Analytica Chimica Acta 711 (2012) 40–45

Contents lists available at SciVerse ScienceDirect

Analytica Chimica Acta

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

A simple and an efficient strategy to synthesize multi-component nanocomposites for biosensor applications

Xiaoquan Lu*, Yan Li, Xia Zhang, Jie Du, Xibin Zhou, Zhonghua Xue, Xiuhui Liu

Key Laboratory of Bioelectrochemistry & Environmental Analysis of Gansu Province, College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou 730070, China

ARTICLE INFO

Article history:
Received 20 August 2011
Received in revised form 27 October 2011
Accepted 2 November 2011
Available online 11 November 2011

Keywords:
One-step
Au–polypyrrole (PPy)/Prussian blue (PB)
Multi-component nanocomposites
Biosensor

ABSTRACT

We demonstrate that core–shell multi-component nanocomposites can be grown in situ at room temperature by a novel one-step approach without adding any reductant and stabilizer. We have presented a one-step method for the synthesis of multi-component nanocomposites in water solution, the multi-component nanocomposites could be produced directly and quickly in an in situ wet-chemical reaction. Here, Au–polypyrrole (PPy)/Prussian blue (PB) nanocomposites have been synthesized successfully under the same circumstance. With the addition of pyrrole monomers into mixture solutions, the autopolymerization of pyrrole into PPy and $AuCl_4^-$ was reduced to elemental Au instantaneously as well as simultaneously. At the same time, PB produced along with elemental Au serving as a catalyst. Furthermore, we investigated the performance of Au–PPy/PB nanocomposites as amperometric sensor toward the reduction of H_2O_2, which displayed high sensitivity, fast response and good stability. The peak current of H_2O_2 increased linearly with the concentration of H_2O_2 in the range from 2.5×10^{-9} to 1.2×10^{-6} M, and the low detection limit of 8.3×10^{-10} M (S/N = 3) was obtained. Therefore, this work provides a new pathway to design and fabricate novel multi-component nanocomposites, which have unique characteristics and hold great applications in the fields of sensors, electrocatalysis and others.

1. Introduction

Nanocomposites are considered to be a group of perspective substances, combining together the different properties of components, leading the way to a new, tunable behavior, and the special characteristics of multi-component nanocomposite has received great attention [1]. Various synthesis methods have been developed as their wide applications [2–4], such as chemical reduction [5], sonochemical reduction [6], laser ablation [7], radiolytic reduction [8], metal evaporation [9], and Ar+ ion sputtering [10], etc. These methods have their own advantages but most synthesis procedure of nanocompositises are multiple steps and need presynthesized precursor. Tsai et al. prepared Au–Ag–Pd nanoparticles by laser irradiation [11]. Perruchot et al. investigated polypyrrole-APS-silica particles which APS was first grafted onto the silica particles then pyrrole coating and polymerization [12]. It is much worthy of being found facile ways to get desired nanocomposites such as one-step method. There are some instances employing one-step method to prepare two-component nanocomposites, for example, CdS/montmo-srillonite [13], multiwalled carbonnanotube/gold [14], poly(styrene-b-caprolactone)/silicate [15], gold-poly(o-phenylenediamine) [16], polyacrylamide-calcium phosphate (PAM-CP) [17]. However, little research through one-step method preparation of three- or multi-component nanocomposites have been reported, limiting their applications to a large extent. Therefore, a great challenge is how to synthesize nanocomposites, not only one-step but also containing multi-component to the future materials research.

