A facile preparation of crystalline GeS$_2$ nanoplates and their photocatalytic activity

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1. Introduction

Due to the unique optical and electronic properties, GeS$_2$ has been regarded as a remarkable functional material. During the past two decades, its potential applications were widely explored in various research fields, such as fiber optics, lithium ion battery, and waveguide materials. Nanomaterials have been proven to possess more outstanding properties in comparison with those of the bulk. Thus, it can be expected that the nanostructured GeS$_2$ will become a subject of particular interest.

Since the discovery of graphene, single or few layered two-dimensional (2D) nanomaterials have attracted growing attention due to their unique physical and chemical properties as well as a wide range of potential applications. Many graphene-like 2D nanomaterials were synthesized, such as germanane, GeTe nanosheets, Ge nanosheets, and MoS$_2$ nanosheets. The common feature of the above materials is that they all can crystallize in layered structures with covalent bonding in each layer and weak interactions between the layers. Crystalline GeS$_2$ possesses similar layered structure, suggesting the possibility to prepare graphene-like GeS$_2$ nanosheets. Unfortunately, there are no reports on the synthesis of GeS$_2$ nanosheets so far. The primary reason is that the synthesis of GeS$_2$ nanomaterials is still in its infancy and is an arduous task although GeS$_2$ nanoparticles and nanowires have been successfully synthesized. Therefore, it is meaningful to pay attention to the preparation of GeS$_2$ nanomaterials for both fundamental and applied interests.

Now, a series of synthetic methods, including sol–gel method, melt quenching method, solvothermal method, thermal decomposition, gas-phase laser photolysis, etc., have been developed to obtain bulk or nanostructured GeS$_2$. However, there exist some shortcomings to be overcome from the practical point of view: (1) crystalline GeS$_2$ can hardly be obtained in sol–gel process or using melt quenching method without further heating treatment at high temperature; (2) when the sol–gel method is used, the purity of product is often unsatisfactory so that special precautions have to be applied to eliminate impurity; (3) hydrogen sulfide is usually used as sulfur precursor; (4) time, organo-ammonium precursors, high temperature as well as costly instruments are required for the preparation of crystalline GeS$_2$. Especially, because the crystallinity is a key to the formation of graphene-like GeS$_2$ nanosheets as well as the potential applications in the field of photocatalysis and photovoltaics, it is highly desirable to develop a new protocol for the enhancement of the product's crystallinity. Simple and effective synthetic technique for the crystalline GeS$_2$ with high purity is still in urgent need.

On the other hand, photocatalytic water splitting to produce hydrogen has received considerable attention, and many highly efficient photocatalysts have been developed. Nanomaterials have been proven to possess more outstanding properties in comparison with those of the bulk. Thus, it can be expected that the nanostructured GeS$_2$ will become a subject of particular interest.

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efficient catalysts have been found [19,20]. GeS$_2$ is a direct semiconductor with a band gap ranging from 2.8 eV to 3.4 eV [21–23], and also has a lot of favorable properties including non-toxicity, high electrical conductivity, considerable thermal and chemical stabilities [2,24]. Therefore, we envision that GeS$_2$ might be a potential photocatalyst for hydrogen production from light-driven water splitting, although, it is still unclear whether GeS$_2$ can be used in the hydrogen evolution from water as a photocatalyst or not.

Herein, crystalline GeS$_2$ nanoplates are synthesized by low temperature solvothermal process. GeCl$_4$ and thioacetamide (TAA) are used as germanium and sulfur precursors, respectively. Meanwhile, the photocatalytic activity of the resulting product for hydrogen evolution from the aqueous solution containing Na$_2$S and K$_2$SO$_3$ is investigated. Meanwhile, the corresponding formation mechanism of GeS$_2$ nanoplates is preliminarily discussed.

2. Experimental

2.1. Materials

Germanium tetrachloride (99.9999%) was purchased from Wuhan Yunjingfei Optical Fiber Materials Co., Ltd., thioacetamide from Adamas Reagent Co., Ltd., Na$_2$O from Shanghai Tongya Chemical Technology Development Co., Ltd. Concentrated hydrochloric acid, ethanol, carbon tetrachloride, acetic acid, chloroplatinic acid and Na$_2$S were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were used as received. Deionized water was used as solvent.

