Ternary Composite MnO₂@MoS₂/Polypyrrole from In-situ Synthesis for Binder-free and Flexible Supercapacitor

Dubin DONG*

Zhejiang A&F University, Hangzhou 311300, China

*Corresponding author: Dubin DONG, 812588636@qq.com
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Abstract: MnO₂@MoS₂/Polypyrrole ternary composite is prepared through hydrothermal methods and a simple oxidation process by using MnO₂@MoS₂ sheet as the substrate and polypyrrole. The ternary composite serves as an electrode for pseudocapacitor which has more superior electrochemical properties compared with the binary complex. The supercapacitor electrode consists of two dimensional MoS₂ layers as load skeleton, MnO₂ providing electrochemical performance and polypyrrole improving high electric conductivity. These three components form a compact structure and synergistic effect leads to enhancing sufficient oxidation reduction for supercapacitor performance. Hence, MnO₂@MoS₂/Polypyrrole structure possesses higher specific capacitance of 490 F/g at a current density of 1 A/g and excellent cycling stability of 90% after 1000 cycles at 1 A/g. Here, Polypyrrole is also used as the binder material, exhibiting mechanical flexibility for electrode. The results of this study provides a simple method to produce an effective material for flexible pseudocapacitor electrodes for higher energy storage devices.

Keywords: flexible supercapacitor; MnO₂@MoS₂/Polypyrrole structure; synergistic effect; electrochemical performance

1 Introduction

Currently, in order to meet the requirement of higher electrochemical energy storage of devices, supercapacitors were attracted increasing attention due to superior performance than batteries (Chen et al., 2013). Supercapacitors were widely studied because of their high power density, fast charging/discharging rate and long cycle life (Ranganatha et al., 2018; Adams et al., 2019). Double electric layer capacitor (EDLC) and pseudocapacitor were typical energy storage types in supercapacitors according to charge storage mechanism (Wang et al., 2016; Lee et al., 2018). The store mechanism of the EDLC based on ion accumulation only took place on interface of materials. On the other hand, pseudocapacitor was generated by the rapid and reversible surface or near-surface redox faradaic reactions of active materials. It had been confirmed that pseudocapacitor had larger charge transfer-reaction, compared with part of EDLC which was formed with conductive porous material, such as carbon-based materials (Chen, 2013; Kim et al., 2016). So pseudocapacitor was a key technological system for higher electrochemical energy storage. Generally, transition-metal oxides, such as MnO₂, were advantageously used for active materials in pseudocapacitors on account of the prominent cation exchange (Li et al., 2011; Yu et al., 2011; Chen et al., 2015). The MnO₂ as typical pseudocapacitive material, had been widely investigated because of its environmental friendliness, low cost, natural availability and high theoretical specific capacitance (1380 F/g). However, highly efficient utilization of MnO₂ in energy application was hindered by instability and poor conductivity. Additionally, the structural collapse or element dissolution of MnO₂ during charge/discharge process could lead to inadequate rate capability. In order to solve these major problems, several strategies were studied on MnO₂ composite materials. Among those studies, it was noted that MnO₂@MoS₂ binary composite materials have been effectively solving the instability of metal oxides through using MoS₂ substrate (Li et al., 2016; Pan et al., 2016; Pan et al., 2017). However, poor conductivity of MnO₂@MoS₂ binary composite materials were not primarily improved. As a substrate, MoS₂ had a 2H phase crystal structure of a monolayer band gap about 1.9 eV, which led to poor conductivity of MnO₂@MoS₂ nanohybrid. Therefore, how to improve Manganese oxides conductivity for supercapacitor based on MoS₂ substrate was a problem.

