Electrochemical performances of Asymmetric super capacitor fabricated by one-dimensional CoMoO₄ nanostructure

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Abstract

We have prepared the CoMoO₄ nanorods (NR) electrode with a specific capacitance (89.5 F g⁻¹) at a current density of 1 mA cm⁻². Moreover, the asymmetric supercapacitor (ASC) has been fabricated by using CoMoO₄ NR as positive electrode and activated carbon (AC) as negative electrode. At a power density of 80 mWcm⁻³, the ASC can deliver an energy density of 0.226 mWh cm⁻³ in the voltage range of 0-1.6V. In addition, the CoMoO₄ NR-based ASC device still remains a high energy density (84.07%) after 5,000 cycles, demonstrating that one-dimensional nanostructures could be promising to achieve the high-energy-density materials.

Keywords: *CoMoO₄ nanorods; Energy density; Asymmetric supercapacitor (ASC)*

1. Introduction

To meet the increasing energy demand, incredible efforts have been made to develop the flexible energy storage and conversion devices with high energy and power density ^[1,2]. Amongst, supercapacitor (SC) has attracted considerable attention for the high power density and excellent safety ^[2,3]. Compared to fuel cells and renewable alternative batteries, the SCs have been widely used in hybrid electric vehicles, industry powergrids and military devices. ^[4,5] However, the lower energy densities of presently existing SCs limit the actual applications. Thus, it still remains a big challenge to obtain a high-energy-density SC.

According to $E=0.5 CV^2$, ^[6-8] the energy density (E) value of SC can be improved by increasing the cell potential (V) and specific capacitance (C). ^[9-12] Herein, V value can be increased through the asymmetric configuration and C value can be increased by developing excellent electrode materials. In most recent years, ternary metal oxides have gained great interest because of their feasible oxidation state, high electrical conductivity and high electrochemical activity, *e.g.* $ZnCo_2O_4$, ^[13,14] Zn_2SnO_4 , ^[15] $NiCo_2O_4$, ^[16-19] $NiMoO_4$, ^[20,21] $MnMoO_4$, ^[22] and so on. Among, $CoMoO_4$ has attracted particular attention due to its excellent electrochemical performances. ^[23,24] Nevertheless, the poor conductivity of $CoMoO_4$ still limit its application in SC and the flexible asymmetric supercapacitors (ASCs) built based on one-dimensional $CoMoO_4$ nanostructure have not been studied extensively.

In this work, we develop flexible asymmetric supercapacitors (ASCs) by using $CoMoO_4$ NR and activated carbon (AC) as positive and negative electrodes, respectively. The as-fabricated ASC shows a high energy density of $0.2263 \text{ mWh cm}^{-3}$ at a power density of 80 mW cm^{-3} , which is superior to many previously reported ASCs. Furthermore, the optimized ASC, with an output voltage of 1.6V, exhibits a

remarkable rate capacitance and a good cycle stability (84.07% of the initial energy density after 5,000 cycles). This work suggests that the high-energy-density capacitor can be developed by one-dimensional nanostructure and asymmetric configuration of electrodes.

2. Experimental

2.1. Sample preparation

The CoMoO₄ NRs were synthesized by a simple hydrothermal method. In detail, 1.5 mmol Co(NO₃)₂•6H₂O was dissolved in 30 mL distilled water, then the solution was stirred at room temperature for 10 min by a magnetic stirrer. After 1.5 mmol of Na₂MoO₄•2H₂O was added to the solution above, the mixture was stirred for 30 min to form a solution. Then, the solution was transferred to a 50-mL Teflon-lined autoclave and was heated at 150 °C for 5 h. After the reaction completed, the sample was collected and washed with distilled water for several times and dried at 60 °C for 24 h.

