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Improved Photoelectrochemical Glucose Oxidation on Graphene Supported CdS Nanoparticles via Decoration of CuO Nanoparticles

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In this work, visible light driven photoelectrochemical glucose sensor was developed by electrochemically deposited CuO nanoparticles (CuO NPs) on graphene (GP)-CdS nanocomposites modified electrode to achieve both the electrocatalytic and photoelectrocatalytic oxidation of glucose. Scanning electron microscopy, electrochemical impedance spectroscopy and cyclic voltammetry were used to characterize the morphology and electrochemical properties of the resultant CuO NPs/GP-CdS nanocomposites. The CV results demonstrated that modification of CuO NPs largely enhanced the photoelectrocatalytic activity of GP-CdS composites toward glucose oxidation in alkaline solution. The glucose detection sensitivity under visible light irradiation is dramatically improved compared to dark condition. Good performance was obtained for the CuO NPs/GP-CdS nanocomposites based glucose sensor. The feasibility of the present method was confirmed by good recovery results for glucose detection in human serum samples.

Keywords: Graphene; CdS, CuO nanoparticles, Glucose, Photoelectrochemical sensor.

1. INTRODUCTION

Glucose, as an indispensable energy source, plays essential roles for maintaining human physilogical health. However, abnormal level of glucose in blood may result in endocrine and metabolic disorders such as diabetes, which threatens many peoples in the worldwide [1,2]. Thus, developing an accurate and reliable method for monitoring of glucose level in daily life is very important to prevent the diabetes mellitus worsening. Many strategies have been proposed for glucose detection, including of fluorescence [3,4], chemiluminescence [5,6], colorimetry [7,8], electrochemistry [2,9-14] and photoelectrochemical method [15,16]. Among these techniques, photoelectrochemical (PEC) measurement coupling photoirradiation with electrochemical detection system is proved to show

advantages of low background signal, simple instrument, low cost, high detection sensitivity and good selectivity [17]. The performance of this PEC glucose sensor is strongly relying on the photoelectrochemical catalytic activity of semiconductor based materials.

As reported, glucose can be oxidized by photocatalysis on photoactive materials such as TiO₂ [18], WO₃ [19], MoS₂ [15], ZnO [20] and CdS [16] nanomaterials. CdS, with a narrow band gap of 2.4 eV, is widely used as photoactive material in constructing PEC based glucose sensor because of its outstanding photoelectrochemical properties. However, the separation efficiency of its photogenerated electron-hole pair's is low [21]. Modification of CdS with highly conductive materials such as graphene (GP) is the commonly used strategy to promote the charge separation and retard the recombination of electron-hole species [22], thus, the photovoltaic conversion efficiency of CdS can be enhanced.

CuO nanostructures comprising nanoparticles and nanowires showing promient electrocatalytic activity toward oxidation of glucose have been intensively used to prepare electrochemical glucose sensors [23-25]. In this work, visible light driven nonenzymatic glucose PEC sensor was developed by electrochemically deposited CuO nanoparticles on GP-CdS nanocomposites modified electrode to achieve both the electrocatalytic and photoelectrocatalytic oxidation of glucose at the resultant CuO NPs/GR-CdS nanocomposites modified electrode. For this nanocomposites, solvothermal method was first used to synthesize CdS nanoparticles decorated GR. CuO NPs were subsequently electrodeposited onto glassy carbon electrode (GCE) modified with GP-CdS nanocomposites by potential cycling in a solution with Cu²⁺ involved. The electrocatalytic and photoelectrocatalytic activity of obtained CuO NPs/GR-CdS nanocomposites toward glucose oxidation was investigated in dark and under visible-light irradiation, respectively. The fabricated CuO NPs/GR-CdS nanocomposites modified electrode exhibited higher photoelectrocatalytic activity toward glucose oxidation than GP-CdS under visible light illumination. In addition, an enhanced electrochemical response of CuO NPs/GR-CdS nanocomposites for glucose under visible-light irradiation was obtained compared to that in dark condition. Therefore, a nonenzymatic PEC glucose sensor with high performance based on CuO NPs/GR-CdS nanocomposites was demonstrated.

2. EXPERIMENTAL SECTION

2.1. Reagents and apparatus

GO was purchased from Nanjing XFNANO Materials Tech Co., Ltd. Glucose and interference species were purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO), CuSO4.5H₂O, NaOH and Cd(CH₃COO)₂.2H₂O were purchased from Aladdin Chemical Reagent Co. All of these reagents were of analytical grade and used as received.

