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$ZnWO_4$ nanocrystals/reduced graphene oxide hybrids: Synthesis and their application for Li ion batteries

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$ZnWO_4$, as an environment-friendly and economic material, has the potential for Li ion batteries (LIB) application. In this paper, a facile method has been developed to synthesize $ZnWO_4$ supported on the reduced graphene oxide (RGO) to improve its LIB performance. The cuboid-like $ZnWO_4$ nanocrystals are prepared by directly adding Na_2WO_4 powders into the graphene oxide/Zn aqueous solution followed by a hydrothermal treatment. The high-resolution TEM, XRD and XPS characterizations were employed to demonstrate structural information of the as-prepared $ZnWO_4$/RGO hybrids carefully. Besides, we also discussed the LIB properties of the hybrids based on the detailed galvanostatic charge-discharge cycling tests. As a result, the specific capacity of the as-prepared $ZnWO_4$/RGO hybrids reached more than 477.3 mA h g^{-1} after 40 cycles at a current density of 100 mA g^{-1} (only less than 159 mA g^{-1} for bare $ZnWO_4$). During the whole cyclic process, the coulombic efficiency steadily kept the values higher than 90%.

$ZnWO_4$, graphene, hybrid, Li-ion battery, anode

1 Introduction

With the increasing demand on energy, Li ion batteries have received much attention owing to their great potential for general use in powering and hybrid electric vehicles. Metal oxide always exhibit higher specific capacities than the commercial graphite, and thus they have been intensively studied as LIB anodes [1−5]. Among various metal oxides, ZnO is a special compund, although its specific capacity is not good enough. If ZnO is combined with other transition metal oxides to form double salts, the composites will show desired LIB performances. For instance, $ZnFe_2O_4$ [6], Zn_2GeO_4 [7], $ZnSnO_3$ [8] and $ZnWO_4$ [9] have been widely studied. However, their large volume change during the charge-discharge process is still a general drawback which limited their practical applications as anode materials.

Recently, an effective way to resolve this problem has been suggested, loading the anode materials on the surface of graphene to improve their cyclabilities. Graphene is monolayer of carbon atoms with a tight packing of honeycomb lattice. Its unique properties, including low-cost, high surface area, flexibility, chemical stability and high electrical conductivity, make it an ideal substrate to form supporting materials. A large number of graphene-metal oxide hybrid materials have been prepared and studied, such as graphene-Mn_3O_4 [10, 11], graphene-Fe_3O_4 [12, 13], and graphene-SnO_2 [14, 15]. The enhanced Li-ion battery performance is reflected by the improvement of both cyclability and capacity.

Here, we show a low-cost and environment friendly metal tungstates $ZnWO_4$. This compound has a wolframite-type monoclinic structure belonging to the $P_{2/c}$ space group and it has two formula units per primitive cell, which can be described as consisting of hexagonal close-packed oxygen

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atoms with certain octahedral sites filled by Zn^{2+} and W^{6+} cations in an ordered fashion [9]. It has been applied in the fields of photocatalysts, optical fibers and gas sensors [16–18]. Very recently, Kim' group also found that $ZnWO_4$ is a good LIB anode material by carbon coating. To the best of our knowledge, there is still no report about the fabrication of $ZnWO_4$/reduced graphene oxide (RGO) hybrid nanocompositse used in LIB area [9].

2 Experimental

2.1 Synthesis of GO

GO was synthesized from natural graphite powder according to a modified Hummers method [19]. Briefly, 0.9 g of graphite powder was added into a mixture of 7.2 mL of 98% H_2SO_4, 1.5 g of $K_2S_2O_8$, and 1.5 g of P_2O_5. The solution was kept at 80 °C for 4.5 h, followed by thoroughly washing with water. Thereafter, the as-treated graphite was put into a 250 mL beaker, to which 0.5 g of $NaNO_3$ and 23 mL of H_2SO_4 (98%) were added while keeping the beaker in an ice bath. Subsequently, 3 g of $KMnO_4$ was added slowly. After 5 min, the ice bath was removed and the solution was heated up to and kept at 35 ℃ under a vigorous stirring for 2 h, followed by the slow addition of 46 mL of water. Finally, 40 mL of water and 5 mL of H_2O_2 was added, followed by water washing and filtration. The exfoliation of graphene oxide was then dispersed in water (5 mg mL^{-1}) under sonication for 2 h to yield a homogeneous suspension.

2.2 Synthesis of $ZnWO_4$/GO

1 mmol of $Zn(NO_3)_3$ was dissolved in 20 mL of H_2O, followed by adding 10 mL of GO aqueous solution. After stirring for 5 min, 1 mmol of Na_2WO_4 powder was added. The mixture was hydrothermally treated in autoclaves at 160 ℃ for 12 h.

