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Green synthesis of silver nanoparticles on nitrogen-doped graphene for hydrogen peroxide detection

Ye Tian[a], Fengli Wang[b], Yanxia Liu[b], Fu Pang[c], Xiao Zhang[b,*]

[a] Department of Physics, College of Science, Hebei North University, Zhangjiakou, Hebei 075000, China
[b] College of Information Science and Engineering, Hebei North University, Zhangjiakou, Hebei 075000, China
[c] Department of Electrical Engineering, Zhangjiakou Vocational College of Technology, Zhangjiakou, Hebei 075000, China

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ABSTRACT

We developed a novel Ag nanoparticles (NPs) supported on N-doped graphene (AgNPs/N-G) hybrid material that was used as an electrochemical sensor for H_2O_2 detection. AgNPs/N-G was synthesized by an environmentally friendly strategy with urea as the N-dopant and vitamin C as the reducing agent. Electrochemical measurements revealed a lower electrical resistance and higher electrocatalytic activity of AgNPs/N-G than undoped counterparts (AgNPs/reduced graphene oxide (rGO)). The AgNPs/N-G based sensor exhibited a fast response time (<2 s), a wide linear range (0.1-126.4 mM) and a low detection limit (1.2 μM). Moreover, the proposed sensor exhibited satisfying selectivity, reproducibility, and stability. These results indicated that AgNPs/N-G modified electrode could act as a promising nonenzymatic sensor for H_2O_2 detection.

1. Introduction

Hydrogen peroxide (H_2O_2), a common oxidizing agent and also an essential intermediate [1], is widely used in clinical, biomedical, environmental, pharmaceutical, and many other fields. However, H_2O_2 can induce potentially serious diseases in the body, such as cancer, infarction, atherosclerosis, and so on, posing a threat to the public health [2]. Therefore, the development of a technique for accurate, fast and reliable detection of H_2O_2 is of great importance. Many methods for the sensitive detection of H_2O_2 have been developed, such as chemiluminescence [3], spectrophotometry [4], fluorometry [5], and electrochemical method [6]. Among these methods, electrochemical method is considered as the most promising approach because of its high sensitivity, convenient operation and low cost. Meanwhile, research has shown that the nonenzymatic sensors can well avoid the disadvantages of enzymatic sensors, such as instability and poor reproducibility, providing an effective way for improving the electrocatalytic activity and selectivity toward the effective detection of H_2O_2[7].

The nonenzymatic sensors by using noble metal nanoparticles (NPs), such as Au, Ag, Pt, Pd, etc, have received increasing attention due to their high electrocatalytic activities [8]. Among these noble metal NPs, AgNPs have aroused growing interest in sensor applications because of their unique properties of biocompatibility, low toxicity and sustainable electrocatalytical activity [9]. Unfortunately, strong van der Waals force between AgNPs causes severe aggregations, resulting in a sharp loss in available electrochemical activity and detection sensitivity. In response to aggregation problem, AgNPs are usually immobilized on various organic/inorganic support materials [10–13], which are confirmed to be an effective strategy in protecting these metal NPs against agglomeration and improving their electrocatalytic activity and stability. Recently, graphene has been demonstrated as an advanced support material for metal or metal oxide NPs owing to its unique properties including large specific surface area, excellent electric conductivity and high chemical stability, and resulting NPs/graphene hybrids show great potential for diverse applications [14–16]. In particular, AgNPs/graphene hybrid has been prepared by various methods and used for the construction of nonenzymatic H_2O_2 sensor, exhibiting greatly improved electrochemical sensing performances [17–20].

On the other hand, chemical doping of graphene with heteroatoms can effectively tune its intrinsic properties [21]. Many studies have revealed that nitrogen doping graphene (N-G) further increases its conductivity and electrochemical performance [22–24]. Recent investigations have suggested that N-G provides a high efficiency in lithium ion batteries and supercapacitor [25,26], and also has a powerful electrocatalytic activity for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) [27]. In addition, the introduction of heteroatoms can provide more active sites and better chemical binding to anchor NPs, resulting

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* Corresponding author. Tel.: +86 3515623587.
E-mail address: Zhangxiao83690@163.com (X. Zhang).

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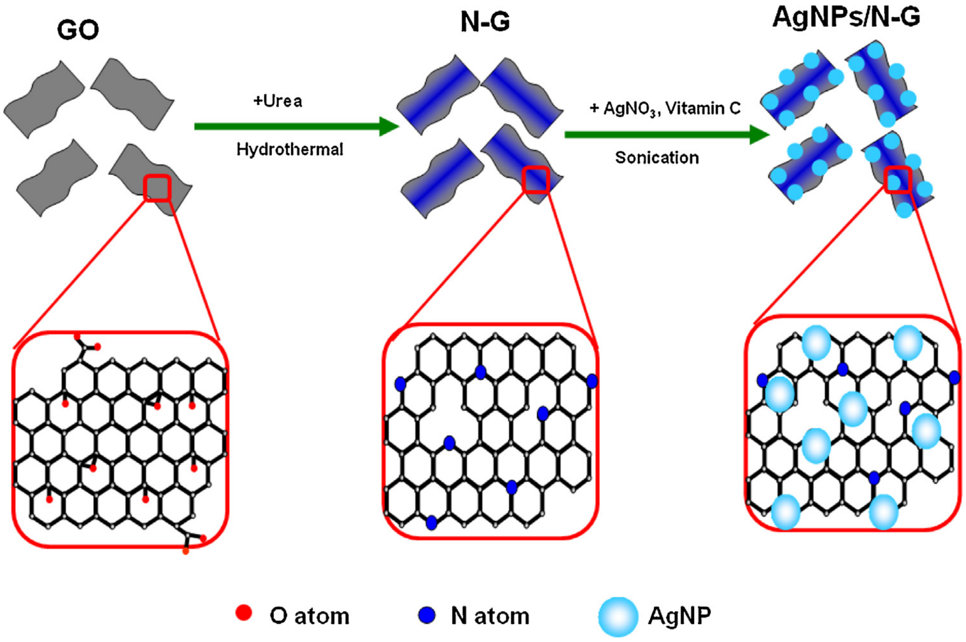