2.2. Characterization

The morphology of the sample was characterized by scanning electron microscope (SEM, Hitachi, SU-1510) using an accelerating voltage of 15 kV. The fine surface structure of the sample was characterized by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F) equipped an electron diffraction (ED) attachment with an acceleration voltage of 200 kV. The crystal phase of the sample was characterized by X-ray diffraction (XRD, Rigaku D/max-2550VB) with graphite monochromatized Cu K_α radiation ($\lambda = 0.154\text{nm}$). X-ray photoelectron spectroscopy (XPS) measurements were done on a VG ESCALAB MKII XPS system with Mg K_α source and a charge neutralizer. All the binding energies were referenced to the C1s peak at 284.8 eV of the surface adventitious carbon. Nitrogen adsorption–desorption isotherms were obtained at 77 K using the Autosorb-iQ physicoadsorption apparatus (Quantachrome). Surface area was calculated by the Brunauer-Emmett-Teller (BET).

2.3. Electrochemical measurements

All the electrochemical measurements were carried out on a CHI 660D electrochemical workstation. The working electrode consists of 80 wt % of CoMoO₄ NR, 10 wt% of carbon black and 10 wt% of polyvinylidene fluoride (PVDF). The powders were mixed with 0.3 mL of N-methylpyrrolidinone (NMP) to form a uniform slurry. The resulting slurry was coated onto carbon fibre (CF) and dried at 60 °C overnight. A Pt wire and a standard saturated calomel electrode (SCE) were used as a counter electrode and a reference electrode, respectively. A standard three-electrode cell was used, in which 1 M KOH aqueous solution was used as the electrolyte solution.

Cyclic voltammetry (CV) and chronopotentiometry (CP) were conducted in a potential range of -0.1-0.4 V (vs. S.C.E). Electrochemical impedance spectroscopy (EIS) was performed from 0.1 Hz to 100 KHz at an alternating current voltage amplitude of 5 mV.

2.4. Fabrication of asymmetric supercapacitor (ASC)

Typically, 80 wt% active carbon (AC) was mixed with 20 wt% PVDF to form a uniform slurry, and then the slurry was coated onto carbon fibre (CF). The AC@CF negative electrode was combined with the CoMoO₄@CF positive electrode to assemble the full ASC cell, with 1 M KOH as the electrolyte. The mass ratio of positive and negative electrodes is based on the charge balance theory ($Q^+ = Q^-$). The specific capacitance, energy and power densities of the ASC were all calculated on base of the total mass of both negative and positive electrodes.

3. Results and Discussion

3.1. Characterization of CoMoO₄ NR

Fig. 1 CoMoO₄ nanorods (NR): (a) XRD patterns; (b) Energy-dispersive X-ray spectrum (EDS) (the inset of the element composition); (c) Survey X-ray photoelectron spectroscopy (XPS) spectra; (d) Co 2p XPS; (e) Mo 3d XPS; (f) O 1s

XPS spectra

CoMoO₄ NR can be easily prepared through the simple hydrothermal method. The X-ray diffraction (XRD) analysis is used to demonstrate the crystal phase of the sample. As shown in Fig. 1a, all diffraction peaks of the sample can be assigned to monoclinic CoMoO₄ (JCPDS file no. 21-0868). The energy-dispersive X-ray spectroscopy (EDS) of CoMoO₄ NR confirms that the atom ratio of Co:Mo:O was approximately 1:1:4, in agreement with that of CoMoO₄ (Fig. 1b).