2.2. Synthesis of GeS$_2$ nanoplates

GeS$_2$ nanoplates were prepared by low temperature solvothermal process. In a typical procedure, TAA (0.494 g, 6.58 mmol) from Shanghai Tongya Chemical Technology Development Co., Ltd. Concentrated hydrochloric acid, ethanol, carbon tetrachloride, acetic acid, chloroplatinic acid and Na$_2$S were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were used as received. Deionized water was used as solvent.

2.3. Photocatalytic hydrogen evolution

The photocatalytic reaction was carried out in a gas-closed system with a reactor made of quartz. A 300 W xenon lamp was used as a light source. The distance between the lamp and the reactor is 2 cm. In a typical experiment, the as-prepared GeS$_2$ nanoplates (60 mg) was added into the aqueous solution (60 mL) containing Na$_2$S (0.1 mol L$^{-1}$) and K$_2$SO$_3$ (0.1 mol L$^{-1}$). The mixture was sonicated for 15 min to form a homogeneous suspension. Then, chloroplatinic acid aqueous solution (227 µL, 10 mg mL$^{-1}$) was dropped into the above mixture. After the gas-closed system was evacuated, the suspension was irradiated for 30 min to prepare the GeS$_2$ nanoplates loaded with Pt. Finally, the amounts of hydrogen produced were measured with a gas chromatograph (GC-7900, China, molecular sieve 5Å, TCD) using N$_2$ as a carrier gas, after a certain period of irradiation.

2.4. Characterization

X-ray diffraction (XRD) patterns were recorded on a PAN analytical X Pert Pro MRD X-ray diffractometer using Cu Kα radiation (λ = 0.15406 nm, Ni filter) in θ/θ configuration, assisted by the XPert Data Collector program for data collection (Netherlands). XRD patterns were identified using the PDF-2004 Database of JCPDS. The samples for XRD were supported on glass substrates. The Fourier transform infrared (FT-IR) spectrum was recorded with a Nicolet 6700 FT-IR spectrometer (USA). Raman spectrum was measured using a Thermo Scientific DXR Raman microscope with a 532 nm DPSS laser and a 50× objective (NA = 0.42) (USA). UV–vis–NIR spectrum was recorded with a Shimadzu UV-3600 UV–vis–NIR spectrometer (Japan). The energy-dispersion X-ray analysis (EDX) was taken using a Hitachi S3400N scanning electron microscope (Japan). The high resolution transmission electron microscope (HRTEM) images were taken on a JEOL 2100F transmission electron microscope (Japan). The N$_2$ adsorption and desorption isotherm was measured on a Micromeritics ASAP-2020 nitrogen adsorption apparatus (USA). The X-ray photoelectron spectra (XPS) were recorded with a Shimadzu Kratos AXIS Ultra DLD X-ray photoelectron spectrometer (Japan).

3. Results and discussion

Fig. 1 shows the XRD pattern of the as-prepared GeS$_2$ nanoplates. As seen from Fig. 1, the peak positions of the sample are matched well with those of the orthorhombic β-GeS$_2$ (JCPDS No. 26-0693). And the strong peaks at 2θ = 15.43°, 17.03°, 24.81°, 26.47° and 31.66° are corresponding to the (111), (220), (151), (311) and (171) planes of β-GeS$_2$, respectively. The lattice constants calculated from the diffraction pattern are $a = 11.74$ Å, $b = 22.47$ Å and $c = 6.88$ Å, in good agreement with the reported values [25]. Moreover, the diffraction peaks are fairly strong and sharp, and no evidence of crystalline impurities, such as GeO, GeO$_2$, GeS and S, is found in the pattern. These results indicate that the crystalline orthorhombic β-GeS$_2$ with high phase-purity can be obtained by low temperature solvothermal process.

Fig. 2A and B shows the TEM images of the crystalline GeS$_2$ nanoplates. From Fig. 2A and B, it can be clearly observed that the irregular nanoplates with average lateral dimensions of 840(±310) nm × 620(±240) nm were prepared. Meanwhile, it can be also found the as-prepared nanoplates are actually a result of oriented stacking of several thinner nanosheets. Moreover, some lattice fringes are observed from the HRTEM image of the nanoplate (Fig. 2C), suggesting that the as-prepared nanoplates have a good crystallinity. Furthermore, the spacing between two conjoint planes is about 0.586 nm and 0.294 nm, corresponding to the (111) and (171) plane of orthorhombic β-GeS$_2$, respectively, which coincides with the XRD result.

