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Facile Synthesis of Ultrathin CuCo₂S₄ Nanosheets for High-Performance Supercapacitors

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Two-dimensional (2D) structural $CuCo_2S_4$ exhibits great potential for applications in the renewable energy and catalysis fields. However, the fabrication of $CuCo_2S_4$ nanosheets remains a great challenge, and studies focussed on $CuCo_2S_4$ nanosheets used for supercapacitors are seldom reported. In this work, for the first time, polyvinylpyrrolidone (PVP) was used to level the sulfurization rate and reactivity of Cu and Co ions in a glycerol solution. As a result, the crystallographic growth direction of $CuCo_2S_4$ was controlled to be a sheet. Furthermore, the obtained $CuCo_2S_4$ nanosheets mainly exhibited an ultrathin thickness of approximately 15 nm. From the electrochemical measurements, the specific capacitance of the $CuCo_2S_4$ nanosheet was 1742 F g⁻¹ at a current density of 10 A g⁻¹. The capacitance retention was 93.4% at 10 A g⁻¹ for 2000 cycles. In addition, the $CuCo_2S_4$ nanosheet//rGO asymmetric supercapacitor exhibited an energy density of approximately 45.6 Wh kg⁻¹ at a power density of 748.2 W kg⁻¹. After 5000 cycles at a current density of 10 A g⁻¹.

Keywords: supercapacitors, CuCo₂S₄ nanosheet, polyvinylpyrrolidone, glycerol, solvothermal method

1. INTRODUCTION

Rapid fossil fuel consumption and serious environmental pollution have seriously hampered the development of science, technology and society [1, 2]. To solve this problem, as a promising energy conversion device, supercapacitors (SCs) have gained great attention due to their superior electrochemical properties such as high-power output, fast recharging rate and excellent cycling stability [3-5]. Active electrode materials, such as carbonaceous materials [6, 7], transition metal oxides [8, 9] and conductive polymers [10, 11], have been intensively investigated for their application as SCs. To date, SCs have been widely used in hybrid vehicles, industrial equipment and electricity systems. However, their energy density is obviously lower than that of rechargeable batteries. To

exploit the further application of SCs, massive studies have been devoted to improving their energy density [12-15].

Recently, it has been confirmed that transition metal sulfides possess the ability to undergo a reversible redox reaction in alkaline electrolytes. The present correlative studies mainly focus on the binary metal sulfides such as MnS, CoS, NiS and MoS₂, which exhibit greater conductivity and higher energy density than transition metal oxides [16-19]. To develop novel electrode materials, the ternary metal sulfides receive extensive attention due to their synergistic effects with two metal ions and the crystal structure. Specifically, the spinel structural CuCo₂S₄ exhibits an ultrahigh specific capacitance and cycling stability as a pseudocapacitive material. Seyyed and co-workers synthesized CuCo₂S₄ hollow nanoneedle arrays on a Ni foam, which revealed a specific capacitance of 2163 F g⁻¹ at a current density of 6 mA cm⁻² [20]. Zhu and co-workers synthesized mesoporous CuCo₂S₄, which exhibited a specific capacitance of 752 F g⁻¹ at a current density of 2 A g⁻¹ [21]. Wang and co-workers synthesized sphere-like CuCo₂S₄ nanostructure on a Ti wire, which showed 53.5 mF cm⁻² at a current density of 0.17 mA cm⁻² [22].

