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Electrospun palladium (IV)-doped copper oxide composite nanofibers for non-enzymatic glucose sensors

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ABSTRACT

Pd (IV)-doped CuO oxide composite nanofibers (PCNFs) have been successfully fabricated via electrospinning and then employed to construct an amperometric non-enzymatic glucose sensor. The PCNFs based glucose sensors display distinctly enhanced electrocatalytic activity towards the oxidation of glucose, showing significantly lower overvoltage (0.32 V) and ultrafast (1 s) and ultrasensitive current (1061.4 μA mM^{-1} cm^{-2}) response with a lower detection limit of 1.9×10^{-8} M (S/N = 3). Additionally, excellent selectivity, reproducibility and stability have also been obtained. These results indicate that PCNFs are promising candidates for amperometric non-enzymatic glucose detection.

1. Introduction

The past several decades have witnessed the big progress on fabricating sensitive devices for fast and reliable monitoring glucose and carbohydrates driven by their practical applications in treating and controlling diabetes [1,2]. Among those devices, amperometric glucose biosensors with glucose oxidase (GO*x*) [3] and without GOx [4] have been the subject of considerable interest because a low detection limit can be achieved easily. Especially, the enzymeless glucose sensors have gained special focus taking the advantages of good stability, simplicity, reproducibility and so on [5]. Recently, bimetallic materials are of particular interest for non-enzymatic glucose detection owing to the improved electrocatalytic ability of pure metal anodes occurs as a consequence of the introduction of the other elements [6–8]. However, at nano-scale, these metallic nanomaterials based electrodes usually suffer from the stable problems (easy oxidization or poisoning) or high cost, which hinders their practical applications [9,10]. On the other hand, oxides based glucose sensors have been widely investigated for non-enzymatic detecting owing to their good stability [11,12]. Prompted by the high electrocatalytic ability of pure metallic nanomaterials and the good stability of oxides, in this communication, we demonstrate a novel type of ultrasensitive and stable enzymeless glucose sensor based on bimetal oxides of palladium-doped copper oxide composite nanofibers (PCNFs) via electrospinning [13]. Ultrafast response with a lower detection limit at a lower applied potential can be obtained based on our sensor.

2. Experimental

D-Glucose, cupric acetate, palladium chloride, polyvinyl alcohol (PVA, M_w = 70,000–75,000), NaOH and ethylene glycol were purchased from Beijing Chemical Co. (China). Uric acid (UA), L-ascorbic acid (AA), dopamine (DA), Triton-X100 and Nafion (Nf) (v/v, 5%) were obtained from Sigma–Aldrich. All chemicals were used as received without any further purification. Distilled water was used in all experiments.

PCNFs were fabricated through electrospinning and followed by calcination. In a typical procedure [14], 0.4 g of cupric acetate and 0.02 g palladium chloride were added slowly into 7.6 g of a PVA solution (7.9 wt.%) with 0.01 g of Triton-X100. Then, the solution was kept under vigorous magnetic stirring for 12 h, and a viscous gel was obtained. Finally, the as-prepared gel was loaded into a syringe and connected to a high-voltage power supply for electrospinning. An electric potential of 15 kV was applied between the orifice and the ground at a distance of 20 cm. Then, calcination (500 °C in air for 5 h) was used to treat the as-spun composite fibers to remove the organic constituents of PVA and to convert the precursor into PCNFs.

The modified electrode was prepared as follows: glassy carbon (GC) electrodes (3 mm diameter) were carefully polished with a diamond pad/3 μm polishing suspension, rinsed with distilled

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water and ethanol, and then dried under ambient nitrogen gas. The as-prepared nanofibers (1 mg) were dissolved in 200 μL ethylene glycol. After ultrasonication (2 min), uniformly dispersed PCNFs were obtained. After dipping 5 μL PCNFs solution onto the electrode surface, the electrode was dried at 80 °C. Subsequently, 5 μL Nafion (Nf) (v/v, 1%) solution was dropped onto the modified electrode to form a film.

The crystal structures of the products were determined by X-ray powder diffraction (XRD) using an X-ray diffractometer (Siemens D5005, Munich, Germany). Analysis of the X-ray photoelectron spectra (XPS) was performed on an ESCLABMKII using Mg as excitation source. The morphologies of the electrospun nanofibers were viewed by scanning electron microscopy (SEM, SHIMADZU SSX-550, Japan). Transmission electron microscopy observations (TEM, Model JEM-2000EX, JEOL) were performed with an accelerating voltage of 200 kV. All electrochemical measurements were performed on a CHI 660C electrochemical workstation (Shanghai, China) with a conventional three-electrode system composed of a platinum auxiliary, a saturated calomel electrode reference (SCE), and modified glassy carbon working electrodes. All electrochemical experiments were performed in 0.1 M NaOH solutions (5 mL) under nitrogen atmosphere at room temperature. Glucose concentration was controlled by adding desired concentration of glucose into the NaOH solution.

