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SDBS-assisted hydrothermal treatment of TiO_2 with improved photocatalytic activity

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ABSTRACT

To meet the practical application, it is still a challenge to prepare TiO_2 with excellent photocatalytic performance. Therefore, in this work, TiO_2 photocatalyst with enhanced sunlight-driven photocatalytic activity was facilely obtained after hydrothermal treatment of TiO_2 with the assistance of sodium dodecyl benzene sulfonate (SDBS). TiO_2 and SDBS-TiO_2 were characterized by Brunauer–Emmett–Teller (BET) method, X-ray diffraction (XRD), UV–Vis diffuse reflectance spectra (DRS), scanning electron microscopy (SEM), surface photovoltage (SPV) spectroscopy and X-ray photoelectron spectroscopy (XPS), respectively. The photocatalytic performance of the photocatalysts toward Rhodamine B (RhB) discolorization was evaluated. The results display that a much higher photo-induced charge separation rate, active free radicals and surface hydroxyl radical content were produced in the SDBS-TiO_2 photocatalytic system. The results further reveal that the photocatalytic performance of SDBS-TiO_2 is more than two times of that of the reference TiO_2.

1. Introduction

TiO_2 has emerged as one of the most promising photocatalysts for environment purification due to its predominant properties [1]. However, the photocatalytic efficiency of TiO_2 is far from satisfied to meet the practical application because of the fast recombination of photo-generated electron-hole pairs [2,3]. Therefore, various strategies have been exploited to improve the photocatalytic performance of TiO_2. According to the principle of photocatalysis, the photocatalytic reaction mainly takes place on the surface of the catalyst [4,5], therefore it is apparent that the surface properties will inevitably influence the transportation of electrons and holes in TiO_2, significantly affecting the photocatalytic activity. Thus, it is feasible to promote the photocatalytic performance of TiO_2 by modulating the surface properties through chemical treatments.

Herein, we reported a simple and effective method to adjust the photocatalytic property of TiO_2 by hydrothermal treatment with the assistance of SDBS. The results substantially reveal that SDBS-assisted hydrothermal treatment of TiO_2 can dramatically enhance the separation rate of photo-generated charge pairs, the formation of active free radicals and the hydroxyl content on the surface, boosting the photocatalytic performance of TiO_2.

2. Experimental section

All chemicals (analytical grade reagents) were obtained from Chengdu Kelong Chemical Reagent Factory and used as received. All the experiments were done using deionized water. TiO_2 powder was prepared following the procedures as described in the Ref. [6]. 2 g TiO_2 was dispersed in 60 mL deionized water with sonication, then 0.04 g SDBS was added into the suspension system mentioned above under intensely stirring. The above mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave and maintained at 453 K for 24 h, then naturally cooled to room temperature. The solid was filtered, washed with deionized water many times, and then dispersed in absolute ethanol and dried at 353 k in air overnight. The sample was named as SDBS-TiO_2. The pure TiO_2 was also treated as the method mentioned above without the presence of SDBS.

The Brunauer–Emmett–Teller (BET) surface areas were measured on a SSA-4200 automatic surface analyzer (Builder, China). Crystal structures of the samples were detected on a DX-2600 X-ray diffractometer using Cu/Kα radiation, 40 kV, 20 mA. The morphologies were taken on a JSM-5900 LV scanning electron microscopy (SEM). X-ray photoelectron spectroscopy (XPS)

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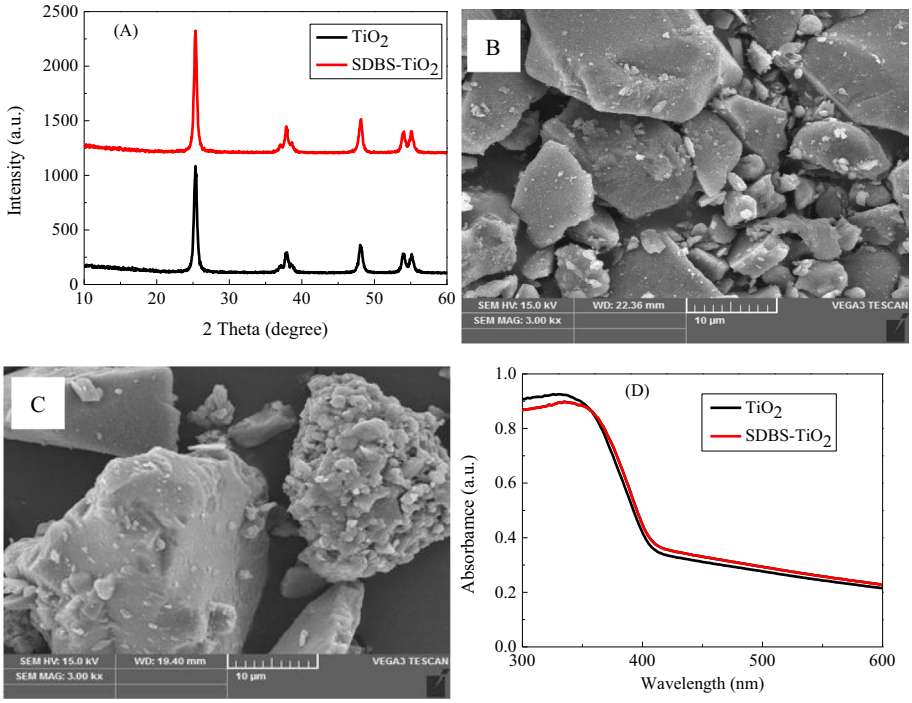

