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$In₄SnS₈$ ultrathin nanosheets: a ternary sulfide with fast adsorption–visible-light photocatalysis dual function†

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Ultrathin In_4SnS_8 nanosheets have been successfully synthesized via a facile thermal decomposition

method. The average thickness of these In_4SnS_8 nanosheets is only 3.8 nm, comprising about five atomically thick layers. To our knowledge, this is the thinnest In₄SnS₈ nanosheet synthesized using Received 24th November 2016 Accepted 29th December 2016

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a solution-phase chemical method. The resulting ultrathin $ln_4 SnS_8$ nanosheets exhibit fast adsorptionvisible-light photocatalysis dual function for various organic dyes, suggesting their potential application in environmental remediation, solar energy conversion, and advanced optical/electric nanodevices.

Introduction

The advances in graphene technology have stimulated the synthesis and characterization of various two dimensional nanomaterials such as transition metal oxides,¹ metal chalcogenides, 2 and organic compounds, $3-5$ in the field of nanotechnology. To obtain these 2D nanomaterials, tremendous efforts have been made and various physical and chemical synthesis methods have been developed, such as mechanical and liquidphase exfoliations, $6-8$ ion-intercalation^{9,10} and exfoliation, $11-15$ chemical vapor deposition (CVD) ,¹⁶⁻¹⁸ and solution-phase chemical syntheses,¹⁹ etc. However, simple, effective synthetic methods and well-defined 2D nanostructures are still being pursued. PAPER

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Metal sulfides, as a typical class of semiconductor, have attracted much attention due to their extraordinary chemical/ physical properties and multiple potential applications. In particular, ternary or quaternary metal sulfides (TQMS) have been extensively studied because of their unique optoelectronic and catalytic properties, as well as their other advantages such as low cost, earth-abundance, and low toxicity. These benefits offer TQMS increased opportunities in meeting the requirements of some special applications. For example, ZnIn_2S_4 with a band gap of 2.3 eV (ref. 20 and 21) and $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ with a tunable band gap within the visible light region $22,23$ have been applied in visible-light photocatalysis. CuInS₂ (ref. 24) and $Cu₂ZnSnS₄$ (ref. 25 and 26) with band gaps of 1.5 eV have been used in low-cost photovoltaic devices. $CuInS₂-ZnS$ with low toxicity and broad emission bands²⁷ has been used in light emitting devices. Compared with 0D quantum dots, 2D ultrathin TQMS nanosheets exhibit improved conductivity, flexibility, and high surface area, which are key elements for some applications. However, although the synthesis of TQMS nanocrystals has been widely reported recently, the controlled and convenient synthesis of TQMS with ultrathin 2D structures still remains a great challenge.

Here, we prepared 2D ultrathin $In₄SnS₈$ nanosheets via a facile thermal decomposition method. The ultrathin In_4SnS_8 nanosheets show fast adsorption–visible-light photocatalysis dual function for various organic dyes.

Experimental section

Chemicals

Indium trichloride $[InCl₃·4H₂O, 99.995%)$, tin(w)chloride dihydrate (SnCl₄ \cdot 5H₂O, 98%), sodium diethyldithiocarbamate $((C_2H_5)_2NCS_2Na \cdot 3H_2O, Na(DDTC)$, oleylamine (OM, 80–90%), octadecylene (ODE, \geq 95.0%) absolute ethanol (AR), cyclohexane (99.5%), and acetic acid (AR) were all purchased from Sinopharm Chemical Reagent Company. All the chemicals were used as received without further purification.

Synthesis of $In(DDTC)_3$ and $Sn(DDTC)_4$

For synthesizing In(DDTC)₃, 10 mmol of InCl₃ \cdot 4H₂O was dissolved in 100 mL of distilled water. Then 100 mL aqueous solution containing 30 mmol of Na(DDTC) \cdot 3H₂O was dropped into the $InCl₃$ aqueous solution and the mixture was magnetically stirred for 1 h. The resulting white solution was then allowed to stand under ambient conditions. After 3 h, the resulting white precipitate was filtered, washed with distilled water and dried in an oven at 60 °C. Sn(DDTC)₄ was also prepared using the same method as that depicted above, with InCl₃ \cdot 4H₂O replaced by SnCl₄ \cdot 5H₂O.

