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Facile fabrication of titanium dioxide/fullerene nanocomposite and its enhanced visible photocatalytic activity

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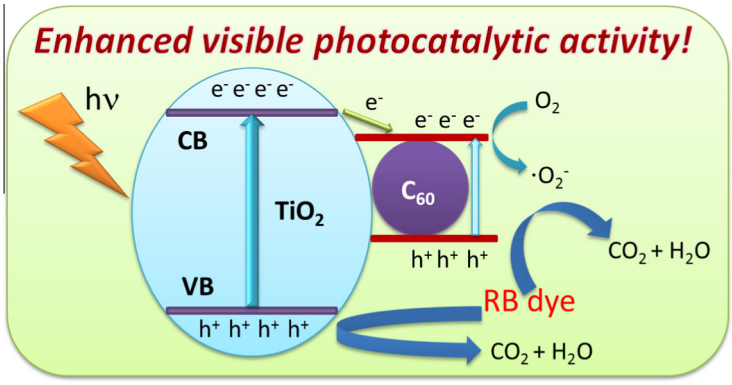
GRAPHICAL ABSTRACT

TiO_2/fullerene nanocomposite was facilely prepared and showed an enhanced visible photocatalytic activity.



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ABSTRACT

Titanium dioxide (TiO_2)/fullerene hybrid nanocomposite was facilely fabricated by mixing TiO_2 and polycarboxylic acid functionalized fullerene under an ultrasonication–evaporation method. It was found that the TiO_2/fullerene composite could serve as an efficient and reusable photocatalyst for degradation of rhodamine B dye under visible light ($\lambda > 400$ nm). The as-prepared photocatalyst was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and diffuse reflection spectroscopy (DRS). The degradation experiments revealed that the photocatalytic activity strongly depends on the contents of fullerene from 0.5% to 3% mass ratio. The incorporation of fullerene into TiO_2 efficiently extended the absorption spectrum of photocatalyst to visible light region, enhanced the adsorption capacity and degradation efficiency, resulting from a synergistic effect of fullerene and TiO_2. The trapping experiments demonstrated that both the photo-generated hole (h^+) and the reactive oxygen species such as superoxide anion radical ($^{\cdot}O_2^-$) were involved in the photocatalytic reaction.

1. Introduction

Environmental pollution, such as water and air pollution, has become a very serious problem all over the world. Photocatalysis of semiconductor has been considered to be one of the most

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promising treatment approaches in solving the problem, due to it is an eco-friendly technique [1–4]. For example, ZnO [5,6], Ag-based materials [7,8], and TiO_2 [9] have been extensively used to photocatalytically decompose organic dyes or treat the wasterwater. As one of the most widely used photocatalysts, TiO_2 owns beneficial characteristics such as high photocatalytic efficiency, chemical stability, low cost, and non-toxicity [2,10–12]. However, the relatively large band gap of TiO_2 makes it only ultraviolet light active, largely limited the well utilization of the solar energy [12]. Furthermore, it has been considered that the quantum efficiency of photocatalysis of TiO_2 is relatively low due to the fast recombination rate between photo-generated electron–hole pairs [2,12]. Thus, much research has been dedicated to the construction of TiO_2 nanocomposite materials to improve the photocatalytic performance [12]. Metal such as transition metal [13] and rare earth metal [14] doped TiO_2 or non-metal such as N- [15] and C-doped [16] TiO_2, has been extensively employed to enhance its photocatalytic activity.

Due to the strong adsorption capacity and good electron accepting ability, nanocarbon materials such as carbon nanotubes (CNTs) and graphene have been usually used to fabricate the composite materials with TiO_2 [16,17]. For example, CNTs [18–21] and graphene [22–25] have been used to modify TiO_2 to improve the visible photocatalytic performance via facilitating the visible light absorption and decreasing the recombination rate of photogenerated hole–electron pairs, respectively. Fullerene (C_{60}), one of the nanocarbon materials, could efficiently promote a rapid photo-induced charge separation and retard charge recombination, making it promising as an excellent electron-acceptor [26–29]. Furthermore, C_{60} adsorbed on inert matrix such as SiO_2 has been directly used as a photocatalyst for pollutant degradation [30–32]. Thus the combination of semiconductor such as TiO_2 and fullerene could produce novel efficient photocatalysts. However, only a few examples have been reported for utilization of semiconductor/fullerene composite on photocatalysts [33–39], where a complicated procedure such as electrodeposition [33], hydrothermal method [35] or sol–gel approach [36,37] was usually employed.

