In$_2$SnS$_8$ ultrathin nanosheets: a ternary sulfide with fast adsorption–visible-light photocatalysis dual function†

Shuling Shen,* Long Li, Zhujun Wu, Minquan Sun, Zhihong Tang and Junhe Yang*

Ultrathin In$_2$SnS$_8$ nanosheets have been successfully synthesized via a facile thermal decomposition method. The average thickness of these In$_2$SnS$_8$ nanosheets is only 3.8 nm, comprising about five atomically thick layers. To our knowledge, this is the thinnest In$_2$SnS$_8$ nanosheet synthesized using a solution-phase chemical method. The resulting ultrathin In$_2$SnS$_8$ nanosheets exhibit fast adsorption–visible-light photocatalysis dual function for various organic dyes, suggesting their potential application in environmental remediation, solar energy conversion, and advanced optical/electric nanodevices.

Experimental section

Chemicals

Indium trichloride ([InCl$_3$]$\cdot$4H$_2$O, 99.995%), tin(IV) chloride dihydrate (SnCl$_4$$\cdot$5H$_2$O, 98%), sodium diethyldithiocarbamate ([C$_2$H$_4$$_2$NCS$_2$Na$\cdot$3H$_2$O, Na(DDTC))], oleylamine (OM, 80–90%), octadecene (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 InCl$_3$$\cdot$4H$_2$O was dissolved in 100 mL of distilled water. Then 100 mL aqueous solution containing 30 mmol of Na(DDTC)$\cdot$3H$_2$O was dropped into the InCl$_3$ aqueous solution and the mixture was magnetically stirred for 1 h. The resulting white solution was then allowed to stand under ambient conditions. After 3 h, the resulting white precipitate was filtered, washed with distilled water and dried in an oven at 60 ºC. Sn(DDTC)$_4$ was also prepared using the same method as that depicted above, with InCl$_3$$\cdot$4H$_2$O replaced by SnCl$_4$$\cdot$5H$_2$O.

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Synthesis of In$_4$SnS$_8$ nanosheets

In$_4$SnS$_8$ nanosheets were synthesized via a thermal decomposition method. 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 °C at a rate of 15 °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 In$_4$SnS$_8$ nanosheets were treated in acetic acid to remove the stabilizing surfactant OM on the surface of the In$_4$SnS$_8$ nanosheets. Typically, the obtained samples were immersed in acetic acid at 70 °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 In$_4$SnS$_8$ nanosheets. 20 mg photocatalyst powder was dispersed in 100 mL aqueous solution containing 10 ppm of dye at room temperature (25 ± 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 ($\lambda > 420$ 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 Kz 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 Kz X-ray source ($h\nu = 1486.6$ 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.

Results and discussion

Fig. 1a–c depicts the morphology of the In$_4$SnS$_8$ 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 Sn$_2$ or Sn$_3$ 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 In$_4$SnS$_8$, 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 In$_4$SnS$_8$, indicating the confined growth of the In$_4$SnS$_8$ nanosheets along the (100) direction. In addition, the energy-dispersive X-ray spectroscopy (EDS) data (Fig. S1†) further verify the formation of the In$_4$SnS$_8$ 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 In$_4$SnS$_8$ 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 In$_4$SnS$_8$ monolayer is 0.697 nm (Fig. 2c), suggesting the obtained In$_4$SnS$_8$ nanosheets comprise about five atomically thick layers. To our knowledge, these are the thinnest In$_4$SnS$_8$ 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 432.3 eV correspond to In 3d$_{5/2}$ and In 3d$_{3/2}$, respectively, suggesting the presence of In$^{3+}$ 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
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. 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 In₄SnS₈ 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 In₄SnS₈ nanocrystals. According to above results, the mechanism for the formation of the In₄SnS₈ 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 In₄SnS₈ 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 range.

**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.
region. The intrinsic absorption edge of these In$_4$SnS$_8$ nano-sheets shows an obvious blue shift with respect to the reported values for flower-like In$_4$SnS$_8$ microspheres,$^{30}$ suggesting the presence of a quantum confinement in the band structure due to the ultrathin thickness of the In$_4$SnS$_8$ nanosheets. In addition, Wang et al.$^{30}$ reported that the flower-like In$_4$SnS$_8$ microspheres with specific surface areas of 24.7 m$^2$ g$^{-1}$ exhibited excellent removal efficiency of Cr(VI). The specific surface area of our In$_4$SnS$_8$ nanosheets is 40.34 m$^2$ g$^{-1}$, which is much higher than that of flower-like In$_4$SnS$_8$ microspheres. The
ultrathin 2D structure, large surface area and visible-light response of the In₄SnS₈ 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. When the molecular weight is larger, the dispersion force is stronger and the adsorption 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 In₄SnS₈ 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 as-prepared 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 In₄SnS₈ 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 filter is only slightly higher than that of OG on the In₄SnS₈ 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
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 °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. 5† of the In₄SnS₈ nanosheets after recycling indicates that after four cycles, the In₄SnS₈ nanosheets maintain their film like structure, but are more

| Dyes          | Molecular weight | Adsorption rate |
|---------------|------------------|-----------------|
| Congo red     | 696.68           | 99.1%           |
| Azure II      | 625.68           | 98.8%           |
| Amido black 10B | 616.49         | 97%             |
| 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 In₄SnS₈ nanosheets mainly involves two steps: (1) the nonpolar dye molecules are adsorbed on the surface of the ultrathin In₄SnS₈ 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 In₄SnS₈ (−0.76 eV (ref. 30)) is more negative than the standard redox potential of (O₂/H₂O) (−0.33 eV vs. NHE), suggesting that electrons at the CB of In₄SnS₈ can reduce O₂ to O₂⁻. 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⁻/H₂O) (1.99 eV vs. NHE), 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. 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. S6f 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).

![Scheme 2](image_url)

**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 In₄SnS₈ ultrathin nanosheets may have potential applications in environmental remediation and solar energy conversion.

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