Hydrothermal synthesis of flower-like molybdenum disulfide microspheres and their application in electrochemical supercapacitors

Fangping Wang, Guifang Li, Jinfeng Zheng, Jing Ma, Caixia Yang and Qizhao Wang

Three-dimensional flower-like molybdenum disulfide microspheres composed of nanosheets were prepared by a hydrothermal method using ammonium molybdate as the molybdenum source and thiourea as the sulfur source. Structural and morphological characterizations were performed by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray (EDX) spectroscopy and X-ray photoelectron spectroscopy (XPS). The electrochemical properties of MoS2 electrode were studied by performing cyclic voltammetry (CV), galvanostatic charge–discharge analysis and electrochemical impedance spectroscopy (EIS). When used as an electrode material for supercapacitor, the hybrid MoS2 showed a high specific capacity of 518.7 F g⁻¹ at a current density of 1 A g⁻¹ and 275 F g⁻¹ at a high discharge current density of 10 A g⁻¹. In addition, a symmetric supercapacitor composed of MoS2 as positive and negative electrodes was prepared, which exhibited a high energy density of 12.46 Wh kg⁻¹ at a power density of 70 W kg⁻¹ and still maintains an impressive energy density of 6.42 Wh kg⁻¹ at a large power density of 7000 W kg⁻¹. The outstanding performance of the MoS2 electrode material indicates its great potential for applications in high-performance energy storage systems.

1. Introduction

Supercapacitors, also known as electrochemical capacitors, have gathered growing interest of researchers in the era of miniaturization of devices.¹,² These present fascinating properties of higher energy density, higher power density, longer life, lower toxicity than batteries, and so on, compared with those of traditional capacitors.³–⁶ According to the charge–discharge mechanisms, SCs can be divided into electrical double-layer capacitors (EDLCs) and pseudocapacitors.⁷–⁸ Pseudocapacitance arises from reversible faradaic reactions of redox active materials, such as transition metal oxides, hydroxides, and sulfides. Among those materials, ruthenium oxide (RuO₂) has exhibited excellent pseudocapacitive performance, but the toxicity and high cost of RuO₂ restrict its widespread commercial application.⁹–¹⁰ The low cost active material MnO₂ can also achieve a high specific capacitance; however, MnO₂-based pseudocapacitors suffer from poor electrical conductivity and cyclic stability.¹¹ Application of nanosized sulfides in the energy storage devices, such as fuel cells, solar energy pools, lithium-ion batteries, and supercapacitors, have aroused widespread interest among researchers. At present, carbon materials (such as activated carbon), transition metal oxides (nickel oxide, etc.), and conductive polymers are often used as electrode materials for supercapacitors.¹²,¹³ However, the growing demand for energy storage devices has prompted researchers to develop new types of electrode materials. Therefore, the research of nanometer-scale metal sulfide as the material of supercapacitor electrode has become a new field. For example, cobalt sulfide (CoS, CoS₂), nickel sulfide (NiS, NiS₂, Ni₃S₄), molybdenum sulfide (MoS₂), copper sulfide (CuS, Cu₂S), and vanadium sulfide (VS, VS₂) have been used as supercapacitors electrode materials.¹⁴–¹⁶ In particular, MoS₂ has aroused interest among other transition metal sulfides due to its layered structure and inherent conductivity,¹⁷ and it is considered to be a suitable replacement for graphene and carbon nanotubes in energy storage applications. In addition, molybdenum-based materials (such as MoO₃, MoO₂, and MoS₂) exhibit various valences and rich chemical properties, making them viable candidate materials for electrochemical applications.¹⁸

MoS₂ is a transition metal sulfide with a layered structure, where a metal molybdenum layer is sandwiched between two sulfur layers; the layers are connected by weak van der Waals forces and the interlayer S–Mo–S atoms are strongly covalently linked.¹⁹–²¹ MoS₂ possesses unique physicochemical properties due to its unique atomic and electronic structure. It is mainly used in the solid lubricants, catalysts, supercapacitors and
lithium-ion batteries. Among these, the research on the application of MoS$_2$ as a supercapacitor electrode material is the most extensive. For example, Soon et al. found that the MoS$_2$ nanofilm presented an electric double layer capacitance behavior. Ma et al. reported that nano-MoS$_2$ intercalated in polypyrrole could improve its capacitance performance. Cao et al. fabricated micro-supercapacitors using coated MoS$_2$ nanofilms, and showed that MoS$_2$ has excellent electrochemical performance in aqueous electrolytes.

