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A highly selective electrochemical sensor for chloramphenicol based on three-dimensional reduced graphene oxide architectures

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ABSTRACT

Chloramphenicol (CAP), as a broad-spectrum antibiotic, has been worldwide banned for using in the food producing animals due to its overuse may cause severe threats to public health. It is therefore highly desirable to develop facile, selective and sensitive biosensor for CAP detection and monitoring in drug and foodstuff samples. In this work, three-dimensional reduced graphene oxide (3DRGO) architectures were prepared through a green and template-free approach and used as active electrode materials to develop a highly selective electrochemical sensor for CAP detection. The spontaneous reduction and assembly of graphene oxide via zinc foil was completed at room temperature, followed by washing with diluted hydrogen chloride solution, to produce 3DRGO. The as-prepared 3DRGO were characterized by scanning electron microscopy (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. An electrochemical biosensor for CAP was constructed based on 3DRGO-modified glass carbon electrode (3DRGO/GCE). It was revealed that the present 3DRGO/GCE sensor exhibited a remarkable performance with a detection range of 1–113 μmol L^{-1} and a detection limit of 0.15 μmol L^{-1} at physiological pH 7.4. Moreover, the sensor showed an excellent selectivity, stability, reproducibility, and satisfying recovery result for CAP detection in real samples.

1. Introduction

As a new class of nanocarbon material, graphene has attracted tremendous attention due to its excellent properties such as extraordinary electrical conductivity, fast electron transfer kinetics, high surface area and remarkable mechanical strength [1–3]. These features make graphene a promising electrode material for various applications, such as electrochemical sensing, catalysis and energy storage [4–8]. However, when used as an electrode material, two-dimensional graphene usually exhibits a dramatically decreased surface area that hindered the practical application, because these graphene nanosheets tend to stack and form agglomerates [9]. To increase the accessible surface area of graphene material and facilitate its practical applications, many efforts have been devoted to construct three-dimensional (3D) graphene materials [10–16]. Recently, 3D graphene architectures have been successfully fabricated by various methods such as self-assembly, template-assisted synthesis as well as chemical vapor deposition (CVD) [17–21]. For example, 3D layered graphene architectures have been achieved via an ordered self-assembly process by using cross-linking agent of poly(vinyl alcohol) [22]. Yu et al. have prepared 3D graphene electrode materials by polystyrene-spheres-templated approach that showed an enhanced sensitivity for dopamine detection [23]. Kota et al. have reported the fabrication of ice-templated 3D graphene material and achieved excellent supercapacitive performances [24]. 3D graphene nanostructures have also been synthesized through CVD by using porous nickel foam as a substrate, and used to construct a dopamine biosensor that exhibited remarkably improved sensing performance [25]. Although the 3D graphene nanostructures have been emerged as promising materials for various applications, the complicate construction conditions and additional templates are usually involved. Therefore, the development of simple and green methods for 3D graphene architectures fabrication is still a challenging task.

Chloramphenicol (CAP), a broad-spectrum antibiotic that is effective against to a wide variety of bacteria, has been extensively used since the 1950s for the treatment of infectious diseases in both humans and animals [26–28]. However, the overuse of antibiotics would result in accumulation of antibiotics in food and water that may cause severe threats to public health [28]. For example, it has been known that the CAP may cause bone marrow depression, aplastic anemia, cardiovascular collapse, etc. [26–29]. Thus the use of CAP in the food producing animals has been worldwide banned in recent years. But the fact is that CAP is still illegally used in cows to control mastitis and other animal diseases

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because of its low cost and high effectiveness [30]. Therefore, it is highly desirable to develop facile, selective and sensitive analytical methods for CAP detection and monitoring in drug and foodstuff samples.

Various analytical methods, such as liquid chromatography (LC) [31], gas chromatography (GC) [32], LC-mass spectrometry (LC-MS) [33], GC–MS [34], electrophoresis [35], Raman scattering [36], and chemiluminescence [37], have been developed for CAP detection. Nevertheless, the requirements for complicated analytical procedures, expensive instruments, tedious separation steps limit the extensive routine applications of these methods. Alternatively, electrochemical method for CAP detection offers the advantages of fast analysis, good sensitivity, simple operation, and low cost [38–40]. In this regard, various electrode materials, such as self-doped polyaniline intercalated molybdenum disulfide [41], nitrogen-doped graphene nanosheets decorated with gold nanoparticles [42], titanium nitride–reduced graphene oxide nanohybrids [43], magnetic hollow porous nanoparticles [44], silver nanoparticles/sulfonated functionalized graphene [45], and 1,5-diaminonaphthalene polymer modified aptamer [46], have been employed for determination of CAP. Most of these reported electrode materials either require complicated preparation processes or show poor sensitivity, and therefore the electrochemical sensing performances still need to be improved for a practical application.

Here we will report a facile preparation of three-dimensional reduced graphene oxide (3DRGO) architecture via green and template-free approach, and its application in construction of electrochemical biosensor for CAP. The as-prepared 3DRGO materials were fully characterized and their sensing performance was investigated by electrochemical determination of CAP, which showed an excellent selectivity, stability, reproducibility, and satisfying recovery result for CAP detection in real samples.

