Electronic Supplementary Material (ESI) for ChemComm.

Dopamine-Mo^{VI} complexation-assisted large-scale aqueous synthesis of single-layer MoS_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 ($Na_2MoO_4.2H_2O$), sodium tungstate dihydrate ($Na_2WO_4.2H_2O$), ferric chloride hexahydrate ($FeCl_3.6H_2O$) and bulk MoS_2 powder (< 2μm) were purchased from Sigma-Aldrich (USA) and used as received. Electrolyte (1M $LiPF_6$ 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 $SLMoS_2$/C composite

The $SLMoS_2$/C composite was synthesized using hydrothermal method. Typically, 300 mg Na_2MoO_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_3O_4/C and WO_2/C composites

1 mmol $Na_2WO_4.2H_2O$ and $FeCl_3.6H_2O$ 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 ^oC 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 ^oC 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.

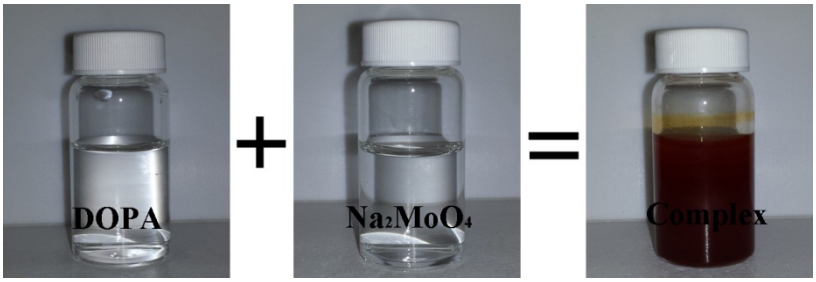

Fig. S1. Photo images of DOPA-HCl, Na_2MoO_4 and DMC solutions.

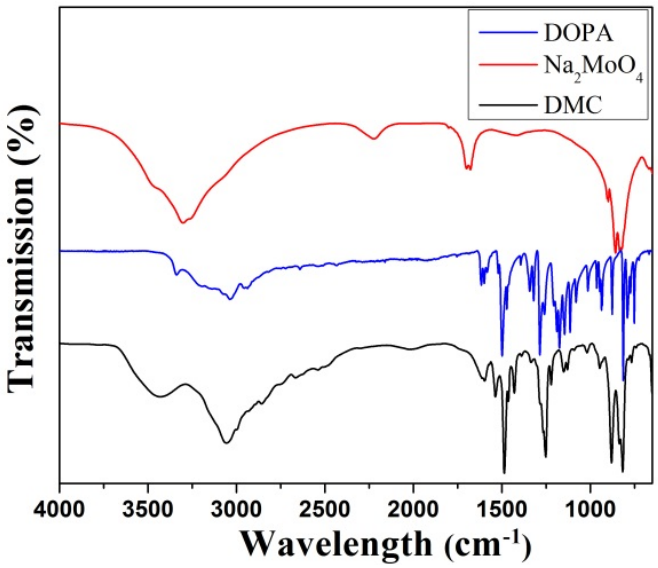

Fig. S2. FTIR spectra of DOPA-HCl, Na_2MoO_4 and DMC.

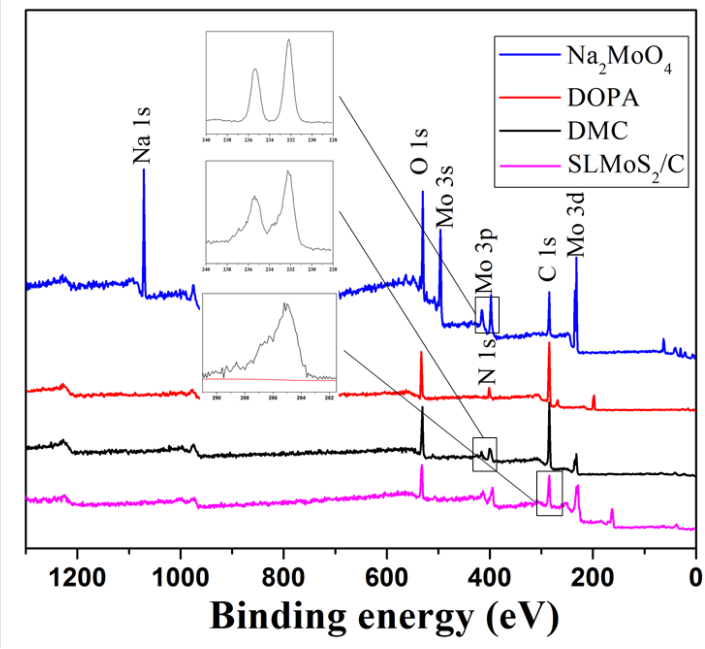

Fig. S3. XPS spectra of DOPA-HCl, Na_2MoO_4, DMC and $SLMoS_2/C$.

