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# Self-assembled molybdenum disulfide nanoflowers regulated by lithium sulfate for high performance supercapacitors†

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Recently, molybdenum disulfide (MoS<sub>2</sub>) has been extensively investigated as a promising pseudocapacitor electrode material. However, MoS<sub>2</sub> usually exhibits inferior rate capability and cyclability, which restrain its practical application in energy storage. In this work, MoS<sub>2</sub> nanoflowers regulated by Li<sub>2</sub>SO<sub>4</sub> (L-MoS<sub>2</sub>) are successfully fabricated *via* intercalating solvated Li ions. *Via* appropriate intercalation of Li<sub>2</sub>SO<sub>4</sub>, MoS<sub>2</sub> nanosheets could self-assemble to form L-MoS<sub>2</sub> nanoflowers with an interlayer spacing of 0.65 nm. Due to the large specific surface area (23.7 m<sup>2</sup> g<sup>-1</sup>) and high 1T phase content (77.5%), L-MoS<sub>2</sub> as supercapacitor electrode delivers a maximum specific capacitance of 356.7 F g<sup>-1</sup> at 1 A g<sup>-1</sup> and maintains 49.8% of capacitance retention at 20 A g<sup>-1</sup>. Moreover, the assembled L-MoS<sub>2</sub> symmetric supercapacitor (SSC) device displays an energy density of 6.5 W h kg<sup>-1</sup> and 79.6% of capacitance retention after 3000 cycles.

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## 1. Introduction

Molybdenum disulfide (MoS<sub>2</sub>), a typical two-dimensional (2D) transition metal chalcogenide, which is composed of S–Mo–S layers vertically stacked *via* weak van der Waals attraction.<sup>1</sup> Owing to the characteristics of high theoretical capacity and electrochemical activity, relatively large and easily expanded interlayer distance, easy preparation, and low cost, MoS<sub>2</sub> has been extensively investigated in the field of supercapacitors, batteries and electrocatalysts.<sup>2–7</sup> However, MoS<sub>2</sub> usually suffers from serious stacking and agglomeration problems during the preparation process, which leads to formation of many inaccessible active sites.<sup>8</sup> As a pseudocapacitive electrode material of supercapacitors, the low conductivity and large volume variation during repeated charge/discharge cycles also give rise to inferior rate capability and cycling stability of MoS<sub>2</sub>, which restrains its practical application in energy storage.<sup>9</sup> Therefore, much efforts are devoted to ameliorating the capacitive performances of MoS<sub>2</sub>.

To address the aforementioned drawbacks, endowing MoS<sub>2</sub> with various kinds of nanostructures can improve its electrochemical performances. The nanostructure design can

effectively avoid the stacking and agglomeration problems of MoS<sub>2</sub> and expose more electroactive sites, which is beneficial to increasing the contact area with electrolyte ions. For instance, Kesavan *et al.* synthesized MoS<sub>2</sub> nanosheets *via* topochemical sulfurization, which revealed a high capacitance of 119.38 F g<sup>-1</sup> and good cyclability of 95.1% over 2000 cycles.<sup>10</sup> Wei *et al.* fabricated MoS<sub>2</sub> nanoflowers *via* adding sodium chloride, which displayed a high capacity of 1120 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup> and 96% of capacitance retention after 2000 cycles.<sup>11</sup> Broadening the interlayer spacing of MoS<sub>2</sub> is also an effective method to enhance the rate capability and cycling stability, since large interlayer spacing can afford rapid diffusion transportation of electrolyte ions between MoS<sub>2</sub> bilayers. Wang *et al.* prepared MoS<sub>2</sub> micro flowers with an interlayer spacing of 0.94 nm by reactant conversion-intercalation strategy, which delivered a specific capacity of 246.8 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup>.<sup>12</sup> Cai *et al.* fabricated PEDOT@MoS<sub>2</sub> composite with an interlayer spacing of 1.02 nm *via* electrochemical co-deposition method, which exhibited a high specific capacity of 4418 mF cm<sup>-2</sup> at 2 mA cm<sup>-2</sup> and 100% of capacitance retention after 10 000 cycles.<sup>13</sup> In addition, the usually synthesized MoS<sub>2</sub> is stable semi-conducting phase (2H-MoS<sub>2</sub>) with low conductivity, while metallic phase (1T-MoS<sub>2</sub>) is thermodynamically metastable but reveals better conductivity and hydrophilicity than 2H-MoS<sub>2</sub>.<sup>14–16</sup> Therefore, developing 1T phase dominated hybrid phase MoS<sub>2</sub> is the optimal strategy to ameliorate the electrochemical properties of MoS<sub>2</sub>. For example, Li *et al.* prepared high purity MoS<sub>2</sub> nanosheets with 83.6% of 1T phase, which achieved a high capacitance of 392 F g<sup>-1</sup> at 1 A g<sup>-1</sup> and 83% of capacitance retention after 10 000 cycles.<sup>17</sup> Although some

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progresses have been made in enhancing the electrochemical performances of MoS<sub>2</sub>-based electrodes, however, the preparation process of MoS<sub>2</sub> usually requires a high hydrothermal reaction temperature (usually above 200 °C), and the specific capacity and rate capability of MoS<sub>2</sub>-based electrodes is still unsatisfactory, it is urgent to develop simple and low temperature strategies to ameliorate the specific capacity and rate capability of MoS<sub>2</sub>-based electrodes.

Inspired by the above literature, in this work, MoS<sub>2</sub> nanoflowers regulated by Li<sub>2</sub>SO<sub>4</sub> (L-MoS<sub>2</sub>) are successfully fabricated *via* intercalating solvated Li ions in a relatively low hydrothermal reaction temperature (180 °C). Under appropriate intercalation of Li<sub>2</sub>SO<sub>4</sub>, MoS<sub>2</sub> nanosheets could self-assemble to form L-MoS<sub>2</sub> nanoflowers with an interlayer spacing of 0.65 nm. Due to the large specific surface area (23.7 m<sup>2</sup> g<sup>-1</sup>) and high 1T phase content (77.5%), L-MoS<sub>2</sub> as supercapacitor electrode delivers a maximum specific capacitance of 356.7 F g<sup>-1</sup> at 1 A g<sup>-1</sup> and maintains 49.8% of initial capacity at 20 A g<sup>-1</sup>. Moreover, the assembled L-MoS<sub>2</sub> symmetric supercapacitor (SSC) device displays an energy density of 6.5 W h kg<sup>-1</sup> at 413 W kg<sup>-1</sup> and 79.6% of capacitance retention after 3000 cycles.

