



# The growth of nickel-manganese and cobalt-manganese layered double hydroxides on reduced graphene oxide for supercapacitor



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## ABSTRACT

Pure Ni-Mn layered double hydroxide (LDH), Co-Mn LDH with a flower-like morphology and sandwich-like Ni-Mn LDH/reduced graphene oxide (rGO), Co-Mn LDH/rGO hybrids are fabricated via a simple co-precipitation method. In the hybrids, Ni-Mn and Co-Mn hydroxide nanoflakes are tightly anchored on the both surfaces of rGO, leading to the composites with high specific surface areas. Electrochemical measurements prove that rGO can improve the capacitance and cyclic stability of the hybrid materials and that Ni-Mn LDH delivers a much higher specific capacitance but a worse cycling performance than Co-Mn LDH. A high specific capacitance of  $1635 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$  and a high rate retention of 71% at  $10 \text{ A g}^{-1}$  are achieved for Ni-Mn LDH/rGO. A hybrid capacitor with Ni-Mn LDH/rGO as positive electrode and activated carbon as negative electrode is assembled. It possesses a specific capacitance of  $84.26 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$  and an energy density of  $33.8 \text{ Wh kg}^{-1}$  within a potential window of 1.7 V.

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## 1. Introduction

Recently, tremendous efforts have been devoted to exploring renewable and high-performance electrode materials for electrochemical capacitors (ECs)/supercapacitors. Layered double hydroxides (LDHs) are unusual layered materials consisting of positively-charged hydrotalcite-like layers, weakly bound, charge compensating anions and water molecules in the interlayer region. Owing to the layered structure, they usually possess high specific surface area, which can facilitate fast ion transfer. This offers them great superiority in electrochemical fields [1–6]. The LDHs containing Ni, Co, Mn, etc, have proved themselves to be one of the most promising electrode materials for ECs due to their high specific capacitance, long life span, low cost and easy synthesis. Many investigations have been performed to synthesize Ni-Mn LDH and Co-Mn LDH and measure their electrochemical performances. Various synthesis methods have been thus developed. For example, Anandan's group reported the sonochemical synthesis of Ni-Mn LDH [7]. Sim et al. used a reverse micelle method to synthesize colloidal Ni-Mn LDH [8]. Hierarchical Ni-Mn LDH nanosheets could be grown on Ni foam by a one-step method at

$80^\circ\text{C}$ , as reported by Guo and co-workers [9]. Electrodeposition method was applied by Jagadale to fabricate Co-Mn LDH [10]. Some above methods are complex, unsuitable for large scale fabrication or resulting in the impurity. Thus, a facile time-/energy-saving method to synthesize pure Ni-Mn LDH and Co-Mn LDH is urgently needed. We know that co-precipitation, hydrothermal method, anion exchange and calcination-rehydration are common methods to synthesis LDHs. Among them, co-precipitation is much more energy-saving, environmentally friendly, and easily carried out.

It is well-known that the electrochemical performance of LDHs can be further improved if they are combined with carbon materials to form a composite [11–14]. Carbon materials are usually used as electrical double-layer capacitive electrode materials or as additives in transition metal oxides/hydroxides. As additives, carbon materials can provide large surface areas, prevent oxides/hydroxides from agglomeration, facilitate electrical conductivity, and enhance mechanical stability. Zhao and Wang deposited Co-Mn LDH onto carbon fibers and carbon cloth, respectively [15,16]. The results revealed that the hierarchical configuration of LDHs/carbon could improve the exposure of active sites and enable a fast charge transfer to the electrode/electrolyte interface. Zhao also reported a hierarchical structure composed of Ni-Mn LDH microcrystals grafted on carbon nanotubes (CNTs) backbone with tunable Ni/Mn ratios by an *in situ* growth route [15].

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The electrochemical investigation showed that Ni<sub>3</sub>Mn<sub>1</sub> LDH/CNTs electrode was rather active with the maximum specific capacitance of 2960 F g<sup>-1</sup> [5]. Our group has also fabricated a hierarchical NiCoMn LDH/rGO composite, which could deliver a high capacitance of 912 F g<sup>-1</sup>, much higher than that of pure NiCoMn LDH (772 F g<sup>-1</sup>) [17]. Some other Ni-Mn LDH/carbon composites, such as, ternary NiCo<sub>2</sub>S<sub>4</sub> nanotube/Ni-Mn LDH/3D graphene sponge [18], Ni-Mn LDH/graphene superlattice [19], and sulfidation Ni-Mn LDH/graphene oxide [20] have been recently reported. All these composites exhibited outstanding capacitance and rate performance, indicating their promising potential as electrode materials of ECs.

Herein, we attempt to synthesize pure Ni-Mn LDH, Co-Mn LDH, and their composites with reduced graphene oxide by simple coprecipitation method. In the composites, LDH nanosheets are anchored onto the surfaces of reduced graphene oxide (rGO) to form a hierarchical architecture. Electrochemical tests are carried out to reveal their capacitive performances as electrode materials for ECs. It is found that Ni-Mn LDH/rGO composite can deliver a high capacitance (1635 F g<sup>-1</sup>), a fair rate capability and a long life span. In addition, an asymmetric capacitor is designed with Ni-Mn LDH/rGO and activated carbon (AC) as positive and negative materials, respectively.

