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Nitrogen-doped graphene prepared by a millisecond photo-thermal process and its applications

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ABSTRACT

Doping graphene with heteroatoms such as nitrogen is a significant strategy to improve its electrochemical performance. Here, a unique millisecond photo-thermal process which is simple, safe for preparing N-doped Graphene (NG) under ammonia atmosphere was adopted. The obtained NGs were characterized by X-ray photoelectron spectroscopy (XPS), Raman spectra, Scanning Electron Microscope (SEM), and electrochemical techniques. The nitrogen content of the NG can as 14 times as that of original rGO according to the XPS results. The intensity ratio of D band to G band in Raman spectra is increased from 1.12 to 1.18, which also demonstrates the doping of nitrogen atoms and creation of some structure defects. The SEM picture clearly demonstrates that the space between graphene planes was significant enlarged. Furthermore, nitrogen adsorption/desorption test indicated that the specific surface area of NG ($267.3\,m^2\,g^{-1}$) is much higher than that of original rGO ($198.9\,m^2\,g^{-1}$), which indicates more surfaces are available after photo-thermal process. The electro-catalysis activity of the NG was characterized by electrochemical reduction of hydrogen peroxide (2 electron process) and oxygen (4 electron process). The hydrogen peroxide reduction potential at the NG electrode was 200 mV positive shift and the peak current increase 15 times compare to bare glassy carbon electrode. The oxygen reduction reaction (ORR) testes shows an obvious reductive peak in -0.39 V vs Ag/AgCl on the NG electrode, which demonstrated that the NG also has the catalysis effect on four-electron process. As well as that, the obtained NG was also used to assemble supercapacitances, it was found that the specific capacitance of NG achieved as high as 350 F g^{-1} with well cyclic stability and rate capability.

1. Introduction

Graphene, a two-dimensional sp^2-hybridized carbon material, has great promising applications in many fields [1]. Due to its unique physical and chemical properties, such as high specific surface area, favorable conductivity, excellent mechanical strength and feasibility of modification, graphene is considered to be an ideal candidate for the preparation of redox catalyzes and supercapacitor [2–6]. In order to improve its performance, much attention has been paid on its functional modification, recently. Usually, the modification strategies include doping with heteroatoms, combining with other electrochemical active materials, such as conductivity polymers, metal nanoparticles, metal oxides and etc. [7–10]. These methods mainly use the synergy or multi-functional effect of the ingredients. However, the preparation of composite materials sometimes damage parts of excellent properties of graphene, such as power density and cyclic stability [11–14]. Therefore, it is necessary to develop an alternative method to improve the electrochemical performances of graphene.

Chemical doping with heteroatoms is an effective method to intrinsically alter the physical/chemical properties of graphene, such as altering the electronic distribution and enriching the free charge carrier densities which would enhance the electrical or thermal conductivities [15–20]. In fact, this method is a common strategy to tailor the properties for carbon materials (0D nanodot, 1D nanotube, 2D graphene and 3D graphite). For example, after nitrogen plasma treatment, nitrogen-doped carbon nanotubes have a significant improvement in oxygen reduction kinetics which shows excellent performance in fuel cells and biosensors [21–23]. As well as that, the sulfur and nitrogen di-doped graphene presented a significant improve in supercapacitor performance [24–26]. Among the numerous dopants, such as boron, nitrogen,

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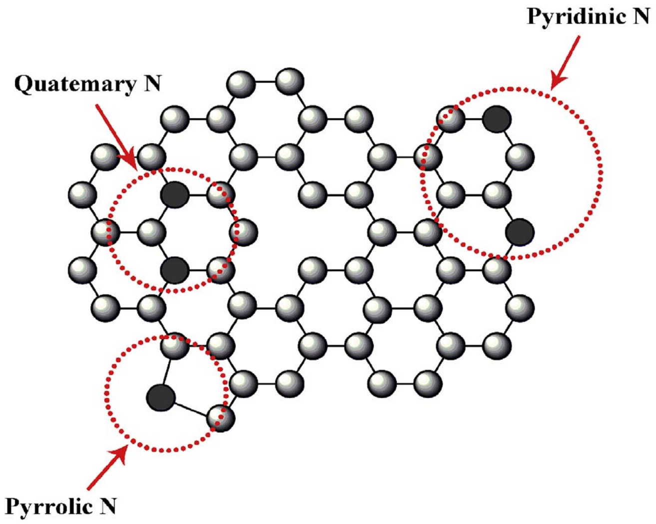

Fig. 1. Graphical representation of nitrogen-doped graphene. The hollow balls represent for carbon atoms and solid balls represent for nitrogen atoms.

oxygen, sulfur and etc., nitrogen atoms are considered to be an appropriate candidate for doping graphene because the atomic size of nitrogen is matched with carbon atoms and five valence electrons of each nitrogen atom are available to form strong valence bonds with carbon atoms [15,27–29]. Generally, when nitrogen atoms were doped into graphene, there are three bonding configurations within the carbon lattice, as shown in Fig. 1 including pyrrolic N, pyridinic N and quaternary N (also called graohitic N). Specifically, pyrrolic N refers to the N atoms bond in to five-member ring at the edges or defects of graphene and contributes two p electrons to the π system. Pyridinic N bonds with two C atoms which also exist in the edges or defects of graphene and contribute one p electron to the π system. Quaternary N refers to N atoms which substitute for C atoms in graphene lattice [15,22].

