Synthesis of Highly Active Si-doped TiO₂ Nanotube/SnS Hybrids for Photocatalytic Degradation of Toxic Dyes

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Synthesis of highly active Si-doped TiO₂ nanotube/SnS hybrids for photocatalytic degradation of toxic dyes

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Abstract: Heterostructures with nanoscale sizes have great superiorities in photocatalytic environment decontaminant because of their efficient interface charge transfer and great surface area. This work reports the facile fabrication of nano-tubular TiO₂ and Si-doped TiO₂ (NTs) hybridizing SnS nanocrystallites and their high-efficient photocatalytic activity. The fabricated nanostructures show wide light absorption in the UV-visible region. The S_{BET} , light absorption, hydrophilicity, and photo-induced super hydrophilicity were enhanced by Si-doping and SnS modification. Moreover, high-efficient interface charge transfer was produced after the SnS modification and further enhanced by the Si doping because of band structure modulation. Thus, the Si-doped TiO₂ nanotubes/SnS heterostructures showed a remarkably enhanced photocatalytic and Fenton-like photocatalytic activities in dye wastewater treatment than the TiO₂ NTs. This work suggests potential materials and their facile fabrication process for the photocatalytic application of environmental decontamination.

Keywords: nanotubes; semiconductor; heterojunction; photocatalytic properties;
interface effect

1. Introduction

TiO₂ nanomaterials have been proverbially used in environmental decontamination as potential photocatalysts. To improve their photocatalysis and mineralization, many methods including various dopings were used to enlarge the wavelength range of absorbed light by narrowing the bandgap of TiO₂ (Lindgren et al 2003; Nishijima et al 2007; Umebayashi et al 2002; Ahmad et al 2013; Fa et al 2013). Constructing hybrid materials with other semiconductors has also been widely used in enhancing photocatalytic activity (Zhang et al 2012; György et al 2014; Wang et al 2013; Li et al 2012; Wang et al 2014; Park et al 2013; Eshaghi and Eshaghi 2012). Hydrophilicity and photo-induced hydrophilicity are important factors affecting photocatalysis. It has been reported that Si doping is highly effective in the enhancement of hydrophilicity and photo-induced hydrophilicity and so the enhancement of photocatalysis (Eshaghi and Eshaghi 2012; Lu et al 2011; Eshaghi et al 2011);

The large specific surface area of TiO₂ nanotubes results in enhanced photocatalytic activity compared with other forms of TiO₂ (Adachi et al 2000; Chu et al 2003). TiO₂ nanotubes have been prepared by some methods including utilizing the template effect of nanoporous alumina (Michailowski et al 2001) and some organic compounds (Jung et al 2002; Kobayashi et al 2002) in sol-gel process, seed layer method (Tian et al 2003), hydrothermal treatment in alkaline aqueous solution (Kasuga et al 1998;

Chen et al 2002; Yao et al 2003), and anodization process (Cai et al 2005; Ruan et al 2005; Quan et al 2005; Mor al 2006).

Stannous sulfide (SnS) as a binary semiconductor has some advantages including narrow optical bandgaps, high absorbance in UV-near-infrared region, non-toxic, and inexpensive. Thus, the SnS should be an efficient photocatalyst and can be used to construct efficient hybrids with TiO₂ and TiO₂ nanotubes. The possible charge transfer between SnS and TiO₂ may restrain the recombination of photogenerated electron-hole pairs thereby producing an efficient interface-induced effect, which may dramatically promote photocatalysis.

Thus, this work successfully fabricated nano-tubular TiO₂ and Si-doped TiO₂ (NTs) and NTs/SnS hybrids with simple chemical processes. The fabricated NTs and hybrids showed high-efficient photocatalytic activity and activity resembling a Fenton-like reaction in the disposing waste dye aqueous solution.