Clearly, the morphology of $CuCo_2S_4$ has a huge impact on its electrochemical performance. However, there have been few studies focussed on $CuCo_2S_4$ nanosheets, and the $CuCo_2S_4$ nanosheets used as an active material for SCs have not been previously reported. Since the sulfurization rate and reactivity of Cu and Co ions are seriously influenced by the distinct affinity for elemental S, it is difficult to obtain pure $CuCo_2S_4$ nanosheets. To achieve the purpose, the reactivity of Cu and Co ions should be levelled. Therefore, the ligands in the Cu and Co precursors are vital. In this work, for the first time, polyvinylpyrrolidone (PVP) was used to synthesize $CuCo_2S_4$ nanosheets in a glycerol solution. According to the results of characterization, the $CuCo_2S_4$ thus obtained mainly exposed an ultrathin thickness of approximately 15 nm. As a comparison, the $CuCo_2S_4$ synthesized without PVP exhibited a morphology of agglomerated nanospheres. From the electrochemical measurements, the $CuCo_2S_4$ nanosheets exhibited better performance. The specific capacitance of the $CuCo_2S_4$ nanosheets was 1742 F g⁻¹ at a current density of 10 A g⁻¹. The capacitance retention was 93.4% at 10 A g⁻¹ for 2000 cycles. In addition, the $CuCo_2S_4$ nanosheet//rGO asymmetric supercapacitor exhibited superior performance for practical applications.

2. EXPERIMENT

2.1. Synthesis of the CuCo₂S₄ nanosheets and nanospheres

First, 1 mmol of $C_4H_6CuO_4 \cdot H_2O$, 2 mmol of $C_4H_6CoO_4 \cdot 4H_2O$ and 4 mmol of $CS(NH_2)_2$ were dissolved in 20 ml of glycerol, and then the solution was stirred at 100 °C for 5 h. Next, 0.1 g of polyvinylpyrrolidone (PVP-K30) was dissolved in 5 ml of glycerol and injected into the above solution. Subsequently, the mixture was transferred into a 100 ml Teflon-lined stainless-steel autoclave and heated at 200 °C for 1 h. After cooling to room temperature, the resultant was separated by centrifugation and washed with deionized water. Finally, the $CuCo_2S_4$ nanosheets were dried in a vacuum oven at 60 °C.

As a comparison, $CuCo_2S_4$ nanospheres were synthesized by the similar preparation process. The only difference was that no polyvinylpyrrolidone was injected into the solution.

2.2. Materials characterization

X-ray powder diffraction (XRD) was carried out on a D8 Advance diffractometer (Bruker, Germany) with Cu Ka radiation ($\lambda = 0.15406$ nm). The Raman spectra were recorded with an InVia Raman microscope (Renishaw, UK). The surface morphology and elemental distribution were observed by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) using a ZEISS Merlin Compact spectroscope (ZEISS, Germany). The microstructure was examined by transmission electron microscopy (TEM) using a JEM-2100F (JEM, Japan). The X-ray photoelectron spectroscopy (XPS) spectra were recorded by an ESCALAB 250Xi (ThermoFisher Scientific, America).

2.3. Electrochemical characterization

Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements were recorded with an Autolab-AUT86742. These measurements were carried out in a three-electrode system using 6 M KOH as the electrolyte. A platinum plate and saturated calomel electrode was used as the counter and reference electrodes, respectively.

The working electrode was fabricated by coating active electrode material onto pure nickel foam. The active electrode material was a mixture of $CuCo_2S_4$, super P and polyvinylidene fluoride (PVDF) with a mass ratio of 8:1:1. Then, the electrode was pressed at 10 MPa for 30 s and dried in a vacuum at 100 °C for 24 h. Finally, the specific capacitance of the $CuCo_2S_4$ nanosphere and nanosheet electrode was calculated by the following equation:

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

where C_{sp} , I, Δt , m and ΔV are the specific capacitance (F g⁻¹), discharge current (A), discharge time (s), mass of the active material (g) and potential window (V), respectively.

The $CuCo_2S_4$ nanosheet//rGO asymmetric supercapacitor was fabricated using the $CuCo_2S_4$ nanosheet electrode as a positive electrode and rGO as a negative electrode. The mass ratio of $CuCo_2S_4$ nanosheets and rGO can be calculated by the following equation:

$$\frac{m_+}{m_-} = \frac{C_{S-} \times \Delta V_-}{C_{S+} \times \Delta V_+}$$

where *m* is the mass (g), C_s is the specific capacitance (F g⁻¹) and the ΔV is the potential window (V) of each electrode. As a result, the mass ratio of is approximately 0.2.

