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3D hierarchical $Ni^{2+}/Mn^{2+}/Al^{3+}$ layered triple hydroxide @ nitrogen-doped graphene wrapped hybrids on nickel foam for supercapacitor applications☆

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ABSTRACT

Nickel Foam as a substrate for morphology controllable synthesis of hierarchical nanocomposites with three-dimensional architecture is gaining substantial rank as effective energy materials for high-performance energy conservation and energy conversion devices. Herein, we report our findings in fabrication of 3D hierarchical, $Ni^{2+}/Mn^{2+}/Al^{3+}$- layered triple hydroxide @ nitrogen-doped graphene wrapped hybrid on a nickel foam (marked as NMA-L@NG-NF) electrode, via a two-step hydrothermal method: primarily in situ hydrothermal growth of NiMnAl-LTH nanosheets over the surface of nickel foam, followed by secondary hydrothermal wrapping of NG graphene over the surface of NiMnAl-L@NF. The phase purity, structure, morphology and functionalities of the synthesized NMA-L@NG-NF hybrid electrodes were characterized comprehensively by XRD, FT-IR, Raman, XPS, EDS and SEM techniques. The results show that the obtained structure (NMA-L@NG-NF) possessed hierarchical flower-like configuration, which were self-assembled from LTH nanosheets and grafted successfully onto the framework of NF substrate during the hydrothermal process. Moreover, when tested as a binder-free electrode in a half cell three-electrode configuration, the NMA-L@NG-NF hybrid display significantly high specific capacity (452 mAh/g at 5 A/g), the excellent rate capability (75.8% at 20 A/g), the excellent cycling stability (91.4% of its initial capacity was retains at a current density of 10 A/g after 5000 cycles, with ~ 100% Coulombic efficiency) and very low R_{CT} value (0.34 Ω before and 0.62 Ω after 5000 charge discharge cycle from impedance measurements). It could be anticipated that the synthesized NMA-L@NG-NF hybrid is thus a highly promising electrode by virtue of their outstanding applications in high-performance energy storage and energy conversion devices.

1. Introduction

Advancement in the field of high-performance energy conservation and energy conversion devices ignites the use of more effective devices for the next generation energy storage applications, such as supercapacitors, fuel cells and secondary batteries [1–3]. Supercapacitors (SCs) or ultracapacitors the promising candidate of energy storage devices which enclose electric double-layer capacitors (EDLCs, containing constructive materials of carbon i.e. Graphene,) and pseudocapacitors (containing transition metal oxides/hydroxides) have the potential of holding high electrochemical characteristics, containing high specific capacitance/capacity, high power density, short charging time and long operational life [4–6]. Moreover realization of high-performance of supercapacitor electrodes intensely depends on the types and properties of energy materials to be used for its fabrication. Among the transition metal hydroxides, metallic layered double hydroxides (LDH), whose structure can be characterized by the general formula $[M^{2+}_{1-x} + M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}{\cdot}mH_2O$, (where M^{2+} and M^{3+} are divalent and trivalent metal cations and A^{n-} is charge balancing interlayer anion), are gaining substantial rank as an effective supercapacitors electrode materials. This is due to their unique properties such as, specific chemical composition flexibility, high surface area, redox capacity, anion exchange capability, water-rich feature, low cost, non-toxic landscape, and structure versatility to achieve the standard capacity values [7–9]. However, despite the exceptional properties, unluckily, the obvious practical electrochemical performances of LDH are hampered by the relative poor electronic conductivity, relative low mass diffusion, aggregation of nanosheets, and bad cycle stability [10]. In addition the

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specific capacity, rate capability and energy density are rather poor at high current density, which makes it less effective to be used as an electrode energy material for their application in high performance SCs [11]. To impede the above confines, first commonly used synthetic strategy is, in situ crystallization and ex situ hybridization method of fabricating LDH with shaped carbon-based nanomaterials, such as carbon nanotubes, activated carbon, porous carbon, graphene and functionalized graphene, which has been already remain a favorable choice of different researchers owning to the significant advantages, compare with mono LDH electrode materials [12–17]. Similarly, the second approach is chemical doping, chemical doping of heteroatoms (B, N, P, O, S, Se, F, Cl, Br, and I) into graphene-based materials is an effective and significant way of tailoring their properties for emerging applications in photo electrochemical reactions, semiconductor,electronics, optoelectronics, energy conversion and conservation, catalysis, biomedicine, and sensing [18–23]. Among these elements, nitrogen-doped graphene (NG) has been widely investigated due to the closest possessions of N to C with respect to dimension and number of valence shell electronic configurations and therefore can be easily accommodate into the graphene lattice framework leading to p-and n-type doping, respectively [24]. Likewise, third synthetic strategy is non-conventional slurry-coating approach. Most of LDH based electrodes are usually binder-enriched electrodes prepared by the conventional slurry-coating technique. However, their performances are not adequate because of the poor intrinsic conductivity, extra contact resistance, aggregation of active species, and the presence of "dead surface" resulting from the introduction of a conductive agent and a polymer binder in the conventional electrode fabrication [25,26]. A hot growing idea is to directly grown electroactive nanomaterial on conductive substrates such as nickel foam (NF) incorporated electrodes (without adding of conductive additives and binders), which can overwhelmed those complications and are proven to be an effective approach to accomplishing further enhancement in their electrochemical performance [27–31].

