



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: [www.elsevier.com/locate/cattod](http://www.elsevier.com/locate/cattod)



## The effect of solvent in the sol–gel synthesis of visible light-activated, sulfur-doped TiO<sub>2</sub> nanostructured porous films for water treatment

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### ARTICLE INFO

#### Article history:

Received 6 September 2013

Received in revised form

16 November 2013

Accepted 26 November 2013

Available online xxx

#### Keywords:

Cyanotoxin

Nonmetal doping

Sol–gel

Solvent

TiO<sub>2</sub>

Water treatment

### ABSTRACT

The effects of solvent on the synthesis of visible light-activated, sulfur-doped TiO<sub>2</sub> (S–TiO<sub>2</sub>) films were studied. Four different polar, protic solvents, isopropanol, 1-butanol, ethanol, and methanol (iPrOH, BtOH, EtOH, and MeOH), were chosen as the solvent in four titania sol–gel preparations. The films were characterized by X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM), atomic force microscopy (AFM), environmental scanning electron microscopy (ESEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), Ultraviolet (UV)–vis diffuse reflectance, and porosimetry. The structural, morphological, and porous characteristics of the sulfur-doped TiO<sub>2</sub> films were correlated with solvent physical properties such as the dielectric constant (*D*-value) and the saturated vapor pressure. According to XPS and FT-IR, S<sup>6+</sup>/S<sup>4+</sup> cations replaced Ti<sup>4+</sup> ions in the lattice of TiO<sub>2</sub>, resulting in the formation of localized states within the bandgap of TiO<sub>2</sub>. The optical absorption edge for all S–TiO<sub>2</sub> films was significantly shifted toward the visible light region. The solvent *D*-value has a negligible effect on the bandgap energy change and the doping states of the prepared S–TiO<sub>2</sub> samples. S–TiO<sub>2</sub> films synthesized using MeOH (S–TiO<sub>2</sub>–MeOH), despite their lower Brunauer, Emmett, and Teller (BET) surface area and porosity compared to the other films, showed the highest photocatalytic activity for the degradation of the hepatotoxin microcystin-LR (MC-LR) under visible light irradiation due to their high surface roughness and large pore size. The tailor-designed structure of the S–TiO<sub>2</sub>–MeOH film contributed to the high photocatalytic degradation rates of MC-LR. The larger pore size of the S–TiO<sub>2</sub>–MeOH films allowed easier transport of MC-LR inside the porous film, while the higher film surface roughness could increase nano-interfacial interactions between MC-LR and surface active sites. These results indicate that the structural and morphological properties of S–TiO<sub>2</sub> photocatalysts can be tailor-designed using different solvents in the sol–gel synthesis, while inducing negligible effects on the sulfur doping and the visible light activation of TiO<sub>2</sub>. Therefore, the enhancement of photocatalytic activity of S–TiO<sub>2</sub> films can be achieved by judicious choice of the main solvent for the sol–gel method.

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### 1. Introduction

Titanium dioxide (titania, TiO<sub>2</sub>) has been intensively studied and utilized in many applications due to its unique physicochemical properties such as low toxicity, high thermal- and chemical-stability, low cost, and relatively high photocatalytic activity [1,2]. TiO<sub>2</sub> photocatalysts have been widely used for environmental

applications, such as water treatment [2], air purification [3], and soil remediation [4], since Fujishima and Honda discovered photoinduced water cleavage by TiO<sub>2</sub> [5]. However, conventional TiO<sub>2</sub> can be excited only by UV light (4–5% of the solar spectrum) for photocatalytic reactions due to the large bandgap of TiO<sub>2</sub> (~3.2 eV for anatase) [2,6]. Therefore, extending TiO<sub>2</sub> light absorption into the visible light region (~45% of solar spectrum) has been extensively studied [2,6–13].

Many approaches, including nonmetal doping [2,6–8] and transition metal ion doping [9,10], have been investigated to extend the photoresponse of TiO<sub>2</sub> into the visible light region. For metal ion doping, severe limitations, such as photocorrosion, low thermal

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**Table 1**  
Properties of polar, protic solvents [26].

