Excellent Rate Capability of NiCo$_2$O$_4$ with Urchin-Like Nanostructure as Cathode for Asymmetric Supercapacitors

Jijun Zhang, Zexiang Chen* and Yan Wang

School of Optoelectronic Science and Engineering, University of Electronic Science and Technology of China, North Jianshe Road 4, 610054 Chengdu, China

*Corresponding author: E-mail address: zxchen@uestc.edu.cn

Abstract. We report a fabrication of urchin-like nanostructure NiCo$_2$O$_4$ by hydrothermal method and followed by heating treatment method for cathode of asymmetric supercapacitors application. The sodium-p-styrenesulfonate (PSS) played a pivotal role in synthesizing the urchin-like nanostructure. The formation of NiCo$_2$O$_4$ with urchin-like nanostructure was showed by the scanning electron microscope (SEM) and the crystalline structure was characterised by X-ray powder diffraction (XRD). The cyclic voltammetry curves exhibited a similar shape at all different scan rates, implying excellent rate capability. The galvanostatic current charge-discharge curves was also tested. The as-prepared NiCo$_2$O$_4$ electrode exhibited the specific capacitance of 1168 F/g at a current density of 1 A/g (25 mA/cm$^2$) and an excellent rate capability of 733 F/g at 16 A/g (400 mA/cm$^2$). The cycle performance of the NiCo$_2$O$_4$ sample under the current density of 4 A/g is demonstrated which the value remained at 92.75% of the maximum value.

1. Introduction
With the continuous consumption of fossil energy, people begin to look for new alternative energy sources. Although many new energy sources have been developed, traditional energy storage equipment can hardly meet the needs. Supercapacitors have been widely studied as a potential energy storage device. Supercapacitors are characterized by rapid charge and discharge, high power density, excellent cycling performance, environmental friendliness abundant reserves of electrode materials and so on[1-4]. There are two types of supercapacitors, one is the double-layer supercapacitor based on the double-layer energy storage mechanism and the other type is the pseudo capacitor based on Faraday redox reaction[5-7]. Although the double-layer supercapacitors have very high power density and excellent cycle performance, their energy density is very low which is also the main factor limiting its practical application. In contrast, the pseudo capacitor has relatively high energy density, which is the focus of new energy storage equipment. Transition metal oxide is a common electrode material with pseudo capacitance which has very high theoretical specific capacity, high power density and good cycle stability[8-10]. NiCo$_2$O$_4$ is an important cathode electrode material in transition metal oxides, which has very high theoretical specific capacity, good rate capability performance and stable cycle life[11-14]. However, at present, the high theoretical specific capacity and high magnification performance of NiCo$_2$O$_4$ have not really been given full play which the main reason is the low electrochemical activity of NiCo$_2$O$_4$. It has been proved that materials with unique nanostructure can effectively increase the electrochemical activity of the materials[15-17]. Therefore, the synthesis of
NiCo₂O₄ with special nanostructures is one of the ways to solve the above problems. In this paper, we synthesized a kind of nanostructure NiCo₂O₄ material with urchin-like by a simple and practical method of hydrothermal reaction and followed by heat treatment. The as-prepared NiCo₂O₄ was used for the cathode materials of asymmetric supercapacitors which exhibited excellent electrochemical properties. The electrochemical tests were carried out by three-electrode system in the KOH electrolyte of 6 mol/L which exhibited the high specific capacitance of 1168 F/g at the current density of 1 A/g (25 mA/cm²) and an excellent rate capability of 733 F/g at 16 A/g (400 mA/cm²). The cycle performance of the NiCo₂O₄ sample under the current density of 4 A g⁻¹ is demonstrated which has an excellent cycle stability.

2. Experimental detail

2.1. NiCo₂O₄ Synthesis

All the reagents are analytically grade without additional treatment for purification. In a typical experimental procedure, firstly, Co(NO₃)₂·6H₂O and Ni(NO₃)₂·6H₂O were respectively configured into an aqueous solution of 1 mol/L. Taking 2 mL Ni(NO₃)₂ solution and 4 mL Co(NO₃)₂ solution into 34 mL deionized water with constant magnetic stirring for 5 min. And then 0.04 g sodium-p-styrenesulfonate (PSS) and 18 mmol urea were added into the solution. After magnetic stirring for 15 min, the obtained solution was transferred to a 50 ml hydrothermal reactor. The hydrothermal reactor is then heated to 90 °C and held at 90 °C for 12 hours. When the reaction is over, taking out the reaction products and centrifugal washing with ethanol and deionized water for several times. The product is then dried at 80 °C for 8h. The as-prepared NiCo₂O₄ was obtained by heat treatment at 350 °C for 2 h with heating speed of 2 °C/min in air.

