## **Electronic Supplementary Information**

# Celastrol-modified TiO<sub>2</sub> nanoparticles: Effects of celastrol on the particles

### size and visible-light photocatalytic activity

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#### 1. Experimental Section

Laser Raman spectra were collected under ambient conditions using an HR Lab Raman 800 system. A diode-pumped solid-state laser (at an excitation wavelength of 532 nm) was used for excitation.

BET surface area was characterized by an  $N_2$  adsorption–desorption isotherm (ASAP-2020 Micromeritics Co., USA) at 77K. The samples were degassed at 180 °C prior to BET measurements. The BET surface area was calculated from the linear part of the Brunauer-Emmett-Teller (BET) plot.

The effects of main active radical species ( $h^+$  and  $\bullet O_2^-$ ) suspected to be involved in the photocatalytic process were investigated under visible light using a quantity of appropriate species quenchers.<sup>1</sup> The dosages of the species quenchers were all 1 mmol/L.

#### 2. Experimental results

The anatase crystal structure of  $TiO_2$  nanoparticles in all the nanocomposites was confirmed by X-ray powder diffraction measurements and by Raman spectroscopy. As shown in Fig. S1, the Raman spectrum of pure  $TiO_2$  and CSL-modified  $TiO_2$  nanoparticles contains four Raman peaks in the range of 100–800 cm<sup>-1</sup>, including a very intense band at 150 cm<sup>-1</sup> (Eg vibration mode) and three strong bands at 395 cm<sup>-1</sup> (B1g), 509 cm<sup>-1</sup> (A1g) and 632 cm<sup>-1</sup> (Eg), can be clearly observed, which correspond to the characteristic vibrations for anatase  $TiO_2$ . On the one hand, the relative intensity of the  $TiO_2$  bands decreases with increase of the CSL content in the nanoparticles, indicating a decrease in the average size and crystallization of the as-prepared CSL-modified  $TiO_2$  nanoparticles.<sup>1</sup> On the other hand, a small shift was observed compared to that of pure anatase  $TiO_2$ , which may be due to the CSL on the surfaces of the  $TiO_2$  nanoparticles. In the spectrum of CSL-modified  $TiO_2$ , the Raman bands assigned to C=O, C-C were observed at 525 cm<sup>-1</sup> and 796 cm<sup>-1</sup>.



Fig. S1 The Raman spectra of pure TiO<sub>2</sub> and CSL-modified TiO<sub>2</sub> nanoparticles.

Specific surface area of the as-prepared samples was characterized by nitrogen adsorption-desorption isotherm measurements. Fig. S2 shows the nitrogen sorption isotherms curves of pure TiO<sub>2</sub>, 0.5% and 2.0% CSL-modified TiO<sub>2</sub>. It can be observed from Fig. S2 that the nitrogen adsorption–desorption isotherms of the samples are of type IV (Brunauer–Deming–Deming–Teller (BDDT) classification) with two hysteresis loops.<sup>3</sup> With increasing of CSL amount, the adsorption isotherms of the photocatalysts shift upward, indicating the increase in the BET specific surface areas. This is consistent with the calculation results, ascribed to the presence of CSL prevent the growth of anatase TiO<sub>2</sub> particles. With increasing CSL from 0, 0.5 to 2.0, the BET surface area increases from 74.7, 185.4 to 248.1 m<sup>2</sup>/g, respectively. This is due to the decrease in the crystallite sizes of the CSL-modified TiO<sub>2</sub> particles.



Fig. S2  $N_2$  adsorption/desorption isotherms of the as-prepared pure TiO<sub>2</sub> and CSL-modified TiO<sub>2</sub> samples.

It is generally accepted that a large number of main reactive oxygen species including  $h^+$ , •OH and •O<sub>2</sub><sup>-</sup> involved in photocatalytic process. A series of comparison experiments were carried out between the original degradation of MB by 2.0% CSL-modified TiO<sub>2</sub> and those obtained after addition of quenchers in the initial solution, under other identical conditions. The results are displayed in Fig. S3. It is clear to observer that in the presence of benzoquinone (a quencher of •O<sub>2</sub><sup>-)4</sup> or ammonium oxalate (a quencher of h<sup>+</sup>)<sup>5</sup>, the photodegradation of MB was inhibited significantly compared with no quencher at the same conditions. From the results, one can conclude that the •O<sub>2</sub><sup>-</sup> radicals and h<sup>+</sup> almost played the same role for MB degradation.



**Fig. S3** The influence of different quenchers on the MB degradation in the presence of 2.0% CSL-modified TiO<sub>2</sub>.

#### References

- [1] a) H. L. Lin, J. Cao, B. D. Luo, B. Y. Xu, S. F. Chen, *Catalysis Communications*, 2012, 21, 91–95; b) J. Cao, B. D. Luo, H. L. Lin, B. Y. Xu, S. F. Chen, *Journal of Hazardous Materials*, 2012, 217–218, 107–115.
- [2] a) J. Zhang, M. J. Li, Z. C. Feng, J. Chen, C. Li, *The Journal of Physical Chemistry B*, 2006, 110, 927–935; b) Z. Y. Wang, B. B. Huang, Y. Dai, Y. Y. Liu, X. Y. Zhang, X. Y. Qin, J. P. Wang, Z. K. Zheng, H. F. Cheng, *CrystEngComm*, 2012, 14, 1687-1692.
- [3] a) F. Jiao, P. G. Bruce, *Angewandte Chemie International Edition*, 2004, 43, 5958-5961; b)
  K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniewska, *Pure and Applied Chemistry*, 1985, 57, 603-619.
- [4] G. T. Li, K. H. Wong, X. W. Zhang, C. Hu, J. C. Yu, R. C. Y. Chan, P. K. Wong, *Chemosphere*, 2009, 76, 1185–1191.
- [5] W. M. Wu, S. J. Liang, Y. Chen, L. J. Shen, H. R. Zheng, L. Wu, *Catalysis Communication*, 2012, 17, 39–42.