In particular, the structure of the electrode directly affects its electrochemical properties. Generally, the electrochemical electrode is 2-dimensional and suffers from inadequate contact with electrolyte and low surface-area-utilization efficiency. Numerous efforts have been made to design three-dimensional (3D) electrodes, such as MoS$_2$/mesoporous carbon spheres. Recently, there have been some reports related to NiCo$_2$S$_4$ and polypyrrole could improve its capacitance performance. Cao et al. reported that nano-MoS$_2$ intercalated in CH$_4$N$_2$S were obtained from Tianjin Kaixin Chemical Industry Co. Ltd. All the chemical reagents were of analytical purity and used without any further purification.

In this paper, the morphologically regular flower-like molybdenum disulfide microspheres were successfully synthesized by a hydrothermal method (Fig. 1). The as-prepared MoS$_2$ was directly used as a supercapacitor electrode and exhibited high specific capacitance (518.7 F g$^{-1}$ at current density of 1 A g$^{-1}$) and excellent cycling performance (88.2% retention after 2500 cycles). In addition, a high performance symmetric supercapacitor was successfully fabricated by using MoS$_2$ as both positive electrode and negative electrode, which exhibited a high energy density of 12.46 Wh kg$^{-1}$ at power density of 70 W kg$^{-1}$.

2. Experimental section

2.1. Materials

Ammonium molybdate ([NH$_4$]$_6$Mo$_7$O$_{24}$·4H$_2$O) and thiourea (CH$_4$N$_2$S) were obtained from Tianjin Kaixin Chemical Industry Co. Ltd. All the chemical reagents were of analytical purity and used without any further purification.

2.2. Synthesis of MoS$_2$

In a typical process, 0.8 g of ammonium molybdate and 5.12 g thiourea were dissolved into 80 mL deionized water and stirred until the solution was clear and transparent. The solution was transferred into 100 mL PTFE-lined stainless steel autoclave and heated at 200 $^\circ$C for different time periods (8 h, 16 h, and 24 h). The obtained MoS$_2$ was flushed with water and ethanol, in sequence, and then dried at 70 $^\circ$C for 12 h. The MoS$_2$ electrode materials were denoted as MoS$_2$-8, MoS$_2$-16, and MoS$_2$-24, according to the hydrothermal treatment time.

2.3. Material characterization

The morphology and microstructure of the samples were characterized by field-emission scanning electron microscopy (FESEM JSM-6701F, Japan), transmission electron microscopy (TEM; JEOL, JEM-2010, Japan), and X-ray diffraction (XRD, D/MAX-2400, Japan) with Cu K$_\alpha$ radiation ($\lambda$ = 1.5418 Å) operating at 40 kV, 100 mA. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a PHI 5702 spectrometer using a standard Al K$_\alpha$ X-ray source of 300 W and an analyser pass energy of 29.35 eV.

2.4. Electrode preparation and electrochemical characterization

The electrochemical properties of the MoS$_2$ nanostructures were investigated in 1 M Na$_2$SO$_4$ solution using a three-electrode system in an electrochemical work station (CHI660E, Shanghai). Initially, 8 mg of MoS$_2$-16 was dispersed in 400 μL of 0.5 wt% Nafion solution by ultrasonication to obtain a well dispersed suspension. Then, 6 μL of the suspension was drop-casted onto the pre-treated glassy carbon electrode (GCE) and left to dry at room temperature. Saturated calomel electrode, platinum wire, and a loadable glassy carbon electrode (L) were respectively the reference, the counter, and the working electrodes. Cyclic voltammetry (CV) in the range −0.3 to 0.5 V was performed at different scan rates. Galvanostatic charge–discharge curves were recorded in the potential range of −0.3 to 0.5 V at different constant current density. The cycle life tests were performed by galvanostatic charge–discharge measurements with a constant current density of 4 A g$^{-1}$ for 2500 cycles. Electrochemical impedance spectroscopy (EIS) was performed in the frequency range of 0.01 Hz to 100 kHz with 5 mV amplitude at current open circuit voltage.

