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Highly dispersed carbon nanotube in new ionic liquid-graphene oxides aqueous dispersions for ultrasensitive dopamine detection

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ABSTRACT

Graphite oxide (GO) is a pH-dependent amphiphile with hydrophilic edges and a more hydrophobic basal plane. It was found that when the hydrophobic prototype ionic liquid (IL) of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) was added into GO water, it experienced changes from coagulation to being redispersed in water phase by constantly turning its pH to alkali condition. Then new aqueous dispersions of GO-[BMIM][PF_6] "water" formed after facile sonicate. The introduction of [BMIM][PF_6] not only minimize the defects of poor electrical conductivity of GO and more interesting is that the carbon nanotube (CNT) can be highly dispersed in this GO-[BMIM][PF_6] water through a simple and facile ultrasonic method at room temperature, forming a new composite of GO-[BMIM][PF_6]-CNT with high dispersibility. This novel composite enhanced its electrochemical signal obviously in the measurement of dopamine (DA) in biological systems and exhibited a wider linear response ranging from 8.0×10^{-12}–1.5×10^{-5} M. The detection limit of 3.0×10^{-12} M at a signal to-noise ratio of 3 was two orders of magnitude lower than that reported previously.

1. Introduction

Dopamine (DA) is a common pharmaceutical compound usually used to treat central nervous system disorders, such as schizophrenia and Parkinson's disease [1] which is essential for the normal functions of the central nervous system. Hence, the determination of DA is important to diagnose, monitor, and prevent these diseases. While the determination remains a challenge because of its coexistence with high concentrations biomolecules of uric acid (UA) and ascorbic acid (AA) in biological samples. To solve this problem, many electrochemistry methods have been used to detect DA [2,3]. However, many of these methods do not meet the growing requirements for developing more selective and sensitive sensors for DA. Therefore, it is significative to design sensors that are specific, selective and sensitive towards the determination of DA.

Carbon nanotubes (CNTs) have been widely utilized in the detection of biomolecules, owing to their unique structures [4], high stabilities and remarkable electrical properties [5,6]. However, they are heavily entangled with one another which make them tend to form irreversible agglomerates and restrict their processing and applications [4]. Hence effective dispersion of the CNTs is strongly needed before any further applications can be applied. Generally, covalent dispersion method typically involves deteriorate or contaminate the functional carbon surfaces; while the noncovalent approach is more promising and the π-π stacking with aromatic molecules has already been the most common method.

Grapheme oxide (GO) is an interesting option, it actually an amphiphile with hydrophilic edges and a more hydrophobic basal plane retaining the potential of strong π-π interaction with other conjugated sp_2 network structures which make it can serve as a dispersing agent for effective dispersion carbon materials and form all-carbon nanocomposites by a simple and facile ultrasonic method [7–11]. However, the poor electrical conductivity of GO greatly restricted the applications of CNT-GO composite especially in the electrochemical detection application [12]. Therefore, seeking proper materials to minimize the defects of GO and increasing the conductivity of the composite has become a great challenge.

Recently, it is found that the imidazolium based ionic liquids (ILs) can also be used to disperse SCNTs easily by mechanical milling [4] which is a simple method. However, the limitations lie in high concentration requirement of the ILs [13]. It has been reported that GO can act as a surfactant sheet to stabilize oil droplets in water [14]. In order to take full advantage of high

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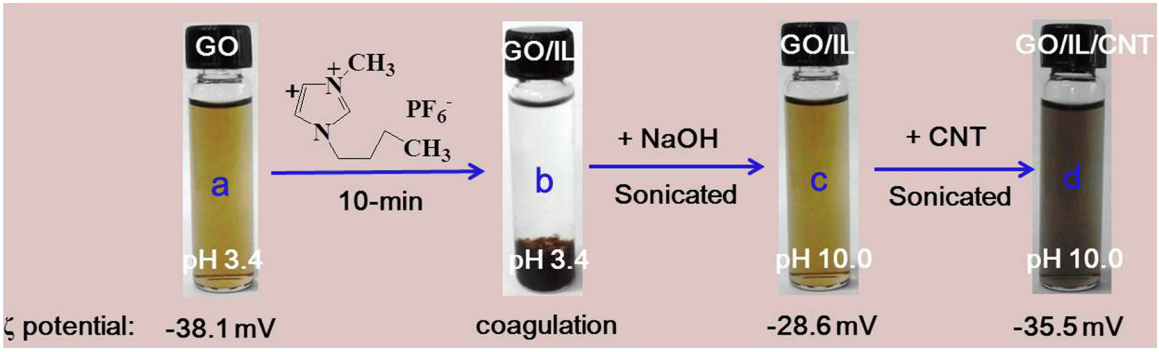

