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Communication

Reduced graphene oxide wrapped hollow molybdenum trioxide nanorod for high performance lithium-ion batteries

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ABSTRACT

Reduced graphene oxide wrapped hollow molybdenum trioxide nanorods (MoO₃@rGO) have been fabricated by a facile process. The MoO₃@rGO shows improved lithium storage performance. It could deliver a high reversible capacity (842 mAh/g at 0.1 A/g), excellent cycling stability (778 mAh/g at 0.1 A/g after 200 cycles) and excellent rate capability (455 mAh/g at 2 A/g). The excellent electrochemical performance could be attributed as the special core (MoO₃)/sheath (rGO) structure, which could accommodate the volume change of MoO₃ during lithiation/delithiation process. In addition, the rGO coating layer could improve the electronic conductivity of MoO₃.

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Lithium-ion batteries (LIBs) have been widely used in portable devices and energy storage systems due to their high energy density, light weight and long cycle life [1]. It is well known that graphite is the most conventional anode material for LIBs, but it shows a limited theoretical capacity of 372 mAh/g, which is unable to meet the demand for electric vehicles (EVs) and large-scale energy storage systems [2]. Recently, much effort has been devoted to find new materials with high capacity, good rate capability and good cycling stability to replace graphite anode [3–9]. Molybdenum trioxide (MoO₃) with a high theoretical specific capacities of 1117 mAh/g, has been regarded as a promising candidate of traditional graphite for next-generation LIBs. However, MoO₃ suffers from serious capacity fading and poor rate capability due to the large volume change, the aggregation of the transition nanoparticles during lithiation/delithiation process and low intrinsic electronic conductivity gravely affected its applications [10]. Decreasing the size of MoO₃ particles has been demonstrated as an effective strategy to improve the electrochemical performances of MoO₃, because the nanosized particles could shorten the diffusion length of Li ions and mitigate the volume variation of the electrode during Li ions intercalation and deintercalation process.

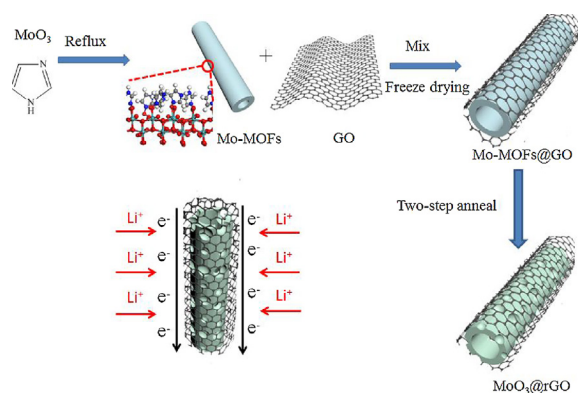
Nanosized MoO₃ particles with different morphologies including nanoparticles [11], nanowires [12], nanobelts [13] have been reported, showing improve lithium storage performance. Among these morphologies, one dimensional (1D) nanostructure allows for better accommodation of the huge volume changes, leading to fracture free structure after repeated cycles. In addition, 1D nanostructure could provide fast charge transport pathway for both ions and electrons [14–16]. Designing of porous structure and carbon coating are another most popular strategy to improve the electrochemical performances of MoO₃ [17].

Graphene is a 2D carbon material with high surface area, chemical stability, and outstanding electronic conductivity, exhibiting excellent energy storage performance [18]. Meanwhile, reduced graphene oxide (rGO) shows an excellent electric conductivity, which has been applied to enhance electric conductivity of electrode materials [4,6,19,20]. Designing graphene coated 1D MoO₃ should be a promising approach to realize high performance lithium storage. Recently, metal-organic frameworks (MOFs) with unique characteristics have been widely studied [21–23]. MOFs have been used as templates and precursors to synthesize various porous nanomaterials [24–26]. Herein, we designed and synthesized reduced graphene oxide wrapped hollow molybdenum trioxide nanorods (denoted as MoO₃@rGO) by simply mixing molybdenum-based MOFs (Mo-MOFs) with graphene oxide (GO) followed by a two-step annealing process. When used as anode material in LIBs, the MoO₃@rGO shows a high

