In situ reduction of WS₂ nanosheets for WS₂/reduced Graphene Oxide composite with superior Li-ion storage

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Abstract: Two-dimensional transition-metal dichalcogenides, such as tungsten disulfide (WS₂), 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 WS₂, restacking between WS₂ nanosheets, low electronic conductivity and brittle nature of WS₂ severely limit its Li-ion batteries application. Here, we adopt a one-pot method for synthesizing of WS₂/reduced Graphene Oxide (rGO) composite to improve the battery performance dramatically. The WS₂/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 WS₂ 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 WS₂, not only avoiding the restacking between WS₂ nanosheets and improving the conductive properties, but also promoting the reduction of WO₃ effectively. Our work may provide a possible route to avoid oxygen impurities in transition metal dichalcogenides.

Keywords: Amorphous materials, Chalcogenides, Composite materials, Fourier transform infrared spectroscopy (FTIR), Electrochemical properties.

1. Introduction

Few-layers of 2D graphene-like nanosheets, notably the layered transition metal dichalcogenides (TMDCs, MoS₂, WS₂, etc.), have been recently receiving interest for lithium storage due to their fast-ion conductivities.^[1] Among these TMDCs, tungsten disulfide (WS₂) is an interesting graphene-like semiconductor material, with a layered structure formed by unit S-W-S atomic trilayers through 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, WS₂ is a suitable candidate as an electrochemical electrode.^{[9][13]}

In term of preparation, conventionally mono- or few-layered WS₂ can be obtained by mechanical exfoliation or grown by chemical vapor deposition (CVD).^{[14][18]} Chemical methods for large-scale synthesis of layered WS₂ have also been reported.^{[2], [19], [20]} However, oxidized impurities, such as WO_x precursor or WO₃, invariably exist in the product and phase-pure WS₂ has been difficultly obtained. For sulfurization, the direct use

of H_2S still generally requires temperatures in excess of $800\text{ }^\circ\text{C}$ to drive the reaction. Thermal H_2S sulfurization of polycrystalline tungsten has produced WS_2 at temperatures as low as $550\text{ }^\circ\text{C}$ by use of a Ni promoter. Recently, H_2S plasma sulfurization of WO_3 at a low-temperature ($500\text{ }^\circ\text{C}$) 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 .

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. 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.

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 K α radiation at 40 kV and 40 mA at 2 θ 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 μ W. 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 (WS₂, WS₂/rGO composite) was prepared with super carbon black and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10, diluted in N-methyl-pyrrolidone (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

Figure 1. SEM images of (a) WS₂ and (b) WS₂/rGO composite; (c) TEM and (d) HRTEM image of WS₂/rGO composite, HRTEM image corresponding to the section red encircled in (c).

To investigate the morphology and microstructure of the as-prepared WS₂ and WS₂/rGO composite sample, field emission scanning electron microscopy (FESEM) and

transmission electron microscopy (TEM) were applied. As shown in the SEM images, morphologies of WS₂ (Figure 1a) and WS₂/rGO composite (Figure 1b) are some different, due to the existence of Graphene which serves as a supporter of WS₂. Figure 1c shows a TEM image of WS₂/rGO composite, typical WS₂ fragment (in red circle) was attached to large area of Graphene, confirming the SEM results. Figure 1d shows a HRTEM image of the section red encircled in Figure 1c, detailing the crystal structure of WS₂, and a spacing distance of about 6.40 Å corresponding to the lattice plane (002) of WS₂ can be observed.

Figure 2. (a) XRD pattern, (b) FTIR spectrum and (c) Raman spectrum of WS₂ and WS₂/rGO composite.

XRD was applied to investigate the crystal structures and composition of the samples.

The XRD pattern in Figure 2a shows two curves corresponding to WS₂ (black curve) and WS₂/rGO composite (red curve). Three peaks at 14.4°, 33.6°, and 58.4° may be assigned to diffractions of the (002), (100) and (110) planes of WS₂ (JCPDS card no. 08-0237), respectively. However, there are also four small peaks shown in the black curve, at 23.9°, 28.1°, 36.6° and 69.7°, corresponding to diffractions of the (100), (200), (201) and (222) planes of WO₃ (JCPDS card no. 85-2459). These results indicate that the WS₂ products contain WO₃. When the GO solution was added to form WS₂/rGO composite, the peaks of WO₃ were obviated. FTIR analysis is employed to study the changes of the functional groups on graphene. Figure 2b shows the FTIR spectrum of GO and WS₂/rGO composite, indicating the existence of -OH (~3450 cm⁻¹, ~1630 cm⁻¹, ~1400 cm⁻¹), C=O (1720 cm⁻¹) and other oxygen-containing functional groups on GO surface.^{[23] [25] [26]} There are two main absorption peaks of WS₂/rGO composite different from GO: The peak at ~3150 cm⁻¹ can be assigned to -OH attach to graphene, differing from that -OH of adsorbed water (~3450 cm⁻¹) on graphene. Another peak at ~1050 cm⁻¹ assigned to C-OH (alcoholic hydroxyl group) in GO disappeared in WS₂/rGO composite. This change may be related to the transferring of WO₃ to WS₂. Raman spectroscopy was carried out to further confirm the formation of the samples. Figure 2c shows two peaks observed at 353 cm⁻¹ and 418 cm⁻¹, which are correspond to the E_{2g}¹ and A_{1g} modes of WS₂ respectively. E_{2g}¹ is an in-plane optical mode, while A_{1g} corresponds to out-of plane vibrations of the sulfur atoms.^{[22] [27] [28]} Peaks at ~1330 cm⁻¹ and ~1550 cm⁻¹ are assigned to the D band and G band in Graphene,^[25] different from the curve of bare WS₂.

