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# Poly(3,4-ethylenedioxythiophene)/MoS<sub>2</sub> nanocomposites with enhanced electrochemical capacitance performance

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Composites based on conducting polymers and two-dimensional (2D) layer structure transition metal oxides are expected to realize the combination of good mechanical properties and excellent capacitance. Here poly(3,4-ethylenedioxythiophene)/molybdenum disulfide (PEDOT/MoS<sub>2</sub>) intercalated composites were successfully synthesized *via in situ* polymerization in the presence of ammonium persulfate (APS). The thermal stability, conductivity and capacitance performance are improved significantly with increasing fraction of MoS<sub>2</sub>. When the content of MoS<sub>2</sub> was 45% in weight, the maximum weight loss velocity temperature is 365 °C which is 52 °C higher than that of PEDOT; the specific capacitance was 405 F g<sup>-1</sup>, about 4 times that of a PEDOT electrode; also the capacity retention was around 90% after 1000 cycles. This study provides a facile preparation method of organic/inorganic nanocomposites with enhanced electrochemical capacitance performance.

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## 1 Introduction

Supercapacitors possess outstanding properties such as the high power density typical of conventional capacitors together with the high energy density typical of rechargeable batteries. In addition, supercapacitors also exhibit fast charge–discharge processes and a long cycle life. These advantages mean they are expected to become an efficient and practical energy storage device.<sup>1</sup> Research into supercapacitors is largely focused on improving performance, reducing cost and improving the environmental friendliness of the devices. The most commonly used electrode materials include carbon material,<sup>2</sup> transition metal oxides<sup>3,4</sup> and conductive polymers.<sup>5–8</sup> There are limitations to a single species used for electrodes active materials, like carbon nanotubes, graphene and its derivatives typically have lower specific capacitances than conductive polymers, ruthenium dioxide (RuO<sub>2</sub>) can suffer from poisoning, and conductive polymers usually possess poor cycle stability. These factors limit their application as electrode materials in supercapacitors.<sup>9,10</sup> Composites of conductive polymers and inorganic materials offer a promising combination of cycle stability, cost-efficiency and good capacitance performance.<sup>11,12</sup>

Supercapacitors work based on two charge-storage mechanisms: surface ion adsorption (electric double layer

capacitance) and redox reactions (pseudocapacitance).<sup>13</sup> Conducting polymers are so-called pseudocapacitors, *i.e.*, they store charge, not only in the electrical double layer, but also faradaically in the polymer matrix.<sup>14</sup> Among these conductive polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) possess the potential to be used as an electrode due to its superior conductivity and stability.<sup>15</sup> Additionally, PEDOT has a larger electrochemical window compared to other conducting polymers. It has been reported that PEDOT can be composited with transition metal oxide, graphene and carbon materials to prepare electrode materials.<sup>16–18</sup> Two-dimensional (2D) layered compounds such as graphite and transition metal oxides can offer a large surface area to storage charge, resulting in good characteristics for electric double layer capacitance.<sup>19,20</sup> Molybdenum disulfide (MoS<sub>2</sub>) is a typical 2D layered material that is non-toxic, available at low cost and has been confirmed to have high specific capacity and cycle stability when used as an anode material.<sup>21</sup> The layered MoS<sub>2</sub> can be anticipated to exhibit good capacitive properties due to its sheetlike morphology, which provides a large surface area for double-layer charge storage. In addition, the transition metal Mo center can exhibit a range of oxidation states from +2 to +6, providing it pseudocapacitance abilities similar to RuO<sub>2</sub>. Composites based on PEDOT and 2D layered MoS<sub>2</sub> are expected to offer the synergetic combination of good mechanical properties and excellent capacitance derived from both charge-storage mechanisms.

Conjugated polymer/MoS<sub>2</sub> composites can be prepared by means of the exfoliating/restacking technique of Li<sub>x</sub>MoS<sub>2</sub>. First, MoS<sub>2</sub> was intercalated by lithium to form Li<sub>x</sub>MoS<sub>2</sub> and exfoliated into the single-molecule-layer MoS<sub>2</sub> suspension in water, and then in the process of MoS<sub>2</sub> restacked, polymers can be