Besides, we resort to X-ray photoelectron spectroscopy (XPS) measurements to insight the chemical states and elemental composition of the sample. The typical survey XPS spectra (Fig. 1c) reveal the coexistence of Mo, Co, C and O elements in both samples. The Co 2p XPS spectra (Fig. 1d) of CoMoO₄ NR presents two major peaks at 780.2 eV and 795.3 eV with a spinning energy of 15 eV, corresponding to the Co 2p_{3/2} and Co 2p_{1/2}, respectively.^[25-27] In the case of CoMoO₄ NR, the peaks of Co 2p_{3/2} and Co 2p_{1/2} locate at 780.8 eV and 796.7 eV, respectively; which are in good agreement with the reported results.^[28,29] From the Mo 3d XPS spectra (Fig. 1e), we notice two peaks at about 232.15 eV and 235.25 eV, corresponding to Mo 3d_{5/2} and Mo 3d_{3/2}, respectively.^[30-32] The O 1s peaks at 529.98 eV and 530.3 eV indicate the existence of O²⁻ species (Fig. 1f).^[33]

Furthermore, the sample has been characterized by scanning electron microscopy (SEM) and high-resolution transmission microscopy (HRTEM) (Fig. 2). Fig. 2a and 2b show that the CoMoO₄ NRs are 1-2 μm long and their average diameters are about 200 nm. The interplanar spacing is determined to be 0.277 nm, corresponding to the (-131) planes of CoMoO₄ (Fig. 2c), indicating the nanorods grow preferentially along [131] direction. The single-crystalline nature of the CoMoO₄ NR can be revealed by

the selected area electron diffraction (SAED) patterns (Fig. 2d) and the clear diffraction spots can be identified as the (-131) and (002) planes of the CoMoO_4 .

Fig. 2 SEM, HRTEM images and electron diffraction patterns (ED) of CoMoO_4 NR: (a) SEM image; (b) TEM image; (c) Lattice fringe images; (d) ED patterns

3.2. CoMoO_4 NR electrode

The electrochemical properties of CoMoO_4 NR electrodes are investigated by the electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and chronopotentiometry (CP). Herein, CVs are measured in 1 M KOH aqueous solution in a three-electrode system. Fig. 3a shows the CV curves of CoMoO_4 NR at different scanning rates ($5\text{--}100\text{ mVs}^{-1}$). A pair of redox peaks can be observed in each CV curve, suggesting a typical pseudo-capacitive behavior. In the alkaline electrolyte solution, such Faradic redox reactions can be attributed to the mutual conversion between Co^{2+}

and Co^{3+} . [22, 34] It can be seen that the peak current increases, but the shape of the CV curves is not influenced by increasing the scanning rate, which suggests an improved electron-transfer efficiency in the host material. Besides, as the scanning rate increases, the anodic peaks shift to higher potential while the cathodic peaks shift to lower potential due to greater ohmic overpotential; but the CV curves still showed symmetrical redox shape, indicating stable and fast redox reaction.

Fig. 3 Electrochemical properties of CoMoO_4 NR: (a) Cyclic voltammetry (CV) curves; (b) Galvanostatic charge-discharge curves; (c) Specific capacitances at different current densities; (d) Cycle stability

Fig. 3b shows the galvanostatic charge–discharge curves at the current densities from 1 to 10 mA cm^{-2} . The nonlinear charge/discharge profile could be attributed to the pseudo-capacitive behavior. [35,36] The specific capacitance of electrode is calculated according to the following equation:

