Chemical Engineering Journal 289 (2016) 85–92

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Mesoporous graphene-layered double hydroxides free-standing films for enhanced flexible supercapacitors

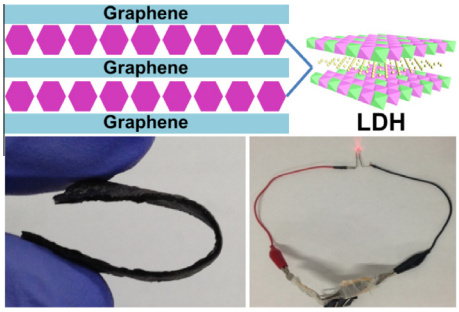
Ruikang Zhang, Hongli An, Zhenhua Li, Mingfei Shao *, Jingbin Han, Min Wei

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

HIGHLIGHTS

- Free-standing graphene oxide/layered double hydroxide (LDH) films were fabricated by flow-directed assembly.
- Mesoporous reduced graphene oxide (rGO)/LDH films formed after a reduction process.
- Embedded LDH nanosheets act as mesopore-creating guest.
- Flexible rGO/CoAl-LDH//rGO all-solid-state asymmetric SC demonstrates an excellent performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 October 2015
Received in revised form 12 December 2015
Accepted 22 December 2015
Available online 2 January 2016

Keywords:
Free-standing film
Graphene
LDH
Mesoporous
Supercapacitor

ABSTRACT

Two-dimensional graphene materials as supercapacitors electrode have attracted tremendous attention owing to their high surface area and exceptionally electrical conductivity, while it is still a great challenge to achieve desired mesoporous graphene electrodes as the easy aggregation of graphene nanosheets. Here we report the design and fabrication of mesoporous free-standing reduced graphene oxide (rGO)-based films by introducing layered double hydroxides (LDHs) nanoplatelets into the interlayer of rGO nanosheets. The nanostructures regular evolutions of rGO/CoAl-LDH free-standing film due to the embedding of LDHs were rationally investigated with detail experiments. Moreover, the flexible all-solid-state asymmetric supercapacitor device fabricated by using rGO/CoAl-LDH as positive electrode demonstrates a superior performance compared to most reported rGO-based free-standing film electrodes. The results presented here provide valuable insights into exploring mesoporous graphene-based free-standing architectures for highly-efficient and stable energy storage devices.

1. Introduction

Portable and flexible electronic equipment such as rollup displays and wearable devices have attracted increasing attentions, which stimulates strong interest in the exploit of new power resources with efficient energy output and satisfactory mechanical properties [1–3]. Electrochemical capacitors (ECs) or supercapacitors (SCs) are considered promising candidates for energy storage due to their advantages of higher power performance and better cycling lifespan over conventional batteries and dielectric capacitors [4–8]. In the search for new electrode materials, two dimensional (2D) nanomaterials present significant promise to achieve efficient flexible SCs, owing to their high surface areas as well as good electrochemical properties. Typically, graphene, as an ideal atom-thick 2D material, is expected to be potential building blocks of flexible SCs with the benefits of large surface area, remarkable conductivity and good mechanical properties [9–12]. Previous advances in graphene-based SCs have shown various film-like structures, such as free-standing [13–15] or supported thin films

* Corresponding author. Tel.: +86 10 64412131; fax: +86 10 64425385.
E-mail address: shaomf@mail.buct.edu.cn (M. Shao).

http://dx.doi.org/10.1016/j.cej.2015.12.088
1385-8947/

[16–19]. The suitable mesopores (especially 2–5 nm) of the electrode materials are critical to ease the mass transfer of electrolytes for fast redox reactions [20–23]. However, it is still a great challenge to achieve mesoporous graphene electrodes due to their easy self-aggregation through strong π–π stacking, which largely restrict their electrochemical overall performances.

To the fabrication of free-standing (denoted as FS) mesoporous graphene-based films, some interesting efforts have been demonstrated either by introduction of a nonvolatile liquid electrolyte [24] or by chemical activation [25]. The purpose of above strategies is to introduce a molecular guest among the graphene nanosheets so as to control the mesopore-size distribution of the obtained graphene films and thus enhance their charge–discharge properties. Despite of all these progresses, the power output of SCs constructed by porous graphene films is still unsatisfactory, mainly limited by their intrinsic electrical double-layer capacitors (EDLCs). Layered double hydroxides (LDHs) are a typical class of 2D structure anionic clays, which have been reported as excellent candidates for SCs owing to their high specific capacity and low cost [26–31]. However, the performances of LDHs materials for supercapacitors are usually limited by the poor conductivity and easy aggregation. To solve this problem, hybridizing LDHs with conducting materials, such as rGO, so as to improve the charge mobility and long-term stability, has attracted increasing interests. Although LDH/rGO materials have been widely investigated, most of the reported LDH/rGO are powdered materials with random dispersion [32–34], which cannot undergo fast redox reactions and meet the requirement of flexibility. This inspires us to further explore a flexible LDH/graphene free-standing film with ordered stacking and mesoporous nanostructure. The excellent conductivity of graphene can stimulate the electrochemically-active sites of LDHs and supply the rapid electrons transmission network, giving rise to greatly enhanced energy and power output.