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inserted into the layered host MoS<sub>2</sub> in the following two ways: (1) direct insertion approach, where the polymer are first dispersed in solvent and then inserted into the MoS<sub>2</sub> layered structure; (2) *in situ* intercalation/polymerization approach, where the intercalated monomer was inserted first, followed the monomer polymerized in the present of MoS<sub>2</sub>. As for the former, polyaniline (PANI) and its intercalation compounds PANI/MoS<sub>2</sub> have been prepared by mixing a solution of PANI and a suspension of single-layer MoS<sub>2</sub>.<sup>22,23</sup> However, the effect of mixing is dependant on the solubility of the conjugated polymer. For most conjugated polymers, poor solubility limits their application in composites. *In situ* intercalation/polymerization are the facile approach for the fabrication of conjugated polymer/MoS<sub>2</sub> composites. The composites of MoS<sub>2</sub> and conjugated polymers such as polypyrrole, polythiophene and its derivates have been prepared by this method.<sup>24–26</sup> The study on PEDOT/MoS<sub>2</sub> composites used for capacitor has not been reported.

The purpose of this work is to enhance the capacitance properties of PEDOT electrode materials *via* introduction of 2D layer MoS<sub>2</sub>. PEDOT/MoS<sub>2</sub> intercalated composites were synthesized *via in situ* polymerization in a single layer suspension of MoS<sub>2</sub> with APS as an oxidizing agent. The structure, thermal stability and capacitance performance were examined and the relationship between structure and properties are discussed. The well-defined intercalated structures of PEDOT/MoS<sub>2</sub> composites exhibit improved thermal stabilities and capacitance properties. It can be deduced that a synergistic effect occurs between PEDOT and MoS<sub>2</sub> interlayer.

## 2 Experimental

### 2.1 Materials

EDOT monomer (99%), *N*-butyllithium (1.6 M solution in hexane) was obtained from Aladdin industrial Inc. MoS<sub>2</sub> (99%) is from Hefei Kehua Fine Chemical Industry Research Institute. APS, methanol and acetone are from Sinopharm Chemical Reagent Co., Ltd.

### 2.2 Synthesis of PEDOT/MoS<sub>2</sub> nanocomposites

The suspension of single layer MoS<sub>2</sub> was prepared based on the literature.<sup>27</sup> Commercial raw 2H-MoS<sub>2</sub> was soaked in 1.5 equivalents butyllithium and kept in a nitrogen atmosphere for 3 days. The Li<sub>x</sub>MoS<sub>2</sub> product was then exfoliated in water (~100 mL) through a redox reaction. 0.8 mL EDOT was added into a three-necked flask with the different number of single layer MoS<sub>2</sub> suspension (10, 20, 30 mL). This solution was stirred until a homogeneous distribution was obtained. 3.42 g of APS (EDOT-APS molar ratio is 1 : 2) was dissolved into deionized water and added dropwise to the flask followed by mechanical stirring for 72 h at the room temperature. The reaction product was washed using a methanol-acetone mixture (methanol-acetone volume ratio is 2 : 1) followed by distilled water and then put into a vacuum drying oven for desiccation (24 h at 60 °C). The PEDOT/MoS<sub>2</sub> intercalated composites with 14 wt%, 30 wt% and 45 wt% contents of MoS<sub>2</sub> were named PEDOT/MoS<sub>2</sub>-14, PEDOT/MoS<sub>2</sub>-30, PEDOT/MoS<sub>2</sub>-45, respectively.

PEDOT without acid doping was also synthesized as above for comparison.

### 2.3 Characterization

X-ray diffraction (XRD) data were recorded using a Rigaku D/Max-2550 diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The morphology of MoS<sub>2</sub> and PEDOT/MoS<sub>2</sub> nanocomposites was examined using a field emission scanning electron microscope (FE-SEM, SU8020, Hitachi, Japan), operated at an acceleration voltage of 5 kV and equipped with an energy-dispersive X-ray (EDX) spectrometer and a field emission transmission electron microscope (FE-TEM, JEM-2100F, JEOL, Japan, operated at an accelerating voltage of 200 kV). The surface chemical properties of PEDOT/MoS<sub>2</sub> nanocomposites were investigated using EDX spectrometer. The thermal stabilities of all PEDOT/MoS<sub>2</sub> samples were characterized using a TG 209 F3 (Netzsch, Germany) with a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere. Electrical conductivity at room temperature was determined using a conventional four-probe method on pressed pellets, formed under a pressure of 20 MPa with a diameter of 10 mm. Cyclic voltammetry (CV), constant current charge-discharge tests and electrochemical impedance spectroscopy (EIS) experiments were conducted using a CHI660B electrochemical workstation with a three-electrode system. The working electrode was prepared by mixing the PEDOT/MoS<sub>2</sub> powder, carbon black and polyvinylidene fluoride (PVDF) binder (85 : 10 : 5 by weight). The mixture (~0.007 g) was pressed onto the steel mesh (~30 mm<sup>2</sup>), and dried under vacuum for 3 h at 60 °C. The thickness of the working electrode is about 0.3 mm. We can think these values are constant. Blank platinum was used as the counter electrode. Ag/AgCl was used as the reference electrode. Experiments were carried out at ambient temperature using 1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution as an electrolyte.

