

# Photoelectrochemical Non-Enzymatic Detection of Glucose at Graphene Supported CdS Nanowires via Decoration of CuO Nanoparticles under visible light

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Received: 1 July 2019 / Accepted: 23 August 2019 / Published: 7 October 2019

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Graphene@CdS nanowires (GP@CdS NWs) was synthesized by electrostatic assembly and hydrothermal method, and then decorated with CuO nanoparticles via electrodeposition on substrate of glassy carbon electrode to construct a photoelectrochemical enzyme-free glucose sensor. Scanning electron microscopy, electrochemical impedance spectroscopy and cyclic voltammetry were used to characterize the morphology and electrochemical properties of the above ternary CuO/GP@CdS NWs nanocomposites. The integration of photosensitive material GP@CdS NWs with electrocatalytic materials of CuO makes the nanocomposites show prominent photoelectrocatalytic activity toward glucose oxidation in alkaline solution. A 2.45 times increase in sensitivity under visible light irradiation was observed compared to dark condition. As a photoelectrochemical platform for non-enzymatic glucose sensing, the CuO/GP@CdS NWs modified electrode exhibited advantages, such as high detection sensitivity, wide linear concentration range, low detection limit and acceptable anti-interference ability. Good recovery obtained for glucose analysis in human serum sample suggested the validity of the proposed method for real sample analysis.

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

## 1. INTRODUCTION

As a main energy source of living organisms, glucose plays a vital role in different areas including clinical diagnostics, biotechnology, pharmaceutical and food industries [1-3]. Importantly, the amount of glucose in human blood behaves as a biomarker in the clinical therapy of diabetes mellitus [4,5]. Therefore, there is an urgent need to develop highly efficient and accurate method for glucose detection. Electrochemical glucose sensors have gained enormous attention due to its favorable features such as high sensitivity, good selectivity, low cost and convenient operation. Non-enzymatic

and enzymatic sensors are the two frequently used strategies for electrochemical monitoring glucose. However, the enzymatic glucose sensor is limited by its poor durability and stability because it is vulnerable to external experimental conditions [6]. In recent years, various nanostructured materials for direct electrocatalyzing oxidation of glucose has been proposed to develop non-enzymatic glucose sensors [7-12].

CuO is a promising material in construction of non-enzymatic glucose sensors owing to its good electrochemical activity, large surface area, and the possibility of improving electron transfer reactions. Various CuO nanostructures such as nanowires and nanoparticles have been prepared to show prominent electrocatalytic activities toward oxidation of glucose through the mediated reaction of  $\text{Cu}^{2+}/\text{Cu}^{3+}$  [13-16]. However, the performance of the present CuO based non-enzymatic glucose sensor need to be further improved.

Photoelectrochemical (PEC) measurement, characterized by its ultrahigh sensitivity and low background signal, is a potential analytical technique for chemical and biological analysis [17-20]. CdS, as a semiconductor with a narrow band gap of 2.4 eV, is one of the most widely studied photoactive materials in the PEC sensing under visible light irradiation. To further improve the photogenerated electron-hole pair's separation efficiency of CdS, the incorporation of more conductive materials, such as Au or Pt nanoparticles as well as carbon materials is the mostly adopted method [21-23]. Graphene (GR), with a high electron transfer rate and zero band gap [24], has been widely explored as a support for loading CdS nanomaterials to promote the charge transport and enhance the charge separation, and thus improve the PEC sensing performances.

In this work, CdS nanowires (CdS NWs) were synthesized by hydrothermal method, and then was further functionalized with amino groups to make it positively charged. Subsequently, CdS NWs were incorporated with graphene oxide (GO) through electrostatic assembly. After a thermal reduction process, GR@CdS NWs composites were prepared. CuO nanoparticles were then electrodeposited onto surface of GR@CdS NWs by potential cycling in a solution with  $\text{Cu}^{2+}$  ion involved to form CuO/GR@CdS NWs nanocomposites. The electrocatalytic activity of obtained nanocomposites modified electrode toward oxidation of glucose was studied in the dark and under visible-light irradiation. The results showed that an enhanced electrochemical response of glucose under visible-light irradiation was obtained compared to that of dark condition. An excellent performance including high sensitivity, good selectivity, high stability and reproducibility for glucose detection was achieved on CuO/GR@CdS NWs nanocomposites. Finally, satisfactory recovery results were found when the nanocomposites modified electrode was used for glucose determination in human serum samples, indicating the good accuracy of the developed method.

