Preparation and Application of CQDs/Ni(OH)$_2$0.75H$_2$O as Electrodes in Supercapacitors

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Abstract. In this paper, a hydrothermal synthesis method for preparation Carbon Quantum Dots (CQDs)/Ni(OH)$_2$0.75H$_2$O composite electrode material, and loaded on Nickel Foam (NF) by rolling method. The crystal phase, structure, morphology and the reaction process were characterized by X-ray diffractometer (XRD) and scanning electron microscopy (SEM). The electrochemical properties of the composite were measured by cyclic voltammetry impedance spectroscopy and couple method charge-discharge techniques. The results showed that the composites material was evenly adhered to nickel foam. When the current density is 1 A g$^{-1}$, the specific capacity of CQDs / Ni (OH)$_2$0.75H$_2$O composite can reach 2115.4 Fg$^{-1}$, which is close to 5 times of Ni (OH)$_2$0.75 H$_2$O electrode material.

Keywords. Ni(OH)$_2$0.75H$_2$O. carbon quantum dots. hydrothermal synthesis method. supercapacitor.

1. Introduction

With the emergence of environmental pollution problems caused by the large-scale use of non-renewable energy, green and sustainable energy such as solar, wind and tidal energy are needed to replace non-renewable energy. However, these sustainable energy resources are unstable and have many uncontrollable risk factors, which are inconvenient in their practical applications. Therefore, it is required to develop various energy storage devices in order to collect the random fluctuations of renewable energy [1-3]. As an energy storage device, supercapacitor has become one of the hot research areas in energy field, because it combines the characteristics of large capacity, high power density, long-term recycling, short charging time, and so on [4-5].

There are two types of supercapacitors and one is double-layer capacitor, in which ions are adsorbed on the surface of the electrode material during charging and desorbed during discharging, which is a reversible process. And the working process of double-layer supercapacitor is a pure physical adsorption process, in which charge is stored and released continuously for the energy storage [6]. The other one is a pseudo-capacitor, in which the charge is transferred during the redox process and the chemical energy and electrical energy are converted to achieve energy storage. Pseudo-capacitors can store more energy under the same conditions [7-8]. Therefore, the selection of electrode materials in this experiment is based on pseudo-capacitor capacitor.

In practical applications, pseudo-capacitive electrode materials usually require at least the following conditions: multivalent, low cost and redox reactions taking place easily [9]. In the transition
metals, nickel not only accords with the above characteristics, but also has a higher theoretical capacitance and is environmentally friendly, too. Therefore, nickel is suitable as the electrode material of pseudo-capacitor [10].

Carbon quantum dots (CQDs) are zero-dimensional nano-materials with strong adsorption capacity, large surface area, many active sites and good crystallization behavior. Additionally, CQDs can promote transport of electrolyte ions and increase the rate of charge transport in the electrode materials, which have great development potential as supercapacitors [11-12].

In this work, CQDs/Ni(OH)$_2$0.75H$_2$O was prepared by the hydrothermal method and the conductivity property of Ni(OH)$_2$0.75H$_2$O was highly improved.

2. Experimental

2.1. Pretreatment of Electrodes
Nickel foam foils were cut into the size of (10 × 30) mm$^2$, then were ultrasonically cleaned in acetone for 15 min, then ultrasonically cleaned in 3 mol·L$^{-1}$HCl for 20 min, finally ultrasonically cleaned in ethanol and distilled water alternately for several times, and then put it into the vacuum drying oven for drying at 60 ℃.

2.2. Preparation of Electrode Materials
Ni(NO$_3$)$_2$·6H$_2$O (0.7270 g, 0.025 moL·L$^{-1}$), NH$_4$F(0.1480 g, 0.04 moL·L$^{-1}$), CH$_4$N$_2$O(0.6426 g, 0.107 moL·L$^{-1}$) and distilled water (90 mL) were added to a 250mL beaker. CQDs and 10 mL ethanol were added to 50 mL beaker and ultrasound was applied for 10 min to make CQDs completely soluble in ethanol. The above two solutions were mixed and stirred using a magnetic stirrer for 120 minutes, then the mixed solution was transferred to a high temperature reactor, which was further heated to 120 ℃ and sealed for 8 h. After filtration, the electrode materials were obtained and washed with distilled water, and the final products were transferred to a constant temperature drying chamber at 60 ℃ for 4 hours.

2.3. Structural Analysis of Electrode Materials
The morphology of the samples was characterized by a transmission electron microscope (TEM). The crystalline structure of the samples was characterized by X-ray diffraction (XRD).

