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Synthesis and photocatalytic property of SnO_2/TiO_2 nanotubes composites

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Abstract

SnO_2/TiO_2 nanotubes composite photocatalysts with different SnO_2 contents were successfully synthesized by means of a simple solvothermal process. The synthesized products were characterized physically by X-ray diffraction (XRD) and high-resolution transmission electron microscope (HRTEM). The composite photocatalysts can not only make the target pollutant, methylene blue (MB), adsorbed at a high concentration level around the surface of the composites but also decrease the recombination rate of electron–hole pairs so as to achieve good photocatalytic performance. The effect of SnO_2 contents on the photocatalytic activities of the composites was also investigated. The results showed that the SnO_2/TiO_2 nanotubes composite photocatalyst with 5 wt.% SnO_2 loading had the highest photocatalytic efficiency.

Keywords: SnO_2/TiO_2 nanotubes composites; Photocatalytic reaction; Methylene blue

1. Introduction

Photocatalytical1y decomposing organic pollutants utilizing an oxide semiconductor to generate clean environment has been a dream of humankind for several decades [1,2]. Particularly, TiO_2 having a crystal form of anatase is known to be one of the most effective photocatalysts for the treatment of polluted water, and its photocatalytic behavior has been studied extensively [3,4]. However, the large band gap in TiO_2 and high recombination rate of the photogenerated electron/hole pairs hinder its further application in industry. To solve these problems, numerous efforts have been attempted to improve its photocatalytic activity by modifying the surface or bulk properties of TiO_2, such as doping, codeposition of metals, surface chelation, mixing of two semiconductors, etc. [5–7].

Among the coupled semiconductor photocatalysts, many efforts have been devoted to the SnO_2/TiO_2 system [8,9]. The relatively high photocatalytic activity of SnO_2/TiO_2 coupled oxide should be attributed to better charge separation. It is well known that the proper placement of the individual semiconductor is essential for the charge separation to ensure high photocatalytic activity due to fast electron transfer from TiO_2 to SnO_2. The bandgaps of SnO_2 and TiO_2 are 3.8 and 3.2 eV, respectively [8]. When the two semiconductor particles are coupled, the conduction band (CB) of SnO_2 (E_{CB} for $SnO_2 = 0$ V versus NHE at pH 7) is lower than that of the TiO_2 (E_{CB} for $TiO_2 = -0.5$ V versus NHE at pH 7), the former acts as a sink for photogenerated electrons. Since the photogenerated holes move in the opposite direction, they accumulate in the valence band of the TiO_2 particles, thereby increasing the efficiency of charge separation [9].

It has been reported that TiO_2 with higher specific surface area demonstrated a better photocatalytic performance than the simple TiO_2 particles [10]. Therefore, it is of great interest to find a special technique that enables the photocatalyst with higher specific surface area to decompose pollutants with high reaction rate and may be easily applied to industry. TiO_2 nanotubes have been found to give some advantages for TiO_2 nanoparticles because of their larger specific area surface [11]. TiO_2 nanotubes make a high concentration environment of target pollutants around photocatalysts, hence, increasing the collision probability between pollutants and photocatalysts [11,12].

In this study, we prepared the SnO_2/TiO_2 nanotubes composite photocatalysts that offer considerably higher photocatalytic

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efficiency than that of pure TiO_2 nanotubes toward the oxidation of methylene blue in aqueous solution. The influence of the SnO_2 contents on the photocatalytic activity of the composite photocatalysts was investigated.

2. Experimental

2.1. Synthesis of the SnO_2/TiO_2 nanotubes composite photocatalysts

All chemicals were of analytical grade and used without further purification. The method employed for the synthesis of TiO_2 nanotubes was the same as described in Refs. [11–13], except where otherwise indicated. The distilled deionized water was used for preparing solutions. In the classical synthesis, 0.8 g pure TiO_2 powders of anatase phase were mixed with 10 M KOH aqueous solution in a Teflon-lined autoclave at 200 °C for 24 h. The resulted product was treated with 0.1 M HCl and further washed with distilled water and ethanol until the pH reached around 7. The snow-white sample was dried at 78 °C for 7 h.