## 2. EXPERIMENTAL SECTION

### 2.1. Reagents and apparatus

GO was purchased from Nanjing XFNANO Materials Tech Co., Ltd. 3-aminopropyltrimethoxysilane (APTMS), glucose and interference species were purchased from Sigma-Aldrich.

CuSO<sub>4</sub>·5H<sub>2</sub>O, CdCl<sub>2</sub>, NaOH and sodium diethyldithiocarbamate trihydrate (C<sub>5</sub>H<sub>10</sub>NNaS<sub>2</sub>·3H<sub>2</sub>O) 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) 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/GR@CdS NWs nanocomposites modified glassy carbon electrode (CuO/GR@CdS NWs/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 NWs nanocomposites

Firstly, cadmium diethyldithiocarbamate was prepared by the reaction of C<sub>5</sub>H<sub>10</sub>NNaS<sub>2</sub>·3H<sub>2</sub>O and CdCl<sub>2</sub> to form precipitate. 1.124 g of the obtained precipitate was transferred into a 50 mL Teflon-lined stainless steel autoclave with the subsequent addition of 40 mL ethylenediamine. Afterwards, the autoclave was sealed and maintained at 180 °C for 24 h, and then allowed to cool down to room temperature naturally. The collected yellow sediment was rinsed with deionized water and ethanol to remove the residual solvent. After dried in 60 °C for 12 h, CdS NWs was obtained.

0.4 g of the resulting CdS NWs was dispersed into 200 mL ethanol and ultrasonicated for 30 min. Subsequently, 2 mL of APTMS was added and the mixture was heated to 60 °C for refluxing 4 h. The resultant APTMS functionalized CdS NWs was rinsed with absolute ethanol for three times. Through this process, positively charged CdS NWs was obtained.

The negatively charged GO solution was added into the above CdS NWs with a weight ration of 0.05: 1. The pH of the mixture was adjusted to 6.0 and incubated for 30 min. Under electrostatic assembly, the GO@CdS NWs nanocomposite was obtained. After that, 0.4 g of GO@CdS NWs nanocomposite was added into an autoclave with 20 mL ethanol and 60 mL distilled water involved. The autoclave was maintained at 120 °C for 12 h to get the GP@CdS NWs nanocomposites through the following rinsing and drying steps.

## 2.3. Preparation of CuO/GR@CdS NWs modified electrode

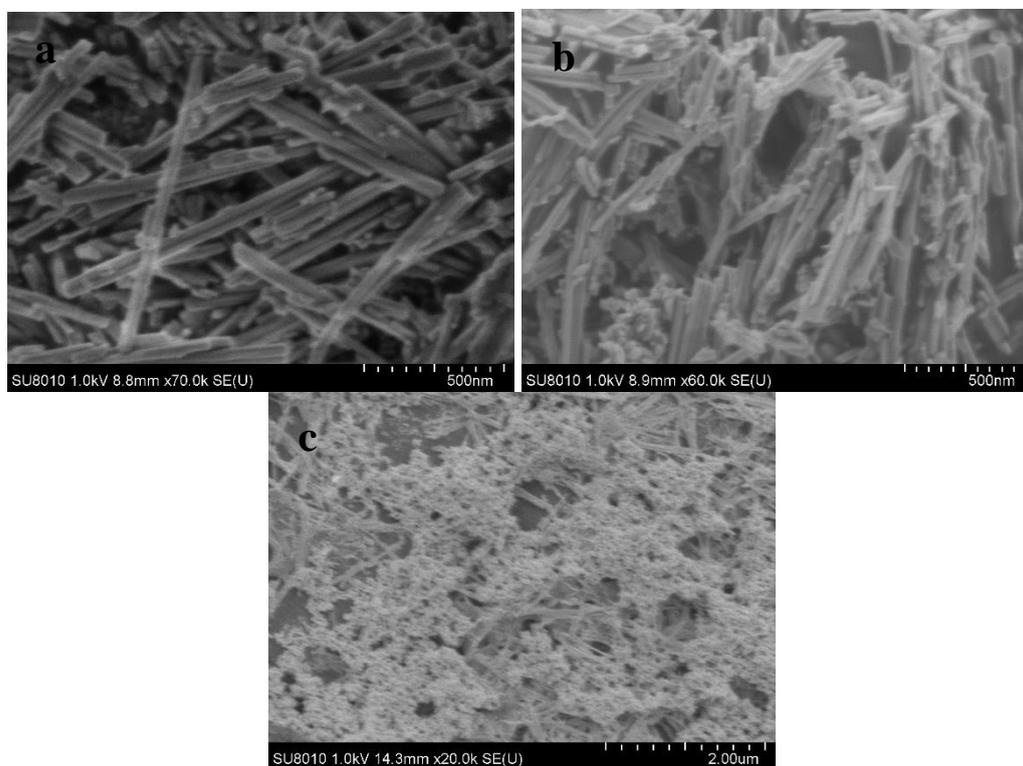
The glassy carbon electrode (GCE) was pretreated by polishing with 0.3 and 0.05 μm alumina slurries respectively. The electrode was placed in ethanol and water container under ultrasonic bathing to remove adsorbed particles. A 2 μL portion of the prepared GP@CdS NWs dispersion (5 mg/mL) was dropped onto a pretreated GCE and dried at room temperature to obtain the GP@CdS NWs/GCE. Before electrodeposition of CuO, the GP@CdS NWs/GCE was treated by potential cycling between -1.5 and 0 V for 20 cycles at scan rate of 100 mV s<sup>-1</sup> in 0.1 M KCl solution. CuO nanoparticles were

