Communication

Architecture of Co-layered double hydroxide nanocages/graphene composite electrode with high electrochemical performance for supercapacitor

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ABSTRACT

A facile hydrolysis method was applied to fabricate high-performance Co-layered double hydroxide (LDH) nanocages/graphene composites for supercapacitors. The materials exhibit enhanced rate capability than the counterpart electrode free of graphene while maintaining a high specific capacitance. In addition, such Co-LDH nanocages/graphene composites display an excellent cycling stability; the capacitance retention of Co-LDH nanocages/graphene composite electrode remains 90.4% after 10000 cycles at a current density of 2 A g^{-1}. The integration of high capacity of double hydroxide and outstanding conductivity of graphene makes the delicately-designed composites promising candidates for electrode materials for supercapacitors.

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Electrochemical capacitors (ECs), i.e., supercapacitors, have drawn much attention in energy storage applications owing to their high power density, fast charge/discharge rate and excellent cycling stability compared with other chemical energy storage devices [1,2]. Basically, ECs can be divided into electrochemical double layer capacitors (EDLCs) and pseudocapacitors [3]. For EDLCs, carbon-based materials, such as carbon aerogels [4], carbon nanotubes [5,6], graphene [7,8] and other carbon-related materials [9] are the primary electrode materials because of their large surface area, excellent electrical conductivity, and extraordinary cycling stability. However, their capacitances are relatively low due to the inherent limitation of the electrostatic surface charging mechanism. In contrast, the specific capacitance of pseudocapacitors is much higher than that of EDLCs as electrode materials of pseudocapacitors (including conducting polymers [10–12], transition metal oxides [13–16] and their relative composites [17–19]), which hold higher theoretical capacity owing to fast and reversible faradaic reactions at the electrode/electrolyte interface, affording

optimum supercapacitive properties than carbon-based materials [20,21]. Therefore, advanced pseudocapacitive materials based on transition-metal oxides/hydroxides have been receiving wide attention.

Metallic layered double hydroxides (LDHs), which are also called hydrotalcite-like clay, consist of divalent and trivalent metal cation layers that coordinated to hydroxide anions [22–26]. A general formula of LDH has been proposed, i.e., $[M_{1-X}^{2+}M^{3+}(OH)_2]^{X+}[A_{n-x/n} \cdot mH_2O]^{X+}$, where M^{2+}, M^{3+} and A^{n-} are bivalent, trivalent metal cation and the charge-balancing anion, respectively [27,28]. LDHs have been involved within a wide range of applications, such as separation, drug delivery and catalysts. LDHs have also attracted increasing interests as promising electrode materials for supercapacitors due to their relatively high specific capacitances, high redox activity, low cost, and their environmentally friendly nature [23,29]. Even though the aforementioned advantages, the rate capabilities of LDHs at a high current density are rather poor due to their intrinsic semi-conductor nature, which degrades their overall performance as active materials for ECs [23,30]. In addition, the volume change during charge/discharge cycles may result in active material exfoliation or peeling off, which will further limit the long-term running stability. In order to upgrade the performance of LDHs in ECs, these

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issues should be properly addressed. The design of rational morphology and structure feature of LDH materials is one effective method to buffer the volume change and obtain larger surface area and accessible channels that facilitate ion diffusion and transfer [31]; on the other hand, the incorporation of high conductive nanostructured carbon materials (such as carbon nanotube, graphene) into the LDH composites cannot only improve the rate capability, but also prevent LDH from agglomeration to enhance the cyclability [21,32,33]. Herein, Co-LDH/graphene composites with a variety of mass ratios were fabricated by a facile hydrolysis method. Among carbon materials, graphene holds large specific surface area and high conductivity. The combination of high capacity of double hydroxides and outstanding conductivity of graphene would improve their electrochemical performance due to their synergistic effects. The surface area of the composite is larger than pure Co-LDH electrode, which will facilitate ion diffusion and transfer. The prepared Co-LDH/graphene composites display excellent cycling stability and their capacitance retention as the electrode can reach 90.4% after 10,000 cycles at a current density of 2 A g^{-1}. Most importantly, the composite exhibits enhanced rate capability than a Co-LDH electrode while maintaining a high specific capacitance.

All raw chemicals were used without further purification. ZIF-67 nanoparticles as the precursor were prepared as follows. Cobalt nitrate hexahydrate (249 mg) were dissolved in methanol (25.0 mL) to form a solution. 2-Methylimidazole (328 mg) was dissolved in methanol (25.0 mL) to generate another clear solution. The latter of clear solution was poured into the former of pink solution rapidly under stirring and then stirring was stopped immediately after mixing with the component solutions. The solution was aged at room temperature for 24 h. After that, almost all of the purple precipitate settled at the bottom. The obtained powders were collected by centrifugation, washed with methanol three times and dried completely at 60 °C.

The as-prepared ZIF-67 was transferred into a round bottom flask containing 100 mg cobalt nitrate and 25.0 mL ethanol for 1 h under stirring at 40 °C. Finally, the product named as Co-LDH was collected by centrifugation, washed with anhydrous ethanol and dried at 60 °C overnight.