Fig. 1. XRD patterns of the photocatalysts (A), SEM of the photocatalysts (B) TiO_2; (C) SDBS-TiO_2 and UV–Vis DRS of the samples (D).

measurements were carried out on an XSAM 800 using Mg Kα at 12 kV and 12 mA. SPV experiments were performed on a home-built apparatus as described in the Ref. [7]. The measurement of $\cdot O_2^-$ was followed the procedures as described in the Ref. [8] using nitrotetrazolium blue chloride (NBT) method. Photocatalytic activities of the samples were tested by decolorization of RhB aqueous solution. A 500 W Xe lamp was used as a light source. 50 mg photocatalyst was added into a 50 mL RhB aqueous solution (10 mg L^{-1}), the initial pH of RhB solution was 6.0.

3. Results and discussion

The XRD patterns of TiO_2 were exhibited in Fig. 1A. It is evident that all the strong patterns can be allocated as the pure anatase-type TiO_2, which fits well with the reported data (JCPDS No. 89-4921), and no peaks of impurity were detected, implying relative high purity of the sample. The SEM images of photocatalysts are shown in Fig. 1B and C. Both TiO_2 and SDBS-TiO_2 exhibits irregular lump-like morphology, no relative abundant pores were observed in the particles, resulting in the relative low specific surface area. The specific surface areas of TiO_2 and SDBS-TiO_2 are 42 m^2/g and 30 m^2/g, respectively. The results indicate that TiO_2 treated by hydrothermal routine with the assistance of SDBS exhibits lower specific surface area than that of TiO_2. The underlying mechanism needs to be further revealed. Combined with the results of photocatalytic evaluation, S_{BET} is not the vital factor for the promoted photocatalytic activity.

As shown in Fig. 1D, two photocatalysts have similar UV–Vis diffuse reflectance characteristics, which demonstrates that the bandgap of TiO_2 cannot be effectively altered by SDBS during the hydrothermal treatment and it is clear that the response ability to light is not the primary factor to determine the difference in photocatalytic performance. Although the photocatalysts exhibit similar UV–Vis diffuse reflectance spectra, as shown in Fig. 2 (inset), the SPV responses of TiO_2 and SDBS-TiO_2 samples display great difference. Two photocatalysts display obvious SPV response from 300 to 375 nm, however, SDBS-TiO_2 possesses stronger SPV response than TiO_2, which indicates that SDBS alter the surface trapping states (surface net charge) of TiO_2 during the hydrothermal treatment, surface net charge can drive the flow of electrons and holes in different directions, greatly boosting the charge separation rate and resulting in stronger SPV responses. After illumination of light whose energy is greater than E_g of a semiconductor, then electrons and holes can be generated. If the photo-generated electrons and holes can be effectively separated before recombination, then electrons and holes will migrate to the surface of semiconductor, initiating the photocatalytic reactions. Commonly, strong SPV response corresponds to high separation rate of photo-generated charge pairs [9], relative high separation rate of photo-induced charge pairs can generate more active free radicals (h^+, $\cdot O_2^-$ and ·OH), which is beneficial to the corresponding photocatalytic activity. According to the principle of NBT

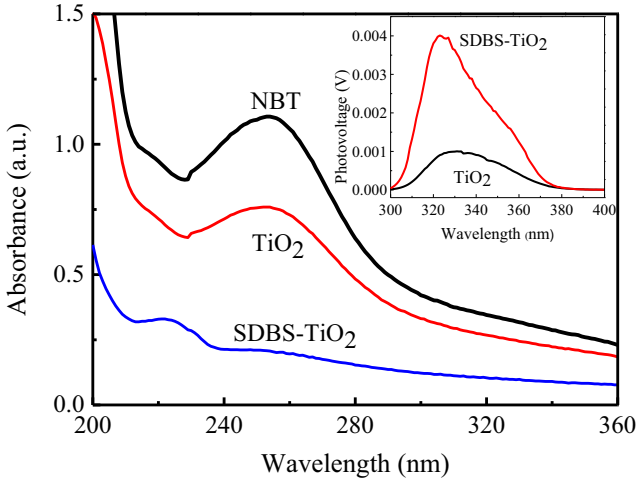

Fig. 2. Absorbance of NBT in different photocatalytic systems (illumination time = 2 h, NBT dosage = 0.05 mmol/L), the inset is the SPS responses of the samples.