Review

Nitrogen-doped graphene: Synthesis, characterizations and energy applications

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ABSTRACT

Nitrogen-doped (N-doped) graphene has attracted increasing attentions because of the significantly enhanced properties in physic, chemistry, biology and material science, as compared with those of pristine graphene. By date, N-doped graphene has opened up an exciting new field in the science and technology of two-dimensional materials. From the viewpoints of chemistry and materials, this article presents an overview on the recent progress of N-doped graphene, including the typical synthesis methods, characterization techniques, and various applications in energy fields. The challenges and perspective of N-doped graphene are also discussed. We expect that this review will provide new insights into the further development and practical applications of N-doped graphene.

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1. Introduction

Graphene, a two-dimensional (2D) sheet sp^2-hybridized carbon with special properties, such as planar structure, high surface area, excellent electrical and optical properties, and great mechanical properties (Young's modulus ∼1.0 TPa and a fracture strength ∼130 GPa) [1,2], has attracted so much attention since it was firstly exfoliated in experiment by Novoselov and Geim et al. [3,4]. During the last decade, great efforts were devoted to investigate the possible applications of graphene based on those above excellent properties. For example, hollow Pt-Ni decorated on graphene was fabricated, and the resultant composite exhibited much higher electrocatalytic activity as compared with bare Pt-Ni catalyst, owning to the significantly enhanced electrical conductivity and reduced particle aggregations [5]. Pt/graphene [6], Fe_3O_4/graphene [7], CoSe/graphene [8], and PtRuNi/graphene [9] were also synthesized, and all of them show the obviously improved performances.

The structures and properties of carbonaceous materials can be effectively tailored by heteroatoms doping. Following this line of thought, doping nitrogen (N) atoms into graphene can significantly affect the properties and performance of graphene-based materials. Peng et al. firstly reported the fabrication of nitrogen-doped (N-doped) graphene, and adopted it as the electrocatalysts in oxygen reduction reaction (ORR) [10]. It was revealed that the N-doped graphene exhibits superior electrocatalytic activity than most of other electrocatalysts. This has attracted great attention and further made N-doped graphene a hot topic. Just from that time, N-doped graphene developed rapidly. By date, many synthesis methods, including chemical vapor deposition (CVD) [11–20], thermal annealing [21–36], pyrolysis [37–41], arc-discharge [42–44], plasma treatment [45–47], N_2H_4 treatment [48–50], hydrothermal method [51–54], solvothermal method [55–58], microwave-assisted hydrothermal [59–61], wet chemical synthesis [62], microwave treatment [63], flame treatment [64], supercritical reaction method [65] and lyophilization-assisted heat treatment [66], have been exploited to prepare N-doped graphene. Graphene sheets doped with N atoms would generate three kinds of common bonding configurations within the lattice, including pyridinic N, graphitic N and pyrrolic N [67]. Among them, the mostly widely discussed was pyridinic N and pyrrolic N. Luo et al. reported the synthesis of single layer graphene doped with pure pyridinic N by thermal CVD of hydrogen and ethylene on Cu foils in the presence of ammonia [68]. Such pyridinic N doping in carbon materials was generally considered to be responsible for their enhancement of ORR activities. Zhang et al. synthesized the N-doped graphene through the thermal annealing method [69], and the resultant material shows a higher electrochemical activity towards methanol oxidation than Pt. These results demonstrated that N doping can really enhance the properties of graphene as compared with those of pristine graphene. Because of the intriguing structures and properties, N-doped graphene has been widely used in the fields of electronics [70], fuel cells [71], secondary batteries [72–74], supercapacitors [75,76], medical domain [77], and so on, and most of the materials can satisfy the expectations.

Recently, several reviews on graphene and graphene-based materials have been reported [1,78]. However, to the best known of our knowledge, a review of N-doped graphene includes the synthesis methods, characterization techniques, energy applications, as well as challenges and perspectives, is still emergently needed. From the viewpoints of chemistry and materials, this article will present an overview on the recent progress of N-doped graphene.