The energy density and power density of this asymmetric supercapacitor were calculated by the following equation:

$$\begin{split} E_m &= \frac{C_{SP} \times \Delta V^2}{\frac{2 \times 3.6}{E_m \times 3600}} \\ P_m &= \frac{t_{dis}}{t_{dis}} \end{split}$$

where E_m and P_m are the energy density (Wh kg⁻¹) and power density (W kg⁻¹), respectively. ΔV is the potential window (V) and t_{dis} is the discharge time(s).

3. RESULTS AND DISCUSSION

3.1. Morphological analysis

Fig. 1a shows the morphology of the $CuCo_2S_4$ nanospheres, which have an average size of 1 μ m. A detailed image is illustrated in Fig. 1b, which reveals that these nanospheres are comprised of numerous nanosheets. Fig. 1c shows the morphology of the $CuCo_2S_4$ nanosheets, and a detailed image is illustrated in Fig. 1d. Clearly, these $CuCo_2S_4$ nanosheets show an average diameter of 500 nm and a thickness of approximately 15 nm. To further investigate the microstructure, a TEM image of the $CuCo_2S_4$ nanosheet was captured and is shown in Fig. 1e. In addition, Fig. 1f shows an HR-TEM image of $CuCo_2S_4$ nanosheets with an interplanar distance of 0.29 nm corresponding to the (1 1 3) plane of $CuCo_2S_4$.

These morphological results indicate that the crystallographic growth direction of $CuCo_2S_4$ was controlled to be a sheet during the incipient reaction. This finding is attributed to the ligand effect of the hydroxyl in the glycerol solution, which levelled the sulfurization rates and reactivity of Cu and Co ions. However, during the crystal growth process, the ligand effect of glycerol was not enough. These nanosheets became agglomerate nanospheres.





Figure 1. An SEM image of $CuCo_2S_4$ nanospheres (a) and a detailed image (b); an SEM image of $CuCo_2S_4$ nanosheets (c) and a detailed image (d); and a TEM image of $CuCo_2S_4$ nanosheets (e) and an HR-TEM image (f).

Although similar studies were reported that use an alcohol group, nitroxyl or amidogen, to synthesize sheet electrode active materials [23-25], this is the first investigation of the use of PVP as the active agent to synthesize $CuCo_2S_4$. As a result, the $CuCo_2S_4$ synthesized in a solution with PVP appeared as nanosheets.

3.2. Structural characterization and elemental composition

To further investigate the structure of the $CuCo_2S_4$ nanosheets and nanospheres, XRD patterns were captured and are shown in Fig. 2a. The apparent peaks at $2\theta = 26.6^{\circ}$, 31.3° , 38.0° , 47.0° , 49.9° and 54.8° correspond to the (0 2 2), (1 1 3), (0 0 4), (2 2 4), (1 1 5) and (0 4 4) planes of $CuCo_2S_4$ (JCPDS card No. 42-1450), respectively. In addition, the $CuCo_2S_4$ nanosheets exhibit a higher crystallinity than that of the $CuCo_2S_4$ nanosheets. These structures correspond to a uniform sheet morphology for the $CuCo_2S_4$ nanosheets and an agglomerate morphology for the $CuCo_2S_4$ nanosheets.



Figure 2. (a) The XRD patterns of the $CuCo_2S_4$ nanosheets and nanospheres, and (b) the Raman spectra of the $CuCo_2S_4$ nanosheets and nanospheres.