SnO_2/TiO_2 nanotubes composite photocatalysts were synthesized by means of the solvothermal method as followings: certain amount of $SnCl_4{\cdot}5H_2O$ was dissolved in absolute ethanol and agitated at room temperature for 30 min to form the well-proportioned solution and then the proper TiO_2 nanotubes were dispersed in the above solution, stirred for 15 min and then ultrasonically treated for 10 min. After well mixed, the mixture was kept in a Teflon-lined autoclave with a stainless steel shell. This autoclave was heated to 160 °C at 10 °C/min in an oven. The autoclave was cooled to room temperature naturally after keeping at 160 °C for 16 h. The prepared products were filtered, washed repeatedly with distilled water and ethanol, and then dried at 80 °C. By changing the added amount of TiO_2 nanotubes to synthesize the SnO_2/TiO_2 nanotubes composites with 2, 5, 10, 15 wt.% SnO_2 loadings, labeled by S_2T, S_5T, $S_{10}T$, $S_{15}T$, respectively, while pure TiO_2 nanotubes are labeled by S_0T.

2.2. Characterization of the SnO_2/TiO_2 nanotubes composite photocatalysts

The prepared SnO_2/TiO_2 nanotubes composite photocatalysts were characterized by X-ray diffraction (XRD, Max 18^{XCE}, Japan) using a Cu Kα source (λ = 0.154056 nm), scanning electronic microscope (SEM, LEO1430VP, Germany) and high-resolution transmission electron microscope (HRTEM, JEOL 2010 F). The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) of the samples was obtained from nitrogen adsorption–desorption data (Micromeritics, ASAP-2010, America). To investigate the light absorption properties of photocatalysts, UV–vis diffuse reflectance spectra were carried out, in the wavelength range of 200–800 nm, using a U-3010 spectrophotometer (Japan). The pure powdered Al_2O_3 was used as a reference sample.

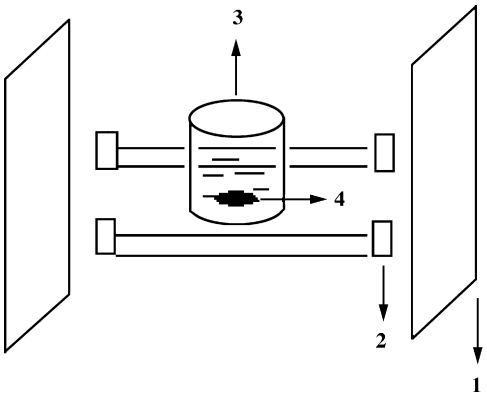

Fig. 1. Photocatalytic reactor. (1) Aluminium reflector, (2) quartz UV lamps (30 W), (3) quartz reactor and (4) magneton.

2.3. Adsorption behavior of MB on the synthesized photocatalysts

To determine the adsorption behavior of MB on the synthesized photocatalysts, the suspensions were prepared by mixing 10 ml aliquots of MB solutions of the same initial concentrations (5×10^{-5} mol/l) with given weight (0.050 g) of different photocatalysts. The suspensions were kept overnight in the dark and filtered after being centrifuged. The absorbance of the filtrated was then measured at the maximum band 464 nm of MB to determine the concentration of MB. The extent of equilibrium adsorption was determined from the decrease in the MB concentration detected after filtration.

2.4. Photocatalytic activity measurements

The photocatalytic properties of SnO_2/TiO_2 nanotubes composite photocatalysts were evaluated by photo-degradation of MB aqueous solution. All photocatalytic reactions were performed under ultraviolet irradiation by using two 30 W ultraviolet lamps and maintaining constant magnetic stirring, and 100 ml of MB solution with initial concentration of 5×10^{-5} mol/l was mixed with 0.050 g as-prepared photocatalyst in a quartz reactor (Fig. 1). The solution was stirred for 10 min in dark to allow the system to reach an adsorption/desorption equilibrium, then analytical samples were drawn from the reaction suspensions every 5 min during the whole irradiation. The concentrations of MB solution were analyzed by UV–vis spectrophotometer (UV-2450, Japan and absorption at λ_{max} = 664 nm for MB).

