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Supercapacitive behavior of electrostatic self-assembly reduced graphene oxide/CoAl-layered double hydroxides nanocomposites

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ABSTRACT

Graphene oxide/CoAl-layered double hydroxide (GO/CoAl-LDHs) composites were successfully prepared by a face-to-face electrostatic self-assembly method. Positively charged colloidal CoAl-LDHs nanosheets (CoAl-LDH-NS) and negatively charged colloidal GO nanosheets were uniformly mixed; then CoAl-LDH-NS were assembled on GO nanosheets via electrostatic attraction to prepare GO/CoAl-LDHs composites. The GO/CoAl-LDHs composites were then transformed to the reduced graphene oxide/CoAl-layered double hydroxide (RGO/CoAl-LDHs) composites with a hydrothermal method. The results showed that the content of RGO has a remarkable influence on the capacitive properties of composites. Among the composites with different RGO content, the RGO/CoAl-LDHs composite containing 12.0 wt% RGO displayed a maximum specific capacitance of 825 F g^{-1} at low current density of 1 A g^{-1}, while that of pure CoAl-LDHs was 552 F g^{-1}. The capacitance retention of the RGO/CoAl-LDHs composite from 1 A g^{-1} to 8 A g^{-1} is found to be 62.3%, whereas that of pure CoAl-LDHs is only 31.9%. Face-to-face self-assembling between positively charged CoAl-LDH-NS and negatively charged GO nanosheets can effectively reduce the self-agglomeration of GO nanosheets and avoid CoAl-LDH-NS stacking together, which lead to improvement of the capacitive performance.

1. Introduction

Layered double hydroxides (LDHs), known as anionic clays or hydrotalcite-like compounds, are typical two-dimensional (2D) nanomaterials [1]. LDHs are promising for next-generation supercapacitors that Faradaic pseudocapacitance and electrical double layered capacitance can be simultaneously acquired because of their electrochemically active sites and abundant slabs. Meanwhile, due to their flexible ion-exchange ability and tunable composition, they have attracted interest in the application of electrode materials for supercapacitors [2–9]. Based on Faradaic electrochemical reaction, LDHs containing electro-actives species should theoretically have large specific capacity in aqueous alkaline electrolytes [10]. CoAl-LDHs, with a divalent Co^{2+} ion and a trivalent Al^{3+} ion, is one of the most commonly studied LDHs, which could contribute to the faradaic redox reaction due to the conversion of Co^{2+} and Co^{3+} [11,12]. Therefore, CoAl-LDHs can be considered as an active material during the pseudocapacitive process, however, the achieved capacity of LDHs is often far below (1/10–1/5) its theoretical capacity due to poor electronic conductivity [13,14]. To synthesize a composite of LDHs with other active materials can be an ideal way to facilitate the transfer of electrons and ions. In recent studies, nanostructured carbon materials, such as carbon nanotubes (CNTs), carbon fiber and graphene, have been considered as intercalation materials of LDHs. For example, Huang et al. prepared composites by simply mixing CoAl-Layered double hydroxides and graphene oxide nanosheets with a maximum specific capacitance of 581.6 F g^{-1} at 2 A g^{-1} [11]. He et al. fabricated GNS/NiCoAl-LDH composites by a facile hydrothermal method that mixing the $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and urea solution with GO, exhibited a specific capacitance of 1736 F g^{-1} at 2 A g^{-1}

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[15], however, it is unavoidable that LDHs and carbon materials could always stack together with themselves via van der Waals forces and diminish the capacitance performance. A lot of efforts have been devoted to prevent the above situation. Zhang et al. prepared porous CoAl-LDH nanosheets/graphene composite as electrode material for supercapacitors by facile and one-pot gas–liquid interfacial method, which exhibited a specific capacitance of 341.2 F g^{-1} at 10 A g^{-1} [16]. Li et al. used γ-Al_2O_3-coated CNTs as a support to grow NiAl-LDHs and the small NiAl-LDHs nanosheets can directly grow on the surface of CNTs to form NiAl-LDHs/CNTs composite, which yield a specific capacitance of 1500 F g^{-1} at 1 A g^{-1} [17]. Ge et al. prepared self-assembled NiAl-LDH/GO superlattice by a co-feeding protocol with a specific capacity of 129 Ah/kg at 1 A g^{-1}, which is about 2 times that of NiAl-LDH [18].

In this paper, we prepared GO/CoAl-LDHs composites by means of electrostatic self-assembly method. Since LDHs materials are a class of lamellar crystals and unlike van der Waals heterostructures, LDH layers are positively charged. The hydrated exchangeable anions are located in the interlayer gallery for keeping charge balance [19,20]. CoAl-LDHs could be exfoliated into positively charged CoAl-LDHs-NS by continuous stirring in formamide. Due to the presence of oxygen-containing groups, GO could also be exfoliated into negatively charged GO nanosheets via ultrasonicating in deionized water. The GO/CoAl-LDHs composites obtained from CoAl-LDHs-NS and GO nanosheets are expected to be prepared by face-to-face self-assembly method due to the fact that the delaminated layered CoAl-LDHs and GO are nanosheets with opposite charges.

The face-to-face self-assembly method has the following advantages: a) negatively charged GO nanosheets mixing with positively charged CoAl-LDHs-NS face-to-face via electrostatic self-assembly method effectively improves the surface area utilization rate of GO nanosheets, which could make maximum contact with Co atoms and lead to a fast electron transport during charge–discharge processes. b) The self-assembly process can decrease the restacking of CoAl-LDHs-NS and avoid aggregation of RGO nanosheets, which increase the interlayer spacing and offer abundant space for the diffusion of an electrolyte. As a result, it optimizes the electrical conductivities of the composites [11].

