

Preparation of Bi-doped TiO₂ modified by TEA and Its Enhanced Photocatalytic Properties under visible light illumination

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Abstract. Bi-doped TiO₂ powders were synthesised by sol-gel method and triethanolamine(TEA) was added to the Bi-doped TiO₂ colloid to improve the performance of prepared photocatalyst. The powder samples were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and UV-vis spectroscopy, respectively. The results show that the addition of TEA influenced both the morphology and the light absorption performance of the catalysts. The photocatalytic activity was investigated by employing methylene blue (MB) as the target pollutant under visible light illumination. Compared with Bi-doped TiO₂, the samples modified by TEA exhibited an enhanced photocatalytic activity. The enhanced photocatalytic activity observed could be attributed to the porous surface and the red shift of visible light absorption which was caused by a narrowing of bandgap of semiconductor.

Introduction

Semiconductor heterogeneous photocatalysis has been widely studied and recognized as a highly efficient and promising advanced oxidization technology for the degradation of environmental contaminants for several decades. TiO₂ is the most popular photocatalyst because of its high reactivity, chemical stability under ultraviolet light, nontoxicity, and low cost. The applications of TiO₂ photocatalytic technology on degradation of pollutants [1], splitting of water, as well as electro-optical conversion and other fields [2-3], have been receiving great attention. However, TiO₂ can be excited only under illumination with UV light at wavelengths of less than 387nm because of the wide band gap [1-3]. Several techniques for improving the photoresponse of oxide electrodes, which have led to higher sunlight conversion efficiency, have already been proposed. Combing TiO₂ with other materials [4] can improve its PEC performance. Surface noble metal [5] modified TiO₂ exhibited higher photocatalytic activity. Ion doping [6] has frequently been applied to extend photo-response into the visible region. Some researches [7-11] indicated that Bi³⁺ ions could successfully incorporated into TiO₂ and extended the absorption of TiO₂ into visible light region. Xu et al. [8] found that the formation of Bi₄Ti₃O₁₂ phase in Bi-doped TiO₂ could inhibit the recombination of electrons/holes and enhance photogenerated holes migrating to the surface. The red shift of absorption spectra for Bi-doped TiO₂ was also observed. Wu et al. reported [9] that after Bi doping, the hydrogen photogeneration rate increased by a factor of ca. 10, and the decolorization rate for RhB increased two times under visible light radiation (>420 nm). Further research implied that Bi doping increased photoinduced charge separation and resulted in a relatively lower overpotential for H₂ photoevolution. The electronic properties and photocatalytic activity of S and Bi-doped anatase TiO₂ are investigated by first-principles density functional theory calculations [10]. In Bi/S-doped TiO₂, both S 3p acceptor states and partially occupied Bi 6s donor states hybridized with S 3p appear simultaneously; this observation suggests that photocatalytic efficiency would be improved significantly due to greater separation of electron-hole pairs. Bi, C and N codoped TiO₂ photocatalysts were prepared by doping TiO₂ with BiCl₃ and KSCN in a sol-gel process [11]. It was found that the cation and the anion affected the properties of TiO₂ differently. The optical absorption onset of TiO₂ red shifted in the presence of Bi³⁺, while long tail occurred in the presence of SCN⁻. We

have reported [12] before that after addition of TEA into the respective sol at room temperature, nitrogen and (Co, N)-codoped TiO₂ sols were obtained. Thus on the basis of similar considerations, in this paper, TEA was selected to modified the Bi-doped TiO₂, we expect further improvement in the performance of Bi-doped TiO₂ by the addition of TEA during the prepared process. The powder samples were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and UV-vis spectroscopy, respectively. The photocatalytic degradation of MB was carried out under visible light illumination using the prepared powders.

Experimental Section

Preparation and characterization. The pure TiO₂ sample was obtained by means of a sol-gel method elsewhere described [12]. In short, a light yellow TiO₂ colloidal solution was obtained by dropping solution A (ethanol at pH 2 achieved by means of 50 mL of HCl) into solution B (Ti precursor colloid and ethanol) with stirring for 30 mins. Appropriate amount of Bi(NO₃)₃ was added to the above colloids with to a form stable Bi-TiO₂ colloid solution. TEA was selected as the source of N element and added to the above colloid drop by drop with strong stirring. All the colloid were calcined at 500 °C to obtain the powder samples. The as-prepared powders were then characterized by the scanning electron microscope (SEM, FEI Sirion-200, Holland) and energy dispersive X-ray spectroscopy (EDS). UV-vis absorption spectrum was obtained with a UV-vis spectrophotometer (Hatachi U-3010, Japan) with a bare ITO glass as reference.