2.3 Synthesis of bare $ZnWO_4$

1 mmol of $Zn(NO_3)_3$ was dissolved in 20 mL of H_2O followed by adding 1 mmol of Na_2WO_4 powder. The mixture was hydrothermally treated in autoclaves at 160 ℃ for 12 h.

2.4 Characterization

The HRTEM images were recorded by a Philips TF-F20 transmission electron microscope operating at 200 kV. XPS measurement was performed on an ESCALAB-MKII 250 photoelectron spectrometer (VG Co.) with Al Kα X-ray radiation for excitation.

2.5 Electrochemical measurements

The test cell consisted of a working electrode and a lithium foil which were separated by a Celgard 2400 membrane. The electrolyte solution was prepared by dissolving 1 M of $LiPF_6$ in EC-DMC (1:1, *w*/*w*). The working electrodes were prepared by casting slurry containing 80% active material, 10% acetylene black and 10% polyvinylidene fluoride (PVDF) onto a copper foil. After vacuum drying at 80 ℃ for about 24 h, the electrode disks were punched and weighed. Each electrode has approximately 1–3 mg of active material. Galvanostatic charge-discharge cycling tests were performed using a LAND CT2001A multi-channel battery testing system in the voltage range between 0.01 and 3 V at room temperature.

3 Results and discussion

In this paper, we developed a facile hydrothermal method to synthesize $ZnWO_4$/RGO hybrid material in one pot. First, $Zn(NO_3)_2$ aqueous solution and GO aqueous solution were mixed together followed by addition of Na_2WO_4 powder directly. After stirring for a few minutes, the mixture was treated in hydrothermal conditions at 160 °C for 12 h, which afforded well-crystallized $ZnWO_4$ cuboids distributed on RGO sheets uniformly. The synthesis process is illustrated in Figure 1.

The X-ray diffraction (XRD) patterns of $ZnWO_4$/RGO hybrids, bare $ZnWO_4$ and GO are shown in Figure 2. Compared with the characteristic diffraction peak of disordered GO, the peak at 2θ = 10.6° disappeared in $ZnWO_4$/RGO, indicating the complete reduction of GO. The peaks at 2θ = 18.9°, 30.5°, 36.3° and 52.5° can be indexed into (100), (111), (021) and (122) reflections (JCPDS No. 15-0774) of the crystallized $ZnWO_4$, respectively.

The transmission electron microscope (TEM) images in Figure 3 show that the as-obtained $ZnWO_4$ cuboids distributed on RGO surface uniformly. There is no scattered $ZnWO_4$ cuboids could be found outside the RGO nanosheets. The continuous and clear lattice fringe spacings suggest that the cuboids are small single crystals. Compared with the previous work, the as-obtained $ZnWO_4$ cuboids have a much smaller partcile size, which could be attributed to the hard templating effect of GO in the *in situ* growth process. The

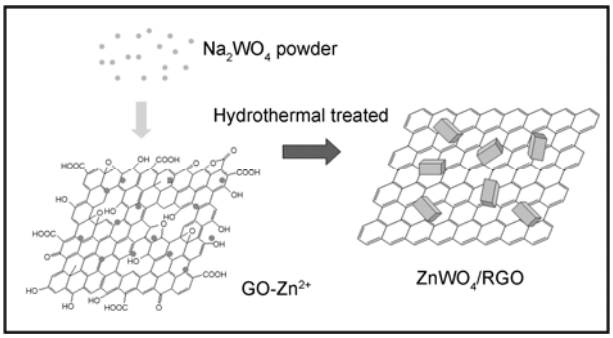

Figure 1 Synthesis process of $ZnWO_4$/RGO hybrids.

GO surface can hold small $ZnWO_4$ crystals strongly and separate them from each other effectively which can limit the mass transformation during the growth process. The lattice fringe spacing is 0.468 nm corresponds well to the characteristic (100) planes of $ZnWO_4$.

In order to find out the oxidation state of carbon in the final products, XPS analysis has been taken and shown in Figure 4. The peaks associated with C–C (284.6 eV) become predominant, while the peaks related to the oxidized carbon species such as C–OH (285.2 eV), C–O (286.7 eV) and O–C=O (288.4 eV) are greatly weakened. These results indicate that GO has been well deoxygenated to form graphene. The Zn 2p binding energy peaks, such as those at 1046.1 and 1023.1 eV, are consistent with Zn $2p_{1/2}$ and $2p_{3/2}$ state, respectively. The major peaks at 36.1 eV and 38.3 eV can be assigned to the $4f_{7/2}$ and $4f_{5/2}$ states of W metals [20].