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Synthesis of $In₄SnS₈$ nanosheets

 $In₄SnS₈$ nanosheets were synthesized via a thermal decomposition method.²⁸ In a typical procedure, 0.1 mmol of $Sn(DDTC)_4$ and 0.4 mmol of $In(DDTC)_3$ were added into 20 mmol of OM solvent in a three-necked flask (100 mL). The slurry was heated to 120 °C under vacuum with vigorous magnetic stirring. Afterward, the slurry was heated to 240 \degree C at a rate of 15 \degree C min^{-1} and was then maintained at this temperature for 1 h under N_2 atmosphere. Then the reaction system was cooled down to room temperature naturally. The resultant mixture was centrifugally separated, and then the precipitates were washed with ethanol twice. The products were collected and stored in cyclohexane.

Because the adsorption and photocatalysis experiments were all carried out in aqueous solution, the obtained $In₄SnS₈$ nanosheets were treated in acetic acid to remove the stabilizing surfactant OM on the surface of the $In₄SnS₈$ nanosheets. Typically, the obtained samples were immersed in acetic acid at 70 \degree C for 10 h. The resulting photocatalysts were collected by centrifugation, washed with ethanol, and then dried at room temperature in the dark.

Removal of organic dyes

Adsorption performance of $In₄SnS₈$ nanosheets. 20 mg photocatalyst powder was dispersed in 100 mL aqueous solution containing 10 ppm of dye at room temperature (25 \pm 2° C). The suspension was placed in the dark under magnetic stirring at a speed of 300 rpm. At a given interval, a 5 mL aliquot of the suspension was taken and centrifuged. The adsorption of dye was monitored by measuring the absorption band of the dye on a UV-visible spectrophotometer. The adsorption rate was evaluated according to C/C_0 (C_0 is the initial density of dye; C is the density of dye after adsorption).

Photocatalytic degradation of dyes. Photocatalytic tests were carried out in an aqueous solution at ambient temperature. The light source was a 300 W Xe lamp with a UV cut off filter (λ > 420 nm) to allow only visible light to transmit. Briefly, 20 mg photocatalyst powder was dispersed in a 100 mL aqueous solution containing 10 ppm of dye. The solution was placed in the dark to reach adsorption-desorption equilibrium. After that, the suspension was irradiated under visible light from the above glass reactor at a distance of 10 cm. The temperature of the reaction system was kept at room temperature by using a water cooling system. At a given irradiation time interval, 5 mL of the suspension was collected and centrifuged to separate the photocatalyst. Photodegradation was monitored by measuring the absorption band of the dye on a UV-visible spectrophotometer. The degradation rate was evaluated according to C/C_0 (C_0 is the density of dye after adsorption equilibrium; C is the density of dye after reaction). To evaluate the stability of the photocatalyst, after the photochemical reaction, the photocatalyst was separated from the suspension, washed with water, and dried at 60 C in the dark, and then the recovered photocatalyst was used for the next run of the photoreaction under the same conditions.

Characterization. The morphology and size of the obtained sample were examined on a Tecnai G2 F30 S-Twin transmission electron microscope (TEM, FEI, USA) operated at 200 kV. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance powder X-ray diffractometer at a scanning rate of 4° min⁻¹, with Cu K α radiation ($\lambda = 1.5406$ Å) in the range of 20-70°. X-ray photoelectron spectra (XPS) were recorded using a PHI 5000 Versaprobe spectrometer fitted with a monochromated Al K α X-ray source ($hv = 1486.6$ eV). The XPS binding energies were calibrated by referencing the C 1s to 284.6 eV. UV-vis absorption spectra were obtained on a Lambda 25 UV-vis-NIR spectrometer (PerkinElmer, USA), and photoluminescence (PL) spectra were collected on a fluorescence spectrometer (HITACHI, F-4600) at room temperature. **SSC Arbanes** Symbolsty are considered to a chromad of compassion are considered on 12/30 S yields are arband on 12/30 S are arband on 12/30 S yields are arband on 12/30 S yields are arband on 12/30 S yields are arband on

Results and discussion

Fig. 1a–c depicts the morphology of the $In₄SnS₈$ nanosheets. Large film structures of tens of micrometres in size are obtained (Fig. 1a), and clear basic features of the film are nanosheets with wrinkles (white arrows) and rags (red arrows). In the TEM image, the wrinkles induced by the surface tension of the nanosheets are more obvious, due to the ultrathin nature of the nanosheets, which is quite similar to graphene (Fig. 1b and c).

