Electronic Supplementary Material (ESI) for RSC Advances.

Enhanced photocurrent of ZnO nanorods array sensitized with graphene quantum dots

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Experimental section

GQDs were synthesized from graphite oxide (GO) powder by using a facile one-step solvothermal method.[1, 2] GO powder was prepared from natural graphite powder by a modified Hummers method reported in previous works.[3, 4] In a typical synthesis, GO powder (1.5 g) was dispersed in 75 ml of N, N-Dimethylformamide (DMF) with the aid of ultrasonication 500 W for 1 hour. Then the suspension was transferred to a Teflon-lined autoclave (125 mL) and kept at 200 ℃ for 8 h. After cooled to room temperature naturally, the mixture was vacuum-filtered using a 0.22 μm microporous membrane and the brown solution was collected. Finally, employing rotary evaporating at reduced pressure, the concentrated GQDs dispersion in DMF was obtained.

The preparation process of ZNRA was similar to our previous reports.[5, 6] Briefly, the ZnO sol was dropped on the interdigital Au electrodes and spin-coated with 2000 rpm for 30 s. After each coating process, the film was preheated at 300 ℃ for 5 min in air to transform sol to gel. This process was repeated 3 times. Finally, the film was annealed in muffle furnace at 500 ℃ for 1 hour for enhanced crystallization. The obtained ZnO seed layer on interdigital Au electrodes was then immersed into a 0.05 M $Zn(NO_3)_2 \cdot 6H_2O$ and 0.05 M hexamethylenetetramine solution and kept at 90 ℃ for 3 hours. After that, the sample was taken out and cooled to room temperature, and then washed with the ultra-pure water, ethanol and dried at room temperature. GQDs suspension in DMF was spin-coated on the ZNRA to obtain GQDs coated ZNRA and for enhancing the adhesion of GQDs on ZNRA, the GQDs coated ZNRA were heated at 100 ℃ for 10 min in air for each run. Ultimately, the sample was dried at 60 ℃ in air for several hours. The content of GQDs was controlled via repeating the spin-coating process.

Transmission electron microscopy (TEM) investigations were conducted on a JEOL 2100 FEG microscope at 200 keV. Scanning electron microscope (SEM) analyses were performed on a field emission scanning electron microanalyzer (JEOL-6701F) at 5 kV. UV-vis absorption spectrum of GQDs suspension was carried out on a Hitachi U-3010 UV-vis spectrophotometer. Photoluminescence (PL) spectrum was carried out on an F-4500 fluorescence spectrophotometer under 365 nm wavelength light excitation. The photoresponse behaviors of pure and GQDs modified ZNRA were conducted on a Keithley 2400 power source and an electrochemical working station (CHI660D, Shanghai, China). The ultraviolet radiation with wavelengths of 254 and 365 nm was generated by a triple purpose ultraviolet analyzer. The surface chemical species of GQDs on ZNRA were examined on a Perkin-Elmer PHI-5702 multifunctional x-ray photoelectron spectroscope (XPS, Physical Electronics, USA) using $\mathrm{Al}K\alpha$ radiation of 1486.6 eV as the excitation source. All the XPS spectra were calibrated by using Au $4f_{7/2}$ at 84.0 eV.

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2 S. Zhu, J. Zhang, C. Qiao, S. Tang, Y. Li, W. Yuan, B. Li, L. Tian, F. Liu, R. Hu, H. Gao, H. Wei, H. Zhang, H. Sun and B. Yang, *Chem. Commun.*, 2011, **47**, 6858-6860.

3 X. Yan, J. Chen, J. Yang, Q. Xue and P. Miele, *ACS Appl. Mater. Interfaces*, 2010, **2**, 2521-2529.

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5 J. T. Chen, J. Wang, R. F. Zhuo, D. Yan, J. J. Feng, F. Zhang and P. X. Yan, *Appl. Surf. Sci.*, 2009, **255**, 3959-3964.

6 J. T. Chen, J. Wang, F. Zhang, G. A. Zhang, Z. G. Wu and P. X.Yan, *J. Cryst. Growth*, 2008, **310**, 2627-2632.

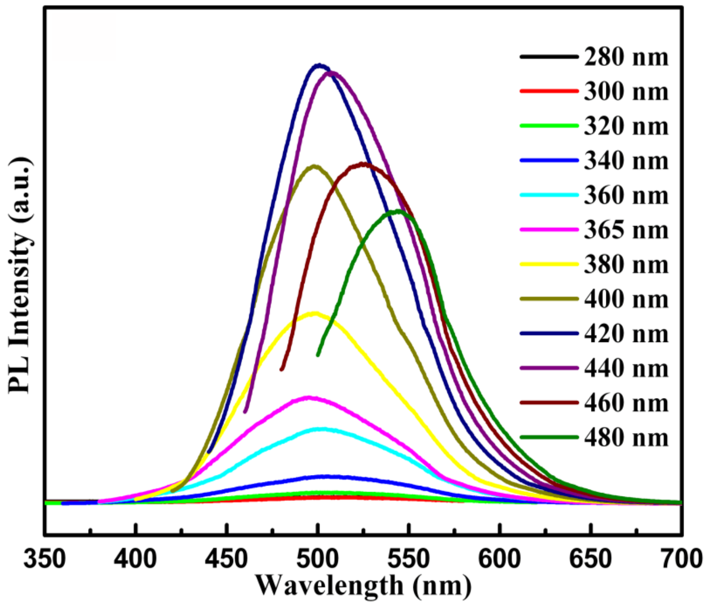

Fig. S1 The excitation-dependent PL spectra of GQDs in DMF, which were excited at wavelengths from 280 to 480 nm.