2.2. As-prepared NiCo₂O₄ characterization

The X-ray diffractometer (X’Pert Pro, CuKa λ = 0.15405 nm) was used to characterize the crystal structure of the urchin-like nanostructure NiCo₂O₄ powder. The nanoscale morphology of as-prepared NiCo₂O₄ was detected by scanning electron microscope (SEM, Inspect F).

2.3. Electrochemical Measurements

The electrochemical performance was tested in three-electrode test system in a in the KOH electrolyte of 6 mol/L. The platinum foil was used as the counter electrode and the Hg/HgO electrode as the counter electrodes. For preparing a cathode electrode of as-prepared NiCo₂O₄, the super-p was used as the conductive material and the Teflon was used as the adhesive. The mass ratio of NiCo₂O₄, super-p and Teflon is 80:15:5 in ethanol forming a uniform slurry. After that, the slurry was scraped onto the nickel foam and dried at 80 °C for 12 h. Then the electrode was pressed into electrode sheet using a compactor with 150 °C for 15 min. The active material area of the electrode was 1 cm × 1 cm, and the mass load of NiCo₂O₄ cathode electrode was 25 mg/cm². The RST5201F electrochemical workstation (Zhengzhou Shiruisi Instrument Technology Co., Ltd., Zhengzhou, China) was used to carry out the electrochemical measurements.

3. Result and discussion

3.1. Formation and Characteristics of the as-prepared NiCo₂O₄

The scheme and evolution of nanostructure NiCo₂O₄ with urchin-like were shown in figure 1 which the field emission scanning electron microscope was used for the nanoscale morphology of the as-prepared NiCo₂O₄ with different hydrothermal reaction time. At the beginning of the hydrothermal reaction, the nanoscale crystallites were formed with the participation of the PSS. And then with the growth of nanocrystals, the nanostructure of the as-prepared NiCo₂O₄ turns into rod-like structure. As the reaction time goes by, in the reaction time of 12 h, the rod-like structure was further grown into
urchin-like NiCo$_2$O$_4$ precursor. Finally with the heating treatment, the urchin-like NiCo$_2$O$_4$ was formed.

![Figure 1. Evolution of urchin-like NiCo$_2$O$_4$ structure and the FSEM images of different hydrothermal reaction time for 3 h, 7 h and 12 h.](image)

The X-ray powder diffraction was used for characterizing the crystal structure of the as-prepared NiCo$_2$O$_4$ as shown in figure 2. It can be seen that nearly no other diffraction peak appears in the as-prepared NiCo$_2$O$_4$, which indicated that the as-prepared sample has a high degree of purity. The diffraction peaks of as-prepared NiCo$_2$O$_4$ are observed in the position of 18.91°, 31.15°, 36.70°, 38.40°, 44.62°, 55.44°, 59.09°, 64.98° and 68.31°, in accord with the (1 1 1), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1), (4 4 0) and (5 3 1) planes of NiCo$_2$O$_4$ respectively (JCPDS 200781), which also indicates that the nano-structure of urchin-like sample is the NiCo$_2$O$_4$ crystals.

![Figure 2. XRD patterns of as-prepared NiCo$_2$O$_4$.](image)

