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Short communication

# Enhanced electrochemiluminescence sensing platform using nitrogen-doped graphene as a novel two-dimensional mat of silver nanoparticles

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ABSTRACT

This communication clearly highlights the importance and necessity for a comparison investigation between nitrogen-doped graphene (N–G) and graphene as a two-dimensional mat of metal nanoparticles (NPs). We presented Ag NPs as a model of metal NPs for fabricating Ag/N–G and Ag/graphene nanocomposites, respectively. Compared with Ag/graphene nanocomposites, the Ag/N–G nanocomposites could facilitate the electrochemical redox process of $S_2O_8^{2-}$, and showed improved electrochemiluminescence (ECL) performances including increasing ~2.25-fold ECL intensity and decreasing ~330 mV onset potential of $S_2O_8^{2-}$, respectively. Further, the as-prepared pentachlorophenol ECL sensor based on Ag/N–G nanocomposites showed a wider linear range and lower detection limit than those of the Ag/graphene nanocomposites. This study could be potentially useful for understanding the role of N–G in electrochemistry, and opening a new aspect for exploring and developing potential application of N–G based materials in electrocatalysis and sensing fields.



## 1. Introduction

Nitrogen-doped graphene (N–G), a novel kind of graphene derivatives, has received considerable interests due to its advantages superior to graphene including much larger functional surface area, higher ratio of surface active groups to volume, and higher electrical conductivity [1]. In particular, as a new desirable two-dimensional mat, N–G possesses more chemically active sites for further anchoring metals [2,3] metallic oxides [4–6] and other metallic compounds [7]. For example, Liang et al. [5] fabricated $SnO_2$/N–G nanocomposite as a high-performance electrode material for Li-ion batteries, which showed higher capacity than $SnO_2$. Yang and coworkers [6] found that the ultrathin $MnO_2$/N–G nanocomposite displayed enhanced electrochemical capacitive performances than $MnO_2$. Yang et al. [2] reported that the Au/N–G nanocomposite facilitated robust immobilization of antibodies, promoted electron transfer and exhibited excellent electrochemical activity, and the proposed immunosensor displayed excellent analytical performance for metalloproteinase-2 detection. Further, our recent study [3] proved that compared with pure Cu NPs, the Cu/N–G nanocomposite showed enhanced electrocatalytic activity to glucose oxidation, and the presented sensor showed excellent performances for glucose detection including wide linear range, low detection limit, high sensitivity and fast response time. All these results indicated that just like graphene, N–G could be used as a two-dimensional mat to fabricated N–G-based materials, which showed improved electrochemical performances. However, the comparison investigation between N–G and graphene as the two-dimensional mat in the electrochemical research has rarely been reported which is of great theoretic and applicable value.

Electrochemiluminescence (ECL) has gradually become an important and powerful analytical tool in many fields, such as environmental pollutant determination, pharmaceutical analysis and immunoassay owing to its distinct advantages of simplicity, rapidity, sensitivity, controllability and low background [8–10]. Among the different ECL types that have been classified, the kind of cathodic ECL reaction systems involving peroxydisulfate ($S_2O_8^{2-}$) plays an important role [11,12]. Although the ECL of $S_2O_8^{2-}$ solution is quite simple and cheap, its ECL application in sensing was still scarce due to the relatively weak ECL intensity. Therefore, it is very urgent to explore more effective methods to improve the ECL of $S_2O_8^{2-}$ and further develop the ECL applications of $S_2O_8^{2-}$ solution.

In this communication, Ag NPs as a model of metal NPs for fabricating Ag/N–G and Ag/graphene nanocomposites were presented, and the ECL performance between Ag/N–G and Ag/graphene in $K_2S_2O_8$ solution was compared. Using pentachlorophenol

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(PCP) as an analyte model, Ag/N–G-based ECL sensor exhibited a wider linear range and lower detection limit than that of Ag/graphene, which could broaden the application of N–G-based material in the electrocatalytic and sensing fields.

## 2. Experimental

### 2.1. Chemicals and reagents

Graphite was purchased from Qingdao Tianhe Graphite Co., Ltd. PCP was purchased from Sigama Aldrich. $AgNO_3$, $K_2S_2O_8$ and glycine were purchased from Sinopharm Chemical Reagent Co., Ltd. Graphene oxide (GO) was prepared using modified Hummers method from graphite powders [13]. 0.1 M phosphate buffered solution (PBS, pH 7.0) was prepared by mixing stock standard solutions of $NaH_2PO_4$ and $Na_2HPO_4$. All the PBS solutions were air-saturated and doubly distilled water (18.2 MΩ; Millpore Co.) was used in all experiments and to prepare all buffers.

### 2.2. Apparatus

The morphologies were performed via transmission electron microscopy (TEM, Hitach H800, Japan). X-ray diffraction (XRD) was acquired on an X'Pert X-ray diffraction spectrometer (Philips, USA). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo VG Scientific ESCALAB 250 spectrometer with a Mg *K*α radiator. The ECL emission was detected using a model MPI-A electro-chemiluminescence analyzer (Xi'an Remex Analysis Instrument Co. Ltd. Xi'an, China) with 800 V photomultiplier tube voltage. The conventional three-electrode system was employed with a modified glassy carbon electrode (GCE) as the working electrode, an Ag/AgCl (saturated KCl) as reference electrode and a Pt wire as the counter electrode.

