Amorphous CoMoS₄ for a valuable energy storage material candidate

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Abstract

The amorphous CoMoS₄ is prepared using a simple precipitation method and for the first time used as a supercapacitor material. Surprisingly, it possesses very good electrochemical behavior owing to its amorphous structure and multiple oxidation states. In a three-electrode system, the ratio capacitance of CoMoS₄ sample can reach 661 F g⁻¹ at a current density of 1 A g⁻¹. In the actual application of CoMoS₄, the CoMoS₄ symmetric device shows the ratio capacitance of 142 F g⁻¹ at 2 A g⁻¹; the assembled CoMoS₄//rGO hybrid supercapacitor also owns a high ratio capacitance of 68 F g⁻¹ at 1 A g⁻¹ with energy and power densities of 27.2 Wh kg⁻¹ at 400 W kg⁻¹ and 17 Wh kg⁻¹ at 2400 W kg⁻¹. Further the hybrid supercapacitor has good capacitance retention (86% after 10000 cycles), low internal and Warburg resistances.

Keywords: amorphous; capacitance; hybrid supercapacitor

1. Introduction

The ever-growing demand for energy, as well as the tremendous growth of

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consumer electronic devices and hybrid electric vehicles, has greatly stimulated scientists to explore high-performance energy conversion and storage devices [1]. However, the Li-ion batteries and fuel cells alone cannot meet all the requirements of performances and technologies [2]. Therefore, supercapacitors have created a great deal of research interest due to their high energy and power densities, quick charge/discharge process and long cycle longevity [3-5].

The transition metal oxides have been generally regarded as the effective electrode materials on account of their high theoretical capacities, low costs and toxicities [6-7]. Many material like NiO [8], CoO/Co₃O₄ [9], MnO₂ [10] and MoO₃ [11] have been reported to exhibit very good supercapacitive properties. Unfortunately, the poor conductivity of these oxides hinders their employment in high-rate capability devices along with rapid electron transport [12]. Surprisingly, the transition metal sulfides have higher conductivities than their corresponding oxides [13]. The transition metal sulfides, such as NiS/Ni₃S₂ [14-15], CoS [16] and MoS₂ [17] have been widely used in supercapacitors and shown outstanding performances. Moreover, in accordance with binary metal oxides, the binary metal sulfides with their multiple redox reactions tend to have better electrochemical behaviors than single component metal sulfides [18]. However, among the binary metal sulfides, there are few reports about applying other binary metal sulfides in supercapacitors apart from NiCo₂S₄, to our best knowledge. Therefore, the development of some new and high-performance binary metal sulfides as supercapacitive materials is still necessary. The abundance of Co and Mo in nature as well as the high theoretical capacities of CoS (or CoO) and

MoS₂ (or MoO₂) make CoMoS₄ ideal candidates for further investigation. In fact, it has been investigated for using in dye-sensitized solar cells [19] and secondary lithium batteries [20].

In this work, the CoMoS₄ sample was prepared using a very easy precipitation method. The CoMoS₄ was then characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), energy dispersive spectrometry (EDS), elemental mapping analyses and Raman analysis. Moreover, it is the first time to explore the supercapacitive performances of CoMoS₄ to our knowledge. It is well known that the electrochemical properties of an electrode material not only rely on its nature, conductivity and surface area but also on the electrolyte. Since the aqueous electrolyte is low cost, safe, environmentally friendly and has good cycling performance [21], 1 M KOH was used as the electrolyte.

The capacitances of the prepared CoMoS₄ were determined in a three-electrode setup. In order to better understand the actual properties of CoMoS₄, a symmetric device using CoMoS₄ as both the positive and negative electrode materials was also studied in a two-electrode cell. Further, a hybrid supercapacitor was assembled with CoMoS₄ as the positive electrode and reduced graphene oxide (rGO) as the negative electrode and characterized. Both the rGO and activated carbon are common negative electrode materials in hybrid supercapacitors [22-24]. The CoMoS₄/rGO hybrid supercapacitor was investigated to have high energy and power density.