## 2. Results and discussion

### 2.1. Characterization

In this work, L-MoS<sub>2</sub> nanoflowers were self-assembled from MoS<sub>2</sub> nanosheets by intercalating moderate amount of Li<sub>2</sub>SO<sub>4</sub> and the detailed preparation process of L-MoS<sub>2</sub> nanoflowers is shown in the ESI.† The morphologies of the obtained samples were first observed by scanning electron microscope (SEM). When Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O was not added in the hydrothermal reaction, the obtained MoS<sub>2</sub> is composed of intersecting nanosheets with thickness about 20 nm and reveals an obvious stacking/agglomeration phenomenon, as illustrated in Fig. S1a and b.† When 0.64 g Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O was added in the hydrothermal reaction, the solvated Li ions carrying water molecules intercalated into the MoS<sub>2</sub> bilayers, broadening the interlayer spacing of MoS<sub>2</sub> and introducing negative charges on the MoS<sub>2</sub> nanosheets.<sup>18</sup> The strong electrostatic repulsive force between negative charges on adjacent MoS<sub>2</sub> nanosheets affects the growth of MoS<sub>2</sub> and induces the self-assembly of MoS<sub>2</sub> nanosheets to form L-MoS<sub>2</sub> nanoflowers. As present in Fig. 1, the SEM images of L-MoS<sub>2</sub> exhibit perfect nanoflowers-like architecture without distinct agglomeration phenomenon. According to the four-probe tests, the conductivity of L-MoS<sub>2</sub> powder is 0.15 S cm<sup>-1</sup>, which is higher than that of MoS<sub>2</sub> powder (0.11 S cm<sup>-1</sup>). It is

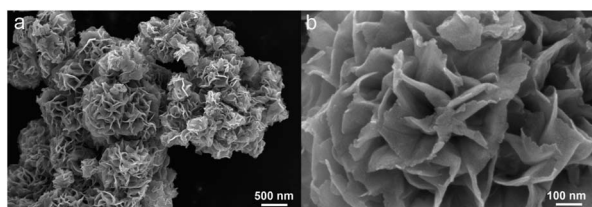


Fig. 1 SEM images of L-MoS<sub>2</sub> nanoflowers (a and b).

noteworthy that the amount of Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O added manifests an obvious effect on the morphology of L-MoS<sub>2</sub>. When the amount of Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O added was 0.32 g, the solvated Li ions intercalated into the MoS<sub>2</sub> bilayers, introducing fewer negative charges on the MoS<sub>2</sub> nanosheets. The relatively weak electrostatic repulsive force between negative charges on adjacent MoS<sub>2</sub> nanosheets only induces partial self-assembly of MoS<sub>2</sub> nanosheets to form nanoflowers, leading to the resultant L-MoS<sub>2</sub>-2.5 still presents stacking/agglomeration due to interlayer van der Waals attraction, as verified by the SEM images in Fig. S1c and d.† When the amount of Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O added was 0.96 g, the solvated Li ions intercalated into the MoS<sub>2</sub> bilayers, introducing more negative charges on the MoS<sub>2</sub> nanosheets. The stronger electrostatic repulsive force between negative charges on adjacent MoS<sub>2</sub> nanosheets induces the disorderly growth of MoS<sub>2</sub> nanosheets, which inevitably leads to the local collapse and agglomeration of the obtained L-MoS<sub>2</sub>-7.5, as proved by the SEM images in Fig. S1e and f.†

The micro morphology of the samples was further observed by transmission electron microscope (TEM) tests. The TEM image in Fig. 2a further affirms that L-MoS<sub>2</sub> is self-assembled from thin and porous MoS<sub>2</sub> nanosheets. The high-resolution TEM (HRTEM) image in Fig. 2b exhibits an interlayer spacing of 0.65 nm, assigning to the (002) plane of 2H-MoS<sub>2</sub>. Furthermore, the discontinuous lattice fringes marked within the dotted circles in Fig. 2b demonstrate the existence of abundant defects, which could be originated from the intercalation of Li ions. The TEM images of MoS<sub>2</sub> are shown in Fig. S2.† It can be seen that the interlayer spacing of (002) plane for MoS<sub>2</sub> is 0.64 nm. The high-angle annular dark-field scanning TEM (HAADF-STEM) image and the corresponding element mapping images in Fig. 2c confirm the homogenous distribution of Mo and S elements in L-MoS<sub>2</sub>.

The crystallinity of L-MoS<sub>2</sub> and MoS<sub>2</sub> was analyzed by X-ray diffractometer (XRD). In Fig. 3a, L-MoS<sub>2</sub> and MoS<sub>2</sub> display identical diffraction peaks around 2θ of 13.5°, 32.5°, 35.7° and 57.4°, which can be respectively corresponded to the (002),

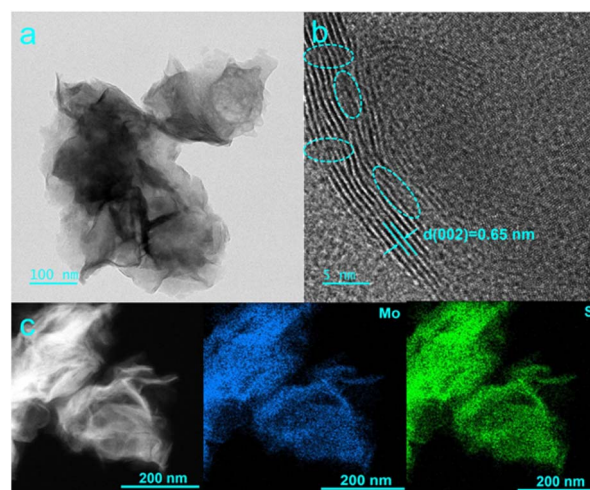


Fig. 2 (a) TEM, (b) HRTEM, (c) HAADF-STEM and corresponding element mapping images of L-MoS<sub>2</sub> nanoflowers.