To further clarify the structure and composition, the EDX analysis (Fig. S1) and the XPS spectra (Fig. 3) of the as-prepared material were conducted. The EDX result shows that the sample contains the elements of Ge and S. The Ge/S ratio is very close to the stoichiometric composition of GeS$_2$ (Ge/S = 1:2) within experimental error.

The Ge 3d high resolution XPS spectrum (Fig. 3A) exhibits that there exists a peak at 32.1 eV. However, the 3d binding energy of Ge$^{4+}$ in GeS$_2$ reported previously is 30.4 eV, 31.4 eV or 36.2 eV [24,26,27]. The observed binding energies are obviously different from the reported values. It was reported in the literatures that the binding energy of Ge$^{4+}$ in the crystalline materials was higher than that in the amorphous materials [26,28]. So, it is reasonable to infer that the shift to higher binding energy might be ascribed to the high crystallinity of the sample. Moreover, the shift to lower binding energy relative to the value [27] reported by Xu and Almeida may be attributed to charging effects of the semiconductors which would make the kinetic energy of the ejected electrons smaller.
decrease \cite{26,29}. Consequently, it can be deduced that germanium exists mainly in the Ge$^{4+}$ state for the sample.

Fig. 3B shows the S 2p high resolution XPS spectrum. From Fig. 3B, it can be found that there exist two fitted peaks at 162.6 eV and 163.8 eV, corresponding to S$_{2p3/2}$ and S$_{2p1/2}$ of the bridging sulfur atoms in GeS$_2$, respectively \cite{30,31}. Moreover, the additional peaks ascribed to sulfur S (164 eV), sulfite SO$_3^{2-}$ (166 eV) and/or sulfate SO$_4^{2-}$ (172 eV) contamination \cite{32,33} are not observed in Fig. 3B, implying the high purity of obtained sample. Based on the above experimental results, it can be affirmed that the sample obtained is GeS$_2$ with high purity.

The FT-IR spectrum and Raman spectrum of the as-prepared GeS$_2$ nanoplates are shown in Fig. 4. The FT-IR spectrum of the sample (Fig. 4A) matches well with that of the pure GeS$_2$ reported in the literature 34. Three obvious absorption peaks were found at around 413 cm$^{-1}$, 430 cm$^{-1}$ and 440 cm$^{-1}$, corresponding to the vibration of Ge–S \cite{35,36}. In addition, no peaks assigned to the vibrations (515 cm$^{-1}$, 555 cm$^{-1}$, 587 cm$^{-1}$ and 885 cm$^{-1}$) of GeO$_2$ was found, suggesting the absence of GeO$_2$. In the case of the Raman spectrum (Fig. 4B), five bands can be identified. The band at 105 cm$^{-1}$ may arise from the bond-bending mode of [GeS$_4$] tetrahedral \cite{37}. The band at 340 cm$^{-1}$ may be assigned to the $\tilde{A}_1$ symmetric stretch mode of the Ge–S–Ge, and the band at 371 cm$^{-1}$ to $\tilde{A}_1$ symmetric stretch mode of [GeS$_4$] tetrahedral \cite{26,38}. The band at 408 cm$^{-1}$ may be ascribed to the vibration of corner sharing [GeS$_4$] tetrahedral \cite{17}, while the band at 434 cm$^{-1}$ may be due to the vibration of edge-shared [GeS$_4$] tetrahedral \cite{37}. These characteristic Raman peaks further indicate the formation of GeS$_2$. Similarly, the characteristic Raman peaks ascribed to GeO$_2$ (416 cm$^{-1}$, 520 cm$^{-1}$, 774 cm$^{-1}$ and 860 cm$^{-1}$) \cite{26,34} could not be found in Fig. 4B either. These results further confirm the high purity of the as-prepared GeS$_2$.

