Talanta 114 (2013) 183–190

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Visible-light-driven photocatalytic and chemical sensing properties of SnS_2 nanoflakes

Ahmad Umar [a,b,*], M.S. Akhtar [c], G.N. Dar [b,e], M. Abaker [b,e], A. Al-Hajry [b,d], S. Baskoutas [e]

[a] Department of Chemistry, College of Science and Arts, Najran University, P.O. Box 1988, Najran 11001, Kingdom of Saudi Arabia
[b] Promising Centre for Sensors and Electronic Devices (PCSED), Najran University, P.O. Box 1988, Najran 11001, Kingdom of Saudi Arabia
[c] New and Renewable Energy Materials Development Center (NewREC), Chonbuk National University, Jeonbuk, South Korea
[d] Department of Physics, Faculty of Sciences and Arts, Najran University, P.O. Box 1988, Najran-11001, Kingdom of Saudi Arabia
[e] Department of Materials Science, University of Patras, Patras, Greece

ARTICLE INFO

Article history:
Received 4 February 2013
Received in revised form
19 March 2013
Accepted 20 March 2013
Available online 28 March 2013

Keywords:
SnS_2
Nanoflakes
Photocatalytic degradation
Rhodamine B
Nitroaniline
Chemical sensors

ABSTRACT

This work demonstrated the successful and facile large-scale synthesis and characterizations of SnS_2 nanoflakes. The detailed morphological studies revealed that the synthesized products were nanoflakes and were grown in large quantity. The XRD pattern and detailed compositional studies confirmed that the synthesized SnS_2 nanoflakes were well-crystalline and possessing hexagonal SnS_2 phase. The synthesized SnS_2 nanoflakes were used as efficient photocatalysts for photocatalytic degradation and effective electron mediators for the fabrication of chemical sensor. The photocatalytic properties of SnS_2 nanoflakes towards the photocatalytic degradation of Rhodamine B dye under visible light irradiation showed reasonably good degradation of ~61%. Moreover, the as-synthesized SnS_2 nanoflakes were used as efficient electron mediators for the fabrication of nitroaniline chemical sensor by simple *I-V* technique. Very high-sensitivity of $\sim 505.82 \pm 0.02\ mAcm^{-2}.(mole/L)^{-1}$ and experimental detection limit of $\sim 15 \times 10^{-6}$ (mole/L) in a short response time of ~10.0 s with LDR in the range of 15.6×10^{-6}–0.5×10^{-3} mole L^{-1} were observed for the fabricated nitroaniline chemical sensor. The observed results indicated that the SnS_2 nanoflakes can efficiently be used as visible-light-driven photocatalysts and the fabrication of ultra-high sensitive chemical sensors.

1. Introduction

The aquatic environmental imbalance mainly occurs by the contamination of water with the harmful non-biodegradable materials [1–3]. Various textile and chemical industries release many harmful organic macromolecules and dyes [4,5]. Particularly the disposable of colored organic waste water from the textile dyeing industries causes a serious problem to aquatic ecosystem and hence contaminate the environment which cause a serious threat to the living organisms [6]. Among various water soluble dyes, Rhodamine B (RhB) with non-volatile nature and bright reddish violet in color are extensively used in various prospect applications such as fluorescence microscopy, flow cytometry, fluorescence correlation spectroscopy and ELISA [7] and also applied for dying cottons, bamboo, weed, stamp pad inks etc. The waste of RhB dye hazardously affects natural environments especially aquatic life and lead the mutagenic effects to humans and other living organisms [8,9]. Conventionally, a biological treatment or degradation process utilizes to decolorize the dyes, but it is ineffective for the complete removal and degradation of dye. Last few years, the catalytic process derived by solar energy or other radiation energy has been studied for the successful degradation of harmful organic dyes into environmental friendly materials [10]. In this regard, because of the unique band gap and various other physical and chemical properties, the nanoscale inorganic semiconductors such as metal oxides, metal sulfides etc. were used as active catalysts for the degradation/oxidation of organic dyes and reported in the literature [11]. The photocatalytic degradation occurs due to the effective separation of excited electron in conduction band (CB) and hole in valance band (VB) under the light illumination, which could capture by some surface species in the surroundings such as hydroxyl or O_2 groups [12]. These catalysts are usually active under the UV-light. Among various semiconducting materials, the metal sulfides have received a great deal of interest as promising photocatalysts under