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Scheme 1. Schematic illustration of the fabrication processes of MoO₃@rGO and schematic diagram of lithium ion diffusion and electron conduction in MoO₃@rGO.

reversible capacity (842 mAh/g at 0.1 A/g), excellent cycling stability (778 mAh/g at 0.1 A/g after 200 cycles) and excellent rate capability (455 mAh/g at 2 A/g).

The entire fabrication process was shown in Scheme 1. Firstly, the synthesis of Mo-MOFs was followed by Pedro Martin-Zarza's work [27]: 3.5 g of MoO₃ and 1.66 g of imidazole were serially mixed in 500 mL of deionized water. And then the mixture was refluxed at 80 °C for 12 h in an oil bath, the precipitate were separated by centrifugation at 6000 rpm for 2 min, rinsed with deionized water for three times. After drying in an oven at 60 °C overnight, the Mo-MOFs were obtained. Then, 0.2 g of Mo-MOFs were mixed with 4 mL GO aqueous solution (~5 mg/mL, pH 1), the mixture was stirred for 6 h. After that the mixture was frozen by liquid nitrogen, and then the frozen sample was transferred to a vacuum freeze dryer immediately. A two-step annealing process had been taken to fabricate MoO₃@rGO. Firstly, the composite of Mo-MOFs and GO was annealed at 600 °C for 6 h with a heating rate of 3 °C/min in N₂ to get MoO₂@rGO. And the MoO₃@rGO can be obtained by the further annealing of MoO₂@rGO under air at 300 °C for 3 h with heating rate of 5 °C/min. For comparison, pure MoO₃ without GO was synthesized by the same experimental conditions.

The battery performance of the electrodes was assessed with CR2032 coin cells. The working electrodes were prepared by the doctor-blade coating of the slurry onto a copper foil. The slurry was formed of active material, acetylene black and polyvinylidene fluoride (PVDF) with a weight ratio of 80:10:10. *N*-Methyl-2-pyrrolidone (NMP) was employed to adjust the viscosity of the slurry. The diameter of electrode slice is 1 cm and the average mass of the electrode slice is about 1.2 mg, so the loading amount of the electrodes is about 1.5 mg/cm². To assemble Li-ion batteries, a Li foil was utilized as counter electrode. The celgard 2400 fibre was used as a separator. The electrolyte was 1 mol/L LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) in a volume ratio of 1:1. The cyclic voltammogram (CV) measurements were performed on CHI 660D electrochemical workstation at a scan rate of 0.2 mV/s. Charge/discharge (0.01–3.0 V) tests were performed on a Neware BTS-610 battery test system under room temperature.

The morphologies of Mo-MOFs, pure MoO₃ and MoO₃@rGO were characterized by Scanning electron microscopy (SEM) (JEOL, Tokyo, Japan) (Fig. 1). Fig. 1a shows the SEM image of the Mo-MOFs. The Mo-MOFs display nanorods morphology with a size of 200–500 nm in diameter and 5–30 μm in length. The SEM images of the pure MoO₃ and MoO₃@rGO are presented in Fig. 1b–d. Both of the MoO₃ and MoO₃@rGO keep the structure of nanorod, while the MoO₃ is composed of many small particles. After coating of reduce graphene oxide (rGO), the nanorod structure of the MoO₃@rGO keep intact. Fig. 1d is the enlarged view of the marked part in

