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Photocatalytic synthesis and synergistic effect of Prussian blue-decorated Au nanoparticles/TiO_2 nanotube arrays for H_2O_2 amperometric sensing

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ABSTRACT

Prussian blue (PB) nanocrystals are decorated on the TiO_2 nanotube arrays (TiNTs) by one-step photocatalytic method. The formed PB-TiNTs composite shows high electrocatalytic activities towards the reduction of H_2O_2. When the TiNTs layer is covered with a layer of Au nanoparticles (AuNPs) before PB decoration, the electrocatalytic activity is significantly enhanced on the as-formed PB-AuNPs/TiNTs nanocomposite, due to the synergistic effect of AuNPs and PB. Compared with PB-TiNTs, the PB-AuNPs/TiNTs based electrode shows improved electrochemical behaviors for H_2O_2 sensing, such as low overpotential, high sensitivity, wide linear range, and decreased detection limitation, and thus provides a simple, promising and cost-effective sensing platform for development of enzyme based biosensors.

1. Introduction

Since the first reports by Zwilling in 1999 [1], TiO_2 nanotube arrays (TiNTs) formed by electrochemical anodization of Ti have generated much interest [2], due to its high photocatalytic efficiency, chemical inertness, surface amphotericity, and nontoxicity. Pioneering work in applying TiNTs in bioelectronics and biosensors explored the catalytic electrochemistry of some model biochemical compounds, such as hemoglobin [3,4], cytochrome c [5], horseradish peroxidase [6,7], levodopa [8], 5-hydroxytryptamine [9]. Hydrogen peroxide (H_2O_2), as a product of industry and atomic power stations, is a chemical threat to the environment on one hand, and, on the other hand, it is the product of enzymatic reactions and is recognized as one of the major factors in the progression of important diseases. Detection of low levels of H_2O_2 is of great importance for modern medicine and environmental protection. However, owing to the poor electrical conductivity and higher detection potential, investigation on preparing of H_2O_2 amperometric sensor by TiNTs based electrode has not been realized yet.

Prussian blue (PB), formula $Fe_4^{III}[Fe^{II}(CN)_6]_3$, because of their high activity and selectivity toward the reduction of H_2O_2 and O_2, is usually considered as an “artificial enzyme peroxidase” and has been extensively used in the construction of electrochemical amperometric biosensors [10,11]. Up to now, many methods have been used to prepare PB-modified electrodes. Xia and coworkers reported to form PB monolayers on gold substrate from an acid ferricyanide solution by electrochemical and photochemical approach [12–14]. Gaitan and coworkers reported to prepare mesoporous TiO_2 and PB modified ITO electrode for H_2O_2 sensing by dip-coating the ITO substrate in a Ti (IV) ethanol-water sol [15]. And then the Prussian blue nanoparticles were decorated by immersing sequence in Fe(II) and $Fe(CN)_6{}^{3-}$ solutions for several times. Recently, we also demonstrated to decorate PB on semiconductor surfaces via photocatalytic deposition or galvanic displacement from a ferricyanide and ferric ions containing solution [16,17]. Such nanoscaled interconnects between semiconductor and PB are considered to be important for applications of semiconductor, such as optoelectronics, clinical diagnosis, ion-selective properties, battery applications, and microelectro-mechanical systems.

In this context a most attractive host for PB is nanotubular TiO_2, as due to its unique photocatalytic properties [18,19], PB can be synthesized by photocatalysis method. Additionally, TiNTs have a defined geometry that can be tuned easily in diameter, aspect ratio, “crystal” structure, and biomedical properties, and therefore versatile nanoscale architectures can be built [20–22]. In the present work, to achieve a H_2O_2 amperometric sensing platform with improved electrocatalytic behaviors, the conjugate of Au nanoparticles and TiNTs (AuNPs/TiNTs) is constructed before PB decoration. Owing to the synergistic effect of the good

