

In-situ growth of micro-cubic Prussian blue–TiO₂ composite film as a highly sensitive H₂O₂ sensor by aerosol co-deposition approach



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ABSTRACT

Assisted by the aerosol co-deposition approach, Prussian blue (PB)–TiO₂ composite film can be *in-situ* formed in one step. The architecture of this film is constructed by two layers: PB–TiO₂ nano-particles as a ground layer and individual PB micro-cubes as a top layer. Together with the strong electrocatalytic ability from regular PB morphology, TiO₂ can denote its high catalysis in H₂O₂ detection attributed by the extinction of band gap since the combination of PB. Under a low operation potential -0.05 V, this sensor exhibits an ultrasensitive ability ($1726.8 \mu\text{A mM}^{-1} \text{cm}^{-2}$), stability and low detection limit ($1.5 \mu\text{M}$) in H₂O₂ analysis. The application of this composite material is hopeful to extend in complex physiological analysis, and the preparation approach is promising to extend in more composite materials *in-situ* synthesis.

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1. Introduction

The purpose of biosensor research is continuously enhancing performance in order to satisfy humans' various demands, such as food and production safety (Raz et al., 2010), clinic treatment (Xu et al., 2010), disease control (Lu et al., 2007). Among lots of physiological activators, hydrogen peroxide (H₂O₂) is an essential detection target which refers to nearly all application fields. In some situation, H₂O₂ is able to provide the positive power (Villegas et al., 2005; Tan et al., 2012), but sometimes, it will be harmful to our body or health (Kitsati et al., 2012; Silva et al., 2012). Accordingly, the improvement of accuracy and sensitivity in H₂O₂ detection is still attracting many attentions from scientists. Characters of modified material are normally crucial to the performance of biosensors. Hence, in order to realize both high performances in sensitivity and accuracy, material selection should be well considered.

Owing to the low detection potential and good electrocatalytic ability to H₂O₂, Prussian blue (PB) is widely called “artificial peroxidase” (Karyakin et al., 2000; Lu et al., 2006). In our previous work, we have focused on the morphology design and control of PB film. Relied on our developed preparation approaches, such as aerosol deposition (Chu et al., 2010), electric field induced self-assembly (Chu et al., 2011) and template hole fill-in method (Chu et al., 2012), PB has already formed various regular

structures. However, although original property of PB is very suitable to serve as a H₂O₂ sensing material, the further improvement is difficult due to its essence limitation. Generally, in order to enhance the performance of one material, another active substance can be doped for assistance (Stankovich et al., 2006; Galan-Vidal et al., 1998). If a high catalytic material can be compatible with PB film, meanwhile the formed film also realizes a regular morphology, the performance can be expected to improve. TiO₂ is a nontoxic oxide with the high catalysis, stability and biocompatibility (Wang et al., 2010). Its application has already referred to biosensor fabrication, but requiring a high detection potential (Cosnier et al., 1997; Cao et al., 2008). This could cause an evident interference from other co-existed compounds in real detection system. While, PB can erase above defects because of its potential reduction function. Thereby, combination of PB and TiO₂ will be desired to possess both high catalysis from TiO₂ and excellent anti-interference from PB. However, with the existence of TiO₂, *in-situ* regular growth of PB is not easy to realize due to the disturbance of assembly and crystallization space.

In this work, we designed to apply aerosols as the reactive unit for co-deposition of TiO₂ and PB because of their small volume and uniform distribution. These properties can separate and decrease the adverse effects of TiO₂ for regular PB crystallization. In one step, uniform PB micro-cubes can be *in-situ* formed on a layer of PB–TiO₂ composite ground film. According to the performance characterizations, the introduction of TiO₂ can reduce 50% of PB surface concentration, but harvesting ca. 50% sensitivity increase in H₂O₂ detection. Moreover, enhancement mechanism is further confirmed that this composition can obviously decrease the band

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gap of TiO₂ to arouse its catalytic function, and regular cubic shape is able to intensify the electrocatalysis of PB film.

2. Experimental section

2.1. Reagents and apparatus

K₄[Fe(CN)₆]·3H₂O (Sigma-Aldrich), FeCl₃·6H₂O (Sigma-Aldrich), Ascorbic acid (Sigma-Aldrich), Uric acid (Sigma-Aldrich) and 30 wt% H₂O₂ (Sinopharm Chemical Reagent Co., Ltd, China) were of analytical grade purity and used without further purification. TiO₂ powder (P25, 80% anatase, 20% rutile) was purchased from Degussa with average size of 21 nm. All solutions were prepared with deionized water.

The electrochemical properties were characterized by electrochemical workstation (CHI 660C, (Shanghai Chenhua, China). All cyclic voltammetry (CV) were operated in 0.05 M phosphate buffer (pH=6.5) with 0.1 M KCl at 25 °C. Pt wire and Ag/AgCl were served as the counter and reference electrodes, respectively. Scanning rate was kept 50 mV/s. Field emission scanning electron microscopy (FESEM) (Hitachi-4800, Japan) characterization were operated to investigate the film morphologies. The spectral properties were studied by UV–vis spectroscopy (PerkinElmer lambda 950, USA). XRD patterns were taken by X-ray diffractometer (Miniflex 600, Japan). Raman spectrum was characterized by Raman spectrometer (Horiba Labram HR 800, Japan).

