Materials Letters 64 (2010) 1720–1723

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Synthesis and enhanced electrochemical properties of pod-shaped gold/silica nanoparticles

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ARTICLE INFO

Article history:
Received 10 February 2010
Accepted 10 May 2010
Available online 20 May 2010

Keywords:
Metal and semiconductor
Nanomaterials
Synthesis
Rod shape
Electrochemistry
Sensors

ABSTRACT

Pod-shaped gold/silica nanoparticles (PGSNPs) were prepared using perfluorooctanoic acid (PFOA) and cetyltrimethylammonium bromide (CTAB) as cotemplates. The PGSNPs were utilized to explore a novel biosensor through coupling myoglobin (Mb) with chitosan (Chi). Compared with Mb–Chi-PSNPs (pod-shaped silica nanoparticles)/GC modified electrode, Mb–Chi-PGSNPs/GC electrode exhibited a pair of much stronger redox peaks at −0.28 V (vs. Ag/AgCl). Moreover, facilitated direct electron transfer of the metalloenzymes with smaller peak-to-peak separation (Δ*Ep*) of about 46 mV was acquired on the PGSNPs-based enzyme electrode. The PGSNPs-based biosensor demonstrated significant electrocatalytic activity for the reduction of hydrogen peroxide with a wide linear range (1–540 μM) and high sensitivity (661 mA cm^{-2} M^{-1}). Together, the Mb–Chi-PGSNPs film is one of ideal candidate materials for direct electrochemistry of redox proteins, and may find potential applications in biomedical, food, and environmental analysis and detection.

1. Introduction

Metal/semiconductor composite nanomaterials have attracted increasing interest because of their novel structures and unique physical and chemical properties [1,2]. It is well known that the intrinsic properties of nanoparticles associate with their compositions, sizes, and shapes [3–5]. Moreover, for composite nanomaterials with two or more components, that one component doped usually amplifies the properties of the other components and even generates new properties [6,7]. Now, metal/semiconductor nanomaterials have been employed to fabricate single-electron transistors [8], nanoelectronic devices [9], spin light-emitting diodes [10], ohmic contact nanodevices [11], etc. However, to the best of our knowledge, metal/semiconductor nanomaterials for immobilizing proteins and constructing electrochemical biosensors have rarely been studied so far although both metal and semiconductor nanomaterials have extensively been utilized to fabricate electrochemical biosensors [12]. Nevertheless, in our latest work, we have used Pt/SWCNTs nanomaterials to construct a H_2O_2 biosensor and demonstrated that the biosensor possesses excellent electrochemical and electrocatalytic properties [13].

In the present work, pod-shaped gold/silica nanoparticles (PGSNPs) were prepared using perfluorooctanoic acid (PFOA) and cetyltrimethylammonium bromide (CTAB) as cotemplates. And that the PGSNPs were for the first time explored to fabricate a novel H_2O_2 biosensor through coupling myoglobin (Mb) with chitosan (Chi). As an inorganic–organic hybrid material, the Mb–Chi-PGSNPs composite can effectively maintain the native structure of Mb and facilitated direct electron transfer of Mb has been achieved. The constructed biosensor was also successfully employed for the detection of H_2O_2 and displayed better electrochemical performances in comparison with PSNPs-based biosensor.

2. Experimental

Chitosan, perfluorooctanoic acid, and tetraethyl orthosilicate were purchased from Sigma-Aldrich, and myoglobin was obtained from Yuanju Biology Science and Technology Co. Ltd (Shanghai, China). Other chemical reagents such as chloroauric acid, cetyltrimethylammonium bromide, sodium citrate, etc. came from Guangdong Guanghua Chemical Reagent Company. All above reagents are analytical grade and used without further purification. All solutions were prepared with water purified in a Milli-Q system (>18.0 MΩ cm). 20 mM of phosphate buffer solution (PBS, pH 7.0) was prepared by mixing 39 mL 20 mM NaH_2PO_4 and 61 mL 20 mM Na_2HPO_4.