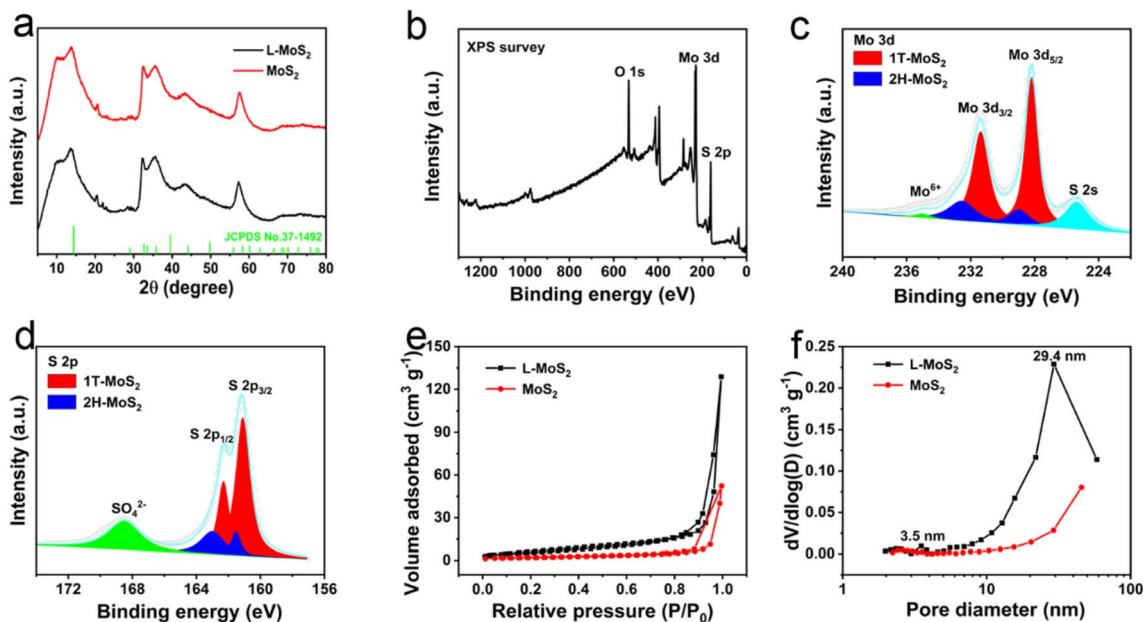


Fig. 3 (a) XRD patterns of L-MoS<sub>2</sub> and MoS<sub>2</sub>. (b) The XPS survey spectrum of L-MoS<sub>2</sub>. The high-resolution (c) Mo 3d, and (d) S 2p XPS spectrum of L-MoS<sub>2</sub>. (e) N<sub>2</sub> adsorption–desorption isotherm curves of L-MoS<sub>2</sub> and MoS<sub>2</sub>. (f) Pore size distribution curves of L-MoS<sub>2</sub> and MoS<sub>2</sub>.

(100), (102) and (110) planes of 2H-MoS<sub>2</sub> (JCPDS no. 37-1492),<sup>19</sup> indicating that the intercalation of solvated Li ions has no distinct effect on the crystallinity of MoS<sub>2</sub>. According to the Bragg equation, the (002) plane interlayer spacing of L-MoS<sub>2</sub> and MoS<sub>2</sub> is respectively calculated to be 6.48 and 6.34 Å, which are in line with the HRTEM results. In addition, the XRD patterns in Fig. S3† reveal that the (002) plane interlayer spacing of L-MoS<sub>2-2.5</sub> and L-MoS<sub>2-7.5</sub> is calculated to be 6.42 and 6.53 Å, respectively, further indicating that the intercalation of MoS<sub>2</sub> with Li<sub>2</sub>SO<sub>4</sub> could broaden the interlayer spacing of MoS<sub>2</sub>. The large interlayer spacing of MoS<sub>2</sub> can afford rapid electrolyte ions transportation in MoS<sub>2</sub>, contributing to improve the rate capability to a certain extent.

X-ray photoelectron spectroscopy (XPS) tests were carried out to identify the chemical states of the samples. The presence of O, Mo, and S elements in L-MoS<sub>2</sub> is demonstrated by the XPS survey spectrum in Fig. 3b. Moreover, the trace amount of Li element in L-MoS<sub>2</sub> can be identified by the high-resolution Li 1s XPS spectrum illustrated in Fig. S4.† The high-resolution Mo 3d spectrum in Fig. 3c displays two peaks at 229.1 eV and 232.7 eV referring to the Mo<sup>4+</sup> 3d<sub>5/2</sub> and Mo<sup>4+</sup> 3d<sub>3/2</sub> of 2H-MoS<sub>2</sub>, while the two peaks located at 228.4 eV and 231.6 eV corresponding to the Mo<sup>4+</sup> 3d<sub>5/2</sub> and Mo<sup>4+</sup> 3d<sub>3/2</sub> of 1T-MoS<sub>2</sub>.<sup>20</sup> The weak peak at 235.1 eV demonstrates the presence of Mo<sup>6+</sup> state, which is likely associated with the oxidation of MoS<sub>2</sub>.<sup>21</sup> The S 2s peak at 225.6 eV is related to the Mo–S bond.<sup>22</sup> Based on the integral area of the deconvoluted Mo 3d spectrum, the content of 1T phase in L-MoS<sub>2</sub> is calculated to be 77.5%. The high-resolution S 2p spectrum in Fig. 3d reveals two peaks at 161.5 eV and 163.0 eV respectively assigns to S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub> of 2H-MoS<sub>2</sub>, while the peak located at 161.1 eV and 162.3 eV could be respectively referred to S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub> of 1T-MoS<sub>2</sub>.<sup>20,23</sup> The

strong SO<sub>4</sub><sup>2-</sup> peak at 168.5 eV could be possibly attributed to oxidation of MoS<sub>2</sub>.<sup>24</sup> In addition, the two peaks of O 1s spectrum for L-MoS<sub>2</sub> at 531.5 and 532.8 eV shown in Fig. S4† could be respectively associated with O–Mo bond and adsorbed water.<sup>25</sup> The high-resolution Mo 3d and S 2p spectra of MoS<sub>2</sub> are illustrated in Fig. S4† and the content of 1T phase in MoS<sub>2</sub> is calculated to be 67.5%. It can be concluded that the intercalation of MoS<sub>2</sub> with solvated Li ions is conducive to increasing the content of 1T phase in MoS<sub>2</sub>, which could be originated from that the negative charges on MoS<sub>2</sub> nanosheets lead to lowered formation energy of 1T phase.<sup>18</sup>