3. Results and discussion

3.1. XRD analysis

The XRD patterns of the prepared photocatalysts are shown in Fig. 2. As shown in Fig. 2(b)–(e), besides the TiO_2 nanotubes diffraction peaks, there exist the tetragonal SnO_2 diffraction peaks, which are presented and indexed in line with the standard spectrum (JCPDS, No.77-0452). Compared to SnO_2/TiO_2 nanotubes composites, the peak intensities of pure TiO_2 nanotubes are much stronger than those of SnO_2/TiO_2 nanotubes

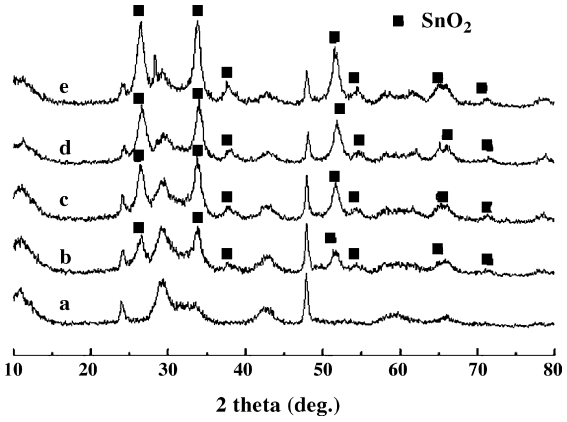

Fig. 2. XRD patterns of S_0T (a), S_2T (b), S_5T (c), $S_{10}T$ (d) and $S_{15}T$ (e).

composites, which indicate that TiO_2 nanotubes have been successfully coated with the SnO_2 and thus the weakened peaks occurred. Moreover, with the increase of the SnO_2 contents, the peak intensities of SnO_2 become stronger and stronger, while the peak intensities of TiO_2 nanotubes turn weaker and weaker.

3.2. The morphology and surface area of samples

3.2.1. The morphology of S_0T

Fig. 3(a) and (b) shows the SEM and HRTEM images of the as-prepared TiO_2 nanotubes, respectively. The external tube diameters fall between 10 and 15 nm and the internal diameters are between 7 and 11 nm. The lengths of nanotubes range from 1 to 2 μm. From Fig. 3(b), it can be clearly seen that the nanotubes possess a hollow inner pore with open tube ends.

Table 1
Surface area for various photocatalysts

	S_{BET} (m^2/g)
S_0T	280.4
S_2T	245.9
S_5T	229.6
$S_{10}T$	211.3
$S_{15}T$	187.8

3.2.2. The morphology of S_5T

Fig. 4(a) shows the SEM image of the as-prepared S_5T. As seen in Fig. 4(a), the composites also have nanotube structure, which is provided by the TiO_2 nanotubes. HRTEM study of S_5T (Fig. 4(b)) reveals that the nanotubes get decorated with evenly distributed SnO_2 nanoparticles without suffering any morphological changes and the thickness of SnO_2 layer is about 1 nm.

3.2.3. The surface areas of as-prepared samples

The surface areas of all photocatalysts in this research are also listed in Table 1. It can be seen that the surface area of pure TiO_2 nanotubes is 280.4 m^2/g. Moreover, the surface areas of the coupled photocatalysts decreased with the increase of

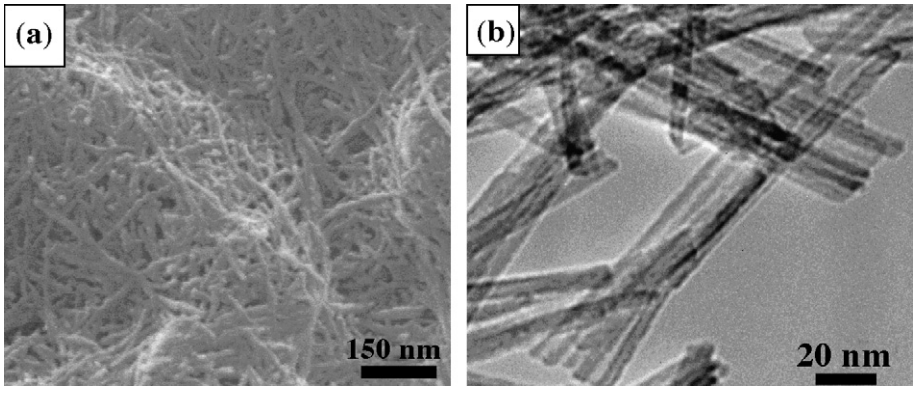

Fig. 3. SEM (a) and HRTEM (b) images of S_0T.