The XRD pattern in Fig. 1d indicates that no other impurities such as SnS or $In₂S₃$ are detected in the sample. The peaks at 28.2°, 33.1°, 48.1°, 50.1° and 58.6° can be indexed to the (6 0 0), (6 0 2), (1 7 4), (0 0 1) and (4 4 6) planes of the tetragonal phase of $In₄SnS₈$, respectively, in agreement with the literature reports.²⁹ The lattice spacing of 0.31 nm in the HRTEM image can be indexed as the (600) plane of tetragonal In₄SnS₈, indicating the confined growth of the In_4SnS_8 nanosheets along the $\langle 100 \rangle$ direction. In addition, the energy-dispersive X-ray spectroscopy (EDS) data (Fig. S1†) further verify the formation of the In_4SnS_8 compound (In : Sn : S atomic ratio $= 3.95 : 1 : 8.07$).

An AFM image was recorded to acquire more information on the nanosheets. Fig. 2a shows the representative AFM image of the edges of the $In₄SnS₈$ nanosheets. The average thickness is determined to be about 3.8 nm according to the height difference at the sites of H1 and H2. The theoretical thickness of an $In₄SnS₈$ monolayer is 0.697 nm (Fig. 2c), suggesting the obtained In_4SnS_8 nanosheets comprise about five atomically thick layers. To our knowledge, these are the thinnest $In₄SnS₈$ nanosheets synthesized via a solution-phase chemical method.

To gain insight into the composition of the nanosheets and the elemental oxidation states present, XPS was performed and the results are shown in Fig. 3. The survey XPS spectrum in Fig. 3a indicates the presence of In, Sn and S components as well as C, O and N impurities. C (C 1s, 284.6 eV), O (O 1s, 531.8 eV) and N (N 1s, 399.6 eV) in the product may be due to absorbed organic ligands of solvent and gaseous molecules. Fig. 3b reveals that the binding energies of 444.7 eV and 452.3 eV correspond to In $3d_{5/2}$ and In $3d_{3/2}$, respectively, suggesting the presence of $In³⁺$ in the sample. Fig. 3c shows that there are two strong peaks at 485.8 eV and 494.2 eV, which can be assigned to Sn $3d_{5/2}$ and Sn $3d_{3/2}$, respectively, confirming the Sn^{4+} oxidation state of the Sn element in the sample. The S

Fig. 1 SEM (a) and TEM (b and c) images and XRD pattern (d) of the In₄SnS₈ nanosheets. The inset in (c) is the HRTEM image of the In₄SnS₈ nanosheets.

2p peak splits into two peaks, and these are located at 161.0 eV and 162.6 eV, indicating that S exists in sulfide phases.

Composition analysis was conducted at the nanoscale to further prove the formation of ternary sulphide $In₄SnS₈$. The EDS elemental mapping images (Fig. 4) directly indicate that In, Sn and S are homogeneously distributed in the nanosheets, which excludes the existence of compositional gradients within the nanosheets or multiphase coexistence. Consequently, the as-synthesized products can be determined to be pure ultrathin $In₄SnS₈$ nanosheets, based on the results of TEM, AFM, XRD, EDS, EDS element mapping and XPS measurements.

It is found that OM plays an important role in the formation of the $In₄SnS₈$ ultrathin nanosheets. In our previous research, we found that OM plays two roles during the formation of low dimensional metal sulfide nanocrystals synthesized using a single-source precursor method: (1) as a catalyst to accelerate the decomposition of single source precursors; (2) as a stabilizer for the growth of low dimensional nanocrystals.19,28 As shown in Fig. S2,† when only ODE is used as the solvent, only $Sn(DDTC)_4$ decomposes and $In(DDTC)_3$ does not decompose (Fig. S2†). When a certain amount of OM is mixed with ODE as the solvent, both $Sn(DDTC)_4$ and $In(DDTC)_3$ decompose and In_4SnS_8 is obtained (Fig. S1†). However, although $In₄SnS₈$ can be formed in the mixture of ODE and OM, the sample does not consist of pure nanosheets, but a mixture of nanoparticles and nanosheets (Fig. S3†). This means that OM can control the nucleation and growth kinetics of In_4SnS_8 nanocrystals. According to above results, the mechanism for the formation of the In_4SnS_8 nanosheets is proposed as shown in Scheme 1: in the presence of sufficient OM, both $Sn(DDTC)_4$ and $In(DDTC)_3$ decompose and $In₄SnS₈$ nuclei form. OM molecules simultaneously selectively adsorb on the (600) plane of newly generated $In₄SnS₈$ nuclei, leading to the formation of two dimensional In_4SnS_8 nanosheets.

Fig. 5 shows the UV-vis absorption and PL spectra of the $In₄SnS₈$ nanosheets. This shows that the $In₄SnS₈$ nanosheets have an intense absorption and emission in the visible light

Fig. 2 (a) AFM image, (b) height profile along the line in AFM image, and (c) the theoretical thickness of In_4SnS_8 monolayer.

