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A green and simple strategy to prepare graphene foam-like three-dimensional porous carbon/Ni nanoparticles for glucose sensing

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ABSTRACT

A green and simple strategy to prepare graphene foam-like three-dimensional (3D) porous carbon/Ni nanoparticles (NiNPs) nanocomposites was developed for glucose detection. The discarded sponge-like natural product, pomelo peel, was employed as novel supporting materials to load a large number of Ni^{2+} by a simple immersing method to form pomelo peel/Ni^{2+} which was then carbonized to construct the graphene foam-like 3D porous carbon/NiNPs nanocomposites. The resulted nanocomposites were carefully characterized by scanning electron microscopy, transmission electron microscopy, N_2 adsorption/desorption isotherms, X–ray powder diffraction, X-ray photoelectron spectroscopy, Raman spectra and electrochemical techniques. The results showed that the NiNPs was acted as the catalyst to result in the transformation of sponge-like pomelo peel into graphene foam-like 3D porous carbon/NiNPs nanocomposites during the carbonization process. The unique catalytic activity, good electrical conductivity as well as the novel structure of the nanocomposites contributed to a perfect electrochemical performance towards the oxidization of glucose, superior to other nanomaterials. The 3D porous carbon/NiNPs nanocomposites were used to construct glucose electrochemical sensor which exhibited a wide linear range (15.84 μM–6.48 mM) and a low detection limit (4.8 μM). This study might provide a novel proposal for preparing perfect electrochemical sensor based on porous carbon materials in the electrochemical sensing.

1. Introduction

Metal or metal oxide nanostructures have been extensively used as mimic enzyme to modify electrode for constructing electrochemical nonenzymatic sensor owing to their nanoscale size, large specific surface area, special structures, low cost, good electrocatalytic activity, etc [1–8]. Especially, transition metal Ni nanostructures have been widely used as electrode materials to construct electrochemical nonenzymatic glucose sensor due to its excellent electrocatalytic activity, low catalytic potential, high selectivity and good electrical conductivity [9–14]. Unfortunately, the Ni nanostructures always formed close-packed structures after they were assembled on electrode surface [15], which would reduce their specific surface area and catalytic activity thus hinder their electrochemical performance.

To alleviate the problem, various carbon nanostructures [16–18], such as two-dimensional (2D) graphene [19–27] and its derivatives [28–32], carbon nanotubes (CNTs) [9,11,33–35], carbon nanofibers [3,32,36] and porous carbon [37–40], were developed to load the Ni nanostructures [41–43] owing to their specific structure and properties (such as high surface area, excellent electrical conductivity, low cost as well as high stability). For example, Zhu et al. prepared CNTs/Ni nanocomposites with nanocluster morphology by magnetron sputtering for glucose sensing [11]. Similarly, Lee et al. synthesized copper–nickel oxide/graphene nanocomposites to prepare a nonenzymatic glucose sensor [44]. However, as compared with the three-dimensional (3D) porous carbon, the performance of the 2D or one-dimensional materials still has some space need to improve. An apparent pitfall of these fabricated sensors was the weak mechanical stability and the poor durability because they easily suffered from the agglomeration, deformation and collapse for extended periods of time under applied potential. Furthermore, the desired maximization of sensitivity as well as excellent selectivity still remains a great challenge [10].

Nowadays, 3D porous carbon derived from waste biomass has been developed for biosensing owing to their unique properties, such as ultra-high surface area, hierarchical pores, low toxicity, excellent electrical conductivity and lots of surface functional

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groups and trace elements [45–49]. For example, a 3D macroporous carbon derived from kenaf stem (3D-KSCs) was proposed as a novel supporting material to load Prussian blue nanoparticles (NPs), CuNiNPs and CoNPs as electrochemical sensing platform [50,51]. The pumpkin stems-derived carbon with high surface areas was also prepared for electrochemical sensing [52]. Compared with 2D materials, the 3D porous structures not only enhanced mass transfer, but also improved the mechanical stability and distribution of the loaded nanomaterials. Furthermore, the 3D self-supported networks with interlaced bridging frameworks might result in the negligible change of Ni nanocomposites after numerous reduplicative measurements, which guarantied the repeatability and long-term stability of the sensor accordingly [10].

Herein, a novel and efficient 3D porous carbon/NiNPs was proposed by carbonating the Ni^{2+} loaded pomelo peel for the nonenzymatic determination of glucose (denoted as 3D PPPC/NiNPs). The sponge-like porous structure of the pomelo peel is very beneficial to the loading of NiNPs which acted as a catalyst to result in the transformation of sponge-like pomelo peel into graphene foam-like 3D porous carbon/NiNPs nanocomposites during the carbonization process. As compared with the previous 3D porous carbon, the 3D-PPPC/NiNPs nanocomposites possessed graphene foam-like structure and good catalytic properties for the oxidation of glucose. Then, the 3D PPPC/NiNPs nanocomposites were further employed as electrode materials for glucose biosensing, and exhibiting good performance.

2. Experimental

2.1. Reagents

The fresh pomelo peels came from sha'tian farm (Fujian Province, China). $NiCl_2$ was purchased from China National Pharmaceutical Group (Shanghai, China). Glucose, NaOH and other chemicals were purchased from Beijing Chemical Reagent Factory (Beijing, China). All reagents (analytical grade) were used as received without further purification. 0.1 M NaOH solution was used as the supporting electrolyte. All the solutions were prepared by ultrapure water (18.2 MΩ cm^{-1}), purified by a Millipore-Q System.