Fig. 1. Schematic diagram of the synthesis procedure of AgNPs/N-G.

in enhanced electrocatalytic activity and stability in comparison to undoped counterparts [28]. For example, Liang *et al.* [27] reported that the Co_3O_4/N-G showed surpassingly higher synergistic catalytic activity than Co_3O_4 or N-G alone, and Co_3O_4/graphene for ORR and OER. Borowiec *et al.* [29] fabricated AuNPs/N-G that exhibited a better electrocatalytic performance for chloramphenicol response than AuNPs/graphene. Jiang *et al.* [30] found that the CuNPs/N-G showed much enhanced electrochemical sensing to glucose due to the integration of N-G compared with pure CuNPs. Therefore, considering the outstanding electrocatalytic properties of N-G and AgNPs, it is reasonable to expect that AgNPs/N-G hybrid would possess a good electrochemical activity toward the electrochemical sensing of H_2O_2. Although a number of researches have been reported on the decoration of AgNPs on graphene or reduced graphene oxide (rGO) [31–34], few studies have managed to support AgNPs on N-G [35]. To the best of our knowledge, no attention has been paid to employ AgNPs/N-G as an electrochemical sensor for detection of H_2O_2.

In this study, AgNPs/N-G hybrid was used as a new electrode material for nonenzymatic sensing of H_2O_2. AgNPs/N-G was prepared through an environmentally friendly method (Fig. 1), in which N-G sheets were first obtained by using urea as the N-dopant, then AgNPs were deposited on N-G to form AgNPs/N-G by an *in-situ* chemical reduction method with vitamin C as the reducing agent. The morphology, structure and electrochemical properties of as-prepared AgNPs/N-G were examined in detail. *It was found that the AgNPs/N-G modified glass carbon electrode (GCE) exhibited excellent sensing performances for electrochemical detection of* H_2O_2.

2. Experimental

2.1. Synthesis of N-G

Graphite powder was provided by Qingdao Dongkai Grapite Co., Ltd. (Qing dao, China). All the chemicals were purchased from Tianjin Chemical Reagent Co., Ltd. (Tianjin, China), and used without further purification. GO was prepared from graphite according to the modified Hummer's method [36]. N-G was synthesized by a solvothermal route using urea as the nitrogen dopant [37]. In a typical procedure, 2 g of GO was dispersed in 500 mL of water under sonication for 1 h, then 50 g of urea was added into the GO solution under sonication for another 1 h. The above solution was sealed in a Teflon-lined autoclave and treated at 170 °C for 8 h. After the autoclave cooled down, the solid product was collected by centrifugation, washed repeatedly with distilled water and dried at 60 °C for 24 h. The undoped graphene or rGO was also prepared through the same procedure as N-G without adding ammonia in the first step.

2.2. Synthesis of Ag NPs/N-G.

AgNPs/N-G was synthesized by an *in-situ* chemical reduction method which involved the chemical reduction of $AgNO_3$ with vitamin C as reducing agent at room temperature. In brief, 1 g of N-G was dispersed in 100 *mL* of distilled water under sonication for 2 h, followed by the addition of 0.1 g of $AgNO_3$ under sonication for 5 min. Then, 50 mg of vitamin C was slowly added to the above suspension under continuous sonication for 20 min. Subsequently, the sediment was collected by centrifugation, washed repeatedly with distilled water and dried at 60 °C for 24 h. AgNPs/rGO was prepared through the same procedure as AgNPs/N-G by replacing N-G with rGO in the first step. AgNPs were also prepared through the same procedure as AgNPs/N-G without adding N-G in the first step.

2.3. Characterizations and electrochemical measurements

The as-synthesized samples were characterized by transmission electron microscopy (TEM, JEM-2100), X-Ray diffraction (XRD, Bruker D8 Avance), X-ray photoelectron spectroscopy (XPS, PHI 5000C), Raman spectroscope (Alpha 300R, WITEC), and thermogravimetric analysis (TGA, Q50 TGA). All the electrochemical experiments were carried out at room temperature. Cyclic voltammetric and amperometric measurements were performed on a PGSTAT-302N electrochemical workstation with a conventional three-electrode system, in which bared or modified GCE, Ag/AgCl electrode, and Pt wire were used as working electrode, reference electrode and counter electrode, respectively. Electrochemical impedance spectroscopy (EIS) was conducted on a Solartron SI1260 Impedance Analyzer. The GCE (3 mm in diameter) was polished with 0.3 and 0.05 mm alumina powder, respectively, and rinsed