

Research Article

Yuhong Qian, Yiting Wang, and Li Wang*

Preparation of cuprous oxide-supported silver-modified reduced graphene oxide nanocomposites for non-enzymatic electrochemical sensor

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Abstract: We constructed a non-enzymatic H_2O_2 sensor based on cuprous oxide-supported silver-modified reduced graphene oxide nanocomposites. It was found that the sensor exhibited good performances for sensing H_2O_2 with a detection limit of $0.34 \mu\text{M}$ and a wide detection range of $1\text{--}310 \mu\text{M}$. The combination of graphene with silver and cuprous oxide improved the sensor's sensitivity for detecting H_2O_2 , with good repeatability, selectivity, and stability. The synthesis method of this nanocomposite provides a new idea for the green preparation of graphene-based nanocomposites and a new method for the construction of a new electrochemical sensor platform.

Keywords: cuprous oxide, silver, reduced graphene oxide, sensor

1 Introduction

Rapid and sensitive methods for detecting H_2O_2 have broad application prospects in the fields of food, medicine, chemical industry, and environmental protection and have attracted much attention in recent years [1–3]. Among many methods for detecting H_2O_2 , the electrochemical method is considered promising because of its high sensitivity and simple operation [4]. With the development of materials science and nanotechnology, nanomaterials with mimetic enzymatic activities have been widely used for the modification of chemical electrodes

to fabricate non-enzymatic sensors and biosensors. It has been reported that some nanomaterials such as two-dimensional (2D) materials, metallic nanoparticles, metal oxides, and others reveal potential enzymatic activity that is similar to natural enzymes, and therefore, could catalyze the oxidation and reduction of H_2O_2 that could be done by natural enzymes previously [5–8].

Graphene is a material with sp^2 hybrid connected carbon atoms closely packed into a single-layer 2D cellular lattice structure. Due to the excellent optical, electrical, and mechanical properties of graphene, graphene and graphene-based hybrid materials have been widely applied to materials science, micro-nano processing, energy, biomedicine, and drug delivery [9–11]. Graphene is considered to be a revolutionary material for the future. Previously, graphene-based non-enzymatic electrochemical sensors for high-performance detection of H_2O_2 and glucose have been reported [12]. In some cases, to improve the sensing performance, other metallic and metal oxide nanoparticles have been incorporated with graphene to form 2D nanocomposites, which exhibited synergistic effects for enhancing the electrochemical sensing efficiency [13–15].

Silver (Ag) nanomaterials have been widely applied in the fields of surface-enhanced Raman scattering (SERS), transparent conductive films, catalysts, sensors, and antibacterial sterilization due to their unique electrical, optical, thermal, catalytic, and elastic properties [16–20]. Cuprous oxide (Cu_2O) is a low-cost, environment-friendly p-type semiconductor with a narrow band gap [21], and therefore Cu_2O -based materials have been used widely in catalysis, sensors, solar cells, lithium-ion batteries, and water splitting [22–25]. The combination of Ag with Cu_2O has attracted strong attention, and Ag- Cu_2O nanocomposites for different purposes have been synthesized [26–28]. For instance, Luo et al. used Ag nanoparticles to decorate the surface of the prepared Cu_2O cubes. The $\text{Cu}_2\text{O}/\text{Ag}$ heterostructures within the cellulose nanofibril

* Corresponding author: Li Wang, College of Chemistry, Jilin Normal University, Siping, 136000, China, e-mail: liwang@jlnu.edu.cn

Yuhong Qian, Yiting Wang: College of Chemistry, Jilin Normal University, Siping, 136000, China

network were employed as an SERS substrate for efficient sensing of methylene blue [29]. Hu and coworkers prepared a series of Cu₂O/Ag heterojunctions using a simple microwave-assisted green route. The study of antibacterial behavior against *Escherichia coli* and *Staphylococcus aureus* indicated that the heterojunction exhibited much better antibacterial performance than the pristine Cu₂O due to the synergistic effect of Cu₂O and Ag [30]. The combination of graphene with Ag and Cu₂O may lead to unique nanomaterials with novel functions [20,31,32]. For example, Sharma et al. synthesized ternary nanocomposites composed of Ag-Cu₂O and reduced graphene oxide (rGO) using Benedict's solution and glucose solution without any toxic reagent, surfactant, or special treatment [33]. The resulting Ag-Cu₂O/rGO nanocomposites exhibited good photocatalytic performance for the photodegradation of methyl orange.