The Raman spectra are shown in Fig. 2b and three main peaks are obviously observed. The Raman peak at 473 cm⁻¹ is assigned to the Cu-S bond [26, 27]. The other two peaks at 514 cm⁻¹ and

 680 cm^{-1} are assigned to the Co-S bond [28]. The higher peak intensity of the CuCo₂S₄ nanosheets demonstrates a higher crystallinity, and the blueshift of the CuCo₂S₄ nanospheres corresponds to a disordered structure containing more residual stress.

The EDS analysis of CuCo₂S₄ nanosheets is shown in Fig. 3a and the EDS mapping demonstrates the homogeneous elemental distribution of Cu, Co and S. To investigate the oxidation of Cu, Co and S, an XPS survey was performed and is shown in detail. Fig. 3b illustrates the fine spectrum of Cu 2p. The binding energies at 951.8 and 931.8 eV are assigned to the spin–orbit doublets for the $2p_{1/2}$ and $2p_{3/2}$ peaks of Cu⁺, and the binding energies at 954.1 and 932.4 eV are assigned to the $2p_{1/2}$ and $2p_{3/2}$ peaks of Cu²⁺, respectively [29]. Fine spectrum of Co 2p is shown in Fig. 3c, and the binding energies at 795.7 and 778.9 eV are assigned to the spin–orbit doublets for the $2p_{1/2}$ and $2p_{3/2}$ peaks of Co²⁺, respectively [30]. In addition, the satellite peaks of Co²⁺ exist at 801.2 and 780.9 eV. For the fine spectrum of S 2p shown in Fig. 3d, the binding energies at 161.7 and 161.0 eV are attributed to the spin–orbit doublets for $2p_{1/2}$ and $2p_{3/2}$ peaks of S²⁻ exists at 168.6 eV [31]. Furthermore, the binding energy at 162.8 eV is assigned to S bound to Cu [32].



Figure 3. (a) EDS analysis of the $CuCo_2S_4$ nanosheets; and the XPS fine spectra of (b) Cu 2p, (c) Co 2p and (d) S 2p.

3.3. Electrochemical measurements with a three-electrode system

The electrochemical properties of the $CuCo_2S_4$ nanosphere and nanosheet electrode were estimated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical

impedance spectroscopy (EIS) measurements with a three-electrode system. Fig. 4a illustrates the CV curves of the CuCo₂S₄ nanosphere electrode at different scan rates from 5 to 50 mV s⁻¹ with a potential window from -0.2 to 0.4 V. Clearly, a pair of redox peaks can obviously be observed in these curves, and this is the typical characteristic of pseudocapacitive SCs. Fig. 4b illustrates the CV curves of the CuCo₂S₄ nanosheet electrode, which exhibits a similar shape as the CuCo₂S₄ nanosphere electrode. However, the CuCo₂S₄ nanosheet electrode reveals the higher peak current density at the same scan rate. To investigate the electrochemical reaction mechanism, the anodic and cathodic peak current densities and the square root of scan rates demonstrates the typical charge transfer process of the pseudocapacitive SCs [33, 34]. Fig. 4d illustrates the CV curves of the CuCo₂S₄ nanosphere and nanosheet electrodes at the same scan rate of 5 mV s⁻¹. Since the integral area of CV curve can be used to estimate the specific capacitance, naturally, the CuCo₂S₄ nanosheet electrode reveals the higher



Figure 4. (a) CV curves of the $CuCo_2S_4$ nanosphere electrode, (b) CV curves of the $CuCo_2S_4$ nanosheet electrode, (c) peak current densities against the square root of scan rates (A and C represent the anodic and cathodic peak current density, respectively), and (d) CV curves of the $CuCo_2S_4$ nanosphere and nanosheet electrodes at the same scan rate of 5 mV s⁻¹.

