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Ultrahigh energy density and stable supercapacitor with 2D NiCoAl Layered double hydroxide

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ABSTRACT

NiCoAl layered double hydroxides (NiCoAl-LDHs) with different morphology, structure, size and pseudocapacior properties have been prepared by tuning the ratio of metallic elements via a hydrothermal method. The optimized element proportion of 2D $NiCo_2Al$-LDH consisting of hexagonal nanosheets delivers a significantly enhanced specific capacitance 2369.4 F g^{-1} at a current density of 1 A g^{-1}. A circle-like growth mechanism is proposed to explain the formation of the 2D $NiCo_2Al$-LDH structures. Its 2D structure and the synergistic effect of three metallic elements assure its high electrochemical performance. An asymmetric supercapacitor (ASC) based on $NiCo_2Al$-LDH exhibits an ultra-high energy density of 91.0 Wh kg^{-1} at a power density of 758.2 W kg^{-1} as well as long-term stability (92% of its initial capacitance retention at 8 A g^{-1} over 5000 cycles), outperforming most of LDH and metal oxides ASCs.

1. Introduction

Owing to the controversy between low power density of secondary battery and the ever-growing demand for electrochemical energy storage, it is vital to find a new alternative energy storage device [1,2]. Electrochemical capacitor, also referred to as a supercapacitor, is one of the kinds of electrochemical energy storage devices which have widely been considered as a potential substitute for secondary battery at high power applications. This is specifically due to its apparent benefits including fast charge/discharge rates, long life as well as high power density [3]. Presently, the biggest challenge in promoting the supercapacitor application is its lower energy density [4]. One of the most effectual methods of improving the energy density of supercapacitor is to enhance the specific capacitance through the use of pseudocapacitive materials or by increasing the operating voltage through constructing of an asymmetric supercapacitor (ASC) which is capable of combining the potential windows of two electrodes coated with different active materials [5,6]. The intrinsic specific capacitance for conventional cost effective pseudocapacitive materials, including MnO_2, NiO, $Ni(OH)_2$, Co_3O_4, $Co(OH)_2$, Fe_3O_4, and their binary systems are obtained in laboratory and generally have less than 1000 F g^{-1} [7,8]. Of late, metallic layered double hydroxides (LDHs) with a class of hydrotalcite-like structure anionic clays such as CoAl-LDH [9], NiAl-LDH [10], NiMn-LDH [11], and CoNi-LDH [12,13] have emerged as the new electrode materials. They are capable of easily attaining higher capacitance of than 1000 F g^{-1} or even up to 2000 F g^{-1}. In addition, these types of materials that contain water in the host structures exhibit good conductivity as well as high proton mobility [14]. More recently, other LDH materials have identified, including tris metallic elements of Ni, Co and Al and which can also be defined as layered double hydroxides (NiCoAl-LDHs) or layered triple hydroxides (NiCoAl-LTHs) [15]. Nonetheless, the NiCoAl-LDHs with more metallic elements did not display a higher specific capacitance. For instance, Gupta et al. fabricated new NiCoAl-LDHs by potentiostatic deposition method in which its maximum specific capacitance obtained at 1 A g^{-1} was 1263 F g^{-1} [15]. Further, Qiu et al. also constructed NiCoAl-LDH@CNT (carbon nanotube) and NiCoAl-LDH@CNT/RGO (reduced graphene oxide) materials by a simple urea precipitation method. From this, they obtained the highest specific capacitance to be 1035 and 1188 F g^{-1}

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at 1 A g^{-1}, respectively [16,17]. These previous findings can be attributed to the structure, elementary composition and proportion of NiCoAl-LDHs.

In the present study, we prepare 2D $NiCo_2Al$-LDH with nanosheets by using the hydrothermal method. As-prepared 2D $NiCo_2Al$-LDH presents a significantly enhanced specific capacitance of 2369.4 F g^{-1} at 1 A g^{-1}. This is considerably a higher value as compared with the findings of the previous reports on ternary-component layered double hydroxides (as shown in Table S1). Even though the existence of Al^{3+} in the LDH could slightly bring down or approach its specific capacitance relative to the NiCo-LDH (2682, 2360 and 2614 F g^{-1}) [12,13,18] and NiMn-LDH (2960 F g^{-1}) [11], the addition of typically trivalent Al^{3+} can help in stabilizing the α-nickel hydroxides and facilitating the reaction between α- and γ-nickel hydroxides. This helps to improve the cycling stability of the $NiCo_2Al$-LDH structure [14]. Additionally, an ASC based on 2D $NiCo_2Al$-LDH is considered as a positive electrode, while the active carbon (AC) as a negative electrode. This demonstrated an ultrahigh energy density of 91.0 Wh kg^{-1} at a power density of 758.2 W kg^{-1} as well as a high power density of 22.7 kW kg^{-1} at 50.5 Wh kg^{-1}, in addition to long-term stability. Thus, the 2D $NiCo_2Al$-LDH nanosheets will be the most promising materials for high performance supercapacitors.

