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Short communication

Enhanced hydrogen peroxide sensing by incorporating manganese dioxide nanowire with silver nanoparticles

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ABSTRACT

We reported a synthesis of manganese dioxide–silver hybrid nanowire. The fast development of detecting small molecules inspired us to study the electrochemical properties of the nanocomposite. The hybrid nanowire was fabricated as a novel nonenzymatic hydrogen peroxide sensor with rapid, stable, and reliable response with a detection limit of 0.24 μM. The enhanced electrochemical signal characteristic of silver can be easily distinguished which can be assigned to the small amount decoration of silver nanoparticles on the nanowire.

1. Introduction

The rapid, accurate, reliable, and sensitive determination of hydrogen peroxide is of great importance in many fields [1–3]. Among various analysis methods, electrochemical route exhibits advantages such as selectivity, low cost, efficiency, and easy to operate. Therefore, many enzyme was developed to fabricate the electrochemical sensor detecting H_2O_2 reduction [4,5]. However, the applications of enzyme-based biosensors were limited by the relatively high cost and crucial demands for environment [6]. With the development of nanoscience and nanotechnology, various nanomaterials were found to own the abilities to catalyze the reduction of H_2O_2, and were developed to fabricate electrochemical sensors towards H_2O_2 reduction, among which Ag nanomaterials were considered as excellent candidates [7–10]. Compton and coworkers have intensively investigated the electrochemical behavior and kinetic research of Ag nanoparticles towards hydrogen peroxide reduction [7–9]. Besides that, MnO_2 nanomaterials have also been attracting certain attention in this area recently [11–13]. It is known that hybrid nanomaterial might endow the integrity with enhanced activity compared with single component [14]. So assembling Ag nanomaterials on MnO_2 nanostructure was desirable for expecting to possess enhanced performance compared with MnO_2 only [15]. To the best of our knowledge, Ag nanoparticle decorated MnO_2 nanowire has never been reported before.

Herein, we assembled Ag nanoparticles on MnO_2 nanowire to obtain the hybrid nanowire. The product was fabricated to an electrochemical sensor towards H_2O_2 reduction, which was proved to exhibit well-performed electrocatalytic activity. Though Ag amount was quite little, the electrochemical signal could still be greatly enhanced which made the sensor more applicable.

2. Experimental section

2.1. Materials

Chemicals were all purchased of analytical grade and used as received without any purification. Water used throughout the whole experiments was ultrapure water with resistivity of no less than 18.2 MΩ cm.

2.2. Synthesis of hybrid nanowire

MnO_2 nanowire and Ag nanoparticles were synthesized according to the literature previously reported with slight modifications [16,17]. Briefly, 0.1 M $MnSO_4$ and 0.1 M $KMnO_4$ were dissolved in water (10 mL), followed by adding 333 μL of 60% H_2SO_4. The mixture was vigorously stirred for 30 min, transferred to a Teflon-lined stainless autoclave, and kept at 150 °C for 36 h. The autoclave was cooled to room temperature. The product was centrifuged, washed and dried. Ag nanoparticles were obtained after adding 3 mL of 0.01 M $NaBH_4$ solution into 100 mL aqueous solution containing 0.25 mM $AgNO_3$ and 0.25 mM sodium citrate under vigorous stirring.

Subsequently, MnO_2 nanowire (30 mg) was suspended in methanol (10 mL), followed by adding 150 μL of (3-aminopropyl)triethoxysilane (APTES) and stayed still overnight. The solution was centrifuged,

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washed and redispersed in water. The APTES-functionalized MnO_2 solution and Ag sol were mixed together and stirred. The product was centrifuged, washed and redispersed in a concentration of 3.2 mg/mL.

2.3. Apparatus

Transmission electron microscopy (TEM) images were obtained on a HITACHI H-7650 EM operated at 100 kV. X-ray photoelectron spectroscopy (XPS) analyses were performed on an ESCALAB-MKII spectrometer (United Kingdom). Electrochemical measurements were all operated on a CHI 660E electrochemical analyzer (Chenhua Co., Shanghai, China) in a conventional three-electrode cell, which includes a saturated calomel electrode as reference electrode, a platinum wire as counter electrode, and a bare or modified glassy carbon electrode (GCE, 3 mm in diameter) as working electrode. The modified GCE was fabricated by casting certain amount of the desired solution, followed by pipetting 10 μL of 0.5 wt.% Nafion. Phosphate buffer solution (PBS, 0.2 M, pH 7.0) is used as supporting electrolyte, and high-purity nitrogen was bubbled for 20 min prior to starting the experiments.

3. Results and discussion

TEM was helpful to identify the morphology of nanomaterial. Fig. 1 shows the typical TEM images of MnO_2 (A) and MnO_2–Ag nanowires (B). From Fig. 1A, it can be obviously seen that nanowire was successfully synthesized with an average diameter of 20 nm, and the surface was relatively smooth. After the assembly of Ag nanoparticles, it can be clearly seen that the surface of nanowire becomes rougher, and small nanodots can be easily observed from Fig. 1B, indicating the successful fabrication of hybrid nanowire.