The porous architecture of L-MoS<sub>2</sub> and MoS<sub>2</sub> was investigated by N<sub>2</sub> absorption/desorption tests. In Fig. 3e, L-MoS<sub>2</sub> and MoS<sub>2</sub> exhibit a type-IV isotherm with an obvious hysteresis loop at high relative pressures, verifying the existence of mesopores.<sup>26</sup> The specific surface area of L-MoS<sub>2</sub> and MoS<sub>2</sub> is calculated to be 23.7 and 7.5 m<sup>2</sup> g<sup>-1</sup>, respectively. Compared with MoS<sub>2</sub>, the pore size distribution curve of L-MoS<sub>2</sub> in Fig. 3f exhibits a bimodal pore size distribution. The narrow distribution centered at 3.5 nm might be related to the pores on the MoS<sub>2</sub> nanosheets, whereas the wide distribution centered at 29.4 nm could be ascribed to the void space formed by the self-assemble of MoS<sub>2</sub> nanosheets.<sup>6</sup> Therefore, the large specific surface area and bimodal pore size distribution are beneficial to increasing the contact area with electrolyte ions and affording fast ions transportation, and then ameliorating the specific capacitance and rate capability of L-MoS<sub>2</sub>.<sup>20,27</sup>

## 2.2. Electrochemical performance

The electrochemical performances of L-MoS<sub>2</sub> and MoS<sub>2</sub> as supercapacitor electrodes were firstly studied in three-electrode system using 2 M KOH as electrolyte. In this work, nickel foam



was used as a current collector due to its high conductivity and porosity. After applying L-MoS<sub>2</sub> powder and MoS<sub>2</sub> powder to nickel foam, the conductivity of obtained L-MoS<sub>2</sub> and MoS<sub>2</sub> electrode is 0.96 kS cm<sup>-1</sup> and 0.82 kS cm<sup>-1</sup>, respectively. The cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) curves of nickel foam alone are illustrated in Fig. S5.† According to the CV and GCD test results, the contribution of foam nickel to capacitance could be negligible. The CV curves of L-MoS<sub>2</sub> and MoS<sub>2</sub> are compared at a scan rate of 20 mV s<sup>-1</sup>, as present in Fig. 4a. It can be observed that both L-MoS<sub>2</sub> and MoS<sub>2</sub> reveal a anodic peak at 0.52 V and cathodic peak at 0.28 V, manifesting the pseudocapacitive nature of L-MoS<sub>2</sub> and MoS<sub>2</sub>.<sup>28</sup> Moreover, L-MoS<sub>2</sub> exhibits a larger integral area of CV curve than that of MoS<sub>2</sub> at the same scan rate, signifying the higher specific capacitance of L-MoS<sub>2</sub>. Fig. 4b shows the CV curves of L-MoS<sub>2</sub> at different scan rates. Obviously, all the CV curves display a pair of distinct redox peaks and the anodic peaks and cathodic peaks gradually move away mutually as the scan rate increases, which may be associated with the polarization phenomenon and internal resistance in L-MoS<sub>2</sub> electrode.<sup>29</sup> The GCD curves of L-MoS<sub>2</sub> and MoS<sub>2</sub> at a current density of 1 A g<sup>-1</sup> are compared in Fig. 4c. The L-MoS<sub>2</sub> displays longer discharge time than that of MoS<sub>2</sub>, further verifying the higher specific capacitance of L-MoS<sub>2</sub> after intercalating moderate amount of Li<sub>2</sub>SO<sub>4</sub>. All GCD curves in Fig. 4d are nearly symmetric, indicating that L-MoS<sub>2</sub> possesses a highly electrochemical reversibility.<sup>30</sup> The CV and GCD curves of MoS<sub>2</sub> reveal similar variation tendency with L-MoS<sub>2</sub>, as illustrated in Fig. S6.† The specific capacitances of L-MoS<sub>2</sub> and MoS<sub>2</sub> calculated from the GCD curves are provided in Fig. 4e. It can be found that all the specific capacitances decrease with increasing the current density, which might be

related to the limitation of K ions transportation at high current density.<sup>31</sup> At a current density of 1 A g<sup>-1</sup>, L-MoS<sub>2</sub> achieves a specific capacitance of 356.7 F g<sup>-1</sup>, which is larger than that of MoS<sub>2</sub> (282.8 F g<sup>-1</sup>). When the current density is 20 A g<sup>-1</sup>, L-MoS<sub>2</sub> still maintains a specific capacitance of 177.7 F g<sup>-1</sup>, exhibiting a favorable rate capability with 49.8% of capacitance retention, which is better than that of MoS<sub>2</sub> (35.6%). In addition, the intercalation amount of Li<sub>2</sub>SO<sub>4</sub> has a significant effect on the electrochemical properties of L-MoS<sub>2</sub>. As present in Fig. S7,† all the specific capacitances of L-MoS<sub>2</sub>-2.5 and L-MoS<sub>2</sub>-7.5 are inferior than that of L-MoS<sub>2</sub> under the same current density, which could be associated with the morphology and interlayer spacing of L-MoS<sub>2</sub>. Compared with L-MoS<sub>2</sub>, L-MoS<sub>2</sub>-2.5 exhibits smaller layer spacing with obvious stacking/agglomeration, which is adverse for the transportation of electrolyte ions into L-MoS<sub>2</sub>-2.5, resulting in lower specific capacitance than L-MoS<sub>2</sub>. Although the interlayer spacing of L-MoS<sub>2</sub>-7.5 is greater than that of L-MoS<sub>2</sub>, the local collapse structure of L-MoS<sub>2</sub>-7.5 and excessive Li ions between the L-MoS<sub>2</sub>-7.5 bilayers can hinder the rapid transportation of electrolyte ions within it, leading to significantly lower specific capacitance than L-MoS<sub>2</sub>. Electrochemical impedance spectroscopy (EIS) measurements were conducted to study the kinetics of L-MoS<sub>2</sub> and MoS<sub>2</sub>. In Nyquist plot, the intercept value on the horizontal axis at high-frequency region corresponds to the equivalent series resistance (*R*<sub>s</sub>) and the diameter of the semicircle represents the charge transfer resistance (*R*<sub>ct</sub>).<sup>32,33</sup> In Fig. 4f, the *R*<sub>s</sub> value of L-MoS<sub>2</sub> (0.73 Ω) is less than that of MoS<sub>2</sub> (0.85 Ω), implying that the intercalation of solvated Li ions contributes to the transportation of electrolyte ions in L-MoS<sub>2</sub>. Moreover, no obvious semicircle can be found in Nyquist plots, indicating that *R*<sub>ct</sub> is negligible and

