Short Communication

Effect of Si doping on the photocatalytic activity and photoelectrochemical property of TiO$_2$ nanoparticles

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ARTICLE INFO

ABSTRACT

Si-doped TiO$_2$ nanoparticles with anatase crystalline phase were prepared by a hydrothermal method using acetic acid as the solvent. Photoelectrochemical studies showed that the photocurrent value for the 15% Si-doped TiO$_2$ electrode (54.4 μA) was much higher than that of the pure TiO$_2$ electrode (16.7 μA). In addition, the 15% Si-doped TiO$_2$ nanoparticles displayed the highest photocatalytic activity under ultraviolet light irradiation. So doping suitable amount of Si in TiO$_2$ nanoparticles was profitable for transferring photogenerated electrons and inhibiting the recombination of photogenerated electrons and holes. As a result, the photocatalytic activity of TiO$_2$ nanoparticles was improved.

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1. Introduction

Commercial dyes have been widely used in industry, such as textile, foodstuff and leather etc, and become an integral part of industrial effluents. Most of these dyes are toxic and potentially carcinogenic in nature and their removal from industrial effluents is a major environmental problem. In fact, various approaches have been developed to eliminate and degrade them, such as biodegradation, coagulation, adsorption, membrane process and advanced oxidation process [1]. Photocatalytic degradation using a semiconductor as the photocatalyst is a part of advanced oxidation process which has proven to be a green technology for the degradation of organic pollutants.

It is known that among various oxide semiconductor photocatalysts, TiO$_2$ is the most widely used one due to its optical and electronic properties, low cost, chemical stability and non-toxicity [2]. However, the photocatalytic efficiency of pure TiO$_2$ is very low because of the fast recombination of photogenerated electrons and holes as well as poor activation of TiO$_2$ by visible light, which makes the progress in the extensive application be impeded [3]. In order to overcome these deficiencies, several available techniques such as metal loading, metal ion doping, anion doping, mixing of two semiconductors with large and small band gap energies and sensitization by visible light sensitizers [4–8] have been developed. In particular, doping of Si
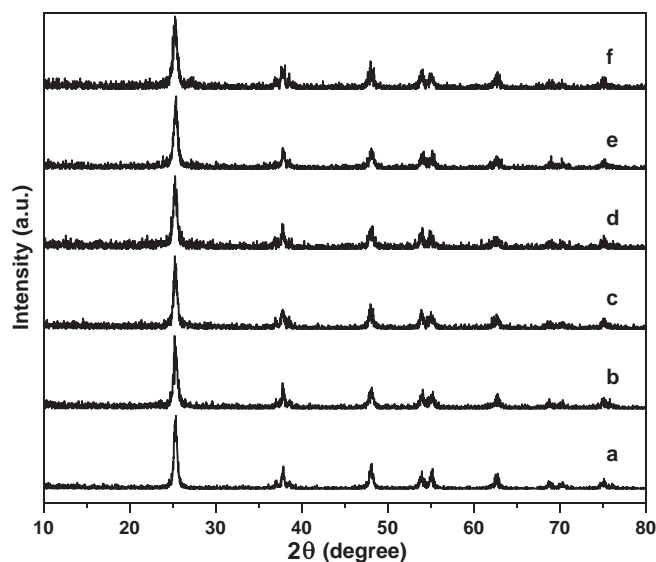

Fig. 1. XRD patterns of pure TiO$_2$ (a), 5% Si–TiO$_2$ (b), 10% Si–TiO$_2$ (c), 15% Si–TiO$_2$ (d), 20% Si–TiO$_2$ (e), and 25% Si–TiO$_2$ (f).