### 3.2. Electrochemical analysis of NiCo$_2$O$_4$ electrode

The electrochemical performance of urchin-like nanostructure NiCo$_2$O$_4$ cathode electrode were measurement by a three-electrode system in the KOH aqueous electrolyte of 6 mol/L. The cyclic voltammetry measurements of the urchin-like nanostructure NiCo$_2$O$_4$ cathode electrode were tested as
shown in figure 3. The scan rates of the CV measurements were from 5 to 100 mV/s. In figure 3, it can be seen that all different scan rates of the CV curves show a similar shape which revealed typical pseudocapacitive characteristics, indicating the excellent rate capability of the urchin-like nanostructure NiCo$_2$O$_4$ cathode electrode. In addition, a series of peaks were detected in the CV curves, which is mainly due to the redox reaction of M-O/M-O-OH (M represents Ni or Co)[18-20]. With the increase of scan rates, the redox peak shifts to a little bit, but the shift distance is still lower than the change range of scan rates, revealing the low resistance of the urchin-like nanostructure NiCo$_2$O$_4$ cathode electrode, which was likely due to the fine electrical contact of Ni foam substrate and NiCo$_2$O$_4$, and the excellent electrical transmission performance of the NiCo$_2$O$_4$ electrode[21-23].

![Figure 3. CV curves of the NiCo$_2$O$_4$ electrode.](image)

To further investigate the electrochemical performance of the urchin-like nanostructure NiCo$_2$O$_4$ cathode electrode, the galvanostatic charge-discharge performance was also tested at different rate current densities. Through the galvanostatic charge-discharge measurements, a series of galvanostatic charge-discharge curves were obtained as shown in figure 4. From figure 4, it can be found that the charge-discharge curves at different rate current densities are basically symmetrical, which indicated that the urchin-like nanostructure NiCo$_2$O$_4$ cathode electrode has excellent rate capability. In addition, the charging platform is higher than the discharging platform which is due to the internal resistance of the urchin-like nanostructure NiCo$_2$O$_4$ cathode electrode. The specific capacitances could be calculated from the discharging platform of the galvanostatic charge-discharge curves. The calculated specific capacitance of the urchin-like nanostructure NiCo$_2$O$_4$ cathode electrode were 1169, 1092, 992, 850, 733 and 533 F/g at 1, 2, 4, 8, 16 and 32 A/g, respectively. The urchin-like nanostructure NiCo$_2$O$_4$ cathode electrode shows remarkable rate capability, and the retention of the capacity is 85 % at the current density of 4 A/g. In addition, when the current density increases to 16 A/g, the retention of the capacity still can retain 62.7 %. At the current density of 32 A/g, the capacity retention is 46 %. The capacity has a large attenuation under such large current density, which is probably caused by the setting of the potential window and the charging and discharging potential of the electrode material itself. The prominent rate capability of the NiCo$_2$O$_4$ cathode electrode could be contributed to urchin-like nanostructure of the NiCo$_2$O$_4$. The novel nanostructure can indeed increase the electrical contact between the electrolyte and the NiCo$_2$O$_4$ materials, which provides more electrochemical active area for the redox reactions, making the improvement of rate capability.
The electrochemical cycling stability of electrode materials has a great influence on the performance of supercapacitors. The cycle stability performance of the NiCo$_2$O$_4$ cathode electrode is shown in figure 5. At the current density of 4 A/g, the cyclic galvanostatic charge-discharge measurement was carried out for 800 cycles. The obtained data is plotted as the cycle stability curve as shown in figure 5. It can be found that the trend of the curve is to increase first, then stabilize and then slowly decay. In the initial 100 cycles, the curve shows an upward trend, which is probably due to the continuous redox reaction to increase the effective active area of the NiCo$_2$O$_4$ material, so as to increase the specific capacity of the NiCo$_2$O$_4$ cathode electrode[24, 25]. In the intermediate stage, the specific capacity tends to be stable, which may be due to the continuous redox reaction makes the material basically be fully activated. The slow attenuation in the final stage is probably due to the gradual loss of stickiness of the electrode binder after cyclic charging and discharging, resulting in the shedding of some electrode materials. The retention capacity rate was 92.75 % in the final, which could indicate a singularly high crystallinity of the urchin-like nanostructure NiCo$_2$O$_4$ and also imply the remarkable cycling stability of the NiCo$_2$O$_4$ cathode electrode.
4. Conclusion

In summary, we presented a fabrication of urchin-like nanostructure NiCo$_2$O$_4$ by hydrothermal method and followed by heating treatment method for cathode of asymmetric supercapacitors application. The as-prepared NiCo$_2$O$_4$ electrode exhibited the specific capacitance of 1168 F/g at 1 A/g (25 mA/cm$^2$) and even at 16 A/g (400 mA/cm$^2$), the retention rate of the specific capacitance is 62.7 % which implied an excellent rate capability. The CV curves shew similar shapes at different scan rates, implying typical pseudocapacitive characteristics and remarkable rate capability. The cycle stability of the NiCo$_2$O$_4$ sample under 4 A g$^{-1}$ is demonstrated which the value remained at 92.75 % of the maximum value. In conclusion, the unique urchin-like nanostructure of NiCo$_2$O$_4$ indeed improves the performance of NiCo$_2$O$_4$ cathode electrode for asymmetric supercapacitors.

