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Fabrication of the Cu_2O/polyvinyl pyrrolidone-graphene modified glassy carbon-rotating disk electrode and its application for sensitive detection of herbicide paraquat

Xiaoliang Ye, Yonge Gu, Chunming Wang*

Department of Chemistry, Lanzhou University, Lanzhou 730000, PR China

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ABSTRACT

A polyvinyl pyrrolidone (PVP) functionalized graphene nanosheets (GNs) and cuprous oxide (Cu_2O) sub-microparticles (micro-Cu_2O/PVP-GNs) modified glassy carbon-rotating disk electrode (GC-RDE) was successfully fabricated. The electrochemical sensor based on PVP-GNs and micro-Cu_2O was then developed for the investigation of the electrochemical behavior and the sensitive detection of herbicide paraquat (PQ). By cyclic voltammetry (CV) and differential pulse voltammetry (DPV), it was found that the modified electrode provided an electron-transfer microenvironment to accelerate the electrochemical catalytic reaction of PQ. The DPV signals of PQ on the micro-Cu_2O/PVP-GNs modified GC-RDE were significantly enhanced. The enhanced DPV signals represented the excellent analytical performance of PQ detection in the range of 1.0×10^{-6}–2.0×10^{-4} mol L^{-1}, with a low limit of detection (LOD) of 2.65×10^{-7} mol L^{-1} (S/N = 3), and the acceptable reproducibility (RSD = 2.02%, n = 5). The proposed method has been used to determine the residual amount of PQ in cabbage leaves samples. By the treatment of the experimental data, the electrochemical reaction mechanism of PQ involves a diffusion-controlled quasi-reversible process and a two-electron-transfer process.

1. Introduction

PQ (1,1′-dimethyl-4,4′-dipyridylium ion), also known as methyl viologen, is a popular herbicide that is used widely all over the world. PQ is a foliage contact herbicide with desiccant and defoliant action, and used in the control of a variety of plants such as cabbages. The toxicity of PQ is essentially related to its rapid reduction and is extremely hazardous for human health, causing frequent accidental and suicidal poisoning [1–3]. Generally, literature reports showed that PQ has been analyzed using a wide range of techniques, such as spectrophotometry [4], molecules surface-enhanced Raman spectroscopy [5,6], high performance liquid chromatography–mass spectrography (HPLC–GC) [7], fluorescence emission spectrometry [8], optical sensor [9], gas chromatography–mass spectrometry (GC–MS) [10] and flow analysis [11]. However, some of these methods and techniques are time-consuming, expensive or required complicated pretreatment, which limits their further applications. Compared with these methods, electrochemical methods are supposed to be a good choice because of their high sensitivity, good stability, simplicity and low cost. In recent years, the electrochemical determination of PQ has been performed utilizing different electrode surfaces including carbon paste electrode [12], glassy carbon electrode [13] and the techniques based on various chemically modified electrodes [14–16]. However, for all we know, the modification on GC-RDE with both micro-Cu_2O and GNs to achieve sensitive, fast and facile determination of PQ remains a challenge.

Cu_2O, with a band gap of 2.17 eV [17], is attracting considerable research interests for its potential applications in sensing [18], solar conversions [19], catalytic activity [20] and anode material for lithium ion batteries [21]. Although some researchers have aimed at the morphology of Cu_2O [22,23], more studies have been reported that Cu_2O has a great potential application in sensitive determination of organic pollutants [24–26] for its excellent electrocatalytic activity. Moreover, it is reported in our previous work that Cu_2O also performed the high selectivity and the potential high photo-electrocatalytic property in the electrocatalytic determination of *p*-nitrophenol [25]. However, as a *p*-type semiconductor, the pure Cu_2O is not suitable for sensitive detection because the conductivity of Cu_2O is not so good. In contrast, graphene nanosheets, a single layer of carbon atoms in a closely packed honeycomb two-dimensional lattice, has attracted enormous attentions since it was first reported in 2004 [27]. Due to the novel properties such as good mechanical strength, large specific surface area and high conductivity, GNs has exhibited potential applications in nanoelectronic devices [28], transparent conductors [29], sensors [30,31],

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* Corresponding author. Tel.: +86 931 8911895; fax: +86 931 8912582.
E-mail address: wangcm@lzu.edu.cn (C. Wang).