2.4. Preparation of the Working Electrode
10 mg of the prepared electrode material and 80 mg of acetylene black were added into the mortar, which were grinded with 1 ~ 2 drops anhydrous ethanol until the mixture became dry, and anhydrous ethanol was added repeatedly. After grinding for 2 hours, 5% PTFE (the mass ratio of acetylene black: sample: PTFE is 8:1:1) was added to grind the whole mixture into a ball of viscous material, which was transferred to the glass plate and rolled. Then, some of the rolled samples were transferred to the nickel foam foil, which were further pressed with the tablet press machine to stick well on the surface of the nickel foam foil to form the working electrode. Finally, the working electrode was dried at 60℃ in the constant temperature oven for 2 hours before measuring its electrochemical properties.

2.5. Electrochemical Measurement
The electrochemical properties were measured by electrochemical workstation performing the following steps:
(1) Cyclic voltammetry: the voltage range was 0 ~ 0.6 V, and the scanning speed was 10 MV s$^{-1}$ ~ 50 MV s$^{-1}$ with 10mV as an interval
(2) Charge and discharge under constant current: and the current density was 1 a · g$^{-1}$ ~ 5 a · g$^{-1}$ with 1 A as an interval.
(3) AC impedance: the frequency range was 10-2 Hz ~ 105 Hz, and the amplitude was 5 mV.
3. Results and Discussion

3.1. Morphology and Structure Characterization

In order to further study the micro state of electrode materials, nickel hydroxide Ni(OH)$_2$·0.75H$_2$O, carbon quantum dots CQDS and composite CQDS / Ni(OH)$_2$·0.75H$_2$O were characterized by SEM. The SEM images of Ni(OH)$_2$·0.75H$_2$O and CQDS were shown in figure 1(a) and figure 1(b) respectively. It could be seen from the figures that Ni(OH)$_2$·0.75H$_2$O was a stacked lamellar structure and CQDS was a spherical structure. Figure 1(c) show the SEM of CQDS / Ni(OH)$_2$·0.75H$_2$O composite. It could be seen from the figure that Ni(OH)$_2$·0.75H$_2$O was dispersed and attached to the surface of CQDS, which could increase the surface area of the composite and improve its chemical properties.

![Figure 1](image_url)

Figure 1. SEM images of Ni(OH)$_2$·0.75H$_2$O, CQDS and CQDS / Ni(OH)$_2$·0.75H$_2$O.

In order to further analyze the final form of the experimental products, the products doped by carbon quantum dots were characterized by XRD and compared with the samples without doping.

Firstly, the characterization of the hydrothermal experimental products of nickel was obtained and analyzed. As a result, it was found that the diffraction peak of the product was basically consistent with the JCPDS no.38-0715 card, so the main component of the product was Ni(OH)$_2$·0.75H$_2$O.

Then, by comparing the XRD characterization of CQDS / Ni(OH)$_2$·0.75H$_2$O with Ni(OH)$_2$·0.75H$_2$O, it was also found that the diffraction peak of the product doped by carbon quantum dots existed a weaker diffraction peak near 27 degrees, which was not found for the undoped product. Since the characteristic diffraction peak of carbon quantum dots is 27.5 degrees [13], it could be identified that this peak was the diffraction peak of carbon quantum dots. However, the diffraction peak intensity was
weak, which may be because the diffraction peak intensity after doping was small. Therefore, when measuring the diffraction peak, the diffraction peak of carbon quantum dots could not be clearly shown on figure 2 due to the high intensity of $\text{Ni(OH)}_{2.75\text{H}_2\text{O}}$ diffraction peak.

![Figure 2. X-ray diffraction (XRD) of CQDs/ Ni(OH)$_{2.75\text{H}_2\text{O}}$ and Ni(OH)$_2$0.75H$_2$O.](attachment:figure2.png)

3.2. Electrochemical Measurement

3.2.1. Cyclic Voltammetry. Since the pseudo-capacitor stores energy by redox reaction, two obvious peaks could be observed from the cyclic voltammetry curves of the two substances prepared in the experiment, and the left peak was the reduction peak while the right peak was the oxidation peak. The corresponding electrochemical reaction equation was [14]:

$$\text{Ni(OH)}_2 + \text{OH}^- \rightleftharpoons \text{NiOOH} + \text{H}_2\text{O} + e^- \quad (1)$$

As shown in figure 3, it could be observed that the closed area of each curve gradually increased when the scanning rate of Ni(OH)$_{2.75\text{H}_2\text{O}}$ increased from 10mV · s$^{-1}$ to 50mV · s$^{-1}$, but the oxidation peak potential gradually shifted to the right and the reduction peak potential gradually shifted to the left, due to the electrode impedance. However, the oxidation-reduction peak of CQDs/ Ni(OH)$_{2.75\text{H}_2\text{O}}$ composite electrode as shown in figure 4 changed little due to the chemical interaction between oxygen-containing functional groups in carbon quantum dots and nickel hydroxide or the van der Waals force between carbon quantum dots and nickel hydroxide. As shown in figure 5. It could be concluded that CQDs/ Ni(OH)$_{2.75\text{H}_2\text{O}}$ composite electrode shew the characteristics of low electrode impedance, fast and stable electron and ion transport rate [15].
Figure 3. CV curves of Ni(OH)$_2$·0.75 H$_2$O with scanning rate of 10 ~ 50 mV·s$^{-1}$.