* Corresponding author at: Najran University, Centre for Advanced Materials and Nanoengineering (CAMNE), Centre for Advanced Materials and Najran 11001, Saudi Arabia. Tel.: +966 534 574597.
E-mail address: ahmadumar786@gmail.com (A. Umar).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.03.050

the visible light illumination [13]. Domen et al. demonstrated a high photo-activity for hydrogen evolution over the surface of synthesized nanostructured CdS under visible light [14].

Recently, the IV–VI group semiconductors such as tin sulfides (SnS, SnS_2) have received much attention owing to their strong anisotropy of optical properties and potential applications in solar cells as well as electrical switchings [15–20]. Among large number of binary tin sulfides (SnS, SnS_2, Sn_2S_3, Sn_3S_4, Sn_4S SnS and SnS_2), the SnS_2 possesses special place due to its own properties and wide applications in solar cells, lithium-ion batteries, optoelectronics, photoluminescence and so on [21]. The SnS_2 is an *n*-type semiconductor and is receiving much attention owing to its layered hexagonal CdI_2-type crystal structure with two layers of close-packed sulfur anions and tin cations sandwiched between them in an octahedral coordination manner. Due to its absorption tunable band gap of 2.2 eV, the crystalline SnS_2 could be a promising photocatalytic material for the photocatalytic degradation of organic dyes in the presence of visible-light [22]. Moreover, SnS_2 nanomaterials possess good oxidative and thermal stability in acid and neutral environment [23,24].

In this work, we demonstrate the facile and large-scale synthesis of well-crystalline SnS_2 nanoflakes by simple hydrothermal process. The synthesized nanoflakes were characterized in detail in terms of their morphological, structural and compositional properties. The as-synthesized nanoflakes were used as efficient photocatalysts for photocatalytic degradation of Rhodamine B dye under visible light. Moreover, the prepared nanoflakes were used as efficient electron mediators for the fabrication of nitroaniline chemical sensor by simple *I–V* technique.

2. Experimental details

2.1. Synthesis of SnS_2 nanoflakes

All the chemicals utilized for the synthesis of SnS_2 nanoflakes were purchased from Sigma-Aldrich and used without further purification. Distilled water (DW) was used for all the synthesis process. Well-crystalline SnS_2 nanoflakes were synthesized by facile low-temperature hydrothermal process. In a typical reaction process, aqueous solutions of 0.02 M $SnCl_4$ $5H_2O$ and 0.05 mol/L thiourea, both prepared in 50 mL DI water, were mixed well under constant stirring. After constant and vigerous stirring for 30 min, the resultant solution was transferred to teflon lined autoclave, sealed and heated upto 140 °C for 3 h. After desired reaction time, the autoclave was allowed to cool at room-temperature and finally yellowish precipitate was obtained which was extensively washed several times with DW, ethanol and acetone, sequentially and dried at 55 °C for 3 h. During the reaction, the thiourea reacts with water and produces H_2S which is further reacted with Sn^{4+} ions obtained from $SnCl_4$. The chemical reactions involved in the synthesis process can be written as:

$$NH_2CSNH_2+2H_2O \rightarrow 2NH_3+H_2S+CO_2$$

$$Sn^{4+}+H_2S \rightarrow SnS_2\downarrow+4H^+$$

The dried powder was then characterized in detail in terms of their morphological, structural and compositional properties and utilized as efficient photocatalyst for photocatalytic degradation of Rhodamine B and as an electron mediator for the fabrication of reproducible and highly sensitive nitro-aniline chemical sensor.