grown on the surface of GP@CdS NWs/GCE by CV in electrodeposition solutions with 10 mM of  $\text{CuSO}_4$  and 0.1 M KCl involved by scanning in the potential range of -1.5 to 0.5 V for 10 cycles at  $50 \text{ mV s}^{-1}$ . The direct electrodeposition of CuO nanoparticles on bare GCE surface was denoted as CuO modified electrode (CuO/GCE) for comparison experiment.

### 3. RESULTS AND DISCUSSION

#### 3.1. Morphological characterization

Fig. 1 shows SEM images of CdS NWs (a), GP@CdS NWs (b) and CuO/GP@CdS NWs (c) modified electrode. As observed, the obtained CdS NWs exhibit a nanowire morphology with diameters of about 20~40 nm. The length of CdS NWs can extend to 1  $\mu\text{m}$ . After electrostatic assembly of CdS NWs with GO to form GP@CdS NWs composites, 1D nanowires and 2D sheet-like morphology can both be seen. With the further electrodeposition of CuO, nanoparticles with aggregated structure were decorated onto GP@CdS NWs surface, indicating the successful formation of the ternary CuO/GP@CdS NWs nanocomposites.

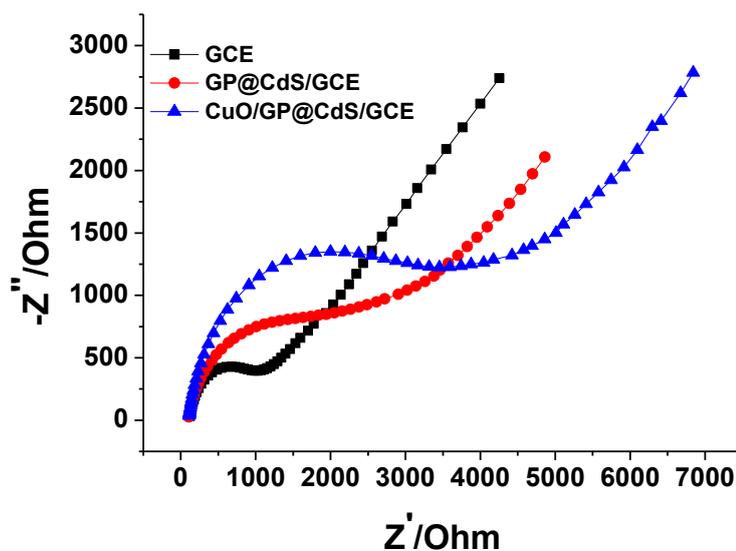


**Figure 1.** SEM images of CdS NWs (a), GP@CdS NWs (b) and CuO/GP@CdS NWs (c) modified electrode.

#### 3.2. EIS characterization

EIS is an effective technique for revealing the interface properties of electrodes modified with

