Supporting Information

PEGME-bonded SnO_2 quantum dots for excellent photocatalytic activity

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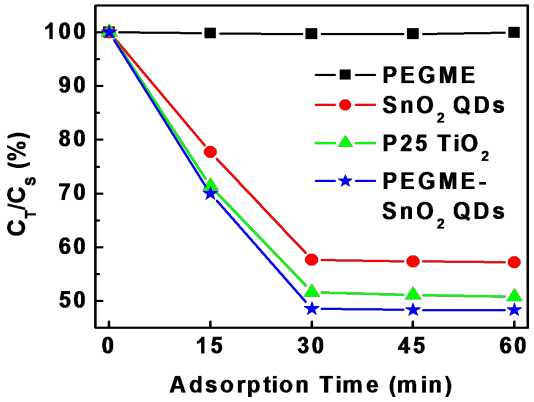


Fig. S1. The adsorption-desorption equilibrium curves of the photocatalysts to RhB dye.

Here, C_S is the concentration of the fresh RhB dye aqueous solution; C_T is the testing concentration of the RhB dye aqueous solution. Therefore, C_T / C_S means the degree of adsorption of photocatalysts to RhB dye. When the C_T / C_S keep unchanged, the adsorption-desorption processes are in equilibrium. It could be clearly found that it could ensure these systems reaching adsorption-desorption equilibrium when the dark adsorption time was set as 1h.

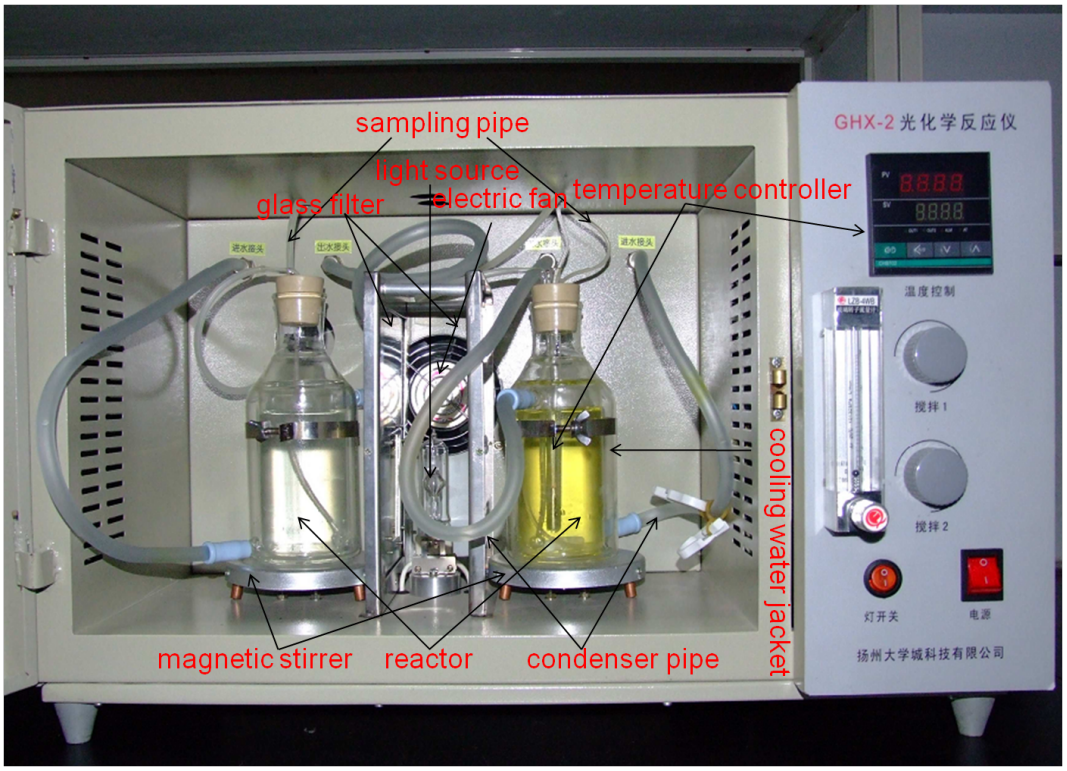


Fig. S2. Schematic of the photocatalytic reactor.

The photocatalytic experiments were carried out in a GHX-2 photochemical reactor, which includes mainly four parts: light source system including a 300 W high-pressure mercury lamp, two (λ>254 nm) cutoff filters on both sides and cooling attachments such as electric fan; reactor (two-layer Pyrex glass bottles of 400 mL capacity, the space between the two layers is filled with circulating water to cool the reactor); magnetic stirrer; and temperature controller. In each experiment, the distance between the Xe lamp and the reactor was set to be 5.8 cm, and the reaction temperature was 25 °C. The light intensity in the center position of the reactor was measured to be about 150 $mWcm^{-2}$ using an UV-light radiometer (UV-B, Photoelectric Instrument Factory of Beijing Normal University, China) over the wavelength in the range of 230-275 nm.

Photonic efficiencies of catalysts.