The $ZnWO_4$/RGO hybrid material and bare $ZnWO_4$ nanoparticles were mixed with carbon black and polyvinyldifluoride (PVDF) in a weight ratio of 80:10:10 for preparing a working electrode. The electrochemical measurements were carried out in coin cells with a Li foil as the

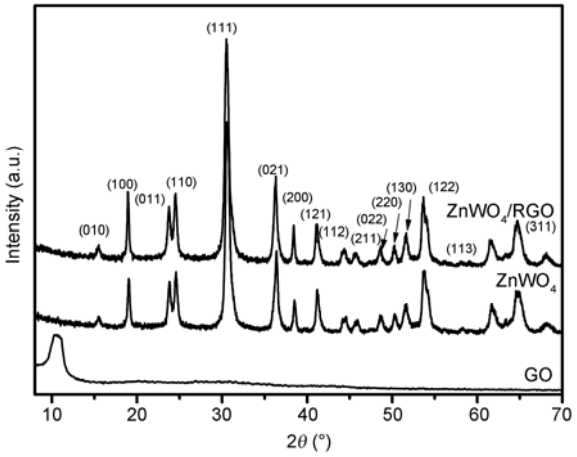

Figure 2 XRD spectra of $ZnWO_4$/RGO hybrids, bare $ZnWO_4$ and GO.

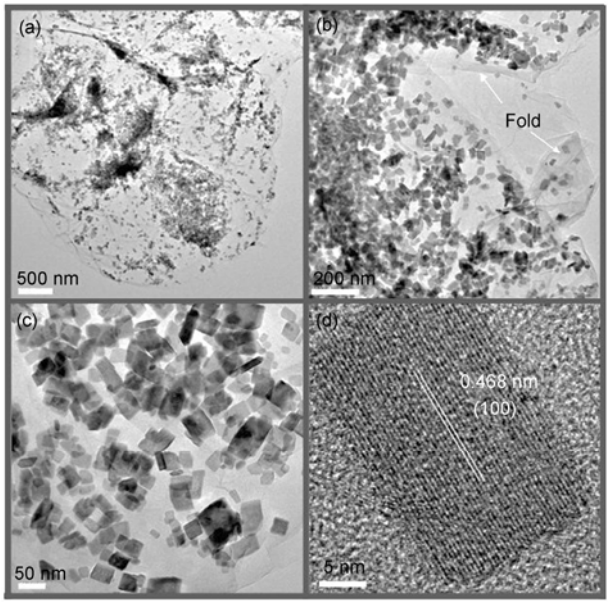

Figure 3 TEM images of $ZnWO_4$/RGO hybrids.

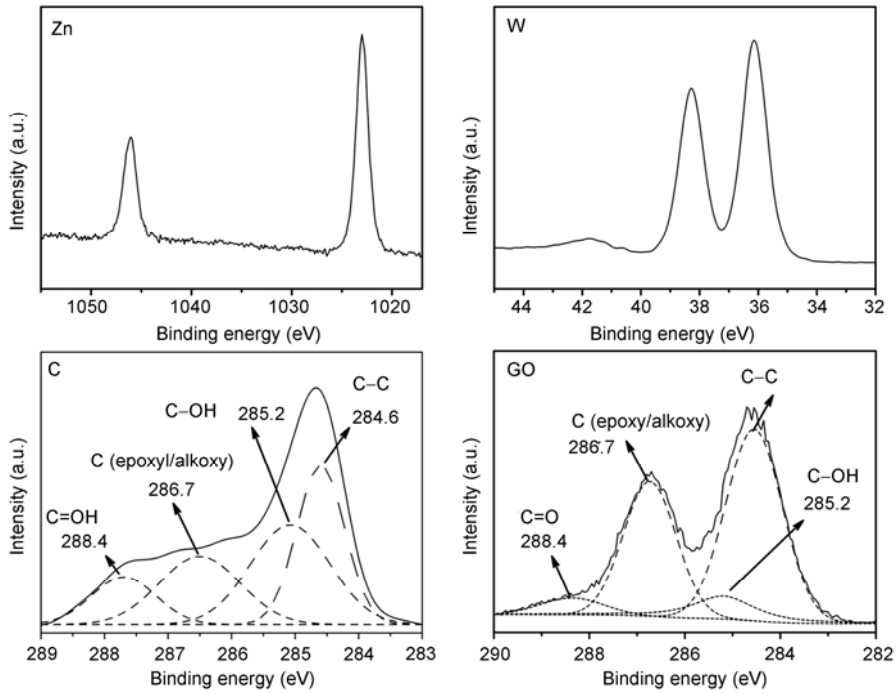

Figure 4 XPS spectra of ZnWO4/RGO hybrids.