different materials. A typical EIS plot involves a semi-circle part and a linear part. The diameter of the semi-circle part is related with the electron transfer process ( $R_{et}$ ). Fig. 2 compares the Nyquist plots of the bare GCE (a), GP@CdS NWs/GCE (b) and CuO/GP@CdS NWs/GCE (c) in 1 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$  and 0.1 M KCl solution in the frequency range of 0.1 Hz–10 kHz. As can be seen, the  $R_{et}$  value of the bare GCE is the smallest. After modification of GP@CdS NWs, the  $R_{et}$  value of the GP@CdS NWs/GCE increased obviously, indicating that the immobilization of GP@CdS NWs composites blocks the interfacial electron transfer due to a thick layer of semi-conductive CdS NWs covered. With the subsequent decoration of CuO nanoparticles, the  $R_{et}$  value of the CuO/GP@CdS NWs/GCE further increased significantly arising from the semiconducting properties of electrodeposited CuO. Furthermore, the gradual increase of the  $R_{et}$  value suggest the successful modification of GP@CdS NWs composites and CuO nanoparticles on electrode surface. The EIS result is similar with that for electrode modified with rGO/CdS/CoO<sub>x</sub> hybrid [23].

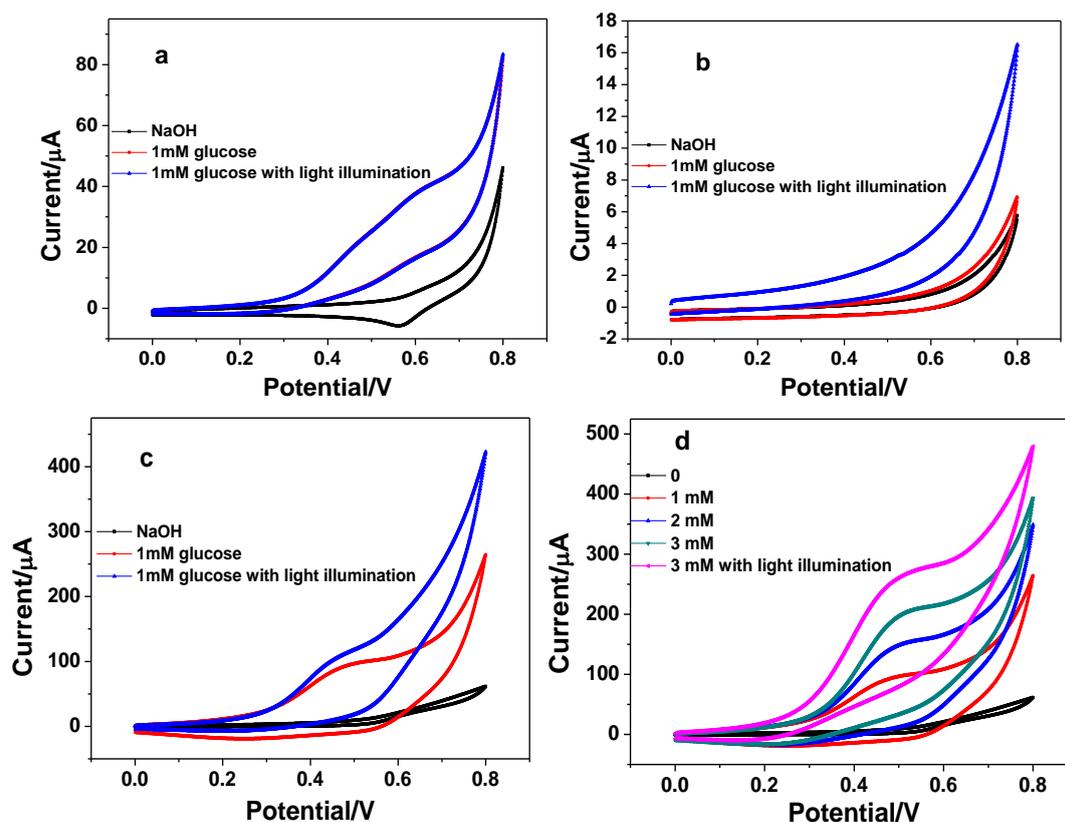


**Figure 2.** EIS of the bare GCE (a), GP@CdS NWs/GCE (b) and CuO/GP@CdS NWs/GCE (c) in 1 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$  and 0.1 M KCl solution in the frequency range of 0.1 Hz–10 kHz.