In this work, we used the catalytic activity of Ag nanoparticles on H₂O₂ to modify rGO and then combined the products with Cu₂O to form Cu₂O/Ag-rGO nanocomposites. It was found that the nanocomposites exhibited good electrocatalytic properties for H₂O₂. The results showed that our method was simple and green, and the sensor based on the Cu₂O/Ag-rGO nanocomposites had the advantages of high sensitivity, high selectivity, and a wide detection range. This method provides not only a highly selective and sensitive electrochemical detection platform for the detection of H₂O₂, but also a new idea for the application of graphene-based metal nanocomposites in the field of electrochemical biosensors.

2 Experimental sections

2.1 Reagents and materials

Ethanol (>99.9%, analytically pure), polyvinylpyrrolidone (PVP, K30, $M_w = 30,000\text{--}40,000$), hydrogen peroxide (H₂O₂, 30 wt%), silver nitrate, copper nitrate, sodium citrate dihydrate (1 wt%), hydrazine hydrate (40%, analytically pure), concentrated nitric acid (68 wt%), glucose (analytically pure), and ascorbic acid (AA, >99.7%, analytically pure) were purchased from Beijing Chemical Plant. Monolayer graphene oxide (GO) aqueous dispersion (10 mg·g⁻¹) was purchased from Hangzhou Gaosen Technology Co., Ltd. Dopamine hydrochloride (98%, analytically pure) was purchased from Aladdin Reagent Co., Ltd., and uric acid (UA, analytically pure) was purchased from Sigma Aldrich Chemical Reagent Co., Ltd. All reagents

were used directly without purification. Ultrapure water was used in the experiment.

2.2 Preparation of Cu₂O/Ag-rGO nanocomposites

2.2.1 Preparation of the Ag-rGO composite

After ultrasonic treatment of 0.1 mg·mL⁻¹ of monolayer GO solution, 30 mL of the treated solution was taken and poured into a three-port flask, and then water was added up to 200 mL. Next, 36 mg of silver nitrate was added to the three-port flask and heated until the solution boiled. Then, 4 mL of sodium citrate solution was quickly added and stirred. Finally, the temperature was adjusted to 85°C and heated for 40 min to obtain the Ag-rGO composite structure.

2.2.2 Preparation of the Cu₂O/Ag-rGO composite

One gram of PVP was added to 50 mL of 0.04 M copper nitrate solution and stirred until PVP was fully dissolved. Then, 20 mL of the prepared Ag-rGO solution was added to this solution. Next, 68 µL of hydrazine hydrate was added to this solution and stirred. The obtained product was centrifuged and washed with water.

2.3 Instruments

The morphology of the obtained nanocomposites was investigated by an S-4800 scanning electron microscope (SEM) and a TECNAI G2 high-resolution transmission electron microscope (TEM). The crystalline nature of the nanostructures was analyzed using a Rigaku D/max 2500 V X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) analyses were carried out on an Escalab-MkII energy spectrometer.

2.4 Detection of H₂O₂

H₂O₂ aqueous solutions with different concentrations were prepared by diluting H₂O₂ in a gradient. All electrochemical properties of the samples were tested by a CHI 760e electrochemical analyzer (Shanghai Chenhua

Instrument Co., Ltd.) with the conventional three-electrode system. Saturated calomel electrode was used as the reference electrode, platinum wire as the counter electrode, and modified glassy carbon electrode (GCE) as the working electrode. The 3 mm diameter GCE was polished with alumina slurry, and then ultrasonically washed in water and ethanol for 5 min. When preparing the H_2O_2 sensor, 4 μL of $\text{Cu}_2\text{O}/\text{Ag-rGO}$ solution was dropped on the clean GCE surface and dried in the air. In the control experiment, 4 μL of 1 $\text{mg}\cdot\text{mL}^{-1}$ rGO solution was dropped on the bare GCE and dried as the working electrode. In the selective test, 5 μL of glucose, AA, UA, and dopamine (DA) were used as control. The current change in the system was investigated under the same experimental conditions as those for H_2O_2 . Before the experiment, N_2 was pumped into the 0.1 M phosphate-buffered saline (PBS) solution ($\text{pH} = 7.0$) to remove the oxygen in the buffer and N_2 was used in the whole electrochemical measurements.