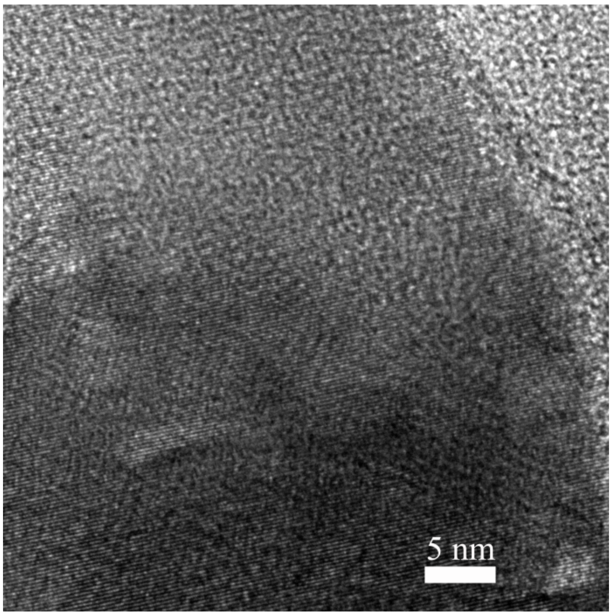

Fig. S2 HR-TEM image of ZNRA.

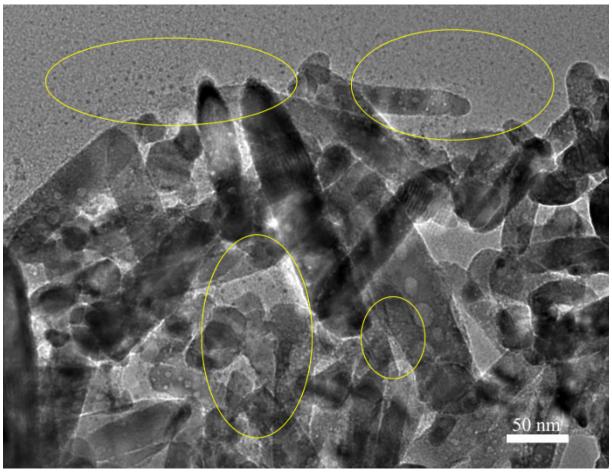

Fig. S3 TEM image of GQDs coated ZNRA. The sample for TEM test was prepared by scraping and ultrasound in ethanol. The GQDs has fallen off from ZNRA. The GQDs can be observed in the TEM image, which confirms successful deposition on surface of ZNRA.

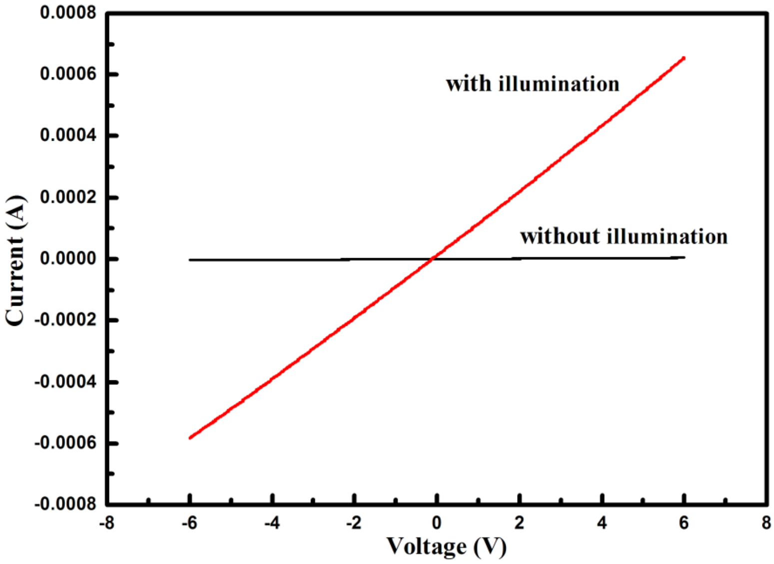

Fig. S4 I-V behavior of GQDs coated ZNRA without and with UV illumination of 365 nm light.

