Electronic Supplementary Information

Dramatic daylight induced photocatalytic performance of carbon quantum dots decorated N-doped ZnO with suppressed photocorrosion

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Experimental details

2.1. Preparation of ZnO photocatalyst: All the chemicals were of analytical grade and used as received without further purification. *T*ypically, about 1.25g of zinc acetate dihydrate was dissolved in 125 ml of double distilled water (DDW). Ammonia solution was added drop-wise to keep the solution should be above pH ~10. White precipitates were formed and it gets disappeared upon further addition of ammonia solution. The resultant clear solution was filtered to remove any foreign particles. It was further diluted with 50 ml of DDW and kept at 60 °C on a constant temperature bath for 26 h. White crystals of ZnO were collected, washed with distilled water and ethanol several times and dried at 100 °C for 70 min [1].

2.2. Preparation of CQD/ZnO photocatalyst: a facile one-step wet chemical method was used to synthesis CQDs with a slight modification of process under reflux [2]. Typically, 50 mg of carbon black pigment (HIBLACK Orion) was put into the mixture of 13 mL H_2SO_4 and 6.5 mL HNO_3 at room temperature and sonicated for few minutes for better dispersion. The reaction was maintained

at 240 °C for 2 h and the resulting mixer was allowed to cool naturally to room temperature. Then, the reaction mixture was neutralized and dialyzed for 2 days to isolated CQDs. Particle size of CQD was about 2.5 nm. For CQD/ZnO photocatalyst, a required amount (10 μL) of CQD solution was mixed with 50 mg of ZnO crystals dispersed in 25 mL of ethanol and stirred for 30 min at room temperature. Filtered and washed with DDW and ethanol several times. The collected products (ivory white) were dried at 100 °C for 70 min.

2.3. Photocatalytic measurement: 0.5 mg of photocatalyst was suspended in 100 mL of malachite green (MG) aqueous solution (1.0×10^{-4} M), and then the mixture was taken in a glass beaker and agitated in the absence of light for 30 min to establish an absorption-desorption equilibrium. After a given daylight exposure time, about 5 mL of the mixture was withdrawn and the catalysts were separated from the suspensions in prior to measure the photodegradation. Dye degradation was measured by considering chances in the absorption band of MG dye at 612 nm with respect to light exposure time. Photocatalytic measurements were performed under UV lamp (Philips, 18W TLD), visible (Philips, 18W CFL) and daylight sources. The daylight intensity ($33\times10^{3} \pm 5000$ lx) was measured by digital lux-meter between Sep to Oct 2014 (11 am to 2 pm). All the experiments were undertaken in triplicate with errors below 4% and average values were reported.

2.4. Characterization: The powder X-ray diffractograms (XRD) patterns of the samples were recorded by a Rigaku using Cu Kα radiation (λ = 0.1546 nm) monochromated by a nickel filter. Morphology was investigated by field emission scanning electron microscopy (FESEM, SUPRA-40VP equipped with an EDXS system) and high resolution transmission electron microscopy (HRTEM, JEOL-2010). X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD (Kratos. Inc), Monochromatic Al Kα radiation (1486.6 eV, 150 W). Raman spectra were collected on Raman spectroscope (nano-Raman, NTEGRA) equipped with a synapse CCD detector and a confocal Olympus microscope. Photocatalytic activity measurement was analyzed with an UV-vis spectrometer (UV-2550, Shimadzu).

Additional Figures:

