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Preparation of $CdIn_2S_4$ microspheres and application for photocatalytic reduction of carbon dioxide

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ABSTRACT

A series of novel microspheres of $CdIn_2S_4$ were prepared by hydrothermal process, among them the $CdIn_2S_4$ synthesized from L-cysteine exhibited higher photocatalytic activity for CO_2 reduction and has potential application for using visible light. Characterization of X-ray diffractometer (XRD), UV–vis absorption spectrometry (UV–vis), field emission scanning electron microscopy (FE-SEM), transmission electron microscope (TEM) and N_2 sorption analysis resulted in the crystal morphology, light absorption band and porous geometry. The mechanism of photocatalytic reduction of CO_2 in methanol over $CdIn_2S_4$ was also proposed. The narrow band gap of the as prepared catalyst promoted reducing CO_2 to dimethoxymethane and methyl formate in methanol.

1. Introduction

Since a variety of human activities, such as electric power generation and transportation, CO_2 emission has increased greatly and caused environmental problems seriously, the greenhouse effect has changed the global climate. In order to abate total amount of CO_2 emitted, various technologies have been exploring. Photocatalytically reducing CO_2 came into notice due to utilizing solar energy and conversing CO_2 to valuable chemicals or fuel. By now TiO_2 acted as an inexpensive and easily obtained material has been employed in many photocatalytic reactions, but its wider band gap hinders in utilizing solar energy. Many researchers, therefore, modified the TiO_2 by doping and compositing Ag_2S Au–Ag in TiO_2, etc. [1–4] or synthesizing novel materials, including $ZnIn_2S_4$, Zn_2SnO_4, etc. [5,6].

Up to date, many efforts have been focused on the photocatalytic reduction of CO_2. Zhou et al. reported that square nanoplates of Bi_2WO_6 benefited photocatalytic reduction of CO_2 into CH_4 [7]. Liang et al. used grapheme-TiO_2 nanocomposite for photocatalytically reducing CO_2 [8]. But the conversion rate of CO_2 to hydrocarbons is still low. Developing novel photocatalysts to efficiently conversing CO_2 will be severe challenge.

$CdIn_2S_4$, belonging to ternary semiconductors of chalcogenide AB_2X_4 and being considered to have potential applications in solar cells and optoelectronic devices [9], has been used for H_2 evolution, bacterial inactivation and degradation of methyl orange [10–13]. To the best of our knowledge, the $CdIn_2S_4$ nanocrystals for CO_2 photocatalytic reduction have not been reported.

In our previous work, methyl formate (MF) was produced through photocatalytic reduction of CO_2 on Ag loaded $SrTiO_3$ in the presence of methanol [14]. In our present work, a chemically stable $CdIn_2S_4$ was synthesized using L-cysteine as sulfur resource via a facile hydrothermal process. The obtained microspheric $CdIn_2S_4$ that was composed of many nano sheets had a considerable photocatalytic activity for photocatalytically reducing CO_2 to quantificationally modulated dimethoxymethane (DMM) and methyl formate (MF), as a new finding, we exposed their reaction mechanism.

2. Experimental

2.1. Synthesis of $CdIn_2S_4$

Three kinds of $CdIn_2S_4$ powders were prepared by hydrothermally synthetic method. All reagents were purchased from Tianjin Benchmark Chemical Reagent Company and used without further

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purification. Firstly, $InCl_3 \cdot 4H_2O$, $CdCl_2 \cdot 2.5H_2O$, L-cysteine or thioacetamide or thiourea with a molar ratio of 2:1:4 were dissolved in 55 ml deionized water to obtain three transparent liquids via magnetically stirring for 15 min. Then, each of them was poured into a 75 ml of Teflon-lined stainless steel autoclave. Subsequently, the three autoclaves were kept at 180 °C for 48 h and cooled down to the room temperature. The obtained brown precipitates were collected after centrifugal separation. Finally, three catalysts were obtained by washing the solid precipitates with absolute ethyl alcohol and deionized water for three times and drying at 80 °C over night.

2.2. Characterization

The as prepared $CdIn_2S_4$ powders were characterized by a Rigaku D X-ray powder diffractometer with Cu Kα radiation at a scan rate of 2 min^{-1}. FE-SEM of JEOL-JSM6700F and HR-TEM of Tecnai G2 F20 were employed out to observe the morphology. Spectra of UV–vis by Shimadzu UV-2550 were obtained using Ba_2SO_4 as a reflectance standard. The surface areas were measured by BET of APP V-Sorb 2800P using nitrogen sorption at 77 K.

2.3. Photocatalytic reaction

Photocatalytic reactions were taken place in a slurry reactor with quartz window and cooling water jacket. Before irritation 0.02 g $CdIn_2S_4$ and 20 ml methanol were put into the reactor. Under stirring, the CO_2 was bubbled through the suspension at a rate of 200 ml/min for 30 min to sweep the air in the reactor and absorbed oxygen in methanol. Then the reactor was sealed and irradiated by a 250 W high pressure mercury lamp over the quartz window at an intensity of 2500 μW/cm^2 reaching the slurry surface. After 10 h irradiation, the concentration of methyl formate and dimethoxymethane in the solution was measured by a gas chromatography (GC) of Agilent 7890A equipped with a flame ionization detector (FID). Comparative tests were implemented under Ar instead of CO_2.