## 3 Results and discussion

### 3.1 Structure and morphology

The structures of PEDOT, restacked MoS<sub>2</sub> and PEDOT/MoS<sub>2</sub> composites were confirmed by FT-IR spectra. As shown in Fig. 1, the presence of peaks at 1382 and 1350 cm<sup>-1</sup> (C-C and C=C stretching vibrations of thiophene ring), 1204 and 1095 cm<sup>-1</sup>

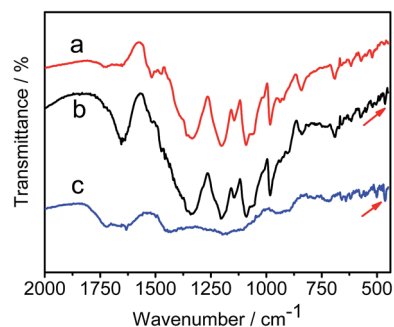


Fig. 1 FT-IR spectra of PEDOT (a), PEDOT/MoS<sub>2</sub> composites (b) and restacked MoS<sub>2</sub> (c).

(C–O–C stretching vibrations in ethylene oxide unit), 984 and 694  $\text{cm}^{-1}$  (C–S stretching vibrations in thiophene ring) prove the formation of PEDOT. The peak at about 465  $\text{cm}^{-1}$  in restacked  $\text{MoS}_2$  is assigned to Mo–S stretching mode of vibration. In comparison with pure PEDOT, the presence of peak at about 465  $\text{cm}^{-1}$  in PEDOT/ $\text{MoS}_2$  composites proves the existence of  $\text{MoS}_2$ . The intercalation of PEDOT into the  $\text{MoS}_2$  host layers is demonstrated by powder X-ray diffraction. Fig. 2a provides the XRD pattern of the dry restacked  $\text{MoS}_2$ . This presents an obvious (002) diffraction peak, indicating that the  $\text{MoS}_2$  layer is still regularly restacked along the  $c$ -axis. The restacked  $\text{MoS}_2$  shows broadened peaks and a shortened (002) diffraction peak, suggesting that the mean crystallite size of the restacked  $\text{MoS}_2$  is much smaller than that of raw bulk 2H- $\text{MoS}_2$ .<sup>28</sup> The typical XRD patterns of PEDOT/ $\text{MoS}_2$  composites are shown in Fig. 2b. The (001) diffraction peak is observed with shifts to lower angles that indicates an increase in inter-layer spacing. The middle strong (001) peak at  $6.54^\circ$  corresponds to  $d = 13.79 \text{ \AA}$ . Compared with bulk  $\text{MoS}_2$ , the interlayer spacing of  $\text{MoS}_2$  in the intercalation composites was expanded by approximately 7.64  $\text{\AA}$  due to the intercalation of PEDOT. The strong  $c$ -axis peaks at  $2\theta = 14.3^\circ$  (Fig. 2b) also reveals that partial  $\text{MoS}_2$  is still regularly restacked along the  $c$ -axis without sandwiching PEDOT, and partially intercalated PEDOT/ $\text{MoS}_2$  composites are obtained in our experiment. The data from the PEDOT/ $\text{MoS}_2$  composites also shows another two broad peaks at  $ca. 2\theta = 18^\circ$  and  $26^\circ$  which are different from those of  $\text{MoS}_2$  and should be attributed to the diffraction patterns of PEDOT,<sup>29</sup> indicating the periodicity parallel and perpendicular characteristics of the polymer chain. Charge storage in  $\text{MoS}_2$  can occur *via* intersheet or intrasheet double-layer charge storage modes,<sup>21</sup> and the well-ordered PEDOT/ $\text{MoS}_2$  intercalation composites offer the potential of being good electrode materials.