Based on the experimental results mentioned above, it can be indicated that the crystalline orthorhombic GeS$_2$ nanoplates with high purity are successfully prepared in the solvothermal process described above. The Brunauer–Emmett–Teller (BET) specific surface area of the GeS$_2$ nanoplates is 5.0 m$^2$ g$^{-1}$. The formation mechanism for the crystalline GeS$_2$ nanoplates is suggested as follows. At first, H$_2$S is generated due to the decomposition of TAA in acetic acid along with heating. Then, the thiolysis of germanium precursor occurs to form the $\text{Ge} \equiv \text{S}$–SH monomers. These monomers react by condensation reactions to generate the complex molecules containing $\text{—SH}$ groups. Subsequently, these complex

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2.png}
\caption{TEM images (A, B) and HRTEM image (C) of the GeS$_2$ nanoplates.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3.png}
\caption{High-resolution XPS spectra (solid lines) of Ge3d (A) and S2p (B) of the GeS$_2$ nanoplates, and curve-fitting analysis (dot lines) of states of S (B).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig4.png}
\caption{FT-IR spectrum (A) and Raman spectrum (B) of the GeS$_2$ nanoplates.}
\end{figure}
molecules further react by condensation reactions to form the nuclei of GeS$_2$ nanoplates. At last, the nuclei grow and link together by the continued condensation of monomers until the GeS$_2$ nanoplates are formed. In this process, $\equiv$Ge–SH which is generated during thiolysis is the monomer that nucleates. The formation of the GeS$_2$ nanoplates depends on the balance between the kinetics of thiolysis and condensation [14,26]. Therein, the solvent acetic acid is critical to the formation of the crystalline GeS$_2$ nanoplates. Firstly, acetic acid can make the condensation rate become slower. Thus, the $\equiv$Ge–SH monomers have enough time to align properly and form a regular crystalline structure when they react by condensation reactions. Secondly, acetic acid can suppress the dissociation of H$_2$S in the reaction system. As a result, the redox reaction between GeCl$_4$ and S$^{2-}$ is hindered so as to avoid the introduction of impurity. The results of control experiments confirm our conjecture proposed above. When cyclohexane, ethanol or toluene was used as the solvent, only mixture with poor crystallinity containing Ge$_3$, GeS, GeO$_2$, S, and Ge can be obtained rather than the crystalline GeS$_2$ nanomaterials.

Fig. 5 shows the UV–vis–NIR absorption spectrum of the crystalline GeS$_2$ nanomaterials. As seen from Fig. 5, the crystalline GeS$_2$ nanomaterials show no absorption peak in near infrared region and a strong absorption band with an edge at approximately 450 nm (2.75 eV) which can be ascribed to the band gap transition. In addition, the edge is very steep, implying that the GeS$_2$ nanomaterials possess relatively high crystallinity [39].

In order to expand the potential application of the crystalline GeS$_2$ nanomaterials, their photocatalytic behavior was examined. Fig. 6 shows the time-course of H$_2$ evolution in the presence of the crystalline GeS$_2$ nanomaterials loaded with Pt under irradiation. From Fig. 6, the crystalline GeS$_2$ nanomaterials loaded with Pt are a notable photocatalyst with the mean rate of H$_2$ evolution of approximately 144 $\mu$mol g$^{-1}$ h$^{-1}$ during 13 h irradiation. Besides, the rate of hydrogen evolution is fast in the first 4 h, and then it gradually decreases. However, the rate of 68 $\mu$mol g$^{-1}$ h$^{-1}$ can be still preserved after irradiated for 11 h. These phenomena indicate that the crystalline GeS$_2$ nanomaterials loaded with Pt will be a promising photocatalyst and keep the activity for a period of time. A possible mechanism may be as follows. At first, when the GeS$_2$ nanomaterials are irradiated, the electrons of GeS$_2$ are excited. These excited electrons make chloroplatinic acid reduce to Pt on the surface of the GeS$_2$ nanomaterials. Then, water molecules are reduced into H$_2$ by the photogenerated electrons on the Pt particles formed on the GeS$_2$ nanomaterials. Therein, Pt particles serve as charge transferring sites and/or active sites in the photocatalytic process.

4. Conclusions

In summary, the crystalline GeS$_2$ nanomaterials have been successfully prepared by the low temperature solvothermal process described above where the solvent acetic acid plays an important role in the formation of the crystalline GeS$_2$ nanomaterials. The as-prepared crystalline GeS$_2$ nanomaterials show considerable photocatalytic activity for hydrogen evolution from water, implying that GeS$_2$ nanomaterials have great potential in the field of hydrogen generation from light-driven water splitting. In addition, this work offers a simple, low temperature approach for the synthesis of crystalline GeS$_2$ nanomaterials. Particularly, it may open a feasible avenue for the preparation of graphene-like GeS$_2$ nanosheets.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jallcom.2014.12.259.

References


