



Research article

Evaluation of SnO₂ for sunlight photocatalytic decontamination of water

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ABSTRACT

The broad bandgap tin (IV) oxide (SnO₂) is the least investigated semiconductor material for photocatalytic water decontamination in sunlight exposure. A detailed study covering the synthesis, characterization and the evaluation of photocatalytic activity of SnO₂, in the natural sunlight exposure, is presented. The structural characterization by XRD revealed the formation of phase pure tetragonal SnO₂ with the average crystallite size of ~41.5 nm whereas minor Sn²⁺ states in the material were identified by XPS analysis. As explored by diffuse reflectance (DR) and photoluminescence (PL) spectroscopy, the material exhibited a distinct absorption edge at ~3.4 eV. The morphological and microstructure analysis of the synthesized SnO₂ was carried out by FESEM and HRTEM. The electrochemical impedance spectroscopy (EIS) and chronopotentiometry (CP) predicted the better charge transport and retention ability of the material under illumination whereas the Mott-Schottky extrapolation prophesied the *n*-type behavior with the flat-band potential of –0.60 V. The photocatalytic activity of SnO₂ was assessed in the exposure of complete spectrum natural sunlight for the removal of 2,4,6-trichlorophenol. The HPLC and TOC analysis monitored the progress of degradation and mineralization whereas the released chloride ions were evaluated by ion chromatography. The effect of the transition metal ions (Fe³⁺, Cu²⁺, Ni²⁺, and Zn²⁺) as electron capture agents and H₂O₂ as ROS generator was explored during the degradation process. The utility of the material for the simultaneous removal of chlorophenols in the mixture was also investigated. The SnO₂ exhibited sustained activity in the repeated use. Based on experimental evidence congregated, the mechanism of the removal process and the efficacy of SnO₂ for sunlight photocatalytic decontamination of water was established.

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1. Introduction

The natural sunlight assisted wastewater decontamination, because of abundance, ever renewability and cost effectiveness is a perspective and rapidly growing area of research for the photocatalytic removal of hazardous toxins from the polluted water

(Chou et al., 2016). The metal oxide semiconductors, due to chemical stability and non-toxic nature are the extensively promised surfaces for the generation of reactive oxygen species (ROS) with the absorption of sunlight photons (Affam and Chaudhuri, 2013; Aslam et al., 2015a; Khaki et al., 2017; Qamar et al., 2015; Salah et al., 2016). Although, several semiconducting metal oxides that includes TiO₂, ZnO, WO₃, Bi₂O₃, CeO₂ etc. have been extensively investigated for the photocatalytic treatment of environmental pollutants (Aslam et al., 2014a, 2016; Hameed et al., 2015; Linsebigler et al., 1995; Nakata and Fujishima, 2012; Ollis and Al-Ekabi, 1993; Schneider et al., 2014; Yin et al., 2009; Zhang et al.,

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2010; Zhong et al., 2014). However, the efforts to explore the impending contestants among the metal oxides for the effective removal of toxicants from the wastewater are still in progress (Dai et al., 2012). Among the semiconductor oxides, SnO₂, due to the comparable optical-electrical and chemical properties, is a least-investigated potential contender in this regard (Diallo et al., 2016; Dimitrov et al., 2010). SnO₂, an *n*-type semiconductor with a wide bandgap has proved its worth in a variety of commercial applications (Das and Jayaraman, 2014; Zhao et al., 2014; Zhou et al., 2014). Although, few reports regarding the photocatalytic activity of SnO₂ for the removal of dyes/phenol are available in the literature (Al-Hamdi et al., 2015; Mendoza-Damián et al., 2015; Singh et al., 2014; Wang et al., 2013; Yao et al., 2014), however, the comprehensive depiction of the photocatalytic behavior of SnO₂ in sunlight exposure, the nature of ROS generated and the efficiency to remove potential pollutants such as chlorophenol derivatives lack. Among the chloro-substituted phenols, 2,4,6-trichlorophenol (TCP), due to stable and non-biodegradable chemical structure, is the substrate of interest in water decontamination (Ghanbari et al., 2016; Peng et al., 2015; Qamar et al., 2016; Xu and Wang, 2015). The pure phase, doped, and composite materials of both TiO₂ and ZnO have been investigated for the photocatalytic removal of TCP (Abbas et al., 2016; Carevic et al., 2016; Gaya et al., 2010; Ji et al., 2013; Rengaraj and Li, 2006; Sood et al., 2015; Sun and Xu, 2009; Wang et al., 2012; Xiong et al., 2005; Yang et al., 2016).

The current study is a detailed evaluation of the photocatalytic activity of surfactant-assisted hydrothermally synthesized SnO₂ in natural sunlight exposure for the photocatalytic decontamination of water. Prior to the photocatalytic studies, the as-synthesized SnO₂ was thoroughly observed by XRD, XPS, FESEM and HRTEM analysis. The optical behavior of the synthesized material was examined by UV–visible diffuse reflectance (DR) and photoluminescence (PL) spectroscopy. The CV, EIS, and CP investigated the electrochemical behavior of SnO₂ in the aqueous medium, both in the dark and under illumination, whereas the valence and conduction band edges were extracted from the Mott-Schottky analysis. The as-synthesized powder was subjected to the actual photocatalytic experiments for the removal of TCP in the exposure of natural sunlight. The experimental results from HPLC, TOC, and IC were linked to propose the mechanism of the degradation process.