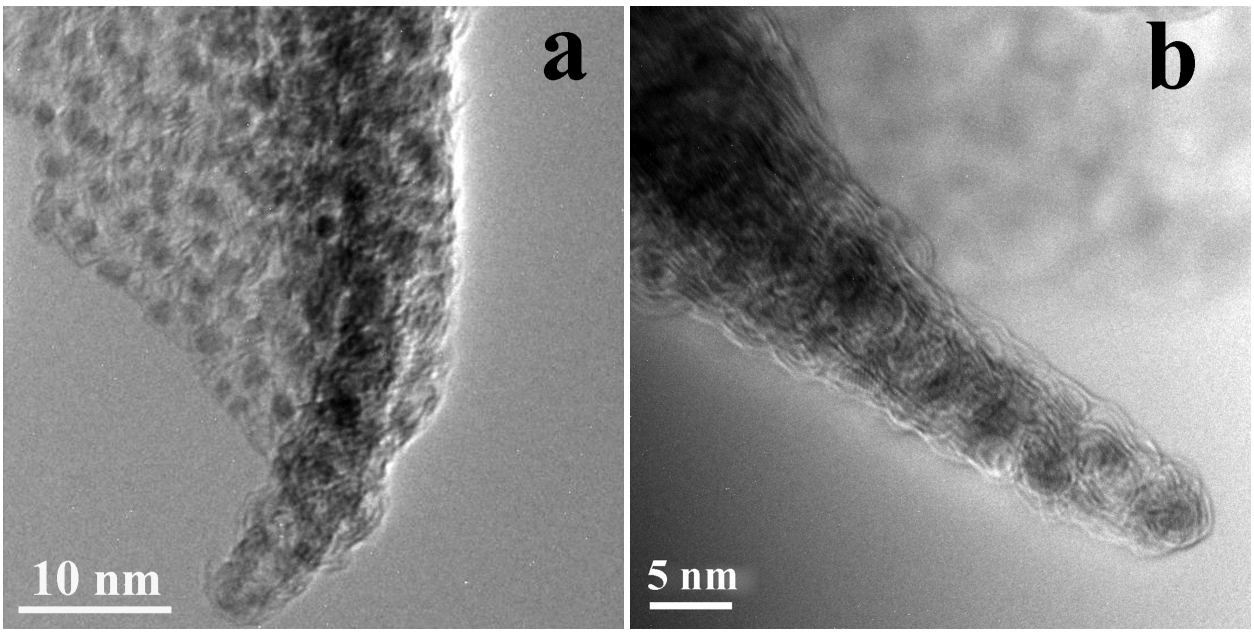

Fig. S4. TEM images of the DMC.

