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A nano-copper electrochemical sensor for sensitive detection of chemical oxygen demand

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ABSTRACT

Copper nanoparticle (nano-Cu) was electrodeposited on the surface of Cu disk electrode under −1 V for 60 s, and then used to construct an electrochemical sensor for chemical oxygen demand (COD). The electrochemical oxidation behavior of glycine, a standard compound for evaluating the COD, was investigated. The potential shifts negatively, and the current increases greatly at the surface of nano-Cu, indicating remarkable enhancement effect on the detection of COD. The analytical conditions such as electrolyte, deposition potential, deposition time and detected potential were studied. As a result, a sensitive, simple and rapid electroanalytical method was developed for COD using amperometric detection. The linear range is from 4.8 to 600 mg L^{-1}, and the limit of detection is as low as 3.6 mg L^{-1}. Moreover, this method exhibits high tolerance level to chloride ion, and 0.02 M chloride ion has no influence. Finally, the sensor was used to detect the COD values of different water samples, and the results were testified by the standard dichromate method.

1. Introduction

Determination of chemical oxygen demand (COD) is very important and interesting because the value of COD indicates the organic pollution in water [1]. COD is defined as the number of oxygen equivalents consumed in the oxidation of organic compounds using strong oxidizing agents such as dichromate or permanganate. Therefore, the commonly used method for the detection of COD is titrimetry using $FeSO_4$ as the titrant. However, the conventional titration method has some intrinsic drawbacks. Firstly, the analysis time is too long (about 2 h) since it requires time-consuming sample refluxing process to achieve complete oxidation. Secondly, the handling is complicated and the reproducibility of results is heavily dependent on the skill of operator. Finally, expensive and toxic reagents (Ag_2SO_4 and $HgSO_4$) were employed, leading health and safety concerns [2,3]. Thus, numerous efforts have been made to overcome these disadvantages, and to develop simple and rapid analytical method for COD.

Recently, the electrochemical treatment of waste water containing organic pollutants has obtained increasing attention [4,5]. The basic principle is to degrade organic pollutants into, ideally, water and carbon dioxide through electrochemical oxidation under high potential. Thus, the value of COD can be calculated from the charge that consumed in the electrochemical degradation of organic pollutants. In order to accomplish complete oxidation and to shorten the oxidation time, thin-layer electrochemical cell was usually employed [6–8]. Compared with the conventional method, the coulometric detection of COD based on exhaustive oxidation was greatly improved on the aspect of analysis time. However, the exhaustive oxidation of organic pollutants into water and carbon dioxide is still difficult and requires long time (about 20–30 min) even in the thin-layer electrochemical cell.

To further shorten the analysis time and for handling convenience, amperometric detection of COD based on measuring the current during the electrochemical oxidation of organic pollutants has been developed. However, the direct oxidation of organic species using ordinary electrodes such as metal and carbon electrodes is almost impossible because the required high potentials usually result in the oxidation of water. In order to lower the oxidation overpotential and to fulfill the direct detection of COD, a number of novel electrodes have been reported. For example, a graphite-polystyrene composite electrode containing silver(II) oxide and copper(II) oxide with the limit of detection (LOD) of 4.3 mg L^{-1} [9], a rotating Pt ring-Pt/PbO_2 disk electrode with LOD of 15 mg L^{-1} [10], a F-PbO_2 modified electrode with LOD of 15 mg L^{-1} [11], a nano-PbO_2 modified electrode with LOD of 20 mg L^{-1} [12], a Ti/TiO_2 electrode with LOD of 16 mg L^{-1} [13,14], a Rh_2O_3/Ti electrode with LOD of 20 mg L^{-1} [15], a boron-doped diamond electrode coupled with flow injection [16], and a long-time (about 15 min) activated copper electrode with LOD of 20.3 mg L^{-1} [17], have been

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developed for the detection of COD. However, the amperometric detection of COD using nano-copper electrode is still missing.

Herein, the copper nanoparticle (nano-Cu) was successfully prepared on the surface of Cu disk electrode using controlled-potential reduction. Compared with the Cu disk electrode, the nano-Cu electrode showed a strong enhancement effect on the detection of COD, and greatly increased the oxidation current signal. The analytical parameters were optimized, and a novel electrochemical sensor with high sensitivity and rapid response was developed for COD. The nano-Cu sensor was successfully used in water sample analysis and exhibited promising application.

2. Experimental

2.1. Reagents

All the chemicals were of analytical grade and used directly. $CuSO_4$, H_2SO_4, NaOH, glycine, $K_2Cr_2O_7$, Ag_2SO_4, $HgSO_4$ and $(NH_4)_2Fe(SO_4)_2$ were purchased from the Sinopharm Group Chemical Reagent Co. Ltd., China. The stock solution of glycine (7.5 g L^{-1}) was prepared using re-distilled water.

2.2. Instruments

Electrochemical measurements were conducted on an EC 550 Electrochemical Workstation (Gaoss Union Co. Ltd., China) with a conventional three-electrode system. The working electrode is a nano-Cu modified Cu disk electrode, the reference electrode is a saturated calomel electrode (SCE), and the counter electrode is a platinum wire. Scanning electron microscopy (SEM) was performed with a Quanta 200 microscope (FEI Company, Netherlands).