2. Experimental

2.1. Fabrication of the TiO₂ and Si-doped TiO₂ nanotubes

A solvothermal process was used to synthesize the TiO₂ nanoparticles (NPs). Butyltitanate (C₁₆H₃₆O₄Ti, 0.02 moles) was first added into the solution of N-heptane (15 ml), polyvinyl alcohol-4000 (1.5 g), and a little acetylacetone (~1 mL). The solution was ultrasonically stirred for 30 min and then became the transparent gel. The gel was successively treated at 150 °C for 12 h and 180 °C for 3 h in a 30 ml hydrothermal kettle. The NPs were finally obtained after filtrating, washing with

deionized water several times, and drying at 80 °C for 3 h. Similarly, Si-doped TiO₂ nanoparticles (Si-doped NPs) were prepared after substituting ethyl orthosilicate for 30 at.% butyl titanate. The nano-tubular TiO₂ and Si-doped TiO₂ nanotubes (NTs) were fabricated by using the hydrothermal process at 110 °C for 24 h in a 8 mole·l⁻¹ NaOH aqueous solution. The obtained samples were filtered and repeatedly washed with deionized water until the washing liquid shows neutral pH. The obtained nanotubes were dried at 80 °C for 3 h and then heat-treated at 400 °C for 40 min to transfer the nanotubes from amorphous to crystalline state. Finally, the nanotubes were fully ground.

2.2. Fabrication of the SnS/nanotubes hybrids

Successive ionic adsorption and reaction methods were used to fabricate the nanotube/SnS hybrids. The Sn²⁺ aqueous solution was first prepared with the stannous chloride (SnCl₂·2H₂O), deionized water, and a little hydrochloric acid (HCl, 37%, ~3 mL). Meanwhile, a thioacetamide (C₂H₅NS) aqueous solution was fabricated in another beaker. Afterward, the thioacetamide aqueous solution and Sn²⁺ aqueous solution were by turns dropwise added into the 50 ml deionized water containing 0.5 g NTs in a constant ultrasonic condition. The SnS nanoparticles were fastly formed because of the very large solubility product constant of SnS. After each dropping, 0.5 min time interval was spent to fully disperse the Sn²⁺ cation and thioacetamide, adsorb Sn²⁺ cations onto the NTs surface, and/or react the Sn²⁺ cations with S²⁻ ions. Such a process was repeatedly performed to achieve the SnS/NTs molar ratio of 0.01. Finally, the hybrids were obtained after filtrating, washing with deionized water for

several times, and drying at 80 °C for 6 h in an oven.

2.3. Characterizations

The crystallographic structures of all the samples were analyzed using a D/Max-2200PC X-ray diffractometer (XRD, Rigaku, Japan) utilizing a $\text{CuK}_{\alpha 1}$ beam ($\lambda=0.15406$ nm). The nanostructures were also characterized by an X-ray energy dispersive spectra (EDS), and JEM-3010 transmission electron microscopy (TEM, Japan), Vector-22 infrared spectroscopy (Bruker, Germany), and Cary100 UV-Vis UV-vis spectrophotometer (Angilent, USA). The S_{BET} was measured with Gemini VII2390 surface area analyzers (Micromeritics Instrument, Shanghai, China).

2.4. Photocatalytic activity analysis

Photocatalytic experiments were carried out using a UV lamp (250 W, emission wavelength: ~315-490 nm) as an illumination light source at room temperature (~20 °C). The malachite green (MG) was selected as a substrate and so a dye aqueous solution (5×10^{-6} mol./l) was prepared in deionized water. In each experiment, the photocatalyst of 50 mg was used to photodegrade 50 ml MG aqueous solution. 1 ml H_2O_2 aqueous solution (H_2O_2 : 30 %) was added into each 50 ml dye aqueous solution to study the effect of H_2O_2 (Fenton-like reaction). After each constant time interval, ~2 mL solution was taken out to measure the absorbance using a 752N spectrophotometer (China) at ~617 nm. Similarly, the NGB aqueous solution (5×10^{-6} mol./l) was photo-degraded under the same conditions.