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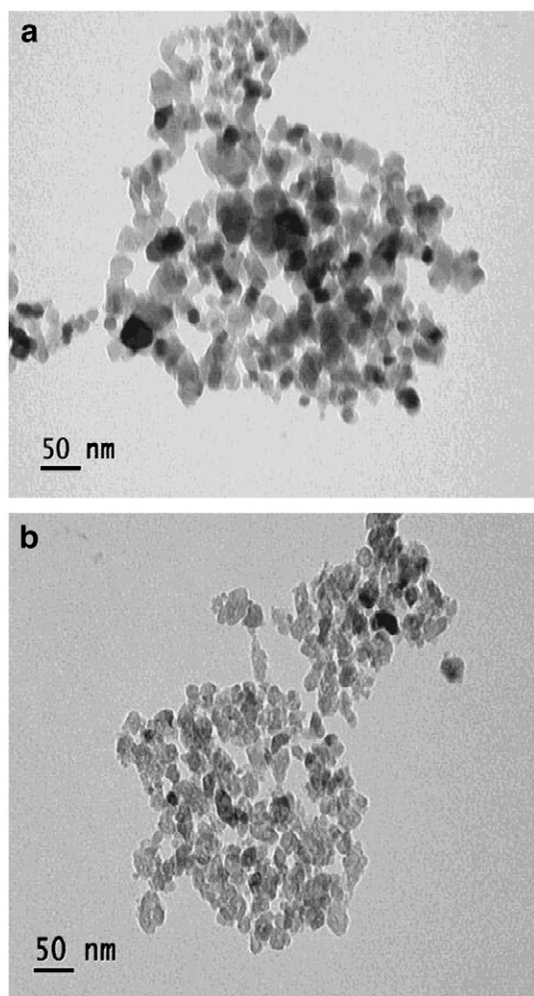E-mail address: jinmu@ecust.edu.cn (J. Mu).

Fig. 2. TEM images of pure TiO₂ (a) and 15% Si—TiO₂ (b).

2. Experimental

2.1. Preparation of Si-doped TiO₂ nanoparticles and their electrodes

Si-doped TiO₂ nanoparticles were prepared by a hydrothermal method using acetic acid as the solvent [21]. The Si-doped TiO₂ nanoparticles are denoted as x% Si—TiO₂ (x% is mole per cent of Si). An indium–tin oxide (ITO) glass slide was used as the electrode substrate. The x% Si-TiO₂/ITO electrodes with an active area of 1 cm² were prepared by the dip-coating method. The detailed procedures were described in the Supplementary data.

2.2. Characterization

The obtained samples were characterized by powder X-ray diffraction (XRD), transmission electron microscope (TEM), energy dispersive X-ray analysis (EDX), Fourier transform infrared spectroscopy (FT-IR) and solid diffuse reflection spectra (DRS). Details are given in the Supplementary data.

2.3. Photoelectrochemical measurements

Electrochemical experiments were carried out in an electrochemical cell using x% Si-TiO₂/ITO as the working electrode, a Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. A 0.1 mol L⁻¹ NaOH aqueous solution purged with N₂ was used as the electrolyte and a 300 W Hg lamp served as the UV light source. Linear sweep voltammetry was performed on a PCI4/300 electrochemical analyzer (Gamry, USA) with a scan rate of 5 mV s⁻¹. All measurements were carried out at 25 °C.

2.4. Photocatalytic experiments

The photocatalytic activity of Si-doped TiO₂ nanoparticles was evaluated by the photocatalytic degradation of methyl orange (MO) aqueous solution (4.6×10^{-5} mol L⁻¹) under UV light irradiation and analyzed by a UV–vis spectrophotometer (Unico UV-2102 PCS, China). The detailed procedures were described in the Supplementary data.
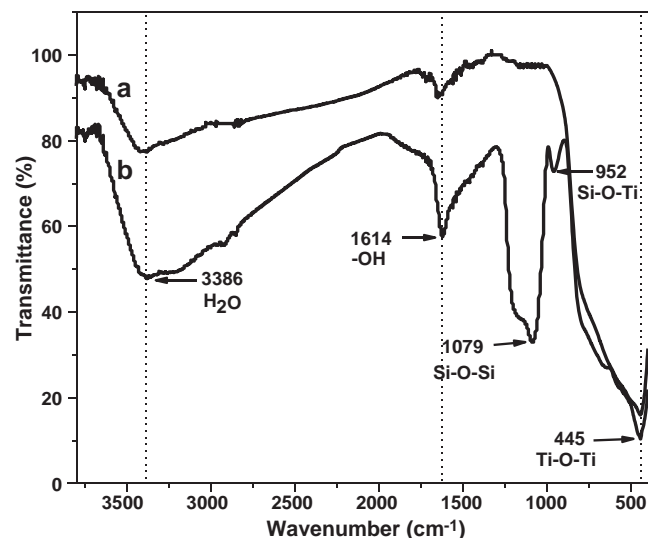
element in TiO₂ can greatly enhance its photocatalytic activity [9–16]. For example, Liu et al.[17] reported that the photocatalytic performance of Si-doped TiO₂ nanocrystals with an addition amount of 10 wt,% exceeded commercialized Degussa P25 by a factor of 3 times when used for the decomposition of formaldehyde. Thus, Si-doped TiO₂ nanoparticles are a promising material for photochemical and photocatalytic applications. However, there are few studies about correlation of photoelectrochemical property with photocatalytic activity of TiO₂ nanoparticles to elucidate the effect of Si doping.

