



# Determination of copper ions using a phytic acid/polypyrrole nanowires modified glassy carbon electrode



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## ABSTRACT

This study reports a sensitive electro-analytical method for the determination of trace amounts of  $\text{Cu}^{2+}$  using a phytate functionalized polypyrrole nanowires (PPy NWs) modified glass carbon electrode. The phytic acid/polypyrrole (PA/PPy) NWs were prepared by an electrostatic adsorption and ultrasonic mixing. The results showed that both PPy NWs and PA/PPy NWs modified glassy carbon electrodes have electrochemical responses toward  $\text{Cu}^{2+}$ . However, owing to the synergistic contribution between the PPy NWs and PA, the PA/PPy NWs modified electrode exhibited higher sensitivity than that of PPy NWs modified electrode. The PA/PPy NWs composites functionalized electrodes showed a good linear relationship with  $\text{Cu}^{2+}$  at concentration ranges of 10–60  $\mu\text{g}\cdot\text{L}^{-1}$ , and the limit of detection ( $S/N = 3$ ) was 3.33  $\mu\text{g}\cdot\text{L}^{-1}$ . In addition, the electrochemical sensor was applied to assay  $\text{Cu}^{2+}$  in real water samples.

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## 1. Introduction

The development of sensitive, simple and reliable methods for determining toxic heavy metal ions in aquatic environment and biological systems is of tremendous interest owing to their deleterious effects on human health and the environment [1]. Among the heavy metal ions, Copper ions ( $\text{Cu}^{2+}$ ) is an essential trace element and plays a crucial role in many biological systems [2]. However, exposure to high level of copper even for a short period of time can cause gastrointestinal disturbance, while long-term exposure causes liver or kidney damage [3]. Additionally,  $\text{Cu}^{2+}$  accumulation in the neuronal cytoplasm may cause Alzheimer's, Parkinson's, and amyotrophic lateral sclerosis diseases [4,5]. The limit of  $\text{Cu}^{2+}$  in drinking water is 1.3 ppm ( $\sim 1.3 \mu\text{g}\cdot\text{L}^{-1}$ ) according to the U.S. Environmental Protection Agency [6]. As a consequence, it is of great significance to have a reliable and sensitive analytical method accurately determines  $\text{Cu}^{2+}$  in biological and environmental systems.

Until now, many techniques have been developed for the determination of  $\text{Cu}^{2+}$ , such as atomic absorption spectroscopy [7,8], inductively coupled plasma spectroscopy [9], ion chromatography [10], chemiluminescence [11], resonance scattering spectrometry [12] and fluorimetric spectrometry [13,14]. However, these methods are not only having some disadvantages such as sophisticated and time-consuming procedures, but also unsuitable for large scale monitoring. Therefore, it is a growing interest to develop a promising method for determining levels of  $\text{Cu}^{2+}$  in biological, toxicological

and environmental samples to overcome most of these difficulties [15]. Electrochemical stripping technique is a very efficient method which has been used for the determination of trace metals, due to the highly sensitive, rapid, simple and *in-situ* analytical technique. Desirable materials for electrode modification are of the greatest importance for the electrochemical detection [16]. As we know, chelation or adsorption plays a key role in the process of nitrogen-containing materials for selective detection of heavy metal ions. Polypyrrole (PPy) has aroused our interest not only it is a well-known nitrogen-containing conducting polymer but also it can be used for biosensors [17–20], composite materials [21–23] and micro-electronic devices [24–25]. Phytic acid (PA) is safely used as an oral cleansing agent, water treatment agent, food additive, and cosmetic additive as it is nontoxic and “green” to the environment [26]. PA caught our sight with 12 acid groups can capture metal ions to form stable complexities [27], while a combination of PPy and chelation agent such as the PA may have an ability to enhance the sensing of heavy metals [28].

Herein, we developed a facile way for selective detection toward  $\text{Cu}^{2+}$  using PA/PPy NWs modified glassy carbon electrode. The structural features of the composites were confirmed by scanning electron microscopy (SEM), Fourier transformed infrared spectroscopy (FTIR) and UV–visible spectroscopy. Operational parameters, such as the pH, deposition potential and deposition time were optimized to detect metal ions. The electrochemical sensor showed excellent selectivity and stability for  $\text{Cu}^{2+}$  determination. Furthermore, the developed sensor exhibited a good electrochemical performance for the selective and simultaneous determination of ultra-trace  $\text{Cu}^{2+}$  in real water samples.