3. Results and Discussion

3.1. Characterization of microstructure

XRD patterns reveal that the NTs are amorphous and anatase (JCPDS: 21-1272) before and after the crystallization at 400 °C, respectively (Fig. 1). The average crystallite sizes were estimated for the crystallized NTs using Scherrer's relation

$$D = 0.9 \frac{\lambda}{\beta \cos \theta} \quad (1)$$

The estimated results of the TiO₂ and Si-doped TiO₂ NTs, are 45.5 nm and 38.9 nm, respectively. Si-doping could interfere with the crystallization of the TiO₂ and so result in a smaller size. Si-doping also shifted the (101) peak, the strongest peak corresponding to the anatase phase, from 2θ=25.06° to 25.08°. This reveals the decrease of the lattice parameter resulting from the smaller covalent radius of Si⁴⁺ (1.11 Å) than Ti⁴⁺ (1.32 Å). After hybridizing SnS, the XRD patterns only illustrate the peaks identified to be the orthorhombic herzenbergite and SnS (JCPDS: 75-0925 and 65-3812). This indicated that the NTs were completely covered by SnS crystallines

The TEM micrographs (Fig. 2) illustrate very small pore and porous structures of the NTs and uniform adherence of nano-scale SnS nanoparticles on the NTs surface. The EDS analysis reveals the S/Sn molar ratio of ~0.93.

3.2. XPS spectra analyses

Figure 3 illustrates the XPS spectra. The survey spectra of the Si-doped TiO₂ NTs and Si-doped TiO₂ NTs/SnS nanostructures (Fig. 3a) shows the peaks corresponded to Ti, Si, C, O, Sn, and S. Two peaks at 456.8 and 462.6 eV (Fig. 3b) assigned to the 2p_{3/2} and 2p_{1/2} electrons of Ti element shift to higher binding energies of 457.8 and

463.6 eV after the modification of SnS, respectively. Similar binding energy upshifts from 100.1 and 100.8 eV to 100.4 and 101.1 eV are also observed for Si 2p peaks (Fig. 3c). These binding energy upshifts reveal the charge transfer from the Si-doped TiO₂ NTs to SnS (Manga et al 2009; Lee et al 2012). Moreover, the Sn 3p peaks only slightly upshift from that of the Sn atom (485.0 eV and 494.0 eV) (Fig. 3d). This could also further confirm that the charges in the Si-doped TiO₂ NTs transferred to the SnS. Furthermore, the Si/Ti molar ratio in the Si-doped TiO₂ NTs determined by the XPS analysis equals 2.3/7.7, indicating more SiO₂ was etched away in the process of hydrothermal treatment in the NaOH aqueous solution.

3.3. FTIR spectra analyses

FTIR spectra show strong peaks at ~3363 cm⁻¹ and ~1628 cm⁻¹ (Fig. 4). The peak at ~3363 cm⁻¹ corresponds to the O–H and H–O–H stretching vibration in the water molecules adsorbed on the surface, whereas the peak at ~1628 cm⁻¹ mainly corresponds to the H–O–H bending vibrations in adsorbed water molecules or O–H deformation vibrations of the surface hydroxyls. The ~3363 cm⁻¹ peak is stronger for the Si-doped TiO₂ NTs than for the TiO₂ NTs, and strongest for the hybrids. This could imply that the Si-doping and SnS modification enhanced the hydrophilicity. Significantly, the peaks at ~3363 and ~1628 cm⁻¹ were enhanced after the UV irradiation (Fig. 4b). This enhancement appears stronger as Si was doped (Fig. 4b). These could imply an obvious photo-induced ultrahydrophilicity and its enhancement with Si doping. The peak at ~1352 cm⁻¹, being greatly reduced after SnS modification, is assigned to the TiO₂.

3.4. Optical property analysis

Figures 5a and 5b show that all the NTs have high transmittance and low reflectance in comparison with the NPs. This is ascribed to the nanotube morphology with thin wall and the rough surface resulting from the NaOH etching, respectively. The spectra also show that the TiO₂ NTs have a low transmittance and a high reflectance compared with the Si-doped TiO₂ NTs, and the SnS reduces the transmittance but raises the reflectance. On basis of the Tauc's relationship (Zaharia et al 2004; Pathan et al 2002), the optical band gap (E_g) of the TiO₂ NPs and the Si-doped TiO₂ NPs equal ~3.24 and 3.34 eV (Fig. 5c). Similarly, the E_g of the TiO₂ NTs and the Si-doped TiO₂ NTs are 3.30 and 3.40 eV, and the E_g of the TiO₂ NTs/SnS and the Si-doped TiO₂ NTs/SnS are ~3.13 and 3.20 eV, respectively (Fig. 5c). The E_g widening resulting from the Si doping could be ascribed to the wider E_g of SiO₂ (8.90 eV) and quantum refinement effect. Whereas, the narrower E_g of the hybrids should be due to the narrow bandgap of the SnS nanoparticles.