Galvanostatic charge-discharge (GCD) measurements were carried out at various current densities from 10 to 50 A g⁻¹. The GCD curves of the $CuCo_2S_4$ nanosphere and nanosheet electrodes are illustrated in Fig. 5a and 5b, respectively. Corresponding to the results of CV curves, the nonlinear shape of GCD curves is attributed to the reversible redox reaction of $CuCo_2S_4$ with OH⁻. The specific capacitances of these two electrodes are shown in Fig. 5c. At discharge current densities of 10, 20, 30, 40 and 50 A g⁻¹, the specific capacitances of the $CuCo_2S_4$ nanosphere electrode are 1138, 909, 796,

698 and 636 F g⁻¹, respectively. On the other hand, the specific capacitances of the CuCo₂S₄ nanosheet electrode at the same discharge current densities are 1742, 1618, 1516, 1433 and 1372 F g⁻¹. Literally, the CuCo₂S₄ nanosheet electrode reveals higher specific capacitances. Furthermore, the capacitance retention of the CuCo₂S₄ nanosheet electrode from 10 to 50 A g⁻¹ is 78.8%, which is higher than that of the CuCo₂S₄ nanosheet electrode (59.9%). It is well known that charge transfer into the interior active material is limited at high-rate GCD measurement [35, 36]. Obviously, the CuCo₂S₄ nanosheet with ultrathin thickness is more suitable for rapid charge transfer.



Figure 5. GCD curves of the $CuCo_2S_4$ (a) nanosphere and (b) nanosheet electrodes; (c) specific capacitance at different current densities; EIS curves of the $CuCo_2S_4$ (d) nanosphere (e) and nanosheet electrodes; and (f) cycling stability.

To further investigate the charge transfer kinetics at the interface of the electrode and electrolyte, electrochemical impedance spectroscopy (EIS) data were collected. Fig. 5d illustrates the EIS curve of the $CuCo_2S_4$ nanosphere electrode, and the equivalent circuit fits well with the raw data.

Reasonably, the equivalent circuit contains the impedance from the electrolyte solution (R_s), the adhesives (R_{ad}) and the reaction resistance (R_{re}) of CuCo₂S₄ with OH⁻ [37]. In addition, the roughness of the working electrode causes an extra influence (R_{ro}). As shown in Fig. 5e, although the CuCo₂S₄ nanosheet electrode reveals the same equivalent circuit, the charge transfer resistance is lower than that of the CuCo₂S₄ nanosphere electrode, which is illustrated in the inset.

To estimate the cycling stability of the $CuCo_2S_4$ nanosphere and nanosheet electrodes, continuous GCD measurements were performed at a current density of 10 A g⁻¹. After 2000 cycles, the capacitance retention of the $CuCo_2S_4$ nanosheet electrode is 93.4%, which is higher than that of the $CuCo_2S_4$ nanosphere electrode (86.8%).

In view of these above characterization and electrochemical measurements, $CuCo_2S_4$ nanosheets exhibit better performance than the nanospheres. The main reason is that the $CuCo_2S_4$ nanosheets with an ultrathin thickness facilitate charge transfer into the interior active material and provide a larger contact area with electrolyte than that of the $CuCo_2S_4$ nanospheres. In addition, the higher crystallinity and more ordered morphology ensure the stability of the $CuCo_2S_4$ nanosheet electrode during electrochemical measurements. Compared with the recent studies, as shown in Table 1, the $CuCo_2S_4$ nanosheets exhibit the better performance than other correlative studies focused on morphology.

Electrode	Specific capacitance	Reference
Cu ₇ S ₄ nanowires	$400 \text{ F g}^{-1} \text{ at } 10 \text{ mV s}^{-1}$	[38]
MnCo ₂ S ₄ nanoneedle	1402 F g^{-1} at 1 A g^{-1}	[39]
Multilayer NiCo ₂ S ₄ @MnO ₂	1338 F g^{-1} at 2 A g^{-1}	[40]
Mesoporous $CuCo_2S_4$	752 F g^{-1} at 2 A g^{-1}	[21]
Sphere-like CuCo ₂ S ₄ @Ti wire	53.5 mF cm ⁻² at 0.17 mA cm ⁻²	[22]
CuCo ₂ S ₄ nanospheres	1138 F g^{-1} at 10 A g^{-1}	This work
CuCo ₂ S ₄ nanosheets	1742 F g^{-1} at 10 A g^{-1}	This work

Table 1. Comparative representation of the specific capacity of recently reported correlative studies.

