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One-step preparation of Ag nanoparticle–decorated coordination polymer nanobelts and their application for enzymeless H_2O_2 detection

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ABSTRACT

In this paper, we report on the one-step preparation of Ag nanoparticle (AgNP)-decorated coordination polymer nanobelts, carried out by direct mixing of an aqueous $AgNO_3$ solution and a N,N-dimethylformamide (DMF) solution of 4,4′-bipyridine (BPD) at room temperature. The construction of an enzymeless H_2O_2 sensor using such nanocomposites with a detection limit of 0.9 μM is also demonstrated.

1. Introduction

Coordination polymers (CPs) are a new class of organic–inorganic hybrid materials, in which metal ions are linked together by organic bridging ligands, and have developed extremely rapidly during the past years [1–4]. They have versatile properties provoked by combining the merits of two sources and are promising materials for molecular storage, separation, catalysis, ion exchange, etc. [5]. On the other hand, H_2O_2 participates in a wide range of enzymatic reactions, playing an important role in the fields of chemistry, biology, clinical control, and environmental protection, and therefore, its detection is of great importance [6–8]. Up to now, many detection techniques have been well developed [9–14]. Among them, electrochemical technique has been proven to be an inexpensive and effective way due to its intrinsic simplicity and high sensitivity and selectivity. Early H_2O_2 sensors involved the use of the intrinsic selectivity and sensitivity of enzymatic reactions where nanostructures are also employed to immobilize the enzymes and at the same time, to reduce the possibility of protein denaturing [15–18]. It has also been shown that Ag nanoparticles (AgNPs) show good catalytic activity toward the reduction of H_2O_2 [19–25], opening the door for the construction of enzymeless H_2O_2 sensors. It has been demonstrated that AgNP–decorated conjugation polymer nanofibers can be used for H_2O_2 detection [26]; however, the preparation of such nanocomposites requires two steps: (1) the direct mix of aqueous $FeCl_3$ and *o*-phenylenediamine (OPD) solutions at room temperature leads to supramolecular microfibrils of OPD dimers generated by the oxidation of OPD monomers by $FeCl_3$; (2) treating the microfibrils with a $AgNO_3$ aqueous solution transform them into nanofibers decorated with AgNPs.

In this paper, by combining the coordination and reducing ability of 4,4′-bipyridine (BPD) and N,N-dimethylformamide (DMF) toward Ag(I), respectively, we develop a one-step preparative strategy toward AgNP–decorated coordination polymer nanobelts (AgNP–CPNBs) for the first time, carried out by direct mixing of an aqueous $AgNO_3$ solution and a DMF solution of BPD at room temperature. It suggests that these AgNP–CPNBs exhibit good catalytic activity toward H_2O_2 reduction. The enzymeless H_2O_2 sensor constructed exhibits a fast amperometric response time of less than 5 s and has a linear detection range from 100 μM to 70 mM and a detection limit of 0.9 μM, respectively.

2. Experimental

All chemicals were purchased from Aladin Ltd. (Shanghai, China) and used as received without further purification. The water used throughout all experiments was purified through a Millipore system. Phosphate buffer saline (PBS) was prepared by mixing stock solutions of NaH_2PO_4 and Na_2HPO_4 and a fresh solution of H_2O_2 was prepared daily. The AgNP–CPNBs were prepared as follows. In a typical experiment, 1 mL of 0.2 M aqueous $AgNO_3$ solution was mixed with 2 mL of 0.1 M DMF solution of BPD under stirring at room temperature, leading to a large amount of white precipitates

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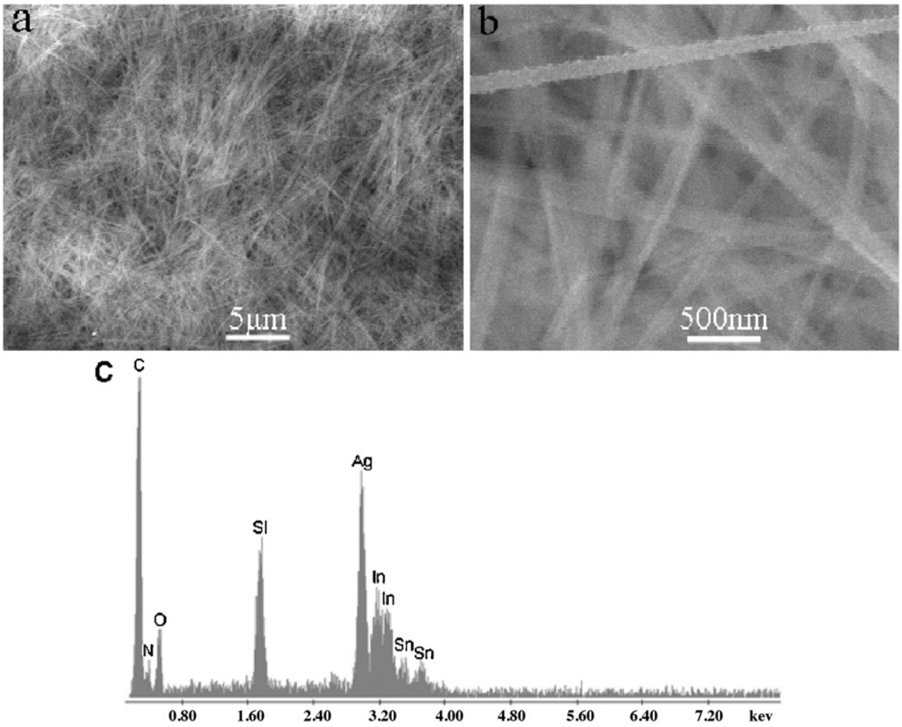