Aiming at these problems, it was key for MnO₂@MoS₂ nanohybrid that poor conductivity was solved and excellent cycling stability and higher specific capacitance were worked` out (Su et al., 2008; Ko et al, 2014; Yang et al., 2016; Xu et al., 2018). In order to promote conductivity, carbonaceous materials and conducting polymers were chosen for conducting materials. Carbonaceous materials had cycle stability and mechanical properties but no binder performance compared with conducting polymers. The advantageous feature of electrochemically active conducting
polymers are adhesion properties in energy storage devices, so no binder would be added in nanohybrid. Conducting polymer polypyrrole (PPy) was used as electrode materials due to low cost, easy preparation, high storage ability, relative environmental stability, great conductivity and large capacitive current (Yao et al., 2013; Bora et al., 2014; Ko et al., 2014; Wang et al., 2014; Ma et al., 2015; Shi et al., 2015). Hence, MnO$_2$@MoS$_2$ was coated with the PPy to obtain a remarkable conducting polymers nanohybrid. As a great conducting polymer, PPy conductive polymer of composite structures was sufficient to improve the conductivity in energy storage and become high quality electrode materials. It was noted that the PPy was compatible with MnO$_2$ in the presence of mild electrolytes. The PPy was mainly involved in the charge storage process, making major effect of conductivity. Moreover, Mo ions, had the range from +2 to +6 oxidation states to generate additional pseudocapacitance because PPy got a synergistic effect here (Bundles et al., 2006; Sharma et al., 2008; Spaldin et al., 2008; Yutaka et al., 2011; Aguirre et al., 2014; Wang et al., 2014). The disadvantage of the PPy about lower cycle life could be weaken by MoS$_2$ as a rigid support. Therefore, design of ternary MnO$_2$@MoS$_2$/PPy pseudo-capacitive electrode could improve the conductivity, increasing the synergy between substances.

In this paper, we developed MnO$_2$@MoS$_2$ binary complex coated with PPy to prepare the ternary MnO$_2$@MoS$_2$/PPy composite here. MnO$_2$ was based on the in-situ interface redox reaction on two-dimensional plane of MoS$_2$. And then pyrrole monomers proceeded in-situ oxidative polymerization on MnO$_2$@MoS$_2$ composite carrier. The synergistic effect between PPy and MnO$_2$@MoS$_2$ was stronger for the potential electrode materials of supercapacitor. Compared with MnO$_2$@MoS$_2$ components, ternary nanocomposites exhibited better rate capability, because the PPy solved the problem of poor conductivity as conducting additives. The PPy provided binder between ternary nanocomposites, so no binder material was added in, rather the electrochemical material remained flexible. Ternary MnO$_2$@MoS$_2$/PPy composite held specific capacitance with 490 F/g at a current density of 1 A/g and cycling stability of 90% after 1000 cycles at 1 A/g. Hence, ternary MnO$_2$@MoS$_2$/PPy composite using a simple preparation method was a promising material for flexible electrochemical electrodes.

2 Materials and Methods

2.1 Materials

Pyrrole monomers was obtained from Aladdin. Ammonium persulphate [(NH$_4$)$_2$S$_2$O$_8$, APS], ethanol, H$_3$MoN$_2$O$_4$, CH$_4$N$_2$S, K$_2$MnO$_4$ and MnSO$_4$ were supplied from Sinopharm Chemical Regent. During the course of the experiment, deionized water was used to prepare the solution. All chemical reagents were in analytical grade used directly without further refinement.

2.2 Methods

2.2.1 Synthesis of MnO$_2$@MoS$_2$/PPy nanocomposites

The MnO$_2$@MoS$_2$/PPy nanocomposites were formed by hydrothermal reaction and the polymerization of pyrrole in-situ oxidation. In a typical process, 45.75 mg H$_3$MoN$_2$O$_4$ and 33.18 mg CH$_4$N$_2$S were dissolved in 50 mL H$_2$O by ultrasonic. The thermal reaction of 220°C was reached to obtain the flake molybdenum sulfide. Next, KMnO$_4$ (0.5 g) and MnSO$_4$ (0.2 g) were transferred into 40 mL MoS$_2$ nanocomposites suspension before hydrothermal route under 140°C about 6 h. The autoclave was then cooled naturally to room temperature and products were washed by ethanol. And then dried in a 60°C oven for 24 h. Then 200 μL pyrrole monomers were added in the above solution. The APS solution (0.41 g/mL) about 800 μL was mixed with a solution of MnO$_2$@MoS$_2$/pyrrole monomers. Afterwards, it was to ensure that the molar ratio of APS to pyrrole monomers was 1:2. The mixed solution was stirred for 12 h. The product was collected by filtration, washed with deionized water and ethanol. Finally, the products were dried in an oven at 60°C.

2.2.2 Characterization

Crystal structures of the materials were determined by X-ray diffraction (XRD) equipped with Cu Kα radiation (λ=0.154 06 nm). The different morphology of PPy/MnO$_2$@MoS$_2$ nanocomposites were characterized by scanning electron microscope (SEM, Quanta FEG 250, USA) and transient electromagnetic method (TEM, Tecnai G$^2$ F20). The X-ray photoelectron spectroscopy (XPS) measurement (Thermo Fisher K-Alpha) was tested with a monochromatic Al Kα radiation (hv=1486.6 eV). Surface area and pore size distribution of the samples were characterized by physical adsorption of N$_2$ at 77 K. Fourier transform infrared (FT-IR) spectra were characterized on a Nicolet Magna-IR 750 spectrometer.