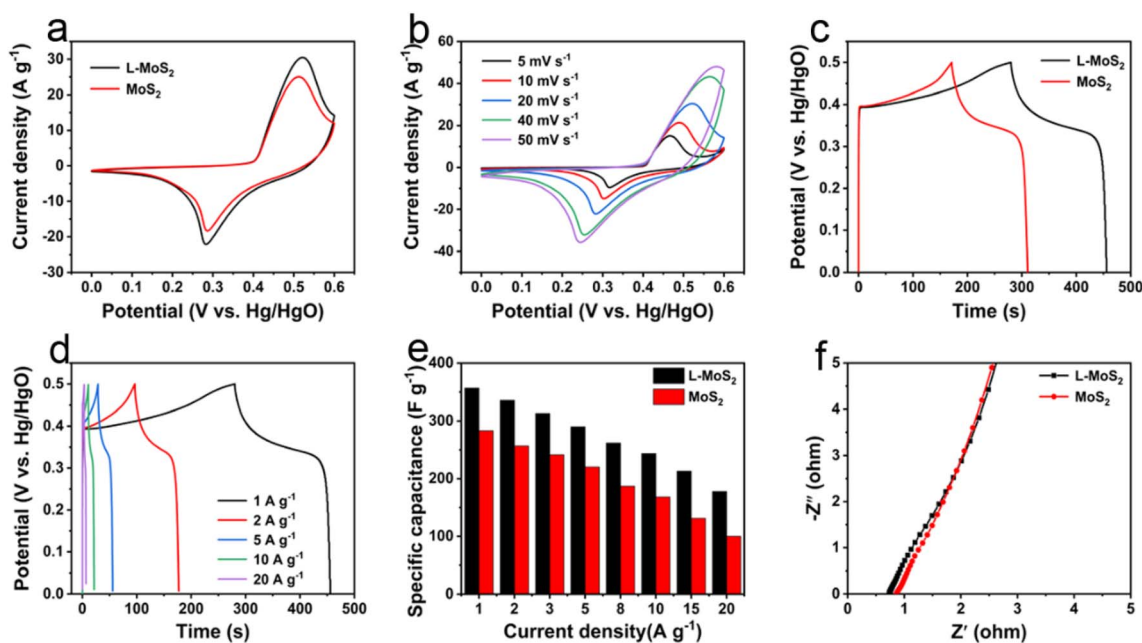


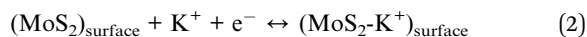
Fig. 4 Electrochemical performances of L-MoS<sub>2</sub> and MoS<sub>2</sub> electrodes in three-electrode system. (a) Comparative CV curves at a scan rate of 20 mV s<sup>-1</sup>. (b) CV curves of L-MoS<sub>2</sub> electrode at different scan rates. (c) Comparative GCD curves at a current density of 1 A g<sup>-1</sup>. (d) GCD curves of L-MoS<sub>2</sub> electrode at different current densities. (e) Specific capacitance versus current density curves. (f) Nyquist plots.



there is a fast electronic transfer during the redox reactions.<sup>34</sup> The cycling stability tests of L-MoS<sub>2</sub> and MoS<sub>2</sub> were carried out at a current density of 10 A g<sup>-1</sup>. As present in Fig. S8,† L-MoS<sub>2</sub> maintains 76.5% of capacitance retention after 3000 cycles, which is higher than that of MoS<sub>2</sub> (48.8%), demonstrating a good cycling stability. The SEM images of L-MoS<sub>2</sub> electrode and MoS<sub>2</sub> electrode after 3000 cycles are illustrated in Fig. S9.† The MoS<sub>2</sub> electrode reveals a dense structure and appears several cracks. Moreover, MoS<sub>2</sub> losses its nanosheet structure and completely turns into nanoparticles after repeated charge/discharge cycles. In comparison, L-MoS<sub>2</sub> electrode still exhibits a loose and porous architecture after cycling, which is conducive to generating a good cycling stability. We summarize the electrochemical performances (specific capacitance, rate capability and cycling stability) of MoS<sub>2</sub>-based electrodes in literature reports with our work. As shown in Table S1,† the electrochemical properties of L-MoS<sub>2</sub> are comparable to the previously reported literature.

Compared with MoS<sub>2</sub>, L-MoS<sub>2</sub> displays superior specific capacitance, rate capability and cycling stability, which could be attributed to the following aspects. First, the self-assembled L-MoS<sub>2</sub> exhibits nanoflowers-like architecture with a large specific surface area of 23.7 m<sup>2</sup> g<sup>-1</sup>, which can expose more electroactive sites and increase the contact area with electrolyte ions. Second, L-MoS<sub>2</sub> possesses an interlayer spacing of 0.65 nm, contributing to rapid transportation of electrolyte ions between L-MoS<sub>2</sub> bilayers. Finally, the high 1T phase content (77.5%) in L-MoS<sub>2</sub> is conducive to improving the conductivity and hydrophilicity, offering fast electronic transfer and large contact area with electrolyte ions.