On the basis of the above considerations, in this contribution our group was motivated to design 3D hierarchical NiMnAl layered triple hydroxide nitrogen-doped graphene-wrapped hybrid on a nickel foam (marked as NMA-L@NG-NF), via a two-step hydrothermal method for innovative functional supercapcitor electrode material. The morphological and supercapacitive properties of the hybrid were briefly investigated and discussed. In comparison hierarchical NiMnAl layered triple hydroxide @ nickel foam without NG (marked as NMA-L@-NF), and NiMnAl-layered triple hydroxide @ nitrogen doped graphene powder (abbreviated as NMA-L@-NG-P) were also fabricated by the same procedure. More importantly, the electrochemical studies of the NMA-L@NG-NF hybrid electrode delivered significantly high specific capacity value (452 mAh/g) reported so far for the LDH based nanocomposites (see Table S1) at very high current density of 5 A/g, the excellent rate capability (75.8% at 20 A/g), the stable capacitance retention (91.4% at a current density of 10 A/g after 5000 cycles, with ~ 100% Coulombic efficiency) and very low R_{CT} value from impedance measurements.

2. Experimental section

2.1. Chemicals and materials

Natural flaky graphite powder (lateral size 45 μm, purity 99%), H_2SO_4, (98.08%), $NaNO_3$, $KMnO_4$, H_2O_2 (30%), HCl (36%), was used to synthesized GO. Ni $(NO_3)_2{\cdot}6H_2O$, $MnCl_2{\cdot}4H_2O$, Al $(NO_3)_3{\cdot}9H_2O$, urea, and ammonia (25%), were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (China) Nickel foam (NF) was bought from Shanghai Tankii Alloy Material Co., Ltd. (purity: > 99.5%, 1 mm: thickness). Water ultra-purified (UP) filtered resistivity (18.2 MΩ cm) was used throughout the experimentation.

2.2. Cleaning of nickel foam

The nickel foam (NF) was cut to a size of 10 mm × 15 mm × 1 mm. Subsequently, it was carefully cleaned with 10% HCL, acetone, and ultrapure water, via an ultrasound bath with 80% amplitude each for 15 min to remove the surface oxide layer. Afterward, the NF was dried in a vacuum oven at 60 °C for 12 h to evaporate solvent.

2.3. Synthesis of 3D hierarchical NiMnAl-LTH nanoplatelet (marked as NMA-LTH)

In a typical procedure, $Ni(NO_3)_2{\cdot}6H_2O$ (0.005 mol), $MnCl_2{\cdot}4H_2O$ (0.0025 mol) and $Al(NO_3)_3{\cdot}9H_2O$, (0.0025 mol) were dissolved in 75 mL of ultrapure water. The mixture was stirred at room temperature until to form a clear light green solution. Subsequently, urea (0.025 mol) was mixed with the solution via a stirring for 0.5 h. The resultant mixture was then transferred into a 100 mL Teflon-lined autoclave vessel and remained at 140 °C in an electronic oven for 10 h. The synthesized NMA-LTH nanoplatelet was washed with ultrapure water and ethanol several times and dried at 60 °C for 12 h in a vacuum oven.

2.4. Synthesis of 3D hierarchical NiMnAl-LTH on nickel foam (marked as NMA-L-@NF)

In situ growth of NMA-LTH nanoplatelet over the surface of nickel foam was sythesized by the homogeneous precipitation hydrothermal method. Typically, $Ni(NO3)_2{\cdot}6H_2O$ (0.005 mol), $MnCl_2{\cdot}4H_2O$ (0.0025 mol) and $Al(NO_3)_3{\cdot}9H_2O$, (0.0025 mol) were dissolved in 75 mL of ultrapure water. The mixture was stirred at room temperature until to form a clear light green solution. Subsequently, urea (0.025 mol) was mixed with the solution via a stirring for 0.5 h. Then, the pretreated nickel foam and the resultant mixture were put into a 100 mL Teflon-lined autoclave vessel and remained at 140 °C in an electric oven for 10 h. After the autoclave vessel naturally cooled down to room temperature, the NMA-L@NF hybrid was rinsed with ultrapure water and ethanol by ultrasonic for several times and dried at 60 °C for 12 h in vacuum oven respectively. The average mass of NMA-L loaded on NF was about ~1.1 mg cm^{-2}, according to the weight difference of NF before and after the first hydrothermal reaction.

2.5. Synthesis of 3D hierarchical NMA-L@NG-NF

A nitrogen-doped graphene (NG) sheets were wrapped on the surface of NMA-L@NF hybrid by hydrothermal method using aqueous ammonia as a reducing agent as well as a nitrogen precursor to synthesize NG [32]. Graphene oxide (GO) was prepared from crude flake graphite by improved Hummers method, details of synthesis is reported in our previous work [33,34]. In detail synthesis, 20 mg of GO was added into 20 mL of ultrapure water (1 mg/mL) followed by 0.5 h of sonication. Then, 1 mL of aqueous ammonia (25%) was added into the exfoliated graphene oxide suspension followed by another 30 min of stirring. Then, the fabricated NMA-L@NF and the resultant NG precursor were transferred into a 25 mL Teflon-lined autoclave vessel and maintained at 110 °C in an electric oven for 6 h. After the autoclave vessel naturally cooled down to room temperature, the NMA-L@NG-NF hybrid was rinsed with ultrapure water and ethanol for several times and dried at 60 °C for 12 h in vacuum oven respectively. The average mass of NG loaded on NMA-L@NF was about ~2 mg cm^{-2}, according to the weight difference of NMA-L@NF before and after the second hydrothermal reaction.

2.6. Synthesis of NMA-L@NG powder (marked as NMA-L@NG-P)

NMA-L@NG-P was synthesized by the ex situ hybridization method. In detail synthesis, $Ni(NO3)_2{\cdot}6H_2O$ (0.005 mol), $MnCl_2{\cdot}4H_2O$