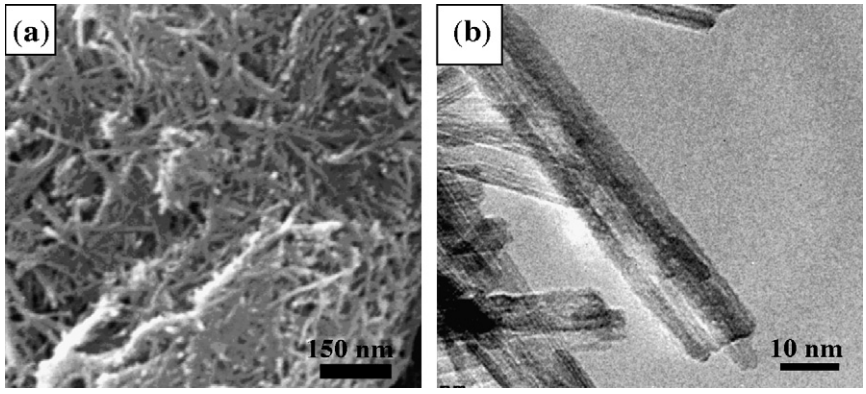

Fig. 4. SEM (a) and HRTEM (b) images of S_5T.

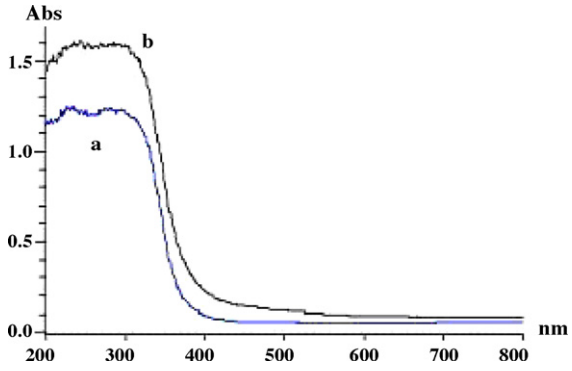

Fig. 5. UV–vis diffuse reflectance spectra of S_0T (a) and S_5T (b).

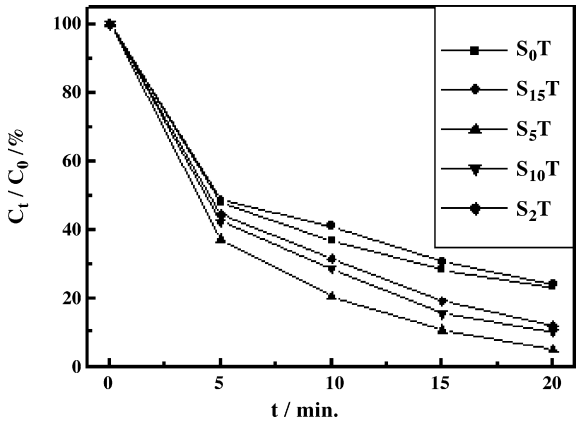

Fig. 6. Effect of as-prepared photocatalysts on the removal efficiency of MB.

SnO_2 contents, indicating that SnO_2 coverage of TiO_2 nanotubes becomes higher while the amount of SnO_2 loadings increases. The increased SnO_2 coverage results in greatly reducing original surface areas and micropore volume of TiO_2 nanotubes. However, the photocatalyst $S_{15}T$ with a maximum content of SnO_2 still has the S_{BET} of 187.8 m^2/g. For the photocatalytic degradation of dilute pollutants, exposed TiO_2 nanotubes surfaces will service as centers of condensing substrates with a physical adsorption process, and the condensed substrates would be degraded by generated hydroxyl radical.

