Dopamine-Mo\textsuperscript{VI} complexation-assisted large-scale aqueous synthesis of single-layer MoS\textsubscript{2}/carbon sandwich structure for ultrafast, long-life lithium-ion batteries

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Experimental Section

Materials

Dopamine hydrochloride (DOPA-HCl), thioacetamide (TAA), sodium molybdate dihydrate (Na\textsubscript{2}MoO\textsubscript{4}.2H\textsubscript{2}O), sodium tungstate dihydrate (Na\textsubscript{2}WO\textsubscript{4}.2H\textsubscript{2}O), ferric chloride hexahydrate (FeCl\textsubscript{3}.6H\textsubscript{2}O) and bulk MoS\textsubscript{2} powder (< 2\textmu m) were purchased from Sigma-Aldrich (USA) and used as received. Electrolyte (1M LiPF\textsubscript{6} in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) at a 1:1 volume ratio) and lithium foil were purchased from Charslton Technologies Pte Ltd (Singapore).

Synthesis of SLMoS\textsubscript{2}/C composite

The SLMoS\textsubscript{2}/C composite was synthesized using hydrothermal method. Typically, 300 mg Na\textsubscript{2}MoO\textsubscript{4}, 900 mg DOPA-HCl and 900 mg TAA were dissolved in 20 ml deionized water, respectively, and then transferred to a 100 ml Teflon-lined autoclave. The suspension was kept at 200 °C for 16 hours. After cooling down, the black precipitates were collected by centrifugation and washed with DI water and ethanol for 3 times. The obtained sample was annealed at 700 °C for 3 hours in argon to eliminate the surface functional groups.

Synthesis of Fe\textsubscript{3}O\textsubscript{4}/C and WO\textsubscript{2}/C composites
1 mmol Na$_2$WO$_4$.2H$_2$O and FeCl$_3$.6H$_2$O were dissolved in 60 ml deionized water and then mixed with 4 mmol DOPA-HCl, respectively. The suspensions were transferred to a 100 ml Teflon-lined autoclave and kept at 160 °C for 16 hours directly. The obtained samples were annealed at 400 °C for 3 hours in argon.

**Characterization**

The morphologies of the samples were studied using a field-emission scanning electron microscope (FESEM, JEOL JSM 7600) at an accelerating voltage of 5 kV and a transmission electron microscope (TEM, JEOL 2100) at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Kratos Analytical AXIS His spectrometer with a monochromatized Al Ka X-ray source (1486.6 eV photons). X-ray diffraction (XRD) patterns were recorded on a Bruker GADDS X-ray diffractometer. Fourier transform infrared spectroscopic (FTIR) measurements were performed using a Shimadzu FTIR IR Prestige-21 using KBr pellets. The compositions of the samples were determined by thermogravimetric analysis (TGA, TA Q500). All the samples were heated from room temperature to 600 °C in air. The UV absorption spectra were measured using a Shimadzu UV-3600 UV–vis–NIR spectrophotometer. Raman spectra were obtained by using WITec CRM200 confocal Raman microscopy system (WITec, Germany) with a laser wavelength of 532 nm.

**Electrochemical measurements**

The electrochemical performances were evaluated with a standard CR2032 coin cell. A Celgard® 2600 membrane is used as the separator. The working electrode was composed of 70 wt% composites, 20 wt% Super P carbon black, and 10 wt% polyvinylidene fluoride. The typical loading of the anode in the electrode was 2 to 3 mg. The electrochemical tests were performed on a NEWARE BTS-5V10mA battery tester. The cells were cycled between
0.005~3.0 V vs Li+/Li. The specific capacity and current density were calculated based on the weight of the SLMoS$_2$/C composite. The cyclic voltammetry (CV) was studied on a PGSTAT302N Autolab electrochemical workstation with a voltage window of 0.005~3.0 V and a scan rate of 0.1 mV/s. The electrochemical impedance spectroscopy (EIS) was measured in the frequency range of $10^{-2}$ to $10^6$ Hz with an AC voltage amplitude of 5 mV.

![Fig. S1. Photo images of DOPA-HCl, Na$_2$MoO$_4$ and DMC solutions.](image)

![Fig. S2. FTIR spectra of DOPA-HCl, Na$_2$MoO$_4$ and DMC.](image)
Fig. S3. XPS spectra of DOPA-HCl, Na$_2$MoO$_4$, DMC and SLMoS$_2$/C.

Fig. S4. TEM images of the DMC.
Fig. S5. FTIR spectra of the DMC-HT and SLMoS$_2$/C.

Fig. S6. TGA curves of (a) SLMoS$_2$/C and (b) DMC-HT. The large weight loss between 200-450 °C is caused by the combustion of carbon and conversion of MoS$_2$ to MoO$_3$ in air.
Fig. S7. (a) SEM and (b) TEM images of DMC-HT.

Fig. S8. TEM images of (a) Fe$_3$O$_4$/C and (b) WO$_2$/C composites after annealing.
In the first discharge, a slope starts at about 1.5 V is indicative of the formation of Li$_x$MoS$_2$. The inconspicuous conversion is caused by the expanded (002) spacing, low crystallinity and disordered structure of SLMoS$_2$. The Li$_x$MoS$_2$ then decomposes into Mo nanoparticles embedded in Li$_2$S matrix, giving a cathodic peak at about 0.5 V. The slope below 0.25 V is
assigned to the formation of a solid electrolyte interphase (SEI) film. During the anodic scanning, 
Li\(^+\) stored within the carbon and defects of SLMoS\(_2\)/C are firstly released, together with the 
partially oxidation of Mo, leading to broad oxidation peaks centered at about 0.5 V and 1.3 V, 
respectively. The pronounced peak at about 2.3 V is associated with the oxidation of Li\(_2\)S to 
sulfur.\(^4\) Therefore, MoS\(_2\) converts to a mixture of sulfur and Mo metal after the first cycle. 
Accordingly in the following cycles, the reduction peak at 2.0 V can be attributed to the 
formation of Li\(_2\)S, and the association of Li\(^+\) ions with Mo is found at 1.0 V.\(^5\) 

![Image showing the cycling performance of the SLMoS\(_2\)/C anode at a current density of 50 mA/g.](image)

Fig. S11. Cycling performance of the SLMoS\(_2\)/C anode at a current density of 50 mA/g.
The Nyquist plots SLMoS\(_2\)/C anodes consist of one semicircle at high and medium frequencies and a straight line at low frequencies, corresponding to the charge transfer resistance at the electrolyte/electrode interface and the solid-state diffusion resistance of Li\(^+\) in the electrode, respectively. After cycling, the interfacial charge-transfer resistance increases because of the SEI layer formed and destruction of the MoS\(_2\) structure during cycling.

references