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Free-standing molybdenum disulfide/graphene composite paper as a binder- and carbon-free anode for lithium-ion batteries

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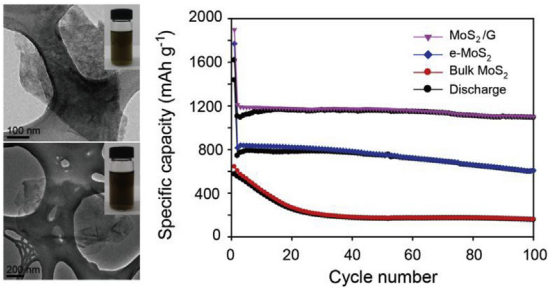
HIGHLIGHTS

- A free-standing MoS_2/graphene (MoS_2/G) composite paper was prepared by a simple vacuum filtration method.
- HADDF-STEM image revealed an alternatively layered structure of MoS_2/G composite paper.
- MoS_2/G paper significantly improved the Li^+ ion storage/release process, compared to the exfoliated MoS_2.

GRAPHICAL ABSTRACT



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ABSTRACT

Two dimensional nanosheets, such as graphene and metal disulfides, have attracted a great deal of attention as anode materials for lithium-ion batteries, owing to their unique capability for lithium-ion storage. In this work, we integrate graphene and MoS_2 nanosheets into a free standing film form using a simple vacuum filtration method. As-prepared composite film could be readily employed as a binder- and carbon-free anode for lithium-ion batteries, removing the polymeric binders and conductive carbon additives that are required for the preparation of conventional electrodes. In addition, the interconnected structure of graphene and MoS_2 sheets provide a good electrical conductivity to the entire film electrode. When tested electrochemical performance as an anode for lithium-ion batteries, the composite film electrode exhibits superior performance compared to the exfoliated MoS_2 electrode, such as 65.8% capacity retention at a high current rate of 1000 mA g^{-1} and 91.1% capacity retention after 100 cycles.

1. Introduction

Lithium-ion batteries (LIBs) are currently being developed as the main power sources for portable electronic devices (*e.g.*, mobile phones and laptops) in our daily life. In addition, ever increasing interest in the widespread of electric vehicles (EVs) and hybrid vehicles (HEVs) has led to demand for development of LIBs with higher energy density, better rate capability, and longer cycling life. Most commercial LIBs are fabricated by assembly of a graphitic anode and an intercalated Li compound cathode (*e.g.*, $LiCoO_2$ or

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$LiMn_2O_4$) with an organic carbonate electrolyte [1]. Although commercial graphite is naturally abundant and has stable cycling performance, its theoretical specific capacity (372 mAh g^{-1}) is relatively low [2]. Hence, various alternative anode materials, such as Si (4200 mAh g^{-1}), Sn (994 mAh g^{-1}), and SnO_2 (782 mAh g^{-1}) have been intensively explored for development of lithium-ion batteries [3–5]. However, large volume expansion (100–300%) of these electrode materials during the repeated alloying and dealloying with Li ions causes pulverization of the electrode and loss of electrical contact, resulting in rapid capacity fading, which has delayed their practical application as electrodes [6].

Molybdenum disulfide (MoS_2), as a two-dimensional (2D) and layered compound, is composed of three atomic (S–Mo–S) layers stacked together through van der Waals interactions. This structure enables the easy intercalation of Li^+ ions between the MoS_2 layers without a significant volume change and exhibits a high theoretical capacity value (670 mAh g^{-1} based on 4 mol of Li ion insertion per formular) [7,8]. A recently developed liquid exfoliation strategy, which is similar to the preparation of graphene derived from graphite, allowed bulk MoS_2 crystals to be exfoliated into mono- or a few layers of MoS_2 [9]. The resulting MoS_2 nanosheets exhibited much better Li storage capabilities than the pristine bulk MoS_2 [10,11]. However, the cyclic stability and rate capability of the most MoS_2-based electrodes are still unsatisfactory due to the intrinsically poor electrical conductivity of the MoS_2. To address this issue, the integration of MoS_2 and carbonaceous materials, such as amorphous carbon, carbon nanotubes (CNTs) and graphene has been attempted, which has led to great improvement in cycling performances of MoS_2-based anodes for LIBs [12–17]. In particular, when using graphene materials, a macroscopically free-standing film form can be easily fabricated using a number of vacuum filtration, solution-casting, and layer-by-layer techniques [18–20]. Such film forms enable elimination of the use of insulating binders, conducting additives, and heavy current collectors in conventional battery structures, which can greatly reduce contact resistance and the total mass of the electrode.

