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聚胺界面修饰改善碳量子点可见光光敏化性能

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Improving the Efficiency of Carbon Quantum Dots as a Visible Light Photosensitizer by Polyamine Interfacial Modification

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Experimental

The treatment of 4BTC5 composite with $NaBH_4$. Sodium borohydride ($NaBH_4$, 400 mg) was mixed with 50 mL solution of 4BTC5 (100 mg) and then stirred for 12 h at room temperature. Excess reductant was washed with water three times by centrifugation then the product was dried in an oven at 333 K overnight.

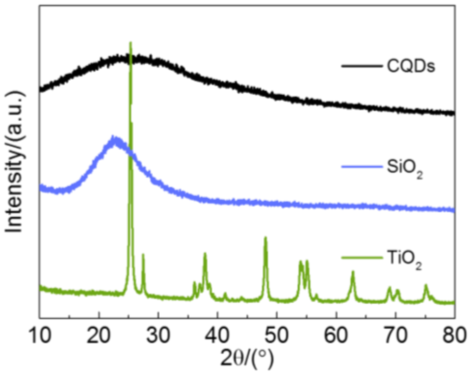

Fig. S1 X-ray diffraction (XRD) patterns of CQDs, SiO_2 and TiO_2 used in the experiments.

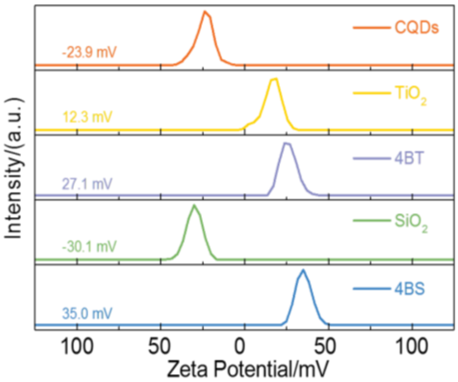

Fig. S2 Zeta potentials of CQDs, TiO_2, 4BT composite, SiO_2 and 4BS composite.

Fig. S3 Photographs of selected samples in the experiments.

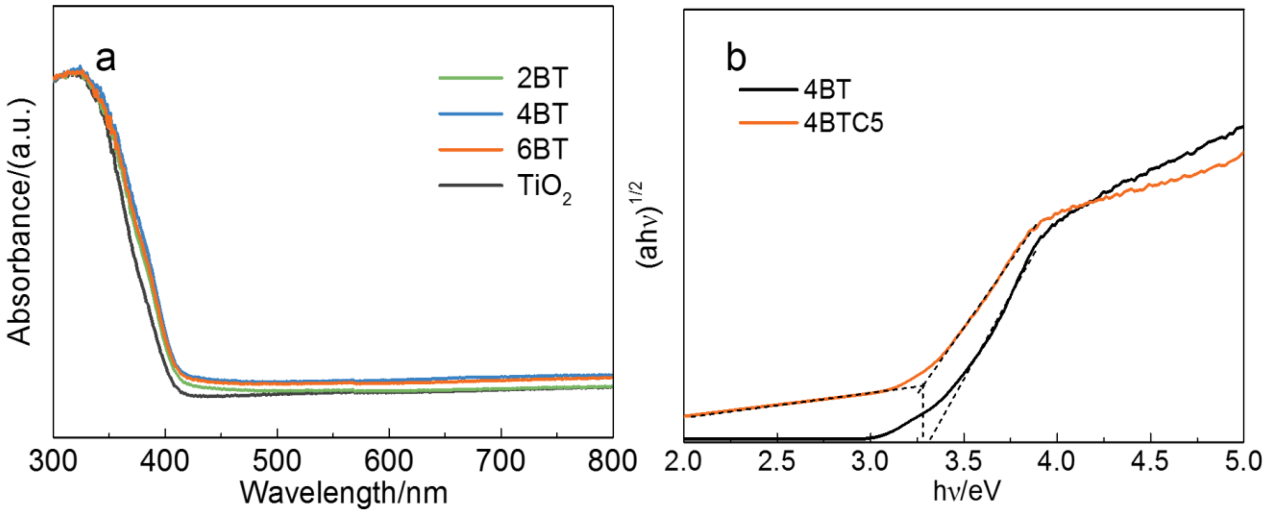

Fig. S4 (a) The UV-vis diffuse reflectance spectra (DRS) of pure TiO_2 and TiO_2 passivated with different amount of BPEI. (b) The corresponding plots of transformed Kubelka-Munk function *versus* the energy of light for 4BTC5 composite in comparison to 4BT composite.