A two-electrode symmetric supercapacitor cell was assembled to measure the device performances. MoS$_2$ was used as the positive electrode and negative electrode. The negative electrode was prepared by the traditional slurry coating method. The mass loading of electroactive material in symmetric supercapacitor was 0.3 mg. The specific capacitances ($C_m$) were calculated according to the following equations:

$$C_m = \frac{I \times t}{m \times \Delta V}$$

Fig. 1  Schematic of the MoS$_2$ synthesized by hydrothermal method.
where \( C_m \) is the specific capacitance, \( I \) is the current of the charge–discharge, \( \Delta t \) [s] is the discharge time, \( \Delta V \) is the voltage window, and \( m \) is the mass of active materials.

In the symmetrical supercapacitors, the corresponding power density \( (P) \) and energy density \( (E) \) were calculated according to the following equations:

\[
E = \frac{C_m \times \Delta V^2}{2} \quad (2)
\]

\[
P = \frac{E}{\Delta t} \quad (3)
\]

### 3. Results and discussion

#### 3.1. Characterization of MoS\(_2\)

Fig. 2 shows the SEM microstructures of the as-prepared MoS\(_2-8\), MoS\(_2-16\), and MoS\(_2-24\). It can be clearly observed from the Fig. 2 that the as-prepared molybdenum disulfide material has a nanoflower-like structure assembled from clear nanoflakes. Different hydrothermal treatment times had a great influence on the size of the molybdenum disulfide nanoflakes and the size of the three-dimensional pore structure. Fig. 2a and b show the SEM microstructures of the MoS\(_2-8\) at low and high magnifications, respectively. It can be seen that the nanosheets are partially adhered together and contained a small amount of block-like structures, resulting in inconspicuous pore structure. MoS\(_2-16\) (Fig. 2c and d) possesses an evenly distributed larger size of nanoflakes, and forms highly open and relatively deep porous nanostructures, making optimal use of the grain surface readily accessible to the liquid electrolyte and providing efficient channels for electron transport. Fig. 2e and f present the low and high magnification SEM image of the MoS\(_2-24\) sample. After a 24 h long hydrothermal process, the nanosheets of MoS\(_2-24\) arranged regularly but too tightly, and some collapsed, resulting in a decrease or disappearance of the pore size in the material, which could degrade the electrochemical performance of the electrode material.

Fig. 3 shows the TEM images for MoS\(_2-16\). As shown in Fig. 3a, the interconnected nanoflakes consist of nano-flowers. As seen in the magnified image (Fig. 3b), MoS\(_2-16\) nanoflakes are very thin, leading to open and porous three-dimensional structures, which are beneficial to electrolyte access and electron transport during electrochemical reactions. These results are in accordance with the SEM images.

The XRD patterns of MoS\(_2-8\), MoS\(_2-16\), and MoS\(_2-24\) hybrids are shown in Fig. 4a. The four diffraction peaks at 14.2°, 32.5°, 35.8°, and 55.4° correspond to the (002), (100), (102), and (106) planes of cubic phase MoS\(_2\) (JCPDS No. 75-1539). Energy-dispersive X-ray (EDX) spectroscopy (Fig. 4b) demonstrates the existence of Mo and S elements. The Raman spectrum of the as-prepared MoS\(_2\) nanoflowers was recorded in this study, as shown in Fig. 4c. At low wave numbers the Raman spectrum of the MoS\(_2\) sample showed peaks at 145, 227, 283, 371 and 403 cm\(^{-1}\), related to the characteristic vibrations of pure metallic phase MoS\(_2\). The main peak associated with Mo–Mo metallic vibration is located at 145 cm\(^{-1}\). Two characteristic peaks are observed at 371 and 403 cm\(^{-1}\), which correspond to the E\(_{2g}\) and A\(_{1g}\) modes of hexagonal MoS\(_2\), and are attributed to the out-of-plane Mo–S phonon mode and the in-plane Mo–S phonon mode, respectively.