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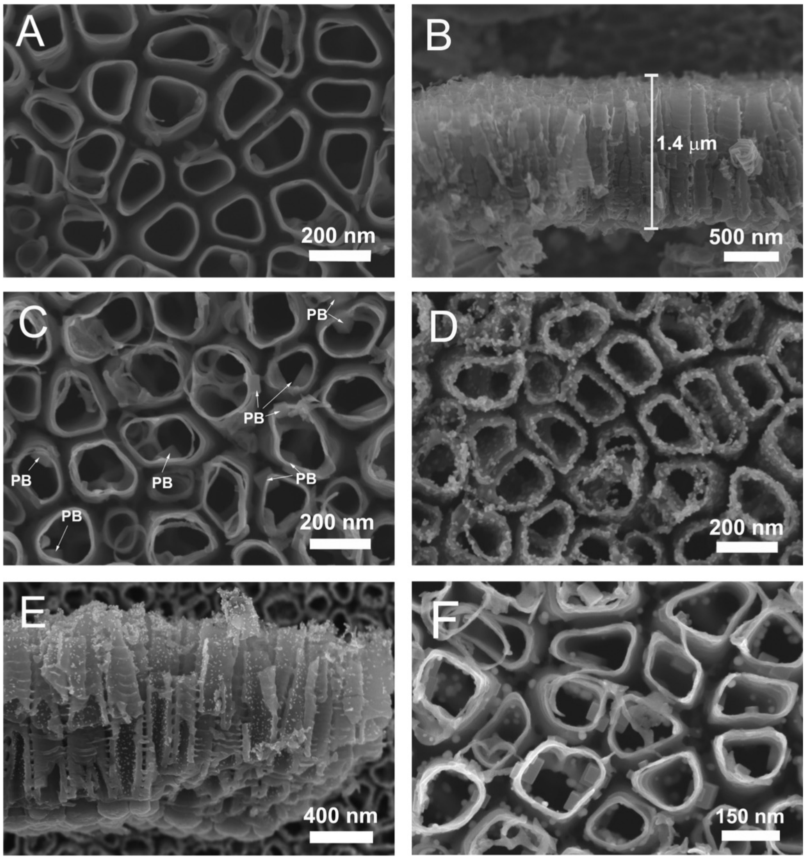

Fig. 1. SEM images of (A) top view and (B) side view of TiNTs, (C) the top view of TiNTs after PB nanocrystals decorated, (D) the top view and (E) side view of TiNTs after Au nanoparticles covering, and (F) the top view after PB nanoparticles decorated onto the AuNPs/TiNTs as-shown in image (E).

electroconductivity of AuNPs and the high electrocatalytic activity of PB, the as-prepared PB-AuNPs/TiNTs based electrode exhibits excellent electrochemical behaviors for sensing H_2O_2.

2. Experimental

For the fabrication of TiO_2 nanotube arrays, Ti foils (0.1 mm thickness, 99.6% purity, Advent) were first degreased by sonication in ethanol and deionized water (DI) and then dried in a nitrogen stream. Anodization was carried out in an electrolyte of glycerol/water (50:50) with 0.27 M NH_4F at 30 V for 3 h where the Ti foils were the working electrode, and a platinum gauze served as the counter electrode. The formed TiO_2 nanotube layers were then annealed at 450 °C in air for 1 h to convert them to an anatase structure.

To Prepare PB-AuNPs/TiNTs, the colloidal AuNPs of ~8 nm diameter were firstly prepared according to the previous protocol [23]. TiNTs were firstly decorated a layer of poly(diallyldimethylammonium chloride) (PDDA) by incubated into 0.05% PDDA aqueous solution for 2 h at room temperature. After washing thoroughly with DI water, the PDDA-modified TiNTs were immersed into 10.0 mL of as-prepared colloidal AuNPs at 4 °C for 4 h. The resulted samples were rinsed with DI water and subsequently placed into a quartz vessel containing 1 mM ferricyanide in the presence of 0.1 M KCl (pH 1.6). Then, the PB decoration was triggered by irradiating the vessel with a commercial UV soruce (300 W Hg lamp) for 90 min. The Hg lamp emits light in the UV-visible spectral region (315 nm – 450 nm), with the strongest peak of the emission line spectrum located at 365 nm. The light source was positioned 20 cm away from the sample, and the average light intensity striking on the surface of the sample was about 100 mW cm^{-2}. The PB-TiNTs samples were prepared by a similar process only without AuNPs decorating step.

The morphologies were characterized using a field-emission scanning electron microscope (FE-SEM, Hitachi S4800). X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer Physical Electronics 5600 spectrometer using Al Ka radiation at 13 kV as excitation source. The IR spectra were recorded on a Nicolet-6700 Fourier IR spectrophotometer (Thermo, USA). The electrochemical measurements were performed using a CHI660D electrochemical workstation (CH Instrument Co. China). The TiNTs acted as the working electrodes (8 mm in electrode diameter). A Pt foil and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. Cyclic voltammetric experiments were carried out in a 10 mM PBS (pH 6.0, containing 0.1 M KCl) with a potential sweep rate of 50 mV s^{-1}.

3. Results and discussion

Under the electrochemical anodization conditions mentioned in the experiment section a ~1.4 μm thick TiNTs with openings of 150 ± 15 nm was obtained. In order to achieve suitable photocatalysis activity and electronic properties, the amorphous TiNTs layer was converted to the anatase phase by annealing at 450 °C [24]. Fig. 1A and B show the top and cross-sectional view of a TiNTs layer after annealing treatment. In Fig. 2A, FTIR spectrum of the resulting PB-TiNTs nanocomposite shows an absorption band at 2089 cm^{-1}, which is attributed to the stretching vibration of -CN group in PB, and is consistent with literature reported elsewhere [11,12]. The chemical composition of the as-synthesized composite nanotubes was further characterized by XPS measurements. In Fig. 2B, the fully scanned spectrum of PB-TiNTs nanocomposite demonstrates the