2.2. Instrumentations

Scanning electron microscopy (SEM) analysis was performed on a XL30 ESEM-FEG SEM equipped with a Phoenix energy dispersive X-ray (EDX) analyzer at an accelerating voltage of 15 kV. X-ray powder diffraction (XRD) data were collected on a D/Max 2500 V/PC X-ray powder diffractometer using Cu Kα radiation (λ = 0.154056 nm, 40 kV, 200 mA). Transmission electron microscopy (TEM) analysis was taken using a JEM-2010 (HR). X-ray photoelectron spectroscopy (XPS) analysis was taken using an AXIS ULTRA DLD at an accelerating voltage of 15 kV to study the elements. Raman spectra were performed at room temperature with a LabRAM HR spectrometer and an argon ion laser operating at a wavelength of 632.8 nm as the excitation (Jobin Yvon Ltd, France).

All electrochemical measurements were performed on a CHI 660C electrochemical workstation (Shanghai, China) at ambient temperature. A common three-electrode system was used containing a bare or nanocomposite modified electrode as the working electrode, a platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE, saturated KCl) as the reference electrode. The cyclic voltammetric experiments were performed in a quiescent solution. And amperometric experiments were taken out in a continuously string solution by a magnetic stirrer. 0.1 M NaOH was used as the supporting electrolyte solution and was inlet with high purity nitrogen for 15 min before electrochemical test, which was to form a nitrogen atmosphere over the solution during measurements.

2.3. Preparation of 3D PPPC/NiNPs nanocomposites

To control the reproducibility for the fabrication of this type of materials, the same position of pomelo was used in the whole experiments. The dried pomelo peels were placed into small beakers, followed by adding 30 mL $NiCl_2$ solution and soaked for 21 days. Then the pomelo peels were removed out and put into vacuum drying oven at 100 °C for 12 h. After that, they were put in a tubular quartz reactor under N_2 atmosphere at 900 °C for 2 h. And then, the samples were cooled down in the N_2 atmosphere to obtain the 3D PPPC/NiNPs nanocomposites. Herein, the 0.02 M, 0.05 M and 0.1 M $NiCl_2$ were used and the obtained corresponding nanocomposites were called as 3D PPPC/$Ni_{0.02}$NPs, 3D PPPC/$Ni_{0.05}$NPs and 3D PPPC/$Ni_{0.1}$NPs, respectively. Furthermore, the 3D PPPC without NiNPs was prepared according to the following procedures. The fresh pomelo peel were firstly cut into regular shape, and then put in a vacuum drying oven (80 °C) for drying, and the carbonization was performed in a tubular quartz reactor under N_2 atmosphere at 900 °C for 2 h, then cooling in the N_2 atmosphere.

2.4. Preparation of 3D PPPC/NiNPs/glassy carbon electrode (GCE)

The GCE (3.0 mm in diameter) was polished carefully with1.0, 0.3 and 0.05 μm alumina powders on felt pads, and then ultrasonically cleaned in water, dried by nitrogen finally. The 3D PPPC/NiNPs suspension was prepared by dispersing PPPC/NiNPs powders in the water of 1 mL, and ultrasonic for 30 min. Then, the 9.7 μL suspension and 0.3 μL nafion solution (3 wt%) were mixed evenly. After that, the 6 μL mixture was dropped on the surface of polished GCE. After drying for 4 h, the 3D PPPC/NiNPs electrodes were obtained.

3. Results and discussions

3.1. Characteristics of the 3D PPPC/NiNPs nanocomposites

Fig. 1A showed the SEM image of the 3D-PPPC. It could be clearly observed that a large number of loose spongy-like 3D macroporous structures arranged in a crisscross pattern with much more pores and larger specific surface area as compared with previously reported 3D-KSC [50]. As shown in the high-magnification SEM image (Inset), there were many folds on the inner wall of the hole and the surface, which was very similar to the structure of graphene. High-resolution TEM image was shown in Fig. 1B, and it clearly revealed that many black and white spots, which indicated the microporous structures of the inner wall of 3D-PPPC. The inset showed that after the carbonization, the 3D-PPPC had a good carbon crystal of C(002). It indicated that this material might have excellent electrical conductivity similar to that of graphite. XPS measurement was performed to probe the chemical composition and chemical status of elements in the 3D-PPPC. Fig. 1C showed the survey scan spectrum of the 3D-PPPC with apparent C1s and O1s peaks and some other elements such as N, S and P (Fig.S1, Supporting information). The chemical composition was estimated to be about 79.97% C, 18.34% O, 0.72% N, 0.54% P, and 0.44% S in the biomass-derived 3D-PPPC, which was found to be responsible for the excellent adsorption for molecules and nanomaterials [53]. The XRD pattern of 3D-PPPC (Fig. 1D) showed clear diffraction peaks at 24.1° and 43.6° which was indexed to the (002) and (100) of carbon (JCPDS card No. 02-0456), similar to that of graphite (Fig. S2. Supporting information). Thus, it could be concluded that the 3D-PPPC had a crystal structure of carbon.