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Hydrothermal One-Step Synthesis of Layered Nickel/Cobalt Double Hydroxide Using Shape-Directing Agent and Homogeneous Precipitating Agent

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Abstract: Nickel/cobalt double hydroxide (Ni/Co-DH) has been prepared by facile hydrothermal one-step synthesis method using hexamethylene tetramine (HMT) as a homogeneous precipitating agent and cetyltrimethylammonium bromide (CTAB) as a shape-directing agent. With the hydrolysis of HMT and the use of CTAB, the Ni/Co-DH could be synthesized without additional alkali source, and in the meantime, the Ni/Co-DH exhibited a controlled mesopore size of 13.4 nm and a large BET surface area of 93.6 m²·g⁻¹. The X-ray diffraction (XRD) pattern displays that the Ni/Co-DH existed as a mixture of α -Ni(OH)₂- β -Co(OH)₂. The scanning electron microscope (SEM) image shows that the as-prepared Ni/Co-DH took on a layered structure, which leads to a maximum specific capacitance of 1902 F·g⁻¹ at a current density of 1 A·g⁻¹. The specific capacitance remained 1250 F·g⁻¹ when the current density increased to 8 A·g⁻¹.

Key words: layered material; cetyltrimethylammonium bromide; nickel/cobalt double hydroxide; electrochemical performance

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Metallic hydroxides as typical pseudocapacitive active species have attracted increasing attention because of their low cost, high redox activity, and environmentally friendly nature^[1-4]. However, they suffer from low electron conductivity and ion conductivity, which restricts their practical applications in high-performance supercapacitors.

To address the above issue, the parameters including specific surface area, morphology, pore size and pore size distribution (PSD) have to be concerned. Metallic hydroxides with porous morphology can have large specific surface area and excellent PSD. Recently, SiO₂, polystyrene, Ni foam are often used as sacrificed materials for fabricating porous metallic hydroxides^[5-9]. Porous morphology like layered structure can provide large interlayer spacing, which allows for fast intercalation/de-intercalation, and guarantees a high electrochemical activity and specific capacitance^[10]. However, the sacrificed materials method for preparing layered metallic hydroxides is complex

and time-consuming. Therefore, a new method for synthesizing layered metallic hydroxides is necessary.

Micelles, dynamic aggregates can alter morphology to different extents depending up on their nature of head group and type of counter-ions^[11]. Surfactant like cetyltrimethylammonium bromide (CTAB) is the amphiphilic molecule, which creates highly anisotropic interfacial regions lining the boundary formed by the highly polar aqueous and nonpolar hydrocarbon regions. By incorporating the substrate into the micellar aggregate, CTAB can affect the morphology of a sample^[12].

Hydrothermal method can conveniently control the morphology and size of materials^[13-15]. It is widely adopted to prepare electrode materials with desirable properties. Hexamethylene tetramine (HMT) can be hydrolyzed to ammonia and formaldehyde during the hydrothermal process. Thus, HMT can play the role of homogeneous precipitation agent and additional alkali source can be avoided. Hence, if hydrothermal

method is adopted and in the meantime both homogeneous precipitation agent and shape-directing agent are used, Ni/Co-DH with special structure can be one-step obtained in a very simple way. Not only the process for preparing suitable sacrificed materials and additional alkali source can be avoided in the synthesizing process of metallic hydroxide, but also Ni/Co-DH with special morphology can be obtained.

Therefore, we have tried to prepare Ni/Co-DH by hydrothermal one-step process accompanied with using both CTAB as a shape-directing agent and HMT as a homogeneous precipitation agent. The as-prepared Ni/Co-DH exhibited a layered structure and excellent electrochemical performance for supercapacitors with high specific capacitance.

1 Experimental

1.1 Synthesis of the Composite

All reagents were AR grade. Firstly, the mixture consisting of 1 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 50 mL of deionized water with 10 mL of glycol, followed by the addition of 0.02 g of CTAB and 0.8 g of HMT. After being sonicating for 1 h, the homogeneous solution was transferred into a 100-mL autoclave and kept at 115 °C for 4 h. After being naturally cooled down to room temperature, the Ni/Co-DH was collected, and washed with deionized water and alcohol for several times, and finally dried at 60 °C in a vacuum oven for 8 h.

