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Simple fabrication and photocatalytic activity of S-doped TiO_2 under low power LED visible light irradiation

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Abstract

A series of S-doped TiO_2 with visible-light photocatalytic activity were prepared by a simple hydrolysis method using titanium tetrachloride ($TiCl_4$) and sodium sulfate (Na_2SO_4) as precursors. The photocatalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), UV–vis diffuse reflectance spectrophotometer (UV–Vis DRS), and X-ray photoelectron spectroscopy (XPS). With the doping of S, photocatalysts with small crystal size, high content of anatase phase were obtained. The result showed that S-doped TiO_2 demonstrate considerably high photoactivity under low power visible LED light irradiation, while undoped TiO_2 and the Degussa P25 have nearly no activity at all. The possible mechanism of S-doped for the visible-light activity was discussed.

Keywords: S-doped TiO_2; Visible-light; Photocatalytic activity

1. Introduction

Photocatalyst has attracted extensive attention for decades due to its potential application in environmental cleaning by decomposition of pollutants [1,2]. TiO_2, among various photocatalysts, is most frequently employed owing to its high photocatalytic activity, structural stability, low cost and non-toxicity [3–5]. However, because of its large band gap (3.20 eV for anatase), titania could only be activated in the UV region by absorbing 2–3% of the solar light [1]. In order to make efficient use of solar light, many researchers paid their much attention to develop TiO_2 photocatalysts with visible light photocatalytic activity [6–11].

Among these methods, modification TiO_2 with various non-metal ions were powerful ways to extend the adsorption light from UV to visible area and to reduce the recombination of photo-generated electrons and vacancies of TiO_2 [9,10]. Since Umebayashi et al. reported that S-doping shifted the absorption edge of TiO_2 to a lower energy [12], thereby exhibiting photocatalytic degradation of methylene blue under visible light irradiation, a large number of researches were carried out on S-doped TiO_2 [13,14]. However, sulfur doping was achieved under high temperature process, using expensive precursors or preparation instruments [14–17]. Except the energy waste, the treatment at such high temperature usually resulted in the low surface area due to the undesirable sintering of nanocrystallites. However, to the best of our knowledge, there were few reports [18] on synthesis S-doped TiO_2 photocatalyst with visible-light response by a simple hydrolysis method which is a promising approach for the preparation of different categories of inorganic materials in a nanocrystalline state. In addition, many researches use 100–500 W high power lamps as light sources in photocatalytic studies. Few studies [19] related to low power light irradiation with monochrome LED were carried out.

In this work, a series of S-doped TiO_2 photocatalysts were prepared using cheap raw material of $TiCl_4$ and Na_2SO_4 by a simple hydrolysis method. The photocatalysts have been characterized by XRD, TEM, FT-IR, XPS and URS. Furthermore, the photocatalytic activity of S-doped titania under irradiation of 12 W monochrome LED lamp was investigated. The obtained products show excellent visible-light photocatalytic activity in degrading methyl orange.

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2. Experimental

2.1. Synthesis

Commercial titanium tetrachloride (99.5% $TiCl_4$, Tianjin Chemical Agent Co.) was used as the main starting material without further purification. Known amount of $TiCl_4$ were added dropwise into distilled water in a ice-water bath under vigorous stirring. Then a small amount Na_2SO_4 aqueous solution was added to the above aqueous solution. The mixture solution was quickly heated to boiling under reflux and stirring. After hydrolysis for 5 h the precipitates formed in the solution were filtered and washed thoroughly with distilled water, and then dried at 60 °C in an oven for 12 h. For comparison, a sample was prepared in the absence of Na_2SO_4 under the same conditions.

2.2. Characterization

The phase structure of the obtained samples were examined by X-ray diffraction (XRD) pattern on a Bruker D8 Advance diffractometer with Cu Kα radiation. The weight of rutile phase in the samples was calculated using the following equation [20]:

$$W_R = \frac{1}{[1 + 0.8(I_A/I_R)]}$$

where W_R is the weight fractions of rutile, I_A and I_R are the peak intensities of anatase (1 0 1) and rutile (1 1 0), respectively. The morphology of the synthesized samples was observed by transmission electron microscopy (TEM) on a Hitachi H-7500, using an accelerating voltage of 25 kV. Fourier transform infrared (FT-IR) spectroscopy measurement was recorded with a Japan SHIMADIU FTIR-8900 equipment, using KBr pellet method. X-ray photoelectron spectroscopy (XPS) measurements were performed in a VG Scientific ESCALAB Mark II spectroscopy to determined the binding state of the O and S ions. The C(1s) level was used as an internal reference at 284.6 eV. Diffuse reflectance UV–Vis spectra were recorded on a Hitachi UV-3010 spectrophotometer equipped with an integrating sphere.

