



Graphene coated with controllable N-doped carbon layer by molecular layer deposition as electrode materials for supercapacitors



Yao Chen ^{a, b}, Zhe Gao ^a, Bin Zhang ^a, Shichao Zhao ^{a, b}, Yong Qin ^{a, *}

^a State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Science, Taiyuan 030001, China

^b University of Chinese Academy of Sciences, Beijing 100039, China

HIGHLIGHTS

- Coating of graphene with uniform polyimide layer by MLD without any surface treatment.
- A new way to fabricate N-doped carbon/graphene composites.
- Synergistic effect of combination of N-doped carbon and graphene.

ARTICLE INFO

Article history:

Received 18 November 2015

Received in revised form

27 February 2016

Accepted 9 March 2016

Keywords:

Graphene

Molecular layer deposition

N-doped carbon

Supercapacitor

ABSTRACT

In this work, graphene is coated with nitrogen-doped carbon layer, which is produced by a carbonization process of aromatic polyimide (PI) films deposited on the surfaces of graphene by molecular layer deposition (MLD). The utilization of MLD not only allows uniform coating of PI layers on the surfaces of pristine graphene without any surface treatment, but also enables homogenous dispersion of doped nitrogen atoms in the carbonized products. The as-prepared N-doped carbon layer coated graphene (NC-G) exhibited remarkable capacitance performance as electrode materials for supercapacitor, showing a high specific capacitance of 290.2 F g⁻¹ at current density of 1 A g⁻¹ in 6 M KOH aqueous electrolyte, meanwhile maintaining good rate performance and stable cycle capability. The NC-G synthesized by this way represents an alternative promising candidate as electrode material for supercapacitors.

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1. Introduction

Currently, carbon materials, such as carbon nanotube (CNT), activated carbon, carbon nanofiber and graphene (G) are attracting considerable interest due to their potential applications in catalyst, gas sensor, water purification, energy storage and so on [1]. For energy storage, they have been regarded as promising candidate as electrode material of supercapacitor, commonly providing high power density, good cycle efficiency and lengthy cycle life [2–5]. Among the carbon family, graphene is particularly attractive because of its large surface area, excellent electrical conductivity, good mechanical and chemical stability [3,6–8]. However, due to limited available specific surface area, the specific capacitance and power density of graphene in practical application are still unsatisfactory. Furthermore, the graphene electrode always presents poor cycling stability. With the intention to improve the energy

storage properties of graphene, considerable efforts have been dedicated to improving the effective specific surface area (SSA) through post treatment as well as novel synthesis methods. Graphene fabricated by microwave irradiation [9] or gas-based hydrazine [2] reduction of graphene oxide, or exfoliated at high temperature via thermal expanding [10] or at relatively low temperature but under vacuum [11] demonstrated exciting potential for high performance due to their rich single or few layered graphene sheets [12]. Post treatment was commonly conducted with KOH activation at high temperature [13], and a surface area as high as 3000 m² g⁻¹ and a specific capacitance of 550 F g⁻¹ can be achieved [6]. However, capacitance performance improvement achieved through the above-mentioned approaches still suffers from poor rate performance, which limits its application at large current density.

Some recent reports demonstrate that carbons doped with heteroatoms display enhanced capacitive performance compared to pristine carbons, meanwhile affording remarkable cycling stability [14–16]. Heteroatom doping (nitrogen, sulfur, phosphorus,

* Corresponding author.

E-mail address: qinyong@sxicc.ac.cn (Y. Qin).

boron or combination of them) is an effective approach to tailor the electronic property of carbons and improve the interfacial interaction between carbon electrode and electrolyte [17–19]. Among them, nitrogen doping has been recommended as the most appealing and effective way. Generally, introduction of nitrogen into carbon matrix can be accomplished by in situ synthesis of N-doped carbons using ammonia [8,19,20], ethylenediamine [21], melamine [19] or complex molecular [22,23] as precursors via chemical vapor deposition method, or treating carbons with nitrogen-containing chemicals under plasma [24,25] or thermal condition [16]. However, these ways usually result in low doping level, high defect density, poor stability, as well as non-uniform distribution of the heteroatoms. In order to overcome these disadvantages, various N-doped carbons were prepared by direct carbonization of nitrogen-containing polymers (eg. Polyimide [25], polyvinylpyridine [26], polyacrylonitriles [27], polyaniline [28] et al.) or biomass derivatives [29–31] to keep nitrogen atom being homogeneously dispersed in the basal plane of carbon matrix. Considering the low conductivity of N-doped carbons fabricated by this way, broad attention has been paid to combining them with graphene [14,32] or CNTs [33]. Such combination can develop their respective advantages, thus achieving high specific capacitance as well as excellent rate capacity. However, in most cases, graphene oxide or functionalized graphene were used as starting materials, which commonly results in various defects and cannot take full advantage of the intrinsic properties of pristine graphene.