1.2 Structure Characterization and Electrochemical Evaluation

The scanning electron microscope (SEM) image was obtained using a Hitachi S4800 SEM (Hitachi, Japan). The X-ray diffraction (XRD) pattern was measured on a X-ray D/max-2200 vpc instrument operated at 40 kV and 20 mA using $\text{Cu } K_\alpha$ radiation source with $\lambda = 0.15406$ nm. The specific surface area was determined by 3H-2000PM2 volumetric adsorption analyzer (Beijing) using nitrogen as adsorption-desorption gas at 77.3 K on the basis of the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was calculated using the Barrett-Jouner-Halenda (BJH) method. Cyclic voltammetry (CV) and galvanostatic charge/discharge tests were

performed on a CHI660E electrochemical workstation (Huakeputian Beijing, China) by employing a three-electrode system, where Pt electrode and Hg/HgO electrode were served as the counter electrode and reference electrode, respectively, and Ni/Co-DH coated glassy carbon (geometric surface area of 0.07 cm^2) was used as the working electrode.

1.3 Fabrication of Working Electrode

The working electrode was prepared by a following procedure: 9.0 mg Ni/Co-DH and 1.0 mg conductive carbon were dispersed in 5 mL isopropanol by sonicating for 30 min to form an ink, and then 5.0 μL of this dispersion ink was pipetted gradually onto a prepolished glassy carbon electrode with a microsyringe. After drying, 5 mL of the diluted Nafion® solution (0.1%, by mass, Aldrich) was used to cover this coated glass carbon electrode to form a uniform electrode layer for electrochemical measurements.

2 Results and discussion

Fig. 1 shows the SEM image of Ni/Co-DH. In Fig. 1, the as-prepared Ni/Co-DH took on a layered structure. During the hydrothermal process, the Ni-Co precursor could be adsorbed and/or bound with the CTAB due to the electrostatic and van der Waals forces. The anisotropic growth enabled the Ni-Co precursor nanosheets to be well interconnected with each other, forming uniform arrays, which in turn, altered the morphology drastically. Such hierarchical architecture is expected to remarkably enhance the electrochemical activity of the Ni/Co-DH by shortening the diffusion and migration paths of electrolyte ions in the charging/discharging process.

The XRD pattern of the as-prepared Ni/Co-DH can be found in Fig. 2. Three intense diffractions appeared at the 2θ values of 11.6° , 33.5° and 59.9° are typical for the rhombo-hedral phase of $\text{Ni}(\text{OH})_2$ (JCPDS:38-0715) and are indexed to the (003), (100) and (110) planes, respectively, which is in accordance with the reported value of $\alpha\text{-Ni}(\text{OH})_2$. The diffractions peaks seen at 33.5° , 37.8° , 59.9° and 71° are typical for the hexagonal phase of $\text{Co}(\text{OH})_2$ (JCPDS:30-0443) and are indexed to the (100), (101), (110) and (112) planes, respectively, which is in accordance with the

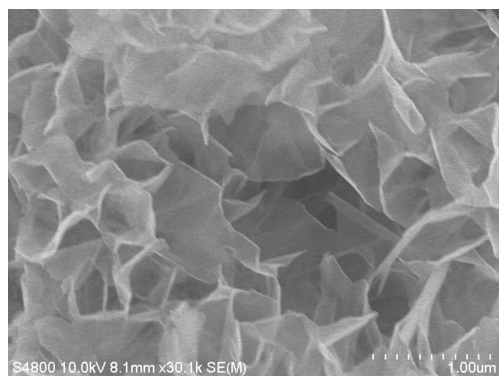


Fig. 1 SEM image of the as-prepared Ni/Co-DH

reported value of β -Co(OH)₂ [16]. Therefore, the Ni/Co-DH sample could be identified as a mixed phase of α -Ni(OH)₂- β -Co(OH)₂.

Nitrogen adsorption-desorption isotherm and BJH pore size distribution plot of Ni/Co-DH sample are shown in Fig. 3. From the examinations of nitrogen adsorption-desorption isotherm (A) and BJH pore size distribution plot (B), three features are worthy being mentioned. First, with the increase of partial pressure, the Ni/Co-DH exhibited a typical H₃-type hysteresis loop, which is the most common for layered particles with slit-shaped pores. And this observation was well-corroborated with the layered morphology of Ni/Co-DH. Second, according to BET plot of nitrogen-adsorption isotherm (A), the specific surface area of Ni/Co-DH was found to be 93.6 m²·g⁻¹, indicating that the as-prepared Ni/Co-DH has a large BET surface area. Third, from the analysis of BJH pore size distribution plot (B), the Ni/Co-DH had a mesopore size of 13.4 nm. Therefore, such a layered

