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A self-adjusting mechanism of schottky junction constructed by zero-bandgap graphene for highly efficient electrochemical biosensing

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ABSTRACT

Constructing schottky junction with zero-bandgap graphene was innovatively achieved by electrochemical reduction and deposition of GO on NiO foam directly. The fabricated 3D graphene/NiO foam exhibited highly efficient sensing performance towards positively charged dopamine molecules. The main mechanism is that the adsorbate-induced charges could change the schottky barrier height, following by selectively enhancing or depressing the electrochemical responses of different charged analytes. The proposed self-adjusting effects of schottky barrier on electrochemical signals were theoretically and experimentally explored in depth. As a result, it can help to break the limitation that analytes with similar redox properties are difficult to distinguish by electrochemical methods

1. Introduction

Highly efficient detection of disease biomarkers is increasingly important for early diagnosis, being well represented by the rapid development of electrochemical methods [1,2]. The interferents with similar redox properties, however, are still difficult to be electrochemically distinguished until now [3]. Many strategies have been developed to enhance the performance of electrochemical biosensors. Enlarging the distinctions among oxidation potentials of different analysts seems to be the simplest approach, but it still limited by their excessive amounts of kinds and is prone to remain stagnant [4,5]. Another possible idea, interestingly, that adjusting the current signals of different analysts under applied potential seems to be neglected and there is little work focusing on it. Since the surface charge state of materials plays a key role in sensing process, heterojunction interfaces are becoming a widely studied topic due to their improved physicochemical and electronic properties, and some wonderful sensing properties have been derived [6]. Wang' group have reported that using schottky contact could realize high-sensitive and fast-response nanowire biosensors in field-effect transistor devices. Moreover, schottky contact area was found as the bottleneck for current transport and schottky barrier height (Φ_B) was the chief functional factor [7]. Inspired by the aforementioned advantages, employing schottky barrier into electrochemical biosensors is very likely to be a promising way to improve detection performance. Unfortunately, there is no comprehensive mechanism or theoretical models about the effects of schottky junction on electrochemical devices have been presented so far.

In addition to the absence of theoretical analysis, another problem is that traditional metal/semiconductor composites with inherent shocttky barrier are always used in form of thin films fabricated on substrates, and the films are difficult to be scraped off the substrates intactly. This means that they could not be easily used as electrode materials. Graphene is well known as a one-atom-thick sp^2-hybridized carbon sheet, every atom in the graphene sheet is a surface atom, hence molecular interaction and electrons transport through graphene could be highly sensitive to any adsorbed molecules [8]. Importantly, graphene is also a zero-gap semi-metal and has outstanding electric properties, it is therefore not surprised that schottky junctions could be effectively constructed between graphene and suitable semiconductors [9,10]. In terms of preparation, various methods have been explored to prepare high-quality graphene [11–13]. Among them, a fast and green method named electrochemical reduction of

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exfoliated graphite oxide (GO) was recently proposed [14,15], which features fabricating graphene on electrode surface directly.

With a wide band gap of about 3.55 eV, p-type NiO exhibits great properties in photocatalysis, fuel cell electrodes and sensors [16–18]. We have reported a facile method of thermal oxidation to fabricate three dimensional (3D) NiO foam, which is helpful to maximize the diffusion of reactants and ions due to its porous architecture. It also has been proved to be a versatile kind of substrate materials for electrochemical biosensors [19]. Moreover, it is basic knowledge that there is a built-in potential at the interface when the work function of the p-type semiconductor is higher than that of the zero-gap material [20]. The work function of NiO is about 5.0–5.6 [21], which is much higher than that of graphene (~4.6) [22]. As a consequence, a depletion region and a built-in potential would be formed at the zero-gap graphene/NiO interface, thereby leading to the band distortion and the construction of schottky junction.

Herein, by employing electrochemical reduction and deposition of GO, we have fabricated zero-bandgap graphene film on 3D NiO foam easily. The schottky junction was constructed at the graphene/NiO interface, and then the effects of employing the p-type schottky barrier as tuning factor for electrochemical detection was explored in-depth. The self-adjusting Φ_B was further confirmed to controllably change all the responses of different charged molecules under redox. Finally, the biosensor based on 3D graphene/NiO foam exhibited excellent performance towards the positively charged biomarker dopamine (DA).

