

# Structural, textural and photocatalytic properties of quantum-sized $\text{In}_2\text{S}_3$ -sensitized Ti-MCM-41 prepared by ion-exchange and sulfidation methods

Shaohua Shen, Liejin Guo\*

State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an, ShaanXi 710049, PR China

Received 1 March 2006; received in revised form 13 April 2006; accepted 10 May 2006

Available online 19 May 2006

## Abstract

$\text{In}_2\text{S}_3$  nanocrystallites were successfully encapsulated into the mesopores of Ti-MCM-41 by a two-step method involving ion-exchange and sulfidation. The X-ray diffraction (XRD) patterns, UV-vis absorption spectra (UV-Vis), high-resolution transmission electron microscopy (HRTEM) and  $\text{N}_2$  adsorption–desorption isotherms were used to characterize the structure of the composite materials. It is found that the diameter of most  $\text{In}_2\text{S}_3$  nanocrystallites is about 2.5 nm, less than the pore size of Ti-MCM-41. The  $\text{In}_2\text{S}_3$  nanocrystallites inside the Ti-MCM-41 host show a significant blue-shift in the UV-vis absorption spectra. Under irradiation of visible light ( $\lambda > 430$  nm), the composite material has much higher photocatalytic activity for hydrogen evolution than bulk  $\text{In}_2\text{S}_3$ . It can be explained by the effective charge-separation in the quantum-sized  $\text{In}_2\text{S}_3$ -sensitized Ti-MCM-41.

© 2006 Elsevier Inc. All rights reserved.

**Keywords:** Ti-MCM-41; Quantum-sized  $\text{In}_2\text{S}_3$ ; Charge separation; Hydrogen evolution; Visible light

## 1. Introduction

Semiconductor metal oxides have received intense research interest for decades because of their activity for the photocatalytic water splitting [1]. Although there has been remarkable progress for photocatalysts working under ultraviolet light [2,3], the progress has rarely extended to the visible light region. Chalcogenides such as CdS have been studied extensively, since they have ideal edge positions of the valence and conduction bands for the reduction of water molecules [4]. Unfortunately, they have a fatal disadvantage of photocorrosion and hence are not useful for practical application. In recent researches [5–7], several new visible-light-driven photocatalyst materials for water splitting have been described. However, the highly efficient photocatalyst for water splitting under visible light irradiation has not been developed yet.

Because of the solid merits of controllable pore size, variable mesostructure, and functional composition, mesoporous

materials have attracted much attention in the fields of pure and applied sciences, since the invention of M41S mesoporous molecular sieves [8]. By utilizing the channel-typed nanospace of mesoporous materials, some unique chemical and physical properties have been introduced, such as selective chemical reactions [9], size-dependent molecular sieving [10], and controlled energy properties [11]. To provide additional functions to siliceous mesoporous materials, researchers have tried to being incorporated inorganic components such as transition metal ions and semiconductor nanocrystals within the framework and/or nanochannels of mesoporous silica materials. Several studies on nanocomposite systems containing inorganic guest species have revealed interesting functional properties in the areas of magnetism [12], optics [13], electronics [14], etc. Also, these derived composites play important role for advanced catalytic applications [15] and, in particular, for photocatalytic hydrogen evolution from water [16]. In the literature, it is thought that stability of the narrow-band-gap sulfide guest can be improved by being incorporated into the siliceous host [17], however, the photocatalytic activity of such composite is quite low, due to the dominant surface charge-recombination

\*Corresponding author. Fax: +86 29 82669033.

E-mail address: [lj-guo@mail.xjtu.edu.cn](mailto:lj-guo@mail.xjtu.edu.cn) (L. Guo).

[18] in quantum-sized semiconductor guest confined in the mesopores of the host.

In other aspects, coupling two semiconductors may lead to an enhanced efficiency of photoinduced charge–carrier separation, as proved by the enhancement of photocatalytic [19] and photoelectrochemical [20] performances in combined materials. As is known, mesoporous silica materials consisting of Si and O atoms do not exhibit any absorption in the UV or visible light range. But then it is possible for silicate molecular sieves to exhibit optic property in the UV region by introducing Ti atoms into the molecular sieves framework. For example, Ti-MCM-41, a mesoporous molecular sieve having MCM-41 structure, shows a characteristic absorption band at 225 nm, which corresponds to the ligand-to-metal (–O–Ti–) electron transfer occurring at isolated Ti atoms [21]. In the case of photocatalysis, sensitizing the wide-band-gap semiconductor with another narrow-band-gap semiconductor has great influence on the charge–carrier recombination time and photoactive transition in the visible light which results in enhanced photocatalytic activity. Moreover, incorporating the narrow-band-gap semiconductor into the mesoporous Ti-MCM-41 host leads to different morphological and crystalline properties of the catalyst. Due to these remarkable reasons, sensitizing Ti-MCM-41 by incorporating some narrow-band-gap semiconductors into the mesopores of Ti-MCM-41 is viewed as one of the promising ways to explore novel catalyst. Two approaches have been generally used to transport precursor molecules or ions for assembly of nanoparticles or nanorods inside the channels of MCM-41 and related mesoporous materials. The first approach involves an ion-exchange procedure [22], the second one uses reversed micelles as an insertion carrier to incorporate nanoparticles into the mesoporous channels [23,24].