Homogenous composites of ZIF-67 and graphene were prepared by ultrasonic dispersion in a beaker containing 10 mL ethanol. The weight ratio of ZIF-67 to graphene varied as 3:1, 3:2 and 1:1, and the resultant composites were named as ZIF-67/G1, ZIF-67/G2, and ZIF-67/G3, respectively. Typically, the graphene was added into 10 mL of ethanol and sealed, ultrasonic treatment for 1 h. Then ZIF-67 was added into the aforementioned suspension and seal, ultrasonic treatment for another 3 h. Finally, the ZIF-67/graphene composites were collected by centrifugation, washed with ethanol and dried completely at 60 °C.

The 20 mg as-prepared ZIF-67/graphene composites (ZIF-67/G1, ZIF-67/G2, and ZIF-67/G3) were transferred into a round bottomed flask containing 100 mg cobalt nitrate and 25.0 mL ethanol for 1 h under stirring at room temperature. Finally, the obtained Co-LDH nanocages/graphene composites named as Co-LDH/G1, Co-LDH/G2, Co-LDH/G3, respectively were collected by centrifugation, washed with anhydrous ethanol and dried at 60 °C overnight.

The surface morphology and microstructure of as-prepared samples were analyzed by a scanning electron microscope (SEM, Hitachi SU8010) and a transmission electron microscope (TEM, JEM-2010F) with an accelerating voltage of 200 kV. The crystalline structures were characterized using a powder X-ray diffraction (Rigaku 2500) system equipped with Cu $K\alpha$ radiation ($\lambda = 0.154$ nm). The diffraction data were collected at a scan rate of 6°/min from 10° to 80°. The surface electronic states of the electrode materials were identified by X-ray photoelectron spectroscopy (XPS, ESCALAB-250). Nitrogen

adsorption–desorption isotherms were obtained using a Quantachrome Autosorb-iQAutomated Gas Sorption System at 77 K. And the specific surface area was calculated by the Brunauer-Emmett-Teller (BET) model.

Electrochemical performance was measured by mixing the sample (Co-LDH, Co-LDH/G1, Co-LDH/G2 and Co-LDH/G3), acetylene black and nafion as the binder at the ratio of 85:10:5 (wt%). Then the mixture was coated onto Ni foam to produce these electrodes. Subsequently, these electrodes were dried at 60 °C in vacuum overnight. The loading amount of these electrodes are ∼2 mg. Electrochemical measurements were carried out on an electrochemical working station (CHI660E, CH instrument, Shanghai) with a three-electrode electrochemical cell. The working electrode was the Co-LDH nanocages/graphene composite. A platinum plate was the counter electrode and a saturated calomel electrode (SCE) was used as reference electrode. The electrolyte was 1.0 M KOH aqueous solution. Then cyclic voltammetry was used to investigate its activity. Its charge/discharge ability was measured by a galvanostatic test.

The specific capacitance of the system was calculated from galvanostatic charge–discharge curves according to equation [21,30]:

$$C_s = \frac{I\Delta t}{m\Delta v}$$

where I (A) is discharging current, Δt (s) is discharging time, ΔV (V) is potential drop during discharging process, and m (g) is mass of the active materials. The mass of active material was achieved by a microbalance (Sartorius BT125D, Hamburger, Germany) with an accuracy of 0.01 mg. And the volumetric capacitance was calculated by using pellet method.

Metal organic frameworks (MOFs) are a new class of highly porous materials with the ability to tune sizes and shapes, which makes MOFs excellent precursors to obtain target products with desired morphologies [34]. Zeolitic imidazolate frameworks (ZIF), as a member of MOFs, show excellent chemical stability and thermal robustness which can be a perfect template to prepare hollow structure [35]. Cobalt ions and methyl imidazole self-assemble to forge ZIF-67 with sod topology, which can be easily removed in polar environment [36,37]. Using the rhombic dodecahedral ZIF-67 as the precursor, hollow polyhedral nanocages were successfully prepared. Panoramic views from the SEM images (Fig. 1a) show that the sample consists of uniform nanocages free of impurity. Magnified SEM images (Fig. 1b) provide clear architectures of the nanocages. The nanosheets assembled with a surface stacking constitute for the polyhedral shell which well maintains the morphology and dimensions of the ZIF-67 templates. ZIF-67 templates were fabricated by mixing cobalt nitrate and 2-methylimidazole in methanol, and the mixture was followed with being aged under ambient conditions for 24 h. The shape of ZIF-67 is a rhombic dodecahedron with a uniform grain size distribution (Fig. S1a). And the XRD pattern of synthesized ZIF-67 matches well with the simulated counterpart (Fig. S2), demonstrating that the as-synthesized ZIF-67 are phase-pure. The component of the Co-LDH nanocages was analyzed using energy dispersive spectroscopy (EDS, Fig. 1g). Only a trace quantity of C is detected in the sample, indicating that the hydrolysis of the ZIF-67 templates was almost completed. Because of the development of nanosheets, its microstructure is fairly difficult to be well identified from the SEM images, and thereof TEM analysis must be applied (Fig. 1c). Co-LDH nanocages can be further observed, from which the inner cavity is clearly revealed by the contrast between the shells and the hollow interiors, consistent with the EDS analysis. Morphology and structure of Co-LDH nanocages/graphene composites whose uniformity of mixing has no more changes compared with ZIF-67/graphene composites (Fig. S1b−d), are shown in Fig. 1(d−f). TEM images have also confirmed the morphology of LDH nanocages and graphene (Fig. S3).