



Electrochemical sensing of nicotine using screen-printed carbon electrodes modified with nitrogen-doped graphene sheets



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ABSTRACT

Rapid and accurate detection of nicotine is important due to its detrimental effects on human beings and recent surge in the usage of electronic cigarettes. In this paper, we report an electrochemical sensor for nicotine detection by using screen-printed carbon electrodes (SPCE) modified with nitrogen-doped graphene sheets (NGS). NGS was synthesized and characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectrometry. Due to the superior electron transfer capability and the doped nitrogen atoms, NGS shows high catalytic activity for the electro-oxidation of nicotine, with a significant decrease in the overpotential. Using the NGS-based nicotine sensor, we obtained detection sensitivity at $0.627 \text{ mA} \cdot \text{cm}^{-2} \text{ mM}^{-1}$ with the limit of detection at 47 nM nicotine. Moreover, the sensor shows favorable selectivity and long-term stability for detecting nicotine in urine and tobacco samples.

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1. Introduction

Nicotine, properly called 3-(1-methyl-2-pyrrolidinyl) pyridine, is an alkaloid primarily found in various plants [1] and a highly tobacco-specific compound in cigarette smoke. It exists in the bodily fluids of the smokers and those non-smokers who are exposed to second-hand smoke. Although it has been found that nicotine may have therapeutic functions towards Tourette syndrome, Parkinson's diseases, depression and attention deficit disorder [2], it is more considered as a hazardous compound with detrimental effects to both smokers and non-smokers, causing a disease, as some studies have shown [3]. Because of these reasons and the fact that the level of nicotine is a crucial factor to judge the quality of cigarette products [4], determination of nicotine amount is of significant importance for medicine, toxicology, and tobacco industry.

Up to now, the primary approach for nicotine detection is based on chromatography, including gas chromatography (GC) [5,6] high performance liquid chromatography (HPLC) [7,8], gas chromatography mass spectrometry (GC-MS) [9,10] and HPLC-MS [11,12]. However, these methods involve complicated sample pretreatment and expensive instruments, limiting their usage. An alternative method is the electrochemical detection that has practical advantages, including rapid analysis, low cost, simple operation, and suitability for real-time detection. Up to till now, various electrochemical sensors have been

investigated for nicotine detection by using carbon-based materials such as electroreduced carboxylated graphene [13], multi-wall carbon nanotubes [14], and nano-carbon [15]. While, the main challenge for the electrochemical nicotine sensors is that the oxidation of nicotine occurs at a very positive potential, which would not only outrange the potential window of typical working electrodes, but also lead to the interference from other molecules in a real-world sample. In order to effectively decrease the overpotential required for the nicotine oxidation as well as to boost the analytical performance of these sensors, other carbon nanomaterials with large surface area, high conductivity, and abundant active sites must be explored.

Graphene has a two-dimensional honeycomb lattice structure, in which adjacent carbon links with each other by σ bonds and has a π orbital contributing to a delocalized network of electrons [16]. Graphene's unique chemical structure and numerous edge-plane sites lead to its ability of fast electron transfer. Besides, graphene possesses other properties such as large specific area and high mechanical strength. To further optimize the properties of graphene and expand its applications, doping graphene with foreign atoms such as nitrogen [17–19], boron [20] and sulfur [21], has been investigated. They have been used in electrochemical sensors for various analytes [22,23].

In this work, we synthesized nitrogen-doped graphene sheets (NGS) in a facile and mild way and used them to modify screen printed carbon electrodes (SPCE) for fabricating an electrochemical nicotine sensor. The reason for choosing SPCEs as the substrate electrodes is the advantages of low cost, mass production, flexibility of design and choice of materials to on-site determination of target analytes [24]. And by taking advantages of the outstanding electron transfer capability from

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graphene and the abundant active sites from the doped nitrogen atoms, NGS facilitates the electrochemical reaction kinetics of nicotine oxidation and significantly decreases the required overpotential. The analytical performance of fabricated NGS modified SPCE (NGS-SPCE) nicotine sensor, including sensitivity, selectivity and stability, was studied and reported here. Finally, the sensor was demonstrated by applying it to nicotine samples.

2. Experimental

2.1. Chemicals and apparatuses

Graphite powder (a purity of 99.9%) was purchased from Shanghai Huayi Co. Nicotine (98.54%) was from Shanghai Jingke Chemical Technology Co., Ltd. A standard solution of nicotine at 1 mg/mL was prepared by diluting the commercial sample into water without further treatment. Uric acid (UA), glucose (Glu) and urea were obtained from Sigma-Aldrich. All chemical reagents used in experiments were at analytical grade without further purification. Ultra-pure water (18.2 M Ω cm), produced by Laboratory Water Purification System, was used for all solution preparation unless noted otherwise.

A transmission electron microscope (TEM, JEM-1400, JEOL) was used to observe the morphology features of the graphene materials. X-ray diffraction (XRD) was performed by using a D/MAX-2550 diffractometer (Rigaku International Co., Japan) with a Cu K α source. X-ray photoelectron spectroscopy (XPS) was carried out using an ESCALAB-250Xi instrument (XPS, Thermo-Fisher, USA) with an Al K α source. InVia Reflex Raman spectrometer (Renishaw Co., UK) was employed to record the Raman spectra of the materials. Gas chromatography-mass spectrometry (GC-MS, Agilent 7890A-5975C) was used as a benchmark method for detecting nicotine concentration in tobacco samples, and for comparison with our sensors.