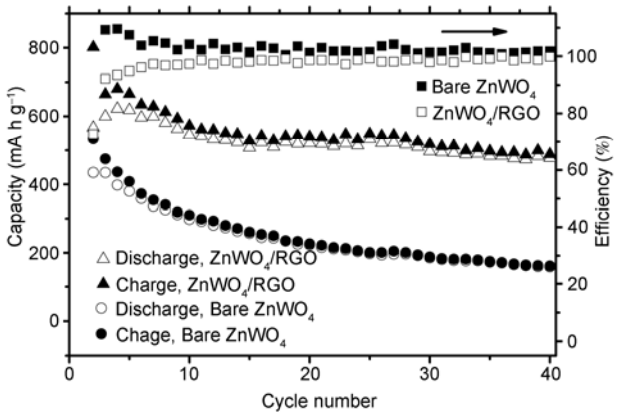

Figure 5 Capacity retentions of $ZnWO_4$/RGO and $ZnWO_4$ for 40 cycles at a current density of 100 mA g^{-1}.

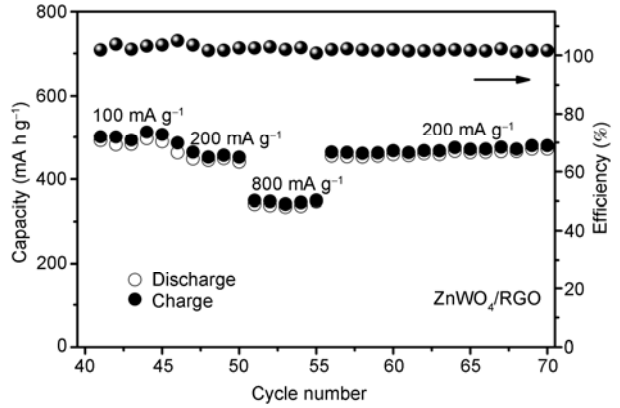

Figure 6 The rate capability test of $ZnWO_4$/RGO.

counter electrode and 1 M $LiPF_6$ in 1:1 ethylene carbonate (EC) and diethyl carbonate (DEC) as the electrolyte. Figure 5 shows the capacity retentions of the $ZnWO_4$/RGO and bare $ZnWO_4$ anode for 40 cycles at a low current density of 100 mA g^{-1} between 3.0 and 0.01 V vs Li^+/Li. The capacities are 566.6, 596.7, 545.3, 521.4, 497, and 477.3 mA h g^{-1} after 1, 5, 10, 20, 30, and 40 cycles for $ZnWO_4$/RGO, respectively. For bare Zn_2GeO_4 nanoparticles, the capacities are 434.8, 359.1, 297.8, 223.7, 185.5, and 159.1 mA h g^{-1} after 1, 5, 10, 20, 30, and 40 cycles, respectively. The capacity decreased fast, which illustrated a serious volume change happened during the charge-discharge process. Notice that the efficiency of $ZnWO_4$/RGO was always slightly below 100%, however, that of $ZnWO_4$ sample was always higher than 100%.

To further evaluate its rate capability, the $ZnWO_4$/RGO hybrids have been first tested at 100 mA g^{-1} for 40 cycles. It can be seen in Figure 6 that they exhibited an excellent rate capability that maintained at 496.9 mA h g^{-1} after another 5 cycles at 100 mA g^{-1}, 440.8 mA h g^{-1} after 5 cycles at 200 mA g^{-1} and 347.4 mA h g^{-1} after 5 cycles at 800 mA h g^{-1}. The as-prepared $ZnWO_4$/RGO hybrids exhibited a desired rate capability.

4 Conclusions

In conclusion, we have demonstrated a facile one-pot aqueous method to synthesis $ZnWO_4$ single crystal short cuboids supported on graphene nanosheets. This featured material has a high specific capacity almost over 500 mA h g^{-1} at a rate of 100 mA g^{-1} in the initial discharge process and excellent retention of the initial capacity in the test of rate capability. During the whole cyclic process, the coulombic efficiency steadily kept the values higher than 90%. Our current results illustrated that the protection by graphene is a very efficient way to enhance the metal oxide's LIB performance. And thus, these $ZnWO_4$ cuboids/RGO hybrid is a good candidate for Li-ion battery cathodes.

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