The photonic efficiency ξ, which is defined as the ratio of the dye degradation rate and the incident photon flux at a given wavelength, is calculated according to Equations (1)-(3) based on the reports of Prof. Yu's, Prof. Mendive's and Prof. Bahnemann's groups.[1-3]

$$\xi = \frac{\text{degradation rate [mol/s]}}{\text{photon flux [mol}h\nu\text{/s]}} = \frac{\Delta C \cdot V}{\Delta t \cdot I_0 \cdot A} \quad (1)$$

$$I_0 = \frac{I \cdot \lambda}{N_A \cdot h \cdot c} \quad (2)$$

So, $$\xi = \frac{\Delta C \cdot V}{\Delta t} \frac{N_A \cdot h \cdot c}{I \cdot \lambda \cdot A} \quad (3)$$

Where $\Delta C / \Delta t$ is the degradation rate, V the volume of the employed test solution, I_0 the photon flux, A the illuminated area (11.05 cm^2), I the light intensity (150 $mWcm^{-2}$), λ the incident wavelength (254 nm), N_A Avogadro's constant, h Planck's constant and c the velocity of light.

Hence, for the reusability of the PEGME-SnO_2 QDs catalyst as shown in Fig. 4 (c), the photonic efficiencies ξ is 0.0058 %, 0.0057 %, 0.0057 % and 0.0057 % for the four cycles, respectively. And for Fig. 5(a), ξ is 0.0046 %, 0.0046 %, 0.0046 %, 0.0058 %, 0.0047 %, 0.0033 % and 0.0029 % for different dosages of PEGME-SnO_2 QDs catalysts, 25, 30, 40, 50, 60, 70 and 100 mg, respectively.

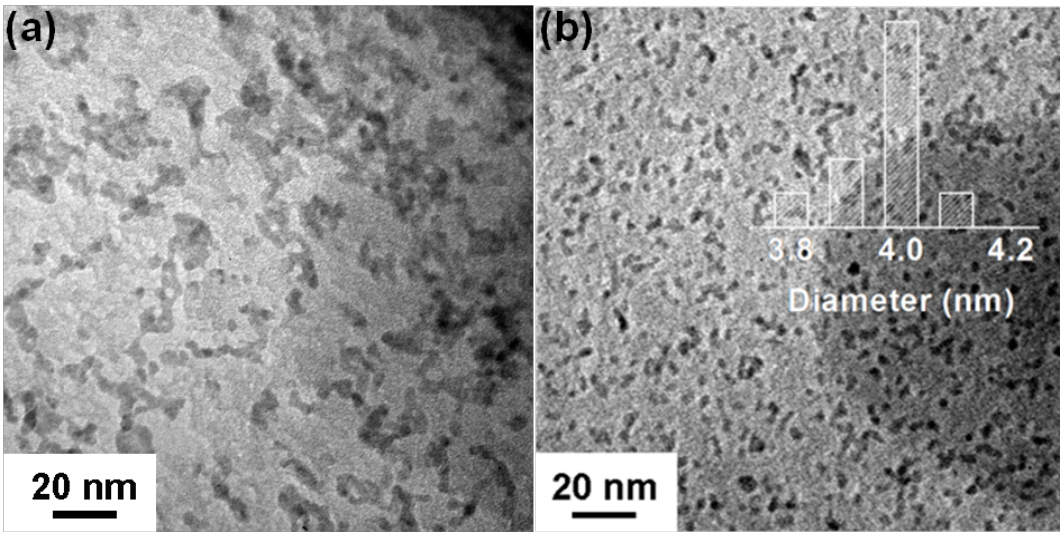


Fig. S3. TEM images of the (a) SnO_2 QDs and (b) PEGME-SnO_2 QDs, the inset is the diameter distribution of the PEGME-SnO_2 QDs.

The TEM images of SnO_2 QDs, PEGME-SnO_2 QDs and the diameter distribution (the inset in (b)) are shown in Fig. S3. It can be found that pure SnO_2 QDs are prone to aggregate as shown in Fig. S3(a). However, after the surface-modification of PEGME, SnO_2 QDs could well dispersed as displayed in Fig. S3 (b). So the PEGME-modification could has an apparent effect on the separation of SnO_2 QDs. Moreover, Fig. S3 (b) could support the formation of almost uniform and monodispersed SnO_2 QDs. It can be seen from the inset of Fig. S3 (b) that PEGME-SnO_2 QDs are in narrow size distribution with diameters around 4 nm, which is similar to the average size calculated from the XRD.

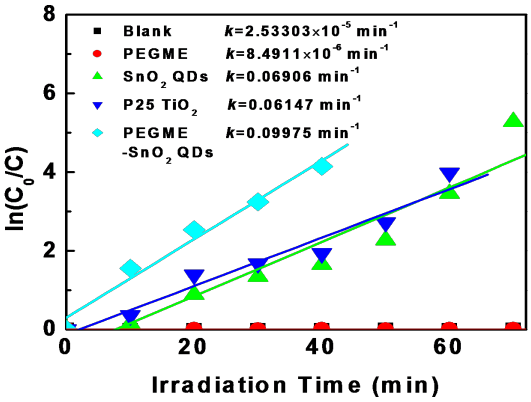


Fig. S4. The apparent reaction rate constants (*k*) of the RhB photodegradation on different photocatalysts.