At present, the reported nitrogen-doped graphene preparation methods are mainly include two types: direct synthesis and post treatment [30]. The direct synthesis methods mainly include chemical vapor deposition (CVD), solvothermal and arc-discharge. In this method, nitrogen contained materials, such as pyrrole or pyridine, which are used to directly synthesize nitrogen-doped graphene or the nitrogen source, such as ammonia, is introduced with the carbon source to synthesize nitrogen-doped graphene [16,31–33]. The post treatment methods, generally apply high energy on graphene to break the C—C bond and doping the nitrogen atoms into graphene plane, mainly including thermal treatment and plasma treatment [34–36]. Comparing with direct synthesis methods, the post treatment methods are supposed to have a better controllability and practicability in produce high performance nitrogen-doped graphene. However, those post treatment methods usually has a significant disadvantage in time-comsuming. As well as that, due to the use of high energy, such as plasma, high temperature or high current, the post treatment methods might have problems of security and huge energy consumption.

Here, we report a novel millisecond photo-thermal method to prepare high performance nitrogen-doped graphene at extremely high speed with no security problem and high energy consumption. The mechanism of photo-thermal process is described below. When exposure under light or other radiation, the energy absorbed by materials is dissipated mainly via three processes: The first one is the radiation relaxation, which suggests the energy re-emits in the form of radiation. The second is charge separation, in which energy is consumed by generating the electron-hole pairs. The last is non-radiation relaxation, where the energy is released by the atomic lattice vibrations known as phonons. It is the third process that gives rise to the phenomenon of photo-thermal [37,38]. For bulk materials, the generated heat from non-radiation relaxation can be dissipated quickly and easily through the whole volume and to the surrounding. However, when the size of material approaches the nanoscale, the heat generated from this photo-thermal processe will be trapped in the individual nanostructures because heat is very difficult to transfer between nanostructure and be released to the environment [39–41]. The photo-thermal is a general phenomenon for materials with a high absorbance, high photo-thermal efficiency, low thermal conductivity and small size. When graphene is exposed to the flash light from a camera flash or xenon lamp, the inability to dissipate heat can lead to a high local temperature. This high temperature could break the C—C bond, create unsaturated carbon and defects on graphene plane [30]. When applied photo-thermal process on graphene under ammonia atmosphere, those unsaturated carbon and defects will react with ammonia to form various types of C—N bond (The schematic diagram is shown in Fig. 2). Here, the millisecond photo-thermal process was applied to prepare nitrogen-doped graphene and the products were characterized. Hydrogen peroxide and oxygen were employed to investigate the electrocatalytic performance of the nitrogen-doped graphene. Oxygen reduction reaction (ORR) is an important process in many energy storage or/and conversion system such as fuel cell. However, traditional noble metal catalysts for ORR are

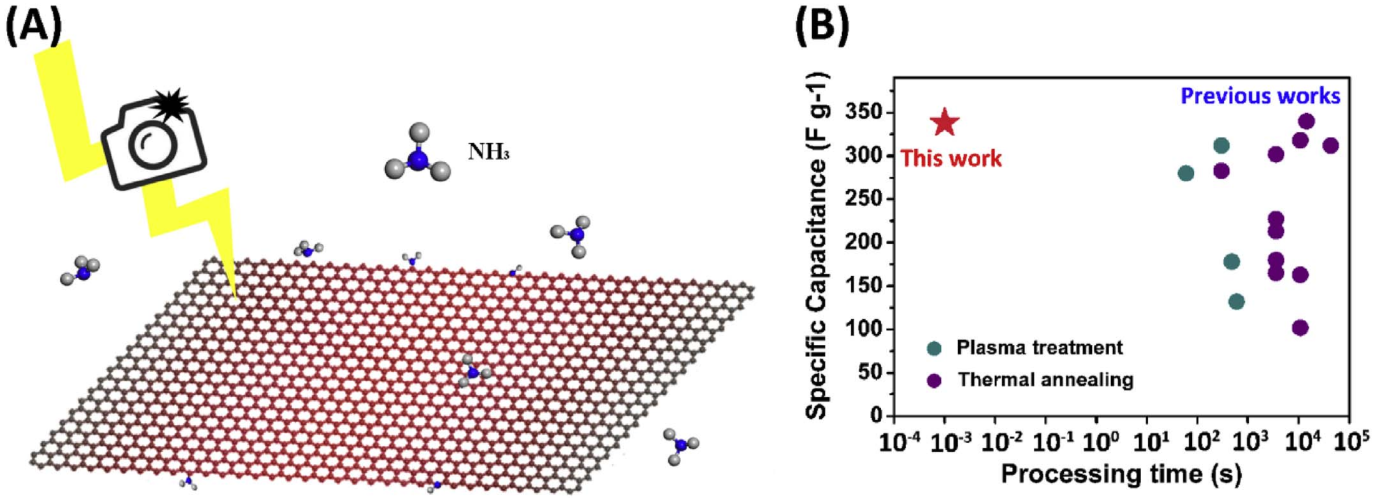

Fig. 2. (A) Is the schematics of graphene photo-thermal processed in ammonia atmosphere (The red color represents the high temperature generated from photo-thermal process). (B) Is the specific capacitance versus processing time of nitrogen doping for the state-of-the-art carbon materials. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)