In this work, we developed a facile ultrasonication–evaporation approach to fabricate a novel TiO_2/fullerene composite photocatalyst, where a poly-carboxylic acid functionalized fullerene C_{60}–$(COOH)_n$ was utilized to modifying the commercial TiO_2 (P25). It was found that the introduction of fullerene C_{60}–$(COOH)_n$ not only extended the absorption spectrum of TiO_2 to visible light region, but also significantly enhanced its adsorption capacity toward pollutant dye. Compared with pure TiO_2 and fullerene, the as-prepared TiO_2/fullerene composite photocatalyst exhibited an enhanced visible activity. The influence of fullerene on the photocatalytic activity of TiO_2/fullerene nanocomposites was examined systematically by considering various mass ratios of fullerene. The catalytic reaction mechanism was also discussed based on the trapping experiments of active species.

2. Experimental

2.1. Preparation of TiO_2/fullerene composite photocatalyst

Fullerene C_{60} (99.5%) was purchased from XFNANO (Nanjing, China) and other reagents as well as solvents (AR) were obtained from Sinopharm Chemical Reagents Corp. (Shanghai, China). TiO_2 (P25) nanoparticle was obtained from Acros. Deionized water was used in all experiments. The TiO_2/fullerene composite photocatalyst was prepared by two steps. Firstly, the poly-carboxylic acid functionalized fullerene C_{60}–$(COOH)_n$ was synthesized by a modified procedure described in the previous report [40–42]. In brief, C_{60} (72 mg, 0.1 mmol), sarcosine (89 mg, 1 mmol) and 4-carboxybenzaldehyde (150 mg, 1 mmol) were refluxed in toluene (30 ml) for 8 h, and the solvent was removed; the residual solid was washed three times by deionized water and dried in vacuum at 40 °C for 24 h. The obtained C_{60}–$(COOH)_n$ was characterized by mass spectrum and the number of carboxylic acid is confirmed to be up to 4 (n = 1–4), where series peaks were detected at m/z = 897, 1074, 1251, and 1428, respectively. Secondly, the mixture of C_{60}–$(COOH)_n$ (1 mg) and TiO_2 (99 mg) was dispersed in 50 ml ethanol under ultrasonication for 30 min; the solvent was removed by rotary evaporation and the obtained TiO_2/fullerene composite powder (mass ratio 1% C_{60}) was dried in vacuum at 40 °C for 24 h. Others photocatalysts with different mass weight ratio of fullerene were obtained by following the similar process with various amounts of fullerene (mass ratio 0.5–3% C_{60}) addition.

2.2. Characterization

X-ray diffraction (XRD) patterns of the samples were obtained on the D/max-2550 PC X-ray diffractometer (Rigaku). The diffuse reflectance spectra (DRS) were recorded on a UV–vis a TU-1901 spectrophotometer (Persee) with $BaSO_4$ as the reflectance standard. Mass spectra were recorded on MALDI-TOF-MS spectrometer (AB Sciex 4700). Transmission electron microscopy (TEM) was performed on JEOL-2100 microscope.

2.3. Photocatalytic properties

In this experiment, rhodamine B (RB), a typical organic dye pollutant in the textile dyeing and printing wastewater, was selected as an example for evaluation of photocatalytic properties of the as-prepared TiO_2/fullerene composite. Briefly, TiO_2/fullerene composite powder (20 mg) was suspended in 20 ml RB solution (10 mg l^{-1}), and the slurry mixture was stirred under dark for 60 min to reach the adsorption–desorption equilibrium; then the quartz reactor was irradiated under the visible light irradiation from a parallel 500 W Xe-lamp, equipped with a 400 nm cutoff filter at room temperature; 1 ml mixture solution was taken out every 30 min, centrifuged and the supernatant was diluted to 3 ml for monitoring the degradation of dye, by measuring the absorbance at 554 nm on the UV–vis spectrophotometer. The percentage of degradation was calculated by C/C_0, where the C represents the concentration of remained dye in solution at the certain irradiation time interval, while the C_0 is the initial concentration of dye solution before irradiation. The used photocatalyst was recovered by the centrifugation and washed alternatively with the deionized water and ethanol three times. The repeated experiment was conducted with recovered catalyst at the same experimental conditions. The same procedure was also employed for pure TiO_2 and fullerene for a comparison study, respectively.

3. Results and discussion

3.1. Characterization of photocatalyst

Fig. 1 presents XRD patterns of the series of TiO_2/fullerene composite photocatalysts. It is obvious that the TiO_2/fullerene nanocomposites with different mass weight ratios of fullerene as well as pure TiO_2 (P25) exhibit similar XRD patterns (Fig. 1(a)–(e)). The well-defined peaks at 25.3°, 37.8°, 48.1°, 54.0°, 55.2°, 62.7°, 69.0°, 70.1°, and 75.1° are readily indexed as (101), (004), (200), (105), (211), (204), (116), (220), and (215) crystal planes of anatase TiO_2 in P25 respectively, whereas the weak diffraction peaks at 27.5 and 36.1 are the characteristic (110) and (101) faces of rutile TiO_2 in P25 [43], implying that the TiO_2 (P25) used in this work is a mixture