Recently, some researchers [18–20] employed linear sweep voltammetry (LSV) technique to study the transfer or recombination behavior of photogenerated electrons and holes in the photocatalyst as well as the variation of photocurrent of a photocatalyst film electrode under dark and light conditions. In fact, the surface and/or the interface states on the TiO₂ nanocrystal film electrode play an important role in the relative electrochemical process that is also included in the photocatalytic reaction such as transfer, capture and exchange of photogenerated electrons. Therefore, considering the photocurrent variation of Si-doped TiO₂ nanoparticles through the LSV technique to study the effect of Si doping on the photocatalytic activity of TiO₂ nanoparticles is really meaningful.

In the present work, we aim to explore the relationship between the photoelectrochemical property and the photocatalytic activity of Si-doped TiO₂ nanoparticles. The effect of Si doping in TiO₂ nanoparticles will be examined from another angle.

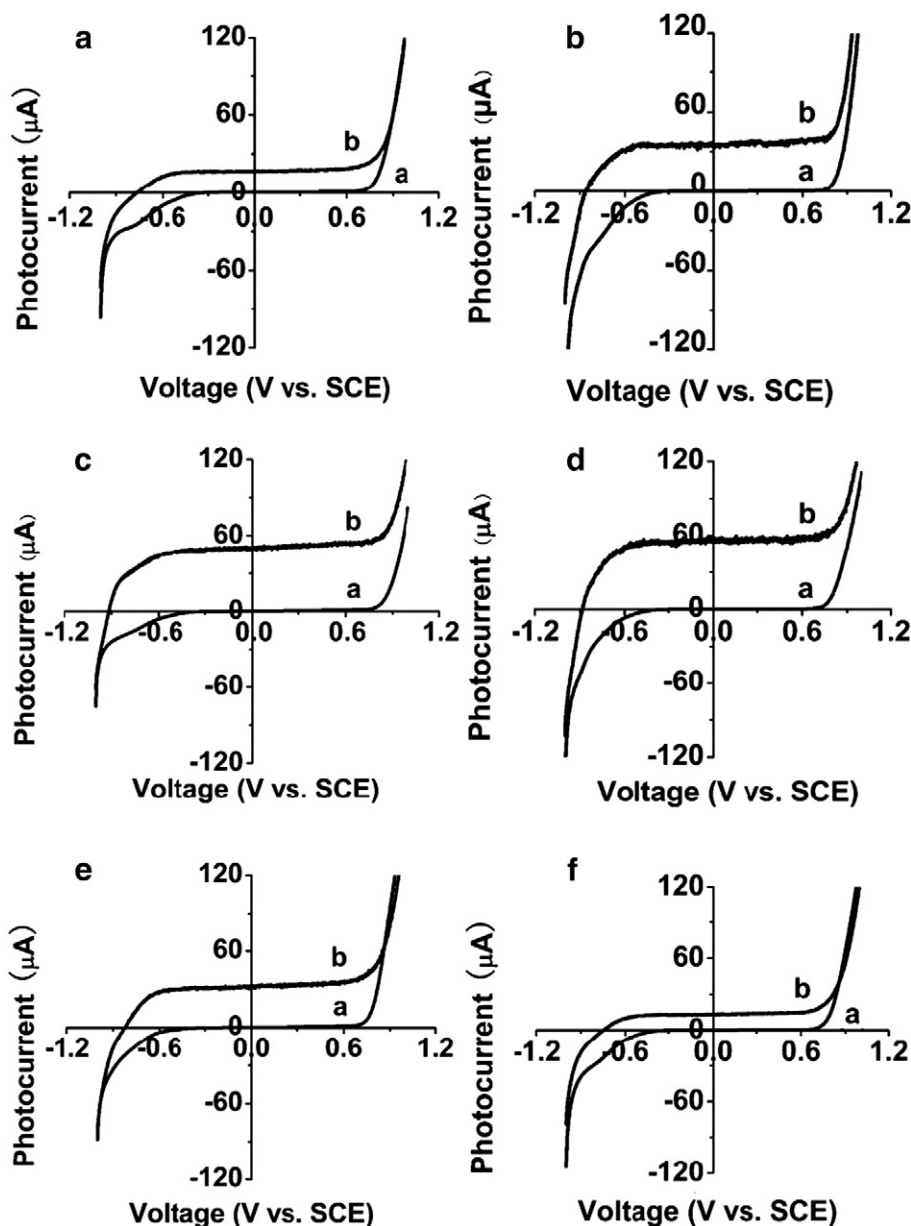**Fig. 3.** FT-IR spectra of pure TiO₂ (a) and 15% Si—TiO₂ (b).