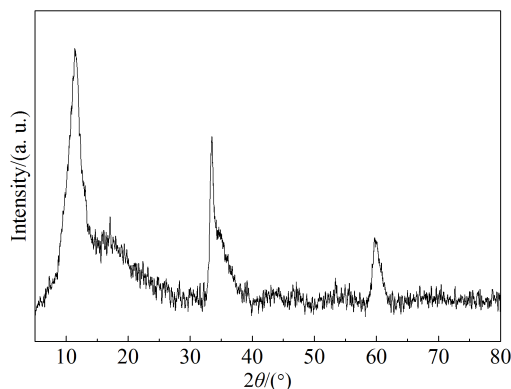


Fig. 2 XRD pattern of the as-prepared Ni/Co-DH

mesopore Ni/Co-DH was supposed to facilitate better transportation of electrolyte through their nanochannels for efficient redox reactions during the charge storage process.

Fig. 4 shows the CV curves of the Ni/Co-DH electrode in 6 mol·L⁻¹ KOH electrolyte with different sweep rates ranging from 1 to 10 mV·s⁻¹ between 0 and 0.6 V (vs. Hg/HgO). The Ni/Co-DH electrode displayed a strong complementary redox peak. Although the widths of both anodic and cathodic peaks broadened with increasing potential scan rate, the potential difference between the anodic and cathodic peaks was small whether at the potential scan rate of 1 or 10 mV·s⁻¹. Therefore, it can be considered as a theoretically reversible process. The as-prepared sample can remain a good electrochemical performance despite increasing scan rate.

According to the CV data, the specific capacitance of the Ni/Co-DH electrode can be calculated using Eq. $C = Q_{V_1 \leftrightarrow V_2} / (w|V_2 - V_1|)$, where V_1 and V_2 are the low and high end potentials in the CV curve, $|V_1 - V_2|$ is the potential window, $Q_{V_1 \leftrightarrow V_2}$ is half of total charge quantity within the CV curve, and w is the total weight of Ni/Co-DH and conductive carbon. Two components contribute to C : Ni/Co-DH through the electrochemical reaction, followed by the conductive carbon inside the electrode layer. Normally, compared to the Ni/Co-DH, the contribution of conductive carbon is negligible. Therefore, in the potential window of 0 ~ 0.6 V (Fig. 4), the calculated specific capacitance based on the weight of Ni/Co-DH is 1905 F·g⁻¹ at 1 mV·s⁻¹.

The first discharge performance of Ni/Co-DH electrode was estimated by galvanostatic charge/discharge measurements in 6 mol·L⁻¹ KOH aqueous solutions at the various current densities of 1 ~ 8 A·g⁻¹ as shown in Fig. 5. Each discharge curve includes two clear voltage steps: a fast potential drop from 0.45 V to 0.35 V and a slow potential decay from 0.35 V to 0.25 V. For the former step which is close to an ideal straight line shape, it corresponds to internal resistance. And the latter represents pseudocapacitive feature arising from redox process of the elec

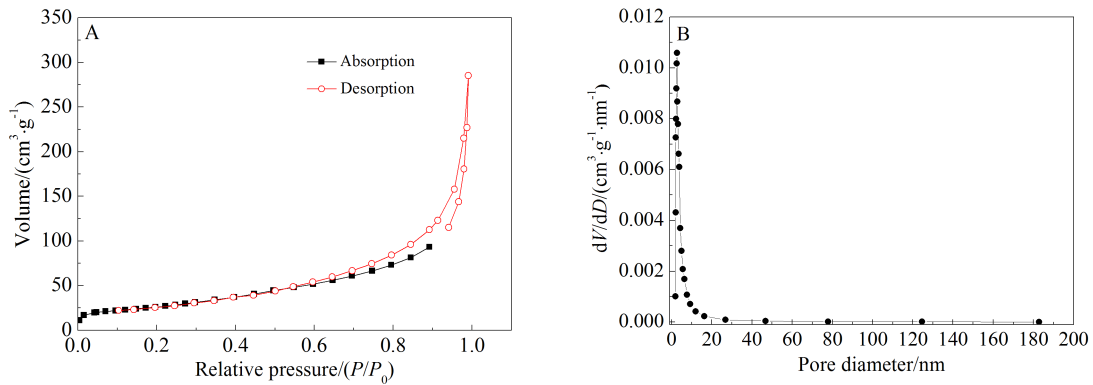


Fig. 3 BET isotherm (A) and BJH pore size distribution profile (B) of the as-prepared Ni/Co-DH

