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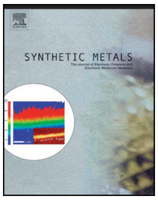

Short Communication

# A facile one-step synthesis of prussian blue/polyaniline/graphene oxide nanocomposites for electrochemical sensing of hydrogen peroxide

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ABSTRACT

Prussian blue/polyaniline/graphene oxide (PB/PANI/GO) nanocomposites were synthesized and used for electrochemical sensing of hydrogen peroxide ($H_2O_2$). PB/PANI/GO nanocomposites were synthesized through a facile one-step approach, where aniline acted as both the precursor of PANI and the reductant for $FeCl_3$–$K_3[Fe(CN)_6]$, therefore making polymerization of aniline and anchoring of PB nanoparticles on PANI/GO occur simultaneously. Then, the nanocomposites were characterized by transmission electron microscopy (TEM), X-ray diffraction spectroscopy (XRD), fourier transform infrared spectroscopy (FTIR) and electrochemical techniques. The results indicated that PB nanoparticles with the size of about 4.0 nm were homogeneously distributed on the surface of PANI/GO, which made the sensor based on PB/PANI/GO exhibit an excellent performance toward $H_2O_2$ detection with a wide linear range of 5.0 μM to 1.275 mM, a sensitivity of 60.16 μA mM$^{-1}$ cm$^{-2}$ and a low detection limit of 1.9 μM (S/N = 3).

## 1. Introduction

The accurate determination of hydrogen peroxide ($H_2O_2$) is important for its wide applications [1,2]. Up to now, many methods were developed to detect $H_2O_2$ [3–6]. In particular, electrochemistry sensors which based on the simple and low cost electrode were extensively studied [7]. Moreover, in order to improve the catalytic activity of sensors for $H_2O_2$ oxidation/reduction, various nanomaterials were employed to modify electrodes due to their large specific surface areas as well as unique electronic and catalytic properties [8–11]. Among nanomaterials, prussian blue (PB) aroused growing interest because of its excellent electrocatalytic activity toward $H_2O_2$ electroreduction [12,13]. In addition, $H_2O_2$ sensors based on PB usually required a low working potential [14], which was beneficial to prevent the interference of other substances. However, the poor stability and low conductivity of PB limited its extensive applications [15]. Recently, it has been reported that hybrid nanomaterial might endow the integrity with enhanced activity compared with single component [16]. Therefore, in order to improve stability, conductivity and catalytic activity of PB, it was desirable to disperse PB on supporting materials with excellent electrical conductivity, large surface area and high stability.

Graphene oxide (GO) was two-dimensional and one-atom-thick sheet material, which exhibited interesting features of large surface area and good stability. PB/GO nanocomposites were investigated [17,18]. Zhang [17] synthesized GO/PB hybrid film by electropolymerizing PB onto the GO modified glassy carbon electrode and then used for electrochemical sensing applications. Li [18] prepared PB/graphene composite film and employed the composite for electrochemical sensing of $H_2O_2$. Compared with PB films and graphene sheets, PB/graphene composite film showed the largest current response to the reduction of $H_2O_2$ due to the synergistic effects between graphene sheets and PB nanoparticles. In addition, polyaniline (PANI) was conductive polymer with excellent electronic properties [19]. Meanwhile, both GO and PANI were functionalized by many groups and these groups can be employed as the anchor sites for nanoparticles, which prevented nanoparticles from aggregating [20,21]. Therefore, the combination of GO with PANI made GO/PANI an advanced support material with excellent electrical conductivity, large surface area and high stability. Up to now, a few examples of synthesis of GO/PANI-based nanocomposites were demonstrated [22,23], where GO/PANI were synthesized first by electrochemical or chemical oxidative polymerization method, then nanoparticles are anchored on the surface of GO/PANI. However, the synthesis of

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GO/PANI-based nanocomposites was complicated. Meanwhile, as far as we know, few studies have managed to support PB on GO/PANI. Therefore, it is still highly necessary to develop a facile one-step approach to synthesize PB/PANI/GO for the determination of $H_2O_2$.

In this paper, PB/PANI/GO nanocomposites were synthesized through spontaneous polymerization of aniline and formation of PB nanoparticles on PANI/GO, where aniline was employed as both the precursor of PANI and the reductant for $FeCl_3$–$K_3[Fe(CN)_6]$. Then, the non-enzymatic $H_2O_2$ sensor based on PB/PANI/GO was fabricated and electrochemical performance of the sensor toward $H_2O_2$ was investigated.

## 2. Experimental

### 2.1. Reagents and materials

Aniline ($C_6H_7N$, 99.9%) and ferric chloride crystal ($FeCl_3·6H_2O$, 99.0%) were purchased from Xi'an Chemical Reagent (Xi'an, China). Graphite powder (99.998%, 325 mesh, Alfa Aesar) and $H_2O_2$ (30% v/v solution) were obtained from Shanghai Yuanju Biotechnology Co., Ltd. (Shanghai, China).

### 2.2. Apparatus

Transmission electron microscopic (TEM) images were carried out by Tecnai $G^2$ F20 S-TWIN (FEI, USA). X ray diffraction (XRD) patterns of the samples were taken by D/MAX 3C (Rigaku, Japan). Fourier transform infrared spectroscopy (FTIR) was recorded with TENSIR 27 (Bruker, German). Electrochemical measurements were carried out in a conventional three-electrode electroanalysis system controlled by CHI 660 electrochemical workstation (Shanghai CH Instrument Co. Ltd., China). A conventional three-electrode cell was used, including a glassy carbon electrode (GCE, geometric area = 0.07 $cm^2$) as the working electrode, a saturated calomel electrode as the reference electrode and platinum foil as the counter electrode. All potentials given in this work were referred to the saturated calomel electrode.