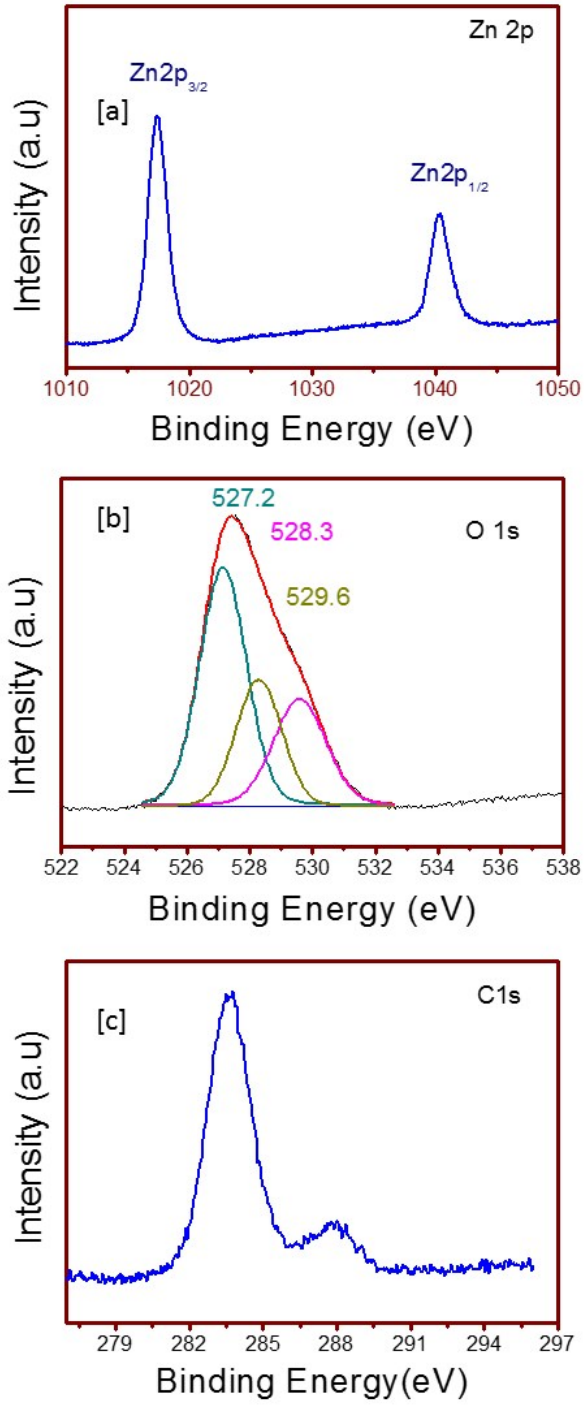

Figure S1. High resolution (a) Zn 2p, (b) O 1s and (c) C 1s core level XPS spectra of CQD/N-ZnO.

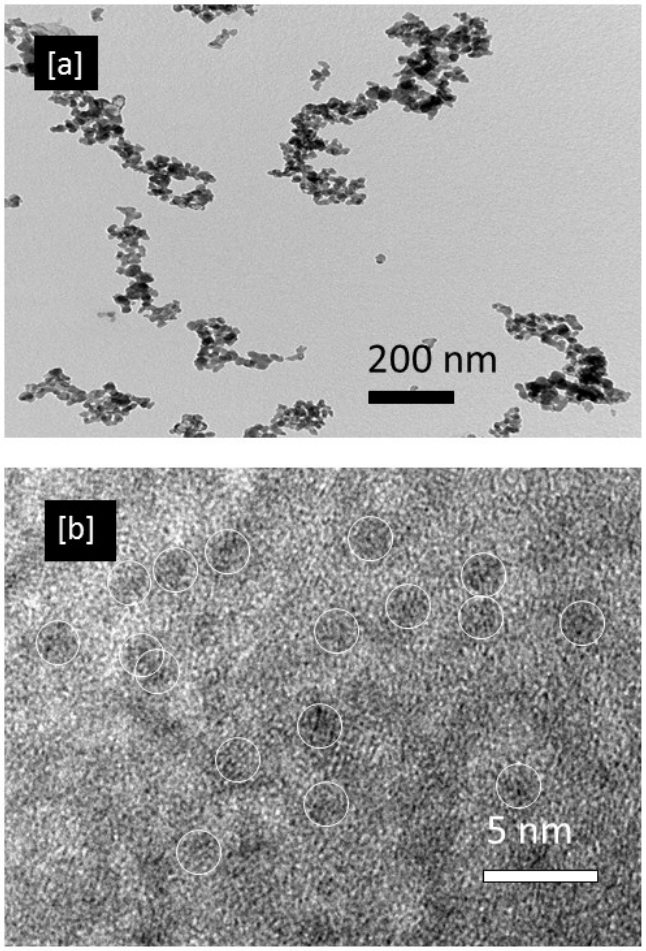

Figure S2. (a) TEM of N-doped ZnO and (b) HRTEM image of CQDs.