2.2.3 Electrochemical characterization

In order to confirm the superior properties of the composite, electrochemical tests in this study were conducted at room temperature in a typical three-electrode configuration. The electrochemical properties including cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) were measured in 1 mol/L Na$_2$SO$_4$ by Pt wire as the counter electrode, Ag/AgCl as reference electrode and MnO$_2$@MoS$_2$/PPy nanocomposites as working electrode. The nanocomposite as flexible materials was bent for supercapacitor device. The CV curves were measured under scan rates of 100 mV/s between 0 and 1 V. The EIS measurement was carried out in the frequency range from

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100 kHz to 0.01 Hz at open circuit potential with an a perturbation of 5 mV. The GCD curves of different nanocomposite and pure PPy, MnO2 and MoS2 were recorded at current densities of 1 Ag⁻¹. The specific capacitance (Cm) of PPy/MnO₂@MoS₂ nanocomposites electrode was calculated from discharging curves by Equation (1):

\[ C_m = \frac{I \Delta t}{m \Delta V} \]  

where \( I \) is the discharging current in the measurement, \( \Delta t \) is the discharging time, \( m \) is the mass of nanocomposites material in a single electrode, and the potential range of \( V \) is the voltage drop upon discharge excluding the internal resistance (IR) drop.

### 3 Results and Discussion

The in-situ synthesis of MnO₂@MoS₂/PPy ternary composite was shown in Fig. 1a, MoS₂ sheet was successfully prepared by hydrothermal reaction after keeping the temperature at 220°C. In this system, H₈MoN₂O₄ and CH₄N₂S provided the source of Mo and S, respectively. During the experimental process, CH₄N₂S was converted to hydrogen sulfide, ammonia and carbon dioxide in hydrothermal solution. More importantly, due to the reductive character, H₂S could react with H₈MoN₂O₄, reducing the chemical valence of molybdenum ion from +6 to +4. The synthesis of MoS₂ sheet follows equations (2) and (3):

\[ \text{CS(NH}_2\text{)}_2\text{+2H}_2\text{O} \rightarrow 2\text{NH}_3\text{+CO}_2\text{+H}_2\text{S} \]  
\[ 4(\text{NH}_2)_2\text{MoO}_4\text{+15H}_2\text{S}+6\text{NH}_3\text{+6CO}_2 \rightarrow 4\text{MoS}_2\text{+(NH}_2\text{)}_2\text{SO}_4\text{+6NH}_4\text{SCN+24H}_2\text{O} \]

Then MnO₂ was formed in-situ growth on as-prepared MoS₂ sheet by hydrothermal method (Fig. 1b). The MnSO₄ and KMnO₄ reacted could be described as Equation (4):

\[ 2\text{KMnO}_4\text{+3MnSO}_4\text{+2H}_2\text{O} \rightarrow 5\text{MnO}_2\text{+2H}_2\text{SO}_4\text{+K}_2\text{SO}_4 \]

The growth of PPy on the 2D sheet surfaces was exhibited in Fig. 1c. Under the oxidation of APS, pyrrole monomers was supported on MnO₂@MoS₂ binary complex sheets through in-situ oxidation polymerization at room temperature. The strong coordination interaction generated between N groups and Mo ion. The MnO₂ particles, in coordination with the MoS₂, formed a rigid support and space for ion permeation. Therefore, charge exchange efficiency and stability of the PPy was improved. The method of in-situ grown provided a strong connection for the ternary structure, as well the possibility of rapid electrolyte penetration.

