



# Sandwich-like graphene/polypyrrole/layered double hydroxide nanowires for high-performance supercapacitors



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## HIGHLIGHTS

- A sandwich-like GPPY/layered double hydroxide nanowires composite was prepared.
- The sufficient space between NiAl-NWs benefits the rate performance and cycle life.
- The ultrathin NiAl-NWs ensure a maximum exposure of active Ni<sup>2+</sup>.
- The optimum E<sub>0V</sub> give rise to a relatively high energy density.

## ARTICLE INFO

### Article history:

Received 29 June 2016

Received in revised form

3 September 2016

Accepted 7 September 2016

Available online 14 September 2016

### Keywords:

Graphene

Polypyrrole

LDH

Supercapacitor

Nanowire

## ABSTRACT

Electrode design in nanoscale is considered to be ultra-important to construct a superb capacitor. Herein, a sandwich-like composite was made by combining graphene/polypyrrole (GPPY) with nickel-aluminum layered double hydroxide nanowires (NiAl-NWs) via a facile hydrothermal method. This sandwich-like architecture is promising in energy storage applications due to three unique features: (1) the conductive GPPY substrate not only effectively prevents the layered double hydroxides species from aggregating, but also considerably facilitates the electron transmission; (2) the ultrathin NiAl-NWs ensure a maximum exposure of active Ni<sup>2+</sup>, which can improve the efficiency of rapid redox reactions even at high current densities; (3) the sufficient space between anisotropic NiAl-NWs can accommodate a large volume change of the nanowires to avoid their collapse or distortion during the reduplicative redox reactions. Keeping all these unique features in mind, when the as-prepared composite was applied to supercapacitors, it presented an enhanced capacitive performance in terms of high specific capacitance (845 F g<sup>-1</sup>), excellent rate performance (67% retained at 30 A g<sup>-1</sup>), remarkable cyclic stability (92% maintained after 5000 cycles) and large energy density (40.1 Wh·Kg<sup>-1</sup>). This accomplishment in the present work inspires an innovative strategy of nanoscale electrode design for high-rate performance supercapacitor electrodes containing pseudocapacitive metal oxide.

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## 1. Introduction

In the last decades, worsening fossil energy depletion and global warming has made it imperative to develop clean, efficient and sustainable energy sources [1–3]. In addition, the ever-growing demand from modern digital communications and electric vehicles or hybrid electric vehicles also promotes the development of alternative energy, as well as new energy storage devices with high

energy density and power density [4,5]. Among numerous energy storage devices, electrochemical capacitors, also being called supercapacitors (SCs), have attracted considerable attention owing to their high power density, long lifespan and safe operation [2,3,5]. The charging-discharging of SCs can be accomplished by non-faradic charge storage accumulation process or faradic charge transfer process [6,7]. Thus, SCs can be divided into electrical double-layer capacitors (EDLCs) and pseudocapacitors. EDLCs, which usually use carbonaceous materials as electrodes [6,8–10], store energy by pure electrostatic charge accumulation at the electrode/electrolyte interface. Therefore, these capacitors often exhibit excellent rate performance at high current density and stability during long period charging-discharging process. For

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instance, an ultra-light hierarchical graphene with a specific surface area of  $835 \text{ m}^2 \text{ g}^{-1}$  was selected as EDLC electrode. It delivers a specific capacitance of  $169 \text{ F g}^{-1}$  at a current density of  $1.5 \text{ A g}^{-1}$  [11]. Upon 5000 cycles at  $3 \text{ A g}^{-1}$ , this graphene based supercapacitor shows a robust retention of more than 92% of its initial capacitance. In addition, a bagasse-derived hierarchical structured carbon with higher surface area of  $2296 \text{ m}^2 \text{ g}^{-1}$  exhibits enhanced capacitive performance ( $320 \text{ F g}^{-1}$  at  $0.5 \text{ A g}^{-1}$ ). 70.8% of its initial capacitance can still be maintained even at a high current density of  $50 \text{ A g}^{-1}$  [12]. However, the specific capacitance of carbonaceous materials based EDLCs is usually less than  $350 \text{ F g}^{-1}$  [8–12], resulting in a low energy density, which limits the applications of EDLCs. Thus, further boosting the energy density while maintaining a high power density still remains to be a major challenge. Compared to EDLCs, pseudocapacitors present 10–100 times higher specific capacitance (per unit surface area) because of reversible redox reactions. To date, considerable efforts have been devoted to explore pseudocapacitive materials with excellent energy storage performance [13–15].

