Synthetic Metals 213 (2016) 73–77

Contents lists available at ScienceDirect

Synthetic Metals

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

Short communication

Facile assembly of polypyrrole/Prussian blue aerogels for hydrogen peroxide reduction

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ARTICLE INFO

Article history:
Received 5 December 2015
Accepted 7 January 2016
Available online 21 January 2016

Keywords:
Polypyrrole
Prussian blue
Aerogels
H_2O_2 reduction

ABSTRACT

Three-dimensional self-standing polypyrrole/Prussian blue (PPy/PB) aerogel monoliths have been fabricated through self-assembly of PPy/PB hydrogel precursors and subsequent freeze-drying. The hydrogel precursors are synthesized using methyl orange as the self-degraded template in the presence of ferricyanide as the oxidant. The morphology, crystalline structure and chemical composition of the resulting PPy/PB aerogels have been investigated by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). Moreover, the as-prepared PPy/PB aerogels exhibit well-defined response in the electrocatalytic reduction of hydrogen peroxide (H_2O_2) owing to the combination of the electrochemical properties of PB and the conductivity of PPy in the aerogels. These aerogels with the multifunctional quality are expected to have wide applications in sensor and other related fields.

1. Introduction

The family of Prussian blue (PB) is a kind of important functional inorganic materials composed of transition-metal hexacyanometalates with a face-centered cubic lattice of transition metal ion centers bridged by electron-rich cyanide groups. PB is the simplest representative for which both of the metal ion centers are iron. They have received great attention due to their particular structures and excellent properties of magnetic adjustment, electrochromism, and electrochemical modulation in recent years [1,2]. Moreover, PB can be used in the field of electrochemical sensors owing to its high activity and good selectivity toward the electrochemical reduction of hydrogen peroxide (H_2O_2) [3,4]. The good selective electrocatalysis toward reduction of H_2O_2 may be ascribed to the unique zeolite-like structure of PB, which only permits small molecules to diffuse onto the lattice gap [5]. However, several disadvantages of PB, such as low stability and poor conductivity, have restricted its efficient application in electrochemical sensors to some extent.

Recently conducting polymers have attracted tremendous interest because of their low cost, ease of synthesis and good conductivity. They have been applied to increase the conductivity of the electrochemical-active PB. For example, polypyrrole (PPy) and poly(o-phenylenediamine) films are electropolymerized on a PB-modified electrode to fabricate glucose biosensor [6]. Wallace et al. have also reported that PB films can be formed under and above PPy film as a mediator system [7]. PPy/PB core/shell nanoparticles with enhanced photofluorescent characteristics are prepared via miniemulsion polymerization using a complicated ferrate surfactant [8]. Although the pioneer works about the synthesis of PPy/PB hybrids in the form of film or powder are exciting, PPy/PB hybrid with three-dimensional aerogel monoliths are rarely reported. It is well-known that more efficient contacts between electrolytes with electroactive materials in the aerogels with high porosity and large specific surface area are favorable to the electrochemical process. However, it is still a big challenge to prepare PPy/PB aerogels owing to the lack of the corresponding hydrogel precursors.

In our previous work, PPy hydrogels with three-dimensional network have been fabricated when dye molecules as templates and common ferric salts as oxidants [9]. Herein, PPy/PB hybrid aerogels are prepared by freeze-drying of their hydrogel precursors made by using methyl orange (MO) in the presence of potassium ferricyanide. Assembling PB into three-dimensional PPy network may integrate the conducting property of PPy and electrocatalytic characteristic of PB. It is expected that PPy/PB aerogels show good electrocatalysis toward reduction of H_2O_2.

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http://dx.doi.org/10.1016/j.synthmet.2016.01.006
0379-6779/

2. Experimental

2.1. Materials

Methyl orange (MO), potassium ferricyanide ($K_3[Fe(CN)_6]$), and hydrochloric acid (HCl) were purchased from Sinopharm Chemical Reagent Co., Ltd., and used without further purification. Pyrrole monomer was distilled under reduced pressure before use.

2.2. Fabrication of PPy/PB aerogels

0.05 g MO was dispersed in 15 mL HCl aqueous solution with the pH value of 4. A certain amount of $K_3[Fe(CN)_6]$ was added, and the solution was stirred and then kept static for 2 h. Then, pyrrole monomer (105 μL) was added to the above solution. The resulting mixture was stirred for several minutes and the reaction was kept without stirring. The molar ratio of pyrrole to $K_3[Fe(CN)_6]$ was 1:2 or 1:5. After 3 h, a small quantity of $FeCl_3$ was added to promote the formation of PB. The reaction was continued to proceed for 12 h. Then, the prepared PPy/PB hydrogel precursors were purified with plenty of deinoized water to remove the residual reactants. Finally, PPy/PB aerogels was obtained after freeze-drying.