3. Results and discussion

3.1. Characterization of photocatalysts

In Fig. 1 the XRD patterns of $CdIn_2S_4$ that prepared with sulfur sources of L-cysteine, thioacetamide and thiourea respectively could refer to the cubic spinel structure of $CdIn_2S_4$ (JCPDS-2760). The broad diffraction peaks in Fig. 1(a) indicated smaller crystals

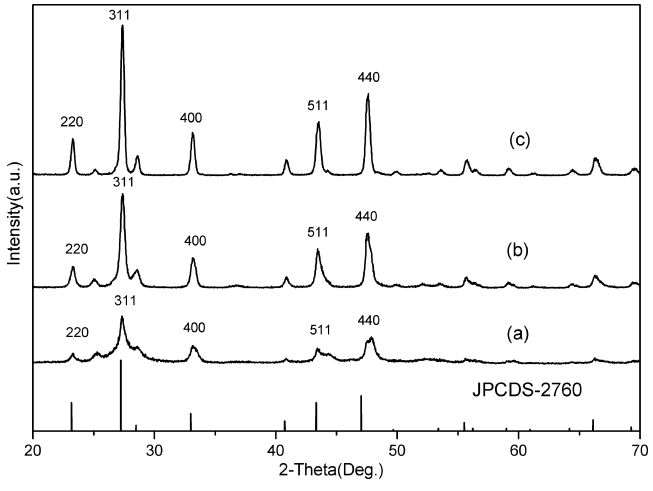

Fig. 1. XRD pattern of $CdIn_2S_4$ prepared with different sulfur source: (a) L-cysteine, (b) thioacetamide and (c) thiourea.

Table 1
Crystal sizes and lattice spacings of $CdIn_2S_4$.

Samples	$CdIn_2S_4$ (L-cysteine)	$CdIn_2S_4$ (thioacetamide)	$CdIn_2S_4$ (thiourea)
Crystal size (nm)	15.92	18.33	25.03
Lattice spacing (Å)	3.2593	3.2574	3.2574

Table 2
Surface areas of $CdIn_2S_4$ samples.

Photocatalyst	$CdIn_2S_4$ (L-cysteine)	$CdIn_2S_4$ (thioacetamide)	$CdIn_2S_4$ (thiourea)
BET surface area (m^2/g)	24.03	23.56	13.20

were formed when L-cysteine was sulfur source. Contrasting three patterns in Fig. 1, we could find that (b) and (c) had stronger and sharper peaks than (a), which meant the crystallinities of the $CdIn_2S_4$ from thioacetamide and thiourea were better than that from L-cysteine.

The facet [3 1 1] was chosen to calculate the crystallite size by using the Debyee–Scherrer equation and lattice spacing, the results are listed in Table 1.

The morphologies and microstructures of the samples were further characterized by SEM and TEM. As shown in Fig. 2(a) and (b), marigold-like $CdIn_2S_4$ spheres with an average diameter of 5 μm were assembled by numerous flakes. Fig. 2(g) and (h) showed the HRTEM images of the $CdIn_2S_4$ synthesized from L-cysteine. The lattice spacings between (3 1 1) and (2 2 0) facets were 3.295 Å and 3.846 Å respectively, which were in accordance with the XRD analysis.

In Fig. 2(c) and (d) the morphologies of $CdIn_2S_4$ synthesized from thioacetamide and thiourea were different from that synthesized from L-cysteine. Although synthesis condition was the same, the $CdIn_2S_4$ from thioacetamide had an average diameter of 4 μm and was composed of dozen of flakes and particles, which were accumulated to form irregular and looser spheres than that from L-cysteine. When sulfur source changed to thiourea, the $CdIn_2S_4$ exhibited much larger diameter of 9 μm, and some bipyramid-like particles aggregated on its spheric surface.

Undoubtedly, coordination ability of sulfur sources plays a key role in morphologies of $CdIn_2S_4$. L-cysteine can coordinate with In^{3+} and $CdIn_2S_4$ strongly to form precursor complexes, but lower coordination abilities are given by thioacetamide and thiourea [15].

The BET specific surface areas of the as-prepared $CdIn_2S_4$ samples were calculated and summarized in Table 2. It is obvious that the $CdIn_2S_4$ synthesized from L-cysteine and thioacetamide had much larger surface area than that from thiourea, and the largest one was $CdIn_2S_4$ synthesized from L-cysteine. The reason could be found by observing the puffy appearance of two samples with larger surface area and the dense appearance of the sample from thiourea in Fig. 2(b), (d) and (f). The smaller crystallite size of sample from L-cysteine also leads to a larger specific surface area. Compared images in Fig. 2, the $CdIn_2S_4$ prepared from L-cysteine has more perfect morphology, which will provide larger irritated area and result in a higher absorbance. Large surface area of microsphere not only provides more active sites, but also enhances the ability of light absorption [16,17].

Fig. 3 showed the UV–vis diffuse reflection spectra (DRS) of the catalysts prepared from three different sulfur sources. The absorption edges of the $CdIn_2S_4$ samples synthesized from L-cysteine, thiourea and thioacetamide were 737, 592 and 605 nm, the corresponding band gaps were 1.68, 2.09 and 2.05 eV, respectively. The smaller value of absorption edge of the sample from L-cysteine could contribute to its smaller crystal size and regular morphology, which reflected an opened architecture constituted