3.5. Photocatalysis and Fenton-like photocatalysis

3.5.1. Photocatalysis

The dye concentration files under the UV lamp irradiation time (Fig. 6) indicate that the Si-doped TiO₂ NTs and Si-doped TiO₂ NTs/SnS showed larger photodegradation efficiency respectively than the TiO₂ NTs and TiO₂ NTs/SnS to both NGB and MG. This reveals an excellent Si-doping effect. Moreover, the SnS modification also results in a remarkable enhancement in photocatalytic activity. As a comparison, the TiO₂ NTs and TiO₂ NTs/SnS show a remarkably larger photocatalytic

activity than the CuS-GO/TiO₂ hybrids [12]. Besides, the TiO₂ NTs/SnS and Si-doped TiO₂ NTs/SnS hybrids show a lower absorbance but higher photodegradation to MG than the NTs. Meanwhile, the Si-doped TiO₂ NTs/SnS hybrids also show a most rapid photodegradation but a lower absorbance to the NGB.

3.5.2. Effect of H₂O₂

A dramatically enhanced photodegradation process was observed after adding H₂O₂ (Fig. 7), showing a well-known photo-Fenton-like reaction. The Fenton-like photocatalytic activity is enhanced by Si doping and SnS modification.

3.5.3. Mechanisms on photocatalysis of the hybrids

The enhancement of the photocatalytic activity resulting from Si doping and SnS decoration could mainly be ascribed to the increases in the hydrophilicity and the efficient charge transfer between the NTs and SnS. The interface charge transfer is related to the band energy alignment at the interface. The absolute work functions (χ) are estimated to equal 5.81, 6.47, and 5.13 eV, respectively. Thus, the band levels (E_c and E_v) are given with the following relations (Butler and Ginley 1978):

$$E_c = \chi + \frac{E_g}{2} \quad (2)$$

$$E_v = \chi - \frac{E_g}{2} \quad (3)$$

In which, the E_g of pure TiO₂ NTs, SiO₂, and SnS equal 3.3 eV, 8.90 eV, and 1.77 eV (Wang et al 2015). The band alignment is therefore given in Fig. 8a. Although the Si doping may only increase the carrier concentration of the TiO₂ and introduce an impurity level to the TiO₂, the strong SiO₂ peak in the valence band XPS spectra (Fig. 8b) indicated that the SiO₂ had alone band levels. The higher E_v of the SnS (6.12 eV)

than that of SiO₂ (10.21 eV) and TiO₂ NTs (7.41 eV) results in the holes in the NTs transfer to the VB of the SnS. The holes in the VB of the SnS and remained in the VB of the NTs enable to directly oxidize the dye, or produce [•]OH by reacting with surface OH⁻ groups and adsorbed water molecules (Ollis et al 2010; Zhang et al 2013; Christoforidis et al 2015). Meanwhile, the lower *E_c* of the SnS (4.25 eV) than that of the SiO₂ (2.02 eV) and TiO₂ in the NTs (4.16 eV) results in the electron movement from NTs to SnS. The electrons in the CB of SnS lead to direct reduction of the dye or act as a reducing agent producing OH⁻ or O²⁻ (Ollis et al 2010; Christoforidis et al 2015). The electron and holes transferred from the Si-doped TiO₂ NTs to SnS could be more efficient than that from the TiO₂ NTs to SnS due to higher energy level difference. But photogenerated electron transfer from the VB to the CB of SiO₂ needs high excitation energy of 8.9 eV (~139 nm). However, only the visible light of ~579 nm is required when the electrons in the CB of TiO₂ transfer to the CB of SiO₂, and only require the visible lights of ~358 nm is required as the electrons in the VB of SiO₂ transfer to the VB of TiO₂. The high-efficient interface charge transfer restrains the charge recombination and so enhances the photocatalytic activities of the hybrids. The enhancement in photoconductivity (*σ*) with the SnS modification and Si doping (Fig. 8c) can verify this interface-induced effect. The *σ* was calculated utilizing the following relation given in previous literature (Chaki et al 2014).

$$\alpha = \frac{anc}{4\pi} \quad (4)$$

In which, *c* and *n* are light velocity in vacuum and refractive index, respectively. The *n* is estimated by the following relation (Chaki et al 2014).

