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A facile approach towards direct transformation of benzoate into graphene under low temperature and study of its electrochemical properties

Hong Chen, Houwen Xiao, Hui Gao, Xiuhua Zhou, Wengong Zhang, Qidan Ling *

Fujian Key Laboratory of Polymer Materials, College of Materials Science and Engineering, Fujian Normal University, Fuzhou 350007, People's Republic of China

HIGHLIGHTS

- Transformation benzoate into graphene under mild reaction conditions.
- The obtained material shows a high BET surface area of 1240 m^2/g.
- Specific capacitance of the resultant supercapacitor is 202 F/g at 1 A/g.
- Capacitance retention after 1000 galvanostatic charge–discharge cycles is 96%.

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ABSTRACT

A facile approach to transform benzoate into porous few-layered graphene (PFLG) sheets under very mild reaction conditions (800 °C, without high-vacuum) was proposed. The obtained porous few-layered graphene (PFLG) sheets with high BET surface area of 1240 m^2/g and a pore volume of 1.18 cm^3/g was employed as electrodes for supercapacitor. A high specific capacitance of 202 F/g was achieved, and a slow decay rate of 3.8% per cycle during 1000 cycles was detected.

1. Introduction

Graphene [1,2], a monolayer of carbon hexagons consisting of sp^2 bonds, has attracted tremendous attentions for its remarkable mechanical, electrical, and thermal properties and its potential applications in supercapacitor [3–5], sensor [6], solar cell [7], polymer composite [8], hydrogen storage [9], and so on. Up to date, various methods have been investigated to prepare graphenes, including micromechanical exfoliation [10], epitaxial growth on SiC [11], and chemical vapor deposition (CVD) [12], etc. However, these methods are rather intensive energy and capital consumption. Chemical exfoliation of graphene oxide (GO) either by ultrasonic dispersion or rapid thermal expansion followed by chemical reduction provides a low-cost and scalable method to produce bulk quantities of graphene sheets (or more commonly referred as reduced GO (rGO)) [13,14]. Although the redundant functional groups can be removed by the reduction process, but it results in considerable disruption of the electronic structure of graphene [15].

It is well known that heat treatment of carbon-rich substances at the temperatures higher than 2000 °C is able to form well-developed graphitic structure, which is so call graphitization, but such reaction condition is costly and complicated [16]. Herein, we report an easy method for the synthesis of porous few-layered graphene (PFLG) sheets by means of templating method. This method involves direct transformation of benzoate into graphene at a moderate temperature (800 °C). The methodology is based on intercalation of carbon-rich substances into layered double hydroxides (LDH), using lattice orientation/confinement effects [17] to promote graphitization of carbon-rich substances at lower temperatures.

Layered double hydroxides (LDH) [18,19] with a general formula of $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}_{x/n})\cdot mH_2O$ is an anion-exchangeable crystal. The structure of LDH consists of positively

* Corresponding author.
E-mail address: chengh5678@126.com (Q. Ling).

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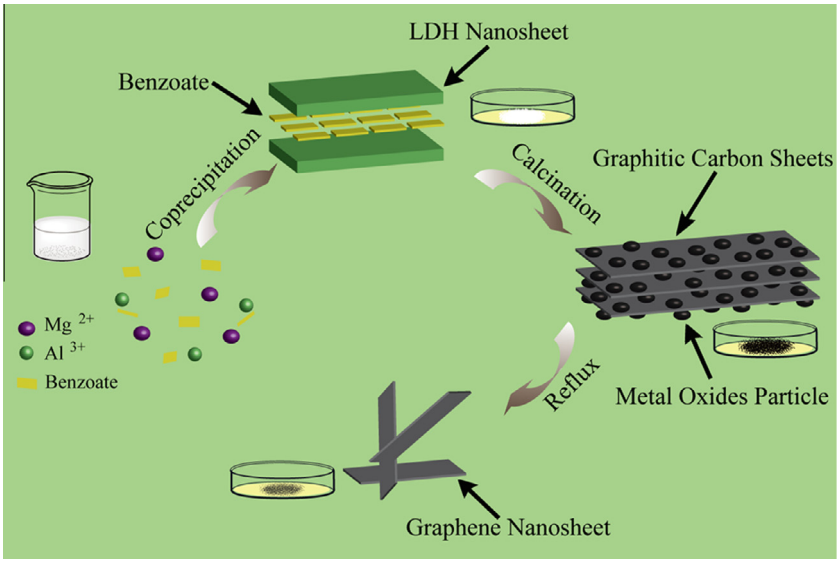

Fig. 1. Schematic illustration showing the experimental steps of the PFLG sheets.