2.2. Pretreatment of Pt electrode

In order to keep the electrode clean, pretreatment was used on the platinum foil surface (7 × 2 mm²). The surface of Pt electrode was first polished as mirror using metallographical sand paper, and then dipped into the Piranha solution (7:3 mixture of H₂SO₄/H₂O₂, v/v) for 30 min and rinsed with water. After ultrasonic washing in water for 30 min, the Pt electrode was ready for use.

2.3. Growth of PB film

For the deposition of PB films, two solutions were prepared. Solution 1: 0.01 M K₄[Fe(CN)₆]+0.1 M KCl+0.1 M HCl. Solution 2: 0.01 M FeCl₃+0.1 M KCl+0.1 M HCl+0.02 g TiO₂. The concentrations of reactive solutions were kept the same as our previous work for comparison (Chu et al., 2010). The adsorption of K₄[Fe(CN)₆] is the most important step for the aerosol deposition approach. Accordingly, in order to protect the freshness of reactive K₄[Fe(CN)₆] and PB formation, we only added TiO₂ powder into FeCl₃ solution. The prepared K₄[Fe(CN)₆] solution and TiO₂/FeCl₃ suspension were respectively filled in two ultrasonic nebulizers (Shanghai Yu Yue Medical Equipment Co., Ltd, China; Size: 240 × 130 × 200 mm³; Power: 50 W; Frequency: 1.7 MHz). As shown in Fig. S1, a Pt electrode was first fixed in one airtight organic glass container. Then, K₄[Fe(CN)₆] aerosol was continuously injected into the container for certain hours. The average injection rate is 1.5 mL min⁻¹. Subsequently, TiO₂/FeCl₃ aerosol was injected for the same time after the former aerosol exhausted. The following description of deposition time is the total time of K₄[Fe(CN)₆] and TiO₂/FeCl₃ deposition periods. The prepared electrodes were cleaned with deionized water and heated at 100 °C for 1 h to dehydrate.

2.4. Density functional theory (DFT) simulation

All the simulative processes were set at the level of DFT by Cambridge sequential total energy package (CASTEP). The Perdew–Burke–Ernzerhof functional (PBE) of gradient-corrected functional

was chosen as the exchange–correlation functional. Ultrasoft pseudopotential was chosen to allow the calculation to run with the lowest possible cutoff energy for basis set. The electronic wavefunctions at each *k*-point were expanded in a plane-wave basis set up to 300 eV. The Monkhorst–Pack *k*-points for the accuracy of the Brillouin zone sampling were set at fine level. The SCF tolerance reached 1 × 10⁻⁶ eV/atom.

3. Results and discussion

3.1. Influence of deposition time

Prussian blue owns different valences of irons (Fe²⁺, Fe³⁺) in its unit cell. Imposing certain potentials can push its electron transfer to realize substance transformation. According to the change amount of electric quantity, the surface concentration of PB on electrode can be calculated. Deposition time is usually essential for the control of formation amount (Taberna et al., 2006; Strohm and Lobmann, 2005). Hence, focusing on different deposition times, CV technology was applied to characterize the sample PB electrodes which are prepared by 5, 6, 7, and 8 h, respectively. From the results of Fig. 1a, we can find that at the ranges of 0.15–0.19 V and 0.23–0.26 V, there are two obvious current peaks. These double peaks reveal the shift processes between Prussian blue (Fe₂[Fe

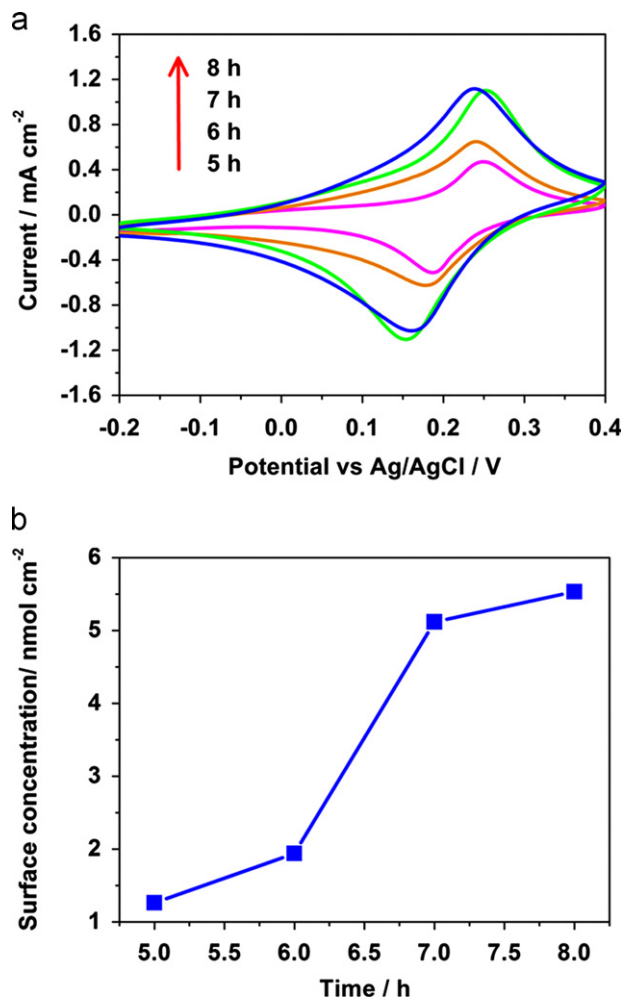


Fig. 1. (a) CV diagram of PB–TiO₂ modified electrodes which were prepared at 35 °C and in 5, 6, 7, and 8 h, respectively; and (b) diagram of calculated PB surface concentrations according to CV results.

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