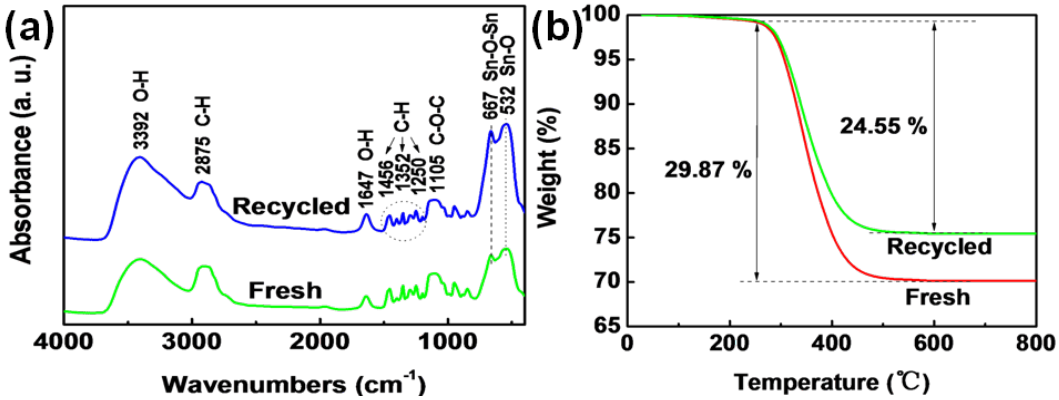
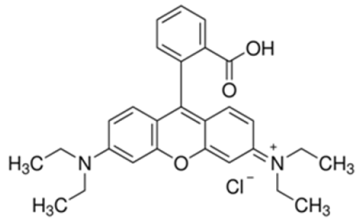


Fig. S5. (a) FT-IR and (b) TGA for fresh and recycled PEGME-SnO_2 QDs catalyst.

Compared with the FT-IR of fresh and recycled PEGME-SnO_2 QDs catalysts in Fig. S5(a), the existence of Sn-O-Sn (667 cm^{-1}), C-O-C (1105 cm^{-1}), C-H (2875 cm^{-1}, 1456 cm^{-1}, 1352 cm^{-1}, and 1250 cm^{-1}) and O-H (3392 cm^{-1} and 1647 cm^{-1}) vibration bonds,[4-6] as well as the almost unchanged Sn-O vibration at around 532 cm^{-1} from the SnO_2 surface,[7] indicating that photocatalytic process has not destroyed the composite of PEGME molecules and SnO_2. This could qualitatively support the stability of PEGME layer on the surface of PEGME-SnO_2 QDs. It could be found from Fig. S5 (b) that, after 4 cycles of photocatalytic process, the mass ratio of PEGME in

PEGME-SnO_2 QDs decreases from 29.87% to 24.55%. The less mass loss (only around 5%) could quantificationally prove the stability of PEGME on the surface of the catalyst. Therefore, the stable recyclability of PEGME-SnO_2 QDs photocatalysts could be supported by the stability of PEGME surface modifiers.



Rhodamine B (RhB)

$$+ \bullet OH \rightarrow CO_2 + H_2O + NO_3^- + NH_4^+ + Cl^-$$

Fig. S6. The molecular structural formula and possible degradation mechanism of RhB.[8]

References

1 X. M. Zhou, J. Y. Lan, G. Liu, K. Deng, Y. L. Yang, G. J. Nie, J. G. Yu and L. J. Zhi, *Angew. Chem. Int. Ed.* 2012, **51**, 178-182.

2 I. Ivanova, J. Schneider, H. Gutzmann, J. O. Kliemann, F. Gärtner, T. Klassen, D. Bahnemann and C. B. Mendive, *Catal. Today* 2013, **209**, 84-90.

3 R. Fateh, R. Dillert and D. Bahnemann, *Langmuir* 2013, **29**, 3730-3739.

4 H. M. Xiong, W. Z. Shen, Z. D. Wang, X. Zhang and Y. Y. Xia, *Chem. Mater.*, 2006, **18**, 3850-3854.

5 H. M. Xiong, W. Z. Shen, B. K. Guo, S. H. Bo, W. J. Cui, L. Q. Chen, H. Li and Y. Y. Xia, *J. Mater. Chem.*, 2011, **21**, 2845-2847.

6 X. Y. Xu, C. X. Xu, Y. Lin, T. Ding, S. J. Fang, Z. L. Shi, W. W. Xia and J. G. Hu, *Appl. Phys. Lett.*, 2012, **100**, 172401.

7 Y. Kobayashi, M. Okamoto and A. Tomita, *J. Mater. Sci.*, 1996, **31**, 6125-6127.

8 L. X. Hu, F. Yang, W. C. Lu, Y. Hao and H. Yuan, *Appl. Catal. B: Environ.*, 2013, **134-135**, 7-18.