



Short communication

Mechanistic study of glucose oxidation on copper sulfide modified glassy carbon electrode



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ABSTRACT

By studying the reduction of hydrogen peroxide and oxidation of glucose on the CuS nanoparticles modified glassy carbon electrode (CuS/chitosan/GCE), a mechanism of the oxidation of glucose was proposed. It was believed that there is no direct electron transfer between glucose and the electrode surface. Although CuS is a weak oxidant, the glucose was oxidized by CuS while Cu(II) was reduced to Cu(I). The produced Cu(I) undergoes two competing reactions. One reaction is the electro-oxidation of Cu(I) to Cu(II) on the electrode surface which induces the increase of the anodic peak current of the Cu(II)/Cu(I) redox couple in the presence of glucose. Another is the oxidation of Cu(I) by dissolved oxygen to produce H₂O₂ which was subsequently reduced on the electrode surface.

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1. Introduction

The electrocatalytic oxidation of glucose has been a research focus because of the great importance of glucose sensing in human blood and their potential use for fuel cell applications [1]. Owing to the nature of enzymes, the most common and serious problem with enzymatic glucose sensors lies in their lack of long-term stability. Most of the enzyme-free glucose sensors are based on noble metals such as gold and platinum. The sensing of glucose with copper or nickel electrodes must be performed in a strong alkaline solution. Recently, the non-enzymatic sensing of glucose on CuO and CuS modified electrode has been intensively studied [2–14]. Copper chalcogenide nanomaterials are not expensive and easy to synthesize. Their size and morphologies can be tuned by simply varying the experimental parameters. The glucose sensors based on CuS or CuO nanomaterials showed high sensitivity, low detection limit and wide linear range in a neutral solution [2–14]. It is a well-known fact that the current of the anodic peak, which is assigned to the Cu(II)/Cu(I) redox couple [2–14], increases as the concentration of glucose increases. However, the mechanism is still unclear although a lot of efforts have been devoted to the application of copper chalcogenide in the glucose sensing.

In this work, we synthesized CuS NPs with a facile aqueous route and fabricated a CuS/chitosan/GCE. By studying the reduction of H₂O₂ and oxidation of glucose on the CuS/chitosan/GCE, a mechanism of the oxidation of glucose was tentatively proposed.

2. Experimental

We dissolve 0.0276 g elemental sulfur in 10 mL DMF under ultrasonic agitation for 10 minutes. We dissolved 0.1476 g CTAB in the solution under hard stirring. The copper foil (5 mm × 20 mm) was rinsed with absolute ethanol, treated in 10% nitric acid solution and then dried with high purity nitrogen gas. We put the prepared solution in ultrasonic bath and immersed the treated copper foil in the solution for 1 h. Under ultrasonic agitation, the solution turned from colorless to black immediately. We centrifuged the solution to obtain the CuS precipitate. The excess CTAB was removed by the following procedure. First, we dispersed the precipitate in 10 mL water under ultrasonic agitation, and then centrifuged the colloid solution and discard the supernatant. We repeated the above procedure for ten times. Finally, we dried the produced precipitate in vacuum oven overnight to obtain the CuS powder. We disperse 5 mg CuS NPs powder in 4 mL 0.2% chitosan 1% acetic acid solution under ultrasonic agitation to obtain a uniform CuS colloid solution. We cast 4 μL CuS colloid solution on the surface of a GCE (ϕ 3 mm). The modified electrode was dried under ambient conditions and washed with water before use.

Cyclic voltammetry (CV) was performed on CHI 660B (Chenhua, Shanghai). A three-electrode system comprising of a platinum wire as the auxiliary, a saturated calomel electrode as the reference and the CuS NPs-modified electrode as the working electrodes was used for all the electrochemical experiments.

The morphology and the crystal structure of the produced CuS NPs were observed with a transmission electron microscope (TEM) and an X-ray diffractometer (XRD). The X-ray diffraction (XRD) patterns

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are obtained by Shimadzu XRD-6000 diffractometer with a Ni filter and Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). TEM experiments were carried out employing Jeol 100CX II transmission electron microscope (TEM), using an accelerating voltage of 100 kV. The samples used for TEM were prepared by dispersing some products in ethanol followed by ultrasonic vibration for 15 min.

3. Results and discussion

We synthesized CuS NPs with a simple aqueous route at ambient conditions. CTAB acts not only as the catalyst for the reaction, but also the capping agent of the produced CuS NPs. The absorption of CTAB on the surface of CuS NPs reduces the surface energy and the interaction forces between the NPs, and thus effectively prevent the aggregation of NPs. Imaging by TEM showed that most of the CuS NPs are spherical (Fig. 1a and b). In order to investigate the electrochemical behaviors of the CuS NPs, the GCE was modified with thin film of CuS NPs. SEM study showed that the CuS NPs are uniformly distributed on the GCE surface (Fig. 1c). Fig. 1d gives the XRD patterns for the CuS prepared with this method. It can be seen that the sample was well crystallized. The diffraction peaks can be perfectly indexed to hexagonal CuS with lattice constants $a = 3.796 \text{ \AA}$ and $c = 16.38 \text{ \AA}$ (JCPDS 78-0876). Broadening of the peaks indicated the nanocrystalline nature of the material.