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capacitors [32] and nanocomposite materials [33,34]. However, the liquid-phase production of GNs-based materials is severely hampered by the poor solubility of GNs, which is chiefly due to the attractive van der Waals forces between GNs and strong π–π stacking [35,36]. Therefore, as recent reports, great efforts have been made to improve their solubility through covalent or non-covalent functionalizations [37–39]. PVP, as a nonionic surfactant, was also chosen to increase the solubility of GNs and to prevent GNs from agglomerated in aqueous solution [39]. Accordingly, functionalizing GNs with PVP could be an effective method to improve the solubility, for the extending application in analysis determination.

In the last decade, many more groups have investigated the integration of Cu_2O on carbonaceous materials. Composites of graphene–Cu_2O [34], single-walled carbon nanotubes–Cu_2O [40] and fullerene–Cu_2O [41] have been synthesized successfully. Since the methods of the composite synthesis have already been developed well, pure Cu_2O microparticles and PVP-GNs here were prepared and reduced separately. The sensor based on micro-Cu_2O/PVP-GNs was fabricated by dropping the dispersions of micro-Cu_2O and PVP-GNs on GC-RDE successively. Besides, RDE is one of the important tools for measuring electrochemical kinetic parameters of more complicated reaction procedures. Meanwhile, the papers of the modified RDE for the organic pollutant determination were rarely seen [42]. Therefore, compared to the common glassy carbon electrode, GC-RDE could amplify the reaction signals for determination and should be a good tool for monitoring the electrode reaction procedure.

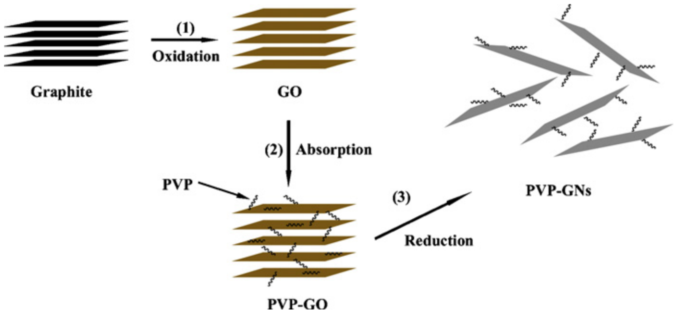
In this work, a highly sensitive, facile and stable electrochemical sensor based on both PVP-GNs and micro-Cu_2O was established for the determination of PQ on GC-RDE. CV was employed to investigate the electrocatalytic ability of PQ, and DPV was introduced to measure electrochemical kinetic parameters and the quantification of PQ on the micro-Cu_2O/PVP-GNs modified GC-RDE. Because of the high catalytic property of micro-Cu_2O and the excellent electric conductivity and solubility of PVP-GNs, the electrochemical signals of the fabricated sensor were significantly amplified which would achieve sensitive PQ detection. In this paper, the electrode reactions of PQ contained two steps, which indicated that the micro-Cu_2O/PVP-GNs modified GC-RDE could be consider as an important way to study the mechanism of the electrocatalytic determination of organic pollutants. Meanwhile, the proposed electrochemical sensor also displayed acceptable reproducibility and good selectivity and could be available for the determination of the residual amount of the PQ in natural samples (cabbage leaves) with satisfactory results.

2. Experimental

2.1. Apparatus and reagents

Nafion-117 (5 wt.%) and graphite powder (KS-10) were purchased from Aldrich reagent company. PVP with a molecular weight of 58,000 (Jkchemical) was used directly. All of the other compounds were of analytical grade and used without further purification. The ultra-pure water was prepared by the Milli-Q system (Milli-pore Inc., nominal resistivity 18.2 MΩ cm). The pure PQ was separated from the commercialized PQ by column chromatography. The sample was obtained through eluting solvents of methanol and ethyl acetate with the ratio of 1:5, 1:3, and 1:1. A 1×10^{-3} mol L^{-1} stock solution of PQ was allocated with Milli-Q water and stored at 4 °C in the dark.