2.3. Photocatalytic activity

The photocatalytic activity of TiO_2 samples under visible light irradiation were performed in a self-constructed photoreactor using methyl orange solution (MO) as the model compound. A 12 W Light Emitting Diode (LED) lamp with a major emission at 460 nm (Tianshengda Optoelectronic Co. Ltd., Shenzhen, China) was used as visible light source. The experiments were carried out in a 250 ml beaker, opening to air and the distance between the lamp and the solution is about 30 cm. A total of 0.08 g photocatalyst powders were added into 100 ml of the methyl orange solution with the concentration of 20 mg/L with ultrasonic treatment for 15 min. Before the photocatalytic degradation, the suspension was magnetically stirred in the dark for 30 min to establish a MO adsorption/desorption equilibrium. The aqueous suspension containing methyl orange and powder catalysts were taken at given intervals time was centrifugally separated at 5000 r/min for 5 min and then filtrated through millipore filter. Finally, the change of concentration of methyl orange was determined with a UV–Vis spectrophotometer, by measuring the absorbance at 464 nm. For comparison, the photocatalytic property of pure TiO_2 and Degussa P25 were also measured.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows XRD patterns of the S-doped TiO_2 and pure TiO_2. It can be seen that the sample prepared in the absent of sulfate is rutile phase (JCPDS, No. 21-1276). The content of anatase phase (JCPDS, No. 21-1272) increases with increasing amount of sulfate. With increasing the amount of sulfate the ratio of anatase titania become higher. When the mole percentage of sulfate to titanium ions is more than 4%, only the anatase phase can be observed in the TiO_2 powder. The results suggest the addition of Na_2SO_4 plays an important role in obtaining anatase phase. The contents of the anatase and rutile phase can be effectively controlled by simply varying the amount of SO_4^{2-} ion.

3.2. Particle morphology

Fig. 2 presents the TEM micrographs of the as-prepared TiO_2 photocatalysts. It is evident that the powders prepared in the absent of SO_4^{2-} ion is needle like with rutile structure. While S-doped TiO_2 are spherical nanoparticles with homogeneous distribution. Therefore the addition of SO_4^{2-} is not only helpful to modify the morphology but also improve the particle distribution. It can be seen that increasing the amount of SO_4^{2-} ion can reduce particle sizes of the S-doped TiO_2. When the mole percentages of sulfate to titanium were at 0.4%,

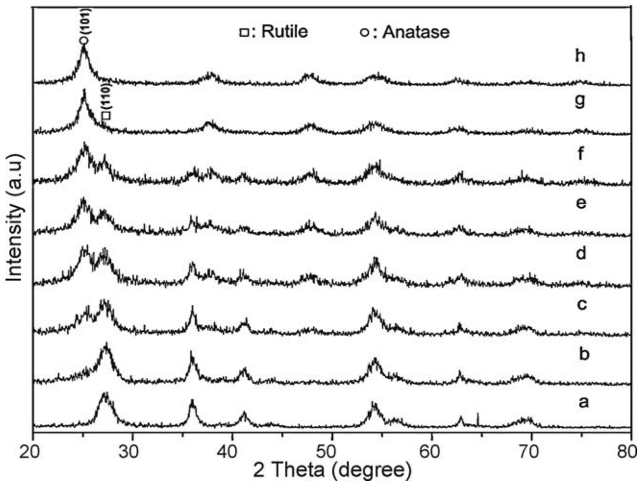


Fig. 1. The XRD patterns of S-doped TiO_2 and undoped TiO_2. a: undoped TiO_2; b: 0.2%S–TiO_2; c: 0.4%S–TiO_2; d: 0.6%S–TiO_2; e: 0.8%S–TiO_2; f: 1%S–TiO_2; g: 2%S–TiO_2; h: 4%S–TiO_2 (*X*%S–TiO_2 *X*-molar ratio).

