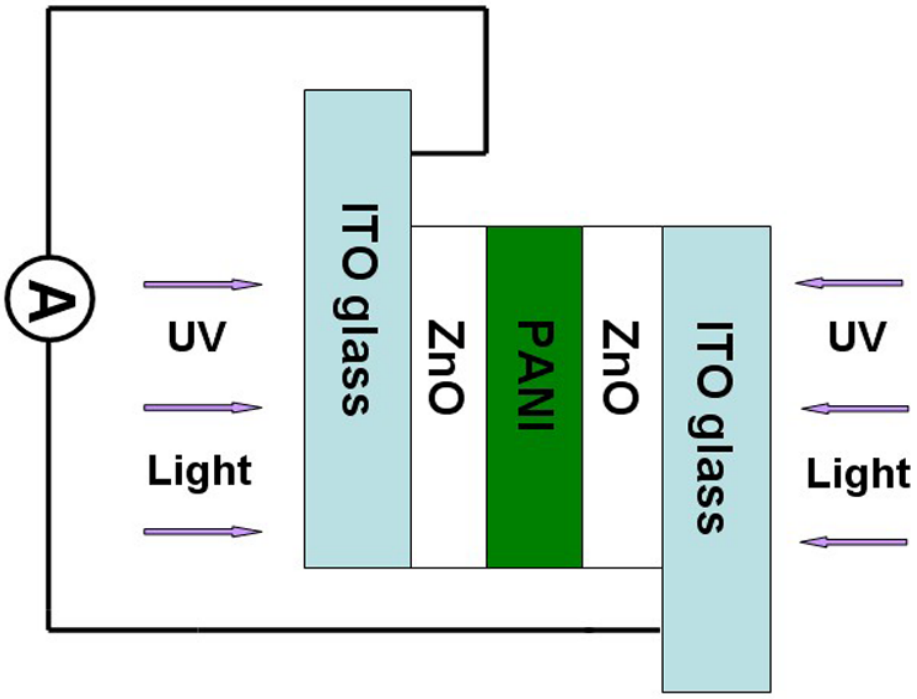

Figure S1 Schematic diagram showing the design and structure of the UV photodetector. Two layers of n-type ZnO nanorods are separated by one layer of p-type PANI nanowires forming a sandwich-structured ZnO/PANI/ZnO device. The ITO substrates with ZnO nanorods are directly connected to an external circuit.

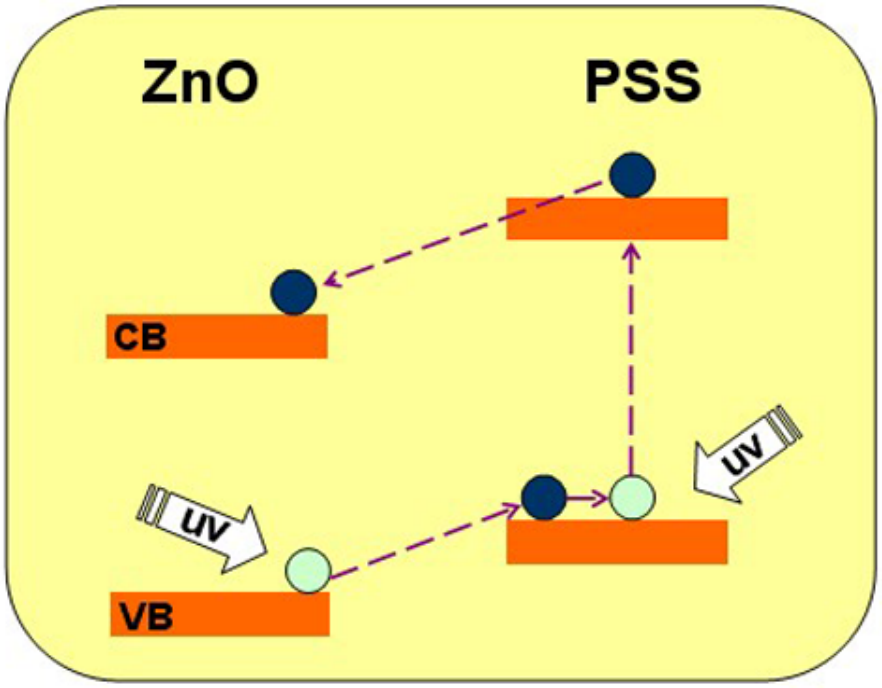

Figure S2 Schematic diagram of the energy states of ZnO and PANI.