In general, there are two charge storage mechanisms for MoS<sub>2</sub> electrode in KOH electrolyte, one is a diffusion-controlled process for intercalation/deintercalation of K<sup>+</sup> into/from the MoS<sub>2</sub> interlayers during the faradaic reaction, the other one is a capacitive process based on the surface adsorption/desorption of K<sup>+</sup> at the MoS<sub>2</sub> electrode/electrolyte interface, as shown in eqn (1) and (2).<sup>9,27</sup>



The CV curves of L-MoS<sub>2</sub> and MoS<sub>2</sub> were analyzed by virtue of the method described in the ESI.† The calculated results shown in Fig. S10† manifest that the charge storage in L-MoS<sub>2</sub> comprises both diffusion-controlled process and capacitive process.<sup>35</sup> At low scan rate of 5 mV s<sup>-1</sup>, the capacitive charge storage contribution ratio of L-MoS<sub>2</sub> is 39.0%, which is higher than that of MoS<sub>2</sub> (34.7%). Moreover, all the capacitive charge storage contribution ratios of L-MoS<sub>2</sub> are larger than MoS<sub>2</sub> at the same scan rate, further verifying the superiority of L-MoS<sub>2</sub>. At 50 mV s<sup>-1</sup>, the capacitive charge storage contribution ratio of L-MoS<sub>2</sub> accounts for 86.2%. Such a high capacitive charge storage contribution ratio is in favor of obtaining superior rate capability.<sup>36</sup>

To further evaluate the practical application of L-MoS<sub>2</sub> in supercapacitor, the SSC device was fabricated using two

identical L-MoS<sub>2</sub> electrodes in 2 M KOH electrolyte. The CV curves of the SSC device in Fig. 5a reveal quasi-rectangular shape and keep the shape unchanged even at the high scan rate of 100 mV s<sup>-1</sup>, demonstrating the superior capacitive behavior of the SSC device.<sup>12</sup> The GCD curves of the SSC device are shown in Fig. 5b. The quasi-triangular characteristic of GCD curves confirms a highly electrochemical reversibility of the SSC device. The specific capacitance of the SSC device is calculated from the GCD curves and illustrated in Fig. 5c. The SSC device could deliver a specific capacitance of 47.3 F g<sup>-1</sup> at 0.8 A g<sup>-1</sup> and 13.0 F g<sup>-1</sup> at 5 A g<sup>-1</sup>. Fig. 5d depicts the Nyquist plot of the SSC device, which displays a distinct semicircle at high frequency region. According to the equivalent circuit model shown in inset of Fig. 5d, the SSC device possesses a small R<sub>s</sub> of 0.48 Ω and R<sub>ct</sub> of 0.81 Ω, manifesting a low resistance and rapid charge transfer in the SSC device.<sup>37</sup> In Fig. 5e, the SSC device reveals 79.6% of capacitance retention and over 94% of coulombic efficiency after 3000 cycles at 2 A g<sup>-1</sup>. The low coulombic efficiency could be due to the side reaction originated from the creation of transition metal and sulfur-containing nanocomposites with low reversibility.<sup>19</sup> The Ragone plot of the SSC device is shown in Fig. 5f. The SSC device exhibits a maximum energy density of 6.5 W h kg<sup>-1</sup> at a power density of 413 W kg<sup>-1</sup>, and keeps 1.8 W h kg<sup>-1</sup> even at 3.2 kW kg<sup>-1</sup>. The energy density and power density of L-MoS<sub>2</sub> SSC device are comparable to MoS<sub>2</sub>-based SSCs in previously reported literature, such as 1T-MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> MXene (6.95 W h kg<sup>-1</sup> at 239.48 W kg<sup>-1</sup>),<sup>16</sup> MoS<sub>2</sub> nanosheets (6.56 W h kg<sup>-1</sup> at 250 W kg<sup>-1</sup>),<sup>10</sup> Cu doped MoS<sub>2</sub> (5.58 W h kg<sup>-1</sup> at 299 W kg<sup>-1</sup>),<sup>38</sup> and MoS<sub>2</sub>-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> (5.1 W h kg<sup>-1</sup> at 298 W kg<sup>-1</sup>).<sup>19</sup> If the masses of nickel foam collector and polypropylene diaphragm are added, the actual energy of the SSC device is only 0.028 W h kg<sup>-1</sup> at a power density of 1.8 W kg<sup>-1</sup>. Therefore, MoS<sub>2</sub>-based free-standing electrodes need to be developed to enhance the actual energy of the SSC device. Self-discharge and leakage current are extremely important parameters to evaluate the practical application of supercapacitors. The self-discharge and leakage current curves of the SSC device are illustrated in Fig. S11.† As shown in Fig. S11a,† the self-discharge of the SSC device could be ascribed to the following aspects. (i) The internal resistance (IR) drop that appears at the initial stage of self-discharge, which is associated with the charging current density and the electrolyte type.<sup>39</sup> (ii) The irreversible parasitic faradaic reaction could be originated from the surface oxygen-containing functional groups of L-MoS<sub>2</sub> electrode.<sup>40</sup> (iii) The charge redistribution caused by the inequality of charge distribution between the surface and inside of L-MoS<sub>2</sub> electrode.<sup>41</sup> According to the previously reported literature,<sup>42</sup> the studied self-discharge time of the SSC device is 10 h. The self-discharge rate could be measured by the open circuit voltage attenuation per unit time (OCV) and the OCV of the SSC device is 63.7 mV h<sup>-1</sup>. In Fig. S11b,† as the current is stabilized, the leakage current of the SSC device is 46.5 μA (8.5 mA g<sup>-1</sup>). If we do not consider the internal short circuit that may occur in assembling the SSC device, the leakage current of the SSC device is mainly derived from the parasitic Faraday reaction near the interfaces of L-