2. Experimental section

2.1. Synthesis of $NiCo_2Al$-DHs

NiCoAl-LDHs were first prepared as follows: The molar ratios of the $Ni(NO_3)_2{\cdot}6H_2O$: $Co(NO_3)_2{\cdot}6H_2O$: $AlCl_3{\cdot}6H_2O$ were fixed at 0:2:1, 0.4:2:1, 1:2:1, 2:2:1, 4:2:1 and 6:2:1. The proportion of Co $(NO_3)_2{\cdot}6H_2O$ together with $AlCl_3{\cdot}6H_2O$ were also fixed at 2.0 and 1.0 mmol. The above mixtures were then dissolved in deionized water to give rise to solutions (40 mL). After that, 4 mmol of urea was added to the solution under vigorous stirring for about 1 hour. Lastly, the above solution was transferred to a Teflon-lined autoclave (50 mL), then, heated to 140 °C. It was then kept for 14 hours. After the reaction, the autoclave was allowed to cool to room temperature. The precipitates were afterwards collected by centrifuge, then they were washed thrice using water as well as ethanol, respectively. Ultimately, they were dried at 60 °C for a period of about 24 hours in order to get the final products.

2.2. Characterization

The structures of as-prepared samples were characterized by the X-ray Diffraction (XRD) analysis using the Bruker AXS D8 Advance diffractometer and with Cu Kα radiation. The morphologies, structures and sizes of the as-prepared samples were observed using the field emission scanning electron microscopy (FESEM, JEOL, JSM-7001F, 10 kV) and then with a transmission electron microscopy (TEM, JEOL, JEM-2100, 200 kV). Afterward, selective area electron diffraction pattern (SAED) was characterized by use of the JEM-2100 microscope. Energy dispersive X-ray spectrometer (EDX, Oxford Instruments Isis300) equipped in the JEM 6490 scanning electron microscope (SEM) together with a Perkin-Elmer ICP-MS SCIEX Elan 900 were also used in analyzing the chemical compositions of Ni, Co and Al of the as-prepared samples. The X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB 250 Xi XPS instrument) and the Fourier transform infrared spectroscopy (FT-IR, Nicolet 380) were then employed in investigating the surface samples' properties and structures. The BET surfaces of the materials were calculated by use of a Belsorp-Mini adsorption apparatus (Bel Japan Inc).

2.3. Electrochemical measurements

The electrochemical examinations of the individual electrodes were performed in a three-electrode system, while the asymmetrical supercapacitors were studied in a two-electrode system. All of the electrochemical tests were carried out in KOH (2 mol L^{-1}) electrolytes. In a three-electrode system, the active materials on nickel meshes, a platinum foil, and a Ag/AgCl electrode were used as working, counter and reference electrodes, respectively. The working electrodes were made of active materials (80 wt%), conductive materials (acetylene black, ATB, 10 wt%) as well as binder (polytetrafluoroethylene, PTFE, 10 wt%). These were all mixed and coated onto the surface of a piece of nickel foam sheet ($1 \times 1\ cm^2$) then dried at 80 °C for about 12 hours. The sheets with active materials were finally pressed under 15 Mpa to get the working electrode. Electrochemical measurements of the asymmetrical supercapacitors composed of NiCoAl-LDHs (~1.4 mg) as the positive electrode and activated carbon, and AC (~6 mg) as the negative electrode, were outperformed in two electrodes. The balance of the charges were positive electrodes and negative electrodes (see our previous report for details) [19,20], whereas the final optimal mass ratio between the electrodes was m(NiCoAl-LDHs): m(AC) ≈ 1:5. The cyclic voltammogram (CV) was measured using a CHI 660E electrochemical workstation. Galvanostatic charge-discharge cycle tests were then carried out on a CT2001A LAND cell test system. The specific capacitance, energy density, and power density of the supercapacitors can be investigated from the charge/discharge test as well as in the following equation (*Eq*) [21].

$$C_m = \frac{2 \times i_m \int Udt}{U^2|_{U_i}^{U_f}} \tag{1}$$

$$E = \frac{i_m \int Udt}{3.6} \tag{2}$$

$$P = \frac{3600 \times E}{t} \tag{3}$$

where C_m is the specific capacitance of the capacitor (F g^{-1}), I_m is the current of the charge-discharge, $\int Udt$ is the integral current area; U is the potential (V) with initial and final values of U_i and U_f, respectively; E is the energy density (Wh kg^{-1}); P is the power density (W kg^{-1}); and t is the discharge time (s).

Table 1
EDX analysis of Ni, Co and Al in NiCoAl-LDHs.

Sample NiCoAl-LDHs	Elemental composition NiCoAl-LDHs (Atomic %) and the approximation ratios (Ni: Co: Al)
Co_2Al-LDH	0: 15.48: 7.64 ≈ 0: 2: 1
$Ni_{0.4}Co_2Al$-LDH	1.58: 7.69: 4.11 ≈ 0.4: 2: 1
$NiCo_2Al$-LDH	1.12: 1.98: 1.05 ≈ 1: 2: 1
Ni_2Co_2Al-LDH	4.99: 5.85: 2.64 ≈ 2: 2: 1
Ni_4Co_2Al-LDH	3.18: 1.55: 0.88 ≈ 4: 2: 1
Ni_6Co_2Al-LDH	5.60: 2.31: 0.93 ≈ 6: 2: 1