2. Experimental

2.1. Chemicals and Materials

Sodium dihydrogen phosphate ($NaH_2PO_4{\cdot}2H_2O$), disodium hydrogen phosphate ($Na_2HPO_4{\cdot}12H_2O$), uric acid (UA) and hemoglobin (Hb) (N ≥ 15.0%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Dopamine (DA) was purchased from Alfa Aesar. Ascorbic acid (AA) was purchased from Bodi Chemical Co. Ltd. (Tianjin, China). Humiseal 948-06G silver conductive paint was manufactured by loka chemicals laboratory. All chemicals or materials were of analytical grade and used directly without any further purification prior to use. Deionized (DI) water with a resistivity greater than 18 MΩ was used throughout the experiments.

2.2. Preparation of 3D NiO foam

A piece of small sized (~1 cm^2) Ni foam was consecutively cleaned by sonication in ethyl alcohol and DI water, followed by drying with compressed nitrogen gas. Then, the obtained sample was annealed at 700 °C for 5 h in air.

2.3. Preparation of 3D Graphene/NiO foam

Firstly, GO was synthesized from graphite power by the modified Hummers' method [23]. Then the as-prepared GO was exfoliated in 0.1 M phosphate buffer solution (PBS, Na_2HPO_4, pH 9.18) by sonication for 30 min to form a homogeneous brown colloidal dispersion with a concentration of 1.0 mg mL^{-1}. This solution would be directly used for the fabrication of Graphene/NiO composite, employing cyclic voltammetric reduction under magnetic string. In this process, a three-electrode system was used. Rinsed by ethanol and DI water twice, the 3D NiO foam served as the working electrode, while a Pt foil and a saturated calomel electrode were used as the counter and reference electrodes, respectively. The scan was from −1.5 V to 1 V at a rate of 100 mV S^{-1}, and the loading of graphene was controlled by the number of potential cycles. After deposition, the working electrode was washed with DI water, and then dried at room temperature.

2.4. Characterization and electrochemical measurement

Scanning electron microscopy (SEM, S-4800) was applied for the morphological investigation of samples. X-ray diffraction (XRD) patterns were obtained on a Bruker D8 ADVANCE X-ray diffractometer fitted with Cu Kα radiation over the 2θ ranges from 2θ = 10° to 70° at the scanning speed of 4°/min. Fourier transform infrared spectra (FTIR) in KBr was carried out in the frequency range of 500–4000 cm^{-1} on a Nicolet 170SX instrument (Madison, WI, USA). Raman spectra was recorded on a Renishaw RM-1000 with excitation from the 514 nm line of an Ar ion laser with a power of about 5 mW. Thermogravimetric analysis (TGA) was performed using a CHNS/O analyzer (Dupont 2200) under an air atmosphere and the samples were heated from 30 to 800 °C at a rate of 10 °C min^{-1}.

All electrochemical experiments were performed in a three-electrode system on a CHI600E workstation (Shanghai Chenhua) at room temperature. The electrode materials of NiO and 3D graphene/NiO foam were immobilized on glassy carbon electrode

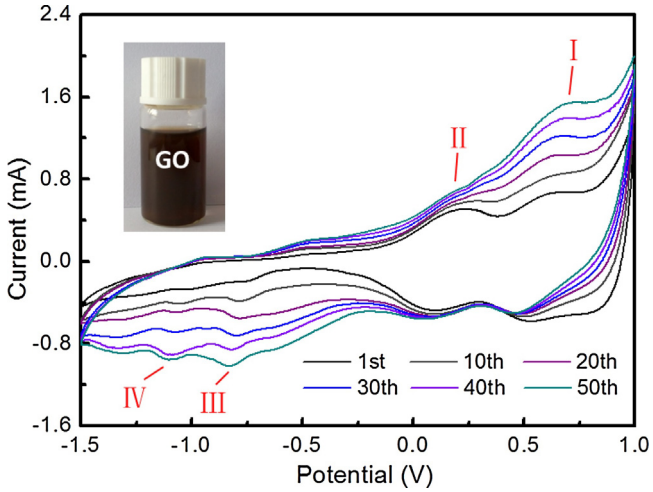

Fig. 1. Typical CVs of 1.0 mg mL^{-1} GO in 0.1 M PBS (pH 9.18) on 3D NiO foam.