2.3. Characterization

The morphology of the aerogel was observed using a JSM-5510LV scanning electron microscopy (SEM). The crystalline structure of the aerogel was characterized by X-ray powder diffraction (XRD, Shimadzu) with monochromatic Cu Kα radiation at room temperature. Conductivities of the compressed samples were measured using a four-probe method. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Impact-420 spectrometer. X-ray photoelectron spectroscopy (XPS) was performed using an AXIS Ultra spectrometer under a base pressure of 1×10^{-9} Torr. Electrochemical experiments were conducted on a CHI 660C electrochemical workstation (Chenhua Instrument Company) with a conventional three-electrode cell. A saturated calomel electrode (SCE) and a platinum wire were used as the reference electrode and the counter electrode, respectively. A modified glassy carbon electrode (GCE) was used as the working electrode. PPy/PB aerogel was dispersed in water to get a homogeneous solution (0.2 mg/mL). Then 10 μL mixture was dropped on the surface of GCE. After that, 2 μL Nafion solution was coated on the above surface and dried in air before use. The solution was purged with highly purified nitrogen prior to the electrochemical measurements.

3. Results and discussion

When $K_3[Fe(CN)_6]$ is used as the oxidant in the polymerization reaction of pyrrole, a cylinder-like whole was observed during the static assembly, which was similar with our previous work about PPy hydrogels prepared using the common ferric salts as the oxidant [9]. And it should be noted that there is no obvious difference for the PPy/PB hydrogel precursors prepared with different molar ratio of pyrrole to $K_3[Fe(CN)_6]$ without stirring for 12 h. However, after freeze-drying, the PPy/PB aerogels prepared with different molar ratio of pyrrole to $K_3[Fe(CN)_6]$ have totally different macroscopic appearance. In the case of the molar ratio of pyrrole to $K_3[Fe(CN)_6]$ 1:2, the resulting PPy/PB aerogel shrink dramatically after freeze-drying and it cannot self-stand, as shown in Fig. 1a. When the molar ratio of pyrrole to $K_3[Fe(CN)_6]$ is changed to 1:5, the self-standing PPy/PB aeerogel with 12 mm in height and 21 mm in diameter is obtained (Fig. 1c). It is unexpected that it can hold a stuff of 200 g, which is as high as about 1350 times of its own weight. It indicates that the amount of the oxidant $K_3[Fe(CN)_6]$ plays an important role in the formation of self-standing PPy/PB aerogels. The corresponding microstructures of the PPy/PB

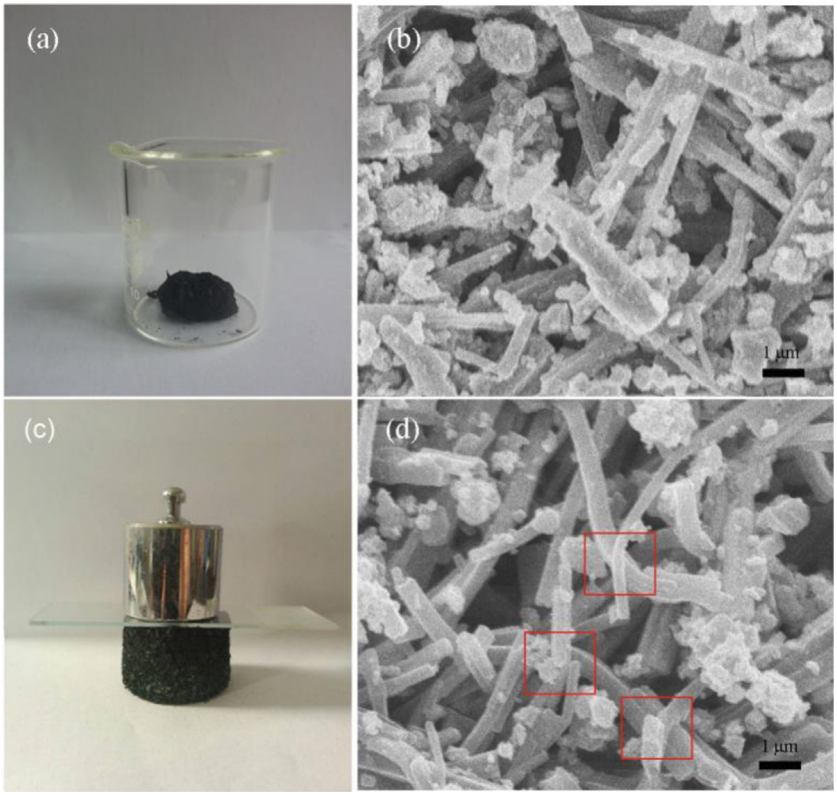

Fig. 1. Photographs and SEM images of PPy/PB aerogels prepared with different molar ratio of pyrrole to $K_3[Fe(CN)_6]$ (a,b) 1:2 and (c,d) 1:5 (For interpretation of the reference to color mentioned in the text, the reader is referred to the web version of this article.).