The morphological characteristics of MnO₂@MoS₂/PPy composite was monitored in SEM, TEM and energy dispersive X-ray spectroscopy (EDS). The results of Fig. 2a revealed that PPy was closely deposited on the surface of MnO₂@MoS₂ sheet. The TEM image (Fig. 2b) of ternary hybrid further presented the uniform loading between MoS₂, MnO₂ and PPy spherical particles. Evidently, MoS₂ was achieved with a suitable layer structure, owning the smooth edge of the film and natural wrinkle after hydrothermal. As marked in the green lines, the high-resolution TEM (HR-TEM) image in inset (b) clearly indicated the lattice fringe spacing of 0.61 nm which could be ascribed to (002) plane of MoS₂. The characteristic of MnO₂@MoS₂ sheet provided rational electrochemically active surface sites for PPy covering. Furthermore, the EDS elemental mappings of N, C, O, S and Mo elements, which were taken from the enclosed area in Fig. 2a, confirmed the composite structure (Fig. 2c). The elements of N and C suggested the presence of the PPy. The S, Mo, O and Mn as the major elements were corresponding to the MoS₂ and MnO₂ which were coexistence in composite. Elemental mapping explicitly reflected enrichment of nanoparticles. A dense PPy was successfully dispersed on MnO₂@MoS₂ sheet. The nanosheets of ternary hybrid would contribute to increasing the surface area of the active material to improve electrochemical performance. In experiments, it was possible that the ternary structure of MnO₂@MoS₂/PPy led to a synergistic effect that further promoted the rapid transport of ions and electrons in the electrolyte for
supercapacitor application. The result of elemental mapping obtained was consistent with SEM and TEM, confirming the experience as well.

The XRD spectra of MnO$_2$@MoS$_2$/PPy composite was represented in Fig. 3. Main diffraction peaks for the as-prepared composite could be indexed to $\alpha$-MnO$_2$ (JCPDS No. 44-0141) and MoS$_2$ (JCPDS No.37-1492). Narrow peak at $2\theta=37.5^\circ$ was an evidence of high $\alpha$-MnO$_2$ crystallinity. The X-ray diffraction data indicated that the interplanar spacing of MoS$_2$ was about 6.1 Å, which was consistent with the value of the HR-TEM image (inset in Fig. 2b). A typical broad peak at $2\theta=25^\circ$ was formed because of PPy which provided abundant conductivity. The broad and strong peak of PPy in spectra was related to the fact that structural characterization with a mass of PPy covered on MnO$_2$@MoS$_2$ sheet. No obvious impurity peak was detected, indicating that the high purity MnO$_2$@MoS$_2$/PPy composite was produced. It was obviously observed that the combination of ternary composite was more balanced. In brief, the result of the XRD demonstrated that PPy was attached onto MnO$_2$@MoS$_2$ sheets successfully.

The FT-IR spectra exhibited more structural information at the molecular level for MnO$_2$, MnO$_2$@MoS$_2$ and MnO$_2$@MoS$_2$/PPy composite (Fig. 3). The MnO$_2$@MoS$_2$/PPy contained the majority of characteristic bands with PPy. The characteristic peak at 470 cm$^{-1}$ was assigned to vibration of Mo-S band. Remarkably, Mn-O vibration was identified at approximately 540 cm$^{-1}$. Besides, the peak at 1184 cm$^{-1}$ was allocated to the C‒C breathing vibration and the bands at 963 cm$^{-1}$ might be related to the presence of polymerized pyrrole. The characteristic peak appeared at 1628 cm$^{-1}$ because of the vibration of C=C/C–C as well. The peak at 1038 cm$^{-1}$ was caused by N‒H in-plane vibration bands of the pyrrole ring. And that the observed peak at 1554 cm$^{-1}$ corresponded to typical pyrrole rings vibration. Another important factor was that the band at 1295 cm$^{-1}$ and 1474 cm$^{-1}$, assigned to the =C–H out-of-plane vibration, which was different from PPy alone at 1480 and 1559 cm$^{-1}$, respectively. Hence, the predominant phenomenon here was that wave moved into lower numbers. Our observation of the difference peak position was between the sample and the pure PPy reported in the literature. One possibility would be that a
The XRD spectra of MnO$_2$@MoS$_2$/PPy composite powders (a), FT-IR spectrum of MnO$_2$, MnO$_2$/MoS$_2$ and MnO$_2$@MoS$_2$/PPy composite (b), XPS survey of MnO$_2$@MoS$_2$/PPy (c) and XPS spectrum of Mn 2p, O 1s, C 1s, N 1s, Mo 3d and S 2p (d)-(i) further confirmed the elemental component and mutual synergies of MnO$_2$@MoS$_2$/PPy composite. Fig. 3e and 3d clearly showed Mn 2p and O 1s. In Fig. 3f, the peaks of C 1s could divide into three peaks at C–C, C–N and C=O which proved the presence of PPy in the compound product. It was worth noting that N 1s peak of N-Mo at 401.6 eV (Fig. 3g) which had coordination interactions with Mo 3p peak at 395.2 and 412.8 eV. This apparent synergism was due to the fact that few PPy was suitable for the appropriate content of Mo and the limited penetration depth of X-ray source. Expect Mo$^{4+}$ 3d$_{5/2}$ and Mo$^{6+}$ 3d$_{3/2}$ at 228.9 eV and 323.2 eV, part of Mo$^{5+}$ and Mo$^{6+}$ appeared, as a consequence of PPy oxidation. Additionally, peaks at 163.1eV and 161.8 eV belonged to the S 2p$_{3/2}$ and S 2p$_{1/2}$. According to the comparison with Mo 3d peaks of previous literature, compared with the semiconducting 2H phase, sheet MoS$_2$ likely had metallic 1T phase with better conductivity after chemical exfoliation.