Fig. 3 XPS spectra of the In₄SnS₈ nanosheets: (a) typical survey spectrum of the In₄SnS₈ nanosheets and high-resolution core level spectra of (b) In 3d, (c) Sn 3d and (d) S 2p.

region. The intrinsic absorption edge of these $In₄SnS₈$ nanosheets shows an obvious blue shift with respect to the reported values for flower-like In_4SnS_8 microspheres,³⁰ suggesting the presence of a quantum confinement in the band structure due to the ultrathin thickness of the $In₄SnS₈$ nanosheets. In addition, Wang et al.³⁰ reported that the flower-like $In₄SnS₈$ microspheres with specific surface areas of 24.7 m^2 g⁻¹ exhibited excellent removal efficiency of $Cr(v)$. The specific surface area of our $\mathrm{In}_4\mathrm{SnS}_8$ nanosheets is 40.34 $\mathrm{m}^2\,\mathrm{g}^{-1},$ which is much higher than that of flower-like $In₄SnS₈$ microspheres. The

Fig. 4 (a) STEM image of the In_4SnS_8 nanosheets, and (b–d) the corresponding In, Sn and S element mapping images.

ultrathin 2D structure, large surface area and visible-light response of the In_4SnS_8 nanosheets make them suitable for photocatalytic applications.

In the photocatalytic degradation test, before irradiation using light, the dye solution containing photocatalyst powder was stirred in the dark to reach absorption equilibrium. It was found that for some dyes, such as methylene blue, congo red, azure II, amido black 10B, and rhodamine B, the adsorption maxima are reached within only 10 min (Fig. 6a). The adsorption rates are all larger than 95%. For congo red, the adsorption rate in 10 min is as high as 99.1%. Simultaneously, it was also observed that for some of the other dyes such as indigotine and orange G (OG), the adsorption maxima are reached in an even longer time of 40 min, with adsorption rates of only 45% and 30%, respectively. The difference in adsorption capacity of the $In₄SnS₈$ nanosheets for the dyes can be attributed to the molecular weights of the dyes (Table 1). With a decrease in the molecular weight of the dye, the adsorption rate decreases. This is because the adsorption of nonpolar dyes on the $In₄SnS₈$ nanosheets mainly belongs to physical adsorption, which is determined by dispersion force.³¹ When the molecular weight is larger, the dispersion force is stronger and the absorption rate is higher. Methylene blue and rhodamine B are polar molecules. The adsorption of these molecules on the $In₄SnS₈$ nanosheets is a chemical adsorption. So, although their molecular weights are small, the adsorption rates are as high as that of the dyes with large molecular weights.

It can be seen from Fig. 6a and Table 1 that the adsorption rate of OG with a small molecular weight is only 30% after 40 min and after this time it reaches absorption equilibrium. In order to completely remove OG, a photocatalytic reaction can be employed by utilizing the visible-light response properties of the $In_{4}SnS_{8}$ nanosheets. It can be seen from Fig. 6b that after 30 min of visible light irradiation, nearly 92% of OG is degraded, showing the excellent photocatalytic activity of the asprepared In₄SnS₈ nanosheets. For comparison, commercial P25 was used as a photocatalyst and the photocatalytic reaction was carried out under the same conditions. The commercial P25 exhibits almost no adsorption for OG and the photodegradation rate of OG over P25 is close to zero under visible-light irradiation. In addition, the photodegradation rates of OG on the $In ₄SnS₈$ nanosheets irradiated under a Xe lamp with a UV cut off filter (visible light) and without a UV cut off filter (UV light and visible light), were also compared. The result shown in Fig. S5† indicates that the photodegradation rate of OG on the $In₄SnS₈$ nanosheets without the UV cut off lter is only slightly higher than that of OG on the In_4SnS_8 nanosheets with the UV cut off filter. This means that the ultrathin $In₄SnS₈$ nanosheets mainly respond to visible light. The above results indicate that the ultrathin $In₄SnS₈$ nanosheets preserve fast adsorption and visible-light photocatalysis dual function for the complete removal of various organic dyes.