$$C = I \Delta t / m \Delta V \quad (1)$$

where I is the discharge current, Δt is the discharge time, ΔV is the voltage range, and m is the mass of active material. Fig. 3c shows the calculated discharge capacitances of CoMoO₄ NR at various current densities. Specifically, the discharge capacitances are 89.5, 35.26, 13.1 8.6 and 8.5 F g⁻¹ at the current densities of 1, 2, 5, 10 and 20 mA cm⁻², respectively. The discharge capacitance significantly decreases with the increase of discharge current density, but the discharge capacitance did not decrease with the current densities of 10 and 20 mA cm⁻². Further, Fig. 3d presents the cycle stability of CoMoO₄ NR electrodes at 10 mA cm⁻² for 4 000 cycles. After 4000 cycles, 80% of capacitance is remained for CoMoO₄ NR, indicating an excellent electrochemical stability. The result suggests that CoMoO₄ NR can be used as an outstanding electrode material. To further understand the electrochemical performances of the electrode, electrochemical impedance spectroscopy (EIS) analysis is carried out, as shown in Fig. 4a. The measured impedance data are fitted and further analyzed by an equivalent electrical circuit (the inset of Fig. 4a), which consists of electrolyte solution resistance (R_s), Warburg impedance (W), charge-transfer impedance (R_{ct}) and a constant phase element (CPE). The CoMoO₄ NR electrode has a small R_{ct} (2.84 Ω), indicating a high electrochemical conductivity. Their excellent electrochemical performances could be attributed to the 1-D nanostructure.^[24, 36] On one hand, the BET area of CoMoO₄ NR is 10.8 m² g⁻¹ (Fig. 4b). It is well known that the high BET area could increase electrolyte/electrode contact area and provide more active sites, which can lead to a high specific capacitance.^[14] On the other hand, the CoMoO₄ nanorods will be beneficial to shorten the diffusion paths for both electrons and ions due to the specific one-dimensional nanostructure, thus leading to fast electron transport and ion diffusion rates during charge–discharge processes.^[34] The results verify that CoMoO₄ NR could be a promising candidate for supercapacitor material.

Fig. 4 (a) Nyquist plot (the inset of the equivalent electrical circuit) and (b) Nitrogen sorption isotherms of CoMoO₄ NRs.

3.3. ASC device

To further evaluate the practical applications of CoMoO₄ NR, the ASC devices are assembled by using CoMoO₄ NR /carbon fiber as the cathode, AC/carbon fiber as the anode, 1 M KOH as the electrolyte solution, and filter paper as the separator. The ASC configure is presented in Fig. 5a. Fig. 5b shows the CV curves of the optimized ASC device fabricated by CoMoO₄ NR at different scanning rates (5, 10, 20, 50 and 100 mVs^{-1}). The operating cell voltage (1.6 V) is much higher than the conventional active carbon (AC)-based symmetric supercapacitors in aqueous electrolytes (0.8-1.0V), which makes it possible to achieve a high energy density. Moreover, it should be worth noting that water splitting can be avoided due to the existence of an overpotential. Fig. 5c presents the galvanostatic charge/discharge curves at different current densities (1.5, 3, 6, 12 and 24 mA cm^{-3}) for the CoMoO₄ NR-based ASC device and Fig. 6 shows the CV curves of positive and negative electrodes, which are tested in a three-electrode cell. Clearly, the nonlinear charge/discharge curves could indicate a typical pseudo-capacitive behavior in CoMoO₄ NR-based ASC device. From the CV curve of the, however, the CV curve of AC@CF electrode presents an

electrochemical double layer behavior (capacitor type). The as-fabricated ASCs can make full use of both capacitive behaviors to enhance the operation voltage window.

According to these results above, the Ragone plots of ASCs describe the relationship between volumetric energy density ($E = (CAU^2/2)$) and volumetric power density ($P=(E/t)$) (Fig. 7a). Notably, our ASC displays a high energy density of 0.226 mWh cm^{-3} at a power density of 80 mW cm^{-3} . Even at a high power density of 640 mW cm^{-3} , the ASC still maintains 0.083 mWh cm^{-3} much superior to those of electric double-layer capacitors.^[11,24] More interestingly, its high energy density is advantageous over the previously reported systems, for example, graphene-based SC (0.06 mWh cm^{-3} at 0.2 W cm^{-3} , PVA/H₃PO₄),^[24] TiN-based SC (0.05 mWh cm^{-3} at 0.1 W cm^{-3} , PVA/KOH),^[11] H-TiO₂@MnO₂//H-TiO₂@C ASC (0.3 mWh cm^{-3} at 0.2 W cm^{-3} , 5M LiCl)^[36,37] and MnO₂@CoMoO₄@Ni ASC (2.26 mWh cm^{-3} at 4 mW/ cm^3).^[38]

Moreover, Fig. 7b exhibits the cycling performance of the ASC device. After 5000 cycles, it can be clearly seen that the discharge capacitance still remains 84.07% of initial specific capacitance, which suggesting the excellent long-term electrochemical stability of ASC device. To conclude, a high energy can be reached for the CoMoO₄ NR-based ASC, which is promising for practical application.