2. Experimental details

The SnO₂ was synthesized by a facile hydrothermal route using SnCl₄ as a precursor. In a typical synthesis of SnO₂, an appropriate amount of SnCl₄·5H₂O (98+%, ACROS organics™) was dissolved in 100 ml of deionized water and added 0.01 g of Triton-X as a surfactant. The metallic ion solution was stirred at 80 °C for 30 min with the dropwise addition of 0.2 M ammonia solution simultaneously till the formation of the white suspension. The resultant suspension was transferred to 200 ml of Teflon-lined stainless-steel autoclave for hydrothermal treatment at 125 °C for 24 h. After cooling to room temperature, the precipitates were centrifuged, filtered and washed with deionized water and finally with 50:50 ethanol-acetone mixture to remove the surfactant and unreacted NH₄OH solution. The filtered precipitates were dried at 60 °C for 24 h. Finally, the dried powder was calcined in a muffle furnace at 400 °C for 4 h at a heating and cooling rate of 10 °C min⁻¹.

The crystal morphology of the as-synthesized SnO₂ was investigated by acquiring the XRD patterns using a Xpert x-ray powder diffractometer (Philips PW1398) with Cu K α radiation source from 10° to 90° (2 θ) with a step of 0.05°. Applying Scherer's equation, on the intense reflections, calculated the average crystallite size of the as-synthesized material. X-ray Photoelectron Spectrometer (PHI

5000 VersaProbe II, ULVAC-PHI Inc.) investigated the probable prevalence of the Sn²⁺ states in the binding energy range of 0 eV–1100 eV. The high-resolution core level peaks were fitted to extract the binding energies. The Field Emission Scanning Electron Microscope (FEI, Quanta FEG 450, Quorum Q150R ES), Quorum technologies coupled with EDX was employed for investigation of the bulk morphology whereas High-Resolution Transmission Electron Microscope (JEM-2100 JEOL, USA) performed the fine microstructure analysis and inter-atomic spaces of the as-synthesized powder. The optical behavior of the as-synthesized powder was investigated by a Perkin Elmer UV–visible diffuse reflectance (DR) spectrophotometer (Lambda 650) in the wavelength range of 200–900 nm. The direct and indirect band gaps of the material were evaluated by applying a Kubelka-Munk transformation on the reflectance data. The evaluated band gaps were validated by Fluorescence spectro-fluorophotometer, FS-2, Sinco, Korea, at an excitation wavelength of 250 nm and recording the emission in 250 nm–850 nm range. The acquired spectra were deconvoluted and fitted for accuracy.

The charge transport in the dark and under illumination in the synthesized material was evaluated by electrochemical impedance spectroscopy (EIS), whereas the Mott-Schottky analysis was performed to evaluate the flat band potential and to specify the semiconducting nature. The stability of the material was assessed by cyclic voltammetry (CV) analysis in positive and negative potential range. For electrochemical measurements, a VSP multi-channel potentiostat (Bio-logic Science Instrument, USA) equipped with glassy carbon (GC), platinum and Ag/AgCl saturated electrodes as working, counter and reference electrodes, respectively. For the modification of GCE (working electrode), a sonicated dispersion of catalyst in chloroform was coated at the surface. The fitting of EIS Nyquist plots was performed by Zfit (Ec-lab software, Bio-logic Science Instruments, USA). A 50-W halogen lamp was used as a source for the measurements under illumination.

To evaluate the adsorption of the 2,4,6-TCP substrate on as-synthesized SnO₂ and to attain the adsorption-desorption equilibrium, a 200 cm³ of the catalyst/TCP suspension containing 50 ppm of the substrate and optimized amount of 100 mg photocatalyst was kept in the dark for 1 h prior to exposure. For photocatalytic experiments, the suspension was exposed to sunlight (900–1100 × 10² lx) in a Pyrex[®] glass reactor (120 × 30 mm) in the fixed period of daylight from 9 a.m. to 3 p.m. Samples were drawn at regular intervals and analyzed by HPLC (SPD-20A, Shimadzu Corporation, Japan) after removing the catalyst using a 0.22 μ m syringe filter. The same sample was subjected to total organic carbon (TOC) measurements using TOC-V_{CPH} total carbon analyzer supplied by Shimadzu Corporation, Japan. The released chloride ions during the course of reaction were monitored by Thermo scientific, USA, ion chromatograph, Dionex (ICS-5000 + EG Eluent Generator) during the degradation/mineralization process.

3. Results and discussion

The powder x-ray diffraction profile of the as-synthesized SnO₂ in the 2 θ range of 10°–90° is presented in Fig. 1a. The sharpness of the diffraction peaks reflected the high crystallinity of the synthesized material and the pattern appeared as the combination of reflections of various intensities. The major reflections at the 2 θ values of ~26.65°, ~33.94°, ~38.01°, ~54.81° and ~57.86° were matched with the JCPDS# 41-1445 representing the tetragonal SnO₂ and assigned to (1 1 0), (1 0 1), (2 0 0), (2 1 1) and (0 0 2) indices of the lattice. The perceived reflections were in sound agreement with that reported in the literature for similar material synthesized by alternative routes (Sun et al., 2011). Additionally, the absence of the reflections due to the other oxides of Sn such as SnO

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