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High-performance supercapacitor based on three-dimensional MoS_2/graphene aerogel composites

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ABSTRACT

Three-dimensional (3D) MoS_2/chemically modified graphene (CMG) aerogel composites are prepared by a hydrothermal reduction reaction. Such 3D architecture enables effective electron and ion transfer and stable distribution of 2D nanosheets. 3D MoS_2/CMG composites are investigated as supercapacitor electrode materials, showing a high specific capacitance of 268 F g^{-1} at 0.5 A g^{-1}, a high rate capability with 87.7% retention up to 15 A g^{-1}, and a good cycle life with 93% retention for 1000 cycles. Electrochemical impedance spectroscopy analysis reveals that the 3D interconnected structure of MoS_2/CMG enhances the charge transfer and facilitates diffusion of electrolyte ions.

1. Introduction

In response to the increasing energy demand in the 21st century, supercapacitors have become promising energy storage devices due to their high power density, rapid charging/discharging time, long cycle life, and simple configuration [1,2]. To date, nanostructured materials with high surface area have been widely applied to improve charge storage and ion diffusion in electrodes of supercapacitors [3]. Two-dimensional (2D) nanosheets, particularly monolayer graphene and metal disulfides (MDSs), are of great interest and importance in development of supercapacitor electrodes due to their high surface area, shortened ion transport, and capability for charge storage [4–8]. The intrinsic specific capacitance of graphene was recently found to be 21 μF cm^{-2} (550 F g^{-1}) based on electric double-layer storage, which is higher than conventional carbon-based materials [9]. However, the practical specific capacitance of CMG-based supercapacitor exhibits lower specific capacitances (100–220 F g^{-1}) than theoretical capacitance values when aqueous and organic electrolytes are used [10–14]. On the other hand, MoS_2 sheets have the potential to charge not only via formation of intra- and intersheet double layers on individual atomic MoS_2 sheets, but also through a Faradaic reaction that originated from a wide range of oxidation states from +2 to +6 on the center Mo atoms, similar to RuO_2 (theoretical capacitance of ~1000 F g^{-1}) [15–18]. MoS_2-based electrodes have typically reached a specific capacitance of around 100 F g^{-1} using an aqueous electrolyte [19–21]. In most cases, the intrinsic poor electrical conductivity of MoS_2 leads to inferior electrochemical performance of supercapacitors. In addition, most 2D nanosheets still suffer from irreversible sheet aggregation owing to intersheet van der Waals forces, which are responsible for a dramatic reduction in specific surface area [22].

The integration of nanobuilding blocks into three-dimensional (3D) frameworks is one of the most promising techniques for transfer of unique properties at the nanoscale to the macroscopic properties of the devices [23–26]. Such 3D architectures (e.g., aerogels, hydrogels, foams, and sponges) have offered large surface area, low density, high electronic and ionic conductivity, and good mechanical properties, which make it an ideal material for advanced energy storage and conversion devices. Inspired by these results, we developed 3D MoS_2/CMG aerogel composites using a hydrothermal assembly. As-prepared composites reversibly stored an electrical charge on their surface with a highly specific capacitance, high rate capability, and long-term cycling performance.

