Supporting Information

Dramatic Visible Light Photocatalytic Degradation Performances Due to

Synergetic Effect of TiO₂ with PDA Nanosphere

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Experimental section

*Preparation of TiO*₂/PDA nanocomposites To prepare TiO₂/PDA nanocomposites is consisted of two major steps. As shown in Fig. S1, the first step was to prepare PDA nanospheres,¹ and the second step was grafting TiO₂ nanoparticles onto the PDA nanospheres. At first, 1.5 mL ammonia aqueous solution (NH₄OH, 28%) was mixed with ethanol (40 mL) and deionized water (90 mL) under mild stirring at 30 °C in a water bath for 30 min. Dopamine hydrochloride (0.50 g) was dissolved in deionized water (10 mL) and then injected into the above mixture solution. The reaction was kept at 30 °C for 20 h. PDA nanosphere was obtained by centrifugation and washed with water for three times. and dried at 60 °C in air over night. Secondly, 20 ml cyclohexane, 6 ml n-butanol, 4 ml polyoxyethylene (10) octylphenyl ether (OP-10), 0.022 ml tetrabutyl titanate and 2 ml HCl (0.1 M) were mixed together to form a dispersed mixture. Then 0.45 g as-prepared PDA nanospheres were added. After stirring for about 30 min, the mixture was finally transferred into a 50 ml Teflon-lined stainless steel autoclave. It was sealed tightly and maintained at 120 °C for 12 h. After that, the products were collected and washed three times using deionized water and absolute ethanol, then dried for 24 h under vacuum at 80 °C. Finally, the powders were collected and calcined at 500 °C for 2 h in a N₂ atmosphere. The as-prepared samples were denoted as 10%-TiO₂/PDA.

Photoelectrode preparation To prepare the working electrodes, 500 mg of the asprepared samples was first dispersed into a mixture of 2.0 mL ethanol and 0.1 mL terpinol and sonicated for 30 min to form a slurry, then the resulting slurry was coated on 2 cm×3 cm FTO glass (2.3 mm, 15 Ω ·square⁻¹, Nippon Sheet Glass, Japan) using a screen-printing method. The photoelectrode film thickness is dependent on the repeating times of the screen printing process. The photoelectrodes were sintered at 300 °C for 30 min in air.

Characterizations X-ray diffraction (XRD) patterns of the as-prepared samples were recorded on an X-ray diffractometer (D/max-IIIA, Japan) using Cu Ka radiation. The surface morphology of as-prepared samples was examined by a scanning electron microscopy (SEM) (LEO1530VP, LEO Company). The UV-vis diffuse reflectance spectroscopy (DRS) of as-prepared samples were obtained from a Hitachi UV-3010 spectrophotometer equipped with an integrating sphere assembly and using the diffuse reflection method and BaSO₄ as a reference to measure all the samples. FTIR absorption spectra were performed with a Nicolet FTIR-170SX spectrometer in the range of 500-4000 cm⁻¹ at room temperature, in transmission mode in a KBr pellet. The each of the chemical nature elements in the TiO₂/PDA nanocomposite has been studied using X-ray photoelectron spectroscopy (XPS) in Krato Axis Ultra DLD spectrometer. The binding energy was referenced to C 1s line at 284.6 eV for calibration.

Photoelectrochemical measurement photocurrent measurements were carried out in a standard electrodes photoelectrochemical cell by an electrochemical workstation (CV-27, BAS). The as-prepared samples, platinumgauze and Ag/AgCl were used as working, counter and reference electrode, respectively. A sodium sulfate solution (0.5 M) is used as electrolyte. The light for the photocurrent was the filtered light ($\lambda > 400$ nm, 150 mW· cm⁻²) from a PLS-SXE 300UV Xe lamp.

Photocatalytic activities measurement The photocatalytic reaction was conducted in a 200 mL cylindrical glass vessel fixed in the XPA-II photochemical reactor. A 1000 W Xe lamp was used as the simulated solar light source (UV-visible light), and a house-made filter was mounted on the lamp to eliminate infrared irradiation. The visible-light was obtained by using the cur-off filter. The cut-off filter was made up of 1 M sodium nitrite solution which can absorb the light with wavelength under 400 nm. This solution was injected into the interlayer of the quartz cool trap and was placed behind the water filter to completely remove the UV portion of the radiation and to supply a visible-light source. MO (20 mg·L⁻¹) was used as contamination. In order to obtain an optimally dispersed system and reach complete adsorption/desorption

equilibration, 20 mg photocatalyst powder dispersed in 200 mL reaction solutions by supersonic for 15 min and then the suspension was magnetically stirred in dark for 1 h. During the photocatalytic reaction, air was blown into the reaction medium at a flow rate of 200 mL·min⁻¹. At regular intervals, 8 mL of the suspension was filtered and then centrifuge. The concentration of the remaining MO was measured by its absorbance (A) at 465 nm with a Hitachi UV-3010 spectrophotometer. The degradation ratio of MO can be calculated by Eq. (1):

$$X\% = (A_0 - A)/A_0 \times 100\%$$
(1)

According to the Langmuir–Hinshelwood kinetics model, thephotocatalytic process of MO can be expressed as the following apparent pseudo-first-order kinetics equation:

$$\ln(C_0/C_t) = K_{app}t \tag{2}$$

Photocatalytic activities cyclic measurement The operation steps are in agreement with the *Photocatalytic activities measurement*, but after each end, the photocatalyst is filtered and dried to repeat the operation.

Photocatalytic active species measurement The terephthalic acid ($C_8H_6O_4$, TA) can be used to confirm the existence of \cdot OH by a fluorescent method, since \cdot OH reacts with TA and generates luminescent TAOH as shown in Eq. (3):²

$$\cdot OH + TA \to TAOH \tag{3}$$

50 mg of as-prepared photocatalyst was added to 160 mL of solution containing 10 mM NaOH and 3 mM TA in a quartz reactor. Prior to photoreaction, the suspension was magnetically stirred in the dark for 1 h to ensure the establishment of an adsorption/desorption equilibrium. The photoreaction was carried out as the foregoing

photocatalytic reaction under UV-visible light without oxygen bubbled into suspension. After photoreaction of 2 h, 8 mL suspension was collected, filtered and centrifuged to remove the photocatalyst particles. Photoluminescence (PL) spectra were measured with a fluorospectrophotometer (SPEX Fluoromax-2) using a Xe lamp as the excitation source at room temperature. Equally weighed powder samples dissolved in terephthalic acid solution were used for PL measurements. The employed excitation light for recording fluorescence spectra was 320 nm.



Fig. S1 Schematic illustration of the synthesis process for TiO₂/PDA.



Fig. S2 XRD patterns of the as-synthetised (a) pure PDA and (b) 10%-TiO₂/PDA.



Fig. S3 FTIR spectra of the as-prepared (a) pure PDA and (b) 10%-TiO₂/PDA.



Fig. S4 UV-vis absorption spectra of the as-obtained samples: (a) PDA; (b) 1%-

TiO₂/PDA; (c)5%-TiO₂/PDA; (d)10%-TiO₂/PDA; (e)20%-TiO₂/PDA.



Fig. S5 Photocatalytic degradation of MO with 10%-TiO₂/PDA under visible light

irradiation for 4 runs.



Fig. S6 XRD patterns of the as-prepared 10%-TiO₂/PDA before and after 4 cycle

experiments.



Fig. S7 PL spectra of the as-prepared samples.

References

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- 2. X. Zhou, B. Jin, L. Li, F. Peng, H. Wang, H. Yu and Y. Fang, Journal of Materials Chemistry, 2012, 22, 17900-17905.