3.4. Electrochemical measurements of the CuCo₂S₄ nanosheet//rGO asymmetric supercapacitor

To evaluate the practical energy storage applications of the $CuCo_2S_4$ nanosheets, the $CuCo_2S_4$ nanosheet electrode was used as a positive electrode, and the rGO was used as a negative electrode to assemble an asymmetric supercapacitor [41, 42]. Fig. 6a shows the CV curves of the $CuCo_2S_4$ nanosheet//rGO asymmetric supercapacitor at different scan rates from 10 to 50 mV s⁻¹ with a potential window from 0 to 1.6 V. The GCD curves at different current densities from 1 to 20 A g⁻¹ are illustrated in Fig. 6b. The linear shape of GCD curves is a typical characteristic of asymmetric supercapacitors. The cycling stability was investigated at a current density of 10 A g⁻¹. After 5000 cycles, the capacitance retention was 91.7%. The energy density and power density were calculated

using GCD curves, and the results were illustrated as a Ragone plot, which is shown in Fig. 6c. At a power density of 748.2 W kg⁻¹, the energy density is 45.6 Wh kg⁻¹. Compared with recent studies, as shown in Table 2, the CuCo₂S₄ nanosheet//rGO asymmetric supercapacitor reveals a superior practicability.



Figure 6. (a) CV curves and (b) GCD curves of the $CuCo_2S_4$ nanosheet//rGO asymmetric supercapacitor; (c) cycling stability at a current density of 10 A g⁻¹, and (d) Ragone plots of the asymmetric supercapacitors.

Table 2. Comparative representation of the energy density with recently reported asymmetric supercapacitors.

Asymmetric supercapacitor	Energy density	Reference
CuCo ₂ S ₄ nanoneedle//AC	44.1 W h kg ⁻¹ at 800 W kg ⁻¹	[20]
Cu ₇ S ₄ nanowires//carbon fibres	$35.0 \text{ W h kg}^{-1} \text{ at } 200 \text{ W kg}^{-1}$	[38]
$MnCo_2S_4$ nanoneedle//rGO	43.0 W h kg ⁻¹ at 801 W kg ⁻¹	[39]
$NiCo_2S_4$ nanosheet//AC	25.5 W h kg ⁻¹ at 334 W kg ⁻¹	[43]
Co ₉ S ₈ layer//AC	31.4 W h kg^{-1} at 200 W kg $^{-1}$	[44]
CuCo ₂ S ₄ nanosheet//rGO	45.6 W h kg ⁻¹ at 748 W kg ⁻¹	This work

The superior electrochemical performance of the $CuCo_2S_4$ nanosheet//rGO asymmetric supercapacitor is attributed to the following synergies. First, the $CuCo_2S_4$ nanosheets ensured an excellent positive electrode with a high specific capacitance and great cycling stability. Furthermore, the appropriate mass ratio of the anode and cathode active materials maintained the charge transfer balance between these two electrodes.

4. CONCLUSIONS

For the first time, polyvinylpyrrolidone (PVP) was used to control the crystallographic growth direction of $CuCo_2S_4$ in a glycerol solution. The obtained $CuCo_2S_4$ nanosheets mainly exposed an average thickness of approximately 15 nm. From the electrochemical measurements, $CuCo_2S_4$ nanosheets facilitated the charge transfer into the interior active material and provided a large contact area with the electrolyte. The specific capacitance of the $CuCo_2S_4$ nanosheets was 1742 F g⁻¹ at a current density of 10 A g⁻¹. The capacitance retention was 93.4% at 10 A g⁻¹ for 2000 cycles. In addition, the $CuCo_2S_4$ nanosheet//rGO asymmetric supercapacitor exhibited an energy density of approximately 45.6 Wh kg⁻¹ at a power density of 748.2 W kg⁻¹. After 5000 cycles at a current density of 10 A g⁻¹, the capacitance retention was 91.7%.