Generally, polymers and metal oxides/hydroxides are explored as pseudocapacitive materials due to their reversible faradic reactions during charging-discharging process. Self-crosslinked polyaniline hydrogels have been synthesized and used as electrode materials [16]. These hydrogels have a high specific capacitance of  $750 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$  due to their high conductivity and 3D gel network. Unfortunately, the volume of conducting polymers frequently expands/contracts during charging-discharging cycles, resulting in inferior lifespan. Transitional metal oxide/hydroxide such as  $\text{MnO}_2$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Co}(\text{OH})_2$ ,  $\text{NiO}$ , and  $\text{Ni}(\text{OH})_2$  with special nanostructures were widely adopted as electrode materials [17–22]. Among them, layered double hydroxides (LDHs) with a general formula of  $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}[\text{A}^{n-}]_x^{n-} \cdot m\text{H}_2\text{O}$  have attracted tremendous attention due to their low cost, environmentally friendly nature and flexible ion exchange ability. But the stack of LDH sheets and semiconductor nature limit the capacitive performance of LDHs. To solve these problems, nanostructured carbon materials have been selected to combine with LDH by many research groups to improve their chemical stability and conductivity. Lei et al. [23] prepared a novel sandwich-like structured Co-Al LDH-carbon nanotube composite by the elegant combination between exfoliated Co-Al LDH nanosheets and modified CNTs. The as-prepared composite exhibited a high specific capacitance of  $884 \text{ F g}^{-1}$ . However, the specific capacitance dropped to  $529 \text{ F g}^{-1}$  at a current density of  $4.3 \text{ A g}^{-1}$ . Goli Nagaraju et al. [15] deposited hierarchical 3D porous Ni-Co LDH on a conductive textile substrate to improve the conductivity. The obtained flexible electrode possesses a high specific capacitance and excellent cyclic stability. But only 57% of its initial capacitance value can be maintained under a current density of  $20 \text{ A g}^{-1}$ . It is obvious that although high specific capacitance can be obtained for these composites, the rate performances are still inferior, which in turn results in poor power-out characteristic [15,23–25]. It is worth to note that choosing a supportive and conductive substrate is vital to forming a well-structured LDH composite, as LDH sheets usually present large size. Graphene seems to be a good substrate due to its high conductivity. However, graphene nanosheets are too flexible to hold up

the bigger LDH sheets. For example, Zheng et al. [26] prepared a Ni-Co-Al LDH/reduced graphene oxide (RGO) by a hydrothermal method. The LDH sheets were disorderly entangled with the corrugated and scrolled RGO nanosheets. As previously reported [27], graphene/polypyrrole nanosheets possesses higher strength and conductivity, which is suitable for supporting large LDH sheets. In addition, the thickness of GPPY can be adjusted via changing the amount of polypyrrole. Thus, GPPY can fulfill different needs in various composites.

Herein, we report for the first time the synthesis of a novel sandwich-like architecture (GPDHW) made of nickel aluminum double hydroxide nanowires (NiAl-NWs) grown in situ on both sides of graphene/polypyrrole nanosheets (GPPY) by a facile and efficient hydrothermal method. In this composite, the GPPY nanosheets serve as substrate for the growth of NiAl-NWs and the NiAl-NWs protect GPPY from aggregation in return, thus constructing fast ion transport channels. The ultrathin NiAl-NWs maximize surface active  $\text{Ni}^{2+}$  to ensure that the rapid redox reactions can be carried out efficiently even at high current densities, leading to an excellent rate performance. In addition, the intertwined nanowires provide sufficient space for rapid ions transport. The space can also accommodate a large volume change of the nanowires to avoid their collapse during charge and discharge cycling. Benefiting from these unique features, the composite exhibits excellent capacitive performance in term of capacity, rate performance and cyclic stability.

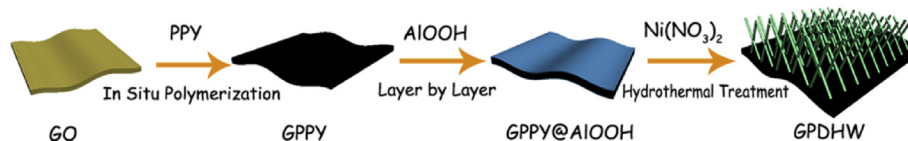
## 2. Experimental section

### 2.1. Reagents

Graphite power was purchased from Qingdao Ruisheng graphite Co., Ltd. Pyrrole was obtained from Sigma-Aldrich. Ferric chloride, aluminium isopropoxide, nitric acid, nickel nitrate and urea were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification.

### 2.2. Synthesis of NiAl-LDH @GO-PPY composites

NiAl-LDH@GO-PPY composite was prepared by the sequentially process in Scheme 1. Firstly, graphene oxide (GO) sheets was prepared by the improved Hummers' method as previously reported [28]. Then, polypyrrole was grown on GO sheets by in situ polymerization of pyrrole based on the previous report [27]. The prepared sample was nominated as GPPY. After obtaining GPPY, graphene/polypyrrole/layered double hydroxide nanowires were prepared through in situ growth of NiAl-LDH nanowires on the surface of GPPY. Briefly, boehmite AlOOH primer sol was firstly prepared by hydrolyzing aluminum isopropoxide according to a previous report [29]. Then, 0.1 g of GPPY was mixed with 20 mL of AlOOH sol under stirring for 12 h. The above process was repeated three times to ensure that GPPY were completely coated by AlOOH sol. Then, the GPPY@AlOOH composite was separated by centrifugation, followed by washing with deionized water and ethanol for several times and drying at room temperature. Finally, as-prepared GPPY@AlOOH powder was dispersed in 30 mL of deionized water



Scheme 1. Schematic diagram for the preparation of GPDHW composite.

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