### 3.3. Electrocatalytic oxidation of glucose on the CuO/GP@CdS NWs/GCE

The electrochemical oxidation of glucose at CuO/GP@CdS NWs/GCE was performed in an alkaline media to investigate the electrocatalytic activity of CuO/GP@CdS NWs nanocomposites. For comparison, CuO/GCE and GP@CdS NWs/GCE were also studied. Fig. 3 shows the cyclic voltammogram (CV) responses of the CuO/GCE (a), GP@CdS NWs/GCE (b) and CuO/GP@CdS NWs/GCE (c) in 0.1 mol/L NaOH with the absence and presence of 1 mM glucose in dark and under visible light irradiation. As observed in Fig. 3(a), the addition of glucose caused a distinct increase for anodic current from a potential of 0.3 V at CuO/GCE due to prominent electrocatalytic activity of CuO toward the oxidation of glucose [14,16]. After exposing to visible light, there is no any change in the anodic current, which indicates photo-inactivity of CuO under visible light irradiation. For GP@CdS NWs/GCE (b), the glucose addition resulted in tiny change in the anodic current. However, an obvious

increase of anodic current can be seen under visible light irradiation. This result reveals the electro-inactivity of GP@CdS NWs but photo-activity toward glucose oxidation because of the formation of hole-electron pairs in GP@CdS NWs composite. For ternary nanocomposite CuO/GP@CdS NWs/GCE (c), the glucose addition leads to a dramatic increase for anodic current from a potential of 0.3 V, the visible light illumination further increase the anodic current from a potential of 0.4 V. In addition, as demonstrated in Fig. 3(d), the anodic peak current at 0.5 V increased with increasing of glucose concentration, and a further increase was observed upon light irradiation. Based on the above results, it can be concluded that the ternary nanocomposite shows effective and excellent photoelectrochemical activity toward glucose oxidation.

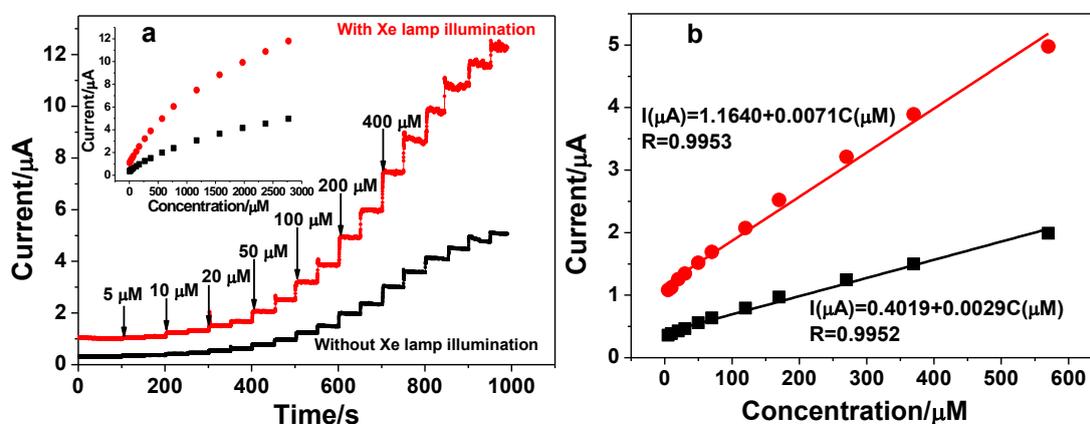


**Figure 3.** CV responses of the CuO/GCE (a), GP@CdS NWs/GCE (b) and CuO/GP@CdS NWs/GCE (c) in 0.1 mol/L NaOH with the absence (black curve) and presence (red curve) of 1 mM glucose in dark and under visible light irradiation (blue curve), (d) is the CVs of CuO/GP@CdS NWs/GCE in dark for 1, 2 and 3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