The chemical and surface states of the Mo and S elements in the as-prepared MoS\(_2-16\) electrodes have been investigated via X-ray photoelectron spectroscopy. The XPS survey spectrum of the MoS\(_2\) electrodes is shown in Fig. 5a, which revealed the presence of Mo 3d, Mo 3p, S 2p, C 1s and O 1s states.\(^{33}\) The C and O signals originated from the CO\(_2\) and H\(_2\)O impurities, as seen in many XPS analyses. The fine fitted spectrum of Mo 3d is shown in Fig. 5b, which revealed the presence of two major peaks at around 228.5 and 232 eV, corresponding to the Mo\(^{4+}\) 3d\(_{5/2}\) and Mo\(^{4+}\) 3d\(_{3/2}\) states, respectively. Small peaks belonging to S 2s in the vicinity of 226 eV are also observed.\(^{34}\) The fine fitted spectrum of S 2p (Fig. 5c) indicated the presence of two major peaks at around 161.5 and 162.9 eV, which corresponds to the S 2p\(_{1/2}\) and S 2p\(_{3/2}\) states, respectively.\(^{35}\) These studies confirm the formation of MoS\(_2\) by the hydrothermal method.

#### 3.2. Electrochemical and energy storage performance

Fig. 6a shows the cyclic voltammetry (CV) curves of MoS\(_2-8\), MoS\(_2-16\) and MoS\(_2-24\) at 10 mV s\(^{-1}\) in 1 M Na\(_2\)SO\(_4\) solution, obtained over the potential range between \(-0.3\) V and 0.5 V. In contrast, the CV curve area of the MoS\(_2-16\) electrode was larger than the electrode area of MoS\(_2-8\) and MoS\(_2-24\). Fig. 6b shows the cyclic voltammetry (CV) curves of MoS\(_2-16\) at different scan rates. On increasing the scanning speed from 10 mV s\(^{-1}\) to 100 mV s\(^{-1}\), the shape of the CV curve did not change significantly, indicating that MoS\(_2-16\) presented better rate performance and small polarization.\(^{36,37}\) Galvanostatic charging-discharging (GCD) technique was also applied to study the electrochemical capacitive properties of MoS\(_2-8\), MoS\(_2-16\) and MoS\(_2-24\) at a current density of 1 A g\(^{-1}\), as shown in Fig. 6c. The longer discharge time of MoS\(_2-16\) electrode again confirmed its enhanced capacitance. Fig. 6d shows the galvanostatic charging-discharge curve (GCD) of MoS\(_2-16\) at various current densities varying from 1 to 10 A g\(^{-1}\), with a potential window range from \(-0.3\) V to 0.5 V. Based on eqn (2), for MoS\(_2-16\) electrode, at a discharge current of 1 A g\(^{-1}\), the specific capacitance reached 518.7 F g\(^{-1}\), while at a high discharge current of 10 A g\(^{-1}\), the specific capacitance was as high as 275 F g\(^{-1}\). Using these GCD curves, the specific capacitances of five electrodes at various current densities were calculated and depicted in Fig. 6e. The calculated specific capacitances of MoS\(_2-16\) electrode were calculated to be 518.7, 415, 363.7, 335, 318.7, and 275 F g\(^{-1}\) at discharge current densities of 1, 2, 3, 4, 5, and 10 A g\(^{-1}\), respectively, which are much higher than those for MoS\(_2-8\) and MoS\(_2-24\) at the same current densities. Table 1 compares the electrochemical performance of the MoS\(_2\) electrode material prepared in this study with that of the MoS\(_2\) electrode material reported in the literature. It can be seen that the electrochemical performance of the MoS\(_2\) electrode material prepared...
Fig. 2  SEM images of (a and b) MoS$_2$-8, (c and d) MoS$_2$-16, and (e and f) MoS$_2$-24.

Fig. 3  TEM images of MoS$_2$-16.
The superior electrochemical behaviors of MoS$_2$-16 nanoflower observed in this study should be partially attributed to its ultrathin and porous features, which can offer even richer electroactive sites, and more efficient and convenient electronic transport.

Electrochemical impedance spectroscopy (EIS) analysis is an important tool to examine the interface resistance of electrode materials for supercapacitors. For an ideal supercapacitor, the Nyquist plot comprises a vertical line, which can be simulated by an equivalent circuit. The semicircle at high frequency region is indicative of interfacial charge transfer resistance. In the equivalent circuit, the series resistance ($R$) depends on electrolyte resistance and electrode electronic resistance. Nyquist plots based on the radius of the high frequency arc on the real axis are shown in Fig. 6f. Clearly, the semicircle over the high frequency range of the MoS$_2$-16 electrode is smaller than that of others, indicating the smaller charge-transfer resistance. Furthermore, the slope of the line for MoS$_2$-16 was larger than that of MoS$_2$-8 and MoS$_2$-24, implying a better capacitive behavior and a lower diffusion resistance of ions in the MoS$_2$-16 electrode material. The differences in the electrochemical properties of MoS$_2$ material are mainly due to disparity in the material electrolyte interface properties and electrolyte ion diffusion rates during the charge–discharge processes, which are in good accordance with its abovementioned electrochemical performance.