The morphology and the chemical surface characteristics of  $\text{MoS}_2$  and PEDOT/ $\text{MoS}_2$  composites were characterized by TEM, SEM and EDX. The TEM image of as-prepared exfoliated  $\text{MoS}_2$  shows thin layered particles with a typical size of 350 nm long and 200 nm wide (Fig. 3a). The 2D lamellar  $\text{MoS}_2$  with higher specific surface area of  $\text{MoS}_2$  is favorable for double layer capacitive properties in comparison with bulk  $\text{MoS}_2$ . These  $\text{MoS}_2$  structures have exhibited typical single-crystal features, as revealed by the SAED pattern (inset in Fig. 3c). The HRTEM

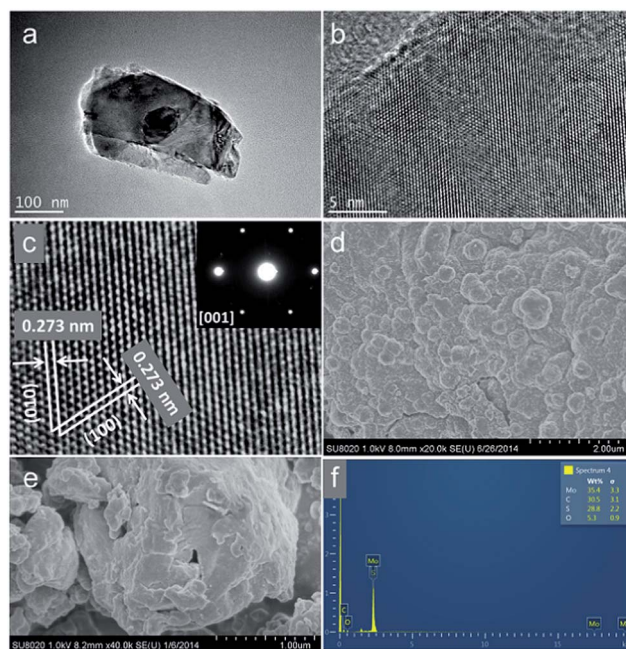


Fig. 3 TEM and HR-TEM images of Li-intercalated  $\text{MoS}_2$  (a–c), SEM of PEDOT/ $\text{MoS}_2$  (d and e), EDX pattern of PEDOT/ $\text{MoS}_2$  (f).

image does show lattice fringes corresponding to  $\text{MoS}_2$  (Fig. 3b), two kinds of lattice spacing of 0.273 nm can be observed in the magnified HRTEM image, corresponding to the (100) and (101) planes of standard  $\text{MoS}_2$ , respectively (Fig. 3c). The combinations of SEM and EDX methodologies not only help to observe PEDOT/ $\text{MoS}_2$ , they also provide information on the two-dimensional, physico-chemical nature of the composites. Scanning electron micrographs of PEDOT/ $\text{MoS}_2$  composites are presented in Fig. 3d and e and EDX spectrograms are shown in Fig. 3f. The morphology of the conjugated polymer strongly depends upon the nature of the anionic oxidizing agents used and preparation methods. As shown in Fig. 3d, PEDOT/ $\text{MoS}_2$  composites took on a uniform state with plate like structure, which is different from the nanoribbon like structure of PEDOT/ $\text{MoS}_2$  composites produced using  $\text{FeCl}_3$  as an oxidizing agent.<sup>26</sup> The existence of Mo, S, C and O are evidenced from EDX analysis performed on the surface of the composites (Fig. 3f), suggesting that  $\text{MoS}_2$  and PEDOT exist in the composites.

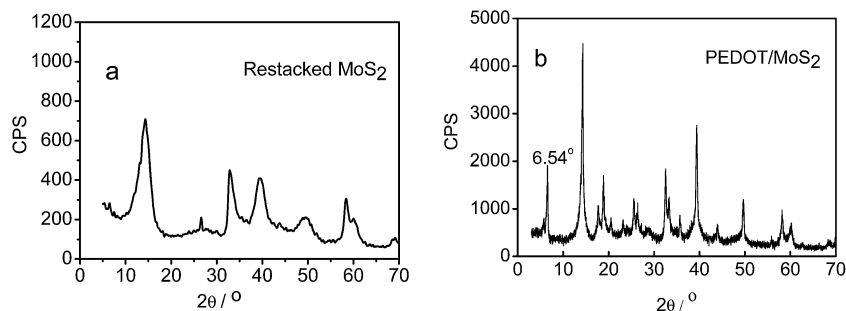


Fig. 2 XRD patterns of restacked  $\text{MoS}_2$  (a) and PEDOT/ $\text{MoS}_2$  composites (b).