2. Preparation of N-doped graphene

The first employed methods for preparing N-doped graphene usually including chemical vapor deposition (CVD) and arc-discharge method, which were reported by Wei et al. [12] and Subrahmanyam et al. [79], respectively. Currently, there are many synthesis methods explored during such a short time. Table 1 summarizes the various methods for preparing N-doped graphene. The N contents, experimental details, applications and advantages for the synthesis/applications of N-doped graphene are also involved. Moreover, we have divided the synthesis methods into the one-step N doping and two-step N doping strategies. The one-step N doping strategy commonly include CVD, flame treatment and solvothermal method, while the two-step N doping strategy mainly include thermal annealing, pyrolysis, N_2H_4 treatment, wet chemical synthesis, microwave treatment, supercritical reaction, hydrothermal method, microwave-assisted hydrothermal method and lyophilization-assisted heat treatment. Detailed discussions on these methods are followed below.

2.1. CVD

CVD is one of the mostly used methods for preparing N-doped graphene [11–20], and it usually includes two precursors, N precursor and graphene precursor. The commonly adopted N precursor was NH_3 [11–14]. However, besides the gas phase precursor, pyridine and polypyrrole were also employed with the presence of carrier gases [15,16,19].

The synthesis procedures usually include the following essentials: first of all, a metal catalyst, like Ni and Cu, and a Si/SiO_2 plate, used as the substrate [11,13,17]. Then, a mixed gas containing carbon precursor and N precursor were introduced with the temperature increasing to a high position [17]. The C and N precursors decomposed and recombined into a new structure that looks like the graphene sheets on the substrate. Therefore, N-doped graphene can be prepared, as schematic illustrated in Fig. 1. The resultant morphology observation shows that most of the structure composed of few layers of graphene monomer, although single layer graphene could be occasionally detected [12].

The mechanism of this method can be postulated that graphene grew on the substrate and N atoms substitutionally doped into the graphene lattice. By incorporating N atoms into graphene, the physic and chemical properties of pristine graphene could be significantly altered [17]. The N contents of this method commonly various from 3.0 to 16 at.%. Moreover, it was reported that the influence factors of CVD includes gas ratio of mixture [12], and deposition conditions [13]. The reported highest N content by using CVD was 16.7 at.% [15], while the lowest N content was 0.25 at.% [17]. Additionally, the N content in N-doped graphene is a very important factor that influences the type of N atoms in graphene. The pyridinic N structure becomes favorable as the N content increases, which plays a key role on the enhancement of electrocatalytic activity and energy storage performance [13].

2.2. Thermal annealing

Thermal annealing is a popular method in the preparation of N-doped graphene owning to the simple and scalable characteristics. The N doping can be achieved through annealing graphene oxide (GO) under NH_3 atmosphere at a comparable high temperature [21–36]. Different temperatures would lead to different N contents as well as the diversity in performance activities [21,23]. The N contents of N-doped graphene prepared through this method usually range from 1.1 to 7.5 at.%.

Besides NH_3, other materials with high N contents were also used as the N precursors. For instance, GO annealed with urea can produce N-doped graphene [30], and the N content could reach as high as 10 at.%. The N content of this method depends mostly on the N content of N precursor. Sometimes, N doping also accompanied with other heteroatoms, such as sulfur and boron atoms, and the resultant products could show synergy effects between the N atoms and other heteroatoms [26,32].

2.3. Pyrolysis

Pyrolysis usually operated under a higher temperature than thermal annealing [37–41]. The pyrolysis of GO and N-containing precursors is a promising method for preparing N-doped reduced GO (rGO). The most extensively used N precursors were polyaniline [37], melamine [38,40,41], and polypyrrole [39]. The common process usually consisted of two steps, the combination between GO and N precursor and followed with pyrolysis of the as-formed composites. This method prone to produce a medium high N content that range from 2.0 to 8.0 at.%. As N-doped porous carbon materials prepared though pyrolysis of ethylenediaminetetraacetic