Photodegradation of MB. The light source was a 500W Xe lamp using a light filter to cut off the uv-light ($\lambda < 420\text{nm}$). All the photodegradation of MB experiments were carried out in a two-compartment Teflon cell equipped with a quartz window. Unless otherwise specified, most experiments were carried out as the following conditions: initial MB concentration $C_0 = 10 \text{ mg dm}^{-3}$, pH = 3.0 ± 0.1 . The supporting electrolyte was 0.5 M Na₂SO₄, diluted H₂SO₄ and NaOH for pH adjustment. Prior to illumination, all the solutions tested were stirred at least for 15 min by bubbling with air to obtain adsorption equilibrium, and kept purging during the experiments. Samples were periodically taken from the anodic compartment for analysis. The concentration of MB was analyzed spectrophotometrically.

Results and Discussion

SEM and EDS analysis. Fig. 1 shows the typical SEM micrographs for both the Bi-TiO₂ and TEA-Bi-TiO₂ powders. After the addition of TEA, the size of the particles decreased slightly and the roughness of the surface also appeared to be porous. The EDS analysis of the Bi-TiO₂ and TEA-Bi-TiO₂ powders is shown in Fig. 2. As we can see, Bi element appeared on the surface of samples, although we used TEA as a doping source of nitrogen, however, no nitrogen was detected here.

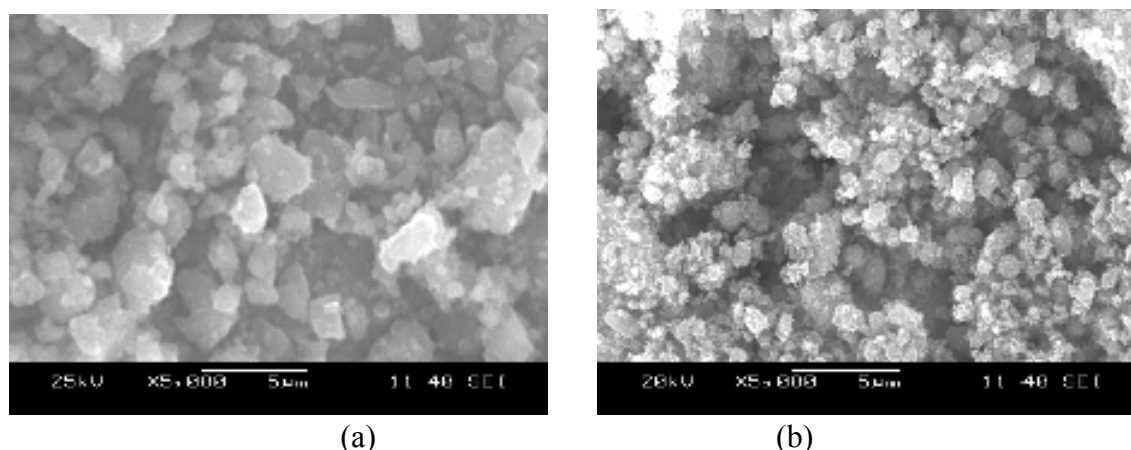
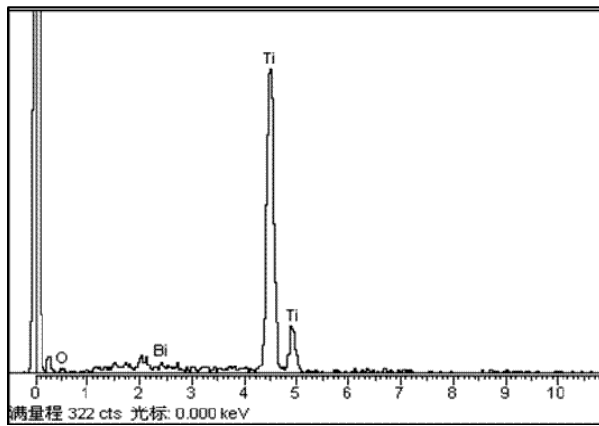
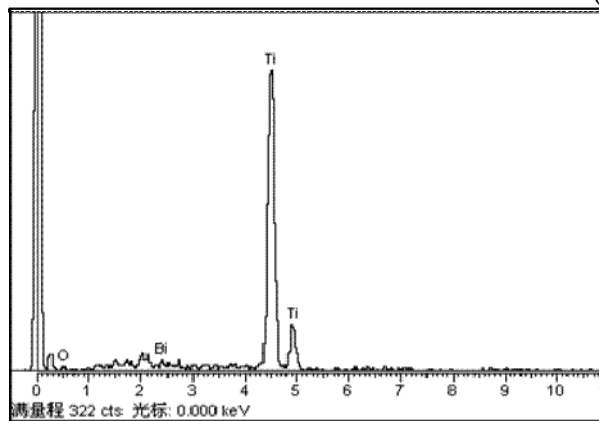


Fig. 1. SEM images of (a) Bi-TiO₂ and (b) TEA-Bi-TiO₂



Element	Wt(%)	At(%)
O	7.80	20.41
Ti	90.76	79.30
Bi	1.44	0.29

(a)