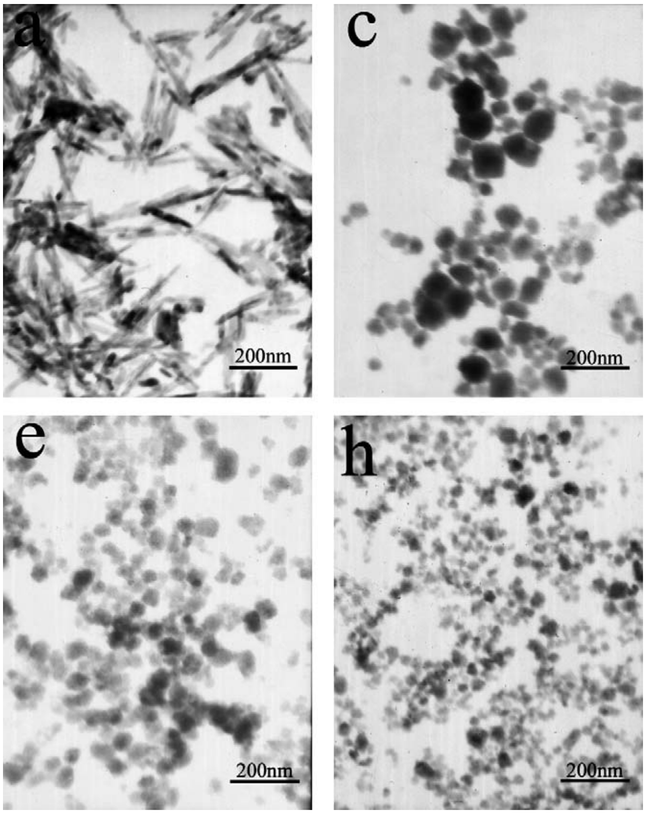


Fig. 2. TEM micrographs of undoped TiO_2 and S-doped TiO_2. a: undoped TiO_2; c: 0.4%S–TiO_2; e: 0.8%S–TiO_2; h: 4%S–TiO_2.

0.8%, 4%, the crystallite sizes of the S-doped TiO_2 were with a average diameter of 35–40 nm, 20–25 nm, 10–15 nm, respectively. It can be presumed that SO_4^{2-} species could possibly interact with the TiO_2 network, and thus hinder the growth of the crystal. Therefore, it is assumed that a small amount of sulfate species is responsible for the lowering of crystallite size.

3.3. FT-IR spectra

In order to reveal the role of sulfate, FT-IR spectra were measured. The infrared spectroscopy of S-doped TiO_2 and pure TiO_2 were represented in Fig. 3. The absorption band at 1626.3 cm^{-1} is attributed to the stretching mode of O–H bonds in absorption water [21]. The peaks corresponding to 1050 and 1131 cm^{-1} are the characteristic frequencies of SO_4^{2-} with bidentate bond [22,23]. After thermal treatment, the peak intensity weakened along with the elimination of physical adsorbed SO_4^{2-}, thus chemisorbed and doped SO_4^{2-} species were remaining existence. Therefore, the most possible doping process is that the SO_4^{2-} incorporated into the network of Ti–O–Ti. The presence of sulfate might be responsible for the formation anatase nucleus and preventing the growth of crystalline size.

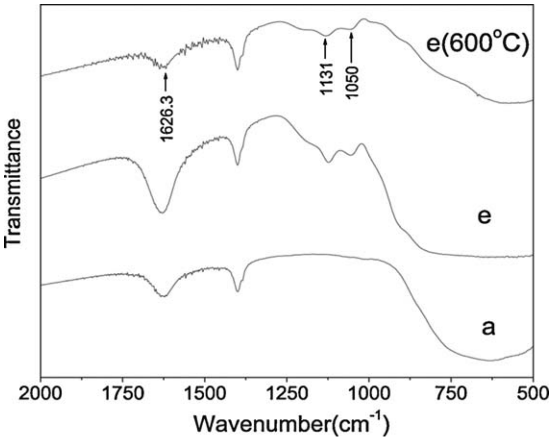


Fig. 3. FT-IR spectra of samples. a: undoped TiO_2; e: 0.8%S–TiO_2.

3.4. XPS analysis

To identify the alteration of surface properties with the addition of sulfur, XPS spectra were performed and shown in Fig. 4. XPS survey spectrum showed that the peak of S 2p around 168.5 eV shifted negatively by 0.5 eV in comparison with standard binding energy of the sulfur in pure SO_4^{2-} (169.0 eV) [24]. Meanwhile, the peak of O 2p around 529.7 eV shifted about 0.5 eV compared with the standard binding energy (529.2 eV) of the oxygen in undoped titania [5]. The result demonstrated that the electrons partially transferred from oxygen to sulfur in S-doped TiO_2 and formed a new band energy structure [5]. The high resolution spectrum of O 1s photoelectron peaks are shown in Fig. 4b. Curve-fitting result suggested that there should exist four kinds of oxygen in S-doped TiO_2. The peaks at around 529.6, 530.4 and 531.6 eV can be attributed to the oxygen in Ti–O–Ti, Ti–O–S and S–O–S linkages, respectively [25], while the peak at around 532.0 eV can be assigned to surface hydroxyl [26]. The difference of the S 2p binding energy indicated that the presence of the Ti–O–S bond which resulted in the change of the chemical circumstance of sulfur, thus SO_4^{2-} could coordinate with TiO_2 in the network which is in well accordance with the FT-IR results.