In a typical procedure for the synthesis of gold/silica nanopods, the mixture solution containing silica nanopods were first prepared according to the previously reported literature [14]. Then, 5 mL $HAuCl_4$ and 4 mL sodium citrate were added and kept stirring at

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doi:10.1016/j.matlet.2010.05.010

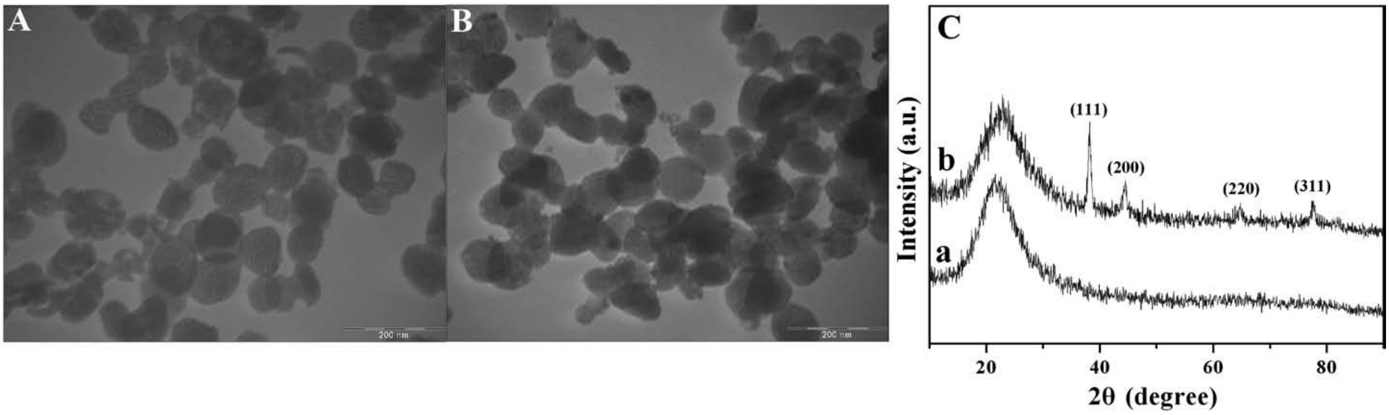

Fig. 1. TEM images of (A) PSNPs and (B) PGSNPs; (C) XRD spectra of (a) PSNPs and (b) PGSNPs.

100 °C for 1 h. Finally, the sample centrifuged with 8000 rpm for 30 min was calcined at 550 °C for 5 h to afford the final product.

In a typical procedure for the preparation of Mb–Chi-PGSNPs/GC modified electrode, glassy carbon (GC) electrode was first polished and cleaned by ultrasonication in ultrapure water and ethanol, respectively. Then, 5 µL of the PBS containing 5 mg/mL Chi dissolving 2% $C_2H_4O_2$, 3 mg/mL Au/SiO_2, and 6 mg/mL Mb was cast onto the surface of the cleaned GC electrode. Finally, a uniform film electrode was formed through putting the as-prepared electrode overnight at room temperature. For comparison, Chi-PGSNPs, Chi–Mb/GC, and Mb–Chi-PSNPs/GC electrodes were also prepared according to the same procedure.

Transmission electron microscopy (TEM) was performed on a Hitachi H-7100. X-ray diffraction (XRD) patterns were recorded on powder samples using a D/max-IIIA (Japan) X-ray diffractometer equipped with Cu Kα radiation ($\lambda = 0.15418$ nm). UV–visible (UV–vis) absorption spectroscopy measurement was carried out with a U-3010 spectrophotometer (Hitachi, Japan). Electrochemical impedance spectroscopy (EIS) spectra were acquired using an AUTOLAB advanced electrochemical system (Swiss). Electrochemical experiments were carried out at room temperature using a CHI 660 electrochemical workstation (CH Instruments, Inc., Austin, USA).

