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Prussian blue/1-butyl-3-methylimidazolium tetrafluoroborate – Graphite felt electrodes for efficient electrocatalytic determination of nitrite

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ABSTRACT

In this study, a novel Prussian blue (PB), ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) and graphite felt (GF) nanocomposite electrode (PB/[Bmim][BF_4]-GF) was obtained by simple methods involving GF placed in a ultrasound bath of [Bmim][BF_4] and then in a PB precursor solution. The electrode showed an efficient activity for electrocatalytic detection of nitrite. [Bmim][BF_4] was ultrasonically immobilized on GF, and played two roles in the fabrication of the electrode: (1) enhancing the synthetic rate of PB from a $K_3[Fe(CN)_6]$ and $FeCl_3$ solution; (2) anchoring PB nanoparticles on the surface of the GF. The PB/[Bmim][BF_4]-GF electrode was characterized by scanning election microscopy (SEM), infrared spectroscopy (IR), X-ray diffraction (XRD) and electrochemical methods, respectively. The as prepared PB/[Bmim][BF_4]-GF electrode exhibited a rapid response of less than 2 s, a very high detection sensitivity of 3.5 A mol^{-1} L, a low detection limit of 1.3×10^{-8} mol L^{-1} as well as excellent stability and selectivity.

1. Introduction

Nitrite is of both environmental and biological importance and is omnipresent within the environmental, food and physiological systems. However, due to its potential toxicity (e.g. promoting the irreversible oxidation of hemoglobin and reducing the blood capacity to transport oxygen [1] or being metabolized to carcinogenic N-nitroso compounds [2]), precise and reliable determination of nitrite has become important for environmental protection and public health. Hence, many methods for nitrite detection such as spectrophotometry [3], chemiluminescence [4], chromatography [5], capillary electrophoresis [6] and electrochemistry [7,8] have been developed. Among all the mentioned methods, electrochemistry has been proven to be one of most favorable for nitrite detection because of its simple apparatus, easy operation and low cost. Additionally, as a kind of electrode material, carbon fiber possesses outstanding comprehensive properties such as very high strength to weight ratio, excellent chemical resistance, superior electrical and thermal conductivities, low cost and conducive to industrial production [9]. Graphite felt (GF), which is a flexible, conductive porous carbon fiber material, can facilitate easy access of electrolytes to the electrodes and the porous surface of its 3D structure can be functionalized to yield a high surface area with tailored properties [10].

Prussian blue (PB), as a classical prototype of mixed-valence transition metal hexacyanometalates, is a well studied material with a wide panel of applications in the fields of electrocatalysis [7], electrochromic display [11], ion selective electrodes [12], charge storage devices [13], catalysis [14], and biosensors [15]. The rate of the conventional synthetic methodology of PB i.e. mixing aqueous solutions of ferric (Fe^{3+}) and ferricyanide ($[Fe(CN)_6]^{3-}$) ions, is so slow that actions are needed to promote the growth of PB in a reasonable time: e.g. using high temperature, or noble metal catalysts (Au, Pt, Ag) [16–18]. Ionic liquids (ILs) may be favorable materials to enhance the reaction rate for they have been used as catalysts in reactions such as controllable synthesis of cellulose acetate [19] and they are an interesting medium for the synthesis and stabilization of nano-sized objects owing to their unique

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physicochemical properties, such as good solubility, relatively low viscosity, high fluidity and excellent thermal and chemical stability. For instance, Larionova et al. synthesized metal ferricyanide magnets $M_3[Fe(CN)_6]_2$/[Rmim][BF_4] (where M^{2+} = Ni^{2+}, Co^{2+} or Mn^{2+}, and [Rmim][BF_4] = 1-alkyl (R)-3-methylimidazolium tetrafluoroborate) and $Fe_4[Fe(CN)_6]_3$/[Rmim][BF_4] using 1-R-3-methylimidazolium salts, which acted as both a stabilizing agent and a solvent [20,21]. Qu et al. reported the synthesis of a new kind of PB type material using $K_3[Fe(CN)_6]$ and [Bmim][$FeCl_4$] as reactants and studied its magnetic properties and electrocatalytic activity in oxidizing sodium nitrite [22]. According to our knowledge, the study of ILs for enhancing the synthetic rate of PB and the detailed electrochemical detection of NO_2^- with GF systems have never been reported so far.

Here, we developed a one-step synthesis method of PB nanoparticles, the synthetic rate of which was promoted by 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) on GF substrate at room temperature, and studied the performance of the corresponding PB/[Bmim][BF_4]-GF electrode for electrocatalytic oxidation of nitrite. Our results indicated that the PB/[Bmim][BF_4]-GF electrode exhibited a great performance for the determination of nitrite, in terms of anodic current increment (regarding the oxidation of sodium nitrite).

2. Experiment

2.1. Reagents and apparatus

GF was obtained from commercially available polyacrylonitrile-based graphite fibers pretreated by nitric acid. [Bmim][BF_4] was purchased from Shanghai Chengjie Chemistry Co. Ltd. (Shanghai, China). Other chemicals were acquired from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). All chemicals were of analytical grade and used as received. All electrolyte solutions were prepared using 0.5 mol L^{-1} KCl.

All electrochemical experiments were carried out on a CHI 618C Electrochemical Workstation (CH Instruments, Shanghai, China) in a standard three-electrode setup with a freestanding GF as the working electrode, a saturated calomel electrode (SCE) (caution: handled with care because of mercury content) as reference electrode and a platinum wire electrode as counter electrode. Scanning electron microscopy (SEM) was performed on a JEOL JSM-6701F. UV–vis spectrophotometry was conducted using an Agilent 8453 UV-spectrophotometer. Power X-ray diffraction (XRD) data were collected using a graphite monochromatic Cu Kα radiation (λ = 0.15406 nm) on a Rigaku D/MAX-2400 X-ray diffractometer. Fourier transform infrared (FTIR) spectroscopy was obtained using KBr pellets after baseline correction on a NICOLET NEXUS-670-FTIR spectrometer.