2. Experimental

Graphite powder was obtained from XFNano (99.9%, Nanjing, China). Chloramphenicol was provided by Amresco (AR, USA). All other chemicals were purchased from Sinopharm (AR, Shanghai, China) and used as received. Phosphate buffered saline (PBS, pH=7.4) was prepared from Na_2HPO_4 (0.1 mol L^{-1}) and KH_2PO_4 (0.1 mol L^{-1}), containing NaCl (0.1 mol L^{-1}) and KCl (0.01 mol L^{-1}).

2.1. Preparation of 3DRGO electrode

The 3DRGO was prepared through spontaneous reduction of graphene oxide via zinc foil at room temperature [14,47]. Briefly, graphene oxide (GO) was firstly produced from graphite powder according to the modified Hummers method [48,49]. The Zn foil was then immersed into an aqueous GO suspension (0.5 mg mL^{-1}, 30 mL) for 7 h without any additives at room temperature. The black deposition formed on Zn foil surface was collected by ultrasonication, cleaned by sinking the graphene materials into diluted HCl under stirring for 30 min. The solid was then collected by centrifugation and washed with water for three times, and finally dried in vacuum at 40 °C overnight to afford the 3DRGO architectures. 3DRGO was then dispersed in ethanol (2.0 mg mL^{-1}) and 3 μL of suspension was transferred on the pre-polished glassy carbon electrode (GCE) to construct the 3DRGO/GCE electrodes. For a comparison, normally reduced graphene oxide (N-RGO) was also prepared by using hydrazine hydrate based on reported procedure [42], and used to similarly construct the N-RGO/GCE electrodes.

2.2. Characterization

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were completed on S-4800 (Hitachi, Japan) and JEM-2100F (JEOL, Japan), respectively. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were recorded on D/max 2550 (Rigaku, Japan) and PHI 5400 (PE, USA), respectively. Raman spectrum was measured on inVia-Reflex (Renishaw, UK). Electrochemical measurements were conducted on CHI-660D electrochemical workstation (Shanghai Chenhua, China) with a common three-electrode system, including GCE or graphene modified GCE as working electrode, Pt wire and saturated calomel electrode (SCE) as counter and reference electrodes, respectively. The cyclic voltammetry (CV) performed from –0.2 to 0.6 V or –1 to 1 V (vs. SCE) with the scan rate of 50 mV s^{-1}. The differential pulse voltammetry (DPV) was carried out in 0.1 mol L^{-1} PBS +0.1 mol L^{-1} KCl at pH 7.4 from −0.4 to −0.7 V (vs. SCE), with step potential of 4 mV, amplitude of 50 mV, pulse width of 0.2 s and pulse period of 0.5 s, respectively. Electrochemical impedance spectroscopy (EIS) was recorded in 0.1 mol L^{-1} KCl solution containing 5 mmol L^{-1} $K_3[Fe(CN)_6]$, where the frequency range is from 0.01 Hz to100 kHz with a signal amplitude of 5 mV and the scan rate of 100 mV s^{-1}. All electrochemical measurements were carried out under nitrogen atmosphere at room temperature.

3. Results and discussion

3.1. Characterization of 3DRGO

The as-prepared 3DRGO materials were characterized by SEM, TEM, XPS, XRD and Raman spectra, respectively. As shown in Fig. 1, porous 3D architectures with obvious ripples and wrinkles on the graphene surface have been revealed by SEM and TEM

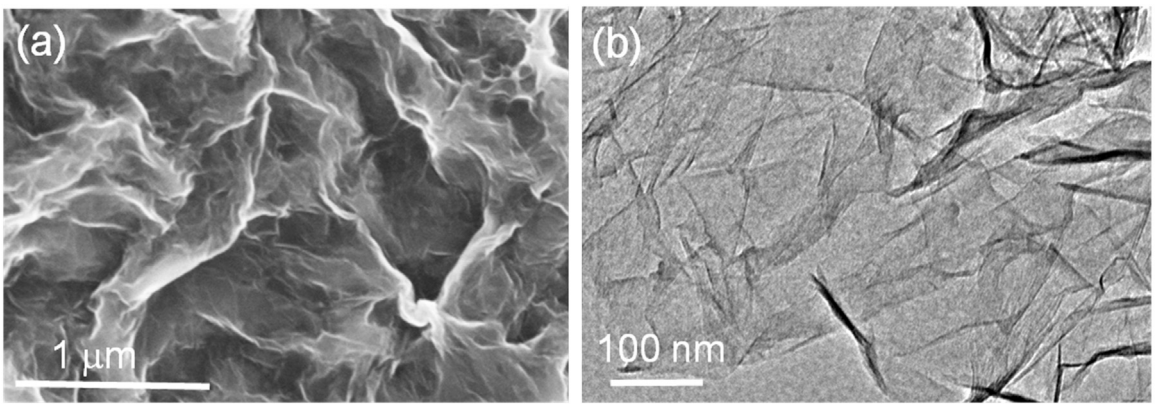

Fig. 1. SEM (a) and TEM (b) images of 3DRGO materials.