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References

- 1. B. Dunn, H. Kamath, J.-M. Tarascon, Science, 334 (2011) 928.
- 2. L. Zhou, Z. Zhuang, H. Zhao, M. Lin, D. Zhao, L. Mai, Adv. Mater., 29 (2017) 1602914.
- 3. L. Peng, P. Xiong, L. Ma, Y. Yuan, Y. Zhu, D. Chen, X. Luo, J. Lu, K. Amine, G. Yu, *Nat. Commun.*, 8 (2017) 15139.
- 4. H. Li, Y. Hou, F. Wang, M.R. Lohe, X. Zhuang, L. Niu, X. Feng, Adv. Energy Mater., 7 (2017) 1601847.
- 5. X. Rui, H. Tan, Q. Yan, Nanoscale, 6 (2014) 9889.
- 6. C. Huang, T. Sun, D. Hulicova-Jurcakova, *ChemSusChem*, 6 (2013) 2330.
- 7. Y. Lv, H. Wang, X. Xu, J. Shi, W. Liu, X. Wang, Chem. Eng. J., 326 (2017) 401.
- 8. S. Li, C. Yu, J. Yang, C. Zhao, M. Zhang, H. Huang, Z. Liu, W. Guo, J. Qiu, *Energy Environ. Sci.*, 10 (2017) 1958.
- 9. Z. Ma, X. Huang, S. Dou, J. Wu, S. Wang, J. Phys. Chem. C, 118 (2014) 17231.
- 10. E.H. Jo, H.D. Jang, H. Chang, S.K. Kim, J.-H. Choi, C.M. Lee, ChemSusChem, 10 (2017) 2210.
- 11. P. Simon, Y. Gogotsi, Nat. Mater., 7 (2008) 845.
- 12. L.-Q. Mai, A. Minhas-Khan, X. Tian, K.M. Hercule, Y.-L. Zhao, X. Lin, X. Xu, *Nat. Commun.*, 4 (2013) 2923.
- 13. X. Peng, H. Liu, Q. Yin, J. Wu, P. Chen, G. Zhang, G. Liu, C. Wu, Y. Xie, *Nat. Commun.*, 7 (2016) 11782.
- 14. C. Zhong, Y. Deng, W. Hu, J. Qiao, L. Zhang, J. Zhang, Chem. Soc. Rev., 44 (2015) 7484.

