



A facile and ultrasensitive photoelectrochemical sensor for copper ions using in-situ electrodeposition of cuprous oxide

Yanxia Qiu^{a,b}, Jing Li^b, Hongbo Li^{b,**}, Qi Zhao^b, Hongmei Wang^b, Hailin Fang^b, Dahe Fan^b, Wei Wang^{a,b,*}

^a School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China

^b School of Chemical and Biological Engineering, Yancheng Institute of Technology, 9 Yinbin Avenue, Yancheng 224051, China

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ABSTRACT

A new and facile photoelectrochemical sensor using in situ electrodeposition of cuprous oxide for copper ions was first constructed. The proposed method is based on the enhanced photocurrent produced by the electrodeposited cubic Cu₂O with the increase of the concentration of copper ions. The prepared films of cubic Cu₂O were successfully characterized by scanning electron microscopy, X-ray diffractometry, and ultraviolet–visible spectroscopy. The fabricated photoelectrochemical sensor showed good performances with a rapid response, facile preparation, excellent stability, a wide linear range (1×10^{-11} – 1×10^{-3} mol L⁻¹), and a low limit of detection (3.33 pmol L⁻¹) at 3 signal-to-noise ratio. It has been successfully applied to the detection of copper ions in environment water sample, which is consistent with the results by inductively coupled plasma-mass spectroscopy. It opens up a novel in situ electrodeposited photoelectrochemical sensing method for metal ions.

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1. Introduction

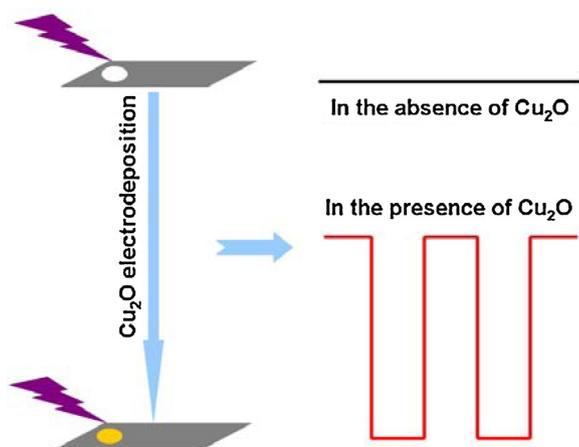
The accumulation of excess amounts of copper ions or their misregulation can cause damage to the liver and kidney [1,2]. Thus, great efforts have been devoted to the detection of copper ions in environmental and biological systems due to their possible toxic effect in the areas of environmental, biological and chemical systems [3]. Except for those conventional analytical approaches such as graphite furnace atomic absorption spectroscopy (GFAAS) [4], inductively coupled plasma-mass spectroscopy (ICP-MS) [5,6], and recently, anodic stripping voltammetry [7], fluorescence detection [8], visual detection [9], and photoelectrochemical strategies have also been reported using CdX (X = S, Te) quantum dots (QDs) [10,11] and ZnO/CdS hierarchical nanospheres [12] as photoelectronic beacons. All the photoelectrochemical (PEC) detection mechanisms of Cu²⁺ in the above literatures were based on the competitive interaction of Cu²⁺ with the CdX (X = S, Te) active materials. Cu_xX (X = S, Te) (x = 1, 2) could form on the active material surface due to the chemical displacement of surface Cd²⁺ by Cu²⁺ resulting from the

lower solubility of Cu_xX (x = 1, 2) than CdX (X = S, Te) [10–12]. Except for the toxic Cd²⁺ effect, electron donors such as Na₂S, ascorbic acid, and triethanolamine were typically added in the above detection to enhance the photocurrent. Alternatively, based on a novel mechanism of the reduction from Cu²⁺ to Cu, the PEC response of AgX/g-C₃N₄ (X = Br, I) hybrid materials [13] can directly detect Cu²⁺ without extra addition of electron donors. However, each of these methods suffers from at least one undesirable limitation such as limited selectivity, low sensitivity, operational complexity, lack of portability, economy or speed. Considering of the low content of Cu²⁺ in river water, it is still a challenge to develop an alternative approach for a facile, portable, selective, sensitive, and environment-friendly detection method of Cu²⁺.

Photoelectrochemical measurement is potentially as sensitive as electrochemiluminescence (ECL) owing to the complete separation of excitation source (light) and detection signal (photocurrent) [14]. Moreover, the utilization of electronic detection makes the photoelectrochemical instruments simpler and low-cost compared with those of the conventional optical methods. Thus, it has attracted considerable interests as a newly developed and promising analytical technique [15–26]. To date, most photoelectrochemical sensing mechanisms are based on the direct or indirect interactions between analytes and the illuminated photoelectrochemical beacons, which lead to the quantitative photocurrent changes of the photoelectrochemical beacons. As one of the semiconductors for photoelectrochemical beacon, Cu₂O is a p-type

* Corresponding author at: School of Chemical and Biological Engineering, Yancheng Institute of Technology, 9 Yinbin Avenue, Yancheng 224051, China. Tel.: +86 515 88298186; fax: +86 515 88298186.

** Corresponding author. Tel.: +86 515 88298186; fax: +86 515 88298186. E-mail addresses: hbli@ycit.edu.cn (H. Li), wangw@ycit.edu.cn (W. Wang).