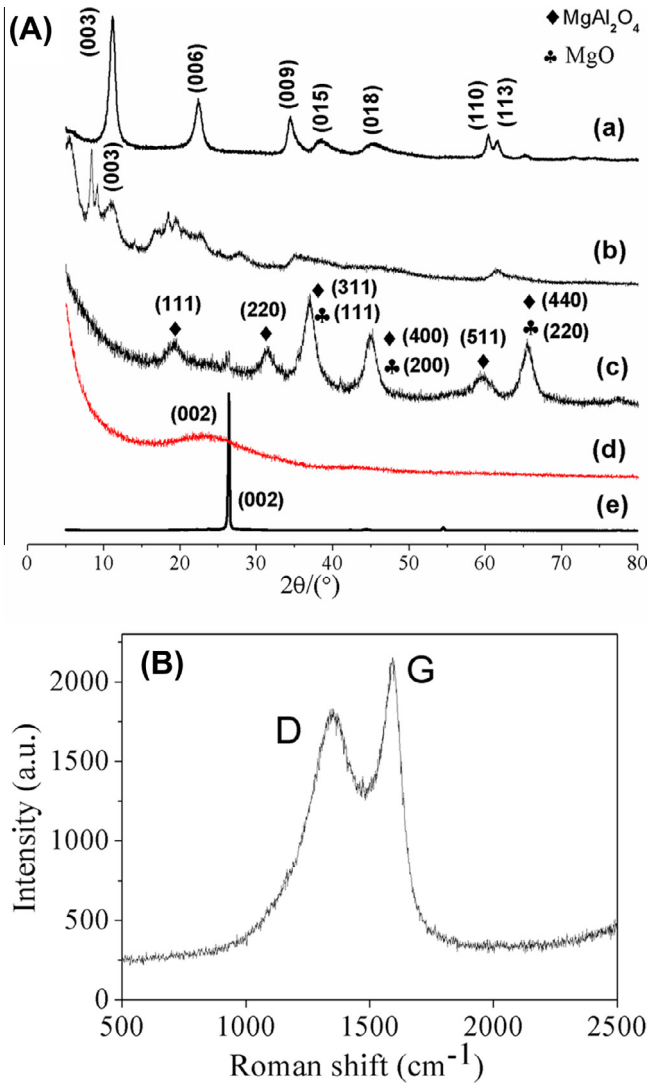

Fig. 2. A. X-ray diffraction patterns of LDH-pristine (a), LDH-BA^- (b), calcined-LDH-BA^- (c), PFLG sheets (d) and pristine graphite (e); B. Raman spectra of the PFLG sheets.

charged brucite ($Mg(OH)_2$)-like layers and interlamellar exchangeable anions, as well as water molecules, located in the interlayer space. M (II) and M (III) are respective divalent and trivalent metal cations in an octahedral hydroxide layers, and A^{n-} is anions between the hydrated interlayer galleries. The highly tunable interlayer compositions coupled with wide possible choice of anionic moieties and/or the variation of the host layer compositions affords a large variety of solids with versatile catalytic and ion exchange/intercalation properties. It is suggested that the heat preservation and lattice orientation effects of the confinement space in LDH enable the lowering of the classical temperature of graphitization and it is expected that, the regular arrangement of carbon atoms will induce the transformation into crystalline structure and the formation of a graphitic sp^2 bonded network [20].

On the basis of this concept, we propose to synthesize PFLG sheets in three steps (Fig. 1): (1) benzoates were intercalated into Mg/Al layered double hydroxides (LDH) by a coprecipitation method to obtain nanohybrids, (2) calcination of the nanohybrids under relative low temperature (800 °C), (3) removal of the formed metal oxides by means of reflux in an acid solution. In step (2), the benzoates confined in the 2D galleries of LDH were converted into amorphous carbon, and then into few-layered graphene sheets. Meanwhile, the layered structure of LDH collapsed and subsequently led to in situ formation of metal oxides on the surface of few-layered graphene sheets.

2. Experimental

2.1. Chemicals

All the reagents and chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification. Deionized water was used throughout the experiments.

2.2. Preparation of porous few-layered graphene (PFLG) sheets

2.2.1. Synthesis of precursor

The samples were synthesized by a coprecipitation method at room temperature and were vigorously stirred.

1.08 g sodium benzoate was dissolved in the distilled water, this was considered as solution A. Solution B was 12.8 g aqueous solution of Mg $(NO_3)_2$ (30% mass ratio). Solution C was 6.25 g aqueous solution of Al $(NO_3)_3$, (30% mass ratio). Solution B and