Furthermore, the elemental composition of PEDOT/MoS<sub>2</sub> can be calculated by EDX measurements, its chemical ratios of Mo, S, C and O are 35.4 wt%, 28.8 wt%, 30.5 wt% and 5.3 wt%, respectively, which is in general agreement with the product expected from the experiment, showing the composites are uniform.

### 3.2 Thermal analysis

The thermal analysis of PEDOT and PEDOT/MoS<sub>2</sub> nanocomposites in N<sub>2</sub> atmosphere was obtained using TGA experiments as shown in Fig. 4. All the samples exhibited slight weight loss in the range of 100–150 °C, which can be ascribed to the loss of water. The mass loss which occurs between 250 °C and 400 °C could be attributed to the combustion and departure of the organic polymer components. The maximum weight loss velocity temperature of pure PEDOT and PEDOT/MoS<sub>2</sub> nanocomposites are seen at 313 °C, 323 °C, 349 °C and 365 °C, respectively. It is clear that the thermal stability of PEDOT/MoS<sub>2</sub> intercalated composites were better than that of PEDOT, and the thermal stability of PEDOT/MoS<sub>2</sub> increased with increasing content of MoS<sub>2</sub>. 2D layered nanomaterials can improve the properties of polymers, including strength, modulus, thermal stability and gas barrier effects.<sup>30</sup> MoS<sub>2</sub> used as 2D layered nanofillers in PEDOT/MoS<sub>2</sub> composites increase the thermal stability of the PEDOT matrix due a physical barrier effect which retards the diffusion of degradation products, gases and heat. The mass loss is followed by a slight continuous weight loss up to 600 °C, which can be attributed to the complete departure of residual polymer components. There is still 31% weight remaining in pure PEDOT when the temperature reaches 800 °C. This should be attributed to the carbonization of the conjugate ring structure of PEDOT at high temperatures. The remaining weight of PEDOT/MoS<sub>2</sub> composites are around 41%, 54% and 62% at 800 °C, respectively. The weight percentage of MoS<sub>2</sub> in PEDOT/MoS<sub>2</sub> intercalation composites can also be determined by TGA. The weight percentage of MoS<sub>2</sub> can be calculated in the following way. After heated to 800 °C, MoS<sub>2</sub> (weight percentage =  $x$ ) and the residual of PEDOT ( $0.31(1 - x)$ ) remains. So we have  $x + 0.31(1 - x) = 0.41, 0.54, \text{ and } 0.62$ . The corresponding weight percentages of MoS<sub>2</sub> are 14%, 30% and 45%, respectively.

### 3.3 Electrical conductivity

Room temperature electrical conductivities were measured on pellets pressed from powders. The conductivity values of

restacked MoS<sub>2</sub>, pure PEDOT and PEDOT/MoS<sub>2</sub> nanocomposites are summarized in Table 1. The measured conductivity values of restacked MoS<sub>2</sub> and PEDOT were  $1.37 \times 10^{-2} \text{ S cm}^{-1}$  and  $2.43 \times 10^{-2} \text{ S cm}^{-1}$ , respectively. However, the measured conductivity values of PEDOT/MoS<sub>2</sub> nanocomposites without any acid doping are an order of magnitude higher than that of each component, *i.e.*, restacked MoS<sub>2</sub> and pure PEDOT. These values increased with increasing amount of MoS<sub>2</sub>. The electrical conductivity values of PEDOT/MoS<sub>2</sub>-14, PEDOT/MoS<sub>2</sub>-30, and PEDOT/MoS<sub>2</sub>-45 are  $5.56 \times 10^{-1} \text{ S cm}^{-1}$ ,  $7.53 \times 10^{-1} \text{ S cm}^{-1}$  and  $9.10 \times 10^{-1} \text{ S cm}^{-1}$ , respectively. The increase of electrical conductivity in intercalated composites is explained by an interaction between conductive PEDOT and MoS<sub>2</sub> layers. The conducting macromolecules of PEDOT with conjugated  $\pi$ -bonds intercalated into the host interlayer of MoS<sub>2</sub> are arranged in a layered arrangement according the XRD analysis as above. This architecture is advantageous for transportation of electrons between the organic and inorganic components. Moreover, intercalation of MoS<sub>2</sub> with lithium results in a structural transformation from trigonal prismatic to octahedral metal coordination and a change in properties from semiconducting to metallic.<sup>31</sup> Increasing the contents of metallic restacked MoS<sub>2</sub> in PEDOT/MoS<sub>2</sub> nanocomposites can improve the conductivity property.

