Preparation and capacitance properties of graphene/NiAl layered double-hydroxide nanocomposite

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A B S T R A C T

Graphene/NiAl layered double-hydroxide (LDH) composite with high capacitive properties has been prepared in a friendly one-step process. It is found that NiAl-LDH is formed in the addition of precipitator agent (NaOH and NaNO₃) by hydrothermal method, at the same time graphene oxide (GO) is reduced to graphene. The morphology and structure of the obtained material are examined by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), transmission electron microscope (TEM), and scanning electron microscope (SEM) techniques. It is revealed that the NiAl–LDH disperses well on the surface of graphene and the formation of NiAl–LDH nanoparticles is beneficial to the peeling of graphene (RGO). More importantly, the addition of NiAl–LDH to graphene endows the materials with desirable specific surface areas and higher porosity. These structural advantages result in higher specific capacitance compared with pristine graphene. Electrochemical property investigations show that the graphene/NiAl–LDH had a higher specific capacitance than graphene.

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1. Introduction

Supercapacitors, also known as electrochemical capacitors or ultracapacitors, have attracted much attention because of their intriguing features including high power density and long cycle life [1–3]. The energy is stored in supercapacitors mainly by electrical double-layer capacitor (EDLCs) and pseudocapacitors [4]. The electrode materials of EDLCs are typically carbon materials with high surface area, while pseudocapacitors are mostly conducting polymers or metal oxides, which transfer the faradic charges between electrolyte and electrode [4]. In order to meet the ever increasing demand for supercapacitors with high electronic performances, it is essential to develop electrodes which are durable, nontoxic and inexpensive. Numerous materials have been investigated and used as electrodes of supercapacitors; they can mainly be divided into three types: (i) carbonaceous materials, (ii) conducting polymers, and (iii) transition metal oxides [5–8]. Among the possible materials, transition metal oxides were studied extensively, such as MnO₂, Co₃O₄, ZnO, and so on [9–18]. Layered double hydroxide (LDH) as a kind of heterostructure nanomaterials have shown superior properties in applications such as catalysis, sorption, medicine, and so on [19–21]. However, layered double hydroxide (LDH), as potential electrochemical active materials, its electrochemical properties is less studied. LDHs are candidates for next-generation electrode materials of supercapacitors because of their abundant slabs and the electrochemically active sites that led to the simultaneous formation of the electrical double-layered capacitance and Faradaic pseudocapacitance. Recently, several groups dedicated to study the electrochemical properties of CoAl–LDH or NiAl–LDH [22–30]. However, pure LDH usually stacks together during the synthesized process or its low conductivity constrains electron transfer; these consequently impact on the performance of electrode materials. So, it is necessary to find an effective method to optimize the electrochemical properties of LDH.

Graphene, a two-dimensional carbon material with unique mechanic and electronic properties, offers promising properties such as high surface area, electrical conductivity, high flexibility, mechanical strength and so on and has drawn extensive attentions since 2004 [31–33]. As a low dimensional material, graphene has a huge theoretical specific area of 2600 m²/g and presents an excellent electrical conductivity of 7200 S/m at room temperature [34–36]. Graphene-based supercapacitors have been reported with high specific capacitance in aqueous solution [30]. However, the agglomeration of graphene always limited its capacitances, so it is urgent to explore novel graphene-based materials to overcome the aggregation and exploit their full potential of electrodes for supercapacitors. A promising prospective is to use graphene as a substrate for growth of functional nanomaterials to form new nanocomposites [30]. Lots of nanocomposites were grown on the graphene substrate such as, NiO, MnO₂, ZnO, and so on. These obtained hybrid nanocomposites showed enhanced electrochemical
performance, because of the combination of pseudocapacitance of the metal oxide and the double-layer capacitance from graphene. Recently, LDH–graphene nanocomposites have attracted intensive attention, because of their low cost, high redox activity, and environmentally friendly nature [30]. However, most conventional synthesis methods for LDH–graphene nanocomposites are either time consuming or involving some toxic precursors, which is not in accordance with the requirements of energy saving and environmental protection. Hence, it is urgent to explore simple and convenient method for synthesizing this kind of material.

In this paper, we reported the preparation of graphene/NiAl layered double-hydroxide composite by a one-step hydrothermal method for the first time. The NiAl/LDHs were dispersed on the surface of graphene. LDH formed by co-deposition method using NaNO₃ and NaOH as precipitating agent. The synthesized graphene/NiAl–LDH was characteristic by transmission electron microscopy (TEM), powder X-ray diffraction (XRD), and so on.