Fig. 4. Photocurrent-potential curves of pure TiO_2 (A), 5% $Si-TiO_2$ (B), 10% $Si-TiO_2$ (C), 15% $Si-TiO_2$ (D), 20% $Si-TiO_2$ (E), 25% $Si-TiO_2$ (F) under dark (a) and UV light irradiation (b). Electrolyte: 0.1 mol L^{-1} NaOH solution, scan rate: 5 mV s^{-1}.

3. Results and discussion

XRD patterns of pure TiO_2 and x% $Si-TiO_2$ are shown in Fig. 1. It can be observed that the diffraction patterns of all x% $Si-TiO_2$ coincide almost with that of pure TiO_2. The peaks at $2\theta = 25.28°$, 37.79°, 48.05°, 53.89°, 55.09°, 62.68°, 68.76°, 70.30° and 75.02° correspond to the (101), (111), (200), (105), (211), (204), (116), (220) and (215) planes of anatase phase of TiO_2 (JCPDS card no. 21–1272). In addition, no peaks from the SiO_2 crystal phase were observed for all x% $Si-TiO_2$ samples, which could be attributed to its amorphous phase [22], or Si as an interstitial atom is well-inserted into the crystal lattice of TiO_2[16].

EDX analysis of 15% Si-TiO_2 nanoparticles (see Fig. S1) shows that the sample is composed of elements Si, Ti and O. The primary particle sizes of pure TiO_2 and 15% Si-TiO_2 are about 20 and 13 nm, respectively, as shown in Fig. 2, which shows that doping Si in TiO_2 nanoparticles can decrease the particle size of TiO_2.

As displayed in FT-IR spectra of pure TiO_2 and 15% $Si-TiO_2$ (Fig. 3), two bands observed at 3386 cm^{-1} and 1614 cm^{-1} are characteristic of O–H bending modes of adsorbed water and hydroxyl groups [21,22], respectively. The band at 445 cm^{-1} is attributed to the Ti–O stretching vibration of crystalline TiO_2 phase [12]. Especially, in the spectrum of 15% Si-TiO_2 nanoparticles, there exists two new bands at 1079 and 952 cm^{-1}, corresponding to the characteristic stretching vibrations of Si–O–Si and Si–O–Ti, respectively [23]. These results show that the Si–O–Ti bond has been formed in the 15% Si-TiO_2 nanoparticles.

Importantly, solid diffuse reflection spectra (see Fig. S3) display that there exists a significant blue-shift of the absorption edge for the 15% Si-TiO_2 sample, which is ascribed to the incorporating of Si into the TiO_2 matrix. It coincides with the result of the literatures reported by Lee et al, and Su et al.[11,16]. The formation of Si–O–Ti bond in the 15% $Si-TiO_2$ can lead to increase of concentration of surface hydroxyl groups (see Fig. 3). The hydroxyl groups can react with holes to

Table 1
Values of photocurrent (I_{ph}) for x% Si—TiO_2/ITO electrodes under UV light irradiation.

x% Si—TiO_2	0	5	10	15	20	25
I_{ph} (μA)	16.7	35.9	50.7	54.9	32.2	12.9

produce hydroxyl radicals. The hydroxyl radicals are a strong oxidant for the degradation of MO [12]. So it would be profitable for enhancing the photocatalytic activity of TiO_2.

