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Short Communication

Visible light-driven binary dyes synergic degradation by iodine-doped TiO_2 nanocrystal film

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ABSTRACT

We report synergistic degradation of fluorescein sodium/rhodamine B or eosin Y/rhodamine B using iodine-doped TiO_2 nanocrystal film (I-TNC) under visible irradiation. The fabricated I-TNC was characterized by SEM, EDS and reflectance spectra. The degradation results showed that when Flu or EO was introduced to I-TNC/RhB system, the degradation ratio of RhB was significantly enhanced, with an eight-fold or five-fold improvement compared with that in I-TNC/RhB system free of sensitizer. The photocatalytic improvement may be explained by the mutually sensitization of binary dyes and narrowed bandgap caused by doping. Active oxygen species were evidenced to be involved in the synergic degradation.

1. Introduction

TiO_2 thin film as efficient photocatalyst has been intensively investigated for organic compound degradation due to its unique properties such as nontoxicity, photostability, high recycle rate and free of costly post-treatment processes [1–6]. In particular, TiO_2 nanocrystal film has gained great attention for the advantages of active surface area and high loading amount. However, such TiO_2 nanocrystal film usually shows poor degradation property under visible-light illumination due to the wide bandgap of pristine TiO_2 [7]. Recent reports have shown that iodine doping can shift the photoresponse from UV to visible region by altering the bulk bandgap of TiO_2 [8–10]. More importantly, iodine dopant also can act as conduction band electron scavenger capable of inhabiting the recombination of electron–hole pairs [11–13]. Very recently, our group reported an iodine-doped TiO_2 nanocrystal photoanode film applied to dye sensitized solar cells [13]. The features of the film i.e. expanded light harvesting, low transfer resistance, prolonged electron lifetime can be considered as favorable influencing factors for improving visible light-induced catalytic capability of film. But to date, iodine-doped TiO_2 nanocrystal film (I-TNC) based system has yet to be reported in pollutant degradation under visible light radiation.

Dye sensitization is another effective method to improve the degradation activity of TiO_2 utilizing visible-light irradiation [14–16]. Although dye-sensitized decomposition in single dye/TiO_2 system has been extensively reported, only a very limited work on synergistic degradation of two or more dyes is involved, even if dyes are extensively coexist in practical wastewater effluents. Recently, Yin et al. [17] reported a synergistic degradation of EO and RhB using a commercial TiO_2 powder as photocatalyst in the TiO_2/EO/RhB system. But in such a system the use of TiO_2 powder will inevitably cause the aggregation of catalyst as well as the difficult post-treatment process [5,6]. Hence, it is highly desirable to seek for a TiO_2 film based system capable of being applicable in the synergistic degradation of binary dyes.

In this work, we reported a new reaction system i.e. I-TNC/binary dyes containing the characteristics of iodine doping, inherent film characteristic, and synergic degradation effect of binary dyes. The experimental results showed that I-TNC exhibited a higher degradation activity than pure TNC either in singly dye system or in binary dyes system. Furthermore, when fluorescein sodium (Flu) or eosin Y (EO) as sensitizer was added into the I-TNC/rhodamine B (RhB) system forming I-TNC/binary dyes system (I-TNC/Flu/RhB or I-TNC/EO/RhB), the degradation ratio of RhB was significantly enhanced, with an eight-fold or five-fold improvement compared with that in the I-TNC/RhB system free of sensitizer and twenty-four-fold with that in pure TNC/RhB system. Besides, active oxygen species involved in the photodegradation process were also examined and analyzed.

2. Experimental

2.1. Preparation and characterization of iodine-doped TiO_2 nanocrystals

Iodine-doped TiO_2 nanocrystal (I-TiO_2 nanocrystals) was synthesized according to an analogous procedure as reported [13]. The

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sample was characterized by transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET) method and X-ray diffraction (XRD) measurements and the details were described in the Supplementary data.

2.2. Preparation and characterization of I-TNC

The TiO_2 nanocrystal paste was obtained by dispersing 0.01 g polyethylene glycol (PEG) 6000 and 0.1 g home-made ZnO nanocrystals [18] into 1 g as-prepared I-TiO_2 nanocrystal colloids by means of sufficient grinding. Note that a tiny tricky is to add a certain amount of PEG and ZnO to the paste for improving the adhesive force of I-TNC with the substrate. The glass used as substrate was ultrasonically cleaned sequentially in ethanol, water, and pretreated with 0.4 M $TiCl_4$ solution at 70 °C for 30 min. The paste was then coated on a 2×2 cm^2 glass by a doctor-blade technique and finally calcined at 500 °C for 1 h to burn off organics and consequently bind TiO_2 onto the substrate. The I-TNC was characterized by field emission scanning electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDS), UV–vis diffuse reflectance spectra (DRS) and the details were described in the Supplementary data.

2.3. Photocatalytic activity measurements

The photocatalytic activity of TiO_2 nanocrystal film (TNC) was evaluated in terms of the degradation of dyes in TNC/single dye or TNC/binary dyes (Flu/RhB or EO/RhB mixture solution) system upon visible irradiation. TNC was immersing in 40 mL aqueous solution containing given concentrations of target organics. A 500 W tungsten halogen lamp with appropriate cutoff filter limiting UV light was used as visible light source (intensity: 120 mW/cm^2). Prior to irradiation, the reaction solution was magnetically stirred in dark for 30 min. The dye concentration changes were monitored with a UV–vis spectrophotometer from their characteristic absorption bands (generally 553 nm for RhB, 487 nm for Flu and 516 nm for EO) [17].