Acknowledgments

This work was supported by National Natural Science Foundation of China (NSFC 51702037) and the Fundamental Research Funds for the Central Universities of China (ZYGX2015KYQD014).

References

[1] Sumanta Kumar M and G Ranga R 2011 J Phys Chem C 115 15646-54
[2] Jun Y, Zhuangjun F, Tong W, Weizhong Q, Milin Z, Fei and W 2010 Carbon 48 3825-33
[3] Zenan Y, Laurene T, Lei Z and Jayan T 2015 Energy Environ Sci 8 702-30
[4] Li Li Z, Xs and Z 2009 Chem Soc Rev 38 2520-31
[5] Shen-Ming C, Rasu R, Veerappan Ma and Ramiah S 2014 Int J Electrochem Sci 9 4072-85
[6] Mingjia Z, Chengcheng X, Jiayong T, Ming L and Nianqiang W 2013 Nanoscale 5 72-88
[7] Cheng Z, Yangwei Z, Yuanyuan L and Jiping L 2013 Nano Lett.13 2078-85
[8] Xingyou L, Akihiko H, Takeshi F and Mingwei C 2011 Nat Nanotechnol.6 232
[9] Raghavan Baby R, Bilal A, Dalaver A and Husam N A 2016 ACS Appl Mater Interfaces 8 18806-14
[10] Yan W, Jin G, Tingfeng W, Junfeng S, Dong W and Ying-Wei Y 2015 Nanomaterials 5 1667-89
[11] Ying L, Jing L, Yanyan W, Li G, Yuefan C, Hongyan Y and Dan X 2014 ACS Appl Mater Interfaces 6 1773-80
[12] Jae-Jin S 2015 J Power Sources 273 110-7
[13] Qifan W, Xianfu W, Jing X, Xia O, Xiaojuan H, Di C, Rongming W and Guozhen S 2014 Nano Energy 8 44-51
[14] Changzhou Y, Jiaoyang L, Linrui H, Xiaogang Z, Laifa S and Xiong Wen L 2012 Adv Funct Mater 22 4592-7
[15] Hao J, Pooy See L and Chunzhong L 2013 Energy Environ Sci 6 41-53
[16] Lele P, Xu P, Borui L, Changzheng W, Yi X and Guihua Y 2013 Nano Lett.13 2151-7
[17] Yuhao W, Ping H, Xiaomei Z, Wen L and Faqin Dong 2014 J Solid State Electrochem 18 665-72
[18] Chenggang W, E Z, Weidong H, Xiaolong D, Jinzhao H, Meng D, Xianqi W, Xiaojing L and Xijin X 2017 Nanomaterials.7 41
[19] Ji-Shi W, Hui D, Peng Z, Yan-Fang S, Jie C, Yong-Gang W and Huan-Ming X 2016 Small 12 5927-34
[20] Yirong Z, Zhibin W, Mingjun J, Weixin S, Hongsaniu H, Xuming Y, Qiyuan C and Xiaobo J 2014 Electrochim Acta 149 144-51
[21] Nousheen I, Xianfeng W, Aijaz Ahmed B, Jianyong Y and Bin D 2016 J Colloid Interface Sci 476 87-93
[22] Xinhong Q, Wenji Z, Gaohong H, Tianfang T, Naixu D and Le W 2017 Chem Eng J 309 426-34.
[23] Tao W, Ying G, Bo Z, Shuhui Y, Hai-Peng Y, Daniel L, Xian-Zhu F, Rong S and Ching-Ping W 2015 J Power Sources 286 371-9
[24] Chi-Chang H, Kuo-Hsin C and Tung-Yu H 2008 J Electrochem Soc 155 F196-F200
[25] Yung-Tai W and Chi-Chang H 2004 J Electrochem Soc 151 A2060-A6