### 3.4. Amperometric detection of glucose at CuO/GP@CdS NWs/GCE

Amperometric technique was used to perform quantitative detection of glucose. Fig.4(a) shows the amperometric responses of CuO/GP@CdS NWs/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. As can be seen from fig.4(a), upon each addition of glucose, stable and stepwise current

increases accordingly and reaches a new equilibrium within 3 s. This rapid response demonstrate efficient catalytic activity of CuO/GP@CdS NWs naocomposites toward glucose oxidation. Obviously, the amperometric current under light illumination is much larger than that in dark condition, indicating more sensitive response for glucose at CuO/GP@CdS NWs/GCE under the help of light illumination. The inset of fig. 4(a) exhibits plots of current response vs glucose concentration. Obviously, a nearly linear and sensitive response was found for the low concentration range of glucose, but the increasing rate for current response vs glucose concentration is lowered for higher concentration of glucose, probably due to the blocked actives sites of CuO/GP@CdS NWs naocomposites by the oxidation product of glucose [10]. The calibration curve of the present method is presented in Fig.4 (b). The obtained calibration equation can be expressed as  $I(\mu\text{A})= 0.4019+0.0029C (\mu\text{M})$  with a correlation coefficient of 0.9952 in the dark condition, and  $I(\mu\text{A})= 1.1640+0.071C (\mu\text{M})$  with a correlation coefficient of 0.9953 under light illumination. The linear response range of glucose is 5-570  $\mu\text{M}$  with a detection sensitivity of  $410 \mu\text{A mM}^{-1} \text{cm}^{-2}$  and  $1005 \mu\text{A mM}^{-1} \text{cm}^{-2}$  in the dark and under visible light irradiation, respectively. A 2.45 times increase in sensitivity suggest an efficient photoelectrochemical catalytic activity of CuO/GP@CdS NWs naocomposites toward glucose oxidation. The limit of detection (LOD) is calculated to be 0.8  $\mu\text{M}$  and 0.4  $\mu\text{M}$  in the dark and light irradiation, respectively.



**Figure 4.** (a) Amperometric responses of CuO/GP@CdS NWs/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 plots of current response vs glucose concentration. (b) The calibration curve of the present method with the data obtained from Fig.4a.

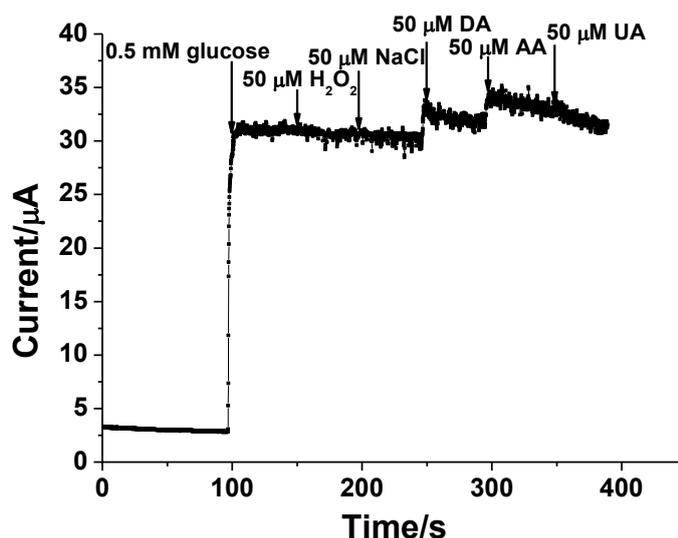
The analytical performance of CuO/GP@CdS NWs based glucose sensor with other reported nanomaterials is compared, the results of which is displayed in Table 1. As observed, the CuO/GP@CdS NWs based glucose sensor has better or comparable features than most of the previously reported glucose sensors listed in Table 1. The sensitivity of the present sensor is much larger than that for Cu<sub>2</sub>O nanocrystals (NCs)/reduced graphene oxide (r-GO), 3D graphene/Co<sub>3</sub>O<sub>4</sub> and Ni-Co oxide/rGO composites. Though rGO/CdS/CoO<sub>x</sub> exhibits an obviously higher sensitivity, the linear concentration range is significantly narrower compared to CuO/GP@CdS NWs nanocomposites. Therefore, the present glucose sensor shows favorable advantages of high sensitivity, low LOD, wide linear concentration range and low detection potential.

**Table 1.** Comparison of the analytical performance of CuO/GP@CdS NWs based glucose sensor with other reported nanomaterials.