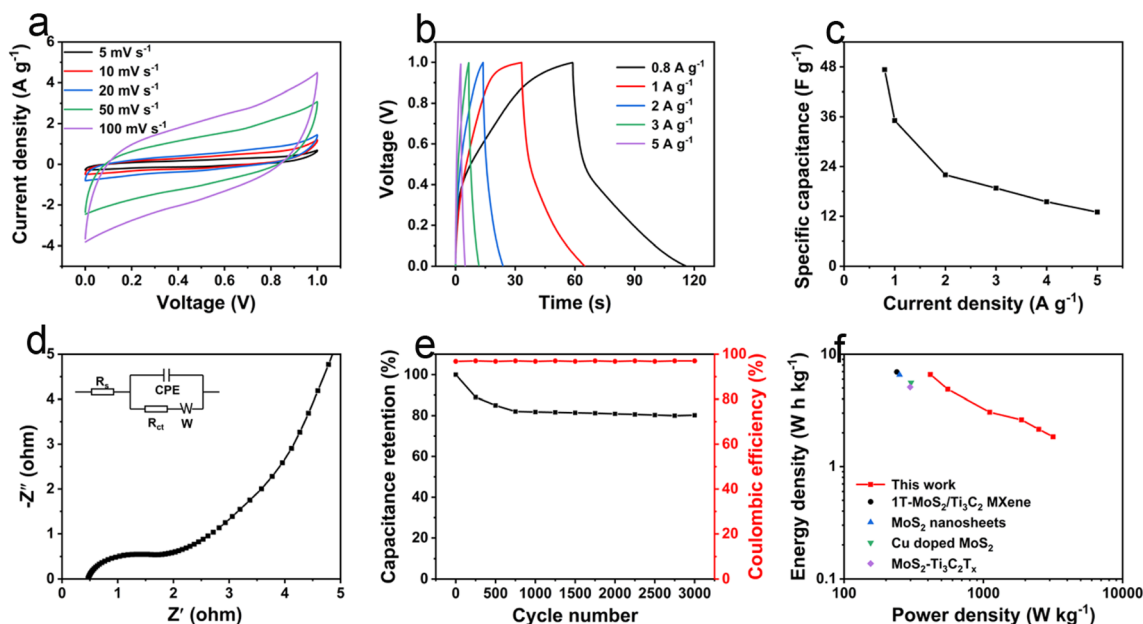


Fig. 5 Electrochemical performances of L-MoS<sub>2</sub> SSC in two-electrode system. (a) CV curves at different scan rates. (b) GCD curves under various current densities. (c) Specific capacitance versus current density curves. (d) Nyquist plot. Inset: the equivalent circuit model. (e) Cycling stability and coulombic efficiency after 3000 cycles at a current density of 2 A g<sup>-1</sup>. (f) Ragone plot.

MoS<sub>2</sub> electrode and electrolyte caused by the surface oxygen-containing functional groups.<sup>42</sup>

### 3. Conclusions

In summary, L-MoS<sub>2</sub> nanoflowers with an interlayer spacing of 0.65 nm are successfully self-assembled from MoS<sub>2</sub> nanosheets under appropriate intercalation of Li<sub>2</sub>SO<sub>4</sub>. Due to the large specific surface area and high content of 1T-MoS<sub>2</sub>, L-MoS<sub>2</sub> electrode delivers a maximum specific capacitance of 356.7 F g<sup>-1</sup> at 1 A g<sup>-1</sup> and keeps 49.8% of capacitance retention at 20 A g<sup>-1</sup>. Moreover, the fabricated L-MoS<sub>2</sub> SSC device displays a highest energy density of 6.5 W h kg<sup>-1</sup> and 79.6% of capacitance retention after 3000 cycles. It is believed that the intercalation of solvated Li ions could also be applicable to develop other 2D materials as advanced electrodes for supercapacitors.

### Author contributions

Yunan Li: conceptualization, data curation, writing – original draft, writing – review & editing. Yang Sun: investigation, data curation. Sen Zhang: investigation, data curation. Xueling Wu: data curation. Meng Song: project administration. Mingli Jiao: funding acquisition. Qi Qin: writing – review & editing. Liwei Mi: funding acquisition, writing – review & editing.

### Conflicts of interest

There are no conflicts to declare.

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### References

- R. Hu, Y. Liao, H. Qiao, J. Li, K. Wang, Z. Huang and X. Qi, *Ceram. Int.*, 2022, **48**, 23498–23503.
- S. W. Bokhari, A. V. Ellis, M. Uceda, S. Wei, M. Pope, S. Zhu, W. Gao and P. C. Sherrell, *J. Energy Storage*, 2022, **56**, 105935.
- W. Jia, H. Wu, Y. Zheng, Z. Liu, G. Cai, J. Wen, G. Hu, T. Tang, X. Li, L. Jiang, Z. Wang, M. Li and H. Huang, *ACS Appl. Energy Mater.*, 2023, **6**, 2570–2581.
- S. Li, C. Huang, L. Gao, Q. Shen, P. Li, X. Qu, L. Jiao and Y. Liu, *Angew. Chem., Int. Ed.*, 2022, **61**, e202211478.
- J. Tian, C. Yang, R. Hao, F. Li, Z. Liu, W. Chen, Y. Lv and C. Lin, *Int. J. Hydrogen Energy*, 2022, **47**, 17871–17878.
- X. Zhu, F. Xia, D. Liu, X. Xiang, J. Wu, J. Lei, J. Li, D. Qu and J. Liu, *Adv. Funct. Mater.*, 2023, **33**, 2207548.
- M. K. Francis, K. Rajesh, P. B. Bhargav and N. Ahmed, *J. Mater. Sci.*, 2023, **58**, 4054–4069.
- Z. Deng, H. Jiang and C. Li, *Small*, 2018, **14**, 1800148.