In comparison with FeCl<sub>3</sub> as oxidizing agent,<sup>26</sup> PEDOT/MoS<sub>2</sub> produced using APS as oxidizing agent in this work showed higher conductivity. The electrical conductivity of composites is related to the particle size and shape.<sup>32</sup> Higher surface area for electron transfer is usually favorable for increasing electron mobility, and the smaller particle size provides a higher surface area for electron transfer. The particle size and shape of synthesized PEDOT depends on the oxidant type, PEDOT nanoparticles using APS as the oxidizing agent showed a smaller particle size and higher electrical conductivity than FeCl<sub>3</sub>. The conductivity of the conjugated polymer is also related to the length of their conjugated chain. The addition of inorganic compounds may decrease the degree of conjugated  $\pi$  bonds in the polymer when using an improper synthesis method.<sup>26,33</sup> APS using as the oxidizing agent can provides a better stability polymerization system in comparison to using FeCl<sub>3</sub> as an oxidizing agent. The progressive conductivity of PEDOT/MoS<sub>2</sub> intercalation composites reported here indicates that the preparation method is a facile approach for organic/inorganic composites.

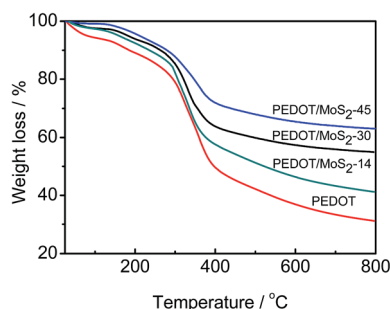


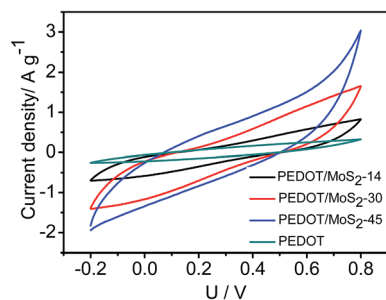
Fig. 4 TGA curves of PEDOT and PEDOT/MoS<sub>2</sub> composites.

### 3.4 Electrochemical characteristics

The electrochemical behavior of the samples when used as active electrode materials was investigated using CV, EIS and constant current charge–discharge tests in 1.0 M H<sub>2</sub>SO<sub>4</sub> aqueous solution. Fig. 5 illustrates the CV performance of pure PEDOT and PEDOT/MoS<sub>2</sub> intercalation composites with different MoS<sub>2</sub> contents at a scan rate of 50 mV s<sup>-1</sup> in the potential window range of -0.2–0.8 V. These data are normalized to the geometric area of the electrode surface. The voltammograms reveal high electrochemical reversibilities of PEDOT and PEDOT/MoS<sub>2</sub> intercalation composites at this

Table 1 The data of electrical conductivities

Sample	Restacked MoS <sub>2</sub>	PEDOT	PEDOT/MoS <sub>2</sub> -14	PEDOT/MoS <sub>2</sub> -30	PEDOT/MoS <sub>2</sub> -45
Conductivity (S cm <sup>-1</sup> )	1.37 × 10 <sup>-2</sup>	2.43 × 10 <sup>-2</sup>	5.56 × 10 <sup>-1</sup>	7.53 × 10 <sup>-1</sup>	9.10 × 10 <sup>-1</sup>

Fig. 5 CV curves of pure PEDOT and PEDOT/MoS<sub>2</sub> composites at scan rate of 50 mV s<sup>-1</sup>.

potential range and sweep rate. In comparison to pure PEDOT, the CV curves PEDOT/MoS<sub>2</sub> intercalation composites show a deviation from the rectangular shape, whereby the CV profile resembles an 'S'-shape, which suggesting the coexistence of charge storage mechanisms with double layer charge storage and pseudocapacitive faradic charging. The curves show no obvious peaks, indicating that the capacitor assembled using a PEDOT/MoS<sub>2</sub> nanocomposite electrode has fast charge and discharge properties.<sup>34</sup> By comparison, the area of the CV curve for the PEDOT/MoS<sub>2</sub> nanocomposite is larger than those of the pure PEDOT electrode, indicating higher specific capacitance and the synergistic effect of PEDOT and MoS<sub>2</sub>. In this case the charge carrier within the electrodes could be more effective and rapid due to the interaction between PEDOT and MoS<sub>2</sub> layers. Furthermore, the CV curve area increases at the same scan rate as the fraction of MoS<sub>2</sub> increases, indicating that the capacitance of PEDOT/MoS<sub>2</sub> nanocomposites increases with the increase in the MoS<sub>2</sub> content. The increase of specific capacitance also suggests that MoS<sub>2</sub> in the composites contributes greatly to the specific capacitance.