Electrode materials	Potential (V)	Sensitivity ( $\mu\text{A mM}^{-1} \text{cm}^{-2}$ )	Linear range (mM)	LOD ( $\mu\text{M}$ )	Ref.
Ni-Co oxide/rGO	0.42	548.9	0.005–8.6	2	25
3D graphene/Co <sub>3</sub> O <sub>4</sub>	0.58	3.39	<0.08	<0.025	26
rGO/CdS/CoOx	0.4	5900	0.001–0.01	0.4	23
Cu <sub>2</sub> O NCs/r-GO	0.6	37.55 $\mu\text{A mM}^{-1}$	0.005–2.095	1	27
CuO/GP@CdS NWs	0.5	1005 ( $71 \mu\text{A mM}^{-1}$ )	0.005–0.57	0.4	This work

### 3.5. Reproducibility, stability, and selectivity of the CuO/GP@CdS NWs based glucose sensor

Five electrodes prepared by the above described method were used to investigate the reproducibility of the present sensor for glucose detection. A 4.56% of relative standard deviation (RSD) for current response of 100  $\mu\text{M}$  glucose was obtained, suggesting an acceptable reproducibility. The long-term storage stability of the CuO/GP@CdS NWs electrode was evaluated by periodically measuring amperometric response of 100  $\mu\text{M}$  glucose for an interval of 5 days. The modified electrode response retained 89% of its initial current after it was kept at 4 °C for one month. Thus, we can conclude that the CuO/GP@CdS NWs electrode have good reproducibility and stability.



**Figure 5.** (a) Amperometric responses of CuO/GP@CdS NWs/GCE holding at potential of 0.5 V for successive additions of 0.5 mM glucose, 50  $\mu\text{M}$  H<sub>2</sub>O<sub>2</sub>, 50  $\mu\text{M}$  NaCl, 50  $\mu\text{M}$  dopamine (DA), 50  $\mu\text{M}$  ascorbic acid (AA), 50  $\mu\text{M}$  uric acid (UA) to 0.1 M NaOH solution under visible light irradiation.

Some compounds such as H<sub>2</sub>O<sub>2</sub>, ascorbic acid (AA), dopamine (DA) and uric acid (UA) that are prone to be oxidized are usually found to coexist with glucose and interfere with the detection of glucose. Cl<sup>-</sup> is also reported to poison the sensing surface [28]. Therefore, the influence of these

possible interferences toward glucose detection was evaluated. Since the normal amount of glucose in human blood (3-8 mM) is nearly 10 times higher than those of DA, AA, UA [29], the molar ratio of 1:10 for glucose and interferences was exploited to carry out interference experiment. Fig. 5 shows amperometric responses of CuO/GP@CdS NWs/GCE holding at potential of 0.5 V for successive additions of 0.5 mM glucose, 50  $\mu$ M H<sub>2</sub>O<sub>2</sub>, 50  $\mu$ M NaCl, 50  $\mu$ M dopamine (DA), 50  $\mu$ M ascorbic acid (AA), 50  $\mu$ M uric acid (UA) to 0.1 M NaOH solution under visible light irradiation. The result shows that H<sub>2</sub>O<sub>2</sub>, 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/GP@CdS NWs/GCE for glucose detection.

### 3.5. Analysis of glucose in human serum samples

In order to evaluate the feasibility of the CuO/GP@CdS NWs/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 certain concentration of glucose (100  $\mu$ L). The determination results are presented in Table 2. As can be seen, the recoveries for glucose are in the range of 96.4%-103.8%, 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 (%)
3.6	2	5.4	96.4
4.8	0.5	5.5	103.8

## 4. CONCLUSIONS

In summary, GP@CdS NWs was prepared by electrostatic assembly of GO and presynthesized amino functionalized CdS NWs followed by a hydrothermal process. The subsequent decoration of CuO nanoparticles on surface of GP@CdS NWs was achieved through electrodeposition method. The resultant CuO/GP@CdS NWs 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/GP@CdS NWs nanocomposites. When the proposed electrode was used as an enzyme-free photoelectrochemical glucose sensor, excellent performance including a high sensitivity (1005  $\mu$ A mM<sup>-1</sup> cm<sup>-2</sup>), wide linear concentration

range (0.005-0.57 mM), low detection limit (0.4  $\mu$ M) good selectivity and stability was obtained. The validity of utilizing the present method for detection of glucose in human serum sample was also demonstrated, the results of which indicated the potential of the proposed method for effective and convenient glucose monitoring and diabetes diagnosis.

#### ACKNOWLEDGMENTS

This work was supported by the Grants from the National Natural Science Foundation of China (21105002, U1704135), the Technology Development Plan Project for Anyang City (21) and the Innovative Foundation for the College students of Anyang Normal University.

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