2. Experimental section

2.1. Preparation of graphene oxide and graphene/NiAl–LDH nanocomposites

Graphene oxide (GO) was prepared from natural graphite powder through a modified Hummers’ method [37]. Graphene/NiAl–LDH nanocomposites were prepared hydrothermally as follows: 0.6 g of GO was dispersed in H₂O and stirred for 12 h to form a homogeneous aqueous dispersion. Then, 0.37 g Al(NO₃)₃ and 0.58 g Ni(NO₃)₂ were added into the GO dispersion followed by stirring at room temperature. NaOH solution (2 M) and NaNO₃ (1 M) were added to the solution slowly and simultaneously for adjusting the pH value in range of 10–11. Then, the mixture was transferred to a 100 mL Teflon-lined autoclave and maintained at 180 °C for 48 h for crystallizing. The products were washed with deionized water for several times and dried at 50 °C for 24 h.

2.2. Material characterizations

Powder X-ray diffraction (XRD) patterns of all samples were carried out by a Rigaku powder diffractometer (D/MAX-RB) using Cu Kα radiation (λ = 0.15418 nm) at a scanning rate of 4°/min in 2θ = 10–70°. The structures of the electrode materials were characterized by transmission electron microscopy (TEM, JEOL 3010) and scanning electron microscopy (SEM, HitachiS–3000N) techniques. Adsorption and desorption isotherms of nitrogen were measured with a NOVA 1200 gas sorption analyser at liquid nitrogen temperature (−196 °C). Before the measurements, the samples were degassed under vacuum condition at 120 °C for 8 h. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area using adsorption data acquired at a relative pressure (P/P₀) range of 0.05–0.25. The pore size distribution curves were calculated from the analysis of the desorption branch of the isotherm based on the Barrett–Joyner–Halenda (BJH) algorithm. The micropore volume and micropore surface area were estimated by a t-plot method.

2.3. Electrochemical measurement

All the electrochemical measurements were carried out in a conventional three-electrode system with 1 M Na₂SO₄ aqueous electrolyte at room temperature. The as-synthesized electrode materials, a platinum wire electrode, and a saturated calomel electrode (SCE) were used as working electrode, counter electrode, and reference electrode, respectively. The working electrode was prepared by mixing sample (80 wt.%) as active material with poly(tetrafluoroethene) (PTFE, 20 wt.%) in ethanol to produce a homogeneous paste. Then, the resulting mixture was coated onto the Ni foam substrate. The foam was dried at 80 °C in air for 12 h to remove the solvent. The electrochemical performances of the as-prepared material electrodes were tested using a cyclic voltammetry (CV) method, galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS) on an electrochemical workstation (CHI 660D, Shanghai CH Instrument Company, China). The measurement was carried out in 1 M Na₂SO₄ aqueous electrolyte at room temperature. CV tests were done between −1.2 V and −0.2 V (vs SCE) at scan rates of 5, 10, 30, 50, and 100 mV s⁻¹. Galvanostatic charge/discharge curves were measured in the potential range of −1 to 0 V at different current densities, and the EIS measurements were carried out in the frequency range from 100 kHz to 0.1 Hz at open circuit potential with an ac perturbation of 5 mV.

3. Results and discussion

3.1. Morphology of GO and NiAl–LDH/RGO

The formation of NiAl–LDH/RGO can be explained as follows (Scheme 1): metal cations were firstly adsorbed on GO surface, using NaOH and NaNO₃ as precipitator agent, then the reduction of GO and the crystallization of LDH crystals happened in one-step process. Fig. 1 shows the XRD patterns of the graphite, GO, as-prepared RGO, and graphene/NiAl–LDH. The diffraction peak of exfoliated GO at 11.17° (001) features a basal spacing of 0.80 nm, showing a well oxidation of graphite to the graphene oxide due to the introduction of oxygen-containing functional groups on the graphite sheets [38]. While for graphene, the peak at 11.17° of GO completely disappears and a broad peak at around 25° representing an interlayer spacing of 0.355 nm is observed. The space is a little larger than the natural graphite (0.334 nm), which maybe because of the partial reduction of graphene oxide. The XRD pattern of hybrid graphene/NiAl–LDH material can be indexed to the hexagonal NiAl–LDH (JCPDS No. 22-0452). The d spacing of the (003) diffraction peak of graphene/NiAl–LDH is 0.754 nm. This indicates that the graphene sheets are effectively exfoliated by the addition of NiAl–LDH hybrid. To confirm the reduction of GO to RGO, FT-IR spectra of GO and RGO are given in supplementary materials (Fig. S1). Besides, thermal stability of NiAl–LDH/graphene has been given in Fig. S2.