2. Experimental

2.1 Materials

$(\text{NH}_4)_2\text{MoO}_4$, $(\text{NH}_4)_2\text{S}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and ethanol were all acquired from Tianjin Jiangtian Chemical Company and used without any further processing.

2.2 Preparation of CoMoS_4

$(\text{NH}_4)_2\text{MoO}_4$ (2.5 g) was placed in a beaker (150 mL) in a water bath at 70 °C. Then an excess of $(\text{NH}_4)_2\text{S}$ solution was added dropwise with stirring to react with the $(\text{NH}_4)_2\text{MoO}_4$. The reaction was monitored by observing the UV-vis absorption peak at 396 nm and when this peak disappeared, the reaction was complete. The mixture was then cooled to a low temperature (~5 °C) to allow the $(\text{NH}_4)_2\text{MoS}_4$ to crystallize. The $(\text{NH}_4)_2\text{MoS}_4$ crystals were separated by centrifugation and rinsed with cold ethanol to obtain the product $(\text{NH}_4)_2\text{MoS}_4$.

The above prepared $(\text{NH}_4)_2\text{MoS}_4$ (4 mmol) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (4 mmol) were dissolved in a solution of distilled water (70 mL) and ethanol (10 mL). The mixture was then stirred at room temperature to yield a CoMoS_4 precipitation. The precipitate was collected by centrifugation, washed with distilled water and ethanol, and dried by a freeze-drying process to obtain CoMoS_4 powder.

2.3 Characterization methods

The UV-vis spectra, XRD patterns, XRF spectra, XPS spectra and SEM images of CoMoS_4 were obtained using a UV-vis spectrophotometer (TU-1901), X-ray diffractometer (BDX3300; Cu K α radiation, voltage: 30 kV and current: 30 mA), XRF

spectrometer (Bruker, S4 Pioneer), XPS spectrometer (PHI1600 ESCA System, Perkin Elmer, US) and a Hitachi Limited S4800 microscope (Japan), respectively. The TEM, SAED, EDS and elemental mapping analyses were performed using a Philips Tecnai G2F20 microscope. Raman analysis was conducted on a DXR Raman spectrometer (US).

Electrochemical measurements, including cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) cycles and electrochemical impedance spectroscopy (EIS), were conducted on a computer controlled workstation (Shanghai Chenhua CHI 660D) in 1 M KOH at room temperature. The electrodes were prepared as follows: an homogeneous slurry of the sample, carbon black and polytetrafluoroethylene emulsion (mass fraction = 60%) with a mass ratio of 75:15:10 was coated on a piece of clean Ni foam (1 cm $\times$ 1 cm). The coated Ni foam was then dried and pressed to obtain an electrode pad.

The performance of CoMoS₄ was investigated with CV and GCD measurements in a three-electrode system, including the prepared CoMoS₄ electrode as the working electrode, a piece of Pt foil with a large-area as the counter electrode and HgO/Hg as the reference electrode. A CoMoS₄ symmetric device was studied by CV and GCD. This device constructed using two CoMoS₄ electrodes as the positive and negative electrodes and the electrodes were separated using a porous separator. A CoMoS₄/rGO hybrid supercapacitor was assembled using the CoMoS₄ and rGO electrodes as the positive and negative electrodes respectively. The hybrid supercapacitor was investigated using CV, GCD and EIS. The EIS measurement was

conducted in the frequency range from 10 mHz to 100 kHz with a potential amplitude of 5 mV at open circuit potential.