Figure 3. XPS spectra of WS₂ and WS₂/rGO composite. (a) Survey scan, (b) W4f and (c) S2p peak, respectively.

XPS spectra are used to further study the chemical composition of the products, shown in Figure 3. Figure 3a show the typical survey spectrum of WS₂ and WS₂/rGO composite. Here, the presence of C, W, S, and O may be observed in both samples. Figure 3b shows a fatal difference of the two samples, two peaks of 4f-level W atoms had left shift to a lower binding energy as it was converted from W-O bound to W-S bound.^{[22], [29]} S Peaks (2p3 at 161.8 eV and 2p1 at 163.0 eV) in Figure 3c are attributed to the -2 valence state of S atoms. All the above characterizations indicated that the added GO by solution may help transfer impurity WO₃ to WS₂ during the composite formation.

Figure 4. Lithium-ion battery measurements: Charge/discharge curves of (a) WS₂ and (b) WS₂/rGO composite; (c) Cycling performance of the two samples at a current density of 0.1 A/g; (d) The specific capacities of bare WS₂ and WS₂/rGO composite at various discharge currents of 0.1, 0.2, 0.4, 0.6 and 0.8 A/g.

Coin cells were assembled to compare the lithium-ion batteries performance of WS₂ and WS₂/rGO composite. The selected discharge/charge curves of WS₂ and WS₂/rGO composite at a current density of 0.1 A/g are shown in Figure 4a and 4b, respectively. The initial discharge capacities of WS₂ are 625.4 mAh/g, while 673.8 mAh/g of the composite. The irreversible initial capacity loss is caused by different factors, such as the formation of solid electrolyte interface (SEI) layer and the decomposition of electrolyte. Both of Figure 4a and 4b also show the second, third, 10th and 30th discharge and charge curves. It

is noted that the specific capacity of WS₂ retained only 169.0 mAh/g after 30 cycles, much lower than that of WS₂/rGO composite, which still retained 543.2 mAh/g. It was an enhancement of 221% in capacity. Bhandavat et al. once synthesized WS₂ nanosheets with an electrochemical capacity of 118 mAh/g after 50 cycles for lithium-ion battery at a current of 0.1 A/g.^[30] This value is quite close to our results. The cycling performances of two samples are shown in Figure 4c. The WS₂ sample (black plots) showed a faster capacity fading, while WS₂/rGO composite (red plots) showed a slight decay after several cycles, which is consistent with the Figure 4a and 4b. The WS₂/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 WS₂ is only 65.5 mAh/g under the same condition. Furthermore, the rate capability of both samples are shown in Figure 4d. High reversible capacity and excellent cycling behavior were observed only for the WS₂/rGO composite. The specific capacities of WS₂ are 784.3 (0.1 A/g), 387.3 (0.2 A/g), 92.7 (0.4 A/g), 21.8 (0.6 A/g), 15.8 mAh/g (0.8 A/g) and returned to 116.4 mAh/g at 0.1 A/g. While the specific capacities WS₂/rGO composite are 758.4 (0.1 A/g), 542.3 (0.2 A/g), 480.1 (0.4 A/g), 441.1 (0.6 A/g), 410.3 mAh/g (0.8 A/g) and returned to 549.1 mAh/g at 0.1 A/g. Our results demonstrated that the added GO can obviously improve the electrical properties of initial WS₂ products, and make better cycling stability and recovery for lithium storage.

4. Conclusion

In summary, we adopt a one-pot method, adding GO solution to the solvothermal

synthesis of WS₂, to obtain WS₂ – reduced Graphene Oxide (rGO) composite. Results show that the added Graphene Oxide is reduced to rGO and constitute stable composite with WS₂, not only avoiding the restacking between WS₂ nanosheets and improving the conductive properties, but also helping transfer impurity WO₃ to WS₂ effectively. Lithium-ion battery measurement demonstrated the capacity of WS₂ electrode could be enhanced by this route, from 65.5 mAh/g to 431.2 mAh/g at a current density of 0.1 A/g after 100 cycles, with a much better stability. The approach may be useful for improvement of other electrode materials.

Acknowledgments

This work was financially supported by the National Basic Research Program of China (973Program: 2013CB932903), the National Science Foundations of China (No. 61205057, No. 61203289), China Postdoctoral Science special Foundation (2012T50488), Qing Lan Project, by the ‘1311 Talent Plan’ Foundation of Nanjing University of Posts and Telecommunications.

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