Fig. 2 gives the morphology and structure of GO and graphene/LDH (SEM and TEM). As can be seen from Fig. 2A that the as-prepared graphene shows a transparent flower-like shape. While for the structure of graphene/LDH (Fig. 2B), with the addition of LDH, it is apparent that it exhibits a layer-like structure. TEM images (Fig. 2C and D) are given to get in-depth study of the structure of the synthesized material. It can be seen that the GO has transparent character due to the thin layered structure with some wrinkles and folds on the surface. While for graphene/LDH, it is clear that the NiAl/LDH nanoplatelets are distributed on the surface of graphene nanosheets and thus effectively prevent the restacking of graphene.

In order to confirm that the formation of graphene/NiAl–LDH prevents the aggregation of graphene nanosheets, nitrogen adsorption and desorption were carried out to obtain the surface area and porous data of the as-synthesized material. The corresponding specific surface area of graphene/NiAl–LDH and graphene is about 122.7 m² g⁻¹ and 56.1 m² g⁻¹, respectively (Fig. 3). From Table 1, the specific area of graphene/NiAl–LDH was higher than graphene,
and this is confirmed that the deposition of NiAl–LDH helped to reduce the restacking of the graphene nanosheets. The pore size analysis of graphene/NiAl–LDH indicates that it comprises a large fraction of mesoporous (2–50 nm), which is thought to be the optimum pore size for electrosorption. Sample with high specific surface area and mesopores is favorable for improving both the main pseudocapacitance of metals and the electric double-layer (EDL) capacitance of graphene because of the easily accessible of the hydrated ions in the electrolyte to the exterior and interior pore surfaces [39,40].

3.2. Electrochemical property

To explore the potential applications of the as-synthesized graphene/NiAl–LDH and graphene, the samples were fabricated as supercapacitor electrodes and characterized by CV, EIS, galvanostatic charge/discharge, and stability measurements.

Cyclic voltammetric tests were used to explore the electrochemical behavior of the obtained graphene/NiAl–LDH and graphene nanocomposites in 1 M Na2SO4 electrolyte between –1.2 and –0.2 V at different scan rates and the results are shown in Fig. 4. As presented in Fig. 4A, the CV curves for graphene (Fig. 4A) are almost ideally rectangular, indicating a typical electrochemical double-layer (EDL) capacitive behavior with fast current response on the voltage reversal at each end potential and high reversibility [41]. While for sample graphene/NiAl–LDH, the CV curves are slightly disordered from the curves of rectangular shape of RGO; however, it is obvious that it shows a larger integrated area than graphene, which results in higher capacitance. The specific capacitances (Cs) were calculated from the CV curves according to the following equation:

\[ C_s = \frac{\int I dV}{m \Delta V} \]

where \( C_s \) is the specific capacitances (F g\(^{-1}\)), \( I \) is the response current (A), \( \Delta V \) is the potential window (V), \( \nu \) is the potential scan rate (mV s\(^{-1}\)), and \( m \) is the mass of the electroactive materials in the electrodes (g). The specific capacitance value calculated from the CV curve at 5 mV s\(^{-1}\) is found to be 203.57 F g\(^{-1}\) and 138.07 F g\(^{-1}\) for graphene/NiAl–LDH and graphene, respectively. The better electrical performance of graphene/NiAl–LDH can be attributed to the pseudocapacitance of NiAl/LDH, the EDL capacitance of RGO, the residual C–O and C=O function groups from the partially reductive of GO and less aggregation of the graphene nanosheets due to the introducing of NiAl–LDH nanocomposites.

In order to further investigate the performance of electrode materials, galvanostatic charge/discharge tests of graphene/NiAl–LDH and graphene were conducted in 1 M Na2SO4 with different current densities in a voltage range of –1 to 0 V, as shown in Fig. 5. The specific capacitances (Cs) of the electrodes can be calculated according to the following equation:

\[ C_s = \frac{It}{\Delta V m} \]