Solvent	Structural formula	Boiling point (°C)	Molecular weight (g mol <sup>-1</sup> )	Dielectric constant	Density (g cm <sup>-3</sup> , 25 °C)	Dipole moment	Vapor pressure(kPa, 25 °C)	Viscosity (mPa s, 25 °C)
iPrOH	(CH <sub>3</sub> ) <sub>2</sub> CHOH	82.2	60.1	19.9	0.782	1.66 D	6.03	2.04
BtOH	C <sub>4</sub> H <sub>9</sub> OH	117.6	74.1	17.5	0.806	1.75 D	0.82	2.57
EtOH	C <sub>2</sub> H <sub>5</sub> OH	78.2	46.1	24.6	0.785	1.66 D	7.89	1.08
MeOH	CH <sub>3</sub> OH	64.5	32.0	32.7	0.787	2.87 D	16.90	0.55

stability, potential metal leaching/toxicity, and increased recombination of charge carriers, have been reported [2,6–8]. Thus, nonmetal doping is a more promising approach to overcome those limitations. Since the synthesis of visible light-activated sulfur-doped TiO<sub>2</sub> was reported by Umebayashi et al. [11], sulfur doping to enhance photocatalytic activity of TiO<sub>2</sub> under visible-light irradiation has attracted extensive attention [10,12,13].

In order to synthesize nonmetal-doped titania, various routes have been used successfully, including seeded growth, chemical vapor deposition (CVD), hydrothermal, and sol-gel methods [2,6–12]. The sol-gel process has been intensively employed to synthesize many metal oxide materials due to several advantages, such as low cost and operating temperature, high chemical homogeneity and purity, and possibility to control material morphology at the nanoscale [14,15]. In particular, the solvent in a sol-gel method for the preparation of a catalyst is an important factor that should be selected carefully. Solvent properties, such as dielectric constant, dipole moment, and saturated vapor pressure, may play important roles in the relevant chemical reactions (e.g. hydrolysis and condensation) related to solution stability, particle size, film morphology, and structural properties of materials [14–16]. Several studies have reported that the stability of colloids and particle shape/size in solution were affected by chemical factors associated with hydrolysis and condensation reactions [17–22].

The investigation of solvent effects in a sol-gel method for synthesizing visible light-activated sulfur-doped TiO<sub>2</sub> thin films is of great interest and is the focus of this study. Four different polar, protic solvents (methanol, ethanol, 1-butanol, and isopropanol) were used for the preparation of four S-TiO<sub>2</sub> sol-gels. The solvents also functioned as in-situ water forming reagents through chemical reaction with sulfuric acid. The S-TiO<sub>2</sub> materials synthesized using different solvents were characterized with XRD, HR-TEM, AFM, XPS, FT-IR, UV-vis diffuse reflectance, and porosimetry. To evaluate the photocatalytic activity of synthesized S-TiO<sub>2</sub>, the degradation of the cyanotoxin microcystin-LR (MC-LR) under visible light irradiation was carried out. This toxin is produced by harmful algal blooms of cyanobacteria, which are commonly found in various water bodies worldwide due to water eutrophication as a result of anthropogenic activities. The presence of cyanobacteria in water can be a potential threat because some species of cyanobacteria are able to produce and release potent toxins. Among these cyanotoxins, the hepatotoxic MC-LR is one of the most toxic and commonly found in surface waters [23,24]. Therefore, in this study MC-LR was chosen as the target compound for the evaluation of the photocatalytic activity of synthesized S-TiO<sub>2</sub> under visible light.