## 2. Experimental

### 2.1. Preparation of materials

Natural flake graphite (500–600 μm, Qingdao Xinghe Graphite Co., Ltd) was used to prepare graphene oxide (GO). By a modified Hummers method, as reported elsewhere [21], oxidation, exfoliation and washing process were carried out on the flake graphite. After centrifugation and standardization, 6 g L<sup>-1</sup> GO suspension was obtained. Then, a specific volume of above GO suspension containing 15 mg GO was dispersed into 250 mL deionized water to form a transparent suspension, followed by the addition of 4 mmol Ni(NO<sub>3</sub>)<sub>2</sub>, 2 mmol Mn(NO<sub>3</sub>)<sub>2</sub> and 18 mmol NH<sub>4</sub>F. Under strong stirring, 18 mL ammonia (1 mol L<sup>-1</sup>) was added dropwise into the above suspension at room temperature in 2 h for the fabrication of LDHs. After being washed and dried at 80 °C, Ni-Mn LDH/rGO was thus obtained. The mass content of rGO in Ni-Mn LDH/rGO

composite was evaluated to be 4.6%, determined by weighing the final product. Pure Ni-Mn LDH could be also prepared by the same process but without using any GO.

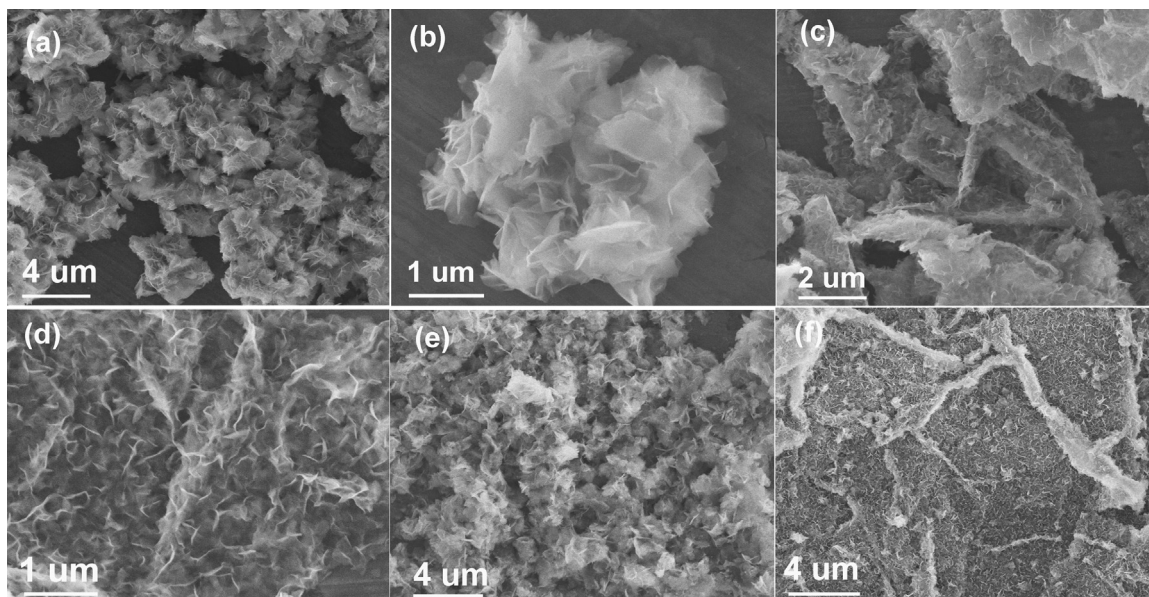
Similarly, pure Co-Mn LDH and Co-Mn LDH/rGO composite could be also fabricated by the same procedure using 4 mmol Co(NO<sub>3</sub>)<sub>2</sub>.

### 2.2. Materials characterization

The structure and morphology of the products were characterized by an X-ray diffractometer (XRD, using Cu-Kα radiation at 40 kV, 40 mA, 3° min<sup>-1</sup>, Shimadzu, LabX XRD-6000) with a secondary graphite monochromator, scanning electron microscope (SEM, Hitachi S-4800), and transmission electron microscope (TEM, Philip-CM200). Fourier transformed infrared spectroscopy (FT-IR, Bruker spectrometer, Tensor 27) was obtained by dispersing the sample in KBr and pressing it into transparent pellets. The specific surface area and pore distribution of the materials were tested by an ASAP 2020 analyzer (Micromeritics Instrument Corporation) by Brunauer-Emmett-Teller (BET) method at 77 K in N<sub>2</sub> with a pre-treatment at 180 °C for over 10 h degassing. X-ray photoelectron spectroscopy (XPS, Thermo, Escalab 250Xi) was measured and the XPS spectra were calibrated by the C 1s line at 284.8 eV. Thermogravimetric (TG) analysis was carried out on an SDT Q600 instrument from 25 to 800 °C with the heating rate of 10 °C min<sup>-1</sup> in air.

### 2.3. Preparation of electrodes and electrochemical characterization

For a three-electrode configuration, the electrode containing as-prepared materials, Ni plate and an Ag/AgCl electrode were used as work electrode, counter electrode and reference electrode, respectively. The work electrode was prepared by mixing the electrode material, acetylene black, polyvinylidene fluoride in a mass ratio of 80:10:10 in *N*-methyl-2-pyrrolidone, which was painted onto a Ni foam substrate (1.5 cm × 1.5 cm) and completely dried at 80 °C in vacuum. The active material loaded on each electrode was about 4 mg. 2 M KOH solution was acted as electrolyte. A salt-bridge was used to connect Ag/AgCl electrode and the electrolyte. Cyclic voltammograms (CV), galvanostatic charge-discharge curves and electrochemical impedance



**Fig. 1.** (a, b) SEM image of pure Ni-Mn LDH, (c, d) SEM image of Ni-Mn LDH/rGO, (e) SEM image of pure Co-Mn LDH, and (f) SEM image of Co-Mn LDH/rGO.

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