Fig. 1. (a) Low and (b) high magnification SEM images and (c) the corresponding EDS of the products thus formed.

immediately. Scanning electron microscopy (SEM) measurements were made on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. Samples for SEM examination were made by placing a drop of the precipitates on a bare indium tin oxide (ITO) and air-dried at room temperature. Electrochemical measurements are performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai). A conventional three-electrode cell is used, including a glassy carbon electrode (GCE, geometric area = 0.07 cm^2) as the working electrode, an Ag/AgCl (saturated KCl) electrode as the reference electrode and platinum foil as the counter electrode. The potentials are measured with an Ag/AgCl electrode as the reference electrode. All the experiments were carried out at ambient temperature. Chitosan of 0.5% was used to immobilize the material onto the surface of electrode, which acted as a fixer herein.

3. Results and discussion

Fig. 1a shows the low magnification SEM image of the products thus formed, indicating that they consist of a large amount of one-dimensional (1D) structures about several tens of micrometers in length. The high magnification SEM image shown in Fig. 1b further reveals that such 1D structures are nanobelts with widths in the range of 50–150 nm. It is important to note that a large quantity of very small nanoparticles is also observed on the nanobelts. The chemical composition of these nanoparticle-decorated nanobelts was determined by the energy-dispersed spectrum (EDS), as shown in Fig. 1c. The peaks of C, N, and Ag are observed, indicating that they are formed from BPD and Ag(I) (other peaks originated from the ITO substrate). The elemental composition of C, N and Ag are measured to be 44.18, 10.04, and 40.08 (total 94.30), respectively, indicating the atom ratio of C:N:Ag is roughly 8:2:1. Such observation suggests that the molar ratio of BPD to Ag in the nanobelts is about 1:1, that is, the content of Ag in the modification layer is about 40.8%. It is well-known that nitrogen ligand can coordinate with Ag(I) [27]. The formation of such nanobelts in our present study can be attributed to coordination-induced assembly from Ag(I) and BPD and a possible formation process is proposed as follows: When Ag(I) and BPD are mixed together, the two nitrogen atoms on the para positions of one BPD molecule can coordinate to two different Ag(I) cations, leading to BPD-bridged structure, and the Ag species contained in the resultant structure can further capture other BPD by coordination interactions along different directions. This coordination-induced assembly process can proceed repeatedly until the depletion of all reactants in the solution, resulting in the formation of large coordination polymer nanobelts, finally. However, the detailed mechanism is not clear at present time and needs further study. It also should be noted that DMF serves not only as a good solvent for BPD, but as a powerful reducing agent to reduce Ag(I) cations into AgNPs [28] which can be adsorbed on the nanobelt via Ag–N interactions [29], leading to AgNP–CPNBs.

It is worth while mentioning that increased incubation time leads to an increase of the AgNPs in size. Fig. 2 shows typical SEM images of the composites after standing under ambient condition over a period of 24 h. The low magnification SEM image shown in Fig. 2a also indicates that they are 1D structures. The high magnification SEM image, however, clearly reveals the formation of nanobelts decorated with large AgNPs, as shown in Fig. 2b. Such observation could be attributed to that more Ag(I) cations are reduced by DMF with the elapse of time.

To demonstrate the sensing application of the AgNP–CPNBs, we constructed an enzymeless H_2O_2 sensor by immobilization of the composites on a glassy carbon electrode (GCE) surface. Fig. 3 shows cyclic voltammetry (CVs) of a bare GCE, a AgNP–CPNBs modified GCE (no standing process applied, AgNP–CPNBs/GCE), and a AgNP–CPNBs-24 h modified GCE (a 24-h standing process applied, AgNP–CPNBs-24 h/GCE) in N_2 saturated 0.2 M PBS at pH 6.5 in the presence of 1.0 mM H_2O_2 (scan rate: 0.02 V/s). The response of the bare GCE toward the reduction of H_2O_2 is pretty weak (about 4 μA in intensity). In contrast, the AgNP–CPNBs/GCE shows a remarkable catalytic reduction current peak of H_2O_2 about 25 μA in intensity at -0.52 V. The dc conductivity of the freshly prepared nanobelts (AgNP–CPNBs), measured at room temperature using standard four-probe method, is in the order of 10^{-7} S cm^{-1}.