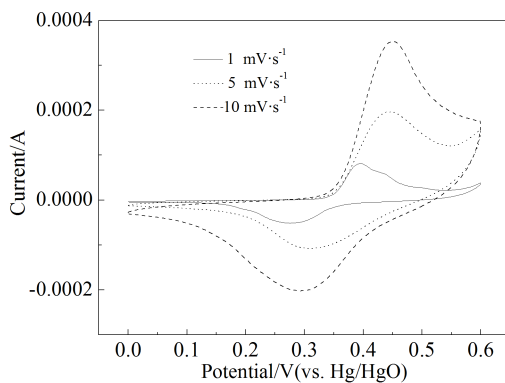


Fig. 4 Cyclic voltammograms of the Ni/Co-DH electrode at different potential scan rates

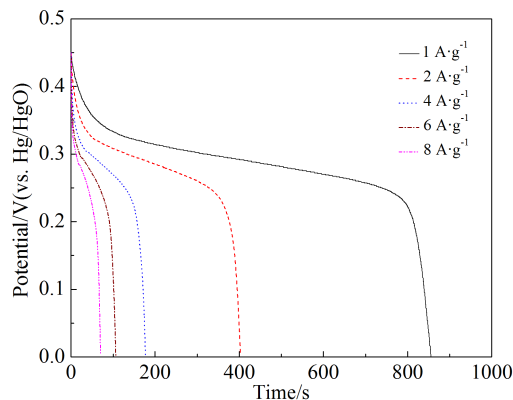


Fig. 5 Discharge curves of the Ni/Co-DH electrode at various current densities

trode. There is obvious deviation of the discharge curve from a straight line, indicating that the capacitance mostly comes from the Faradic redox reaction of Ni and Co electroactive species in the Ni/Co-DH. The specific capacitance values of the Ni/Co-DH were 1902, 1791, 1571, 1415, 1250 $F \cdot g^{-1}$ at 1, 2, 4, 6,

8 $A \cdot g^{-1}$, respectively. This demonstrates that the hydrothermal one-step synthesis method in this work may be an efficient way to prepare Ni/Co-DH hybrid material with excellent electrochemical performance.

3 Conclusions

In this work, the Ni/Co-DH with a layered structure has been synthesized by the hydrothermal one-step synthesis method using hexamethylene tetramine (HMT) as a shape-directing agent and cetyltrimethylammonium bromide (CTAB) as a homogeneous precipitating agent. The unique architecture obtained greatly improved the Faradaic redox reaction and mass transfer process. The Ni/Co-DH based electrode could have a specific capacitance of 1902 $F \cdot g^{-1}$ at the discharge current density of 1 $A \cdot g^{-1}$. Combining shape-directing agent and homogeneous precipitating agent method may be an efficient way to prepare layered Ni/Co-DH materials with excellent electrochemical performance.

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利用均相沉淀剂和形貌导向剂水热一步合成 层状镍钴氢氧化物

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摘要: 本文利用在反应过程中同时添加均相沉淀剂六次甲基四胺和形貌导向剂十六烷基三甲基溴化铵, 结合水热反应的方法一步合成了镍钴氢氧化物. 随着六次甲基四胺的水解, 层状镍钴氢氧化物可以被合成而且避免了额外碱源的使用. 同时, 由于反应过程中十六烷基三甲基溴化铵参与的孔径调节, 合成出来的镍钴氢氧化物具有可控的介孔尺寸 13.4 nm 以及较大的比表面积 $93.6 \text{ m}^2 \cdot \text{g}^{-1}$. X 射线衍射图谱表明合成出来的镍钴氢氧化物构型是 $\alpha\text{-Ni(OH)}_2\text{-}\beta\text{-Co(OH)}_2$. 扫描电镜表明合成出来的镍钴氢氧化物具有层状的结构. 正是因为层状介孔结构的存在, 合成出来的镍钴氢氧化物在 $1 \text{ A} \cdot \text{g}^{-1}$ 电流密度下, 比电容可以高达 $1902 \text{ F} \cdot \text{g}^{-1}$. 即使电流密度提高到 $8 \text{ A} \cdot \text{g}^{-1}$, 镍钴氢氧化物的比电容仍然可以保持在 $1250 \text{ F} \cdot \text{g}^{-1}$.

关键词: 层状材料; 十六烷基三甲基溴化铵; 镍钴氢氧化物; 电化学性能