Electrochemical impedance measurements were used to study the redox processes of the PEDOT/MoS<sub>2</sub> nanocomposites and to evaluate their ionic and electronic conductivity as well as specific capacitance. The Nyquist plots for PEDOT and PEDOT/MoS<sub>2</sub> nanocomposites with different MoS<sub>2</sub> content are shown in Fig. 6. Impedance was tested in the frequency range from 0.05 kHz to 100 kHz at open-circuit potential. The impedance value was composed of the resistance of the electrode, electrolyte and the contact resistance at the interface active material/current collector. There is great similarity in the Nyquist plots for all of these materials. At high frequency, the plots of PEDOT and PEDOT/MoS<sub>2</sub> intercalation composites all show favourable semicircles which is indicative of the charge transfer phenomena of a faradic redox process. The diameter of the semicircle corresponded to interface charge transfer resistance ( $R_{ct}$ ). The  $R_{ct}$  of PEDOT/MoS<sub>2</sub> is smaller than that of PEDOT,

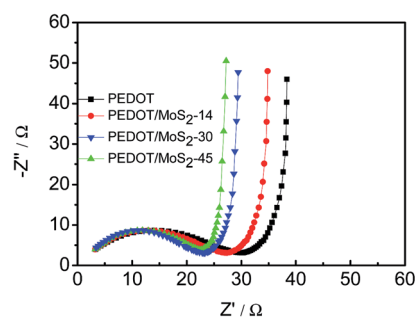
showing PEDOT/MoS<sub>2</sub> composites have the faster charge transfer rates. Meanwhile, the  $R_{ct}$  of PEDOT/MoS<sub>2</sub> composites decreased with increasing fraction of MoS<sub>2</sub>. This indicates that the addition of MoS<sub>2</sub> reduces charge transfer resistance and improves the conductivity of the electrode materials. At low frequency, the line is almost vertical to the real axis in the imaginary part of the impedance demonstrating an ideal capacitive behavior for PEDOT/MoS<sub>2</sub> nanocomposites. This ideal capacitive behavior is attributed to the faradic pseudo-capacitance of the composite electrodes.<sup>35</sup> This conclusion agrees with the capacitance properties above.

### 3.5 Charge-discharge cycling performance

The galvanostatic charge-discharge curves of PEDOT and PEDOT/MoS<sub>2</sub> are displayed in Fig. 7a. It can be observed that all the charge-discharge curves of PEDOT and PEDOT/MoS<sub>2</sub> took on the shapes that closed to a triangle, and show distinct characteristics of reversible charge-discharge. Particularly, PEDOT/MoS<sub>2</sub> composites have longer charge-discharge times than PEDOT as can be ascribed to their high capacitance performances. The specific capacitance can be evaluated using the following equation:<sup>36</sup>

$$C_g = \frac{I\Delta t}{\Delta V \times m}, \quad (1)$$

where  $C_g$  (F g<sup>-1</sup>) is the specific capacitance of the electrode,  $I$  (A) is the discharge current,  $\Delta t$  (s) is the discharge time,  $\Delta V$  (V) is the potential window and  $m$  (g) is the mass of active materials loaded in working electrode. According to the equation, the specific capacitance of PEDOT can be calculated as 109 F g<sup>-1</sup>. The discharge time of PEDOT/MoS<sub>2</sub> composites increased with increasing MoS<sub>2</sub> content. The specific capacitances of PEDOT/MoS<sub>2</sub>-14, PEDOT/MoS<sub>2</sub>-30 and PEDOT/MoS<sub>2</sub>-45 are 208 F g<sup>-1</sup>, 354 F g<sup>-1</sup> and 405 F g<sup>-1</sup>, respectively. The specific capacitance of the PEDOT/MoS<sub>2</sub>-45 sample reached four times that of pure PEDOT. This gives clear proof that a

Fig. 6 Nyquist impedance spectra of pure PEDOT and PEDOT/MoS<sub>2</sub> composites.