3.5. UV–Vis spectra

The UV–Vis diffuse reflectance spectra of the S-doped TiO_2 samples as well as undoped TiO_2 are shown in Fig. 5. It can be seen that the UV–Vis adsorption band wavelength of S-doped TiO_2 shifted to the visible range and the optical band edge exhibits a remarkable red-shift with respect to that of undoped TiO_2 and Degussa P25, indicating that a second absorption edge in the visible region appeared for all prepared S-doped TiO_2. The red shift increases with the rise of the content of sulfate. This may be attributed to the fact that the increase content of sulfate can sufficient coordinate with TiO_2 in the network.

3.6. Photocatalytic activity

To evaluate the photocatalytic activity of S-doped samples, the reactions of MO degradation were performed as photoreaction probes under visible LED light irradiation. Degussa P25 and undoped titania were used as the reference material for comparison.

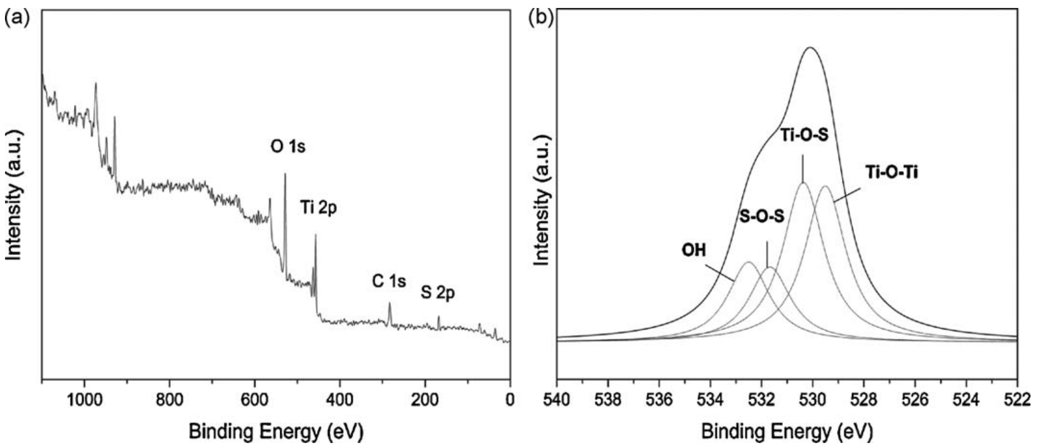


Fig. 4. XPS spectra of 0.8%S–TiO_2. a: survey spectrum; b: O 1s spectrum.

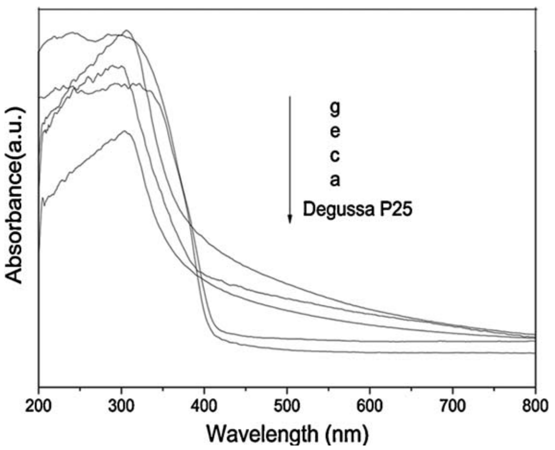


Fig. 5. UV–Vis spectra of samples. a: undoped TiO_2; c: 0.4%S–TiO_2; e: 0.8%S–TiO_2; g: 2%S–TiO_2.

Fig. 6a shows the degradation ratios of MO versus illumination time over different photocatalysts under visible light (460 nm) irradiation. It could be observed that the undoped TiO_2 and the Degussa P25 have nearly no activity under visible light irradiation, agreeing well with the result from the UV–Vis DRS analysis. The S-doped TiO_2 samples demonstrate considerably high photoactivity under low-power LED lamp. Fig. 6b gives the degradation ratio of samples with different sulfate dopant amounts at 5 h. The 0.8%S–TiO_2 photocatalyst shows the highest performance and MO was almost completely eliminated within 5 h.