The electrochemical measurements were studied at room temperature in the same reactor using 10 mL of the stored PQ solution and 90 mL electrolyte of 0.1 mol L^{-1} phosphate buffer solution (PBS, pH 7.0). The electrochemical signals were recorded on a CHI 7101c electrochemical workstation (Shanghai Chenhua Instrument Co., China) which are composed of a platinum-wire auxiliary electrode, a KCl saturated Ag/AgCl reference electrode and the modified GC-RDE working electrode. Field-emission scanning electron microscopy (FESEM) was running on a Kevex JSM-6701 (Tokyo, Japan). The X-ray-diffraction (XRD) data was collected on XRD-6000 (Shimadzu, Tokyo, Japan) using Cu-Kα (1.5406 Å) radiation. X-ray photo-electron spectroscopy (XPS) was performed on a VG Escalab 210 electron spectrometer equipped with Al-Kα X-ray radiations ($h\nu$ = 1486.6 eV) as the source for excitation.



Scheme 1. The proposed schemes of the formation of PVP-GNs composites. (1) Oxidation of graphite (black blocks) to GO (lighter colored blocks) with greater interlayer distance, (2) absorption of PVP on the GO, and (3) formation of PVP-doped GNs by the reduction of PVP-GO. The disordered carbon sheets are simplified to idealized planar model.

2.2. Graphene and cuprous oxide preparation

Graphite-oxide nanosheets (GO) were synthesized from natural graphite powder by a modified Hummers and Offeman method [43] and dispersed in water to form a 300 mL of 0.5 mg mL^{-1} GO dispersion by ultrasonication for 1 h. 3.00 g of PVP was slowly added into the GO dispersion under constantly stirring before the pH was set to 12.00 by adding 2 mol L^{-1} NaOH solution. After magnetic stirring for 5 h, the resulting dispersion was further treated with 3.0 mL of 1 mol L^{-1} hydrazine hydrate and allowed to react for 2 h at 80 °C. Finally, a black precipitation was yielded by 3 times of centrifugation at 15,000 rpm for 10 min and several times of water-washing cycles. The final black precipitation was then dried in vacuum. The diagram of the general synthesis of PVP-GNs composites was depicted in Scheme 1.

The Cu_2O microparticles were fabricated by copper–citrate complex with hydrazine hydrate under alkaline condition at room temperature, as our previous work [25]. In a typical procedure, 200 mL of aqueous solution containing 0.001 mol L^{-1} $CuSO_4 \cdot 5H_2O$ and 0.001 mol L^{-1} $C_6H_5Na_3O_7 \cdot 2H_2O$ (Na_3Cit) was put into 500 mL flask. The pH of the complex solution was then adjusted to 12.00 by adding 2 mol L^{-1} NaOH solution. The solution was further treated with 4.0 mL of 1 mol L^{-1} hydrazine hydrate under magnetic stirring at room temperature for 1 h. A orange yellow powder thus was yielded. Collect the powder and wash it with Milli-Q water several times and then dry in a vacuum at 60 °C for 12 h.

2.3. Fabrication of electrochemical sensor

Before fabrication, non-modified GC-RDE was polished by 0.3 μm alumina slurry to mirror like, and then the mirror like GC-RDE was washed successively with anhydrous alcohol and water in an ultrasonic bath for 3 min, respectively, and dried in N_2 blowing. 5.0 mg PVP-GNs was added into 900 μL anhydrous alcohol and 100 μL Nafion-117 (5 wt.%), followed by ultrasonication for 1 h. A homogeneously dispersed solution (5.0 mg mL^{-1} PVP-GNs) was obtained. As the same, 5.0 mg mL^{-1} micro-Cu_2O dispersion