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## 2. Experimental

### 2.1. Materials

Phytic acid (PA), dodecyltrimethylammonium bromide (CTAB), and ammonium persulfate (APS) were purchased from Sigma-Aldrich. Pyrrole monomer and other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). The Pyrrole monomer was vacuum distillation and preserved against the oxidation impurities in a refrigerator prior to be used. A 0.1 M HAC-NaAc buffer (pH 4.0) served as a supporting electrolyte and was prepared by mixing the appropriate amounts of  $\text{CH}_3\text{COONa}$  and  $\text{CH}_3\text{COOH}$ . Ultrapure water ( $\geq 18 \text{ M}\Omega$ ) was used throughout the experiments. The standard stock solutions of  $\text{Cu}^{2+}$  from Aladdin were diluted into various concentrations using HAC-NaAc buffer solutions.

### 2.2. Fabrication of the modified electrodes

PPy NWs were synthesized according to the reported method with a slight modification [29–31]. A  $0.2 \text{ mol}\cdot\text{L}^{-1}$  HCl aqueous solution containing  $0.01 \text{ mol}\cdot\text{L}^{-1}$  sodium benzenesulfonate,  $0.02 \text{ mol}\cdot\text{L}^{-1}$  CTAB and 0.3 mL pyrrole was prepared first. Subsequently, the solution was degassed with nitrogen for 120 min and kept at  $0\text{--}5^\circ\text{C}$ . In order to obtain the PPy NWs, the precooled APS aqueous solution ( $0.1 \text{ g}\cdot\text{mL}^{-1}$ ) as an oxidizing agent was dripped to the mixture. After reacting for 24 h with stirring, the resulting sediment was centrifuged, washed and dried at  $40^\circ\text{C}$ .

Ultrasonic agitation was used to disperse the synthesized PPy NWs into water to produce a  $2 \text{ mg}\cdot\text{mL}^{-1}$  PPy solution. Then 5 mL PPy dispersion and 5 mL  $0.02 \text{ mol}\cdot\text{L}^{-1}$  PA solution were mixed together and further treated with ultrasonication for another 5 min. Prior to the electrode modification, a glassy carbon electrode (GCE, the diameter of 5 mm) was first polished with  $1.0 \mu\text{m}$ ,  $0.3 \mu\text{m}$  and  $0.05 \mu\text{m}$  alumina slurry, respectively. Then, the GCE was subjected to potential cycling in  $0.50 \text{ mol}\cdot\text{L}^{-1}$   $\text{H}_2\text{SO}_4$  aqueous solution for sufficient cycles to obtain reproducible cyclic voltammograms. After that,  $10 \mu\text{L}$  amount of the above suspension was casted onto the pretreated GCE surface and the solvent was evaporated under an infrared lamp. Finally,  $3 \mu\text{L}$  of Nafion solution was deposited onto the electrode in order to improve film stability and anions-resistant permselectivity [32]. The PA/PPy NWs modified GCE was denoted as PA/PPy/GCE. For comparison, PPy/GCE electrodes were prepared through the same procedures without the addition of PA.

### 2.3. Electrochemical detection

Differential normal pulse voltammetry (DNPV) was performed in  $0.1 \text{ M}$  HAC-NaAc buffer solutions (pH 4.0) containing various

concentrations of  $\text{Cu}^{2+}$ . Prior to the stripping process, a preconcentration and reduction of  $\text{Cu}^{2+}$  into Cu on the surface of the modified electrode at  $-0.5 \text{ V}$  for 300 s. Then, DNPV signals were applied from  $-0.5$  to  $0.5 \text{ V}$ , the pulse amplitude of  $25 \text{ mV}$ , step of  $4 \text{ mV}$ , 1st pulse width of  $0.2 \text{ s}$ , 2nd pulse width of  $0.05 \text{ s}$ , pulse period of  $0.5 \text{ s}$  and sample width of  $0.0167 \text{ s}$ . Subsequently, the electrode was cleaned at  $0.4 \text{ V}$  for  $60 \text{ s}$  in order to remove residual metals.