The stability of photocatalysts is an important factor for their practical application. Therefore, the $In₄SnS₈$ nanosheets were

Scheme 1 Schematic illustration of the formation mechanism of ultrathin In_4SnS_8 nanosheets

Fig. 5 UV-vis absorption (black line) and PL (red line) spectra of the In_4 SnS $_8$ nanosheets.

recycled four times under visible light irradiation to examine their stability. After each reaction, the photocatalyst was collected and washed using deionized water and separated by centrifugation from the aqueous suspension. Afterward, the photocatalysts were dried in a vacuum at 40 \degree C for 10 h and used for the next recycling reaction. Fig. 6c shows that the photodegradation rate can still be maintained above 85% after four cycles. The TEM image in Fig. $S4\dagger$ of the In₄SnS₈ nanosheets after recycling indicates that after four cycles, the $In₄SnS₈$ nanosheets maintain their film like structure, but are more

Fig. 6 (a) The adsorption of various dyes on the In_4SnS_8 nanosheets. (b) Adsorption and visible-light photodegradation rate of OG on the $In₄SnS₈$ nanosheets and P25. (c) Typical time course of the photocatalytic degradation of OG over the In_4SnS_8 nanosheets under visible light.

Table 1 Molecular weights and adsorption rates of various dyes

Dyes	Molecular weight	Adsorption rate
Congo red	696.68	99.1%
Azure II	625.68	98.8%
Amido black	616.49	97%
10B		
Rhodamine B	479	96.8%
Methylene blue	320	98.4%
Indigotine	466.37	45%
Orange G	452.37	30%

aggregated compared with the as-prepared nanosheets. This may be due to the repeated washing and drying during the recycling reaction. HRTEM and XRD measurements indicate that the crystal structure of $In₄SnS₈$ remains unchanged after the recycling test, suggesting the high stability of the $In₄SnS₈$ nanosheets.

Based on the above discussion, the mechanism for dye removal from water using the In_4SnS_8 nanosheets mainly involves two steps: (1) the nonpolar dye molecules are adsorbed on the surface of the ultrathin In_4SnS_8 nanosheets by dispersion force. (2) Under the irradiation of visible light, the electrons in the valence band (VB) of the $In₄SnS₈$ nanosheets are excited to the conduction band (CB). The CB band of In_4SnS_8 (-0.76 eV (ref. 30)) is more negative than the standard redox potential of $(O_2$ / $^{\bullet}O_2^{})$ (–0.33 eV vs. NHE),³² suggesting that electrons at the CB of In₄SnS₈ can reduce O_2 to ' O_2 ⁻. With the help of the superoxide radical, the dye molecules can be translated into $CO₂$ and H₂O, *etc.* The VB potential of $In₄SnS₈$ (1.51 eV (ref. 30)) is more negative than the standard redox potential of $(OH^-/'OH)$ (1.99 eV vs. NHE),³³ suggesting that the generated holes in In₄SnS₈ cannot oxidize OH⁻ or H₂O to the hydroxy radical 'OH. To further confirm the absence of the hydroxy radical, a fluorescence method was adopted using terephthalic acid (TA) as a probe molecule.^{34,35} TA can react with the hydroxy radical to produce the highly fluorescent product, 2-hydroxyterephthalic acid (TAOH), which has a maximum emission intensity in its fluorescence spectra at 425 nm by excitation at 315 nm. However, the result in Fig. S6† indicates that the characteristic peak of TAOH at 425 nm was not detected during the whole irradiation time, meaning no hydroxy radicals were produced under visible light irradiation in the presence of the $In₄SnS₈$ nanosheet photocatalyst, which is consistent with the theoretical analysis (Scheme 2). Paper

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STEP II $In₄SnS₈$ VISIBLE-LIGHT **PHOTOCATALYSIS** ϵ $\left(\mathbf{e} \right)$ VB **CB** \bullet $H₂O$ $O₂$ \cdot O₂ $O₂$ $CO₂+H₂O...$ dye **STEP I ADSORPTION**

Scheme 2 Schematic diagram of the removal of dyes by the ultrathin In4SnS8 nanosheets through adsorption and visible-light photodegradation.

Conclusions

In₄SnS₈ ultrathin nanosheets were synthesized via a facile thermal decomposition process. SEM, TEM and EDS element mapping results indicated the 2D nature of the $In₄SnS₈$ nanosheets. The AFM results indicated that the thickness of the $In₄SnS₈$ nanosheets was only 3.8 nm, consisting of about five atomically thick layers. The $In₄SnS₈$ ultrathin nanosheets exhibited fast and high adsorption capacities for various organic dyes. For nonpolar dyes, the adsorption rates were related to their molecular weights. Nonpolar dyes of small molecular weights and low adsorption rates, such as OG, could be degraded up to 92% under visible light irradiation, using the In₄SnS₈ nanosheets as a photocatalyst. The as-obtained In_4SnS_8 ultrathin nanosheets may have potential applications in environmental remediation and solar energy conversion.

Acknowledgements

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