3. Results and discussion

SEM has been used to characterize the morphologies of pure CuO nanofibers and PCNFs as shown in Fig. 1a and b. From the SEM images, it can be seen that the diameters of the as-prepared nanofibers are ranging from 90 to 140 nm. Fig. 1c and d show the TEM images of the CuO nanofibers and PCNFs, indicating that those fibers have a rough surface and consist of the agglomeration of oxides nanoparticles with average size of about 40 nm.

Fig. 1e shows XRD patterns of the pure CuO nanofibers and PCNFs. The apparent monoclinic structure CuO (JCPDS 5-0661) can be detected in both samples [15]. And there is no indication of the presence of any dopants-related phases for the Pd-doped sample, attributing to the high dispersion or the poor crystallinity of dopants-related nanoparticles. In order to prove the existence of Pd component in the PCNFs, XPS has been used to investigate the bonding characteristics and oxidation states of Pd in the composite nanofibers. As shown in Fig. 1f, the Pd 3d spectrum shows two

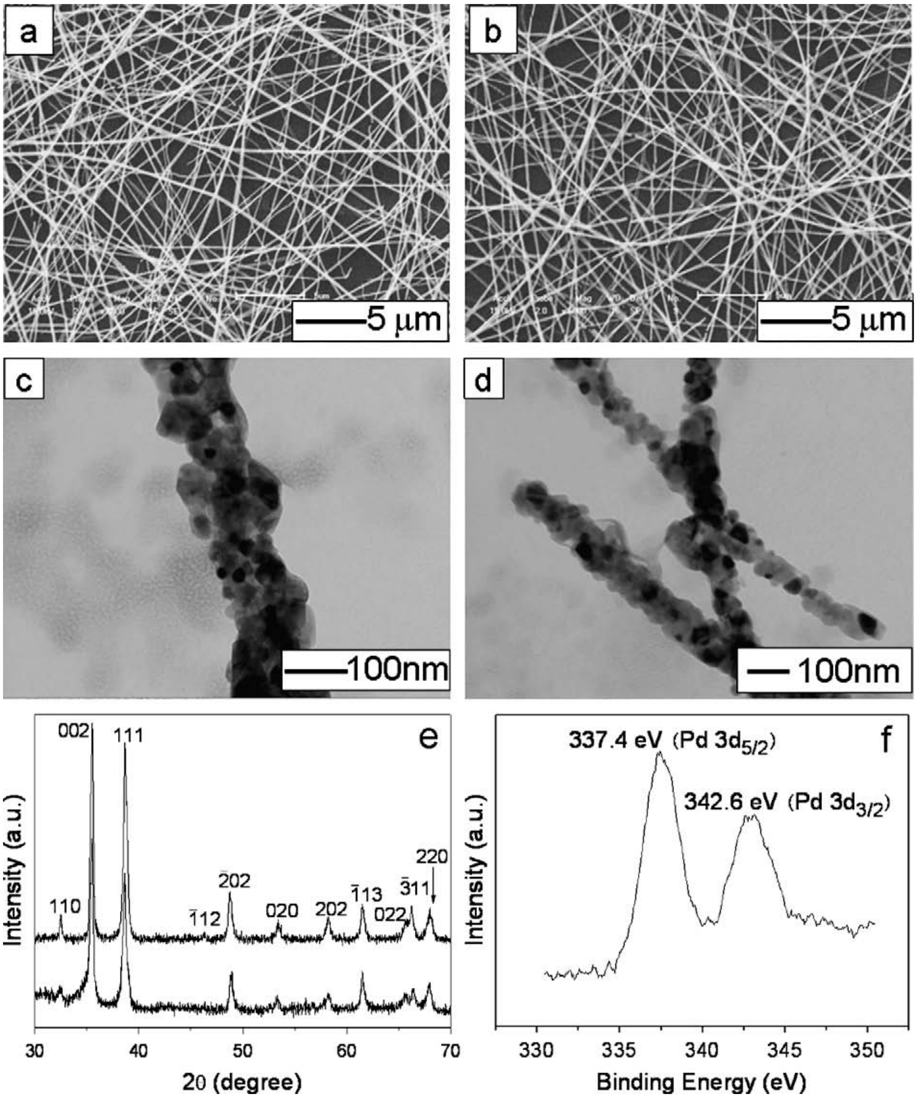

Fig. 1. SEM images of (a) pure CuO nanofibers and (b) PCNFs. TEM images of (c) pure CuO nanofibers and (d) PCNFs. (e) XRD patterns of the products and (f) XPS spectra of Pd 3d for PCNFs.