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Nitrogen-doped carbon-coated molybdenum disulfide nanosheets for high-performance supercapacitor

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ABSTRACT

Although exfoliated MoS_2 sheets have recently demonstrated their great potential for use as electrodes for supercapacitors, they suffer from poor intrinsic electrical conductivity and strong tendency for intersheet aggregation. Here, we develop a synthetic method for preparation of *N*-doped carbon-coated MoS_2 (NC-MoS_2) nanosheets composed of coating of polydopamine and a post carbonization process. Construction of carbon layers on the MoS_2 surface enables effective prevention of sheet aggregation and provide a rapid pathway for electron transfer. As-prepared NC-MoS_2 materials are then characterized by electrochemical measurements to demonstrate the superior performance of the supercapacitor electrodes. The NC-MoS_2 electrode exhibits improved electrochemical performance relative to the exfoliated MoS_2 sheets, with a high specific capacitance (158 F g^{-1}), high rate capability (83% retention), and good cycling life (89% retention) during 1000 cycles.

1. Introduction

Supercapacitors typically store electrical charges by adsorption of electrolyte ions or reversible redox reactions onto the surface of electrode materials. These unique storage mechanisms make them attractive energy-storage systems that can deliver high power density while maintaining a long cycling life [1–3]. In this regard, the features of electrode materials, such as size, morphology, and surface functional groups are essential to achieving high-performance sueprcapacitors [4–6]. Two-dimensional (2D) graphene materials have attracted increasing attention in the development of supercapacitors owing to their large surface area, high electrical conductivity, and excellent electrochemical properties [7–10]. The great potentials of monolayer graphene have stimulated synthesis of other 2D thin materials, including metal dichalcogenides (e.g., WS_2, TiS_2, and MoS_2), oxides, and hydroxides [11–16]. These 2D dichalcogenides can be exfoliated down to a monolayer by solution-based chemical methods similar to those used in production of chemically prepared reduced graphene oxides [11,12,14].

MoS_2 nanosheets have become one of the most promising electrode materials for energy storage devices due to easy accessibility for ion intercalation and high theoretical specific capacitance (>1000 F g^{-1}) [17–26]. More importantly, MoS_2 has the potential to store charges not only by formation of double layers on inter- and intra-sheet of individual MoS_2, but also via faradic reactions on Mo transition metal centers using a wide range of oxidation states from +2 to +6 [20]. Cao et al. reported that the MoS_2-based micro-supercapacitors exhibit a high specific capacitance of 8 mF cm^{-2} (volumetric capacitance of 178 F cm^{-3}) [21]. Despite this previous work, testing of macroscopic electrodes revealed that the specfic capacitance values of MoS_2 were inferior, even though the morphology was controlled, with values of 92.85 F g^{-1} for sphere-like MoS_2 [22] and 129.2 F g^{-1} for flower-like MoS_2 being observed [23]. The poor performance of MoS_2 primarily originates from both the poor electrical conductivity and strong tendency for intersheet aggregation of MoS_2. Although various carbon additives have recently been coupled to MoS_2 nanosheets to improve electrical conductivity [27–29], the restacking and aggregation of exfoliated MoS_2 (e-MoS_2) still remain a challenge in MoS_2-based supercapacitors.

Herein, we report a simple and efficient method for preparation of ultrathin MoS_2 sheets coated with *N*-doped carbon layers from polydopamine. Dopamine, which is composed of catechol and amine functional groups, can spontaneously self-polymerize under alkaline pH values and deposit polydopamine films on any surface of organic and inorganic materials [30]. This polydopamine coating allowed us to efficiently prevent aggregation of MoS_2 sheets and

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provide *N*-doped carbon shells onto the MoS_2 surface by a post carbonization process. Using these unique properties of *N*-doped carbon coated MoS_2 (NC-MoS_2), we demostrate that core–shell structured NC-MoS_2 electrodes showed improved specific capacitance, rate capability, and cycling performance relative to the bare MoS_2.

2. Experimental

2.1. Materials

Molybdenum disulfide, dopamine hydrochloride, *n*-butyl lithium (1.6 M), and tris(hydroxymethyl) aminomethane were obtained from Sigma–Aldrich. Hydrochloric acid and sulfuric acid were purchased from Junsei. All materials were commercially available and employed without further purification.

2.2. Synthesis of NC-MoS_2

Prior to preparation of NC-MoS_2 samples, e-MoS_2 samples were obtained by the lithium intercalation method, as previously described reports [31]. Briefly, MoS_2 flakes (0.1 g) were lithiated by soaking in 1 mL of 1.6 M *n*-butyl lithium under an argon atmosphere for 24 h. The Li_xMoS_2 powder was then obtained by washing several times with de-ionized (DI) water, after which it was dried under vacuum at 60 °C for 24 h. To obtain polydopamine-coated (PDA-MoS_2) sample, the Li_xMoS_2 samples were re-dispersed in 75 mL of tris-buffer solution (10 mM, pH 8.5) through gentle sonication. Next, 150 mg of dopamine hydrochloride was added, and then the mixture was stirred at 80 °C for 2 h. After washing and centrifuging several times, PDA-MoS_2 samples were collected. To obtain the NC-MoS_2, the resulting PDA-MoS_2 was placed in a tubular furnace under N_2 atmosphere and kept to 400 °C for 2 h and 800 °C for 3 g at a heating rate of 1 °C min^{-1} and 5 °C min^{-1} for 3 h, respectively.

