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One-pot green synthesis of Prussian blue nanocubes decorated reduced graphene oxide using mushroom extract for efficient 4-nitrophenol reduction

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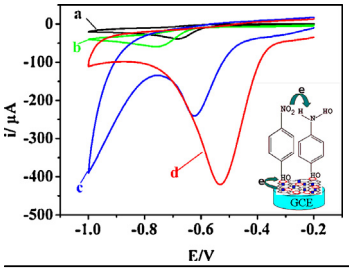
HIGHLIGHTS

- Prussian blue nanocubes/reduced graphene oxide was synthesized by mushroom extract.
- This methodology avoids toxic reagents.
- Detects 4-nitrophenol with low detection.

GRAPHICAL ABSTRACT



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ABSTRACT

One-pot green approach to the synthesis of Prussian blue nanocubes/reduced graphene oxide (PBNCs/RGO) nanocomposite had been attempted. It was based on the extract of mushroom with $K_3[Fe(CN)_6]$ and graphene oxide (GO) as precursors, where the reduction of GO and the deposition of PBNCs occurred simultaneously. The obtained nanocomposite was characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy and electrochemical techniques. With the introduction of β-cyclodextrin (β-CD), the β-CD/PBNCs/RGO system showed linear behavior in the range from 0.01 to 700 μM for 4-nitrophenol with a low detection limit of 2.34 nM (S/N = 3).

1. Introduction

Nitrophenols are a class of anthropogenic, toxic, inhibitory and biorefractory organic compounds which are used extensively in the production of pesticides, dyes and pharmaceuticals [1,2]. In particular, 4-nitrophenol (4-NP), a toxic hydrolysis product of the insecticides parathion and paraoxon, exists not only in wastewater from industries such as refineries, but also in freshwater and marine environments [3]. Because of its toxicity, it was cited in the List of Pollutants of the US Environmental Protection Agency which had set the allowed limit of 4-NP in wastewater at 0.22 μM [4]. Detoxification of water contaminated with 4-NP is a very difficult process since the presence of a nitro-group on the aromatic compound. It confers a strong chemical stability and resistance to microbial degradation [5]. Therefore, 4-NP determination in environmental samples has been of high interest. Chromatography [6,7], enzyme-linked immunosorbent assay (ELISA) [8] and electroanalytical techniques [9–12] are among the techniques reported for 4-NP determination. Electrochemical methods [13–15] have received considerable attention in the determination of 4-NP due to their great advantages, such as simple operation, fast response, good sensitivity and in situ detection.

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Prussian blue (PB), which is the prototypical metal hexacyanoferrate with the formula of $Fe^{III}_4[Fe^{II}(CN)_6]_3$ [16], has been extensively used as the electron-transfer mediator in the electrochemical sensor [17–19]. One of the most attractive features of PB is that its electroactive metal-chelating framework can undergo reversible, stepwise and multi-electron-transfer reactions [20]. However, low stability and poor conductivity of PB have become serious obstacles for its efficient use. To overcome these obstacles, a series of conductive supports such as polymer [19,21–23], carbon nanotubes [23,24], GO [17,25,26] and RGO [27,28] have been used as substrates to assemble PB nanomaterials. Meanwhile, a simple way to increase the stability of the PB-based biosensors is to improve the intimate contact between PB and its conductive support. RGO, a two-dimensional (2D) sheet with fully delocalized π-electrons, has been highlighted as a support for PB, attributing to its large surface area (2630 $m^2 g^{-1}$), good chemical stability and superior electrical conductivity (10^3–10^4 $S m^{-1}$) [27]. In the microstructure of PB, the ferric ions are coordinated to the nitrogen atoms, and the ferrous ions strongly coordinate to the carbon atoms of the bridging cyanide ligands. It was noticed that both carbon atoms in RGO and the CN of PB are conjugated, and then they could act as electron donor and acceptor, respectively. Therefore, π–π stacking interaction should occur between RGO and CN of PB [26]. However, it is difficult to synthesize RGO based nanocomposites using exfoliated RGO directly because it is hydrophobic and tends to agglomerate irreversibly or even restack to form graphite through van der Waals interactions and strong π–π stacking, which limits its further application [29]. In comparison, GO, which has abundant oxygen-containing surface groups, displays good water solubility. Therefore, it offers us a potential precursor for such nanocomposite fabrication. For an example, Zhang et al. immobilized PB on RGO by directly mixing Fe^{3+} and $[Fe(CN)_6]^{3-}$ in the presence of GO in polyethyleneimine aqueous solution [27].