2.2. Fabrication of the PB/[Bmim][BF_4]-GF electrode

The activated GF obtained following a previously reported procedure [17] was incubated in a centrifuge tube with 1.5 mL of an ethanol solution containing 0.14 mL of [Bmim][BF_4] and was placed in an ultrasonic bath for 1 h. It was then dried at 60 °C overnight to remove any residual ethanol. The [Bmim][BF_4] immobilized GF was referred to as [Bmim][BF_4]-GF. Then the [Bmim][BF_4]-GF electrode was immersed in 20 mL of fresh aqueous solution containing 1.0 mmol L^{-1} $K_3[Fe(CN)_6]$, 1.0 mmol L^{-1} $FeCl_3$, 0.1 mol L^{-1} KCl and 0.025 mol L^{-1} HCl for 1 h. Then the electrode was carefully washed by double-distilled water and dried at 90 °C in a vacuum oven for 3 h. Such an electrode was denoted as PB/[Bmim][BF_4]-GF. For comparison, a bare GF was also treated in the same conditions, except [Bmim][BF_4], and this is hereafter referred to as a "PB/GF".

3. Results and discussion

3.1. Characterization of the PB/[Bmim][BF_4]-GF electrodes

The microstructure and morphology of GF, [Bmim][BF_4]-GF, PB/GF and PB/[Bmim][BF_4]-GF electrodes were characterized by SEM. Fig. 1A shows a micrograph of the GF in which a three-dimensional macroporous open-pore structure was observed with diameters of fibers around 7–9 μm (Fig. 1A inset), and on the surface of each GF, lots of gaps and cracks were discovered. No obvious morphological modifications of the fibers were noticed before and after the treatment by [Bmim][BF_4] (Fig. 1A and B). Only few and asymmetrical PB objects have been deposited on GF without [Bmim][BF_4], after immersion in the ferricyanide/ferric solution (Fig. 1C). This deposition can be related to the adsorption of the precursors on oxygen-containing groups on the GF surface [23]. On the contrary, numerous PB was homogeneously deposited on the surface of the [Bmim][BF_4]-GF with an average size of about 40 nm (Fig. 1D) and a three-dimensional hierarchical macroporous open-pore structure was clearly shown in the inset of Fig. 1D. This outcome confirms the promoting effect of [Bmim][BF_4] on the growth process of PB. The highly dispersed PB nanoparticles on high surface area of GF may create a better communication between electrode and analyte. To demonstrate the [Bmim][BF_4] enhancing effect on PB grafting, we followed the absorbance of the reacting ferricyanide/ferric solution at 420 nm during the reaction process, which is the energy of the strongest absorption peak of $[Fe(CN)_6]^{3-}$ [24]. The results obtained are shown in Fig. 1E. Here, the decrease of absorbance at 420 nm was so small that it cannot be detected in the presence of a bare GF in the solution. However, an appreciable change (700%) was observed in the presence of a [Bmim][BF_4]-GF. This behavior indicated that a significant amount of $[Fe(CN)_6]^{3-}$ was consumed to produce PB in the presence of [Bmim][BF_4], and this is in agreement with the SEM results in Fig. 1C and D.

The FTIR spectrum of a PB/[Bmim][BF_4]-GF is exhibited in Fig. 1F, in which the absorption band at 2083 cm^{-1} shows the common characteristics of PB, corresponding to the stretching vibration of the CN groups [16] and the absorption band at 495 cm^{-1} is due to the formation of M-CN-M' [25], both of which indicate that PB exists. The absorption bands at 1615 and 3430 cm^{-1} refer to the H–O–H bending mode and O–H stretching mode, respectively, which indicate the presence of interstitial water. In addition, the absorption bands at 3147 cm^{-1} can be attributed to aromatic C—H stretching, whereas those at 2960 cm^{-1} can be attributed to aliphatic C—H stretching, derived from ILs [26]. The formation of PB/[Bmim][BF_4]-GF and GF are identified by XRD (Fig. 1G). The XRD patterns of the two kinds of materials exhibit diffraction peaks close to 25.8°, 41.2° and 52.5°, which can be attributed to the diffraction of GF, while the peaks near 17.5°, 35° and 40° refers to (2 0 0), (4 0 0) and (4 2 0) reflections of the face-centered-cubic phase of PB (JCPDS card No. 73-0687), demonstrating PB nanoparticles on the GF.

Fig. 2A shows the cyclic voltammetry (CV) response of 0.5 mol L^{-1} KCl at PB/[Bmim][BF_4]-GF, PB/GF and [Bmim][BF_4]-GF between −0.2 and 1.0 V at a scan rate of 50 mV s^{-1}. There are two pairs of redox peaks observed, one at 0.25/0.15 V attributable to the Prussian white (PW)/PB reaction (PW: the oxidation of PB) and one at 0.9/0.8 V attributable to the PB/Berlin green (BG) (BG: the reduction of PB) reaction. The separation of PB/BG oxidation and reduction potentials was only 100 mV and the oxidation peak current was approximately equal to the deoxidization peaks ($i_{pa} \approx i_{pc}$ = 0.78 mA), indicating a reversible process (i.e. a fast charge transfer) occurred at the PB/[Bmim][BF_4]-GF electrode. For comparison, without [Bmim][BF_4], the PB/GF electrode exhibited (11%) smaller peaks, and without PB, [Bmim][BF_4]-GF