The ratio capacitances of the electrode material (C_s , F g⁻¹), the symmetric device ($C_s(d)$, F g⁻¹) and the hybrid supercapacitor ($C_s(hsd)$, F g⁻¹), the energy density (E , Wh kg⁻¹) and power density (P , W kg⁻¹) of the hybrid supercapacitor were determined according to the following equations (1-5) [25-26]:

$$C_s = \frac{i \times \Delta t}{\Delta v \times m} \quad (1)$$

$$C_s(d) = \frac{i \times \Delta t}{\Delta v \times M'} \quad (2)$$

$$C_s(hsd) = \frac{i \times \Delta t}{\Delta v \times M} \quad (3)$$

$$E = \frac{1000}{2 \times 3600} C_s(hsd) (\Delta v)^2 \quad (4)$$

$$P = \frac{3600 \times E}{\Delta t} \quad (5)$$

Where i is the applied constant current (A), Δt is discharge time (s), Δv is the potential window (V) and m , M' and M represent the mass (g) of the active materials in the single electrode, in the two CoMoS₄ electrodes in the symmetric device (g) and in the CoMoS₄ and rGO electrodes of the hybrid supercapacitor, respectively.

3. Results and discussion

When the (NH₄)₂S solution was added to (NH₄)₂MoO₄, the solution color immediately turned to orange due to the formation of MoO₃S₂²⁻, and then the solution gradually turned to red as MoS₄²⁻ was formed. The formation of the (NH₄)₂MoS₄ was monitored using UV-vis spectroscopy. Spectra were recorded every 10 min and the results are shown in Figure 1a. Obviously, the area ratio of absorption peaks at about

396 and 468 nm decreased with increasing time. After 20 min, the absorption peak at about 396 nm fully disappeared, indicating that all the $(\text{NH}_4)_2\text{MoO}_4$ was transformed to $(\text{NH}_4)_2\text{MoS}_4$. In order to ensure that the reaction was complete, the reaction time of 40 min was selected.

The composition of the prepared $(\text{NH}_4)_2\text{MoS}_4$ was also verified by XRD and the patterns is shown in Figure 1b. The typical diffraction peaks at about 14.6° , 17.1° , 18.5° , 23.5° , 25.4° , 29.1° , 31.5° , 40.2° , 45.7° , 53.1° can be indexed to the (011), (120), (200), (220), (022), (040), (311), (142), (431) and (360) crystal planes for $(\text{NH}_4)_2\text{MoS}_4$ (JCPDS: 48-1662) respectively, further confirming successful preparation of $(\text{NH}_4)_2\text{MoS}_4$. The obtained $(\text{NH}_4)_2\text{MoS}_4$ reacted with CoCl_2 at a molar ratio of 1:1 at room temperature to give CoMoS_4 . When the CoCl_2 solution was added to the $(\text{NH}_4)_2\text{MoS}_4$ solution, a precipitate was observed immediately, which is attributed to the occurrence of a replacement reaction. The XRD pattern (Figure 1b) proves that the CoMoS_4 is believed to be amorphous, which is in accordance with the reported result in the literature [27]. In addition, XRF measurement was used to determine the elemental composition of the CoMoS_4 sample. The calculated molar ratio of Co, Mo and S is 1:1.02:3.80, which is close to the stoichiometric ratio of CoMoS_4 .

Figure 1. UV-vis spectra taken during the preparation of $(\text{NH}_4)_2\text{MoS}_4$ (a); XRD patterns of the prepared $(\text{NH}_4)_2\text{MoS}_4$ and CoMoS_4 samples (b)

The chemical composition of the sample can be further verified by XPS analysis and the results are shown in Figure 2. In Figure 2a, the two main peaks located at 797.8 and 779.8 eV in the Co 2p core level spectrum can be attributed to Co 2p_{1/2} and Co 2p_{3/2}, which are in consistent with the presence of Co^{2+} . Moreover, the Co 2p_{3/2} binding energy (779.8 eV) is close to that (779.7 eV) for Co-Mo-S reported by Okamoto et al [28], suggesting that Co^{2+} ions are bonded with MoS_4^{2-} . In Figure 2b, the two peaks centered at 235.5 and 232.4 eV correspond to Mo 3d_{5/2} and Mo 3d_{3/2}, which is in consistent for Mo^{6+} . The peak at 229.0 eV can be assigned to S 2s. The binding energy of 162.9 eV corresponds to S 2p (Figure 2c), which is the characteristic of -2 oxidation state of S. These results are consistent with the characteristics of CoMoS_4 .