Photocurrent-potential curves of pure TiO_2 and x% Si-TiO_2 nanoparticles are shown in Fig. 4. The photocurrent values are zero for all the samples under dark. Under UV irradiation, the photocurrent values for 5%, 10%, 15% and 20% Si-TiO_2/ITO electrodes are much higher than that of the pure TiO_2/ITO electrode (see Table 1). However, the photocurrent value of the 25% Si-TiO_2/ITO electrode (12.9 μA) is lower than that of the pure TiO_2/ITO electrode (16.7 μA). These results show that doping Si into the TiO_2 nanoparticles has both a positive effect and a negative effect on the photocurrent of x% Si-TiO_2/ITO electrodes. One of possible explanations is that Si as an interstitial atom is forced to enter the crystal lattice of TiO_2 to establish a Si–O–Ti bond during the synthesis process [24]. As a transfer bridge, photogenerated electrons can easily move to the surface via the Si–O–Ti bond. This process can facilitate the transfer of photogenerated electrons and the improvement in quantum yield leading to an increase in the photocurrent value. Besides, the doping of Si decreases the particle size of TiO_2 (Fig. 2) and increases the specific surface areas of TiO_2 nanoparticles, implying that more electrons/holes can escape to the surface of Si-TiO_2 nanoparticles. Consequently, the photocurrent value of Si-TiO_2/ITO electrodes is increased. On the contrary, at high Si doping, the excess Si can behave as a recombination center between photogenerated electrons and holes, resulting in a decrease in the photocurrent value. In other words, doping suitable amount of Si in TiO_2 nanoparticles can promote the separation of photogenerated electrons and holes, implying a possible increase of photocatalytic activity of Si-doped TiO_2 nanoparticles as a photocatalyst. Therefore, we evaluated the effect of Si doping on the photocatalytic activity of TiO_2 nanoparticles for the degradation of MO as a model pollutant, as shown in Fig. 5. The results indicate that the 15% Si-TiO_2 nanoparticles display the highest photocatalytic activity for the degradation of MO. That is, the photocatalytic activity of x% Si—TiO_2 nanoparticles is consistent with the photocurrent variation of the x% Si—TiO_2/ITO electrodes.

In addition, the photocatalytic degradation dynamic curves of MO over the 15% Si—TiO_2 nanoparticles and the commercialized Degussa P25 were also measured (see Fig. S2). The results show that the self-

degradation of MO is negligible in the absence of the photocatalyst. Whereas, in the presence of the 15% Si—TiO_2 nanoparticles and P25, the degradation efficiencies of MO are about 98% and 84% under UV light irradiation for 40 min, respectively. These results indicate that the photocatalytic activity of 15% Si-TiO_2 nanoparticles is higher than that of P25.

4. Conclusions

The photoelectrochemical results show that doping of suitable amount Si in TiO_2 nanoparticles facilitates flowing of photogenerated electrons toward cathode. The effect of Si doping on the photocatalytic activity of TiO_2 nanoparticles can be ascribed to the easy transfer and separation of photogenerated electrons and holes. Namely, there is a strong relationship between the photocurrent and photocatalytic activity of a photocatalyst. The photocurrent as an auxiliary parameter can be correlated with the photocatalytic activity of a photocatalyst.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.06.016.