All electrochemical measurements were carried out at CHI1040B electrochemical workstation (CH Instruments Inc.) with a three-electrode system: the prepared NGS-SPCE electrode as a working

electrode, a platinum wire as a counter electrode and an Ag/AgCl (3 M KCl) electrode as a reference electrode. Several techniques, including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronoamperometry (I-t), were carried out for nicotine detection.

2.2. Synthesis of electrode modified material

First, graphene oxide (GO) sheets were synthesized according to the literature [25]. In brief, 1.5 g of graphite powder was added to a solution of 180 mL concentrated H₂SO₄ and 20 mL concentrated H₃PO₄. Then, 9 g of KMnO₄ were slowly added into the mixture. The resulting mixture was subsequently heated to 50 °C and reactions took place under constant stirring for 12 h. The products were cooled down to ambient temperature and placed into an ice bath. Then 1.5 mL of H₂O₂ (30%, v/v) and 400 mL of ultrapure water were added. After being successively washed with hydrochloric acid (10%, v/v) and ultrapure water, the synthetic products were dried in a vacuum oven.

Then, NGS was obtained in term of the literature [26] with a minor modification. 0.1 g of GO prepared above were dispersed into 108 mL of 2% w/w ammonia/water by ultrasonication for 30 min. Afterwards, the mixture was kept stirring for 6 h at 80 °C. The product was then centrifuged, washed with water several times, and dried at 50 °C under vacuum.

For comparison, reduced graphene oxide (RGO) was synthesized in accordance with the method published [27,28]. Briefly, 0.1 g GO were dispersed into 100 mL of water with sonication for 30 min. Then 0.2 g NaBH₄ was added into the dispersion. The mixture was heated at 90 °C for 1 h with constant stirring. Finally, the product was washed with water and dried under vacuum.

2.3. Fabrication of modified electrodes

SPCEs were homemade and have been reported previously [29]. Before use, SPCE was activated in 0.5 M H₂SO₄ by cyclic voltammetry from 1.5 V to 2.0 V for 20 cycles. Then 3 mg of synthesized NGS was

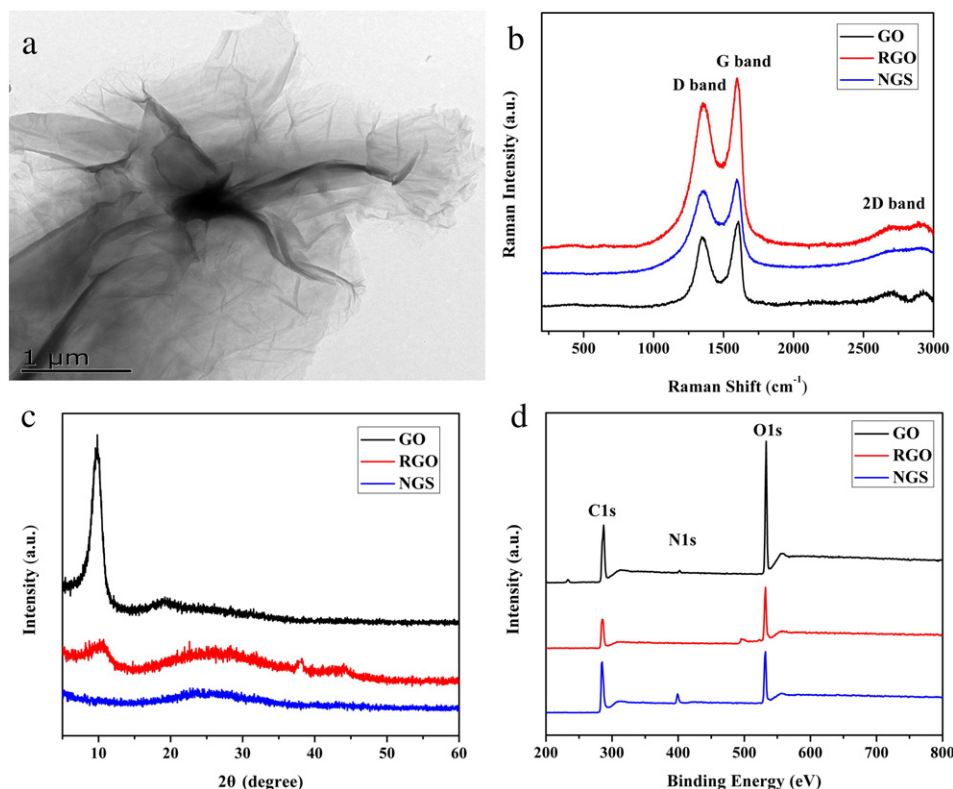


Fig. 1. (a) TEM image of the synthesized NGS; (b) Raman spectra, (c) XRD patterns and (d) XPS spectra of GO, RGO and NGS.

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