The cyclic voltammogram of the CuS/chitosan/GCE in 0.1 M phosphate buffer (pH 7.2) displays a pair of well-defined redox peaks which are assigned to the Cu(II)/Cu(I) redox couple (Fig. 2a) [2–14]. The reduction and oxidation peak currents exhibited a linear relationship with the scan rate from 0.01 to 0.2 Vs^{-1} ($r = 0.995$) (Fig. 2a and b). All these results suggested that the reaction was a surface-confined electrochemical behavior.

Before experiments the phosphate buffer solution was degassed with high purity nitrogen gas for 20 min. Fig. 3a presents the CVs of bare GCE (curve a) and chitosan/GCE (curve b) in the presence of H_2O_2 . For CuS/chitosan/GCE, in the absence of H_2O_2 , there is a pair

of well-defined redox peaks at 0.25 V and 0.42 V (Fig. 3b, curve c). In the presence of H_2O_2 , the CV displays a broad cathodic peak at -0.1 V while the anodic peak current at 0.42 V increases with the addition of H_2O_2 (Fig. 3b, curve d). The cathodic peak at -0.1 V in the presence of H_2O_2 is due to the reduction of H_2O_2 . The peak potential for reduction of H_2O_2 at CuS/chitosan/GCE is more positive than those at other H_2O_2 sensors which have been reported [15,16].

Fig. 3c clearly indicated that, as the concentration of H_2O_2 increased, the peak current of the reduction peaks of H_2O_2 at -0.1 V also increased. The variation of the peak current vs. H_2O_2 concentration is linear in the H_2O_2 concentration range of $1 \times 10^{-4} \text{ M}$ to 10 mM with a correlation coefficient of 0.9925 (Fig. 3d).

Fig. 4a presents the CVs of bare GCE (curve a) and chitosan/GCE (curve b) in the presence of glucose. For CuS/chitosan/GCE, as shown in Fig. 4b, upon the addition of $1 \times 10^{-4} \text{ M}$ glucose into pH 7.2 phosphate buffer, a broad peak at -0.1 V was observed at CuS/chitosan/GC electrode while the oxidation peak at 0.46 V increased. It was discovered that the dissolved oxygen exert great effect on the peak currents at -0.1 V and 0.46 V. After the $1 \times 10^{-4} \text{ M}$ glucose 0.1 M phosphate buffer (pH 7.2) solution was degassed with high purity nitrogen gas for 20 min, the anodic peak at 0.42 V decreased and the cathodic peak at -0.1 V became barely observable (Fig. 4c). In an air-saturated 0.1 M phosphate buffer (pH 7.2) solution, the CVs of CuS/chitosan/GC with successive additions of $1 \times 10^{-4} \text{ M}$ glucose were recorded. As the concentration of glucose increased, both the cathodic peak current at -0.1 V and the anodic peak current at 0.42 V increased (Fig. 4d). The variation of the cathodic peak current at -0.1 V and anodic peak current at 0.42 V vs. glucose concentration is linear in the glucose concentration range of $1 \times 10^{-4} \text{ M}$ to 1 mM with a correlation coefficient of 0.9948 and 0.9903, respectively (Fig. 4e).

The anodic peak at 0.42 V is due to the oxidation of Cu(I). The increase of the anodic peak current with the concentration of glucose has been observed by Liu et al. [13] and Zhang et al. [14]. They ascribed the current increase to the direct electro-oxidation of glucose on the electrode under the catalysis of CuS. However, it is too coincidental

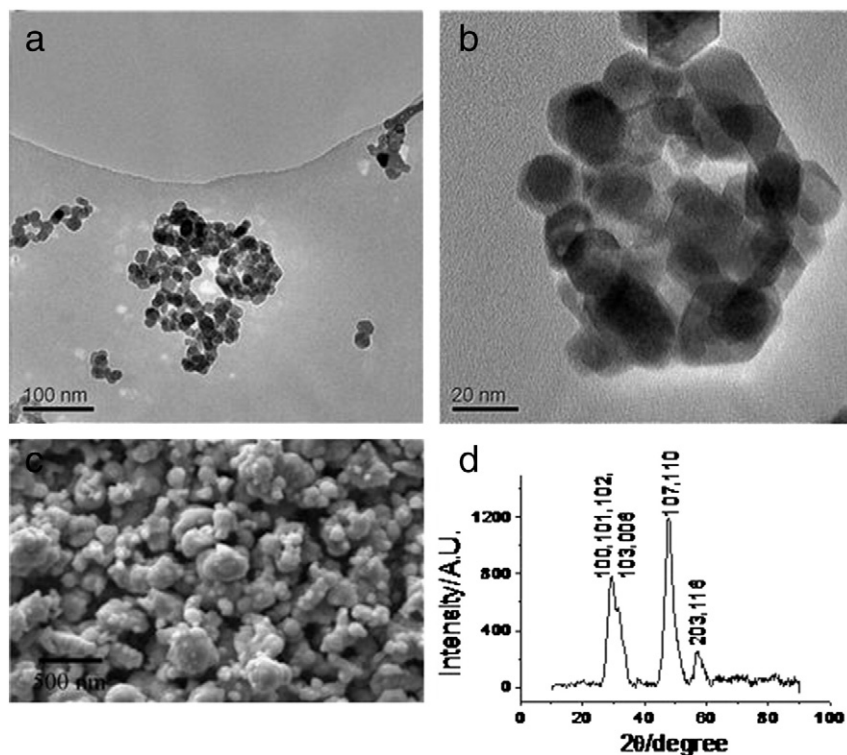


Fig. 1. (a, b) TEM images of the CuS NPs; (c) SEM of the CuS/CS/GCE; (d) XRD data of synthesized CuS NPs.

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