### 2.4. Apparatus

Electrochemical measurements were performed with a CHI760 electrochemical workstation (CH Instruments, China). A three-electrode system was employed with the modified glassy carbon electrode as a working electrode, a saturated calomel electrode (SCE) as a reference electrode and a platinum plate electrode as a counter electrode. The solutions were deoxygenated by bubbling with high-purity  $\text{N}_2$  for at least 10 min before the electrochemical measurements. SEM images were obtained using a JEOL JSM-6700F field emission scanning electron microscopy and Infrared spectra of the PA/PPy NWs were performed on Fourier transformed infrared spectrometer (FTIR, Bruker, Tensor 27).

## 3. Results and discussion

### 3.1. Characterization of PA/PPy nanowires

Fig. 1 shows the representative SEM images of PPy and PA/PPy NWs. It is found that well-defined PPy NWs with the diameters of  $30\text{--}40 \text{ nm}$  and the lengths above  $2 \mu\text{m}$  are obtained by Fig. 1A. Fig. 1B demonstrates that the PA are distribution on PPy NWs, forming a thin layer that coated on the PPy NWs, the small-molecular of phytic acid, so PPy NWs without changing too much.

The chemical structures of PA/PPy and PPy NWs were examined by FT-IR (Fig. 2). The characteristic peaks at  $1547 \text{ cm}^{-1}$  and  $1480 \text{ cm}^{-1}$  are assigned to the fundamental stretching vibration of pyrrole rings [33]. The absorption peaks at  $1295 \text{ cm}^{-1}$  and  $1043 \text{ cm}^{-1}$  are belong to C–N stretching vibration and the C–H deformation vibrations, respectively [34]. The new peak at about  $1645 \text{ cm}^{-1}$  is assigned to the C=O stretching vibration of the carboxylic groups [35]. The incorporation of PA into PPy matrix is certified by the characteristic absorption peaks at  $1176 \text{ cm}^{-1}$ ,  $1064 \text{ cm}^{-1}$ ,  $952 \text{ cm}^{-1}$  and  $854 \text{ cm}^{-1}$ , which are due to the characteristic peaks of PA. By careful comparing the absorption peaks of PA/PPy with those of PPy, the peaks at  $1064 \text{ cm}^{-1}$  is assigned to the vibration of P–OH bonds. The peaks at  $952 \text{ cm}^{-1}$  and  $854 \text{ cm}^{-1}$  are due to the vibration of P–O–C bonds and the enhanced peak at  $1176 \text{ cm}^{-1}$  originates from the vibration of P=O bonds. Based on the above evidence, we can conclude that PA is indeed coupled into the PPy by electrostatic adsorption and ultrasonic mixing.

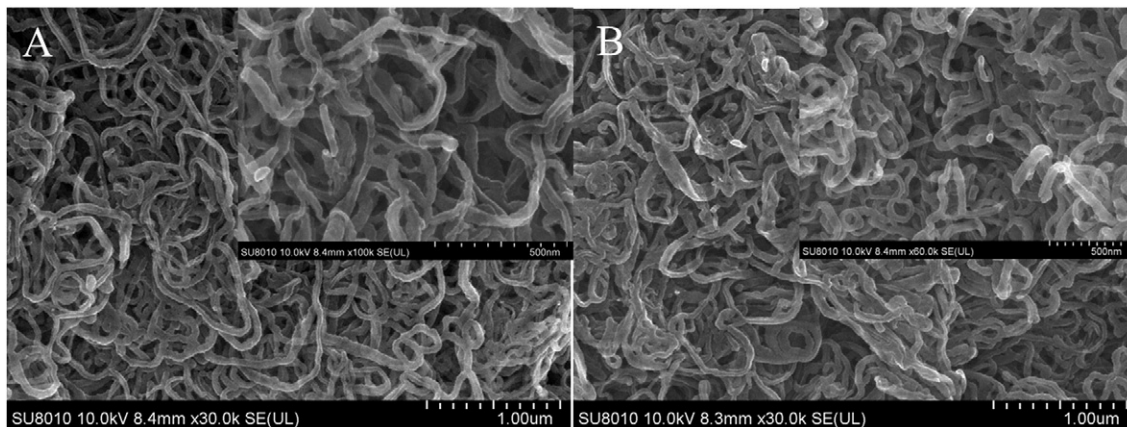


Fig. 1. Surface morphologies of PPy NWs and PA/PPy NWs.

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