The Brunauer-Emmett-Teller (BET) surface areas and pore size distribution were relevant to the specific capacitance. Fig. 4 exhibited a N$_2$ adsorption-desorption isotherm (Fig. 4a) and pore size distribution (Fig. 4b) of MnO$_2$, MnO$_2$/MoS$_2$, MnO$_2$@MoS$_2$/PPy. Nitrogen adsorption-desorption isotherms exhibited type IV isotherms with H3-type hysteresis loops. The observation confirmed that the mesopores existed in all samples which were essentially significant to contribute to capacitance. According to BET analysis, the total specific surface area of synthesized composites was higher than reported in pure MnO$_2$ (42.1 m$^2$/g), MoS$_2$ (40.6 m$^2$/g) and original PPy (41 m$^2$/g). Surface area of MnO$_2$/MoS$_2$/PPy and MnO$_2$/MoS$_2$ were 196 m$^2$/g and 147 m$^2$/g, respectively. Obviously, PPy molecules reduced stacking of MoS$_2$ sheets and led to higher surface area. Moreover, obtained
pore-size distribution (Fig. 4b) indicated that there was distribution within the diameter range both of mesoporous and micropore pore. Meanwhile, pore size distribution of MnO2@MoS2 nanocomposites showed that mainly micropores were larger compared with MnO2@MoS2. The larger micropores were probably formed by the cover of PPy. Larger pores offered lower resistant for ions, leading to increase of the transport and diffusion of electrolyte ions during the rapid charge/discharge process. The MnO2@MoS2/PPy composite with higher surface area and larger porous structures, was potential for the pseudocapacity applications.

**Fig. 4** The N2 adsorption/desorption isotherms of MnO2, MnO2@MoS2, MnO2@MoS2/PPy at 77 K (a) and pore size distribution (b)

Flexible supercapacitor device was prepared to explore the performance of MnO2@MoS2/PPy used for electrode application. Figure 5a showed the schematic diagram of flexible material and digital photographs of MnO2@MoS2/PPy flexible supercapacitor, owing obvious flexibility. It was necessary to point out that the MnO2@MoS2/PPy had no binder such as carbon black additive or Ni collectors because PPy served as a binder. The MnO2@MoS2/PPy could be designed to flexible belt and bent highly in supercapacitor device. This material reduced the weight of the device, so the flexible supercapacitor device displayed outstanding performance.

The CVs measurements were tested for MnO2, MoS2, PPy, MnO2@MoS2, MnO2@MoS2/PPy at scan rates of 100 mV/s for electrochemical performance (Fig. 5b). The pure MnO2 showed poor conductivity because of distorted CV shape. On the contrary, hybrid with nearly rectangular shape had a larger area to show better capacitance behavior. In addition, the current density of the MnO2@MoS2/PPy electrode was much higher compared with the other two current densities under the same sweep. The charge storage mechanism of MnO2 was (MnO2)surface+Na++e– ↔ (MnO2−Na+)surface and charge-discharge possibly achieved through intercalation/deintercalation of Na+. Moreover, MoS2 had a large surface area, which could assist in efficient charge storage electrolyte and electron transport.