## 2. Experimental methods and procedures

### 2.1. Preparation of S-TiO<sub>2</sub> sol-gels, films, and particles

To investigate the effects of solvent choice on the synthesis of visible light-activated, sulfur-doped TiO<sub>2</sub>, a previously reported sol-gel preparation method was modified [25]. A nonionic surfactant (polyoxyethylene (80) sorbitan monooleate, Tween 80, Sigma-Aldrich) was employed as a pore-directing reagent. Four different solvents, methanol (MeOH, HPLC grade, Tedia Company

Inc.), ethanol (EtOH, 200 proof, Decon Lab, Inc.), isopropanol (iPrOH, 99.8%, Pharmco), and 1-butanol (BtOH, 99.5%, Fisher Scientific), were chosen as primary solvents to prepare different sol-gels. Table 1 shows the properties of these polar, protic solvents [26]. The surfactant was dissolved in different solvents, and then titanium (IV) isopropoxide (TTIP, 97%, Sigma-Aldrich) was added as an alkoxide precursor in the mixtures of Tween 80 and the various solvents. Finally, sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 95–98%, Pharmco) was added as a sulfur precursor as well as a water forming reagent through an esterification reaction with the solvent. The sulfate esterification was proven in previous studies [27–29] and the reaction (1) has been postulated to result from the reaction of alcohols with sulfuric acid [27–29].



The solutions were stirred for 24 h at room temperature. All cases produced a yellowish, transparent, and stable solution. The pH value was 3.0 for all prepared solutions. The viscosity of the solutions were 6.48 ± 0.12, 4.99 ± 0.01, 2.88 ± 0.02, and 2.54 ± 0.03 cP for iPrOH, BtOH, EtOH, and MeOH, respectively. The molar ratio of the ingredients was Tween 80:solvent:TTIP:sulfuric acid = 1:45:1:1, and for the reference TiO<sub>2</sub> film, the surfactant was excluded and sulfuric acid was replaced with acetic acid at the same molar ratio. After the solution preparation, the photocatalyst was immobilized on borosilicate glass (Micro slide, Gold Seal) by a dip-coating method (withdrawal velocity of 12.3 ± 0.5 cm min<sup>-1</sup> and effective surface area of 10 cm<sup>2</sup>) when S-TiO<sub>2</sub> thin films were desired. To obtain S-TiO<sub>2</sub> photocatalyst, the immobilized photocatalysts were calcined in a multi-segment programmable, high-temperature furnace (Paragon Model HT-22-D, Thermcraft Inc., Winston-Salem, NC) at 400 °C for 30 min and then removed to cool down naturally. Before the dip-coating, glass substrates were rinsed with Milli-Q grade water and EtOH, and then dried under an infrared lamp. After dip-coating, the coatings were dried under an infrared lamp for 10 min, and then calcined. All prepared films had five layers of coating, each including the dip coating and calcination processes. The total mass of immobilized S-TiO<sub>2</sub> for iPrOH, BtOH, EtOH, and MeOH on the glass substrate was 4.2 ± 0.3, 3.3 ± 0.1, 4.2 ± 0.2, and 5.0 ± 0.5 mg, respectively. The samples prepared using iPrOH, BtOH, EtOH, and MeOH are denoted as S-TiO<sub>2</sub>-iPrOH, S-TiO<sub>2</sub>-BtOH, S-TiO<sub>2</sub>-EtOH, and S-TiO<sub>2</sub>-MeOH, respectively. For characterization of porosity and optical absorption, S-TiO<sub>2</sub> powders were prepared from thick films due to the difficulty of sample collection from the TiO<sub>2</sub> thin films. This approach is useful to rapidly investigate the effect of solvents for sulfur-doped TiO<sub>2</sub> synthesis even though the titania particles may not be exactly the same as those in the thin films [30,31]. For preparation of thick films, the prepared solutions were dried in petri dishes at 90 °C for 6 h and then calcined at 400 °C for 12 h in the programmable high-temperature furnace. The TiO<sub>2</sub> materials were then collected and ground.

### 2.2. Characterization of synthesized S-TiO<sub>2</sub>

An X'Pert PRO (Philips) XRD diffractometer with Cu K (λ = 1.5406 Å) radiation was employed to measure XRD patterns for the synthesized S-TiO<sub>2</sub>. Their crystal structures were determined

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