3.3. UV–vis diffuse reflectance spectra analysis

The room temperature UV–vis diffuse reflectance spectra of S_0T and S_5T were displayed in Fig. 5. Compared to S_0T, S_5T showed much stronger light absorption property in the UV region and further slightly red-shifted to the visible-light region, which further confirms that S_5T owned stronger photocatalytic property than S_0T under UV irradiation. It is known that the process for photocatalysis of semiconductors is the direct absorption of photo by band gap of the material and generates electron–hole pairs in the semiconductor particles. The excitation of an electron from the valence band to conduction band is initiated by light absorption with energy equal to or greater than the band gap of the semiconductor. The narrower band gap is, the more easily an electron is excited from the valence band to the conduction band. The differences in the band gap and light absorption property lead to different photocatalytic behavior. The UV–vis diffuse reflectance spectra are in good agreement with the observed photocatalytic activity.

3.4. Photo-catalytic activity

A preliminary test was done to obtain a few sets of stand control data. The preliminary test was carried out in the dark using the prepared photocatalyst. The results are listed in Table 2. It can be seen that total removal of the model pollutant were not contributed by the effect of photocatalytic degradation alone. A portion of the removal efficiency was attributable to the rapid attainment of adsorption equilibrium of the dye onto the composites, and the S_0T photocatalyst had the highest adsorption property (25.7%). However, when the photocatalytic degradation experiments were carried out under illumination of light, total removal of pollutant was enhanced significantly. Total removal of pollutant can be attributed to more than 50% of photodegradation capability in addition to the above-mentioned surface adsorption effect.

Removal efficiency of MB over the SnO_2/TiO_2 nanotubes composites with different SnO_2 contents is reported in Fig. 6. It can be seen that S_2T displayed higher photocatalytic activity compared to S_0T, and the photocatalytic activity of the SnO_2/TiO_2 nanotubes composite photocatalysts increased with the increase of the SnO_2 content and then decreased slightly. The optimum SnO_2 content was found to be 5 wt.%. Moreover, the photocatalytic activity of $S_{15}T$ was slower than S_0T. This indicated that SnO_2 itself was not effective as photocatalyst, which was in agreement with the previous report that TiO_2 nanotubes showed higher photocatalytic property while pure SnO_2 showed very slow photocatalytic activity [11,14,15]. The high photocatalytic activity of the SnO_2/TiO_2 nanotubes composites is attributed to the following two factors: the one is that

Table 2
Preliminary test and experiments carried out applying optimum parameters

	S_0T	S_2T	S_5T	$S_{10}T$	$S_{15}T$
Initial concentration (10^{-5} mol/l)	5	5	5	5	5
Adsorption removal[a] (10^{-5} mol/l/%)	1.285/25.7	1.265/25.3	1.160/23.2	1.080/21.6	0.960/19.2
Photodegradation removal[b] (10^{-5} mol/l/%)	2.555/51.1	3.150/63.0	3.595/71.9	3.415/68.3	2.845/56.9
Total removal[c] (10^{-5} mol/l/%)	3.840/76.8	4.415/88.3	4.755/95.1	4.495/89.9	3.805/76.1

[a] Total removal in the dark using photocatalyst.
[b] Total removal − adsorption removal = photodegradation removal.
[c] Total removal under light illumination using photocatalyst.

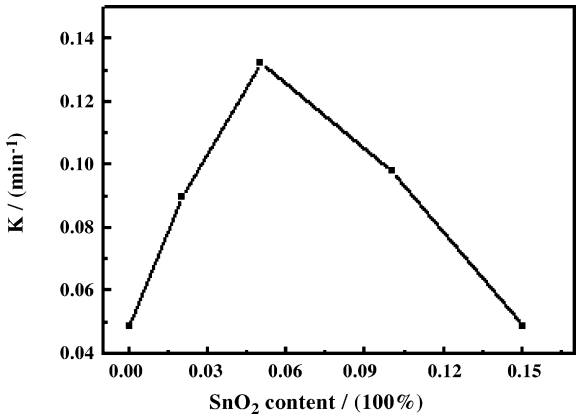

Fig. 7. The photocatalytic activity as a function of the SnO_2 contents for the SnO_2/TiO_2 nanotubes composite photocatalysts. (photocatalytic reaction rate constants (K) were calculated according to the formula: $\ln(C_0/C_t) = Kt$, where C_0 and C_t are the concentrations of MB in the primary stage of experiment and after t minutes UV-irradiation).

