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Growth of three dimensional flower-like molybdenum disulfide hierarchical structures on graphene/carbon nanotube network: An advanced heterostructure for energy storage devices

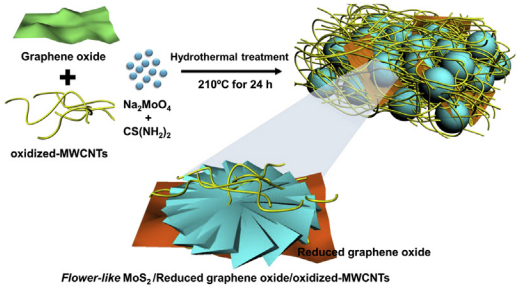
Niranjanmurthi Lingappan, Ngoc Huynh Van, Suok Lee, Dae Joon Kang*

Department of Physics, Sungkyunkwan University, Suwon 440-746, Republic of Korea

HIGHLIGHTS

- Flower-like MoS_2 grown on RGO/o-MWCNT backbone *via* hydrothermal process.
- Flower-like structure with the average size ranging between 1.1~1.3 μm formed.
- Formation and growth mechanism of the structures were investigated in detail.
- The as-prepared hybrid used as an anode for lithium-ion batteries.
- It exhibited enhanced electrochemical performance due to the rationally designed structure.

GRAPHICAL ABSTRACT



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ABSTRACT

We report the design and synthesis of three dimensional flower-like molybdenum disulphide (*f*-MoS_2) hierarchical structures, on reduced graphene oxide (RGO)/oxidized multi-walled carbon nanotube (o-MWCNT) backbone (*f*-MoS_2/RGO/o-MWCNT), through one-pot hydrothermal method. Control experiments reveal that the homogenously distributed o-MWCNTs on RGO play an essential role for the formation of such morphology. As an anode for lithium ion batteries, the *f*-MoS_2/RGO/o-MWCNT hybrid delivers a high reversible capacity of 1275 mAh g^{-1} at the current density of 100 mA g^{-1}, superior rate capability and excellent long cycle life, with capacity retention of 93% after 100 cycles. The outstanding electrochemical performance can be attributed to the large surface area, short diffusion length and continuous electron transport pathway, as a consequence of the intimate contact between *f*-MoS_2, graphene, and o-MWCNTs.

1. Introduction

The rapid depletion of fossil fuels, and environmental pollution have sparked an unprecedented research effort towards the development of high performance energy storage devices [1]. Consequently, there is an urgent need for reliable energy storage systems with high energy and power densities, to meet the ever-growing demands for portable electronics and electric vehicles applications. Undoubtedly, lithium-ion-batteries (LIBs) represent a prominent technology due to their high energy density, lack of memory effect, and environmental friendliness [2]. For high-power applications, the power density, rate capability, and cycling stability

* Corresponding author.
E-mail address: djkang@skku.edu (D.J. Kang).

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should be substantially improved. Thus, exploring new electrode materials and modifying the existing electrode structures have become a primary task for the current research community [3].

Discovery of graphene has stimulated great interest in other two-dimensional (2D) structures, with respect to their unique structure, and unusual properties [4–7]. One of the most fascinating 2D materials, ultrathin molybdenum disulfide (MoS_2) layered structure, has been extensively investigated for diverse applications [8–13]. MoS_2 has a hexagonal crystal structure, with molybdenum atoms sandwiched between two layers of S atoms, which are held together by weak van der Waals interaction [14]. Such weak interlayer interaction renders MoS_2 nanosheet as a prominent host for intercalation chemistry based cathodes [15]. MoS_2 has also been explored as an anode in LIBs based on the conversion-type reaction mechanism [16]. However, while pioneering works have witnessed the superiority of layered structures, the restacking between the sheets significantly reduces its processability, and deteriorates other structural features. In addition, the moderate conductivity limits the electrode kinetics and electron transfer efficiency; this results in low active material utilization, and poor electrochemical performances [17]. The coupling of MoS_2 nanosheets with carbon nanostructures has proven to be an effective strategy to overcome the aforementioned issues [18–21]. Of various carbon nanostructures, graphene has emerged as an advanced material for various energy storage and electronic devices, due to its high carrier mobility, large specific surface area, and excellent chemical stability [22]. Carbon nanotubes also continue to gain unwavering attention, for their excellent conduction, high degree of resiliency, and superior mechanical properties [23].

A current area of interest for both fundamental research and practical applications is the manipulation of 2D structures [24]. In this context, three dimensional (3D) hierarchical structures appear to be a promising platform, because of their ultrahigh surface area [25], better permeability [26] and improved electrical properties [27] which are highly beneficial for catalysis, gas adsorption, and energy storage applications [28–30]. More importantly, 3D structures can significantly reduce the self-aggregation of active materials, and ensure high utilization efficiency [31]. Recently, various 3D MoS_2 hierarchical structures have been demonstrated to exhibit superior electrochemical behaviors due to the fast ion diffusion and ion transport [32–36]. In spite of that, most of these fabrication methods require complex and multiple-steps, and some in some cases; the structure possesses moderate electrical conductivity, which further limits their electrochemical performances. Thus, developing a simple and cost-effective approach for the large-scale synthesis of 3D MoS_2 hierarchical structures with high electrical conductivity is highly desirable for various applications.