According to the results from XRD, FT-IR and XPS, the promoting effect of the S dopant on the photocatalytic activity could be understood by considering the following factors. First of all, based on XPS result, the S dopant modification in the electron-deficient oxygen which could also serve an electron trap to inhibit the recombination between photo-induced electrons and holes. The red shift in the band gap transition of the S-doped TiO_2 sample indicated that S species can narrow the band-gap and then produce a second absorption edge in the visible region [24]. The mechanism of S-doped for the visible-light activity was illustrated as Scheme 1. However, with the increasing of the S-doped content, the position of the new-generated band-gap structures elevated and then could act as recombination centers for electron–hole pairs.

Secondly, the S species were coordinated with TiO_2 in the network producing more acidic sites on the TiO_2 surface. These acidic sites could capture more photo-induced electrons which could effectively protect the photo-induced holes from recombination with electrons [5]. Thus, the quantum efficiency of the TiO_2 photocatalyst was improved, resulting in the higher

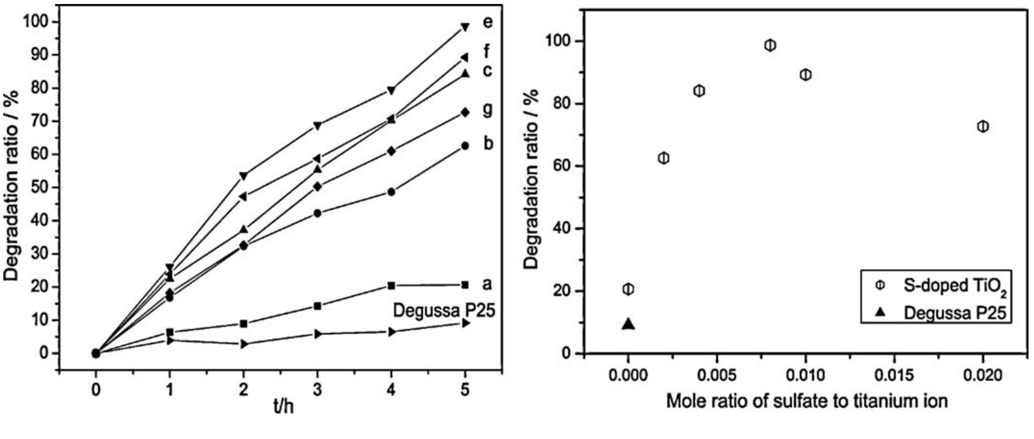
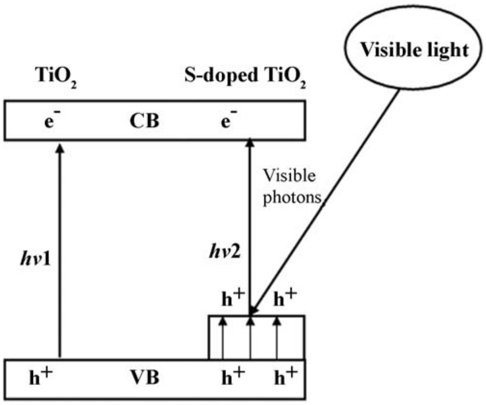


Fig. 6. (a) The photocatalytic activity of the photocatalysts under LED visible light irradiation. a: undoped TiO_2; b: 0.2%S–TiO_2; c: 0.4%S–TiO_2; e: 0.8%S–TiO_2; f: 1%S–TiO_2; g: 2%S–TiO_2. (b) The degradation ratio of samples with different sulfate dopant amounts at 5 h.



Scheme 1. Mechanism of S-doped TiO_2 for the visible-light activity photocatalyst.

photocatalytic activity. Moreover, The TiO_2–0.8%S sample is the mixture of anatase and rutile phase. It is believed that the photocatalytic activity of the mixture of anatase and rutile titania with appropriate ratio is higher than that of the pure anatase titania [21]. Because that the coupling is achieved by the improvement of the charge separation efficiency due to the photoinduced interfacial electron transfer [27].

4. Conclusion

A series of S-doped TiO_2 were synthesized using $TiCl_4$ and Na_2SO_4 as precursors for a simple boiling reflux hydrolysis method. S dopant is helpful to form anatase phase and reduce particle sizes. More importantly the doped sulfur plays a key role in expanding the photoactivity to visible region. The as-prepared S-doped titania show excellent visible-light photocatalytic activity in degrading methyl orange. Further work for the mechanism of S species is being under way.

Acknowledgements

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