Molecular layer deposition (MLD) is a novel gas-phase film deposition technology and allows coating on not only flat surfaces but also complicated substrates in a controllable and homogenous manner. Furthermore, precise control over coating thickness and the composition in molecular level can be provided via this method [34–36]. To date, various kinds of substrates, such as metal oxide [37,38], glass [39], silicon wafer [36], nanocarbon [40,41] and polymer [42], have been coated with diverse MLD materials. In general, the presence of surface active groups or defect sites on substrate is required to initiate film growth. Surface oxidation treatment or attached adhesion layer is usually employed to provide nuclear sites [43–45]. However, some previous researches reported that MLD is also feasible for pristine CNTs, which are rare in surface functional groups owing to the chemical inert nature of highly graphitic carbon. George and coworkers have demonstrated conformal coatings of several metal-organic MLD chemistries including alucone, titanicone, and zincone on bulk quantities CNTs without any surface treatment [40]. Our previous work also confirmed that pure organic polymers, such as polyurea can be directly deposited on CNTs by using MLD [41]. However, there is still no report for direct MLD on pristine graphene.

Herein, we report, for the first time, the deposition of aromatic polyimide (PI) on surfaces of pristine graphene by using MLD. The PI containing electron-rich N atom can attach on the surface and gallery of graphene sheets via hydrogen-bonding or π - π interaction. Subsequently, the as-deposited composites were annealed at high temperature to obtain N-doped carbon layer coated graphene (NC-G). In this study, aromatic polyimide was used as nitrogen source due to its high N content and simple synthesis procedure via MLD. Moreover, this method ensures stable doping of N atom into the composite without destroying the intrinsic properties of pristine graphene. In comparison with graphene, the NC-G exhibits great potential as electrode material for supercapacitor with remarkable capacitive performance.

2. Experimental

2.1. Materials

Graphene (layer number: 3–4, and lateral dimension: 100 nm–3 μ m) purchased from Carmery Materials Technology (China) was prepared by chemical intercalation-thermal expansion method. Both pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenyl ether (ODA) were obtained from J&K Scientific. All of the materials were used as received.

2.2. Preparation of NC-G

The synthesis procedure of NC-G includes the preparation of aromatic PI coated graphene (PI-G) and the following carbonization of the composites, as depicted in Fig. 1. First, PI-G was prepared by MLD of PI on graphene in a homemade hot-wall closed chamber-type atomic layer deposition (ALD) system. PMDA and ODA were used as precursors. Because both PMDA and ODA are solid at room temperature, heating (at 155 °C and 140 °C, respectively) is required to obtain reasonable vapor pressure. The ALD reactor in this study was maintained at 160 °C. A typical PI deposition cycle consists of a sequence of the following steps: PMDA dose, N₂ purge, ODA dose, N₂ purge. The MLD dose, exposure and purging times (in seconds) for PMDA and ODA are 5/10/30 and 3/8/30, respectively. The as-deposited materials with x cycles (x is the cycle number of MLD) were then placed into a furnace and carbonized with a two-step heating procedure to obtain xNC-G. In the first step, temperature was elevated to 300 °C in a heating rate of 3 °C/min and maintained for 1 h to allow complete imidization of the polymer. In the second step, temperature was further increased to 700 °C and held for 1 h to allow full carbonization of the polymer. In addition, pristine graphene, pure N-doped carbon (NC) and their physical mixture were also prepared for comparison. In order to prepare N-doped carbon, potassium bromide plates were used as substrate to deposit PI. After carbonization, the composites were dissolved in deionized water to remove the substrate. The remaining carbon film was then collected and dried under vacuum. Ethanol solution of G and NC with mass ratio of 1:2 and 2:1 were ground in mortar for 30 min to obtain physical mixture of them.

2.3. Characterization

Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) mapping were performed using a JEOL-JEM-2100F microscope. Scanning electron microscopy (SEM) pictures were observed by a Hitachi S4800 field emission scanning microscope operated at 5 kV. Fourier Transform infrared spectroscopy (FTIR) analysis was conducted with a Bruker Tensor

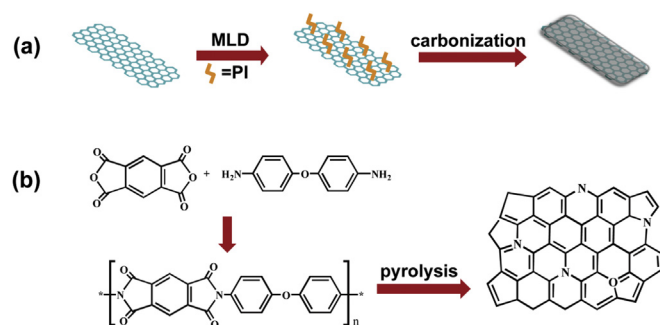


Fig. 1. Synthesis procedure of NC-G. a) Scheme of preparation process for NC-G. b) Chemical structure of polyimide and carbonized product.

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