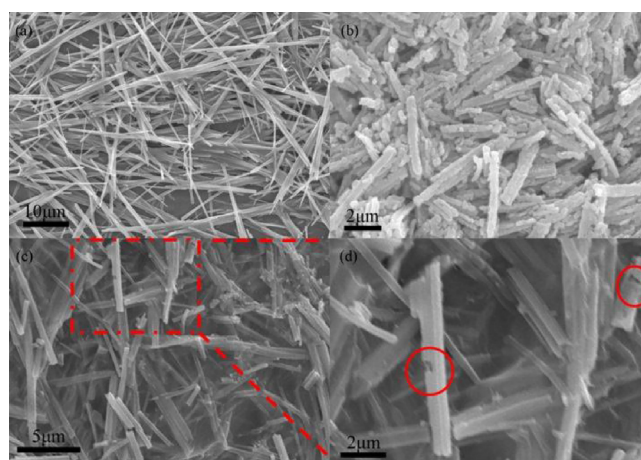


Fig. 1. SEM images of Mo-MOFs (a), pure MoO₃ (b), MoO₃@rGO (c, d).

Fig. 1c. As marked in Fig. 1d, there are two gaps, which suggesting a hollow structure of the nanorod. To further reveal the morphology of MoO₃@rGO, Transmission electron microscopy (TEM) (JEOL, Tokyo, Japan) was conducted. Fig. 2a confirms the hollow structure of the nanorod. Moreover, rGO film completely wrapped the surface of the MoO₃ nanorod. In addition, a number of pores can be observed in the wall of the hollow nanorod. The phase purity and crystallinity of MoO₃@rGO was characterized by X-ray diffraction (XRD) (Philips X'PertPRO SUPER X-ray diffractometer). As shown in Fig. 2b, all of the XRD peaks of MoO₃@rGO can agree well with α -MoO₃ (JCPDS 05-0508) while there is no impure peak can be observed, indicating a good phase purity and crystallinity of MoO₃. Raman spectroscopy was also performed (Fig. 2c). Several peaks can be found at 200–1000 cm⁻¹, which attributed to the stretching and bending of Mo-O bonds, in agreement with previous reports [28,29]. The typical Raman peaks of D and G bands of rGO can also be observed at 1366 and 1601 cm⁻¹ respectively, confirming the presence of rGO [4]. The surface chemistry of the MoO₃@rGO was analyzed by X-ray photoelectron spectroscopy (XPS). Fig. 2d shows the wide scan XPS survey spectrum, indicating that the MoO₃@rGO only contains C, Mo and O elements. The individual spectrum of Mo 3d is shown in Fig. 2e, there are two peaks located at 232.9 and 236.1 eV with an integrated peak area ratio of 3:2, corresponding to Mo(VI) for MoO₃ [30]. As for the spectrum of C 1s (Fig. 2f), expect the C—C bond at 284.8 eV, different oxygen-containing functional groups of the C—O bond at 286.2 eV, the C=O bond at 288.9 eV can also be observed [31].

To evaluate the electrochemical performance of the MoO₃@rGO, galvanostatic charge/discharge measurements and cyclic voltammetry (CV) were performed. For comparison, we also measured galvanostatic charge/discharge of the pure MoO₃. Fig. 3a and b display the initial two galvanostatic discharge-charge profiles of the pure MoO₃ and MoO₃@rGO at a current density of 100 mA/g between 0.01 V and 3 V. The pure MoO₃ delivers capacities of 1st discharge and 1st charge are 1163 mAh/g and 436 mAh/g, respectively, corresponding an initial coulombic efficiency (ICE) of 37%. For MoO₃@rGO, it shows an initial discharge capacity of 1107 mAh/g and an initial charge capacity of 842 mAh/g with an ICE of 76%. The decomposition of electrolyte and the formation of solid electrolyte interface (SEI) are responsible for the low ICE of MoO₃@rGO [32]. The MoO₃@rGO also delivers an excellent cycling stability and rate performance (Fig. 3c–e). Cycling performances of the MoO₃@rGO and pure MoO₃ at current density of 100 mA/g were shown in Fig. 3c. The charge capacity of MoO₃@rGO can maintain 778 mAh/g after 200 cycles showing a capacity retention of 92%, while the pure one can only retain

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