The band-gap energies of all the samples are estimated from the absorption spectra by using the following relationship: $\alpha h\nu = A(h\nu - E_g)^{n/2}$, Where A, α, $h\nu$ and E_g are constant, the absorption coefficient, photon energy, and the band gap energy, respectively; n is determined by the type of the optical transition of a semiconductor (n = 1 for the direct transition and n = 4 for the indirect transition).

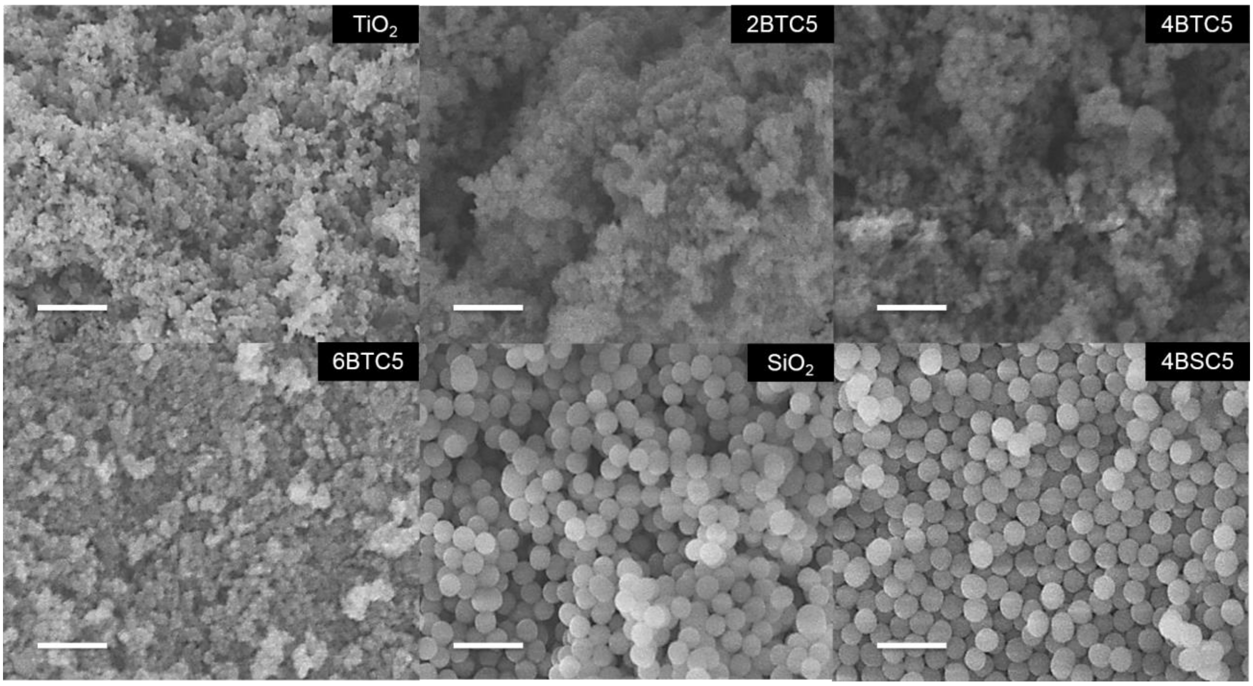

Fig. S5 Scanning electron microscopy (SEM) images of selected samples. The scale bar is 500 nm.