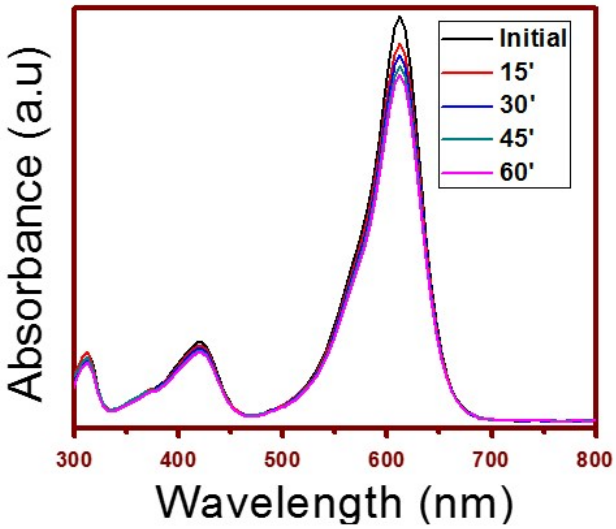

Figure S3. Photocatalytic degradation of MG dye solution under daylight irradiation without catalyst.

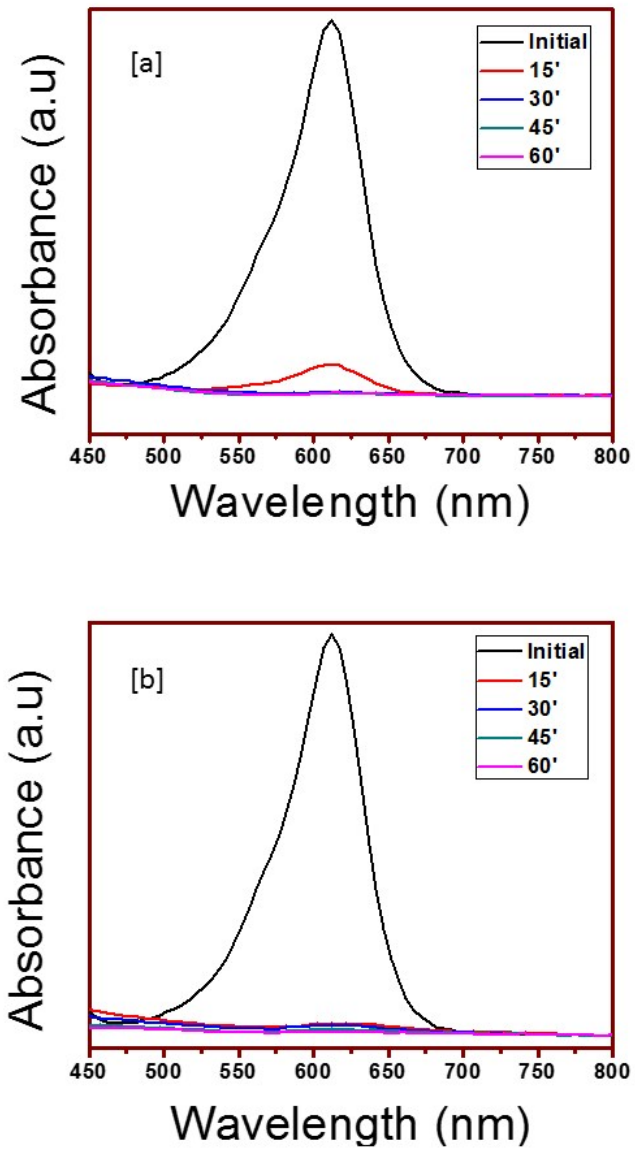

Figure S4. UV-Vis absorption spectra of CQD/N-ZnO photocatalytic degradation on MG dye solution under (a) UV light and (b) visible light irradiation.