Figure 2. Co 2p (a), Mo 3d (b) and S 2p (c) core level spectra of CoMoS₄

The morphology and structure of CoMoS₄ can be observed by SEM and TEM images. Many particles and pores are observed in the SEM images at different magnifications (Figure 3a and b). In the TEM images (Figure 3c-d), there are some nano-flakes. It can be concluded that the CoMoS₄ particles are composed of many nano-flakes. The flake-like and porous structures often hold large surface area, which can improve the contact area between active materials and electrolyte, leading to high capacitance value. The high-resolution TEM photo of CoMoS₄ does not show any diffraction fringes (Figure 3e). Moreover, there is no obvious diffraction rings in the SAED pattern of CoMoS₄ (Figure 3f). These results further indicate that CoMoS₄ is amorphous.

Figure 3. SEM (a-b, scale: 5 μm (a), 1 μm (b)), TEM (c-e, scale: 100 nm (c), 50 nm (d), 5 nm (e)) and SAED (f, scale: 20 nm) images of CoMoS₄

The EDS analysis was also performed to determine the elements in the CoMoS₄

sample and shown in Figure 4a. Four elements Co, Mo, S and Cu were found. The Cu element is from the Cu grid used in the TEM measurement. The Co, Mo and S elements originate in CoMoS_4 and their molar ratio is also close to the stoichiometric proportion of CoMoS_4 . In addition, to intuitively observe the elemental distribution, the elemental mapping of CoMoS_4 was shown in Figure 4b. Obviously, the Co, Mo and S elements are uniformly distributed throughout the CoMoS_4 sample.

(a)

(b)

Figure 4. EDS spectrum (a) and Elemental mapping (b) of CoMoS₄

Raman analysis can provide the accurate data about variations in chemical bond distances as well as mechanical behaviors (strain, stress, etc.). Moreover, it is suitable for a variety of materials on account of the effectiveness and non-destructive feature. Figure 5 shows the Raman spectrum of the obtained CoMoS₄. The band at 932 cm⁻¹ is associated with the Mo-S symmetric stretching mode. The band located at 858 and 812 cm⁻¹ correspond to S asymmetric stretching mode in S-Mo-S bond. The band at 366 cm⁻¹ can be attributed to the Co-S-Mo symmetric stretching mode. The band at 404 cm⁻¹ is associated with the out-of-plane vibration of S atoms in opposite

directions. In addition, all observed peaks in this spectrum are distinguishing from those of CoS_2 [29] and MoS_2 [30] in both position and quantity, i.e. the Raman spectrum of CoMoS_4 has not any signature of CoS_2 and MoS_2 .

Figure 5. Raman spectrum for CoMoS_4

The prepared CoMoS_4 should be supposed to use as an electrode material in supercapacitors owing to the amorphous structure and multiple oxidation states [31]. Figure 6a exhibits the CV curves of CoMoS_4 at different scan rates (from 10 to 100 mV s^{-1}) in a potential window of 0-0.7 V. Some redox peaks appear in the CV curves of CoMoS_4 , indicating that CoMoS_4 stores electric energy by a Faradaic redox mechanism [32]. Meanwhile, the oxidation and reduction peaks shift to more positive and negative potentials at a high scan rate, which may be due to the increased inner diffusion resistance in the electrode material [33]. Moreover, the current subsequently increased at higher scan rates but the shape of CV curves is very similar at all scan rates. This fact reflects the good electrochemical capacitance for CoMoS_4 [34].