Herein, we present the design and fabrication of a sophisticated mesoporous graphene/LDHs FS film *via* flow-directed assembly of graphene oxide (GO)/CoAl-LDH hybrid nanosheets followed by a reduction process, and demonstrate its excellent behavior in the flexible SCs. The graphene nanosheets serve as a conductive and robust network to facilitate the electron collection and fast transport; while embedded LDHs act as mesopore-creating guest to offer high ion-accessible surface area and provide extra pseudocapacitance simultaneously. The obtained asymmetric SC device fabricated by using mesoporous rGO/CoAl-LDH FS film gives a satisfactory overall performance: an energy density of 22.6 Wh kg^{-1} (at 0.09 kW kg^{-1}), a power density of 1.5 kW kg^{-1} (at 6 Wh kg^{-1}) and long life time (5000 cycles); much superior to that of reported rGO-based FS films. Therefore, the hybrid mesoporous FS films prepared by assembly of graphene and LDH nanosheets in this work demonstrate a promising strategy for the fabrication of fine-tuning flexible SCs electrodes in high efficiency energy storage devices.

2. Experimental

2.1. Preparation of CoAl-LDH colloidal suspension

CoAl-LDH nanoplatelets were prepared by a coprecipitation method [35]. Typically, 40 mL of mixed salt solution containing $CoCl_2$ (0.2 M) and $AlCl_3$ (0.1 M) was added into 160 mL of NaOH solution (0.15 M) under vigorous stirring, followed by 30 min stirring. Pure LDH slurry was obtained after centrifuge separation and washing. Then the LDH slurry manually dispersed in 150 mL of deionized water and hydrothermally treated in autoclaves at 100 °C for 12 h, resulting in a stable homogeneous colloidal suspension (~3 mg mL^{-1}).

2.2. Fabrication of rGO/CoAl-LDH FS films

Graphite oxide was prepared using a Hummer's method [36]. After undergoing the exfoliation via sonication for 2 h, the GO colloidal suspension (~6 mg mL^{-1}) was obtained. CoAl-LDH suspension (~3 mg mL^{-1}) with different volume (1 mL, 2 mL, 3 mL and 4 mL) was added into a GO suspension (10 mL, ~6 mg mL^{-1}) to obtain GO/CoAl-LDH colloidal suspention with LDH/GO mass ratios of 5 wt%, 10 wt%, 15 wt% and 20 wt%, respectively. The resulting GO/CoAl-LDH suspention was filtered by using a cellulose filter film (diameter: 6 cm; pore size: 0.2 μm) under vacuum, followed by drying in air for 24 h. A GO/CoAl-LDH FS film was achieved after peeling it off from the cellulose filter. In order to obtain rGO/CoAl-LDH FS film, the GO/LDH FS film was positioned on the upper wall of the Teflon vessel that has been preloaded with hydrazine solution (0.5 mL). The vessel was then sealed inside stainless steel autoclave at 85 °C for 12 h. The rGO/CoAl-LDH FS film was placed at 60 °C for 12 h in vacuum drier to remove gases possibly adsorbed on the surface. Similar method was used to fabricate rGO film without the addition of CoAl-LDH colloidal suspention.

2.3. Preparation of solid electrolyte

The PVA-KOH solid electrolyte was prepared as follows: PVA (5.0 g; molecular weight: 75,000–80,000) and KOH (4.2 g) were dissolved in 50 mL water with vigorous and continuous stirring for 4 h at 85 °C, until a complete dissolution and formation of a jell-like solution. The resulting gel was heated at 60 °C in a vacuum oven to evaporate excess water.

2.4. Fabrication of rGO/CoAl-LDH based SC device

The asymmetric SC device was fabricated by assembly of a PVA-KOH solid electrolyte membrane between the rGO/CoAl-LDH and rGO FS film electrode. Nickel foam were used as the collector. After hot pressing at 60 °C for 5 min, the electrolyte was solidified to produce a sandwich structure.

2.5. Characterization

X-ray diffraction patterns of the samples were collected on a Shimadzu XRD-6000 diffractometer using a Cu Kα source, with a scan step of 10°/min and a scan range between 3° and 70°. The morphology of the samples was investigated using a scanning electron microscope (SEM; Zeiss SUPRA 55) with an accelerating voltage of 20 kV, combined with energy dispersive X-ray spectroscopy (EDX) for the determination of metal composition. Transmission electron microscopy (TEM) images were recorded with Philips Tecnai 20 and JEOL JEM-2010 high-resolution transmission electron microscopes. The accelerating voltage was 200 kV in each case. The surface roughness was studied using the atomic force microscopy (AFM) software (Digital Instruments, Version 6.12).

2.6. Electrochemical performance measurements

Electrodes were tested on a CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Co., China) in a three-electrode electrochemical cell using a 1 M KOH aqueous solution as electrolyte at room temperature. A Pt wire and a SCE were used as the counter and reference electrode, respectively.

The specific capacitance of the FS film samples was calculated from the charge–discharge curves based on the following equation:

$$C = \frac{I \times \Delta t}{m \times \Delta V} \quad (1)$$