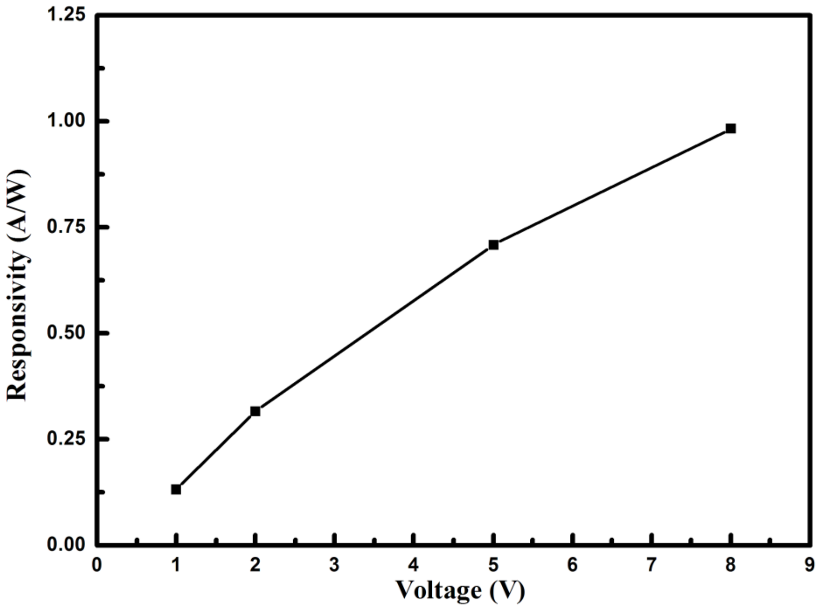

Fig. S5 Responsivity of GQDs coated ZNRA with UV illumination of 365 nm light as a function of applied voltage.

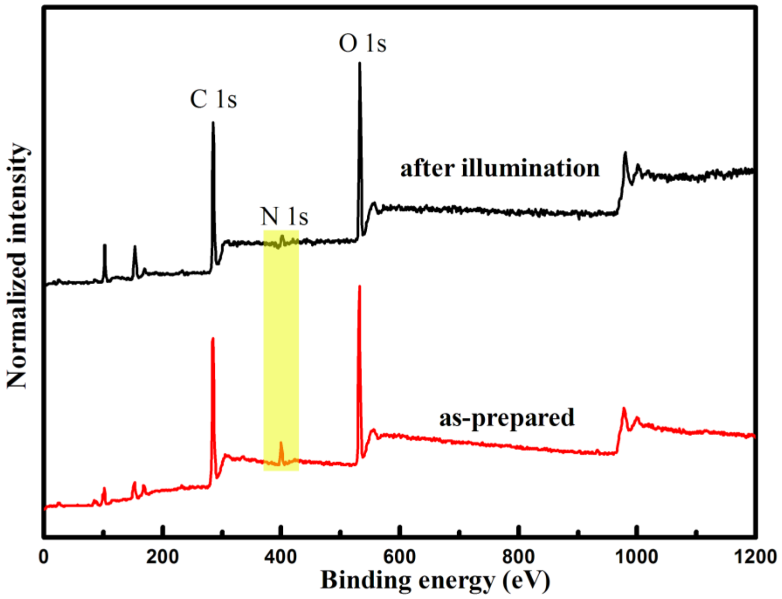

Fig. S6 The XPS full spectra of GQDs on ZNRA before and after UV light illumination. Seen from the spectra, the intensity of N 1s peak weakened after UV light illumination. The GQDs were further reduced by UV light illumination.

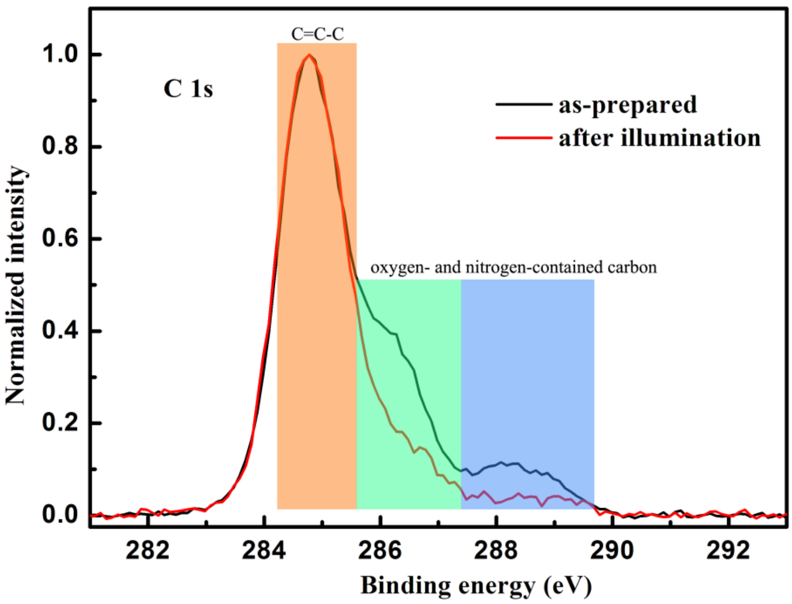

Fig. S7 C 1s core spectra of GQDs coated ZNRA before and after UV light illumination. The GQDs were reduced further and this probably affected the photoresponse behaviors of ZNRA via the interfacial interaction among GQDs and ZNRA.