Preparation of GeS$_2$/graphene nanocomposite with high lithium storage capacity

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Keywords: GeS$_2$; graphene; nanocomposite; lithium ion battery

Abstract. In the present work, the nanocomposite containing GeS$_2$ and reduced graphene oxide was prepared and characterized with XRD, HRTEM and Raman spectroscopy. Meanwhile, the electrochemical performance of the GeS$_2$/graphene nanocomposite, as an anode material, was evaluated by galvanostatic discharge-charge tests. The experimental results indicate that the as-prepared nanocomposite consists of the GeS$_2$ nanosheets and the graphene nanosheets. And the graphene nanosheets are coated with GeS$_2$ nanosheets to form a GeS$_2$-graphene double-layer nanostructure. Moreover, it is also observed that the GeS$_2$/graphene nanocomposite possesses a high initial discharge capacity of 1560.9 mA h g$^{-1}$.

Introduction

Recently, extensive efforts have been devoted to developing lithium ion batteries in order to obtain high-performance power sources for electric vehicle, hybrid electric vehicle, smart grids etc. Therein, GeS$_2$ has been regarded as a remarkable electrode material due to its unique electronic properties [1]. Particularly, the nanostructured GeS$_2$ has become a subject of particular interest in the field of lithium ion battery. On the other hand, graphene as a two-dimensional nanomaterial has been widely applied in the field of lithium ion battery due to large specific surface area and excellent electron transport property [2]. Therefore, the nanocomposite of GeS$_2$ and graphene may be a potential candidate in the field of lithium ion battery, given that the nanocomposite containing GeS$_2$ and graphene may simultaneously possess the direct band gap of GeS$_2$ and the high carrier mobility of graphene. However, there are limited reports on the preparation and electrochemical performance of GeS$_2$/graphene nanocomposite so far.

In the present work, we prepared GeS$_2$/rGO nanocomposites in a low temperature solvothermal process. In addition, the as-prepared GeS$_2$/rGO nanocomposite is investigated as an anode material in order to assess its potential in the field of lithium ion battery.

Experimental

Graphene oxide (GO) was prepared according to the procedure reported in ref. 3 [3]. In a typical preparation process of the nanocomposite containing GeS$_2$ and reduced graphene oxide (GeS$_2$-rGO), thioacetamide (TAA, 6.58 mmol), CTAB (2.74 mmol) and GO (18 mg) were added into a conical flask containing 30 mL acetic acid. After ultrasonic treatment for 5 h, the mixture was transferred into a Teflon-lined vessel (50 mL). Then, GeCl$_4$ (1.32 mmol) was added into the mixture under nitrogen protection. Subsequently, the vessel was sealed in a stainless-steel autoclave and heated to 140 °C for 12 h. After the autoclave was naturally cooled to ambient temperature, the precipitate was collected by centrifugation and washed with ethanol, and water for several times, respectively. Finally, the resulting product was dried at 60 °C for 2 h.
The discharge-charge voltage profile of the sample was investigated using Swagelok-type cells assembled in an argon-filled glovebox. The copper foil coated with a slurry that consisted of 80 wt% active material (GeS$_2$-rGO), 10 wt% poly(vinylidene fluoride) and 10 wt% carbon black was used as the working electrode. The loading mass of GeS$_2$-rGO was about 10 mg cm$^{-2}$. Lithium foil and a glass fiber from Whatman were used as the counter electrode and the separator, respectively. The electrolyte solution was 1 mol·L$^{-1}$ solution of LiPF$_6$ in ethylene carbonate, dimethyl carbonate and diethyl carbonate (1:1:1 in wt%) containing 2 wt% vinylene carbonate. Galvanostatic cycling tests were carried out with an Arbin BT2000 system in the voltage range of 0.01-1.5 V (vs Li$^+$/Li) under a current density of 100 mA g$^{-1}$.

The powder X-ray diffraction (XRD) analysis was made on a PANalytical Xpert Pro MRD X-ray diffractometer using Cu Kα radiation ($\lambda = 0.15406$ nm, Ni filter) in 0/0 configuration, assisted by the X’Pert Data Collector program for data collection (Netherlands). The morphology of the sample was characterized on a JEM-2100F transmission electron microscope (JEOL, Japan). Raman spectra were measured using a Thermo Scientific DXR Raman microscope with a 532 nm DPSS laser and a 50× objective (NA = 0.42) (USA).