3. Results and discussion

Fig. 1A,B gives representative TEM images of PSNPs and PGSNPs produced thus, respectively. The PGSNPs possessed an average width and length of about 80 and 120 nm, respectively, which were consistent with those reported previously [14]. The surfaces of PGSNPs contained a few gold nanospheres with an average diameter of around 12 nm, indicating the formation of PGSNPs. Fig. 1C shows XRD spectra taken from the PSNPs and PGSNPs, respectively. The broad peak ranging from 15 to 30° in 2θ angle (curves a,b) can be attributed to the amorphous nature of the silica [15]. And the diffraction peaks at $2\theta = 38.2°$, 44.4°, 64.6°, and 77.5° (curve b) could be indexed to the (111), (200), (220), and (311) planes of a pure face-centred crystalline structure of Au (JCPDS: 04-0784). The XRD result further suggested the formation of PGSNPs and that silica and gold nanoparticles still retained their crystalline structures in the gold/silica nanopods.

Fig. 2A shows UV–vis absorption spectra of dry Mb and Mb–Chi-PGSNPs films. Compared with dry Mb film (a characteristic peak at around 408 nm, curve a), the Mb spectrum peak in the Mb–Chi-PGSNPs film had the similar position and intensity (curve b), suggesting that the Mb still retained the essential feature of its native secondary structure in the Mb–Chi-PGSNPs film. To evaluate interfacial electron transfer property of different modified electrodes, EIS was preformed. Compared with the bare GC electrode (340 Ω, curve a in Fig. 2B), Chi–Mb/GC electrode possessed a giant transfer resistance (Rct) (about 6.1 kΩ, curve d in Fig. 2B), indicating that Mb hindering electron transfer pathway was successfully immobilized on the surface of the bare GC electrode. Nevertheless, the Rcts at Mb–Chi-PGSNPs/GC or Mb–Chi-PSNPs/GC electrodes dramatically decreased again in comparison with that at the Mb–Chi/GC electrode (curves b,c in Fig. 2B), demonstrating that the PGSNPs or PSNPs were rather helpful to speed the electron transfer between the underlying electrode and the electrolyte. It is especially important to note that the Rct (about 2.1 KΩ, curve b in Fig. 2B) of the PGSNPs-based electrode was much smaller than that (about 3.7 KΩ, curve c in

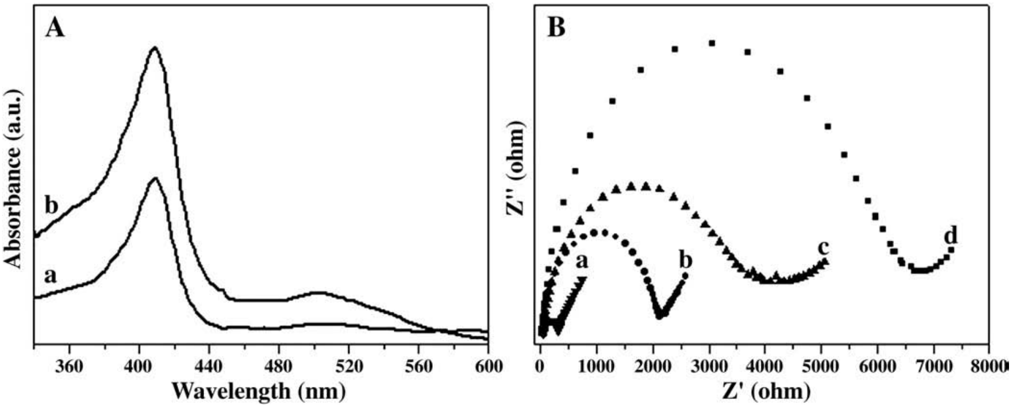

Fig. 2. (A) UV–vis absorption spectra of dry (a) Mb and (b) Mb–Chi-PGSNPs films; (B) EIS spectra of different modified electrodes: (a) bare GC, (b) Mb–Chi-PGSNPs/GC, (c) Mb–Chi-PSNPs/GC, and (d) Chi–Mb/GC.