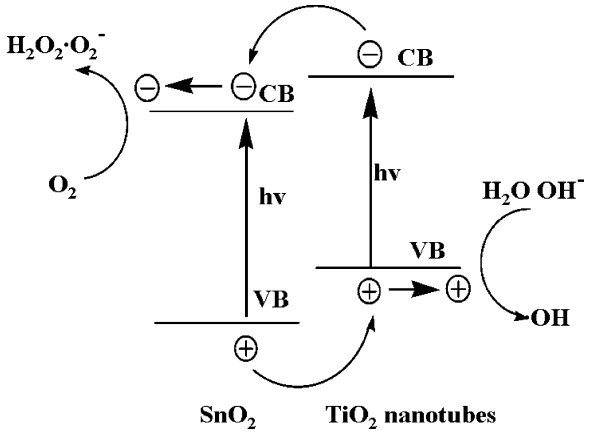

Fig. 8. Schematic diagram of the charge-transfer process in the SnO_2/TiO_2 nanotubes composite photocatalysts.

TiO_2 nanotubes make the target pollutants at a high concentration level around the surface of the composite photocatalysts because of their strong adsorption properties, thus the collision rate between pollutants and photocatalysts is increased; the other is the suppression of the recombination rate of the photogenerated electron–hole pairs due to the existence of SnO_2. Both of the two factors cooperate and make the composite photocatalysts own good photocatalystic performance.

When the SnO_2 content is loaded up to a certain level, such as 15 wt.% SnO_2 loading, a great number of SnO_2 cover the surface of TiO_2 nanotubes, hence decrease the adsorption property of TiO_2 nanotubes, and therefore, the concentration of the target pollutants around of TiO_2 nanotubes is lowered, thus the collision rate between pollutants and photocatalysts is decreased. Moreover, when the loading of SnO_2 is beyond monolayer coverage, the distance of TiO_2 nanotubes from surface of catalyst will increase, so hole and electron cannot be separated effectively. Therefore, the photocatalytic activity of SnO_2/TiO_2 nanotubes will decrease with the increase of SnO_2 contents when the SnO_2 content is loaded up to a certain level.

Fig. 7 shows the effect of the amount of SnO_2 on the photocatalysts on the kinetic constant K. It is obvious that K increases with an increase of SnO_2 contents and the total amount of the SnO_2 is up to ca. 5 wt.%, beyond which a decreasing tendency appears. Therefore, the SnO_2 content should be an important factor affecting the photocatalytic activities of the SnO_2/TiO_2 nanotubes composite photocatalysts, which is in well agreement with the Ref. [15].

In order to further get some information about the degradation mechanism of MB over the composites, we designed the schematic diagram of the charge-transfer process in the SnO_2/TiO_2 nanotubes composite photocatalysts, as shown in Fig. 8. When proper SnO_2 is loaded on TiO_2 nanotubes, during the photocatalytic process, the absorption of a photon by TiO_2 nanotubes leads the promotion of an electron from the valence band to the conduction band of TiO_2 nanotubes (E_{CB} for $SnO_2 = 0$ V versus NHE at pH 7), and then the electron is transferred to the conduction of SnO_2 ($E_{CB} = -0.5$ V versus NHE at pH 7) loaded on the surface of TiO_2 nanotubes. That is to say, the conduction band of SnO_2 acts as a sink for photogenerated electrons. While the photogenerated holes moves in the opposite direction, they accumulate in the valence band of the TiO_2 nanotubes, which increases the efficiency of charge separation [16,17].

4. Conclusions

TiO_2 nanotubes have been prepared in the hydrothermal condition. Further through loading SnO_2 on them by solvothermal process, we have successfully synthesized the SnO_2/TiO_2 nanotubes composite photocatalysts. MB being the target pollutant, we have systemically investigated the photocatalytic performance. The results demonstrated that the composite photocatalyst with proper amount of SnO_2 loading owns better photocatalytic activity than the pure TiO_2 nanotubes. The composite photocatalysts can not only make MB at a high concentration level around the surface of the composite photocatalysts by their strong adsorption properties but also decrease the recombination rate of electron–hole pairs so as to achieve good photocatalytic performance. Moreover, the effect of SnO_2 contents on the photocatalytic activity was also investigated. It was found that the best photocatalytic activity was obtained in the case of 5 wt.% SnO_2 loading.

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