**Results and discussion**

![Image](image.png)

**Figure 1.** XRD pattern of GeS$_2$-rGO.

Fig. 1 shows the XRD pattern of GeS$_2$-rGO. As can be seen from Fig. 1, there exist three strong diffraction peaks at 15.37°, 26.48° and 39.07°, corresponding to the (111), (311) and (191) planes of orthogonal GeS$_2$ (JCPDS card No. 26-0693), respectively. In addition, we can also find two strong diffraction peaks at 28.70° and 33.39°, which may be ascribed to the (330) and (060) planes of monoclinic GeS$_2$ (JCPDS card No. 27-0238). According to the Scherrer’s formula, the average crystallite size of GeS$_2$ is evaluated to be approximately 38 nm. 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 nanostructured GeS$_2$ are formed in the as-prepared sample.

Fig. 2 shows the Raman spectra of GeS$_2$-rGO and GO. From the Raman spectrum of GeS$_2$-rGO, it can be found that there exist two obvious Raman peaks at 1320 cm$^{-1}$ and 1599 cm$^{-1}$. These peaks ought to correspond to the D band and G band of reduced graphene oxide (RGO), respectively [4]. In addition, compared with GO, the intensity ratio of the D band to G band ($I_D/I_G$) of GeS$_2$-rGO increases from 0.93 to 1.86 after solvothermal treatment. Based on the results above, it can be concluded that the GO is successfully reduced to the RGO in the solvothermal process.
Figure 2. Raman spectra of GeS$_2$-rGO and GO.

Figure 3. (a) HRTEM image and (b, c) TEM images of GeS$_2$-rGO.

Fig. 3 shows the TEM images and HRTEM image of GeS$_2$-rGO. From Fig. 3, some nanosheets with puckers can be clearly observed, implying the presence of the RGO. Moreover, it can be found that some irregular black plates are coated on the surface of RGO. Their average lateral dimensions are about 20 nm × 80 nm. Because the Ge atoms and the S atoms are heavier than the C atoms, the GeS$_2$-rich areas on the RGO nanosheets will exhibit relatively blacker images. Therefore, it is reasonable to assume that the black nanoplates are the GeS$_2$ nanoplates in GeS$_2$-rGO. On the other hand, the HRTEM image of GeS$_2$-rGO shows that there exist some lattice fringes in the black areas distributed on the RGO nanosheets. The spacing between two conjoint planes is 0.312 nm, 0.279 nm and 0.297 nm, respectively. Therein, the planes with spacing of 0.312 nm should be assigned to the (330) plane of monoclinic GeS$_2$ (JCPDS card No. 27-0238). The planes with spacing of 0.279 nm and 0.297 nm ought to be the (080) plane and the (202) plane of orthogonal GeS$_2$ (JCPDS card No. 26-0693), respectively. Combined with the results of XRD and Raman spectra, it can be deduced that the as-prepared product is a composite containing GeS$_2$ nanoplates and RGO. And the GeS$_2$ nanoplates are coated on the surface of RGO nanosheets.

Based the experimental results, we presume a possible mechanism for the formation of GeS$_2$-rGO. At first, GO is homogeneously dispersed in the water with the help of CTAB. And thioacetamide is adsorbed on the surface of GO nanosheets. When the reaction system is heated, thioacetamide is
broken down into $S^2^-$. The thiolysis of germanium precursor occurs on the surface of GO to form the $≡$Ge-SH monomers. Then, these monomers further react by condensation reactions to form the nuclei of GeS$_2$. Next, under the induction of GO nanosheets, the nuclei of GeS$_2$ grow and link together on the surface of GO nanosheets to generate the GeS$_2$ nanoplates. Meanwhile, GO is reduced to RGO.

Fig. 4 shows the first discharge-charge voltage profile and the cycle behavior of the as-prepared GeS$_2$/rGO nanocomposite. From Fig. 4A, it can be found that the first discharge capacity of GeS$_2$-rGO is 1560.9 mA h g$^{-1}$ under 100 mA g$^{-1}$. In addition, it can also be observed that there is an extended voltage plateau at about 0.4 V followed by a sloping curve. These results indicate that GeS$_2$-rGO is a potential anode material for lithium ion batteries. However, its specific capacity continuously decreases and reaches 84.1 mA h g$^{-1}$ after 15 cycles (Fig. 4B), indicating poor capacity retention. One possible explanation is that the phase purity of GeS$_2$ is poor. Even so, its ultrahigh first discharge capacity still displays an extensive prospect in the field of lithium ion battery.

![Figure 4. First charge-discharge profile (a) and cycle behavior (b) of GeS$_2$-rGO.](image)

Summary

In summary, the GeS$_2$/rGO nanocomposite can be one-pot prepared in a low temperature solvothermal process. In addition, the GeS$_2$/rGO nanocomposite shows high electrochemical activity towards lithium storage.

Acknowledgements

This work was financially supported by the Key Project of Science and Technology Innovation supported by the Shanghai Committee of Science and Technology (No. 12JC1400102).

References