Fig. 1. Dispersing CNTs in GO-[BMIM][PF_6] (GO-IL) water.

electrical conductivity and wide electrochemical window of the ILs [15], here we extend our study to the behavior of a prototype IL of [BMIM][PF_6] [16–18]. We found that GO can also stabilize the [BMIM][PF_6] in water which is composed of bulky, asymmetrical ions through constantly turning pH to alkali condition, forming new aqueous dispersions of GO-[BMIM][PF_6] water. One may speculate that the CNTs can be more effectively dispersed in this GO-IL water will occur. We exactly found that the CNT-GO-[BMIM][PF_6] composite, thus fabricated, is highly dispersed in water.

Involving only simple ultrasonication processes, it offers an easy manipulation for large-scale solution-dispersed CNT composites and this CNT-GO-[BMIM][PF_6] composite was found to exhibit excellent electrochemical properties toward the detection of DA in the presence of a large excess of uric acid (UA) and ascorbic acid (AA).

2. Experimental

2.1. Reagents

1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) was purchased from Sinopharm Chemical Reagent Co. (China). Multi-walled carbon nanotubes (CNTs, purity > 95%, diameter 40–60 nm) were purchased from Jiangsu JF Advanced Technologies, Inc. (Nanjing, China). Ascorbic acid (AA), DA and uric acid (UA) were purchased from Aladdin Chemical Reagent Co. (China). Human serum were provided by the local hospital and stored at 4 °C. All aqueous solutions were prepared using deionized (DI) water.

GO was synthesized by a modified Hummers' method as reported elsewhere from graphite powder [19]. The dry GO filter cakes were redispersed in water to create a stock solution of 1.0 mg/mL, which may be further diluted to various concentrations. For condition optimization experiments, a certain amount of [BMIM][PF_6] was mixed with 10 mL GO water (0.15 mg/mL). The pH value of GO-IL water was modified by adding HCl (1 M) or NaOH (1 M) solution. The zeta potential was measured with Malvern Instruments' Zetasizer Nano system.

2.2. Apparatus

Scanning electron microscopic (SEM) was running on a Hitachi S-4800 SEM instrument (Japan). The UV-visible (UV-vis) spectrum was recorded by a UV-8000 series UV-visible spectrophotometer obtained from Shanghai Yuan Xi Instrument Co. Ltd., (Shanghai, China). Electrochemical impedance spectroscopy (EIS) was performed on an Autolab potentiostat/galvanostat (PGSTAT30) obtained from Eco Chemie B.V., (Utrecht, Netherlands) with a three-electrode system in H_2SO_4 solution (0.5 M) containing $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (5.0 mM, 1:1) mixture as a redox probe, and

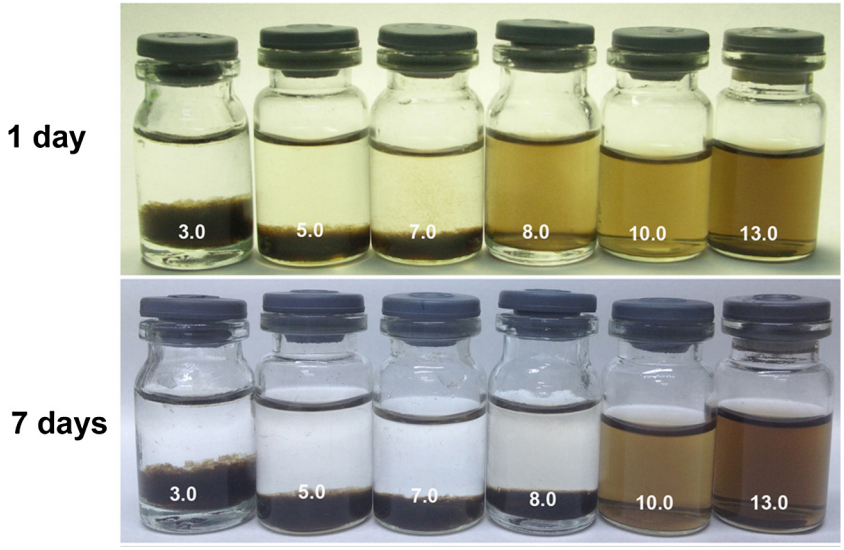

Fig. 2. Photographs of GO-[BMIM][PF_6] with water-bath sonication for 20 min at different pH values and settling for different time.