Prussian blue (PB) is a prototype of mixed valence metal hexacyanoferrates, has played a lot of important roles in the fields of electrocatalysis [18], electroanalysis [19,20], electrochromism [21] and batteries [22,23] for its interesting electrochemical, photophysical, and magnetic properties. Especially in the field of electroanalytical chemistry for constructing PB-based H_2O_2 biosensor, it has proved to be an excellent catalyst for H_2O_2 reduction at low potentials. Among various types of conducting polymers, polypyrrole (PPy) is one of the most important organic conducting polymers because of relatively high conductivity, good environmental stability and ease of preparation [24,25]. It has potential use in fuel cells [26,27], sensors [28–31], batteries [32–34], capacitors [35–37], and corrosion protection [38–40]. Conducting polymers have one distinct advantage that is oxidation polymerization of monomer and reduction of metal salt can be finished in one step [41]. Selvan et al. revealed that Au/PPy core–shell NPs can

---

* Corresponding author. Tel.: +86 931 7971276; fax: +86 931 7971323.
E-mail address: luxq@nwnu.edu.cn (X. Lu).

0003-2670/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.aca.2011.11.005

synthesize by a simple one-step progress [42], and the conductivity and the sensing behavior of PPy could be further improved by imbedding Au nanoparticles (AuNPs) into the PPy matrix [42–44]. In addition, integrating AuNPs into PB can improve the sensing properties of PB [45]. In this paper, we have successfully synthesized a new multi-component nanocomposites by a one-step method. The morphology and composition of Au–PPy/PB core–shell nanocomposites were investigated by Transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), ultraviolet visible spectroscopy (UV–vis) and cyclic voltammetry (CV). Moreover, Au–PPy/PB nanocomposites were immobilized on the GCE and construct a H_2O_2 biosensor. The sensor exhibited high sensitivity, fast response and good stability.

2. Experimental

2.1. Chemicals and apparatus

Pyrrole was purchased from Zhongqin Chemical Reagent Co., Ltd. (Shanghai, China) and purified twice by distillation under the protection of high purity nitrogen and then kept in a refrigerator before use. Potassium ferricyanide was purchased from Xi'an Chemical Reagent Factory (Xi'an, China). Chloroauric acid was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The 0.02 M phosphate buffer solution (PBS), which was made from K_2HPO_4 and KH_2PO_4, was always employed as the supporting electrolyte. All other chemicals were of analytical-reagent grade and used without further purification. All experiments were carried out at room temperature (22 ± 2 °C) and the solutions were prepared by doubly distilled water.

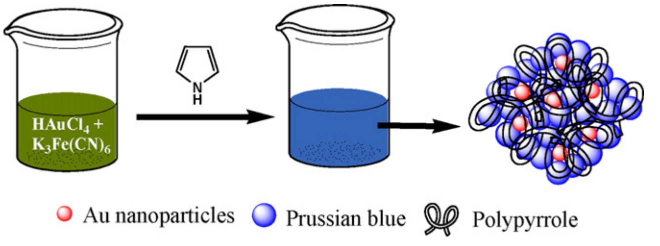
The morphologies of Au–PPy/PB core–shell nanocomposites were observed by TEM (Tecnai G2 F20 U-TWIN, USA). XRD pattern was performed on D/Max-2400 (X-ray Diffractometer, Rigaku Corporation, Tokyo, Japan), UV–vis absorption spectra of Au–PPy/PB core–shell nanocomposites dispersed in distilled water through ultrasonic irradiation were recorded on a UV1102 (Techcomp Bio-Equipment Ltd., Shanghai, China) spectrometer. FTIR spectroscopic measurements were performed on a Nicolet Impact-400 spectrometer using KBr pressed disks. CV and differential pulse voltammetry (DPV) experiments were performed on CHI-832 working station (CHI instrument, Co. Ltd., Austin, USA). A three-electrode system consisting of a sat. Hg/Hg_2Cl_2:KCl reference electrode, a platinum counter electrode as a auxiliary electrode, and a Au–PPy/PB core–shell nanocomposites modified glassy carbon electrode (GCE, $r = 1.75$ mm) was employed for electrochemical measurements.

2.2. Preparation of Au–PPy/PB core–shell nanocomposites

In a typical procedure for the synthesis of Au–PPy/PB nanocomposite, 0.1 M pyrrole aqueous solution was slowly added to a mixed aqueous solution of 1 mM $HAuCl_4$ and 2.5 mM $K_3[Fe(CN)_6]$ at room temperature under vigorous stirring. With the addition of pyrrole aqueous solution, the color changed from green yellow to green blue. The reaction was allowed to proceed for 2 h at room temperature. After the reaction, the mixture was centrifuged, and the precipitate was washed with distilled water for several times. The final product was dried in a vacuum at 60 °C for 24 h.