where \( m \) (g) is the mass of the active material in the film electrode, \( I \) (A) is the discharge current, \( \Delta V \) (V) is the potential window, \( t \) is the discharge time, and \( C_s \) (F g\(^{-1}\)) is the specific capacitance. Table 2 lists the charge/discharge data of the electrode materials calculated from the above equation at different current density. The remarkably increased capacitance of graphene/NiAl–LDH may be caused by the combination of electric double-layer capacitance of RGO and faradic pseudocapacitance of NiAl–LDH. With the increase in the current density, the capacitance of electrode is decreased from 213.6 F g\(^{-1}\) to 80 F g\(^{-1}\). The decreasing trend of the capacitance
indicates that the partial surface of the electrode is inaccessible at the high current density. Besides, it is apparent that for the shapes of the discharge curves of the graphene/NiAl–LDH are deviates from the ideal voltage–time curves. After the $iR$ drop, by the decrease in voltage, the time increasing deviates from a straight line. The phenomenon has already reported by Xu et al., Niu et al., and Beidaghi et al. about electrochemically modified graphite electrodes, porous carbon cloth material, and electrochemically activated carbon microelectrode arrays, respectively [42,43]. The factors contribute to the non-ideal behavior can be illustrated as follows: (i) the pseudocapacitive comes from LDH; (ii) the redistribution of charge within the pores of the activated electrodes during charging or discharging; and (iii) the effect of direct equivalent series resistance (ESR). ESR is an important parameter determining the charged/discharged rate of a supercapacitor, and it can be obtained from the intercept of the plot with real impedance axis.

Fig. 6 shows Nyquist plots of graphene and graphene/NiAl–LDH. For the plots of graphene, a semicircle over the high frequency range and a linear part in the low frequency region can be observed. The semicircle is due to charge-transfer resistance on the electrode/electrolyte interface, while the low frequency region is mainly characterized by purely capacitive behavior. The region

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$V_{total}$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{micropore}$ (cm$^3$ g$^{-1}$)</th>
<th>$S_{micropore}$ (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDH–RGO</td>
<td>122.7</td>
<td>0.164</td>
<td>0.01375</td>
<td>28.93</td>
</tr>
<tr>
<td>RGO</td>
<td>56.1</td>
<td>0.101</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
between the high frequency and low frequency regions is called the Warburg region, and this is the combination of both resistive and capacitive behavior characterized by diffusive resistance. The Nyquist plots for graphene/NiAl–LDH are different from graphene, which possesses the typical plots of carbon material in the high frequency region, and this indicates that the capacitance of graphene/NiAl–LDH nanocomposite is mainly from the pseudocapacitance of NiAl–LDH. At this region, the equivalent series resistance (ESR,

![Graph](image1)

![Graph](image2)

![Graph](image3)

![Graph](image4)

**Fig. 4.** CV curves of RGO (A) and LDH–RGO (B) electrodes at different scan rate; relationship between specific capacitance and the scan rate (RGO (C), LDH–RGO (D)).

![Graph](image5)

**Fig. 5.** Charge–discharge behaviors of RGO (A) and LDH–RGO (B) electrodes at different current density.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Current density</th>
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<tbody>
<tr>
<td>RGO (F g⁻¹)</td>
<td>135.7 71.9 48.6 38.4 30.4</td>
</tr>
<tr>
<td>LDH–RGO (F g⁻¹)</td>
<td>213.6 167 124.9 95.6 80</td>
</tr>
</tbody>
</table>

**Table 2** Specific capacitance values of electrodes RGO and LDH–RGO calculated from charge/discharge curves measured at different current densities.
obtained from the intersection of the Nyquist plot at the x-axis) of graphene is apparently higher than the graphene/NiAl–LDH nanocomposite, and this may due to the higher conductivities of graphene/NiAl–LDH electrode, which makes it showed a specific capacitance of 213.57 F g⁻¹ at a current density of 1 A g⁻¹. Additionally, nearly 100% of the original capacitance was retained after 1000 cycles, indicating a good cycle stability of composite materials. All of the above suggested that the graphene/NiAl–LDH electrode material was a high promising electrode material for supercapacitors with excellent performance.

4. Conclusion

In summary, the graphene/NiAl–LDH was prepared by hydrothermal method in one step as an electrode material. This material takes the advantages both of the electrical double-layer capacitor from graphene and of pseudocapacitance of NiAl–LDH nanoparticles. Compared with the pristine as-synthesized graphene, the present of NiAl–LDH nanocomposites prevents the restacking of graphene and decreases the charge-transfer resistance of graphene/NiAl–LDH electrode, which makes it showed a specific capacitance of 213.57 F g⁻¹ at a current density of 1 A g⁻¹. Additionally, nearly 100% of the original capacitance was retained after 1000 cycles, indicating a good cycle stability of composite materials. All of the above suggested that the graphene/NiAl–LDH electrode material was a high promising electrode material for supercapacitors with excellent performance.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2013.01.013.

References