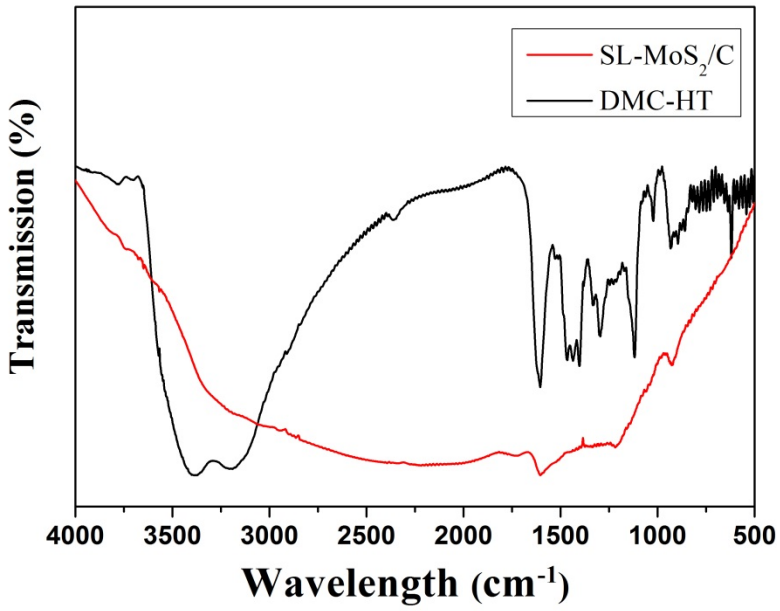

Fig. S5. FTIR spectra of the DMC-HT and SLMoS$_2$/C.

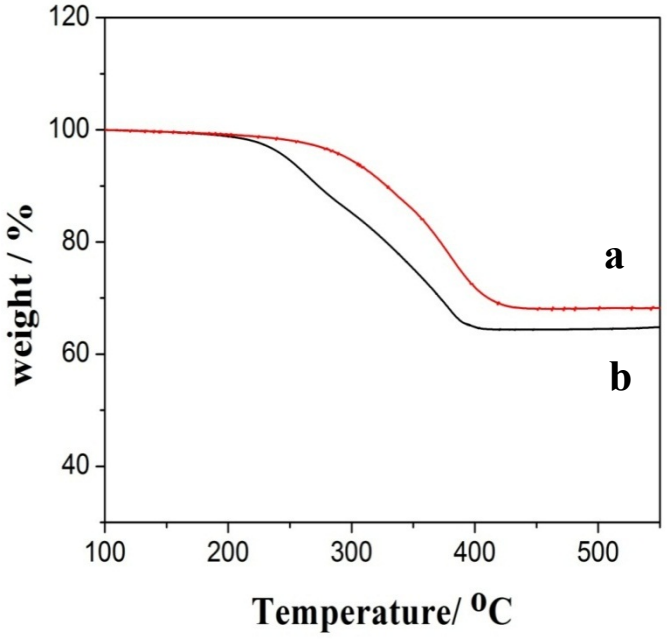

Fig. S6. TGA curves of (a) SLMoS$_2$/C and (b) DMC-HT. The large weight loss between 200-450 °C is caused by the combustion of carbon and conversion of MoS_2 to MoO_3 in air.

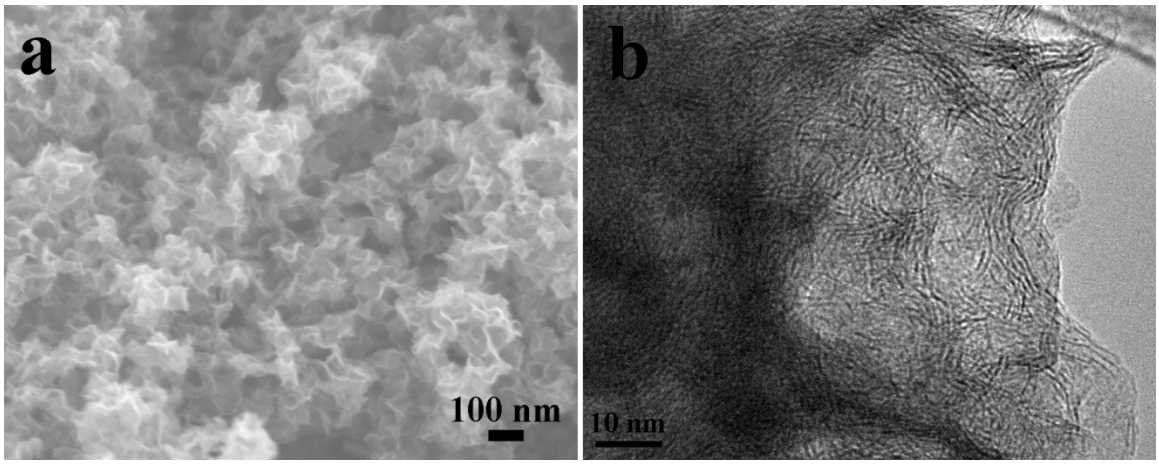

Fig. S7. (a) SEM and (b) TEM images of DMC-HT.