Fig. 5 Flexible asymmetric supercapacitors (ASC): (a) Schematic configuration of ASC; (b) CV curves with a voltage window of 0–1.6 V; (c) Change-discharge curve

Fig. 6 Comparative CV curves of the CoMoO₄@ carbon fibre (CF) electrode and activated carbon (AC) electrode (three-electrode cell, vs. SCE)

Fig. 7 Ragone plots (a) and cycling stability (b) of the CoMoO₄ NR-based ASC

4. Conclusions

CoMoO₄ NR-based ASC delivers a high energy density of 0.226 mWh cm⁻³ at a power density of 80 mW cm⁻³, which has been mainly ascribed to the specific one-dimensional nanostructure that leads to the fast electron transport and ion diffusion rates. Our results demonstrate that a high-energy-density supercapacitor can be achieved by using 1-D nanostructure and the asymmetric configuration.

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References

- [1] J. R. Miller, P. Simon, *Science*, 321 (2008) 651-652.
- [2] P. Simon, Y. Gogotsi, *Nat. Mater.*, 7 (2008) 845-854.
- [3] H. Wang, H. S. Casalongue, Y. Liang, H. Dai, *J. Am. Chem. Soc.*, 132 (2010) 7472-7477.
- [4] G. Yu, L. Hu, M. Vosgueritchian, H. Wang, X. Xie, J. R. McDonough, X. Cui, Y. Cui, Z. Bao, *Nano Lett.*, 11 (2011) 2905-2911.
- [5] N. Yu, H. Yin, W. Zhang, Y. Liu, Z. Tang, M. Zhu, *Adv. Energy. Mater.*, 6 (2016), 201501458
- [6] H. Tang, J. Wang, H. Yin, H. Zhao, D. Wang, Z. Tang, *Adv. Mater.*, 6 (2015)

1117-1123.

- [7] J.-H. Sung, S.-J. Kim, K.-H. Lee, *J. Power Sources*, 124 (2003) 343-350.
- [8] K. Chau, Y. Wong, C. Chan, *Energy Convers. Manage.*, 40 (1999) 1021-1039.
- [9] J. Yan, Z. Fan, W. Sun, G. Ning, T. Wei, Q. Zhang, R. Zhang, L. Zhi, F. Wei, *Adv. Funct. Mater.*, 22 (2012) 2632-2641.
- [10] J. Xu, Q. Wang, X. Wang, Q. Xiang, B. Liang, D. Chen, G. Shen, *ACS nano*, 7 (2013) 5453-5462.
- [11] X. Lu, G. Wang, T. Zhai, M. Yu, S. Xie, Y. Ling, C. Liang, Y. Tong, Y. Li, *Nano Lett.*, 12 (2012) 5376-5381.
- [12] M. Yu, Y. Zeng, Y. Han, X. Cheng, W. Zhao, C. Liang, Y. Tong, H. Tang, X. Lu, *Adv. Funct. Mater.*, 5 (2015) 56-67.
- [13] K. Karthikeyan, D. Kalpana, N. Renganathan, *Ionics*, 15 (2009) 107-110.
- [14] B. Liu, B. Liu, Q. Wang, X. Wang, Q. Xiang, D. Chen, G. Shen, *ACS Appl. Mater. Inter.*, 5 (2013) 10011-10017.
- [15] L. Bao, J. Zang, X. Li, *Nano Lett.*, 11 (2011) 1215-1220.
- [16] C. Yuan, J. Li, L. Hou, X. Zhang, L. Shen, X. W. D. Lou, *Adv. Funct. Mater.*, 22 (2012) 4592-4597.
- [17] L. Huang, D. Chen, Y. Ding, S. Feng, Z. L. Wang, M. Liu, *Nano Lett.*, 13 (2013) 3135-3139.
- [18] G. Zhang, X. W. D. Lou, *Sci. Rep.*, 3 (2013) 77-80.
- [19] Q. Wang, X. Wang, J. Xu, X. Ouyang, X. Hou, D. Chen, R. Wang, G. Shen, *Nano Energy*, 8 (2014) 44-51.
- [20] M.-C. Liu, L.-B. Kong, C. Lu, X.-J. Ma, X.-M. Li, Y.-C. Luo, L. Kang, *J. Mater. Chem. A*, 1 (2013) 1380-1387.
- [21] B. Senthilkumar, K. V. Sankar, R. K. Selvan, M. Danielle, M. Manickam, *RSC*