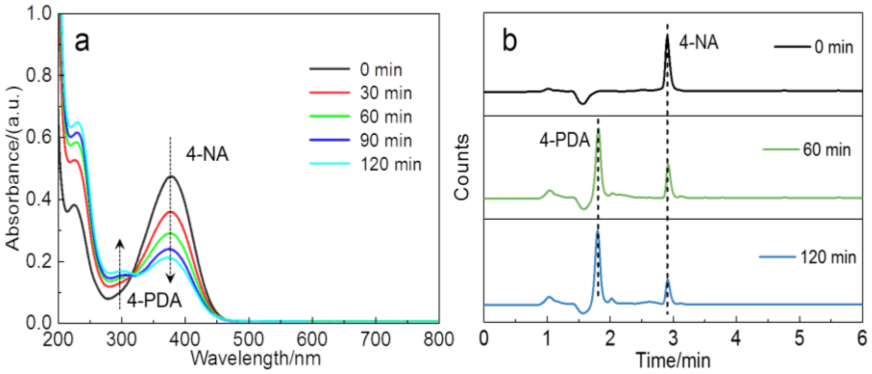

Fig. S6 (a) Time-dependent UV-Vis spectral variation during the photocatalytic reduction of 4-nitroaniline (4-NA) to 4-phenylenediamine (4-PDA) over the 4BTC5 composite under visible light irradiation ($\lambda > 420$ nm) with N_2 purge under ambient conditions, i.e., room temperature and atmospheric pressure. (b) The liquid chromatograph analysis (performed on a Shimadzu High Performance Liquid Chromatograph (HPLC), i.e., HPLC–LC20AT which was equipped with a C18 column and SPD-M20A photo diode array detector) images of 4-nitroaniline in the aqueous phase under visible light irradiation ($\lambda > 420$ nm), which is taken at regular time interval over the 4BTC5 composite at different reaction time: 0, 60 and 120 min.

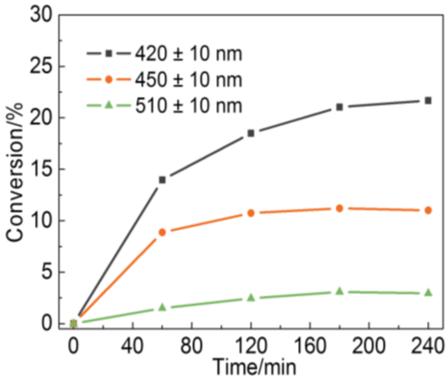

Fig. S7 Photocatalytic performance over 4BTC5 composite under different monochromatic light with the wavelength in the visible light.

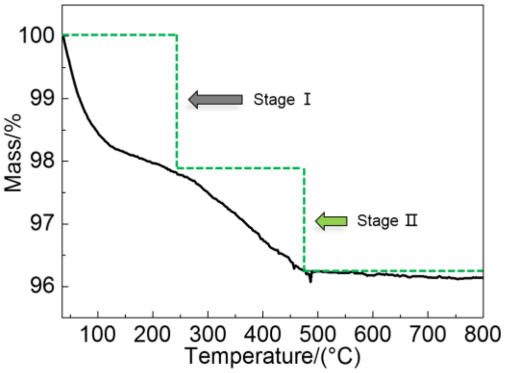

Fig. S8 Thermogravimetric analysis (TGA) profile of the TC composite prepared by impregnation method.

Two weight loss stages under N_2 flow can be categorized as follows. (I) Evaporation of chemisorbed water and some low-temperature volatile carbon residues (100–240 ℃); (II) mass loss from the high-temperature pyrolytic carbon species, that is, combustion of the CQDs (240–480 ℃).

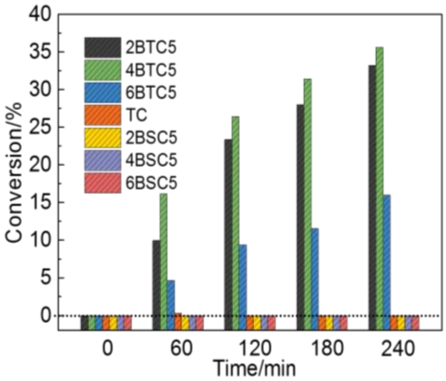

Fig. S9 Photocatalytic performance over TC composites and different amount of BPEI modified TiO_2 (SiO_2) with 5% (*w*) CQDs under visible light irradiation with 440 nm cutoff filter.

We conducted photocatalytic measurements using 440 nm cutoff filter to further prove the photoactivity originated from CQDs in BTC5 composites and exclude the potential that semiconductor TiO_2 was in the excited state.

The complete author lists of references 22 and 31 in the article are as follows:

(22) Sun, Y. P.; Zhou, B.; Lin, Y.; Wang, W.; Fernando, K. A. S.; Pathak, P.; Meziani, M. J.; Harruff, B. A.; Wang, X.; Wang, H.; Luo, P. G.; Yang, H.; Kose, M. E.; Chen, B.; Veca, L. M.; Xie, S. Y. *J. Am. Chem. Soc*. **2006,** *128*, 7756. doi: 10.1021/ja062677d

(31) Huang, W.; Zeng, L.; Yu, X.; Guo, P.; Wang, B.; Ma, Q.; Chang, R. P. H.; Yu, J.; Bedzyk, M. J.; Marks, T. J.; Facchetti, A. *Adv. Funct. Mater*. **2016,** *26*, 6179. doi: 10.1002/adfm.201602069