Fig. 4 (a) XRD pattern of the MoS$_2$-8, MoS$_2$-16, and MoS$_2$-24; (b) EDX spectra of MoS$_2$-16; (c) Raman spectra of MoS$_2$-16.

Fig. 5 (a) XPS survey scanning of MoS$_2$-16. XPS spectra of (b) Mo 3d and (c) S 2p.
The cyclic stability of the electrode material is very important for practical supercapacitor applications. The cycling performance of MoS$_2$-16 electrode was tested by 2500 cycles of continuous galvanostatic charge/discharge at the current density of 4 A g$^{-1}$ (Fig. 6g). Although the specific capacitance gradually decreases with the increase of cycle number, there is still 88.2% retention of the initial capacitance.
Table 1  Comparison of electrochemical properties of different MoS₂ electrode materials

<table>
<thead>
<tr>
<th>Samples</th>
<th>Electrolyte</th>
<th>Current density</th>
<th>Specific capacitance</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS₂ nanosheets</td>
<td>1 M Na₂SO₄</td>
<td>1 A g⁻¹</td>
<td>129.2 F g⁻¹</td>
<td>38</td>
</tr>
<tr>
<td>Sphere like MoS₂</td>
<td>1 M Na₂SO₄</td>
<td>5 mV s⁻¹</td>
<td>106 F g⁻¹</td>
<td>39</td>
</tr>
<tr>
<td>Spherically clustered MoS₂</td>
<td>1 M H₂SO₄</td>
<td>5 mV s⁻¹</td>
<td>113 F g⁻¹</td>
<td>40</td>
</tr>
<tr>
<td>MoS₂ nanospheres</td>
<td>1 M KCl</td>
<td>1 A g⁻¹</td>
<td>122 F g⁻¹</td>
<td>41</td>
</tr>
<tr>
<td>Hollow MoS₂ nanospheres</td>
<td>1 M KCl</td>
<td>0.59 A g⁻¹</td>
<td>144 F g⁻¹</td>
<td>42</td>
</tr>
<tr>
<td>MoS₂ nanolayers</td>
<td>6 M KOH</td>
<td>0.5 A g⁻¹</td>
<td>366.9 F g⁻¹</td>
<td>43</td>
</tr>
<tr>
<td>MoS₂/CMG</td>
<td>1 M Na₂SO₄</td>
<td>0.5 A g⁻¹</td>
<td>268 F g⁻¹</td>
<td>44</td>
</tr>
<tr>
<td>MoS₂/MWCNT</td>
<td>1 M Na₂SO₄</td>
<td>1 A g⁻¹</td>
<td>452.7 F g⁻¹</td>
<td>45</td>
</tr>
<tr>
<td>MoS₂-16</td>
<td>1 M Na₂SO₄</td>
<td>1 A g⁻¹</td>
<td>518.7 F g⁻¹</td>
<td>This work</td>
</tr>
</tbody>
</table>

Fig. 7  (a) CV curves of MoS₂-16/MoS₂-16 measured at different potential windows at a scan rate of 30 mV s⁻¹. (b) CV curves of the SC measured at different scan rates ranging from 20 to 120 mV s⁻¹ in potential window of 0 to 1.6 V. (c) Galvanostatic charge/discharge curves of the SC measure at different current densities from 1 to 10 A g⁻¹. (d) Specific capacitance as a function of the current density of the symmetric supercapacitor. (e) Ragone plots of the SC. (f) Cycling stability of the SC at 1.6 A g⁻¹.
3.3. Electrochemical performances of the MoS$_2$-16//MoS$_2$-16 symmetric supercapacitor