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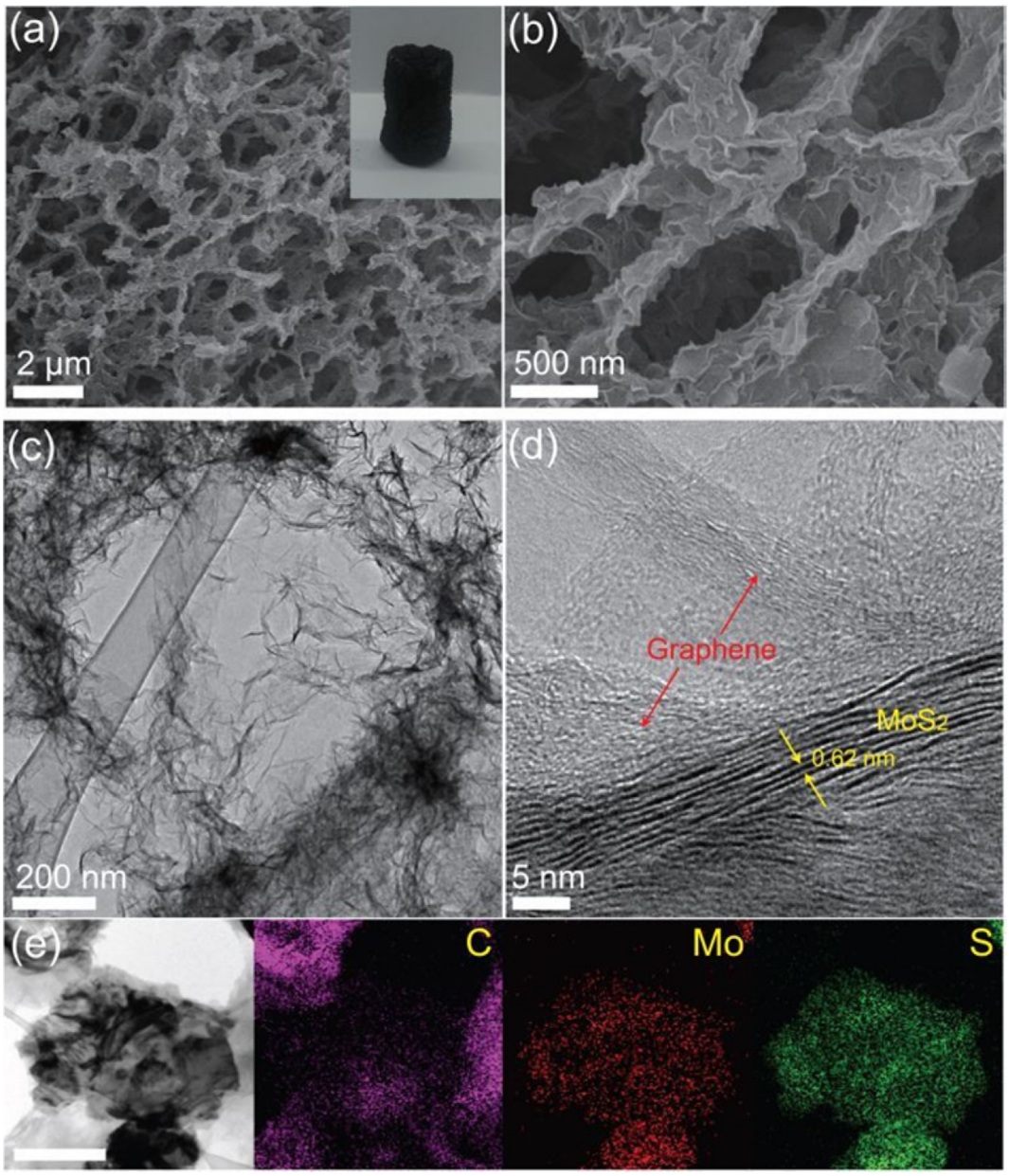

Fig. 1. (a) and (b) SEM images of interior microstructure of 3D MoS_2/CMG composite (Inset of Fig. 1a is photograph image of free-standing 3D MoS_2/CMG composite). (c) Low-magnification and (d) High-resolution TEM images of 3D MoS_2/CMG composite. (e) High-resolution TEM image and EDX mapping images of Mo, S and C signals of 3D MoS_2/CMG composite (scale bar, 1 μm).

2. Experimental section

Graphene oxide (GO) nanosheets were prepared by the modified Hummers method as described in our previous report [27]. MoS_2 nanosheets were obtained using the lithium intercalation method according to a previously reported procedure [28]. 3D MoS_2/CMG aerogel composite was fabricated by a hydrothermal assembly and reduction reaction. Typically a 10 mL MoS_2 (2 mg mL^{-1}) aqueous dispersion was mixed with a 10 mL GO (5 mg mL^{-1}) aqueous dispersion. The mixture of MoS_2/GO was then sonicated for 1 h, after which it was sealed in a Teflon-lined autoclave and heated at 180 °C for 12 h. Finally, the 3D aerogel composite was obtained via a freeze-drying process of the resulting hydrogel.

The morphology and microstructure of 3D MoS_2/CMG samples were investigated using a field emission scanning electron microscope (SEM, Hitachi S-4800) and transmission electron microscope (TEM, JEOL Ltd. JEM2100F) operated at 200 kV. Thermogravimetric analysis (TGA) was conducted using a TGA 92-18 (Setaram) with a heating rate of 10 °C min^{-1}. N_2 adsorption/desorption was determined by Brunauer-Emmett-Teller (BET) measurements using an ASAP-2010 surface area analyzer. X-ray photoelectron spectroscopy (XPS) data were obtained using a Thermo MultiLab 2000 system with an Al Mgα X-ray source at 200 W. The X-ray diffraction (XRD) data were obtained on a Rigaku D/max IIIC (3 kW) with a q/q goniometer equipped with a CuKa radiation generator. The diffraction angle of the diffractograms was in the range of $2\theta = 5°–80°$. The Raman spectra were obtained using an ARAMIS Spectra spectrometer (Horiba Jobin Yvon, France).

Electrochemical characterization was performed in a three-