



Self-assembled porous MoO₂/graphene microspheres towards high performance anodes for lithium ion batteries



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HIGHLIGHTS

- MoO₂/graphene microsphere is synthesized by microwave assisted hydrothermal method.
- Graphene encapsulation driven the self-assembly of 3D porous framework.
- Nanoporous voids enable effective electrolyte penetration.
- Strategic combination of 3D architecture provides superior Li ion storage property.

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ABSTRACT

Three dimensional (3D) porous self-assembled MoO₂/graphene microspheres are successfully synthesized via microwave-assisted hydrothermal process in a short reaction time followed by thermal annealing. Such rationally designed multifunctional hybrid nanostructure is constructed from interconnected MoO₂ nanoparticles (3–5 nm), which is self-assembled into ordered nanoporous microspheres via strong electrostatic attraction between graphene sheets and MoO₂ nanoparticles. The MoO₂/graphene hybrid structure delivers a high reversible capacity with significantly enhanced cycling stability (~1300 mAh g⁻¹ after 80 cycles at C/10 rate) and excellent rate capability (913 and 390 mAh g⁻¹ at 2C and 5C rates, respectively), when used as an anode material. The microspheres are interconnected and well encapsulated by the flexible graphene sheets, which not only accommodates large volume change but also increases the electrical conductivity of the hybrid structure. Moreover, nanoporous voids present in the 3D framework facilitate effective electrolyte penetration and make a direct contact with the active MoO₂ nanoparticles, thereby greatly enhancing lithium ion transport. The strategic combination of self-assembly, nanoporous voids, 3D network and intriguing properties of graphene sheets provides excellent electrochemical performance as anode materials for Lithium ion battery applications.

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1. Introduction

Lithium ion batteries (LIBs), one among the popular rechargeable battery systems, exhibit the advantages of high voltage, long cycle life, low toxicity and high reliability for powering an increasingly diverse range of applications, ranging from portable electronics to electric vehicles (EVs) or hybrid EVs (HEVs) [1]. Current battery system technologies are known to suffer from kinetic problem associated with volumetric strain and intrinsically slow solid state diffusion into the bulk (limits high power

capability), based on micron sized electrode material [2]. In principle, capabilities of safe lithium ion batteries rely largely on the performance of electrodes, particularly anode, for lithium ion storage [3]. A variety of transition metal oxide nanostructured materials (TMO) have the potential to be used as safe and high capacity material, a promising alternative for commercialized graphite anodes (<372 mAh g⁻¹), to meet the ever-growing energy demands [4,5].

Recently, a variety of one-dimensional (1D) TMO nanostructures such as TiO₂, SnO₂, Fe₃O₄, Fe₂O₃, Co₃O₄, and Mn₃O₄ have been explored as potential anodes for their superior reversible capacity [6–11]. Nanomaterial electrodes have several advantages such as short Li ion diffusion distance, large electrode-electrolyte contact area and large surface to volume ratio. Despite these distinct

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advantages, nanomaterials, which are being electrically isolated upon cycling, are suffering from relatively low conductivity and particle agglomeration, which limits the rate performance of the electrode. Integration of carbonaceous matrix into TMO nanostructures can buffer the volume strain due to electrostatic feature of the carbon support. It also increases the electrical conductivity and prevents the particle agglomeration by forming hybrid nanostructures [4,12]. Graphene, a honeycomb network of sp^2 carbon atoms, is one of the most appealing carbon matrix, featuring outstanding electrical conductivity, large specific surface area (theoretical value of $2630 \text{ m}^2 \text{ g}^{-1}$), excellent mechanical flexibility, and high thermal and chemical stability [13,14]. The functional ($-\text{COOH}$ and $-\text{OH}$) groups present in graphene oxide (GO) act as a nucleation site for metal oxides, which facilitates via strong electrostatic bond during hybrid structure formation. Graphene, composite with metal oxide nanostructures of different dimensionality such as zero dimensional (0D) nanoparticles, one dimensional (1D) nanotubes and two dimensional (2D) nanoplates or nanosheets, serves as an excellent support for increasing the electrical conductivity and buffering large volume change of electrode [15,16].

Among various TMOs, molybdenum oxide (MoO_x) is considered as an unusual and attractive anode material for their rich chemistry associated with multiple valence states [17,18]. Molybdenum dioxide (MoO_2) has high theoretical capacity (838 mAh g^{-1} , 4 Li per formula unit), low electrical resistivity, high density (6.5 g cm^{-3}), high melting point, and high chemical stability. However, bulk MoO_2 electrodes are greatly hampered by significant volume change during cycling, which leads to pulverization of the electrode. Numerous electrode designs have emerged to mitigate the adverse mechanical effects and improve the overall electrochemical performance of MoO_2 based anodes. Recently, MoO_2 nanostructures such as ordered mesoporous material [19], nanoparticles [20], nanocrystals [21], nanosheets [22], and nanorods [23], and MoO_2 /carbon hybrid composites such as MoO_2 /carbon nanotube [24], MoO_2 /carbon [25], and MoO_2 /graphene [26] have been investigated as LIB anodes to hold the promise for better electrochemical performance than bulk counterparts. On the other hand, it is a great challenge to synthesize nanomaterials of hierarchical architectures and multi functionalities, or hybrid combinations of various nanomaterials to fulfil the on-board energy demands. The overall device performance is not only based on the development of advanced electrode material but also on the effect of materials engineering for superior electrode architecture. One among them is self-assembled 3D porous hybrid architecture, which exhibits highly specific morphology and remarkable electrochemical performance based on the surface and indigenous material property [27–29].

