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In situ reduction of WS_2 nanosheets for WS_2/reduced graphene oxide composite with superior Li-ion storage

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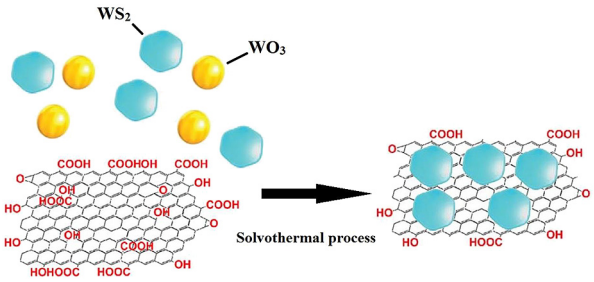
HIGHLIGHTS

- The WS_2/rGO composite were synthesized to improve the battery performance.
- The WS_2/rGO anode shows a capacity of 431.2 mAh/g, much higher than WS_2.
- The added graphene oxide is reduced to rGO, improving the conductive properties.
- The rGO can avoid the restacking, and promote the reduction of WO_3.

GRAPHICAL ABSTRACT



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ABSTRACT

Two-dimensional transition-metal dichalcogenides, such as tungsten disulfide (WS_2), have been actively studied as suitable candidates for anode materials used in lithium ion batteries recently, due to their remarkable ion intercalation properties. However, the difficulties in the synthesis of phase-pure WS_2, restacking between WS_2 nanosheets, low electronic conductivity and brittle nature of WS_2 severely limit its Li-ion batteries application. Here, we adopt a one-pot method for synthesizing of WS_2/reduced Graphene Oxide (rGO) composite to improve the battery performance dramatically. The WS_2/rGO anode shows a stable discharge capacity of 431.2 mAh/g, at a current density of 0.1 A/g after 100 cycles, while the capacity of bare WS_2 is only 65.5 mAh/g under the same condition. The added graphene oxide is reduced to rGO in reaction process and constitute stable composite with WS_2, not only avoiding the restacking between WS_2 nanosheets and improving the conductive properties, but also promoting the reduction of WO_3 effectively. Our work may provide a possible route to avoid oxygen impurities in transition metal dichalcogenides.

1. Introduction

Few-layers of 2D graphene-like nanosheets, notably the layered transition metal dichalcogenides (TMDCs, MoS_2, WS_2, etc.), have been recently receiving interest for lithium storage due to their fast-ion conductivities [1]. Among these TMDCs, tungsten disulfide (WS_2) is an interesting graphene-like semiconductor material, with a layered structure formed by unit S–W–S atomic trilayers through

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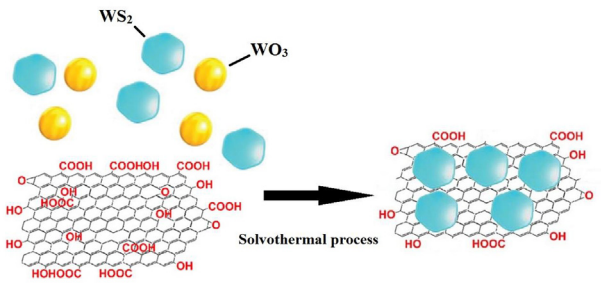
van der Waals interactions [2–5]. And this structure provide great convenience for the insertion and extraction of Li^+ [6–8]. The higher theoretical specific capacity of 433 $mAhg^{-1}$ (4 mol of Li^+ insertion) makes it a potential substitute of commercial graphite (372 $mAhg^{-1}$). With a high intrinsic electric conductivity TMDCs, WS_2 is a suitable candidate as an electrochemical electrode [9–13].

In term of preparation, conventionally mono- or few-layered WS_2 can be obtained by mechanical exfoliation or grown by chemical vapor deposition (CVD) [14–18]. Chemical methods for large-scale synthesis of layered WS_2 have also been reported [2,19,20]. However, oxidized impurities, such as WO_x precursor or WO_3, invariably exist in the product and phase-pure WS_2 has been difficultly obtained. For sulfurization, the direct use of H_2S still generally requires temperatures in excess of 800 °C to drive the reaction. Thermal H_2S sulfurization of polycrystalline tungsten has produced WS_2 at temperatures as low as 550 °C by use of a Ni promoter. Recently, H_2S plasma sulfurization of WO_3 at a low-temperature (500 °C) is used for the preparation of WS_2 [21,22]. Previously, we accept a one-pot method for synthesizing WS_2/reduced Graphene Oxide (rGO) composite [2]. It is found that the WO_3 impurities were obviously reduced. Graphene, the mono-atomic thick honeycomb lattice carbon nanofiller, has excellent mechanical and electrical properties due to its unique structure. The incorporation of graphene into polymer matrices can greatly improve the comprehensive performance of nanocomposite. Especially, graphene oxide (GO), a precursor of graphene, containing many strongly hydrophilic groups including hydroxyls, epoxides and carboxyls on its basal planes and edges, can build strong interaction between the nanocomposite [23,24].