2.3. Preparation of Au–PPy/PB core–shell nanocomposites modified GCE

The GCE was polished with 0.3, and 0.05 μm alumina slurry followed by rinsing with doubly distilled water and drying at room temperature. Au–PPy/PB core–shell nanocomposites were dispersed in distilled water to form a 1.0 mg mL^{-1} solution and ultrasonically treated for 30 min. The colloidal solution (5 μL) was dropped onto the pretreated GCE surface and allowed to dry under the ambient condition.



Scheme 1. Synthetic procedure and chemical structure of the Au–PPy/PB core–shell nanocomposites.

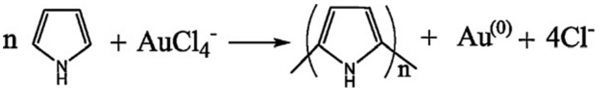
3. Results and discussion

3.1. Characterization of Au–PPy/PB core–shell nanocomposites

The synthetic procedure and the chemical structure of the Au–PPy/PB core–shell nanocomposites are shown in Scheme 1. The Au–PPy/PB core–shell nanocomposites were synthesized successfully by one-step with $HAuCl_4$, $K_3[Fe(CN)]_6$ and pyrrole monomer. Fig. 1(a–d) shows the TEM images of the forming Au–PPy/PB core–shell nanocomposites after 0.1 M pyrrole aqueous solution was added to the mixed solution of 1 mM $HAuCl_4$ and 15–25 mM $K_3[Fe(CN)]_6$ solution. As shown in Fig. 1, the dark spots inside the nanocomposites correspond to Au, that is surrounded by PPy/PB matrix. The concentration of $K_3[Fe(CN)]_6$ has a strong effect on the morphology of the resultant products. In Fig. 1a, $K_3[Fe(CN)]_6$ concentration was 15 mM, the morphology appeared square sheet about 20 nm, AuNPs was around 1–3 nm (Fig. 1a and b), The corresponding EDS spectrum of nanocomposites shows the peaks presence of C, N, K, Au and Fe elements (insert in Fig. 1b). When increasing the concentration to 20 mM, PPy/PB shell presented compact network, AuNPs were uniform distributed in PPy/PB shell and the size was around 2–3 nm. As the concentration reached to 25 mM, such compact-network PPy/PB shell appeared again, but rodlike AuNPs appeared and recessed irregularly into PPy/PB shell, it is about 2 nm width and 40 nm length (Fig. 1d).

15 mM $K_3[Fe(CN)]_6$ is a optimization concentration and has been chosen to do the subsequent experiment. Nevertheless, it is difficult to distinguish PPy and PB around AuNPs, there may be two reasons: the color of PB in the TEM image is light, the other is that PB embraced by PPy fully, which is favourable to avoid the PB leaking and improve the catalysis of PB.

Actually, with the addition of pyrrole monomers into mixture solution, the autopolymerization of pyrrole into PPy and $AuCl_4^-$ was reduced to elemental Au instantaneously and simultaneously (Eq. (1)) [43]. At the same time, PB produced along with elemental Au. The forming of PB involves the reduction of the free ferric ion or the ferric ion in the associated complex, according to Eq. (3), elemental Au acts as a catalyst in this progress [46–48]. This reaction is unfavourable thermodynamically because the standard free-energy change is 173 kJ mol^{-1}. The driving force could be provided only by the subsequent formation of PB (Eq. (2)). The standard free-energy change of the total reaction is −177 kJ mol^{-1}. The reaction mechanisms may be as follows:



(1)

$$K^+ + Fe^{2+}Fe(CN)_6^{3+} \rightarrow KFe^{3+}[Fe^{2+}(CN)_6] \quad (2)$$