- 15. L. Yang, H. Li, H. Liu and Y. Zhang, Int. J. Electrochem. Sci., 12 (2017) 1.
- 16. R. Li, S. Wang, J. Wang, Z. Huang, Phys. Chem. Chem. Phys., 17 (2015) 16434.
- 17. S. Ravi, C.V.V.M. Gopi, H.j. Kim, Dalton Trans., 45 (2016) 12362.
- 18. Y. Wang, Y. Ma, G. Z. Guo, Y. Zhou, Y. Zhang, Y. Sun and Y. Liu, Int. J. Electrochem. Sci., 12 (2017) 2135
- 19. G. Zhang, H. Liu, J. Qu, J. Li, Energy Environ. Sci., 9 (2016) 1190.
- 20. S.E. Moosavifard, S. Fani, M. Rahmanian, Chem. Commun., 52 (2016) 4517.
- 21. Y. Zhu, X. Ji, H. Chen, L. Xi, W. Gong and Y. Liu, RSC Adv., 6 (2016) 84236.
- 22. Q. Wang, X. Liang, D. Yang and D. Zhang, RSC Adv., 7 (2017) 29933.
- 23. K.-J. Huang, J.-Z. Zhang, Y. Fan, J. Alloy. Compd., 625 (2015) 158.
- 24. S.G. Mohamed, S.Y. Attia, H.H. Hassan, Microporous Mesoporous Mater., 251 (2017) 26.
- 25. X. Zhao, X. Li, Y. Zhao, Z. Su, Y. zhang, R. Wang, J. Alloys Compd., 697 (2017) 124.
- 26. A.A. Dubale, A.G. Tamirat, H.-M. Chen, T.A. Berhe, C.-J. Pan, W.-N. Su, B.-J. Hwang, *J. Mater. Chem. A*, 4 (2016) 2205.
- 27. Z. Xu, T. Li, F. Zhang, X. Hong, S. Xie, M. Ye, W. Guo, X. Liu, Nanoscale, 9 (2017) 3826.
- 28. H. Yang, J. Zha, P. Zhang, Y. Xiong, L. Su, F. Ye, RSC Adv., 6 (2016) 66963.
- 29. S. Zhao, Y. Wang, Q. Zhang, Y. Li, L. Gu, Z. Dai, S. Liu, Y.-Q. Lan, M. Han, J. Bao, *Inorg. Chem. Front.*, 3 (2016) 1501.
- 30. Y. Wen, S. Peng, Z. Wang, J. Hao, T. Qin, S. Lu, J. Zhang, D. He, X. Fan, G. Cao, *J. Mater. Chem. A*, 5 (2017) 7144.
- 31. H. Tong, W. Bai, S. Yue, Z. Gao, L. Lu, L. Shen, S. Dong, J. Zhu, J. He, X. Zhang, *J. Mater. Chem. A*, 4 (2016) 11256.
- 32. P.L. Saldanha, R. Brescia, M. Prato, H. Li, M. Povia, L. Manna, V. Lesnyak, *Chem. Mater.*, 26 (2014) 1442.
- 33. V. Augustyn, P. Simon, B. Dunn, Energy Environ. Sci., 7 (2014) 1597.
- 34. P. Xu, J. Liu, P. Yan, C. Miao, K. Ye, K. Cheng, J. Yin, D. Cao, K. Li, G. Wang, *J. Mater. Chem. A*, 4 (2016) 4920.
- 35. L. Sun, X. Wang, W. Liu, K. Zhang, J. Zou, Q. Zhang, J. Power Sources, 315 (2016) 1.
- 36. A. Śliwak, B. Grzyb, N. Díez, G. Gryglewicz, Appl. Surf. Sci., 399 (2017) 265.
- 37. J. Tang, Y. Ge, J. Shen, M. Ye, Chem. Commun., 52 (2016) 1509.
- 38. M.S. Javed, S. Dai, M. Wang, Y. Xi, Q. Lang, D. Guo and C. Hu, Nanoscale, 7 (2015) 13610.
- 39. A.M. Elshahawy, X. Li, H. Zhang, Y. Hu, K.H. Ho, C. Guan and J. Wang, J. Mater. Chem. A, 5 (2017) 7494.
- 40. J. Yang, M. Ma, C. Sun, Y. Zhang, W. Huang and X. Dong, J. Mater. Chem. A, 3 (2015) 1258.
- 41. P. Ahuja, S.K. Ujjain, R. Kanojia, Appl. Surf. Sci., 427 (2018) 102.
- 42. C.H. Ng, H.N. Lim, S. Hayase, Z. Zainal, S. Shafie, N.M. Huang, *Electrochim. Acta*, 229 (2017) 173.
- 43. Z. Wu, X. Pu, X. Ji, Y. Zhu, M. Jing, Q. Chen and F. Jiao, *Electrochim. Acta*, 174 (2015) 238.
- 44. R.B. Rakhi, N.A. Alhebshi, D.H. Anjum and H.N. Alshareef, J. Mater. Chem. A, 2 (2014) 16190.

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