In this paper, in order to constitute stable composite with WS_2 and improve the performance of Lithium-ion batteries, we added GO to the hydrothermal synthesis, to synthesize WS_2/reduced Graphene Oxide (rGO) composite [2]. The results show that the process could not only avoid the restacking between WS_2 nanosheets and improve the conductive properties, but also help transfer impurity WO_3 to WS_2 effectively (Scheme 1), thus bringing in better electrochemical performance for reversible lithium storage. The experimental results confirmed the importance of Graphene in composite for Lithium-ion batteries and provide a possible route to avoid oxygen impurities in transition metal dichalcogenides, such as WS_2.

2. Experimental

All chemicals used were of analytical grade and applied as received without further purification. Tungsten hexachloride (WCl_6), thioacetamide (TAA) were all purchased from Aladdin Industrial Corporation. GO was made by the modified Hummers method, and exfoliated using a high pressure homogenizer.



Scheme 1. Added GO in the hydrothermal synthesis of WS_2 may help transfer impurity WO_3 to WS_2, along with its own reduction.

2.1. Synthesis of WS_2 and WS_2/rGO hybrid composite

In a typical synthesis procedure, 0.8923 g of WCl_6 and 1.6904 g of thioacetamide (TAA) were slowly added to DI water (30 ml) and stirred at room temperature for 1 h. The solution was then transferred into a reaction kettle and maintained at 265 °C for 24 h.

WS_2/rGO hybrid composite were synthesized by the same hydrothermal reaction condition as that for WS_2. A GO solution of 5 mg/mL was added to the mixture of tungsten chloride and thioacetamide, heated up to 265 °C and kept for 24 h.

Both products were cooled to room temperature, centrifuged, washed several times with DI water, dried in vacuum at 60 °C, and then annealed at 300 °C for 3 h under Ar atmosphere.

2.2. Characterization

Field emission scanning electron microscopy (FE-SEM; JSM-7000F) was used to determine the morphology of the samples. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL model JEM2100 instrument at an accelerating voltage of 200 kV. The crystal phase properties of the samples were analyzed with a Bruker D8 Advance X-ray diffractometer (XRD) using Ni-filtered Cu Kα radiation at 40 kV and 40 mA at 2θ ranging from 10° to 90° with a scan rate of 0.02° per second. FTIR spectra was carried on NEXUS870 spectrometer from 2000 cm^{-1} to 200 cm^{-1}. Raman spectra were obtained on a Raman spectrometer (JY T64000) excited by the 514.5 nm line of an Ar^+ laser under 100 μW. X-ray photoelectron spectroscopy (XPS) analysis (PHI5000 Versaprobe) was used to determine the chemical composition of the products.

2.3. Electrochemical measurements

A homogeneous slurry of active material (WS_2, WS_2/rGO composite) was prepared with super carbon black and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10, diluted in N-methylpyrrolidone (NMP). The slurry was then filmed on a copper foil and dried in vacuum at 80 °C for 12 h. The electrodes were pressed to enhance the contact between the active materials and the conductive carbon. Coin cell was assembled in a glove box under argon. The electrochemical active material is around 1 mg. The galvanostatic charge/discharge cycling was performed on LAND-CT2001A battery-test system, at a current density of 0.1 A/g in the voltage range of 0.01 and 3 V (versus Li+/Li).

3. Results and discussion

To investigate the morphology and microstructure of the as-prepared WS_2 and WS_2/rGO composite sample, field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were applied. As shown in the SEM images, morphologies of WS_2 (Fig. 1a) and WS_2/rGO composite (Fig. 1b) are some different, due to the existence of Graphene which serves as a supporter of WS_2. Fig. 1c shows a TEM image of WS_2/rGO composite, typical WS_2 fragment (in red circle) was attached to large area of Graphene, confirming the SEM results. Fig. 1d shows a HRTEM image of the section red encircled in Fig. 1c, detailing the crystal structure of WS_2, and a spacing distance of about 6.40 Å corresponding to the lattice plane (002) of WS_2 can be observed.

XRD was applied to investigate the crystal structures and composition of the samples. The XRD pattern in Fig. 2a shows two curves corresponding to WS_2 (black curve) and WS_2/rGO composite (red curve (in the web version)). Three peaks at 14.4°, 33.6°, and 58.4° may be assigned to diffractions of the (002), (100) and (110)