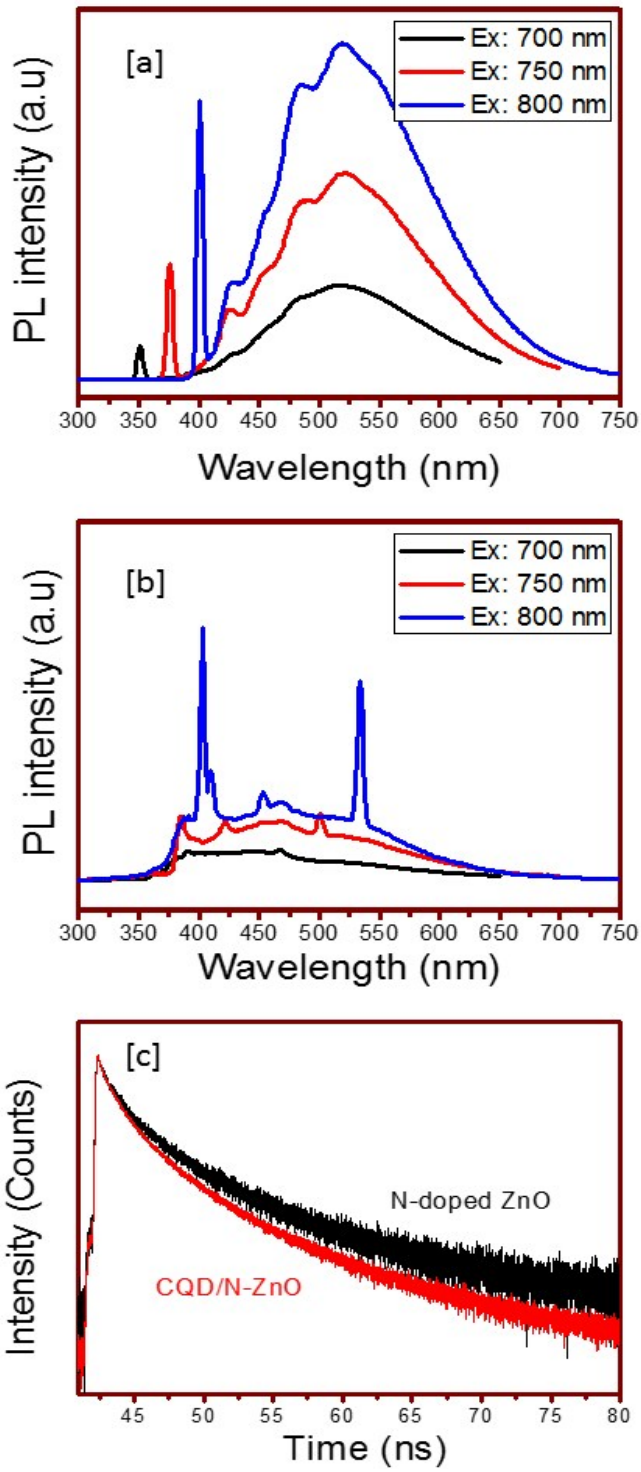

Figure S5. The up-conversion PL emission spectra of (a) pure CQD and (b) CQD/N-ZnO photocatalysts under different excitation wavelength. Time resolved PL spectra of (c) pure N-doped and CQD/N-ZnO photocatalysts.