2.3. Preparation of nano-Cu

Before electrodeposition, the Cu disk electrode with diameter of 3 mm (Gaoss Union Co. Ltd., China) was polished with 0.05 μm alumina slurry, and then sonicated in re-distilled water to give a clean surface. After that, the nano-Cu sensing film was electrodeposited on the surface of Cu disk electrode under −1 V for 60 s in 4 mM $CuSO_4$ containing 1 mM H_2SO_4. Finally, the resulting nano-Cu modified Cu electrode (nano-Cu/Cu) was rinsed with re-distilled water to remove any adsorbed species.

The morphology and the particle size of prepared nano-Cu were characterized using SEM. Fig. 1 shows the SEM images of Cu (A) and nano-Cu/Cu (B). The comparison of these two images clearly indicates that the surface of Cu disk electrode was coated with copper nanoparticles, and the diameter is about 40–80 nm.

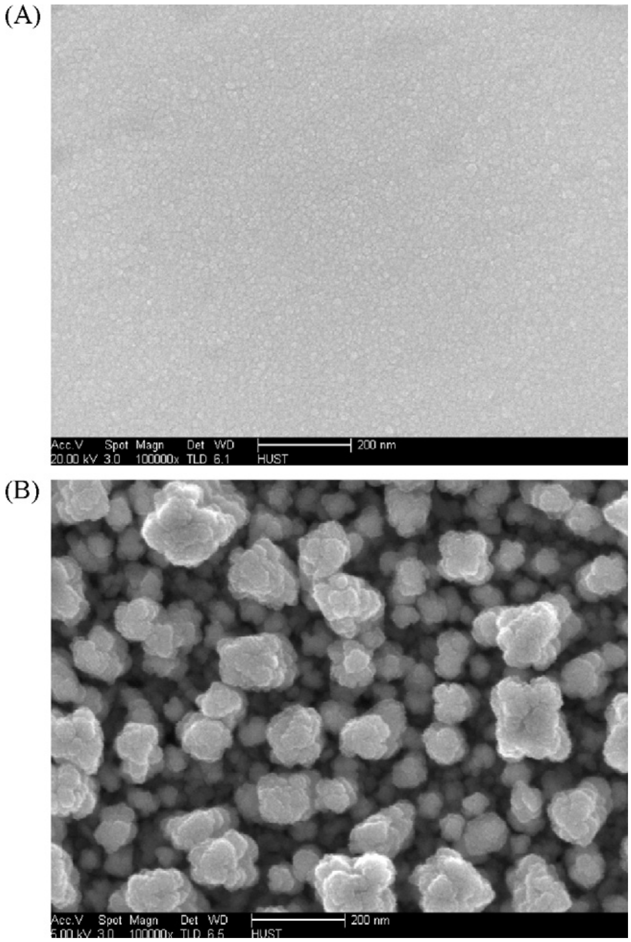

Fig. 1. SEM images of Cu (A) and nano-Cu (B).

2.4. Conventional dichromate method

The conventional dichromate method was also used to determine the value of COD according to the National Standard of China (GB 11914-89). 10 mL sample solution was added into a cuvette, and then refluxed for 2 h in a thermostat at 433 K. After that, the excess of dichromate was determined by titration using $(NH_4)_2Fe(SO_4)_2$ as the titrant. Finally, the value of COD was calculated.

For 150 mg L^{-1} glycine solution, the value of COD was measured to be 98.6 mg L^{-1} of O_2 using the conventional dichromate method, which consists with the theoretic value of 96 mg L^{-1} of O_2 [18].

2.5. Analytical method

The amperometric detection under well-stirred condition was used to measure the value of COD. The detected potential is 0.8 V and the electrolyte is 0.075 M NaOH solution. The observed current was allowed to reach a steady state before addition of standard sample or real sample, and the net increase of current was then measured as the response current. All the experiments were carried out at ambient temperature.

3. Results and discussion

3.1. Electrochemical enhancement effect of nano-Cu

From the definition of COD, it is known that the value of COD reflects the total amount of organic species in water. For simplification, a few of compounds such as glucose, glycine and potassium hydrogen phthalate (KHP) were selected as the standard reagents. Herein, glycine was employed as the standard compound for evaluating the value of COD. The oxidation behavior of glycine at different electrodes was studied using linear sweep voltammetry (LSV), which is shown in Fig. 2. During the potential scan from 0.1 V to 0.7 V, no oxidation peaks were observed for glycine at the glassy carbon disk electrode (GCE), Ti, Pt and Au disk electrodes, all them 3-mm in diameter, suggesting that the oxidation activity of glycine is very poor. However, a very sensitive oxidation peak is observed at the Cu disk electrode, indicating that the oxidation activity of glycine is relatively high at the Cu electrode. As well-known, the properties of metal nanoparticles are quite different from those in bulk metals [19,20]. Therefore, the oxidation activity of glycine may be further improved at the surface of nano-Cu.

Fig. 3 compares the oxidation behavior of glycine at Cu (curve b) and nano-Cu/Cu (curve d) in 0.075 M NaOH. At the nano-Cu surface, the oxidation potential of glycine shifts negatively, and