The GCD curves (Figure 6b) of CoMoS₄ at a potential range from 0 to 0.6 V were recorded at current densities of 1 to 3 A g⁻¹. The nonlinear discharge curves also verify the Faradic nature of CoMoS₄. The corresponding charge and discharge curves are nearly symmetric, suggesting the reversible charge/discharge capability of CoMoS₄ [35]. The ratio capacitances of CoMoS₄ from GCD cycles were calculated according to the equation (1) and are shown in Figure 6c. For current densities of 1, 1.6, 2, 2.4 and 3 A g⁻¹, the ratio capacitances of CoMoS₄ are 661, 554, 490, 449 and 410 F g⁻¹, respectively. Very obviously, the ratio capacitance values are inversely proportional to the scan rates, a common phenomenon. The diffusion time is reduced at a high scan rate, so the electrolyte ions cannot fully access to the inner surface of the active materials for charge storage [36]. The capacitance for CoMoS₄ are superior to those of the component sulfides, including CoS (247.2 F g⁻¹ at 1 A g⁻¹ [37]), CoS₂ (245 F g⁻¹ at 1 A g⁻¹ [38]) and MoS₂ (122 F g⁻¹ at 0.5 A g⁻¹ [39], 142 F g⁻¹ at 0.59 A g⁻¹ [40], 70 F g⁻¹ at 1 A g⁻¹ [41]). They are also higher than those of the similar oxides, such as ultrathin nanosheet-assembled CoMoO₄ with a mesoporous morphology (135 F g⁻¹ at 0.6 A g⁻¹) [42] and hierarchical MnMoO₄/CoMoO₄ hetero structured nanowires (187.1 F g⁻¹ at 1 A g⁻¹) [43]. The high capacitance of CoMoS₄ may be attributed to the multiple oxidation states, the synergistic effect of M (Co and Mo) and high conductivity of sulfides [44].

Figure 6. CV curves (a), GCD curves (b) and the corresponding ratio capacitances (c) of CoMoS₄ in a three-electrode system

Figure 7a and b show the CV and GCD curves of the CoMoS₄ symmetric device at the potential range of 0-1.0 V. In Figure 7c, the ratio capacitances of the symmetric device ($C_s(sd)$, F g⁻¹) using the equation (2) are 160, 142, 125, 114, 99 and 92 F g⁻¹ at 1.8, 2, 2.4, 2.6, 2.8 and 3 A g⁻¹ respectively, higher than some other symmetric supercapacitors, such as a UV induced rGO symmetric capacitor (141.2 F g⁻¹ at 1 A g⁻¹) [45], a MoS₂/PANI based symmetric supercapacitor (124 F g⁻¹ at 1 A g⁻¹) [46] and a α -MnMoO₄ symmetric cell (25 F g⁻¹ at 1.6 A g⁻¹) [47].

Figure 7. CV curves (a), GCD curves (b) and the corresponding ratio capacitances (c) of the CoMoS₄ symmetric device

Figure 8a exhibits the schematic image of the CoMoS₄/rGO hybrid supercapacitor device. The ratio capacitance values of the used rGO in this work are 170, 143, 131, 117, 111 F/g at 1, 1.6, 2, 2.6 and 3 A/g (Figure 8b). The loading mass of CoMoS₄ and rGO are about 3 and 7 mg based on the charge balance, respectively. Figure 8c and d show the CV and GCD curves of the hybrid device in a voltage window of 0-1.6 V. The nearly rectangle CV and triangle GCD curves confirm the good supercapacitive performance. The ratio capacitances of the CoMoS₄/rGO hybrid supercapacitor ($C_s(hsd)$, F g⁻¹) based on equation (3) are 77, 68, 63, 59, 53 and 48 F g⁻¹ at 0.5, 1, 1.5, 2, 2.5 and 3 A g⁻¹ (Figure 8e), higher than those of other similar hybrid supercapacitors, including α -MnO₂/MWCNT//activated carbon (43.3 F g⁻¹ at 1 A g⁻¹) [48] and rGO//CoMoO₄ (26.16 F g⁻¹ at 0.5 mA cm⁻²) [49]. The two key