Here, we report the fabrication of a free-standing MoS_2/graphene (MoS_2/G) composite paper using a simple vacuum filtration method. This sandwiched and layered structure is beneficial for rapid and efficient transfer of electrons and mechanical stability that can accommodate volume change, and thus leading to enhancement of electrochemical performances. As-prepared MoS_2/G composite paper can be directly used as binder- and carbon-free anodes without the need for additives for LIB applications. The MoS_2/G composite exhibited superior electrochemical performances compared to the exfoliated MoS_2 (e-MoS_2); high reversible capacity, high rate capability, and good cycling performance.

2. Experimental

2.1. Chemicals

Graphite powder (<20 μm), MoS_2 powder (~6 μm), *n*-butyllithium solution (1.6 M in hexane), hydrazine solution (65 wt% in water) were purchased from Aldrich. The isopropyl alcohol and hexane was obtained J.T.Baker.

2.2. Preparation of free-standing MoS_2/G composite paper

Free-standing composite papers were prepared by a flow-directed assembly. As staring materials, the graphene oxide (GO) and e-MoS_2 nanosheets were prepared by liquid exfoliation method [21,22]. The e-MoS_2 samples were particularly prepared by exfoliation of lithium-intercalated MoS_2 in solution. Briefly, MoS_2 powder (0.1 g) was purged by Ar gas for 2 h and was then filled with 1.6 M n-butyllithium (1 mL) in a sealed tube. Following an inserting reaction time of 48 h, the Li_xMoS_2 samples were washed several times with n-hexane and filtered to remove unreacted n-butyllithium. Finally, a solid powder was obtained by drying the sample overnight at room temperature under vacuum. As-prepared GO and e-MoS_2 nanosheets were dispersed in 1:1 (v/v) water and isopropyl alcohol solution and then sonicated for 60 min. The composite suspension was subsequently filtered by vacuum filtration through an anodic aluminium oxide membrane (0.2 μm pore size, Whatman). The resultant free-standing MoS_2/GO composite film was dried at room temperature and subsequently peeled off from the membrane. The free-standing MoS_2/G composite paper was obtained by exposure to hydrazine vapour at 80 °C for 10 h, in which the film was left well above the hydrazine solution level to avoid direct wetting.

2.3. Characterization

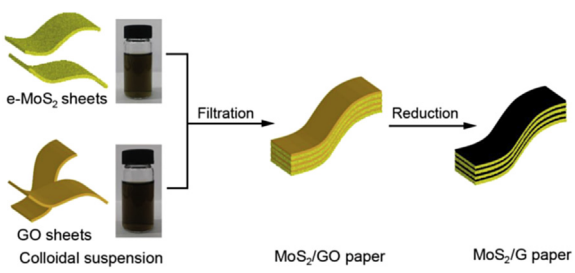
Transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) measurements were carried out using an E.M. 912 Ω energy-filtering TEM (JEM-2200 FS, JEOL). Scanning electron microscopy (SEM) images were obtained using a field emission SEM (S-4800, Hitachi). Raman spectra were measured using a high-resolution dispersive Raman microscope (ARAMIS, Horiba Jobin Yvon) with a 514 nm laser excitation as the light source. X-ray photoelectron spectroscopy (XPS) measurement was conducted using a Thermo MultiLab 2000 system. X-ray diffraction (XRD) data was obtained on a Rigaku D/MAX-2500 (40 kV, 300 mA, Cu Kα radiation).

2.4. Electrochemical measurements

Electrochemical tests were carried out using 2032 coin cells with the MoS_2/G composite paper as the working electrode and lithium foil as the counter electrode at room temperature. The cells were assembled inside an Ar-filled glovebox with 1 M $LiPF_6$ in 1:1 v/v ethylene carbonate/dimethyl carbonate as electrolyte and Celgard 2400 as separator. The cell was optimized with mass ratio of Li cathode to MoS_2/G anode (2.7–2.8). Cyclic voltammetry (CV) was performed using a VersaSTAT 4 (Princeton Applied Research) at scan rate of 0.5 mV s^{-1} in the voltage range of 3–0.01 V (vs. Li/Li^+). Galvanostatic charge/discharge cycles were tested using a WBCS 3000 automatic battery cycler (WonATech) at various current densities in a voltage range of 3–0.01 V (vs. Li/Li^+).

3. Results and discussion

Scheme 1 describes an experimental procedure for the preparation of MoS_2/G composite paper by vacuum filtration. Prior to preparing the MoS_2/G composite paper, the colloidal suspensions of e-MoS_2 and GO sheets were prepared. GOs were synthesized by the



Scheme 1. Schematic layout of an experimental process for the preparation of MoS_2/G composite paper.