



In situ fabrication of nickel aluminum-layered double hydroxide nanosheets/hollow carbon nanofibers composite as a novel electrode material for supercapacitors



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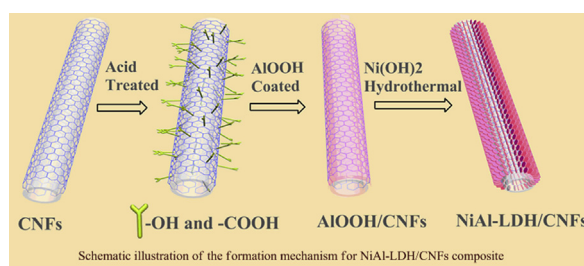
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HIGHLIGHTS

- Nickel aluminum-LDH grown on hollow carbon nanofibers by an in situ growth method.
- NiAl-LDH/CNFs composite presents as three-dimensional network structure.
- The composite exhibited a high specific capacitance of 1613 F g⁻¹ at 1 A g⁻¹.
- Remarkable cycle performance at a current density of 2 A g⁻¹.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper introduces a new design route to fabricate nickel aluminum-layered double hydroxide (NiAl-LDH) nanosheets/hollow carbon nanofibers (CNFs) composite through an in situ growth method. The NiAl-LDH thin layers which grow on hollow carbon nanofibers have an average thickness of 13.6 nm. The galvanostatic charge–discharge test of the NiAl-LDH/CNFs composite yields an impressive specific capacitance of 1613 F g⁻¹ at 1 A g⁻¹ in 6 M KOH solution, the composite shows a remarkable specific capacitance of 1110 F g⁻¹ even at a high current density of 10 A g⁻¹. Furthermore, the composite remains a specific capacitance of 1406 F g⁻¹ after 1000 cycles at 2 A g⁻¹, indicating the composite has excellent high-current capacitive behavior and good cycle stability in compared to pristine NiAl-LDH.

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1. Introduction

The crisis of fossil fuels and deterioration of environment push our society to move towards sustainable and green energy. Supercapacitors (SCs), also known as electrochemical supercapacitors (ESCs) or ultracapacitors, have been attracting intensive attention for their high power density, environment non-toxicity, short

charge–discharge time, and long cycle life [1–3]. In general, SCs are divided into two types according to their energy storage mechanism: electrochemical double layer capacitors (EDLCs) and pseudocapacitors (PCs), which mainly arise from ions stored in the electrode/electrolyte interface and fast surface redox reactions, respectively. To fulfill the higher requirement of future systems, for example, to accomplish the task of high energy output for electric vehicle (EV) and hybrid electric vehicle (HEV), SCs can provide enough energy in a short time, this advantage makes SCs became one of the most promising systems for the next generation high-energy storage systems [4–6]. It is well known that carbon

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materials (carbon nanotubes, graphene and activated carbon, etc.) are typical electrode materials for the EDLCs [7–9]. However, carbon materials have a small specific capacitance in spite of the better rate capability and long cycle life [10]. On the other hand, electrode materials with pseudo-capacitive properties have been intensively studied because of their large specific capacitance and fast redox kinetics, such as metal oxides (RuO_2 , Co_3O_4 , NiO , MnO_2 , etc.), conductive polymers (polyaniline, polypyrrole, polythiophene, etc.), and hydroxides ($\text{Ni}(\text{OH})_2$, $\text{Co}(\text{OH})_2$, etc.) [11–19]. However, PCs have a low conductivity and poor cycle life due to the limited velocity of ion diffusion and electron transfer compared with EDLCs [20,21]. One effective approach to solve these problems is to combine PCs active materials with carbon materials to take full use of the advantages of pseudo-capacitance and double layer capacitance [2,22–25].

Materials with large surface area and highly ordered dimension are expected to exhibit superior performance potential in SCs [4,26,27]. Hollow carbon nanofibers (CNFs), which are relatively inexpensive compared with CNTs, with well arrangement of sp^2 carbon layers, as its excellent electronic, thermal properties, and high electrical conductivity, are regarded as a promising electrode material for SCs [28–31]. Layered double hydroxides (LDH) have exhibited unique electrochemical properties when it used as PCs electrode materials [2,32]. They are usually present in a general formula of $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2][(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}]$, where M^{2+} and M^{3+} are divalent and trivalent metal ions, x is defined as the molar ratio of $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$ and generally has a value ranging from 0.2 to 0.33, A^{n-} are the interlayer anions [33–35]. LDH also have potential application in catalysts [36], precursors [37], environmental protection [38], and drug delivery [39], etc.