Figure 4. CV curves of CQDs/Ni(OH)$_2$·0.75H$_2$O with scanning rate of 10 ~ 50 mV·s$^{-1}$. 
Figure 5. CV curves of CQDs/Ni(OH)$_2$0.75H$_2$O and Ni(OH)$_2$0.75H$_2$O with scanning rate of 50 mV·s$^{-1}$.

3.2.2. Charge and Discharge under Constant Current. As shown in figure 6 and figure 7, the voltage of the two electrode materials gradually rose to 0.52 V during charging under the conditions of voltage range of 0 ~ 0.52 V and current density of 1 ~ 5 a·g$^{-1}$, and there were obvious flat periods in the charging curves. In the discharge process, the potential gradually decreased to 0 V with time, and the plateau period was obvious, which indicated that the material was a pseudo-capacitor.

According to the specific capacitance equation:

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

Where, $C_s$ (F·g$^{-1}$) is the specific capacitance; $I$ (A) is the charge discharge current; $\Delta t$ (s) is the discharge time; $m$ (g) is the mass of the active substance involved in charge and discharge in the working electrode; $\Delta V$ (V) is the total voltage drop.

For instance, the specific capacitance of Ni (OH)$_2$0.75 H$_2$O could be calculated as 492.3 F·g$^{-1}$ according to equation (2) under the current density of 1 a·g$^{-1}$, as shown in figure 6. The proton transfer rate could accelerate as the increasing of the current density, so the protons could be transferred before involving in the reaction. Therefore, the specific capacitance would decrease with the increase of current density [16].

In the same way, the specific capacity of CQDs/Ni(OH)$_2$0.75H$_2$O in figure 7 was calculated to be 2115.4 F·g$^{-1}$ at 1 a·g$^{-1}$. With the increase of current density, the specific capacitance would also decrease.
Figure 6. Charge and discharge curves of Ni (OH)$_2$0.75 H$_2$O under the current density of 1 ~ 5 A·g$^{-1}$.

Figure 7. Charge and discharge curves of CQDs/Ni(OH)$_2$0.75H$_2$O under the current density of 1 ~ 5 A·g$^{-1}$.

The comparison of the discharge curves at 1 A·g$^{-1}$ and 0.52 V of CQDs/Ni(OH)$_2$0.75H$_2$O and Ni(OH)$_2$0.75 H$_2$O were shown in figure 8. Consequently, the conductivity of the composite was increased by the doping of CQDS, and the specific surface area of CQDs/Ni(OH)$_2$0.75H$_2$O and the number of active sites were also increased, which would make the redox reaction could take place more completely, which was reflected in the increase of specific capacitance in the data. According to the comparison of the figure, the specific capacitance ratio of CQDs/Ni(OH)$_2$0.75H$_2$O and Ni(OH)$_2$0.75 H$_2$O was close to 5:1, which indicated that the electrochemical performance of CQDs/Ni(OH)$_2$0.75H$_2$O was significantly improved.
Figure 8. Charge and discharge curves of CQDs/Ni(OH)$_2$0.75H$_2$O and Ni (OH)$_2$0.75 H$_2$O under the current density of 1A· g$^{-1}$.

The AC impedance curves included two parts of high-frequency region and low-frequency region, which represented load transfer process control and diffusion control respectively. The resistance of charge transfer inside the electrode was shown in the high frequency region, while the rate of ion diffusion in the solution was indicated in the low frequency region. The high frequency region was represented by the semicircle radius in the AC impedance curve, and the low frequency region was represented by the linear slope in the AC impedance curve [17]. As shown in figure 9, the radius of CQDs/Ni(OH)$_2$0.75H$_2$O in the high frequency region was small and its slope in the low frequency region was high, which indicated that the internal charge transfer resistance of CQDs/Ni(OH)$_2$0.75H$_2$O composite was small and the ion diffusion rate of electrolyte was better.

Figure 9. AC impedance curves of CQDs/Ni(OH)$_2$0.75H$_2$O and Ni(OH)$_2$0.75 H$_2$O.
4. Conclusions

(1) Carbon quantum dots / nickel hydroxide composite electrode materials were prepared by hydrothermal method. Characterizations of XRD and SEM identified that the final product was CQDs/Ni(OH)$_2$.0.75H$_2$O, which was attached to the CQDS ball in a lamellar structure.

(2) The analysis of cyclic voltammetry (CV), AC impedance (EIS) and constant current charge and discharge (CCD) of the samples indicated that CQDs/Ni(OH)$_2$.0.75H$_2$O composite electrode material owned the characteristics of lower impedance, better ion diffusivity, fast and stable electron and ion transport rate. And the specific capacity could reach 2115.4 f · g$^{-1}$ when the current density was 1 a · g$^{-1}$.

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