In this work, we focus on the preparation and investigation of quantum-sized  $\text{In}_2\text{S}_3$ -sensitized Ti-MCM-41 composite semiconductor. For the synthesis, we used a two-step method involving ion-exchange and sulfidation to incorporate  $\text{In}_2\text{S}_3$  into the mesopores of the Ti-MCM-41. This synthetic method generally allows controlling the texture and the morphological properties of the solid. The size of  $\text{In}_2\text{S}_3$  nanoparticles is quantum-confined by the mesopores of the Ti-MCM-41 and less than the pore size of the Ti-MCM-41. Herein, we investigated the photocatalytic activity of quantum-sized  $\text{In}_2\text{S}_3$ -sensitized Ti-MCM-41 composite semiconductor for hydrogen production from water under visible light irradiation ( $\lambda > 430$  nm). The charge transfer mechanism in quantum-sized  $\text{In}_2\text{S}_3$ -sensitized Ti-MCM-41 was also explored.

## 2. Experimental section

### 2.1. Synthesis

All chemical reagents used in the present experiments were obtained from commercial sources as guaranteed-

graded reagents and used without further purification. A typical synthesis process for preparation of mesoporous silica of Ti-MCM-41 follows the procedure [25] with minor modification: At 40 °C, 1.82 g of cetyltrimethylammonium bromide (CTAB) was dissolved into a solution containing 45 mL of deionized water and 0.42 g of NaOH, then 8.21 mL of tetrahydroxosilicate (TEOS) was added dropwise to the above solution and stirred vigorously for 1 h for the hydrolysis of TEOS. The resulted sol was stirred, and to which 0.25 g of tetrabutyl titanate (TBOT) was added dropwise and stirred at 40 °C for another 1 h. Finally the resulting gel was transferred to a 90-mL Teflon-lined autoclave and held at 100 °C for 3 days. The product obtained was filtered, washed with water and ethanol, and dried in air at 100 °C overnight. The as-synthesized samples were denoted as CTAB@Ti-MCM-41, and calcined at 500 °C in static air for 5 h to remove the template CTAB with a heating rate of 2 °C/min, then white powder Ti-MCM-41 was obtained. The molar ratio of Ti:Si is 0.02.

$\text{In}_2\text{S}_3$  nanoparticles were loaded inside the mesoporous Ti-MCM-41 through ion-exchange and sulfidation according to the literature [22]. The indium (III) methanol (MeOH) solution was prepared by dissolving 1.00 g of  $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$  in 100 mL of MeOH. The resulting solution was added to 1.00 g of the as-synthesized CTAB@Ti-MCM-41 powder. The slurry of the salt precursor and CTAB@Ti-MCM-41 was refluxed while being stirred for 4 h. The ion-exchanged Ti-MCM-41 was recovered by filtration and washed with excess MeOH and distilled water, to make sure that the  $\text{In}^{3+}$  absorbed onto the outer surface of Ti-MCM-41 was washed away. The product was then dried at 70 °C in vacuum for 6 h. Finally, treatment with  $\text{H}_2\text{S}$  at 300 °C for 3 h yielded the desired  $\text{In}_2\text{S}_3$  nanoparticles inside Ti-MCM-41, denoted as  $\text{In}_2\text{S}_3$ @Ti-MCM-41. The content of  $\text{In}_2\text{S}_3$  in the final  $\text{In}_2\text{S}_3$ @Ti-MCM-41 is 7.6 wt%.

Bulk  $\text{In}_2\text{S}_3$  as reference was also prepared by treating 1.00 g of  $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$  with  $\text{H}_2\text{S}$  at 300 °C for 3 h in the muffle oven, product was denoted as bulk  $\text{In}_2\text{S}_3$ .

### 2.2. Characterization

X-ray diffraction (XRD) patterns of the synthesized samples were obtained from a PANalytical X'pert MPD Pro diffractometer using Ni-filtered  $\text{CuK}\alpha$  irradiation (wavelength 1.5406 Å).  $\text{N}_2$  adsorption–desorption isotherms of samples were conducted at 77 K in the Beckman Coulter SA3100 plus instrument. Samples were degassed at 70 °C for 12 h prior to measurements. Pore size, surface area and pore volume of the samples were determined using the Barrett–Joyner–Halenda (BJH) [26], the Brunauer–Emmett–Teller (BET) and Horvath–Kawazoe (HK) [27] methods, respectively. Elemental Analysis was conducted on the Bruker S4 PIONEER X-ray fluorescence spectrum (XRF) using Ru target and 4 kW maximum power. Raman scattering study was performed on the

Download English Version:

<https://daneshyari.com/en/article/1333542>

Download Persian Version:

<https://daneshyari.com/article/1333542>

[Daneshyari.com](https://daneshyari.com)