Microwave-assisted hydrothermal (MAH) process is well known for synthesizing rapid and homogeneous nanostructures, compared to conventional hydrothermal method during which unavoidable temperature gradient occurs. This temperature gradient may adversely affect the particle size distribution and purity of the material. Being energy efficient, microwave heating increases the rate of reaction and kinetics of crystallization and also provides uniform nucleation environment in a short reaction time leading to high quality monodisperse nanocrystals [9,30]. Herein, we report a facile strategy to synthesize self-assembled MoO_2 /graphene hybrid (SA-MGH) microsphere via MAH process followed by thermal annealing. The well assembled 3D porous microsphere is formed from interconnected MoO_2 nanoparticles uniformly dispersed on conducting graphene matrix. In such rationally designed hybrid structure, MoO_2 microspheres have good contact with encapsulated graphene backbone which helps for prolonged cycle life and provides a pathway for charge transfer kinetics. By taking the advantage of unique morphology, graphene

encapsulation, and 3D porous framework, SA-MGH microsphere anode provides exciting possibilities for improving the performance of lithium ion batteries.

2. Experimental

2.1. Synthesis of graphene oxide

Graphene oxide (GO) was prepared by using modified Hummer's method [31,32]. Natural graphite powder (2 g, Aldrich) and sodium nitrate (NaNO_3 -2 g, Aldrich) was added into concentrated sulphuric acid (H_2SO_4 -50 ml, Aldrich) and stirred for 30 min in ice bath. Potassium permanganate (KMnO_4 -7 g, Aldrich) was added, followed by continuous stirring and further, a 100 ml of deionized (DI) water was slowly added into the reaction mixture. After dilution with DI water (300 ml), 30% hydrogen peroxide (H_2O_2 , Aldrich) was added to the mixture. Finally, the solution was filtered and washed with aqueous 5% hydrochloric acid (HCl, Aldrich) to remove residual ions and further washed with DI water to reach neutral pH and overnight dried at 70°C .

2.2. Synthesis of molybdenum dioxide and graphene hybrid composite

The SA-MGH microsphere was synthesized via MAH process followed by thermal annealing and this hybrid synthesis is based on previously reported conventional hydrothermal method [33]. A 120 mg/ml of GO was ultrasonicated for 30 min to form a homogeneous dispersion. Ammonium heptamolybdate tetrahydrate ($\text{AHM}-(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ -5.6 g, Aldrich) was dissolved in aqueous exfoliated GO suspension. Then, ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$ -0.56 g, Aldrich) was added to the above mixture by constant stirring and the pH was adjusted to 1 by adding 1 M HCl. The above mixture was treated in a closed Teflon vessels in MAH reactor (2.45 GHz, 800 W, MARS, CEM Corp.) at a controlled temperature and pressure of 200°C and 500 Torr for 30 min, and the reaction mixture was cooled down to room temperature. The collected reaction mixture was centrifuged, washed thoroughly by DI water and absolute ethanol and dried at 60°C overnight in oven to obtain MoO_2 /graphene composite. The as-prepared MoO_2 /graphene composite was further thermally annealed at 500°C (ramp rate: $10^\circ \text{C min}^{-1}$) for 5 h under nitrogen flow to increase the crystallinity of the material. For comparison, bare MoO_2 nanoparticle and reduced graphene oxide (RGO) were synthesized under the same reaction conditions.

2.3. Materials characterization

Thermo gravimetric and differential thermal (TG/DTA) analysis were conducted with SEICO INST (TG/DTA 7300) in the temperature range of 25 – 700°C at a heating rate of $10^\circ \text{C min}^{-1}$ in air flow. Powder X-ray diffraction (XRD) patterns were collected using D8–Advance, BRUKER MILLER Co diffractometer in the range of $5^\circ < 2\theta < 80^\circ$ using $\text{Cu K}\alpha_1$ irradiation ($\lambda = 1.5406 \text{ \AA}$). The morphology and microstructure of hybrid composites were characterized by field emission scanning electron microscope (FE–SEM, JEOL JSM7000F) and high resolution transmission electron microscope (HR–TEM, JEOL JEM2100F) coupled with Energy Dispersive Spectroscopy (EDS/EDX). Raman spectra were measured by (Renishaw, RM 1000) Raman spectrometer using Ar^+ laser of 514 nm at room temperature. X-ray photoelectron spectroscopy (XPS) measurements were carried out using VG microtech (ESCA, 2000) with a monochromatic $\text{Al K}\alpha$ (1486.6 eV) X-ray source. Nitrogen sorption isotherms were obtained by Micromeritics ASAP 2000 at liquid N_2 temperature. Samples were degassed for 12 h at 323 K before the measurement. The Brunauer–Emmett–Teller (BET)

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