### 2.3. Preparation of samples

Ag/N–G was prepared according to the literature with some modifications [14]. Briefly, 5 mL solution containing 10 mg GO, 30 mg glycine and 15 mg $AgNO_3$ was sonicated for 2 h, and then the resulting mixture was poured into an alumina crucible which was gradually increased from room temperature to 500 °C under argon atmosphere and maintained for 2 h. Ag/graphene was prepared using the same method without adding glycine. Similarly, N–G was prepared without adding silver nitrate, and graphene was prepared using the same treatment without adding silver nitrate and glycine.

### 2.4. Preparation of the modified electrodes

6 μL of 2 mg $mL^{-1}$ Ag/N–G suspension was spread evenly onto the cleaned GCE surface and allowed to dry in ambient air for 24 h. For comparison, N–G/GCE, graphene/GCE and Ag/graphene/GCE were also prepared using a similar procedure.

## 3. Results and discussion

### 3.1. Characterization of the samples

The typical TEM images and the size-distribution histogram of Ag/N–G and Ag/graphene samples (Fig. 1A–C) show that Ag NPs ranging from 30 to 60 nm are evenly distributed on graphene and N–G sheet, respectively. Moreover, in both cases, particles appeared spherical, well dispersed and well-separated. And XRD

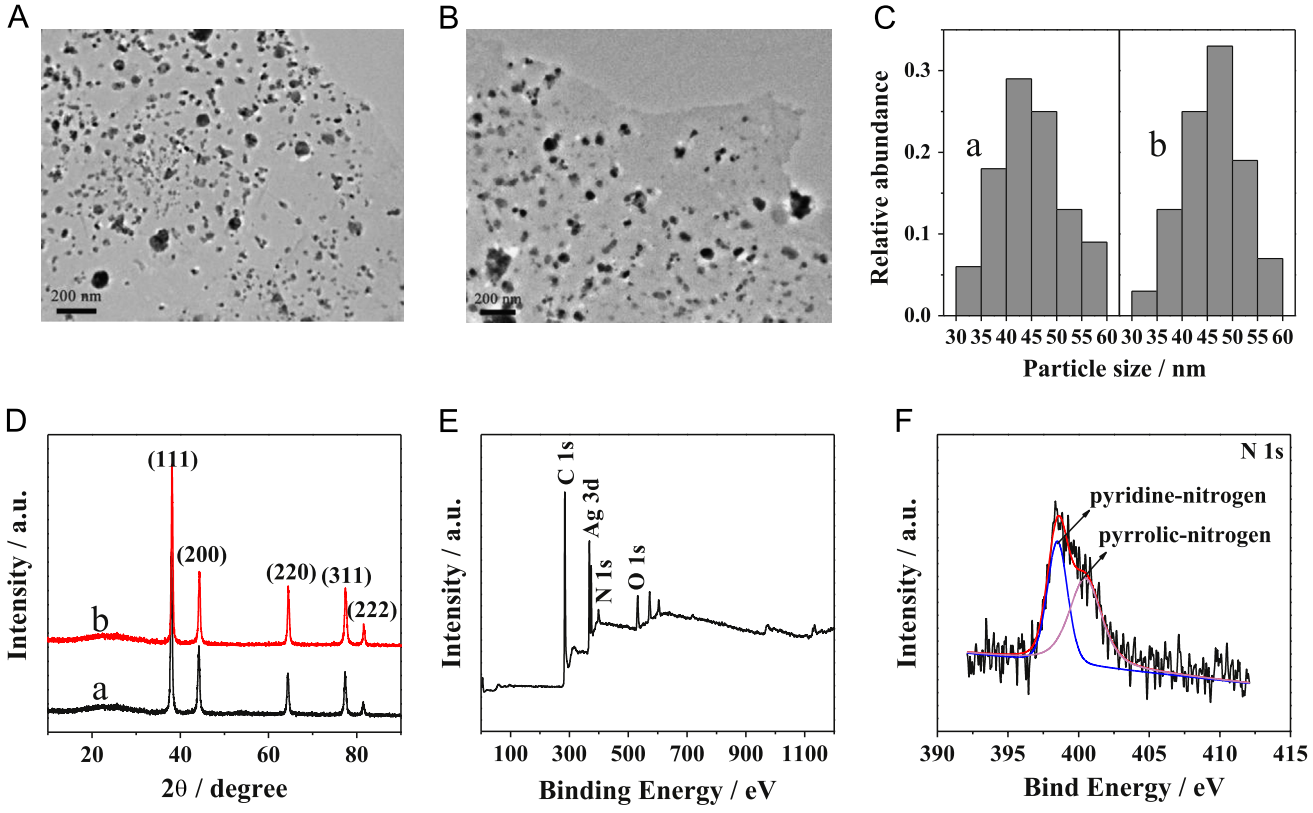


**Fig. 1.** TEM image of (A) Ag/N–G and (B) Ag/graphene. (C) The histogram of particle size distribution for Ag/N–G (a) and Ag-graphene (b). (D) XRD patterns of Ag/graphene (a) and Ag/N–G (b). (E) XPS spectra of Ag/N–G. (F) The high-resolution N 1s spectrum of Ag/N–G.