Scheme 1. Schematic illustration of the proposed photoelectrochemical sensing for copper ions using in situ electrodeposition of cuprous oxide.

semiconductor with a direct band gap of about 2.0 eV and also an economically available material with low toxicity [27]. Moreover, this material is known to have sufficient mobility and a relatively large minority carrier diffusion length [28]. In view of this, we successfully constructed a novel photoelectrochemical sensing for reduced glutathione based on the heterojunction of $\text{Cu}_2\text{O}/\text{ZnO}$ [14]. In that work, the Cu_2O was first introduced into photoelectrochemical sensing, which was electrodeposited on the film of ZnO nanospindles from the electrolyte containing copper ions. Thus, we were inspired to construct a facile photoelectrochemical sensor for copper ions using in situ electrodeposition of cuprous oxide under proper conditions.

In this work, for the first time, we report a facile photoelectrochemical approach for the determination of copper ions with excellent performances. As can be seen from the sensing system in Scheme 1, the working principle is based on the enhanced photocurrent produced by the electrodeposited cubic Cu_2O with the increase of the concentration of copper ions. In order to confirm the selectivity of the as-prepared photoelectrochemical approach, the electrodeposited films of cubic Cu_2O from the electrolyte containing the other conventional ions were also successfully characterized by scanning electron microscopy, X-ray diffractometry and ultraviolet–visible spectroscopy. The results indicated that the present photoelectrochemical sensor had good selectivity, and it also provided a novel, robust, sensitive, and wide linear range strategy for copper ions.

2. Experimental

2.1. Reagents and apparatus

All reagents used were analytical grade and were used directly without purification. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and KNO_3 were purchased from sinopharm chemical reagent Co., Ltd. Different concentrations of $\text{Cu}(\text{NO}_3)_2$ solution were prepared for in-situ electrodeposition of cuprous oxide. In the electrolytic cell, $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ is not only for the supporting electrolyte but also acts as the oxygen source for the electrodeposition of Cu_2O . In this work, 0.1 mol L^{-1} phosphate-buffered saline (PBS) was always employed as the supporting electrolyte for photoelectrochemical determination. Aqueous solutions were prepared with ultrapure water (Milli-Q, Millipore), and the pH value of PBS was 7.0.

Photoelectrochemical measurements were performed with a home-built photoelectrochemical system. Photocurrent was measured by the current–time curve experimental technique on a CHI660D electrochemical workstation (CH Instruments, Shanghai,

China) with a 250 W tungsten halogen lamp light as the irradiation source (simulated sunlight irradiation). The distance between the light source and the photoelectrode was fixed at 10 cm. All experiments were carried out at room temperature using a conventional three electrode system with the modified ITO substrates ($\varphi = 5 \text{ mm}$, resistivity $10 \Omega/\text{sq}$, Zhuhai Kaivo Electronic Components Co. Ltd., China) as the working electrode, a platinum wire as the auxiliary electrode, and a saturated calomel electrode as the reference electrode. Scanning electron microscopy (SEM) was performed using a Hitachi S-4800 scanning electron microscope (Hitachi, Tokyo, Japan). X-ray diffraction (XRD) patterns of Cu_2O were measured in the range of 2θ by step scanning on the Bruker D8 Advance (super speed) diffractometer (Bruker-AEX, Germany) with $\text{Cu K}\alpha$ radiation ($k = 0.15406 \text{ nm}$) operated at 40 kV and 100 mA. UV–vis spectra were recorded at room temperature with a Cary 5000 ultraviolet and visible spectrophotometer (Varian, USA).

2.2. Preparation of Cu_2O nanostructures by electrodeposition

Preparation of Cu_2O nanostructures by electrodeposition was performed on an electrochemical workstation using a standard three-electrode system according to the references [29] with some modifications. Before using the ITO electrode ($1 \text{ cm} \times 4 \text{ cm}$), which was cleaned with the mixed solution containing water, ammonia and hydrogen peroxide with volume ratio of 50:1:1, and it was finally washed by ultrapure water again before electrodeposition and dried in air. The cubic Cu_2O was prepared via cathodic electrodeposition in different concentration of $\text{Cu}(\text{NO}_3)_2$ solution containing $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ with a fixed potential of -0.2 V for 60 min after the electrodeposited Cu_2O nanostructures were rinsed with ultrapure water for three times and dried in air. For controlled experiments, the Cu_2O nanostructures were prepared using the electrodeposition method in $0.01 \text{ mol L}^{-1} \text{ Cu}(\text{NO}_3)_2$ solution containing $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ added with various conventional ions while keeping the other experimental conditions unchanged.

3. Results and discussion

3.1. Characterization of Cu_2O

The morphology of the as-synthesized Cu_2O nanostructures was investigated by field emission scanning electron microscopy (FESEM). Fig. 1(A) showed the high-magnification SEM image of nano- Cu_2O , which revealed the formation of cubic structures. It also can be seen from Fig. 1(B) that the nano- Cu_2O still remains cubic nanostructures while the electrolyte containing various possible interference metal ions. The two FESEM morphologies looked like no obviously changes, which indicate that various conventional metal ions can hardly influence the generation of cubic nano- Cu_2O . This was also confirmed by the X-ray diffraction patterns of cubic Cu_2O in the above two electrolytes.

In order to confirm the generation of the Cu_2O nanostructures in the above two conditions, the XRD spectra of the cubic Cu_2O nanostructure were shown in Fig. 2. As shown in Fig. 2a, the peaks corresponding to the Cu_2O (1 1 1), (2 2 0) planes can be perfectly indexed to the cubic Cu_2O (JCPDS CARD no. 78-2076) with a lattice constant $a = 4.267 \text{ \AA}$. No other peaks were observed except for that of the substrate. This result implies that the products are highly pure. As shown in Fig. 2b, the diffraction peaks of Cu_2O were almost no changes for the electrolyte containing the different metal ions. Briefly, the different metal ions can seldom affect the formation of cubic Cu_2O , which can be explained that the conventional ions can hardly generate the corresponded semiconductors of metal oxide at the potential of -0.2 V .

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