In this paper, we synthesized PBNCs/RGO by an environmental friendly approach. Mushrooms are rich in proteins, vitamins, polysaccharide and amino acids. They are well known for their antioxidant, antimicrobial, anti-inflammatory, antitumor, and anticancer activities [30,31]. They also exhibit reducing properties. Philip [32] and Bhat [33,34] had synthesized gold and silver nanoparticles, using the mushroom extract as reducing and protecting agents. We demonstrated that mushroom extract can reduce GO and $K_3[Fe(CN)_6]$ to RGO and PBNCs for the first time. More importantly, we found that PBNCs/RGO nanocomposites can be prepared by heating GO and $K_3[Fe(CN)_6]$ in mushroom extract solution, where the reduction of GO and the deposition of PBNCs occurred simultaneously. Many efforts have been devoted to combine PB with RGO for the determination of glucose and hydrogen peroxide [17,18,35]. However, to the best of our knowledge, there have been few reports on the use of PBNCs/RGO for the electro-reduction of 4-NP. Due to the formation of inclusion complex between 4-NP and β-CD [36–38], the β-CD/PBNCs/RGO/GCE was developed as an electrochemical sensor to the electro-reduction of 4-NP. This sensor showed a good electrocatalytic performance to 4-NP with wide linear range, low detection limit, good stability and reproducibility.

2. Experimental

2.1. Reagents and apparatus

Mushrooms were purchased from Walmart (Changchun, China). Graphite powder (99%) and 4-NP were obtained from Sinopharm Chemical Regent Co., Ltd. The solution of 4-NP was prepared by dissolving 4-NP into absolute ethanol. All other chemicals were of analytical grade from Shanghai Chemical Factory (Shanghai, China), and all solutions were prepared with distilled water. The pH of solutions was adjusted with HCl.

The samples were characterized using scanning electron microscopy (SEM: Hitachi S-4800), transmission electron microscope (TEM: HITACHI H-600), X-ray diffraction (XRD: D/max2550VB X-ray diffractometer, Rigaku), and Raman spectroscopy (Renishaw with a 632 nm laser).

2.2. Synthesis of nanocomposites

2.2.1. Preparation of mushroom extract

The mushroom extract was obtained based on the literatures [32,39]. The fresh mushrooms (50 g) were washed repeatedly with distilled water to remove organic impurities presented on the surface. The cleaned mushrooms were crushed into small pieces with a sterilized knife. Then, they were added to water (100 mL) and heated at 80 °C for 3 h. The filtrate was cooled to room temperature and used as reducing agent.

2.2.2. Preparation of Prussian blue nanocubes

To mushroom extract of 10 mL solution (pH 1.0), 10 mL of 5 mM $K_3[Fe(CN)_6]$ (pH 1.0) was added under stirring at ambient temperature. The mixture was then heated at 95 °C for about 3 h. The final product was collected by centrifugation and washed with distilled water three times.

2.2.3. Reduction of graphene oxide with mushroom extract

GO was obtained by oxidizing graphite using an improved method published by Marcano et al. [40]. A suspension of GO was obtained at a concentration of 0.5 mg mL^{-1} with the aid of sonicating for 3 h in distilled water. Equal volumes of the above GO and mushroom extract solution were mixed in a flask by stirring for 30 min to obtain a mixture (pH 1.0). Then the flask was put into oil bath at 95 °C, and allowed to react for at least 3 h, According to the color change before and after the reaction, it could be concluded that GO was reduced by mushroom extract. The obtained dispersion was washed several times by distilled water and collected by centrifugation. It was noteworthy that the resulting dispersion of RGO was not agglomerated, indicating that mushroom extract was also a stabilizing agent for RGO.

2.2.4. Synthesis of Prussian blue nanocubes/reduced graphene oxide

To a vigorously stirred mushroom extract (10 mL, pH 1.0), GO (10 mL, 0.5 mg mL^{-1}, pH 1.0) and $K_3[Fe(CN)_6]$ (10 mL, 5 mM) were added. After stirring at room temperature for 30 min, the reaction mixture was stirred at 95 °C for 3 h. The color of the mixture gradually changed, suggesting the formation of PBNCs/RGO. The solid PBNCs/RGO product was isolated by centrifugation.

2.3. Preparation of modified electrodes

β-CD/PBNCs/RGO suspension was prepared by adding 0.5 mg β-CD into 1 mL PBNCs/RGO (0.5 mg mL^{-1}) suspension, and mixed by ultrasonic treatment (150 W) for 20 min. Prior to the modification, the GCE was polished with 1, 0.3 and 0.05 μm alumina slurry. Then, it was washed successively with 1:1 nitric acid, acetone and water in an ultrasonic bath. The β-CD or PBNCs/RGO or β-CD/PBNCs/RGO suspension (0.5 mg mL^{-1}, 5 μL) was dropped on the cleaned GCE surface and dried in air before use.

2.4. Electrochemical measurements

Electrochemical impedance spectra (EIS) measurements were conducted by Princeton Applied Researcher (USA). Electrochemical experiments were performed on a CHI-920c workstation (CH Instruments). A three-electrode cell was employed. A glassy carbon