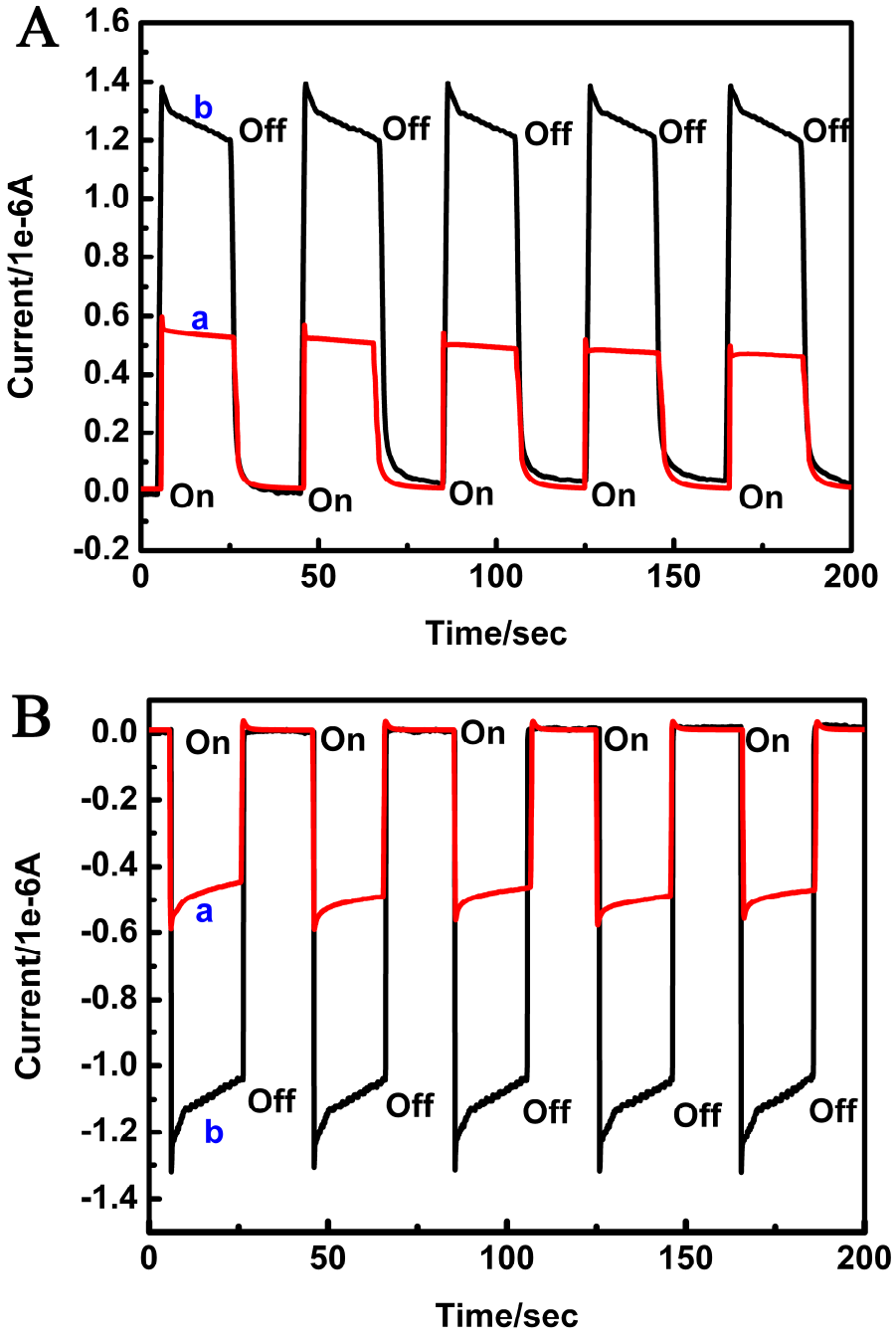

Figure S3 I-t curve of the sandwich-like structure of the ZnO/PANI/ZnO device when subject is irradiated by 8 W (curve a) and 16 W (curve b) UV light from opposite direction, respectively.

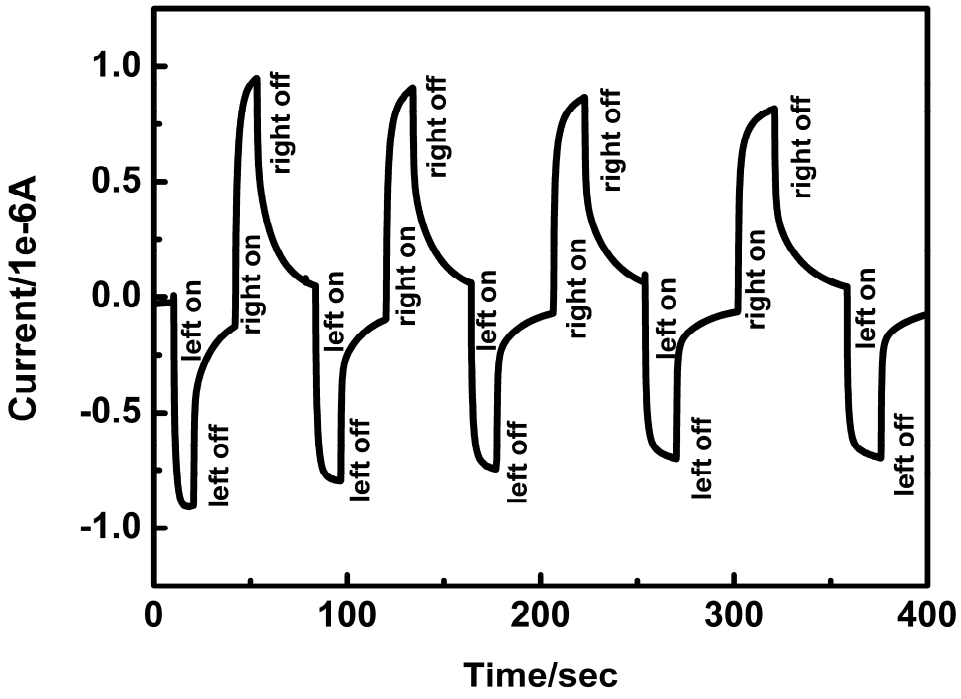

Figure S4 I-t curve of a sandwich-like structure of the TiO_2/PANI/TiO_2 device when subject is irradiated by 8 W UV light from opposite direction.