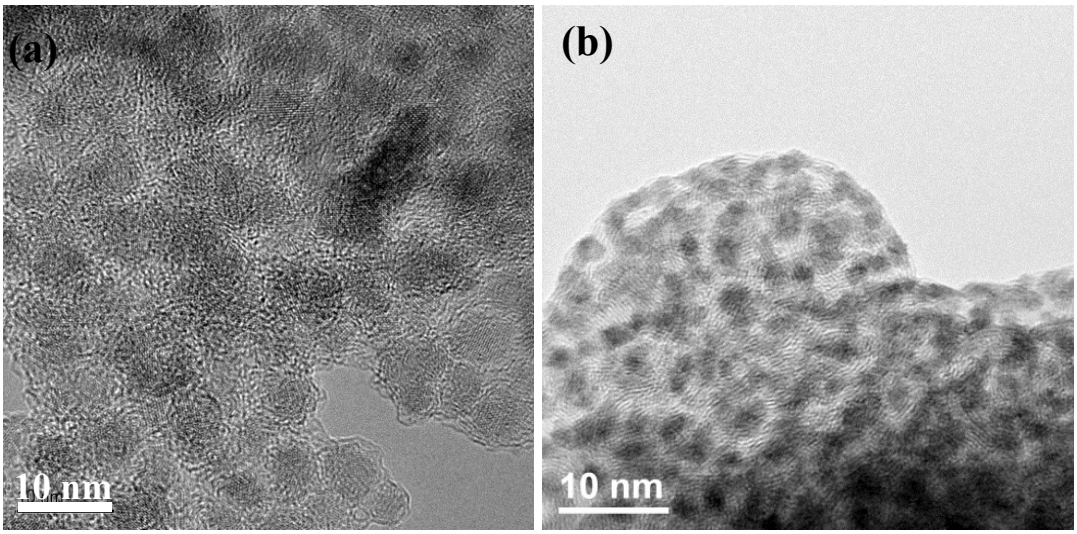

Fig. S8. TEM images of (a) Fe_3O_4/C and (b) WO_2/C composites after annealing.

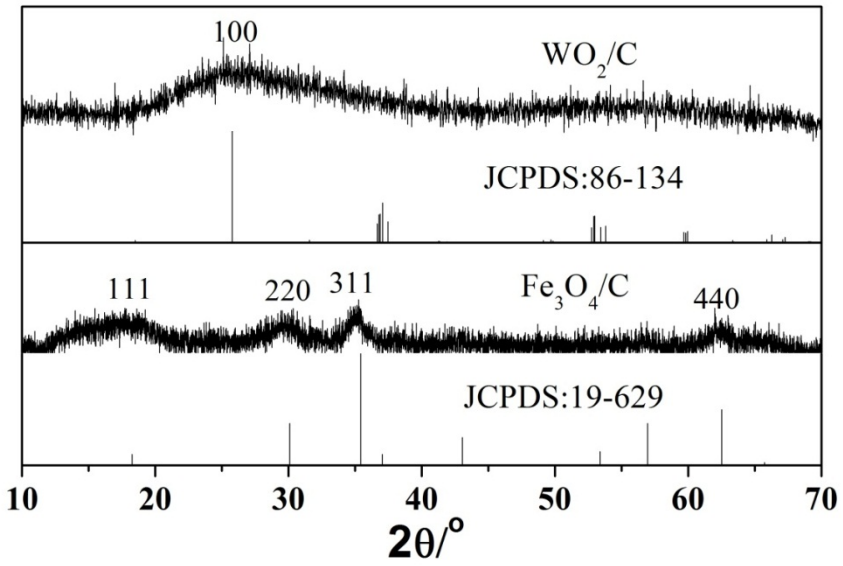

Fig. S9 XRD patterns of Fe_3O_4/C and WO_2/C nanocomposites.