- Adv.*, 3 (2013), 352–357.
- [22] L.-Q. Mai, F. Yang, Y.-L. Zhao, X. Xu, L. Xu, Y.-Z. Luo, *Nat. Commun.*, 2 (2011) 381.
- [23] X. Yu, B. Lu, Z. Xu, *Adv. Mater.*, 26 (2014) 1044-1051.
- [24] G.K. Veerasubramani, K. Krishnamoorthy, S.J. Kim *RSC Adv.*, 5 (2015) 16319–16327.
- [25] Z. Wang, L. Pan, H. Hu, S. Zhao, *CrystEngComm*, 12 (2010) 1899-1904.
- [26] C. Loussot, P. Afanasiev, M. Vrinat, H. Jobic, P. Leverd, *Chem. Mater.*, 18 (2006) 5659-5668.
- [27] J. Xiao, X. Zeng, W. Chen, F. Xiao, S. Wang, *Chem. Commun.*, 49 (2013) 11734-11736.
- [28] J. Xu, P. Gao, T. Zhao, *Energ. Environ. Sci.*, 5 (2012) 5333-5339.
- [29] J. Xiao, L. Wan, S. Yang, F. Xiao, S. Wang, *Nano Lett.*, 14 (2014) 831-838.
- [30] M. Zhang, C. Shao, J. Mu, Z. Zhang, Z. Guo, P. Zhang, Y. Liu, *CrystEngComm*, 14 (2012) 605-612.
- [31] Z. Li, X. Chen, Z.-L. Xue, *Sci. China Chem.*, 56 (2013) 443-450.
- [32] H. Tang, J. Wang, H. Yin, H. Zhao, D. Wang, Z. Tang, *Adv. Mater.*, 27 (2015) 1117-1123.
- [33] M. Yu, W. Wang, C. Li, T. Zhai, X. Lu, Y. Tong, *NPG Asia Mater.*, 6 (2014) e129.
- [34] S. Peng, L. Li, H. B. Wu, S. Madhavi, X. W. D. Lou, *Adv. Energy Mater.*, 5 (2015) 1401172.
- [35] R. Rakhi, W. Chen, D. Cha, H. Alshareef, *Nano Lett.*, 12 (2012) 2559-2567.
- [36] L. Li, S. Peng, H. B. Wu, L. Yu, S. Madhavi and X. W. D. Lou, *Adv. Energy Mater.*, 5 (2015) 1500753.

- [37] X. Lu, M. Yu, G. Wang, T. Zhai, S. Xie, Y. Ling, Y. Tong and Y. Li, *Adv. Mater.*, 25 (2013) 267-272.
- [38] Z. Liu, Z. Zhao, F. Teng, C. Chang, Y. Zhao, Y. Yang, W. Yao, Y. Zhu, Y. Fan, *RSC Adv.*, 6 (2016) 46508-46515.

Graphic Abstract

A flexible asymmetric super capacitor is fabricated by CoMoO_4 nanorods.