The surface morphology of synthesized materials were characterized by scanning electron microscopy (SEM) using Hitachi SU8010 (Japan) equipped with energy dispersive X-ray spectroscopy (EDX) detector for observations. Electrochemical experiments containing electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and amperometric technique were conducted on a CHI 660D electrochemical station (Shanghai Chenhua) with a conventional three-electrode system. The CuO

NPs/GR-CdS nanocomposites modified glassy carbon electrode (CuO NPs/GR-CdS/GCE) was used as the working electrode. A saturated calomel electrode (SCE) and a Pt wire acted as the reference and counter electrodes, respectively. The electrochemical measurement under visible light irradiation was carried out in a quartz cell in the presence of three-electrode system under the irradiation of 300 W Xe lamp.

2.2. Preparation of GR-CdS nanocomposites

5 mg of graphene oxide (GO) was dissolved in 40 mL DMSO under the help of ultrasonication for ten minutes. 0.106 g Cd(CH₃COO)₂.2H₂O was mixed with the above solution. After stirred for 30 min, the resultant solution was transferred into teflon-lined stainless steel autoclave. Then, the autoclave was sealed and maintained at 180 °C for 12 h, and then allowed to cool down to room temperature naturally. The collected sediment was rinsed with deionized ethanol and acetone to remove the residual solvent. After dried in 60 °C for 12 h, GR-CdS nanocomposites was obtained. It was dispersed into water to form a 5 mg/mL GR-CdS dispersion for further use.

2.3. Preparation of CuO NPs/GR-CdS modified electrode

The GCE was pretreated by polishing with 0.3 and 0.05 μ m alumina slurries respectively. The electrode was placed in ethanol and water container under ultrasonic bathing to remove adsorbed particles. A 2 μ L portion of the prepared GP-CdS dispersion (5 mg/mL) was dropped onto a pretreated GCE and dried at room temperature to obtain the GP-CdS/GCE. Before electrodeposition of CuO NPs, the GP-CdS/GCE was treated by potential cycling between -1.5 and 0 V for 20 cycles at scan rate of 100 mV s⁻¹ in 0.1 M KCl solution. CuO NPs were grown on the surface of GP-CdS/GCE by CV in electrodeposition solutions with 10 mM of CuSO4 and 0.1 M KCl involved by scanning in the potential range of -1.5 to 0.5 V for 10 cycles at 50 mV s⁻¹. The direct electrodeposition of CuO NPs on bare GCE surface was denoted as CuO NPs modified electrode (CuO NPs/GCE) for comparison experiment.

3. RESULTS AND DISCUSSION

3.1. Morphological characterization

Fig. 1 shows SEM images of GP-CdS (a), CuO NPs/GP-CdS nanocomposites (b) and the EDX chart of the CuO NPs/GP-CdS nanocomposites. As can be seen, the surface of 2D sheet-like graphene was covered with CdS nanoparticles with diameters of less than 200 nm. Aggregation of CdS nanoparticles was also observed. After electrodeposition of CuO NPs, a large amount of nanoparticles with diameters of about 100 nm were decorated onto GP-CdS surface, indicating the successful formation of the ternary CuO NPs/GP-CdS nanocomposites. From the EDX results, it can be found that the element of Cu, O, C, Cd and S were all present, which further indicated the successful formation of CuO NPs/GP-CdS nanocomposites.



Figure 1. SEM images of GP-CdS (a), CuO NPs/GP-CdS nanocomposites (b) and the EDX chart of the CuO NPs/GP-CdS nanocomposites.

3.2. EIS characterization



Figure 2. EIS of the bare GCE (a), GP-CdS/GCE (b) and CuO NPs/GP-CdS/GCE (c) in 1 mM $Fe(CN)6^{3^-/4^-}$ and 0.1 M KCl solution in the frequency range of 0.1 Hz-10 kHz.

EIS can reflect the interface properties of modified electrodes. For a typical EIS plot, the diameter

of the semi-circle part is corresponding to the electron transfer process (R_{et}). Fig. 2 exhibits the EIS of the bare GCE (a), GP-CdS/GCE (b) and CuO NPs/GP-CdS/GCE (c) in 1 mM Fe(CN) $_{6}^{3-/4-}$ and 0.1 M KCl solution in the frequency range of 0.1 Hz-10 kHz. Obviously, the bare GCE shows the smallest R_{et} value. The modification of GP-CdS makes the R_{et} value of GP-CdS/GCE increased, suggesting that GP-CdS hinders the electron transfer between the electrolyte and electrode because of the semi-conductive properties of CdS [26]. The subsequent modification of CuO NPs on surface of GP-CdS leads to a further increase of R_{et} value, indicating that CuO NPs impede the interfacial electron transfer of electrode.