2.3. Structural characterization

Transmission electron microscopy (TEM), high-angle annular dark-field scanning TEM (HAADF-STEM) images and elemental mapping were conducted using an E.M. 912 Ω energy-filtering TEM (JEM2100F, JEOL Ltd.) at 200 kV. Scanning electron microscopy (SEM) images were obtained using a field emission SEM (S-4800, Hitachi). X-ray photoelectron spectroscopy (XPS) data were obtained using a Thermo MultiLab 2000 system with an Al Mgα X-ray source. X-ray diffraction (XRD) data were collected on a Rigaku D/max 111C (3 kW) with a q/q goniometer equipped with a CuKa radiation generator. The diffraction angle of the diffractograms was in the range of $2\theta = 5–80°$.

2.4. Electrochemical characterization

Prior to being used as a current collector, the Ti foil was rinsed in an ultrasonic bath of a solution of 0.5 M H_2SO_4 for 10 min and then washed with acetone followed by DI water for 10 min. The working electrode, which was composed of a slurry of 80 wt% active material (NC-MoS_2 or e-MoS_2), 10 wt% poly(vinylidenedifluoride) and 10 wt% activated carbon, was coated onto a pretreated Ti foil current collector (≈2.0 mg cm^{-2}) and then dried at 60 °C overnight in a vacuum oven. All electrochemical measurements were performed in a three-electrode electrochemical cell in 1 M Na_2SO_4 at room temperature. A Pt wire and an Ag/AgCl electrode were used as the counter and as the reference electrode, respectively. Cyclic voltammetry (CV) and galvanostatic charge/discharge measurements were performed with a CHI 760E electrochemical workstation (CH Instruments). A life cycling test was taken by galvanostatic charge/discharge measurements at 1 A g^{-1} of current density up to 1000 cycles. Electrochemical impedance spectroscopy (EIS) measurements were performed over a frequency range from 10^5 to 10^{-2} Hz at sinus amplitude of 10 mV using a VersaSTAT 4 (Princeton Applied Research). The as-obtained data were within the error range of ±1%.

3. Results and discussion

Bulk MoS_2 typically has a compacted and layered structure due to the strong intersheet interactions of van der Walls forces (Fig. 1a) [32]. Conformal coating of PDA on e-MoS_2 through oxidative self-polymerization of dopamine led to a stable colloidal dispersion in water and maintained the exfoliated states (Fig. 1b), attributed to deprotonation of catechol —OH groups of PDA [33]. Obviously, the folded MoS_2 sheets were ascribed to the high flexibility of a few layers of MoS_2 (Fig. 1b). The NC-MoS_2 nanosheets were obtained after carbonization of PDA by calcination of the PDA-MoS_2 samples (Fig. 1c). Examination by high resolution-TEM revealed that graphitic carbon layers of ∼2.5 nm were conformally coated on the surface of MoS_2 sheets (Fig. 1d). The uniform coating of *N*-doped carbon was further confimed by element mapping measurements according to the HADDF-STEM image (Fig. 2). The molybdenium and sulfur signals for MoS_2 and nitrogen and carbon signals for *N*-doped carbon completely overlapped.

Fig. 3a shows the XRD patterns of bulk MoS_2 and NC-MoS_2 samples. In contrast to the sharp diffraction peak at 14.2° of bulk MoS_2, the X-ray diffraction (XRD) pattern of the NC-MoS_2 samples show a broad and weak shift peak at 13.95°. These results suggest that MoS_2 nanosheets are still exfoliated after carbonization, which was due to being prevented re-stacking of e-MoS_2 sheets by the carbon layer derived from conformal coating of PDA onto e-MoS_2 sheets. The chemical composition of the NC-MoS_2 was characterized by X-ray photoelectron spectroscopy (XPS) measurements (Fig. 3b). The NC-MoS_2 sample contained newly appeared C 1s, O1s and N1s peaks in response to conformal coating and carbonization of PDA on e-MoS_2, which was in agreement with HADDF-STEM results. The surface elemental composition of NC-MoS_2 was further investigated by high resolution XPS (Fig. 3c). The C1s spectrum of NC-MoS_2 exhibited four different C groups: graphitic C at 284.52 eV, N-sp^2 C at 285. 37 eV, C—OH at 286.15 eV, N-sp^3 C at 287.41 eV, and C=O at 289.59 eV, respectively [34,35]. The N1s spectrum that overlapped with the Mo3p spectrum (396.54 eV) in the range from 390 to 408 eV reveals the local chemical two characteristic peaks (Fig. 3d). The peaks at 399.27 eV corresponds to pyrrolic or pyridonic N, which contributed electron density of two *p*-electron to the π-conjugated system in the graphitic carbon layer [35]. Another N1s peak at 401.64 eV is graphitic N, which is located inside the graphitic carbon plane and bonds with three sp^2 carbon atoms [34,35]. These results demonstrated that PDA was completely converted into an *N*-doped carbon with small amount of oxygen functional groups after carbonization.

The electrochemical performance of NC-MoS_2 was evaluated by CV measurement (Fig. 4). The e-MoS_2 sheets were also tested as a reference sample under identical experimental conditions as those used for NC-MoS_2. Fig. 4 shows the CV curves of the NC-MoS_2 and e-MoS_2 electrodes at a scan rate of 50 mV s^{-1} with a potential window ranging from −0.5 to +0.5 V versus Ag/AgCl in 1 M Na_2SO_4 electrolyte. As expected, the CV of the NC-MoS_2 electrode had a higher integrated area than that of the e-MoS_2 electrode when analyzed at the same scan rate. In addition, the NC-MoS_2 electrode exhibited non-rectangular shape, which is indicative of the combined contribution of faradaic and non-faradaic reactions of the MoS_2 sheet and N-doped carbon. More specifically, MoS_2