221

$$n = \frac{1 + R^{1/2}}{1 - R^{1/2}} \quad (5)$$

223 When H_2O_2 is utilized, the H_2O_2 is believed to have two effects in photocatalysis
 224 (Elmolla and Chaudhuri 2010; Nezamzadeh-Ejhi and Karimi-Shamsabadi 2013).

225 First, it accepts photogenerated electrons from the hybrids to derive OH^- and $\cdot\text{OH}$
 226 radicals (6). Second, it derives OH^- and $\cdot\text{OH}$ radicals with $\cdot\text{O}_2^-$ and $h\nu$ (7 and 8)

230 The derived $\cdot\text{OH}$ radicals act as oxidation, whereas OH^- radicals act as reduction, in
 231 photocatalysis. In the view of equation 6, e^- takes part in the formation reaction of
 232 OH^- and $\cdot\text{OH}$ radicals. So that the increase in numbers of the photo-generated
 233 electrons with the SnS modification results in the enhancement of the Fenton-like
 234 reaction.

235

236 4. Conclusion

237 The TiO_2 and Si-doped TiO_2 NTs were facily fabricated. The thin pore and porous
 238 morphology and large specific surface area were observed for the NTs. The Si-doping
 239 resulted in the bandgap broadening from ~ 3.30 eV to ~ 3.40 eV but dramatical
 240 enhancement of the hydrophilicity and photo-induced ultrahydrophilicity. Meanwhile,
 241 the SnS modification remarkably enhanced the light absorption, hydrophilicity, and
 242 photo-induced ultrahydrophilicity. Moreover, the SnS modification introduced a highly

efficient interface effect that was enhanced by Si doping. These resulted in that the hybrids possessed the dramatically enhanced photocatalytic and photo-Fenton-like catalytic activities in the photodegradation of dye contaminant naphthol green B and malachite green in aqueous solution.

Statements and Declarations

Ethical Approval: All authors declare the manuscript is not submitted to other journal. This work does not involve human participants and/or animals.

Consent to publish: Authors consent to publish all parts of the manuscript and obtain the consent from the responsible authorities at the universities.

Competing interests: Authors Ning Ma and Hai-Yan He declare they have no financial interests. No funding was received for conducting this study.

Author contributions: All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Ning Ma and Hai-Yan He. The first draft of the manuscript was written by Ning Ma and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Availability of data and materials: The data and materials generated in our research all appear in the manuscript and are available to any uses.

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358

Figures

Figure 1

XRD patterns of the (a) TiO₂ NTs, (b) Si-doped TiO₂ NTs, (c) TiO₂ NTs/SnS, and (d) Si-doped TiO₂ NTs/SnS.

Figure 2

TEM micrographs of the (a) TiO_2 NTs, (b) Si-doped TiO_2 NTs, (c) TiO_2 NTs/SnS, and (d) Si-doped TiO_2 NTs/SnS

Figure 3

(a) XPS survey spectra and XPS spectra of (b) Ti 2p, (c) Si 2p, and (d) Sn 3d in the hybrids.

Figure 4

FTIR spectra of the NTs and hybrids (a) before (b) after UV irradiation

Figure 5

(a) Transmittance and (b) reflectance spectra and (c) the plots of $(ah\nu)^2$ versus $h\nu$ of the NTs and hybrids

Figure 6

Concentrations of (a) naphthol green B and (b) malachite green aqueous solution as a function of the reaction time

Figure 7

Concentrations of (a) naphthol green B and (b) malachite green aqueous solution with the H_2O_2 aqueous 20 ml/l as a function of the reaction time

Figure 8

(a) Schematic diagram of energy levels and initial redox process of the hybrids in the process of the UV light excitation, (b) bandgap XPS spectra of TiO_2 NTs and Si-doped TiO_2 NTs and (c) photoconductivity of the NTs and hybrids