To further evaluate the practical application potential of MoS$_2$-16 electrode, an aqueous SC was first assembled using the MoS$_2$-16 electrode as both positive electrode and negative electrode. Fig. 7a shows a series of CV curves collected at 30 mV s$^{-1}$ with an operating SC voltage ranging from 0.8 to 1.6 V to obtain the best operating potential of MoS$_2$-16//MoS$_2$-16. Fig. 7b shows typical CV curves for the SC device corresponding to different sweep rates. With the increment of sweep rate from 20 to 120 mV s$^{-1}$, all the curves presented similar shapes, revealing the splendid high-rate charge–discharge performance of the device.\(^{35-48}\) Fig. 7c shows the typical GCD curves for the cells at various current densities with a potential window of 0–1.4 V. During the charge and discharge processes, the charge curve of MoS$_2$-16//MoS$_2$-16 (SSC) and its corresponding discharge curve are observed to be symmetrical, confirming that it has excellent electrochemical reversibility.\(^{49}\) The calculated specific capacitance values based on the discharge curves are plotted in Fig. 7d, which are 45.7, 43.7, 42.8, 42.3, 39.8, 36.9 and 23.57 F g$^{-1}$ at 0.1, 0.2, 0.3, 0.4, 1, 2, and 10 A g$^{-1}$, respectively. Energy density and power density are important parameters to evaluate the performance of symmetric supercapacitors. Fig. 7e presents the Ragone plot of the as-fabricated MoS$_2$-16//MoS$_2$-16 symmetric device, which describes the relationship between the energy and power densities. The supercapacitor device delivered a high energy density of 12.46 W h kg$^{-1}$ at the power density of 70 W kg$^{-1}$ and still maintained 6.42 W h kg$^{-1}$ at 7 kW kg$^{-1}$. Previously reported literature also reported energy storage tests on these similar electrode materials. The as-fabricated self-charging supercapacitor power cell (SCSPC) delivered a specific capacitance of 18.93 mF cm$^{-2}$ with a specific energy of 37.90 mJ cm$^{-2}$ at a specific power density of 268.91 µW cm$^{-2}$, which were obtained at a constant discharge current of 0.5 mA.\(^{50}\) For the s-MoS$_2$/CNS-based symmetric pseudocapacitor, the equivalent values were 108 F g$^{-1}$, 7.4 W h kg$^{-1}$ and 3700 W kg$^{-1}$.\(^{51}\) The MoS$_2$-based wire-type solid state supercapacitors (WSCSs) device delivered a specific capacitance of 119 µF cm$^{-1}$, and energy density of 8.1 nW h cm$^{-1}$.\(^{52}\) Furthermore, the cycling stability of the as-fabricated SC was performed by repeating the GCD test at a current density of 1.6 A g$^{-1}$. The specific capacitance retention of MoS$_2$-16//MoS$_2$-16 was about 73.5% after 1100 cycles, revealing that this symmetric supercapacitor has eminent cycling stability.

4. Conclusions

In summary, we have designed and successfully fabricated flower-shaped MoS$_2$ microspheres assembled from many nanoflakes. The capacitive properties of flower-shaped molybdenum disulfide microspheres as the material of the supercapacitor electrode were studied. The obtained MoS$_2$-16 nanoflower delivered a high specific capacitance of 518.7 F g$^{-1}$ at a current density of 1 A g$^{-1}$, with capacitance retention of 88.2% after 2500 cycles in alkaline system in a three-electrode cell. To further confirm its practicability, an symmetric supercapacitor was assembled using the MoS$_2$-16 nanoflower as both positive electrode and negative electrode. This supercapacitor delivered a maximum energy density of 12.46 W h kg$^{-1}$ at a power density of 70 W kg$^{-1}$. Even at the highest power density of 7000 W kg$^{-1}$, the MoS$_2$-16//MoS$_2$-16 device still maintained an energy density of 6.42 W h kg$^{-1}$. Such outstanding capacitive behaviors imply the MoS$_2$-16 nanoflower as a promising material for energy storage devices.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We gratefully acknowledge the financial support of this research by the National Natural Science Foundation of China (21065010, 21365019).

References


8. R. Li, S. Wang, Z. Huang, F. Lu and T. He, NiCo$_2$S$_4$@Co(OH)$_2$ core-shell nanotube arrays in situ grown on Ni foam for high performances asymmetric supercapacitors, J. Power Sources, 2016, 312, 156–164.

9. C. C. Hu, K. H. Chang, M. C. Lin and Y. T. Wu, Design and tailoring of the nanotubular arrayed architecture of


38 K. J. Huang, J. Z. Zhang, G. W Shi and Y. M. Liu, Hydrothermal synthesis of molybdenum disulfide