- 9 M. G. Fayed, S. Y. Attia, Y. F. Barakat, E. E. El-Shereafy, M. M. Rashad and S. G. Mohamed, *Sustainable Mater. Technol.*, 2021, **29**, e00306.
- 10 D. Kesavan, V. K. Mariappan, P. Pazhamalai, K. Krishnamoorthy and S. J. Kim, *J. Colloid Interface Sci.*, 2021, **584**, 714–722.
- 11 S. Wei, R. Zhou and G. Wang, *ACS Omega*, 2019, **4**, 15780–15788.
- 12 J. Wang, X. Zheng, Y. Dong, L. Chen, L. Chen and W. He, *Dalton Trans.*, 2023, **52**, 4537–4547.
- 13 Y. Cai, H. Kang, F. Jiang, L. Xu, Y. He, J. Xu, X. Duan, W. Zhou, X. Lu and Q. Xu, *Appl. Surf. Sci.*, 2021, **546**, 149088.
- 14 Z. Lei, J. Zhan, L. Tang, Y. Zhang and Y. Wang, *Adv. Energy Mater.*, 2018, **8**, 1703482.
- 15 F. Wan, X. Wang, C. Tang, C. Jiang, W. Wang, B. Li, Y. Zhang and X. Zhu, *J. Mater. Chem. A*, 2022, **10**, 12258–12268.
- 16 X. Wang, H. Li, H. Li, S. Lin, W. Ding, X. Zhu, Z. Sheng, H. Wang, X. Zhu and Y. Sun, *Adv. Funct. Mater.*, 2020, **30**, 0190302.
- 17 H. Li, H. Li, Z. Wu, L. Zhu, C. Li, S. Lin, X. Zhu and Y. Sun, *J. Mater. Sci. Technol.*, 2022, **123**, 34–40.
- 18 Z. Bo, X. Cheng, H. Yang, X. Guo, J. Yan, K. Cen, Z. Han and L. Dai, *Adv. Energy Mater.*, 2022, **12**, 2103394.
- 19 W. Hou, Y. Sun, Y. Zhang, T. Wang, L. Wu, Y. Du and W. Zhong, *J. Alloys Compd.*, 2021, **859**, 157797.
- 20 H. Niu, Z. Zou, Q. Wang, K. Zhu, K. Ye, G. Wang, D. Cao and J. Yan, *Chem. Eng. J.*, 2020, **399**, 125672.
- 21 Z. Wang, J. Wang, F. Wang, X. Zhang, X. He, S. Liu, Z. Zhang, Z. Zhang and X. Wang, *J. Alloys Compd.*, 2023, **947**, 169505.
- 22 P. Kour, Deeksha and K. Yadav, *J. Alloys Compd.*, 2022, **922**, 166194.
- 23 S. Li, Y. Liu, X. Zhao, K. Cui, Q. Shen, P. Li, X. Qu and L. Jiao, *Angew. Chem., Int. Ed.*, 2021, **60**, 20286–20293.
- 24 Q. Zhang, Y. Song, B. Chen, X. Hu, W. Peng, Y. Li, F. Zhang and X. Fan, *Chem. Eng. J.*, 2023, **454**, 140330.
- 25 X. Gu, L. Zhang, X. Ma, J. Wang, X. Shang, Z. Wang, M. Kandawa-Schulz, W. Song and Y. Wang, *Ionics*, 2022, **28**, 2337–2347.
- 26 I. T. Bello, K. O. Otun, G. Nyongombe, O. Adedokun, G. L. Kabongo and M. S. Dhlamini, *Int. J. Energy Res.*, 2022, **46**, 8908–8918.
- 27 K. B. Pisal, B. M. Babar, S. H. Mujawar, S. S. Mali, C. K. Hong, S. D. Sartale and L. D. Kadam, *Int. J. Energy Res.*, 2022, **46**, 18312–18327.
- 28 N. Joseph, P. Muhammed Shafi and A. Chandra Bose, *New J. Chem.*, 2018, **42**, 12082–12090.
- 29 Y. Yao, J. Wang, X. Ban, C. Chen, Q. Wang, K. Zhu, K. Ye, G. Wang, D. Cao and J. Yan, *EcoMat*, 2023, **5**, e12287.
- 30 S. Liu, Y. Yin, M. Wu, K. S. Hui, K. N. Hui, C.-Y. Ouyang and S. C. Jun, *Small*, 2019, **15**, 1803984.
- 31 K. Le, X. Zhang, Q. Zhao, Y. Liu, P. Yi, S. Xu and W. Liu, *ACS Appl. Mater. Interfaces*, 2021, **13**, 44427–44439.
- 32 M. Rashidi and F. Ghasemi, *Electrochim. Acta*, 2022, **435**, 141379.
- 33 H. Wu, Z. Guo, M. Li, G. Hu, T. Tang, J. Wen, X. Li and H. Huang, *Electrochim. Acta*, 2021, **370**, 137758.
- 34 S. Liu, Y. Yin, D. Ni, K. S. Hui, K. N. Hui, S. Lee, C.-Y. Ouyang and S. C. Jun, *Energy Storage Mater.*, 2019, **19**, 186–196.
- 35 M. S. Javed, X. Zhang, S. Ali, A. Mateen, M. Idrees, M. Sajjad, S. Batool, A. Ahmad, M. Imran, T. Najam and W. Han, *Nano Energy*, 2022, **101**, 107624.
- 36 Z. Tang, J. Dai, W. Wei, Z. Gao, Z. Liang, C. Wu, B. Zeng, Y. Xu, G. Chen, W. Luo, C. Yuan and L. Dai, *Adv. Sci.*, 2022, **9**, 2201685.
- 37 X. Sun, Y. a. Pang, S. Li, Y. Yu, X. Ding, L. Wang and Q. Zhang, *Ceram. Int.*, 2022, **48**, 21317–21326.
- 38 D. Vikraman, S. Hussain, K. Karuppasamy, A. Kathalingam, E.-B. Jo, A. Sanmugam, J. Jung and H.-S. Kim, *J. Alloys Compd.*, 2022, **893**, 162271.
- 39 S. Pu, Z. Wang, Y. Xie, J. Fan, Z. Xu, Y. Wang, H. He, X. Zhang, W. Yang and H. Zhang, *Adv. Funct. Mater.*, 2022, **33**, 2208715.
- 40 M. Haque, Q. Li, A. D. Smith, V. Kuzmenko, P. Rudquist, P. Lundgren and P. Enoksson, *J. Power Sources*, 2020, **453**, 227897.
- 41 W. Shang, W. Yu, X. Xiao, Y. Ma, Y. He, Z. Zhao and P. Tan, *Adv. Powder Mater.*, 2023, **2**, 100075.
- 42 W. Li, X. Yang, Z. Chen, T. Lv, X. Wang and J. Qiu, *Carbon*, 2022, **196**, 136–145.