Herein we demonstrate an effective approach for the large-scale synthesis of flower-like MoS_2 (*f*-MoS_2) hierarchical structures on reduced graphene oxide (RGO)/oxidized-multi-walled carbon nanotubes (o-MWCNTs) backbone (*f*-MoS_2/RGO/o-MWCNT), through one-pot hydrothermal process. Due to the heterogeneous nucleation effect, the ideal combination of RGO/o-MWCNTs results in the formation of flower-like structures. As an anode material for LIBs, the *f*-MoS_2/RGO/o-MWCNT hybrid demonstrates the outstanding electrochemical performances with a highest specific capacity, excellent cycling stability and remarkable rate capability.

2. Experimental

2.1. Synthesis of f-MoS_2/RGO/o-MWCNT hybrid

15 mg of GO and 15 mg of o-MWCNTs (weight ratio, 1:1) were dispersed in 30 mL of DI water, and ultrasonicated for 1 h, in order to obtain homogeneous dispersion. Then, 0.2 g of $Na_2MoO_4.2H_2O$ (1 mmol) and 0.36 g of thiourea (5 mmol) were dissolved in 100 mL of DI water, and the reaction mixture was added into the GO/o-MWCNTs dispersion, and stirred for 1 h. The homogeneous dispersion was then transferred into a 150 mL Teflon-lined autoclave, heated up to 210 °C, and maintained at this temperature for 24 h. The resultant black precipitate was centrifuged, washed three times with DI water, followed by ethanol, and freeze-dried under vacuum. For comparison, MoS_2/RGO and MoS_2/o-MWCNT hybrids were also prepared *via* the same procedure. In the case of MoS_2/RGO, 30 mg of GO was dispersed in DI, and then followed by the same synthetic procedure. In the case of MoS_2/o-MWCNT, 30 mg of o-MWCNTs were dispersed in DI water, and then followed by the above mentioned procedure.

2.2. Characterization

The surface morphology was studied by field-emission scanning electron microscopy (FESEM, Hitachi; JSM6300, Japan), and elemental analysis was performed with energy dispersive X-ray (EDS) spectroscopy. Field emission transmission electron microscope (FETEM) images were acquired with a transmission electron microscope of JEM-1011 at an accelerating voltage of 100 kV. X–ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos AXIS HSi spectrometer with a monochromatized Al Kα X-ray source (1486.6 eV photons), at a constant dwell time of 100 ms, and the energy of 40 eV. The anode voltage and current were set at 15 kV and 10 mA, respectively. Thermogravimetric analysis (TGA) was carried out using a Perkin Elmer Pyris 1 TGA with a heating rate of 10 °C min^{-1} under ambient atmosphere. X-ray diffraction (XRD) patterns were recorded on Rigaku X-ray diffractometer with Cu Kα (λ = 1.5418 A°), and the data were collected in the 2θ of 5°–80°, at a scanning rate of 2 °C min^{-1}. N_2 sorption analysis was recorded from a Quantachrome autosorb iQ2 instrument, equipped with automated gas absorb analyzer, at 77 K using Barrett-Emmett-Teller (BET) calculations for the surface area.

2.3. Electrochemical measurements

The working electrode was fabricated, by mixing the active material (*f*-MoS_2/RGO/o-MWCNT, MoS_2/RGO, MoS_2/o-MWCNT) and polyvinylidene fluoride binder, in the weight ratio of 90:10 in N-mehyl-2-pyrrolidinone, and then coated onto a Cu foil current collector, and dried at 80 °C for 12 h, to remove the solvent. The loading mass of the each electrode was calculated to be ~1.1 mg. Electrochemical measurements were performed, using two-electrode coin-type cells, with lithium foil serving as both counter and reference electrodes, under ambient temperature. The electrolyte was 1 M $LiPF_6$, in a 50:50 (w/w) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Cell assembly was carried out in an argon-filled glove box, with both moisture and oxygen contents below 1.0 ppm. Galvanostatic charge/discharge tests were performed, using a battery tester in the voltage range of 0.001–3.0 V.

3. Results and discussion

Fig. 1 shows the schematic illustration for the synthesis of 3D *f*-MoS_2/RGO/o-MWCNT hybrid. This method utilizes graphene oxide (GO) and o-MWCNTs as carbon precursors, and sodium molybdate and thiourea as inorganic precursors, without any additional template or structure-directing agent. Briefly, the GO and o-MWCNTs were dispersed in DI water and ultrasonicated in order to achieve a homogeneous dispersion. Such pre-dispersed GO/o-MWCNTs mixture can effectively inhibit the agglomeration and restacking of both RGO sheets and MWCNTs, which is advantageous, in that it