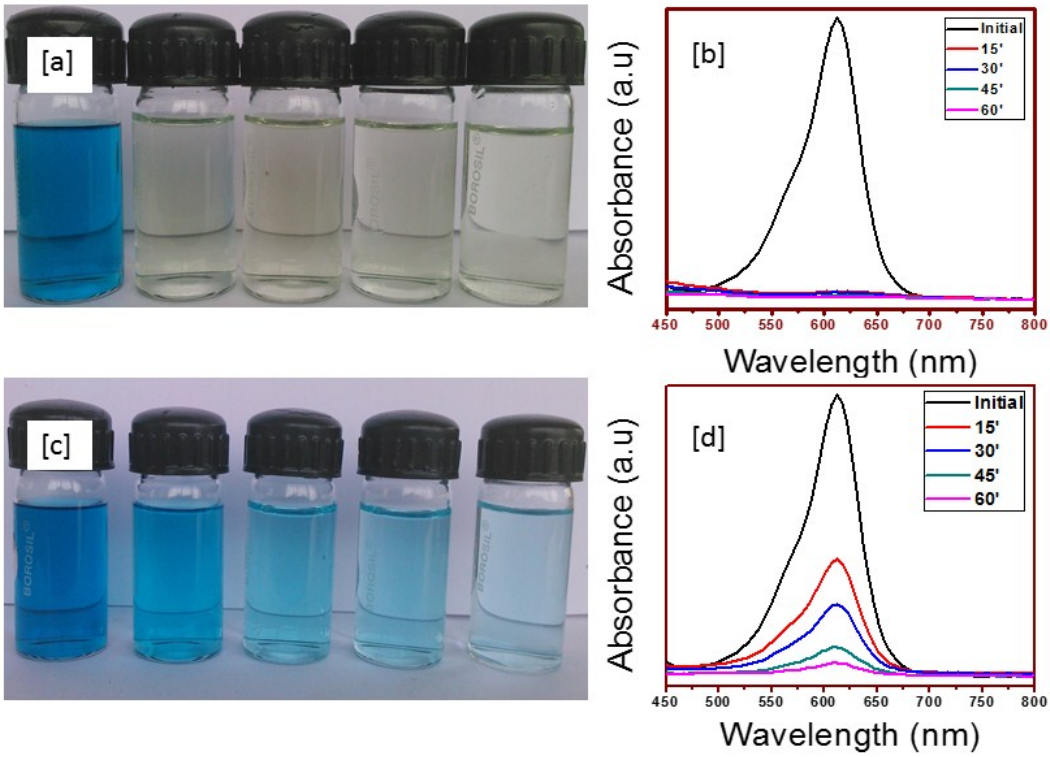

Figure S6. Photographs and UV-Vis absorbance spectra of MG dye degradation in presence of (a-b) CQD/N-ZnO and (c-d) N-doped ZnO photocatalysts, under 0, 15, 30, 45, and 60 min of daylight irradiation.

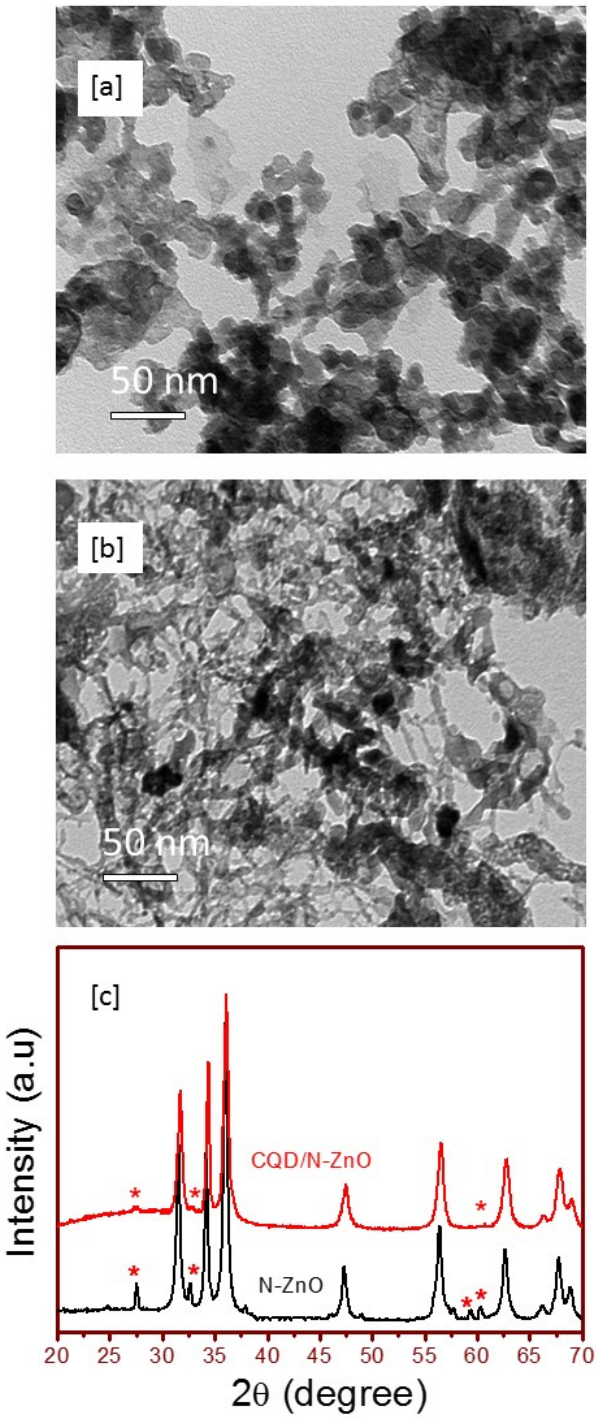

Figure S7. TEM images of (a) CQD/N-ZnO and (b) N-doped ZnO photocatalysts after 4th successive photocatalytic experiments and their respective (c) XRD spectra.

References:

[1] P. Uthirakumar, S. Muthulingam, B. D. Ryu, J. H. Kang, A. Periyasamy, M. Prabakaran, and C. H. Hong, *Curr. Nanosci.,* 2013, 9, 335-40.

[2] J. Peng, W. Gao, B.K. Gupta, Z. Liu, R.A. Rebeca, L.H. Ge, L. Song, L.B. Alemany, X.B. Zhan, G.H. Gao, S.A. Vithayathil, B.A. Kaipparettu, A.A. Marti, T. Hayashi, J.J. Zhu, and P.M. Ajayan, *Nano Lett.,* 2012, 12, 844-49.