3.3. Photoelectrocatalytic activity of CuO NPs/GP-CdS/GCE toward glucose oxidation

The photoelectrocatalytic oxidation of glucose on the CuO NPs/GP-CdS/GCE was carried out in alkaline solution. Fig. 3 presents CV responses of CuO NPs/GCE (a), GP-CdS/GCE (b) and CuO NPs/GP-CdS/GCE (c) in 0.1 mol/L NaOH with the absence and presence of 1 mM glucose in dark and under visible light irradiation. Obviously, for CuO/GCE (Fig. 3a), upon addition of glucose into NaOH solution, a prominent increase for anodic current starting from a potential of about 0.3 V can be found, indicating outstanding electrocatalytic activity of CuO toward glucose oxidation. The visible light illumination leads to indistinct increase for anodic current due to the photo-inactivity of CuO. For GP-CdS/GCE (Fig. 3b), a tiny increase for anodic current upon the addition of glucose, but the visible light irradiation results in an obvious increase for anodic current, the results of which suggest the photoelectrocatalytic activity of GP-CdS for glucose oxidation. After electrodeposition of CuO NPs, the resultant CuO NPs/GP-CdS/GCE shows both electrocatalytic activity and photoelectrocatalytic activity toward oxidation of glucose evidenced from the anodic current increase from a potential of 0.3 V (Fig. 3c) upon addition of glucose in dark condition and visible light illumination. The anodic current caused by glucose oxidation increase accordingly with the increase of glucose concentration, and the visible light illumination further increase the anodic current obviously (Fig. 3d). This results indicate the potential application of CuO NPs/GP-CdS/GCE for photoelectrochemical detection of glucose quantitatively.





Figure 3. CV responses of CuO NPs/GCE (a), GP-CdS/GCE (b) and CuO NPs/GP-CdS/GCE (c) in 0.1 mol/L NaOH with the absence (black curve) and presence (red curve) of 1 mM glucose in dark and under visible light irradiation (blue curve), (d) is the CVs of CuO NPs/GP-CdS/GCE in dark for 1, 2 and 3 mM of glucose and for 3 mM of glucose under visible light irradiation.

The influence of scan rate on anodic current of glucose at 0.4 V was investigated to study the electrochemical reaction kinetics of glucose on CuO NPs/GP-CdS/GCE. As can be seen in Fig. 4, the anodic cuurent of glucose is linearly proportional to the square root of scan rate, indicating the electrochemical reaction of glucose on CuO NPs/GP-CdS/GCE is dominated by diffusion controlled process.



Figure 4. The relationship between anodic current of CuO NPs/GP-CdS/GCE at 0.4 V in 1 mM glucose and the square root of scan rate from 20 mV.s⁻¹ to 300 mV.s⁻¹.

3.4. Optimization of experimental parameters

Fig.5 shows amperometric currents of CuO NPs/GP-CdS/GCE toward succesive additions of 50 \Box M glucose in 0.1 M NaOH at applied potentials of +0.3 V, +0.4 V, +0.5 V and +0.6 V. As observed, the amperometric currents increase rapidly with the applied potential increase from +0.3 V to +0.5 V, and then increase gradualy from +0.5 V to +0.6 V. Considering the possible strong interference at high detection potential [27], +0.5 V was used for amperometric detection of glucose in the following

experiment.



Figure 5. Amperometric currents of CuO NPs/GP-CdS/GCE toward succesive additions of 50 □M glucose in 0.1 M NaOH at applied potentials of +0.3 V, +0.4 V, +0.5 V and +0.6 V.

The concentration of NaOH was optimized to enhance the detection sensitivity of glucose. As can be seen in Fig.6, the amperometric currents of CuO NPs/GP-CdS/GCE increase distinctly with the increase of NaOH concentration from 0.01 to 0.1 M, and then lowed down with the further increase of NaOH concentration from 0.1 to 0.3 M. Therefore, a maximum amperometric currents was obtained in 0.1 M NaOH solution, and it was selected as optimal electrolyte for the subsequent glucose detection.



Figure 6. The influence of concentration of NaOH on amperometric currents of CuO NPs/GP-CdS/GCE toward of 50 □M glucose at potential of 0.5 V.

3.5. Amperometric detection of glucose at CuO NPs/GP-CdS/GCE

The quantitative detection of glucose was carried out by amperometric strategy. Fig.7(a) exhibits the amperometric currents of CuO NPs/GP-CdS/GCE holding at potential of 0.5 V for successive additions of different concentrations of glucose to 0.1 M NaOH solution in dark and under visible light