parameters E and P were determined using the equations (4) and (5). The Ragone plots which relate to E and P are exhibited in Figure 8f. The energy density can reach 27.2 Wh kg^{-1} at the power density of 400 W kg^{-1} , and retains 17 Wh kg^{-1} at the power density of 2400 W kg^{-1} . These values are higher than those of other reported hybrid supercapacitors, such as ZnO/graphene nanoribbon//lacey reduced graphene oxide nanoribbon (9.4 Wh/kg) [50], CoMn LDH/Ni foam//Activated carbon (4.4 Wh/kg and 2500 W/kg) [51] and $\text{NiCo}_2\text{O}_4/\text{NiO}/\text{Fe}_2\text{O}_3$ (19 Wh/kg and 157 W/kg) [52].

The stability of a device can be evaluated using capacitance retention. Figure 8g indicates the capacitance retention of the $\text{CoMoS}_4/\text{rGO}$ hybrid supercapacitor at 80 mV s^{-1} . This device retained about 86% of the initial capacitance after 10000 cycles. This cyclic performance is better than some reported hybrid supercapacitor devices like MnO_2 nanowire/graphene//graphene (79% after 1000 cycles) [53], activated carbon// $\text{Co}_3\text{O}_4@\text{NiMoO}_4$ (1000 cycles, 68.7%) [54], activated carbon//hetero-Ni-Co-S asymmetric device (5000 cycles, 86%) [55] and $\text{Co}_9\text{S}_8/3\text{D}$ graphene//rGO hydrogel (6000 cycles, 86%) [56]. Figures 8h show the Nyquist plots of the $\text{CoMoS}_4/\text{rGO}$ hybrid supercapacitor. The charge transfer resistance (the radius of the high frequency loop) is about 1.1Ω , reflecting a low charge transfer resistance [57]. Moreover, the internal resistance (the real axis intercept) is 1.41Ω , indicating the internal resistance [58]. In addition, the straight line is nearly perpendicular to the real axis, demonstrating low Warburg resistance, which will promote the diffusion of electrolytes into the electrode material and lead to a facile and reversible Faradaic redox.

Figure 7. Schematic image of the CoMoS₄/rGO hybrid supercapacitor (a); specific capacitances of rGO (b); CV (c), GCD curves (d), ratio capacitances (e), Ragone plots (f), capacitance retention after 10000 cycles at 80 mV s⁻¹ (g) and Nyquist plots (h) for

the CoMoS₄/rGO hybrid supercapacitor

4. Conclusions

The amorphous CoMoS₄ was prepared by a simple precipitation method. The CoMoS₄ was used as the electrode material of supercapacitors for the first time and it exhibited the good electrochemical performance. The electrochemical behavior parameters of the CoMoS₄ sample were studied by a three-electrode system. The ratio capacitance of CoMoS₄ can reach 661 F g⁻¹ at a current density of 1 A g⁻¹. In order to determine the actual properties, the CoMoS₄ symmetric device was constructed and showed the ratio capacitance of 142 F g⁻¹ at 2 A g⁻¹. Based on the good performances of CoMoS₄, the CoMoS₄/rGO hybrid supercapacitor was constituted using CoMoS₄ and rGO. The device exhibits good supercapacitive performances: the ratio capacitance is 77 F g⁻¹ at 0.5 A g⁻¹; the energy density can reach 27.2 Wh kg⁻¹ at 400 W kg⁻¹, which retains 17 Wh kg⁻¹ at 2400 W kg⁻¹; capacitance retention is about 86% after 10000 cycles; low internal and Warburg resistances.

Acknowledgements

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