However, the carboxyl, hydroxy and epoxy groups on the edge of GO destroy the conjugate network of GO, which would lead to the defects. Furthermore, other atomic-scale lattice defects modify the electronic structure of GO and serve as strong scattering centers that can affect the electrical transport [21]. Therefore, the reduction of GO is necessary to recover the conjugated plane and improve electrical conductivity. In order to reduce GO to generate RGO with several oxygen containing groups, many reducing agents, such as hydrazine, hydrobromic acid, dimethylhydrazine, etc, are widely used [22–29]. Because of their toxicity and harmfulness, it is imminent to look for a cleaner route for the reduction of GO. To minimize the defect of GO, we prepared GO/CoAl-LDHs composites by means of electrostatic self-assembly method and then generated RGO/CoAl-LDHs composites in hydrothermal conditions [30]. Under high temperature and pressure in a closed system of hydrothermal conditions, the π-conjugated structures of RGO nanosheets were increased, which minimize the defects of GO and improve the conductivity of the material; Furthermore, it is relatively clean compared to chemical reduction using hydrazine or sulfonate, which can introduce non-carbon impurities [31].

The self-assembly process of the RGO/CoAl-LDHs composite is illustrated in Fig. 1. It can be divided into 3 steps. First, the GO and CoAl-LDHs were exfoliated into negatively charged GO nanosheets and positively charged CoAl-LDHs-NS, respectively. Second, CoAl-LDH-NS and GO nanosheets were uniformly mixed, and CoAl-LDH-NS were assembled on GO nanosheets via electrostatic attraction, forming the GO/CoAl-LDHs composite. Finally, the GO/CoAl-LDHs composite was reduced to generate RGO/CoAl-LDHs composite using a hydrothermal method.

2. Experimental section

2.1. Material synthesis

2.1.1. Preparation of negatively charged colloidal GO nanosheets

Graphene oxide (GO) was synthesized from natural flake graphite (Sigma–Aldrich) using a modified Hummers method. In a typical synthesis, the graphite powder (1 g) and $NaNO_3$ (0.5 g) were added to 98% H_2SO_4 (23 mL), which was stirred for half an hour in an ice bath. $KMnO_4$ (3 g) was added gradually under stirring and the temperature of the mixture was kept below 5 °C. Under this temperature, the reaction was maintained for 1.5 h. After that, the above mixture was kept at 35 °C for 2 h. Next, deionized water (40 mL) was gradually added, keeping the reaction in an ice bath. The mixture was then heated at 95 °C for 30 min. Then the mixture was further treated with deionized water (100 mL) and 30% H_2O_2 solution (15 mL). The obtained GO was first washed with 5% HCl solution (800 mL), and then washed with deionized water at 10,000 rpm several times. After filtration and drying in vacuum at 60 °C, the GO was obtained in the form of black flakes [32]. Then, 0.05 g, 0.1 g, 0.15 g and 0.2 g of dried GO were suspended in 100 mL, 200 mL, 300 mL and 400 mL of deionized water, respectively. After ultrasonicating for 3 h, the colloidal GO was prepared. Followed by centrifuging at 6000 rpm for 15 min, the exfoliated negatively charged colloidal GO nanosheets were obtained in the supernatant. The concentration of the GO nanosheets is approximately 0.5 mg mL^{-1}.

2.1.2. Preparation of positively charged colloidal CoAl-LDHs-NS

CoAl-LDHs were prepared by a hydrothermal treatment [33]. $CoCl_2\cdot 6H_2O$ (3.0 mmol), $AlCl_3\cdot 9H_2O$ (1.5 mmol), and arginine (3.0 mmol) were dissolved in deionized water (50 mL) with n (Co^{2+}): n (Al^{3+}) = 2:1. After continuous stirring for 30 min, 4 mmol urea was added to form a stable solution. Then, 2 M NaOH was added to the above solution drop by drop under magnetic stirring to adjust the pH value to reach 13. The aqueous mixture was then transferred to a 100-mL Teflon-lined autoclave and reacted at 160 °C for 12 h. After cooling down to room temperature, the products were filtered and then washed with deionized water and alcohol several times to obtain electrically neutral charged wet CoAl-LDHs products. A typical amount of wet CoAl-LDHs was dispersed into 400 mL of formamide and stirred at a speed of 160 rpm for 2 days. The resulting pink translucent colloidal suspension was further treated by centrifugation at 4000 rpm for 15 min to remove the unexfoliated parts of the CoAl-LDHs. After centrifugation, a pink transparent solution (positively charged CoAl-LDH-NS) was obtained.

2.1.3. Preparation of self-assembly GO/CoAl-LDHs composites

The positively charged CoAl-LDHs-NS and negatively charged GO nanosheets combined with each other face-to-face via the electrostatic self-assembly method. The GO/CoAl-LDHs composite was synthesized by adding a specific amount of negatively charged colloidal GO nanosheets to the positively charged colloidal CoAl-LDHs-NS. Specifically, 100 mL, 200 mL, 300 mL and 400 mL of the prepared 0.5 mg mL^{-1} colloidal GO nanosheets were added to 400 mL of colloidal CoAl-LDHs-NS drop by drop under constant stirring, which were denoted as GO/L-1, GO/L-2, GO/L-3 and GO/L-4, respectively. The precipitation was obtained by centrifugation after incubating for 1 day at room temperature.