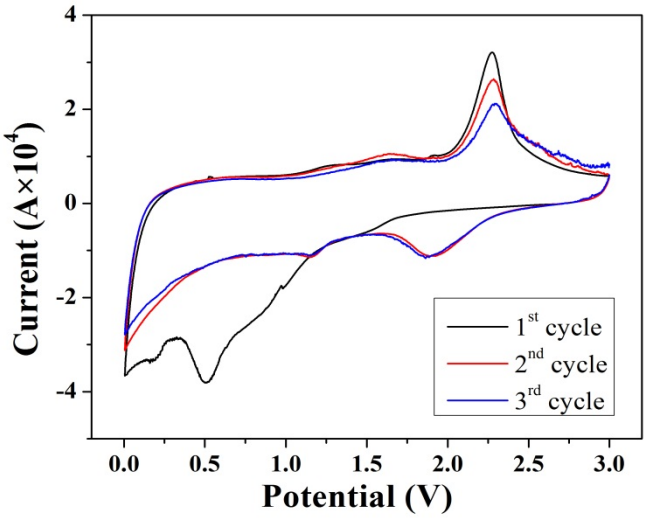

Fig. S10. Cyclic voltammogram of the SLMoS_2/C anode.

In the first discharge, a slope starts at about 1.5 V is indicative of the formation of Li_xMoS_2. The inconspicuous conversion is caused by the expanded (002) spacing, low crystallinity and disordered structure of SLMoS_2.[1-3] The Li_xMoS_2 then decomposes into Mo nanoparticles embedded in Li_2S 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_2S 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_2S, and the association of Li^+ ions with Mo is found at 1.0 V.[5]

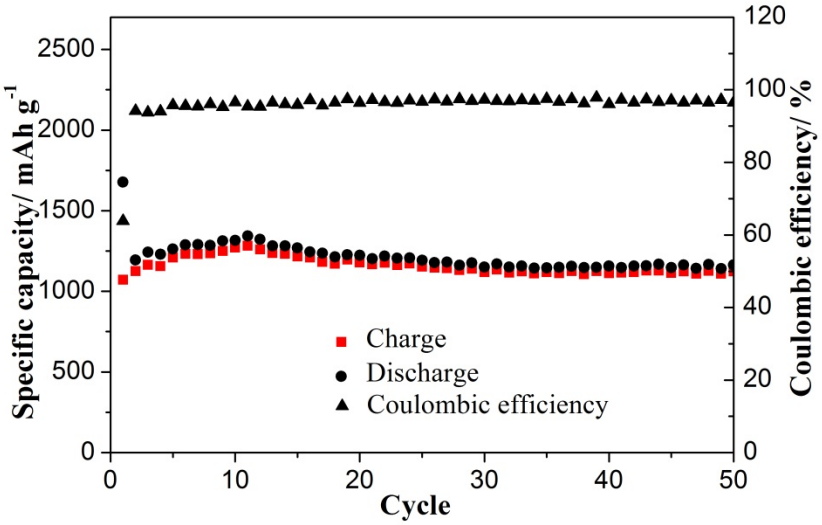

Fig. S11. Cycling performance of the $SLMoS_2/C$ anode at a current density of 50 mA/g.

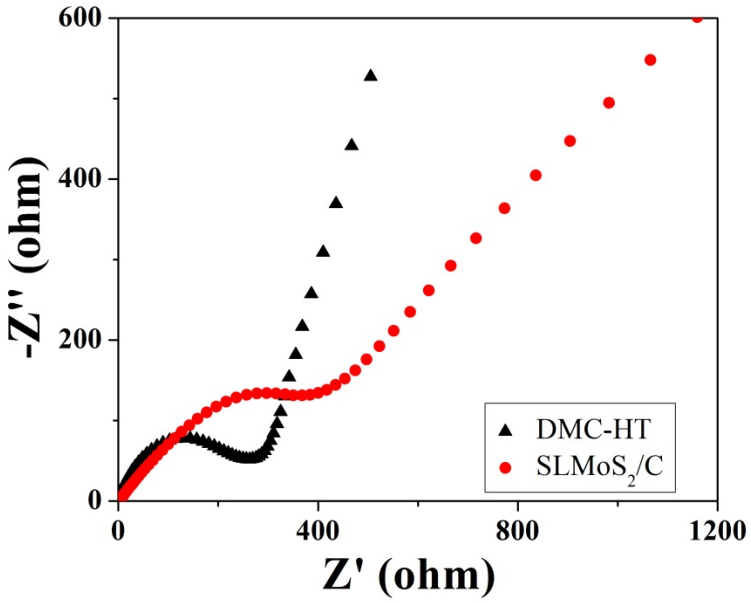

Fig. S12. Nyquist plot of $SLMoS_2/C$ (a) before and (b) after cycles.

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

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