The galvanostatic charge-discharge behaviors were performed on pristine and MnO2@MoS2 and MnO2@MoS2/PPy at the 1 A/g in Fig. 5c. At the same applied current density, the charging and discharging time were measured. As a result, the sample of MnO2@MoS2/PPy showed the highest values of specific capacitance of 450 F/g and lower IR drop, compared with the results of monolithic composites and MnO2@MoS2. Similarly, ternary composites had a high specific capacitance and excellent rate capability compared with the binary complex. The PPy properly mixed nanocomposites resulting in a strong synergistic effect on MnO2@MoS2. The PPy structure was uniformly grown around the monolayer MoS2 structure, offering a substantial electrochemically active surface area for charge transfer. And it also reduced ion diffusion length during the charge/discharge process. The same time, the sheet structure ensured that the electrolyte ions effectively entered the active material, greatly reducing the dead volume. Moreover, galvanostatic charge/discharge curves at various current densities were presented in Fig. 5e at 0.0–1.0 V in a voltage window. Value of ternary composite showed a satisfactory rate performance. Apparently, MnO2/MoS2@PPy ternary composite expressed a wonderful specific capacitance (1050 F/g) at a discharge current of 0.5 A/g and 42 F/g at a discharge current density of 10 A/g. The balance between MnO2/MoS2 and PPy maximized the capacitance and rate performance.

Figure 5d shows specific capacitance of the sample at different scan rates. Specific capacitance value was calculated through the CV curve integral. Note that the specific capacitance of the MnO2@MoS2/PPy ternary composite was the highest of all. The specific capacitance of ternary composite was two or three times of a single substance and better than binary complex. Particularly, the maximum specific capacitance of MnO2@MoS2/PPy ternary composite improved to about 600 F/g at the scan rate of 10 mV/s. The higher specific capacitance of ternary composite was the result of easier charge transfer and an additional contribution of MoS2 as a substrate.
The synergistic effect on the ternary MnO$_2$@MoS$_2$/PPy hybrid composite electrode was further investigated by EIS measurements. Figure 5f shows the resulting Nyquist plots of the EIS spectra for the MnO$_2$@MoS$_2$/PPy composite electrodes, PPy/MoS$_2$, PPy, MnO$_2$, and MoS$_2$. The MnO$_2$@MoS$_2$/PPy electrode had a smaller equivalent
series resistance $R_s$ and charge-transfer resistance $R_t$. This suggested that the MnO$_2$@MoS$_2$/PPy complex had a significant synergistic effect, as compared with the purity components. The lower resistance of the MnO$_2$@MoS$_2$/PPy electrode would exhibit a faster Faraday reaction, which gives rise to better rate capability. Furthermore, the finite slope of the straight line represented the diffusive resistance of the electrolyte in the electrode pores and cation diffusion in the host materials.

The long-term operating stability (Fig. 5g) was carried out to evaluate the performance of the charge and discharge stability. During the charge-discharge cycle, the polymer might degrade because of expansion and contraction. Hence the pure conductive polymer generally possessed a poor long-term stability. A surprising finding of our study was that MnO$_2$@MoS$_2$/PPy ternary composite was extraordinarily stable after long-term cycling. After 1000 cycles, the capacitance of MnO$_2$@MoS$_2$/PPy maintained 90% of its initial value while pure PPy only remained about 40% of its initial capacitance. It was known that the dissolution of active material and the mechanical failure of the electrode would lead to the smaller specific capacitance. However, this composite structure would inhibit the dissolution and agglomeration of the active substance during the cycle test. Excellent synergetic interaction between PPy and MnO$_2$/MoS$_2$ should be the reason for significantly improving cycle stability. On the other hand, the MoS$_2$ served as substrates at the bottom of the compound and was a beneficial role for stability. As a result, ternary composite material had almost no significant loss compared with the initial value. These results suggested the advantages of ternary composites complied the requirements of high capacitance, excellent rate capability and long cycle life.

4 Conclusions
In this study, MnO$_2$@MoS$_2$ was developed by adding PPy to prepare ternary hybrid composites, including MoS$_2$ as the basic framework, manganese dioxide and PPy as the conductive material which contributed to for flexible supercapacitors. Hybrid flexible electrode showed that prominent electrochemical performance could be summarized to following points: (1) Ternary composite structure affected each other and played a synergistic role, so that the electrical energy storage was better than the binary compound. (2) The PPy improved holistic electrical conductivity on the substructure of MnO$_2$@MoS$_2$. (3) The MoS$_2$ sheet with a large active surface ensured the electrochemical stability and ions accessibility of hybrid composites. (4) The PPy covered on MnO$_2$@MoS$_2$ sheet as adhesion. Therefore flexible electrode materials could be in type of bend without any adhesive. According to those features, MnO$_2$@MoS$_2$/PPy was provided with higher capacitance of 490 F/g at a current density of 1 A/g and predominant cycling stability of 90% after 1000 cycles at 20 A/g. Hence, MnO$_2$@MoS$_2$/PPy nanocomposites had unique characteristics and provided a potential electrode material for flexible supercapacitor.

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