References

[1] M.A. Rauf, S. Salman Ashraf, Chem. Eng. J. 151 (2009) 10–18.
[2] M.I. Litter, J.A. Navio, J. Photochem. Photobiol. A 98 (1996) 171–181.
[3] K.Y. Jung, S.B. Park, J. Photochem. Photobiol. A 127 (1999) 117–122.
[4] A. Kudo, Y. Miseki, Chem. Soc. Rev. 38 (2009) 253–278.
[5] X.B. Chen, S.H. Shen, L.J. Guo, S.S. Mao, Chem. Soc. Rev. 110 (2010) 6503–6570.
[6] X.B. Chen, S.S. Mao, Chem. Soc. Rev. 107 (2007) 2891–2959.
[7] T.L. Thompson, J.T. Yates, Chem. Soc. Rev. 106 (2006) 4428–4453.
[8] A. Hagfeldt, G. Boschloo, L.C. Sun, L. Kloo, H. Pettersson, Chem. Soc. Rev. 110 (2010) 6595–6663.
[9] T.V. Nguyen, O.B. Yang, Catal. Today 87 (2003) 69–75.
[10] T.V. Nguyen, S.S. Kim, O.B. Yang, Catal. Commun. 5 (2004) 59–62.
[11] I.J. Lee, T.S. Jung, J.G. Kim, S.H. Ro, C.S. Kim, Y.J. Lee, Y.M. Kim, J.H. Lee, M.S. Kang, J. Ind. Eng. Chem. 14 (2008) 869–873.
[12] R.B. Jin, Z.B. Wu, Y. Liu, B.Q. Jiang, H.Q. Wang, J. Hazard. Mater. 161 (2009) 42–48.
[13] Y. Su, J.S. Wu, X. Quan, S. Chen, Desalination 252 (2010) 143–148.
[14] G. Li, F. Liu, Z. Zhang, J. Alloys Compd. 493 (2010) L1–L7.
[15] H.F. Yu, S.T. Yang, J. Alloys Compd. 492 (2010) 695–700.
[16] Y. Su, S. Chen, X. Quan, H.M. Zhao, Y.B. Zhang, Appl. Surf. Sci. 255 (2008) 2167–2172.
[17] Z.Y. Liu, X. Quan, H.B. Fu, X.Y. Li, K. Yang, Appl. Catal. B 52 (2004) 33–40.
[18] W.D. Zhang, L.C. Jiang, J.S. Ye, J. Phys. Chem. C 113 (2009) 16247–16253.
[19] D. Zhao, T.Y. Peng, M. Liu, L.L. Lu, P. Cai, Microporous Mesoporous Mater. 114 (2008) 166–174.
[20] V. Pore, M. Heikkil, M. Ritala, M. Leskel, S. Areva, J. Photochem. Photobiol. A 177 (2006) 68–75.
[21] Q.F. Chen, D. Jiang, W.M. Shi, D. Wu, Y. Xu, Appl. Surf. Sci. 255 (2009) 7918–7924.
[22] M. Hirano, K. Ota, H. Iwata, Chem. Mater. 16 (2004) 3725–3732.
[23] X.L. Yan, J. He, D.G. Evans, X. Duan, Y.X. Zhu, Appl. Catal. B 55 (2005) 243–252.
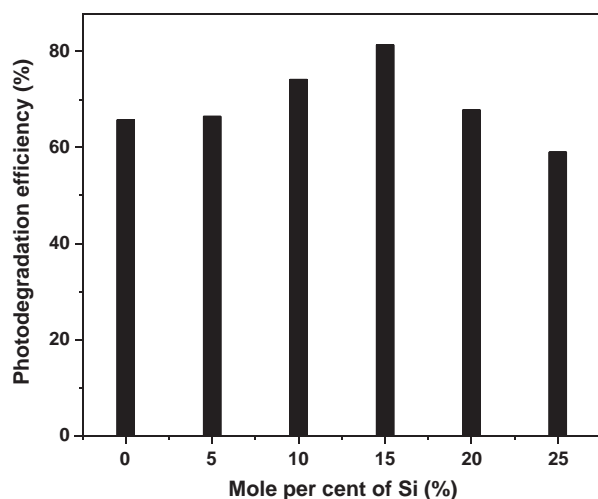[24] Y.J. Zhang, X.F. Li, D. Chen, N.H. Ma, X.S. Hua, H.W. Wang, Scripta Mater. 60 (2009) 543–546.

Fig. 5. Effect of Si-doping amount on the photocatalytic activity of TiO_2 nanoparticles for the degradation of MO under UV light irradiation for 30 min.