3. Results and discussion

3.1. The morphology and structure of I-TiO_2 nanocrystals

Fig. 1a shows the TEM image of I-TiO_2 nanocrystals, illustrated that the as-synthesized I-TiO_2 nanocrystals have a uniform spherical structure with an average diameter of ~15 nm. The XRD patterns of undoped and I-doped TiO_2 nanocrystal powders are shown in Fig. 1b. A series of characteristic peaks of 25.3°, 37.9°, 48.0°, 55.1°, and 62.7° is observed, exhibiting good agreement to anatase crystal planes (JCPDS 21–1272), indicating that the anatase nanocrystalline structure is retained after doping. The average crystallite size calculated from the full width at half-maximum (FWHM) of the (101) peak based on the Scherrer's formula ($d = 0.9\lambda/\beta_{1/2}\ cos\theta$) is within a narrow range of 14–15 nm, and it is well consistent with the TEM image. The physical parameters of prepared samples are summarized in Table 1.

3.2. The morphology and optical properties of I-TNC

The FESEM images of pure TNC and I-TNC as shown in Fig. 1c and d exhibit smooth and homogeneous surface morphology without cracks and big agglomerates, facilitating electron transport between neighboring nanoparticles [13,18,19]. The EDS analysis was conducted to determine the composition of the I-TNC. As shown in Fig. 1e, the film is mainly composed of Ti and O, with a certain amount of iodine dopant, confirming the doping of iodine into TiO_2. The Cl and Zn elements should be ascribed to the $TiCl_4$ used in the pretreatment of substrate and ZnO nanocrystals added in during the preparation of films.

The DRS spectra of I-TNC and pure TNC are presented in Fig. 2a. Compared to pure TNC, the absorption stopping edge of I-TNC sample exhibits a noticeable shift into the long wave region; concomitantly, the color of TNC changes from transparent to yellow (see the inset in Fig. 2a). Generally, the photocatalytic activity is proportional to $(I_\alpha\Phi)^n$ (n = 1 for low light intensity and n = 1/2 for high light intensity), where I_α is the photo numbers absorbed by photocatalyst per second and Φ is the efficiency of the band gap transition [20]. The broadened absorption in the visible light region of I-TNC can increase the $I_\alpha\Phi$ causing an enhanced visible light photocatalytic activity.

To further gain insight into the absorption red-shift of materials originated from I-doping, the band gap energies (E_g) of samples were estimated from UV–vis diffuse reflectance spectra. As shown in Fig. 2b, the plots of the Kubelka–Munk functions (F(R)) [21,22] against the photon energy (E_g) exhibit that the E_g estimated from the intercept of the tangents to the plots is 3.1 and 3.3 eV for I-TNC and pure TNC, respectively. The 0.2 eV band gap narrowing caused by iodine doping facilitates the improvement of the photocatalytic activity, which is further evidenced by the following degradation results.

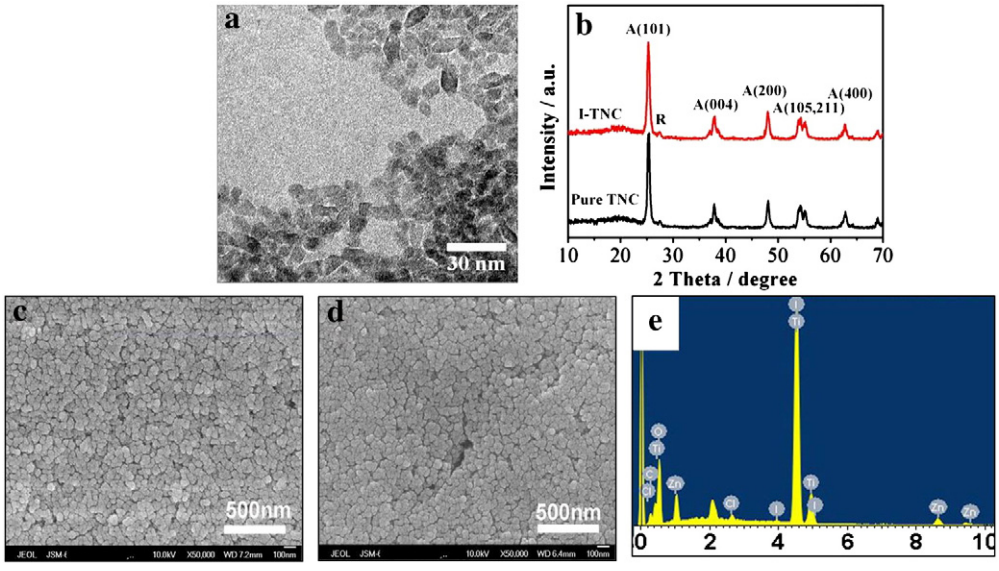

Fig. 1. (a) TEM of I-TiO_2 nanocrystals; (b) XRD patterns of pure TiO_2 and I-TiO_2 nanocrystals; (c) FESEM image of pure TNC; and (d) FESEM image of I-TNC; (e) EDS spectra of I-TNC.