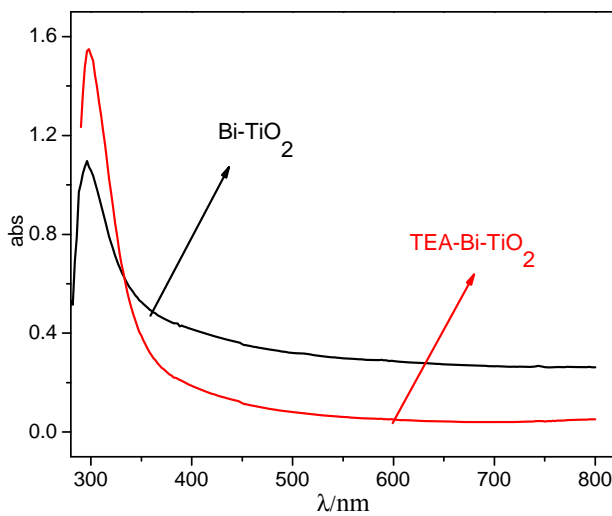


Element	Wt(%)	At(%)
O	11.74	28.71
Ti	87.01	71.06
Bi	1.25	0.23

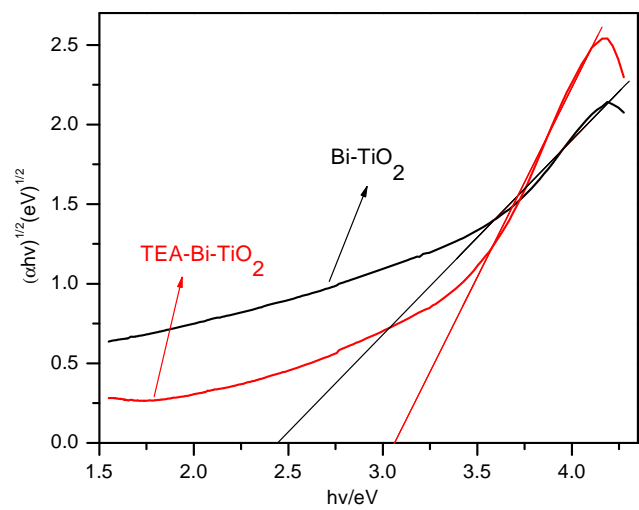
(b)

Fig. 2 EDS analysis of (a) Bi-TiO₂ and (b) TEA-Bi-TiO₂

UV-vis absorption spectrum analysis. The optical absorbance spectra of the powders are shown in Fig. 3a. Compared with Bi-TiO₂, the light absorption of TEA-Bi-TiO₂ decreased in the region of 280-330 nm while increased in the region of 330-800 nm. Some of the studies have proposed that such a red-shift is caused by a narrowing of bandgap of semiconductor[9]. Thus the bandgap was calculated using the $(\alpha h\nu)^{1/2} - h\nu$ plot[9] and the result is shown in Fig. 3b, the bandgap values of Bi-TiO₂ and TEA-Bi-TiO₂ are 3.1 eV and 2.4eV, respectively.



(a)



(b)

Fig. 3 UV-vis absorption spectra of Bi-TiO₂ and TEA-Bi-TiO₂

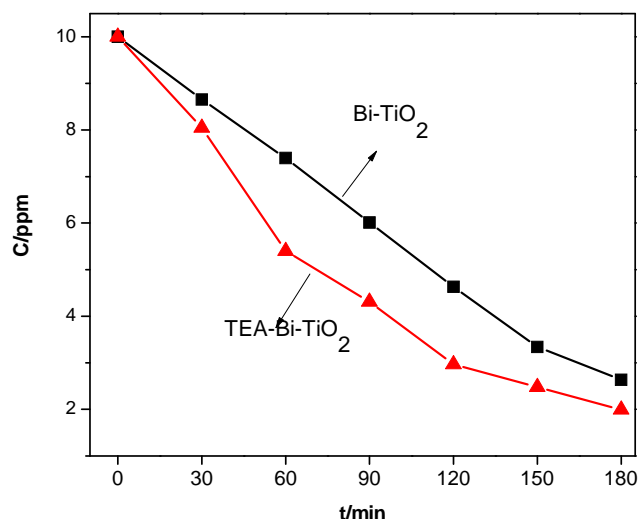


Fig. 4 MB photodegradation rate of Bi-TiO₂ and TEA-Bi-TiO₂

Photogradation of MB. The degradation rate of MB in the solution was shown in Fig. 4. It can be seen that MB was degraded efficiently on both Bi-TiO₂ and TEA-Bi-TiO₂ in 3 hours. The TEA-Bi-TiO₂ exhibited a higher photoactivity than the Bi-doped one as indicated in Fig. 4.

Conclusions

The Bi-doped TiO₂ powders modified by TEA were prepared using sol-gel method. The red-shift light absorption of the TEA-Bi-TiO₂ is caused by a narrowing of bandgap of semiconductor. MB can be effectively oxidized using TEA-Bi-TiO₂ under the illumination of visible light and an enhancement of photocatalytic performance of TEA-Bi-TiO₂ catalyst has been achieved. The enhanced photocatalytic activity observed can be attributed to the higher visible light absorption and larger surface area.

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