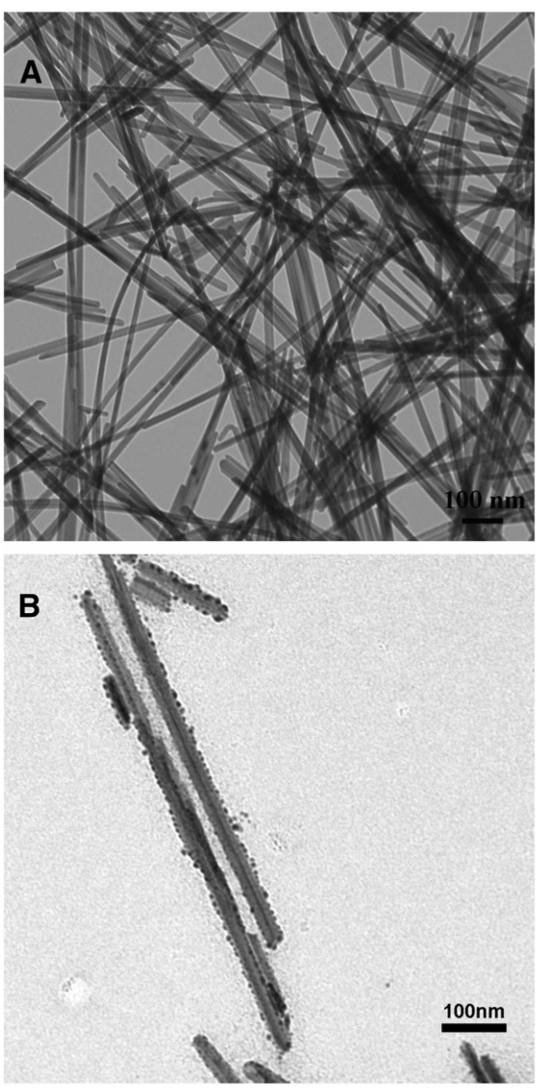

Fig. 1. TEM images of MnO_2 nanowire (A) and MnO_2–Ag hybrid nanowire (B).

The chemical composition of the hybrid nanowire was examined by XPS. Fig. 2 shows the Ag 3d (A) and Mn 2p (B) regions of XPS spectrum of the hybrid. In Fig. 2A, peaks of binding energies at 367.9 and 373.8 eV can be assigned to Ag $3d_{5/2}$ and $3d_{3/2}$, which are in accordance to those for metallic Ag [18]. Besides that, peaks of binding energies at 641.8 and 653.8 eV in Fig. 2B could be ascribed to Mn $2p_{3/2}$ and $2p_{1/2}$, which is in consistence of those for MnO_2 [15]. XPS results show that the hybrid nanowire consists of MnO_2 and Ag.

In recent years, catalytic activity towards H_2O_2 reduction has been found on MnO_2 or Ag nanomaterials [7–13]. Herein, we applied the novel hybrid onto GCE surface to investigate its electrochemical properties. Fig. 3A shows the cyclic voltammetry curves (CVs) of bare (a, b in inset), MnO_2 (a, b) and MnO_2–Ag nanowire (c, d) modified GCEs in PBS without and with 5 mM H_2O_2 at 50 mV/s. As shown in Fig. 3A, MnO_2–Ag nanowire (curve d) exhibits larger current response compared with bare or MnO_2 modified GCEs in pure PBS, indicating that the incorporation of silver might increase the conductivity of the composite, making the composite more applicable. After adding H_2O_2 into PBS, in comparison with bare GCE, both MnO_2 and hybrid nanowires exhibit enhanced activity towards H_2O_2 reduction. Besides that, signal characteristic of Ag can also be detected on hybrid nanowire (curve d), which supports the successful assembly of Ag nanoparticles on nanowires from the side. Note that though Ag amount was quite low in the hybrid nanowire (0.6 μg in 9.6 μg), H_2O_2 reduction current was greatly enlarged compared with that on MnO_2 nanowire, and signal characteristic of silver can be observed easily, showing the significant contribution of silver nanoparticles in the hybrid. In order to further

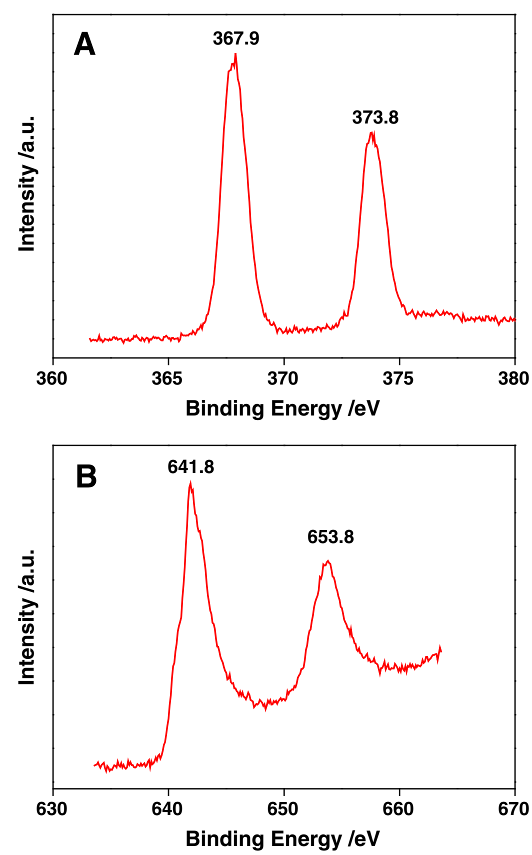

Fig. 2. Ag 3d (A) and Mn 2p (B) regions of XPS spectrum of MnO_2–Ag nanowire.