### 2.3. Synthesis of PB/PANI/GO

GO was synthesized from graphite powder [24]. 100 μL of aniline was added in aqueous solution of GO (50 mL, 0.5 mg/mL) under vigorous stirring for 30 min. Then, 1 mL of 12 M HCl (containing 0.012 g $FeCl_3·6H_2O$ and 0.014 g $K_3[Fe(CN)_6]$) was slowly added into above solution and the solution was stirred for 24 h. After that, the product was separated from solution by centrifugation and was washed for three times by doubly distilled water.

### 2.4. Electrode modification

GCE was prepared by the casting method. 2.0 mg of PB/PANI/GO were dispersed into 1 mL of water and the solution was sonicated for 8 min. After that, 6 μL of PB/PANI/GO solution and 3 μL of Nafion (0.05 wt%) was dropped on the surface of GCE and then dried at room temperature in air.

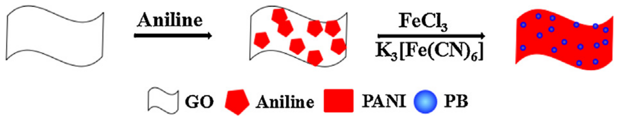

**Fig. 1.** Experimental procedure of synthesis of PB/PANI/GO.

## 3. Results and discussion

### 3.1. Characterizations of PB/PANI/GO

Fig. 1 showed the schematic illustration for the preparation of PB/PANI/GO. PB/PANI/GO were synthesized through spontaneous polymerization of aniline and formation of PB nanoparticles using aniline as both the precursor of PANI and the reductant for $FeCl_3$–$K_3[Fe(CN)_6]$. When adding aniline into GO solution, aniline was adsorbed on the surface of GO through hydrogen bond force [25], which was beneficial for the subsequent polymerization of aniline on the surface of GO. In addition, it was reported that $FeCl_3$–$K_3[Fe(CN)_6]$ was strong oxidant in acidic solution. Therefore, after adding acidic $FeCl_3$–$K_3[Fe(CN)_6]$ into above solution, aniline was polymerized on the surface of GO, meanwhile, $Fe^{3+}$ was reduced to $Fe^{2+}$ by aniline and then PB nanoparticles was obtained through the reaction of $Fe^{2+}$ with $[Fe(CN)_6]^{3-}$. Therefore, PB/PANI/GO were synthesized through a facile one-step approach using aniline as both the precursor of PANI and the reductant for $FeCl_3$–$K_3[Fe(CN)_6]$.

The morphologies of GO and PB/PANI/GO were characterized by TEM. As shown in Fig. 2(A), GO revealed nanosheet structures with wrinkles and folds. In the case of PB/PANI/GO, from Fig. 2(B) and (C), it can be seen that a large number of nanoparticles with the size of about 4.0 nm were homogeneously distributed on the surface of PANI/GO, which benefited from the nucleation sites provided by the functional groups on the surface of PANI/GO. These functional groups prevented PB nanoparticles from aggregating and facilitated the homogeneous distribution. Furthermore, the chemical structural characterization of PB/PANI/GO was investigated by XRD. As shown in Fig. 1(D), PB/PANI/GO revealed some peaks at 24.8°, 35.4°, 43.6°, 54.2° and 57.3°, which were indexed to (220), (400), (422), (600) and (620) planes of PB [26], therefore confirming that the nanoparticles decorated on PANI/GO were PB.

FTIR spectra (Fig. 3) was employed to study the chemical structural characterizations of GO and PB/PANI/GO. It can be seen that GO (curve a) showed absorption peaks at 3417 $cm^{-1}$, 1734 $cm^{-1}$, 1627 $cm^{-1}$ and 1065 $cm^{-1}$ which can be assigned to $—OH$, $C{=}O$, $C{=}C$, $C—O$ stretching, respectively [27]. In the case of PB/PANI/GO (curve b), the new peaks at 1137–1340 $cm^{-1}$ were ascribed to $C{=}N$ stretching vibration and $C—N$ vibrations of PANI [28]. Moreover, comparing with the spectra of GO, PB/PANI/GO also showed two new peak at 2084 $cm^{-1}$ and 498 $cm^{-1}$ due to the stretching modes of $C{\equiv}N$ group and the formation of $Fe^{II}—CN—Fe^{III}$ [15], which confirmed the presence of PB. Therefore, on the basis of the results of TEM, XRD and FTIR characterizations, GO and PB/PANI/GO nanocomposites were successfully prepared.

### 3.2. Electrochemical properties of PB/PANI/GO nanocomposites

Cyclic voltammograms (CVs) were recorded to investigate the electrocatalytic behavior of PB/PANI/GO/GCE. Fig. 4(A) showed CVs obtained at PB/PANI/GO/GCE in 0.5 M KCl solution (HCl, pH 3.0) at a scan rate of 100 mV/s. From Fig. 4(A), it can be seen that PB/PANI/GO/GCE exhibited a pair of well-defined redox peaks with a formal redox potential of 184 mV, which were due to the transitions between PB and Prussian white ($K_2Fe^{II}[Fe^{II}(CN)_6]$) [29]. Moreover, the potential separation of the redox peaks was 19 mV and the potential separation was very close to the theoretical value, indicating that fast charge transfer occurred in PB/PANI/GO composite [18]. The electrochemical stability of PB/PANI/GO/GCE was studied. As shown in Fig. 4(B), no significant current decreased after thirty cycles, indicating the good stability. Furthermore, in order to examined the possible kinetic mechanism of PB/PANI/GO/GCE, the effect of scan rates on the current response was