2.2. Characterizations of as-synthesized SnS_2 nanoflakes

The as-synthesized SnS_2 nanoflakes were characterized in detail by various analytical tools. The general and detailed morphologies of as-synthesized nanoflakes were done by field emission scanning electron microscopy (FESEM; JEOL-JSM-7600 F) and transmission electron microscopy (TEM) equipped with high-resolution TEM (HR-TEM). For HRTEM analysis, the synthesized products were ultrasonically dispersed in acetone and a drop of acetone solution, which contains the SnS_2 nanostructures, was placed on a copper grid and examined. The crystallinity and crystal phases were examined by the X-ray diffraction (XRD; PANanalytical Xpert Pro.) pattern measured with Cu-Kα radiation (λ = 1.54178 Å) in the range of 10–65°. The chemical composition of the as-synthesized SnS_2 nanoflakes was examined by Fourier transform infrared (FT-IR) spectroscopy, measured at room-temperature, in the range of 400–4000 cm^{-1}. To prepare the sample for FTIR measurements, small amount of the as-synthesized SnS_2 nanoflakes was mixed well with the potassium bromide (KBr) and subsequently compressed under high-pressure (~4 t) for pellet preparation. The obtained pellet, composed of SnS_2 nanoflakes and KBr, was used for the FTIR measurements.

2.3. Photocatalytic decomposition of rhodamine B dye using as-synthesized SnS_2 nanoflakes

The photocatalytic performance of the synthesized SnS_2 nanoflakes was examined by studying the photocatalytic decomposition of rhodamine B (RhB) dye. The photocatalytic degradation of RhB dye was performed under the illumination of Xenon arc lamp (300 W, Hamamatus: L 2479), attached with UV cut-off filter of wavelength 400 nm (FSQGG-400) which limited the illumination in a range of 400–800 nm, i.e. visible light. The degradation of RhB dye was calculated by measuring the UV–vis absorbance at 552 nm wavelength at certain time intervals. The photo-catalytic degradation was established in a 250 ml beaker using 150 ml of RhB dye solution (10 ppm). Prior to the light illumination, the prepared RhB dye solution was bubbled with oxygen for 30 min to allow the equilibrium of the system. For the photocatalytic experiments, 150 mg of the as-synthesized SnS_2 nanoflakes as photocatalyst were added to the RhB dye solution and stirred for 10 min for the initial physical adsorption of dye over SnS_2 nanoflakes surfaces. The decomposed dye solution was measured by using (UV–vis spectrophotometer Perkin Elmer-UV/VIS-Lambda 950) after regular time intervals.

2.4. Fabrication and characterization of nitro-aniline chemical sensor by I–V technique

To modify the electrode surface, firstly, the surface of glassy carbon electrode (GCE) was polished with commercially available alumina, followed by rinsing with DW thoroughly. For the GCE surface modification for nitro-aniline chemical sensor, slurry of SnS_2 nanoflakes were made by mixing an appropriate composition of SnS_2 nanoflakes and conducting agent (butyl carbital acetate). Finally, a small amount of the slurry was casted on GCE (surface area 0.0316 cm^2) surface, and then the modified electrode was dried in electric oven at 60 ± 5 °C for 4 h. The sensor analytical performance was investigated using *I–V* technique as discussed in our previous reports [25]. For *I–V* measurements, an electrometer (Keithley, 6517A, USA) was used as a voltage source and the SnS_2 nanoflakes/GCE was used as a working electrode while Pt wire was employed as a counter electrode. The current response was measured from 0.0 to 2.0 V while the time delaying and response time were 1.0 s and 10.0 s, respectively. The amount of 10.0 mL phosphate buffer solution was kept constant for all the measurements. For the concentration studies, a wide range of nitroaniline concentrations (15.6×10^{-6} mol/L–1×10^{-3} mol/L) was used. The sensitivity of the fabricated nitro-aniline chemical sensor was estimated from the slope of the current *versus* concentration from