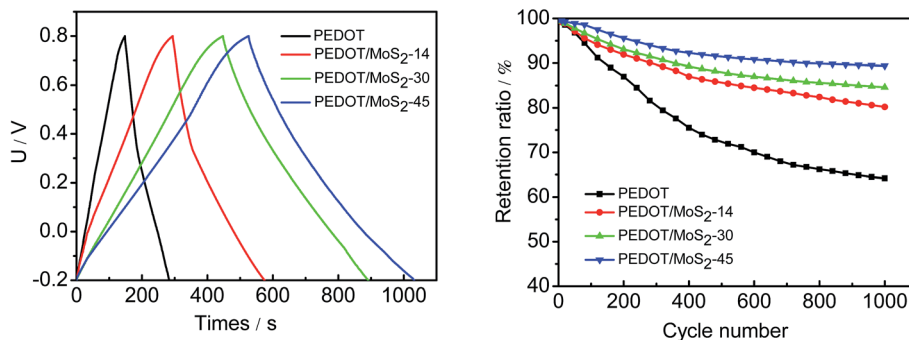


Fig. 7 Galvanostatic charge–discharge curves (a) and cycle stability (b) of electrodes with pure PEDOT and PEDOT/MoS<sub>2</sub> at current density of 0.8 A g<sup>-1</sup>.

synergistic effect of PEDOT and MoS<sub>2</sub> allows a higher capacitance for the composite electrode which derived from both charge-storage mechanisms. Huang *et al.*<sup>37</sup> and Ma *et al.*<sup>38</sup> has reported the composites of PANI/MoS<sub>2</sub> and PPy/MoS<sub>2</sub> respectively, in which the preparation method of conducted polymer/MoS<sub>2</sub> composites is mainly through chemical synthesis from Mo precursors such as sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>·H<sub>2</sub>O). PANI/MoS<sub>2</sub> composites exhibit a specific capacitance of 575 F g<sup>-1</sup> at a current density of 1 A g<sup>-1</sup> in a three-electrode system, which is about two times than that of pure PANI. The composites of PPy and MoS<sub>2</sub> afforded a high specific capacitance of 553.7 F g<sup>-1</sup> at a current density of 1 A g<sup>-1</sup> in a typical three-electrode test, which is also about two times than that of pure PPy. The specific capacitance of these composites all higher than each of the composition, and shows the synergistic effect in conducted polymer/MoS<sub>2</sub> composites. For comparison, the preparation of PEDOT/MoS<sub>2</sub> nanocomposites in this work shows a more effective improvement method in supercapacitance performance.

The cycling stability of PEDOT and PEDOT/MoS<sub>2</sub> nanocomposite electrodes was measured by charge–discharge cycling at a current density of 0.8 A g<sup>-1</sup>. As shown in Fig. 7b, the specific capacitance of PEDOT is only 64% after 1000 charge–discharge cycles, while the PEDOT/MoS<sub>2</sub> nanocomposite electrodes displayed greater cycle stability, with this stability increasing with increasing fraction of MoS<sub>2</sub>. The specific capacitance of the PEDOT/MoS<sub>2</sub>-45 sample decreased only 5% after 200 cycles, holding steady at 90% from 300 cycles to 1000 cycles. This demonstrates that PEDOT/MoS<sub>2</sub>-45 has good long-term cycle stability. These studies suggest that the composite electrodes have fast charge exchange, leading to good cyclic power storage ability. The excellent cycling stability can be explained by the following two reasons: (1) the higher specific surface area of MoS<sub>2</sub> is favorable to the rapid diffusion of ions by providing a low-resistance pathway and (2) the intercalation of conjugated polymer into the MoS<sub>2</sub> interlayer facilitates electron transport during the charging and discharging processes because of its high conductivity. This result is also in agreement with the thermal stability analysis above, *i.e.*, the better thermal stability of PEDOT/MoS<sub>2</sub> brings smaller volume change during the charge–discharge processes.

## 4 Conclusions

A facile synthesis method of PEDOT/MoS<sub>2</sub> nanocomposites has been developed *via in situ* polymerization in the presence of ammonium persulfate. The well-defined intercalated structure of PEDOT/MoS<sub>2</sub> nanocomposites is beneficial to their conductivity, thermal stability and capacitance. The conductivity, thermal stability and the specific capacitances of the PEDOT/MoS<sub>2</sub> nanocomposites were enhanced by increasing the amount of MoS<sub>2</sub>, exhibiting a good synergetic effect between an inorganic layered compound and organic polymer. When the content of MoS<sub>2</sub> was 45% in weight, the specific capacitance achieved was 405 F g<sup>-1</sup>, about 4 times larger than that of a PEDOT electrode. The PEDOT/MoS<sub>2</sub> nanocomposite also retained a capacity of around 90% after 1000 cycles. This work offers a strategy for preparing supercapacitors with high performance and good stability.

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