Recently, LDH and carbon materials composites have been investigated intensively as promising capacitive materials due to high redox activity, enhanced electrochemical performances, environmentally friendliness, and low cost [10,40,41], such as NiAl-LDH/GNS [42], CoAl-LDH/MWCNT [43], CoAl-LDH/GO [46]. For instance, Gao et al. prepared graphene nanosheet/NiAl-LDH composite through a hydrothermal process and the products provide a maximum specific capacitance of 781.5 F g^{-1} at 10 mA cm^{-2} in 6 M KOH solution [2]. Yang et al. reported MWCNT-doped NiCoAl-LDH nanohybrid by a simple urea precipitation method, the specific capacitance of the nanohybrid reaches 1035 F g^{-1} at 1 A g^{-1} in 6 M KOH solution [7]. However, the LDH and carbon materials composites used as active materials of SCs generally have low conductivity, inferior rate capability, and small specific capacitance. These features obstruct the application of SCs.

In this paper, we introduce a new protocol to fabricate the NiAl-LDH/CNFs composite using a situ growth method. As far as I know, this is the first example to obtain the NiAl-LDH/CNFs composite. In our experiments, the NiAl-LDH nanosheets were grown vertically on the surface of hollow carbon nanofibers to form the three-dimensional porous structure which is a key factor to combine the pseudo capacitive of NiAl-LDH with double layer capacitive of hollow carbon nanofibers, the linear CNFs can provide a stable network-like structure during the charge–discharge process, which can facilitate the fast electron transfer and decrease in electrochemical polarization of the active material. Therefore, the NiAl-LDH/CNFs composite can offer an excellent electrochemical performance.

2. Experimental section

2.1. Pretreatment of hollow carbon nanofibers

Hollow carbon nanofibers, with diameters of 100 nm, were purchased from Sigma–Aldrich, which is denoted as CNFs if there is

no special declaration in the following passage. The pristine CNFs were treated with a mixture of concentrated nitric acid and sulfuric acid (in a volume ratio of 1:3) by refluxing in a round-bottom flask for 6 h at 80°C . Then the modified CNFs were filtered and washed with deionized water until $\text{pH} = 7$. Finally, the collected powder was dried at 60°C for 12 h. As a result, a number of negatively charged carboxyl groups were introduced onto the surface of CNFs. The other reagents (analytical grade) were used as received without further purification.

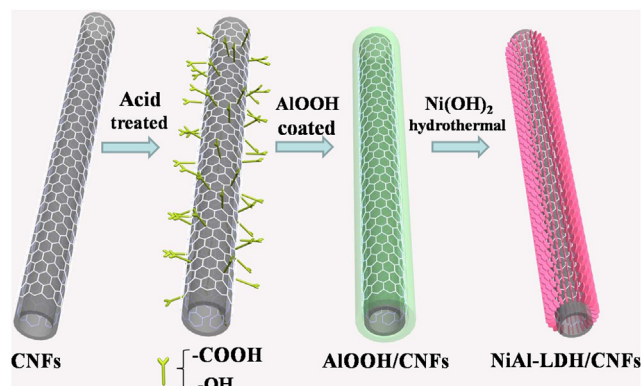
2.2. Synthesis of NiAl-LDH/CNFs composite

The NiAl-LDH/CNFs composite was prepared via a situ growth method. Firstly, the boehmite primer (AlOOH) sol was prepared by hydrolysis process. To be specific, 6 g aluminum isopropoxide ($\text{Al}(\text{OPr})_3$) was added into HNO_3 solution (50 ml, 0.05 M), followed by refluxing in a round-bottom flask for 6 h at 90°C . After that, the CNFs covered with AlOOH to form a shell structure. Typically, the prepared CNFs (0.1 g) were dispersed in 50 ml AlOOH primer sol for 24 h with vigorous agitation, followed by filtration, and then washed thoroughly with ethanol several times, after that dried at room temperature.

NiAl-LDH/CNFs composite was carried out through an in situ growth method. The AlOOH /CNFs (0.1 g) powder was dispersed in 70 ml deionized water by vigorous stirring for 10 min. Then $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.003 mol) and urea (0.01 mol) were added into the above solution. After stirring for about 20 min, the mixed solution was transferred into an autoclave at 100°C for 48 h. Finally, the resulting NiAl-LDH/CNFs composite was separated by centrifugation, rinsed with ethanol and dried at room temperature. The whole synthesis process of the composite is depicted in Scheme 1. For comparison, the pristine NiAl-LDH was synthesized by an identical process to that of the composite without the introduction of CNFs.

2.3. Structural characterization

The structure of the obtained samples were characterized by X-ray diffraction (XRD, Rigaku) using $\text{CuK}\alpha$ radiation at 40 kV and 250 mA, $\lambda = 1.5406 \text{ \AA}$. SEM investigations were performed using a Quanta FEG 250 field emission scanning electron microscope (FEI, Electron Optics, B.V). EDX analyses were performed using an EDAX system. TEM and HRTEM (JEM-2100F) were used to study the morphologies and microstructure properties of samples. Fourier transform-infrared measurements (FT-IR) (Thermo Electron Scientific Instruments, Nicolet 6700, America) were recorded on KBr



Scheme 1. Schematic illustration of the formation mechanism for NiAl-LDH/CNFs composite.

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