irradiation. It is found that stable and stepwise increasing currents with the level of glucose was obtained and the currents reaches a plateau within 4 s. In addition, the visible light illumination enhanced the amperometric current remarkably compared to the dark condition, suggesting efficient photoelectrocatalytic activity of CuO NPs/GP-CdS/GCE toward glucose oxidation. Fig. 7b shows the plots of current response vs glucose concentration. As observed, the current reponse increase rapidly with the concentration of glucose, and then with the further increase of glucose concentration, the increase rate of current reponse is lowered, possibly because the active sites of CuO NPs/GP-CdS nanocomposites is partly blocked by oxidation product of glucose [28]. From the inset of Fig. 7b, the linear concentration range of glucose is 5-750 µM in dark condition and 5-2000 µM under light illumination. Obviously, the light illumination makes the linear concentration of glucose wider than dark condition. The linear concentration range obtained by the present PEC sensor is much wider than other PEC senosrs based on diffferent materials, such as Ni(OH)₂/TiO₂ (0.5-20 µM) [18] and rGO/CdS/CoO_x hybrid (1-10 µM) [16]. The calibration equation in the dark condition can be obtained as $I(\Box A)=2.16747+0.02148C(\Box M)$ with a correlation coefficient of 0.9952, and $I(\mu A)=1.1640+0.071C$ (μM) with a correlation coefficient of 0.9953 under light illumination. The detection sensitivity can be calculated to be $304 \,\mu\text{A mM}^{-1} \,\text{cm}^{-2}$ and 1005 µA mM⁻¹ cm⁻² in the dark and under visible light irradiation, respectively. The obtained sentitivity of the present PEC glucose sensor is higher than other reported PEC sensor based on ZnO nanowires via decorated Pt nanoparticles (928.1 µA mM⁻¹ cm⁻²) [20]. A 3.3 times increase in sensitivity suggest an excellent photoelectrocatalytic activity of CuO NPs/GP-CdS naocomposites toward glucose oxidation. The limit of detection (LOD) in the dark and light irradiation is estimated to be 1 µM and 0.5 µM, respectively.



Figure 7. (a) Amperometric responses of CuO NPs/GP-CdS/GCE holding at potential of 0.5 V for successive additions of different concentrations of glucose to 0.1 M NaOH solution in dark and under visible light irradiation. The inset is enlarged response at response time less than 500 s; (b)The plots of current response vs glucose concentration and the obtained calibration curve in dark and under visible light irradiation, respectively.

Selectivity is an important factor for evaluating an PEC glucose sensor. Some possible interference in the detection of glucose was studied. Fig. 8 shows amperometric responses of CuO NPs/GP-CdS/GCE holding at potential of 0.5 V for successive additions of 0.5 mM glucose, 50 \square M

H₂O₂, 50 \Box M NaCl, 50 \Box M dopamine (DA), 50 \Box M ascorbic acid (AA), 50 \Box M uric acid (UA) to 0.1 M NaOH solution under visible light irradiation. The result indicates that H₂O₂, NaCl and UA have negligible interference on glucose detection. DA and AA caused a current response less than 5% of that of glucose. Therefore, the interference of DA and AA can also be ignored. The above results indicate excellent selectivity and high activity of CuO NPs/GP-CdS/GCE toward glucose detection.



Figure 8. (a) Amperometric responses of CuO NPs/GP-CdS/GCE holding at potential of 0.5 V for successive additions of 0.5 mM glucose, 50 □M H₂O₂, 50 □M NaCl, 50 □M dopamine (DA), 50 □M ascorbic acid (AA), 50 □M uric acid (UA) to 0.1 M NaOH solution under visible light irradiation.

3.6. Analysis of glucose in human serum samples

In order to evaluate the feasibility of the CuO NPs/GP-CdS/GCE for glucose detection, the proposed method was applied for glucose monitoring in human blood serum using standard addition method. Two serum samples were first 100-fold diluted by 0.1 M NaOH solution (10 mL) and subsequently spiked with a certein concentration of glucose (100 \Box L). The determination results are presented in Table 1. As can be seen, the recoveries for glucose are in the range of 95.3%-101.4%, indicating that the proposed method have good accuracy and can be used practically for routine analysis of glucose in real samples.

 Table 2. Determination results for glucose in human serum sample.

Serum sample (mM)	Spiked (mM)	Detected (mM)	Recovery (%)
4.6	4	8.2	95.3
5.4	2	7.5	101.4

4. CONCLUSIONS

This work demonstrated an improved PEC glucose sensor based on GP-CdS nanocomposites via modification of CuO nanoparticles. The resultant CuO NPs/GP-CdS modified electrode shows good

electrocatalytic activity toward glucose oxidation in dark condition, and if under visible light irradiation, the electrochemical current is further enhanced significantly due to photoelectrocatalytic activity of CuO NPs/GP-CdS nanocomposites. The CV results demonstrated that modification of CuO NPs dramatically improved photoelectrocatalytic activities of GP-CdS composites toward glucose oxidation. As an PEC glucose sensor, good performance including a high detection sensitivity (1005 μ A mM⁻¹ cm⁻²), wide linear concentration range (5-2000 μ M), low detection limit (0.5 μ M) and good selectivity was obtained for CuO NPs/GP-CdS composites. The present method for detection of glucose in human serum sample demonstrated good recovery results, suggesting the validity of the present method for effective glucose monitoring.

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