3 Results and discussion

3.1 Characterizations of $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposites

The morphology and crystal structure of $\text{Cu}_2\text{O}/\text{Ag-rGO}$ were characterized by SEM and TEM, as shown in Figure 1. SEM images show that $\text{Cu}_2\text{O}/\text{Ag}$ nanoparticles are spherical in shape with the size of about 50–80 nm and the surface of the particles is rough (Figure 1a and b). To further confirm their micro-configuration and geometrical structure, the morphologies of the as-prepared $\text{Cu}_2\text{O}/\text{Ag}$ nanocomposites were further analyzed by TEM (Figure 1c and d). It can be seen from Figure 1c that most $\text{Cu}_2\text{O}/\text{Ag}$ nanoparticles are supported on rGO nanosheets. The Ag nanoparticles are evenly encapsulated by the rough Cu_2O layer. The evident contrast in the brightness between the dark cores and bright shells indicates the formation of core-shell architecture. Two distinct crystal

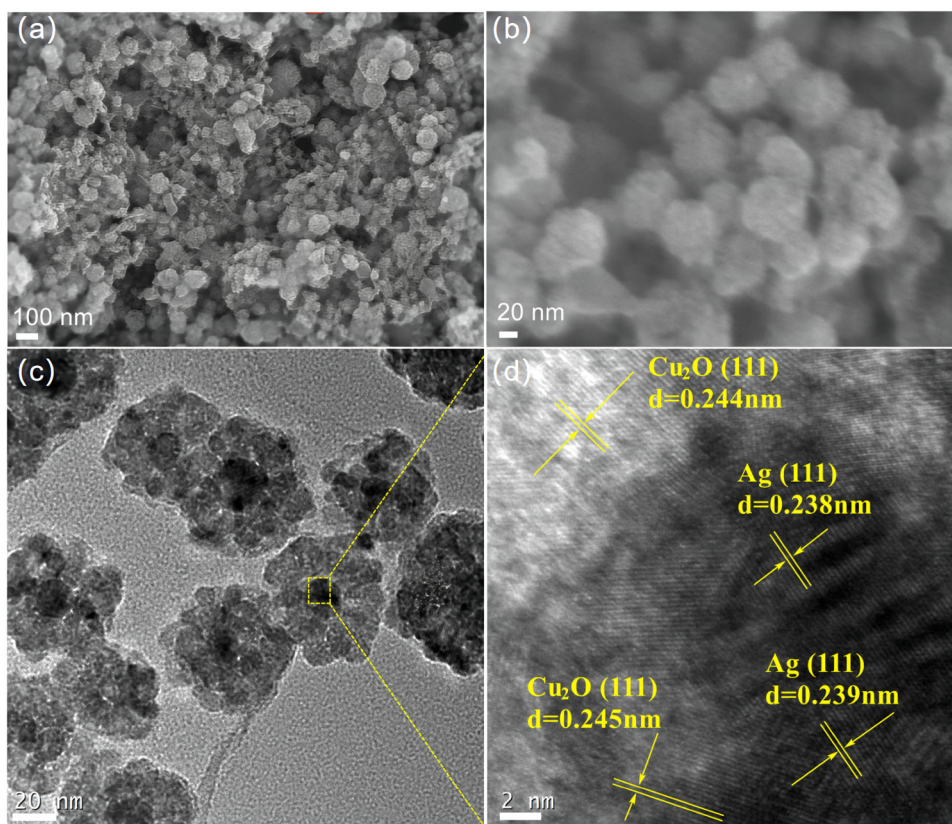


Figure 1: (a and b) SEM and (c and d) TEM images of $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposites.

structures can be observed in Figure 1d. High-resolution transmission electron microscopy shows that the fringe spacing of 0.244 nm is ascribed to (111) facet of Cu_2O nanoparticles, indicating that the exposed crystal facet of Cu_2O nanocrystals is (111) crystal facets. The fringe spacing of 0.238 nm corresponds to the (111) crystal planes of Ag nanoparticles [31].

XRD diffraction pattern shows that the main diffraction peaks of $\text{Cu}_2\text{O}/\text{Ag-rGO}$ in the range of $10\text{--}90^\circ$ are consistent with the previous reports [34], as shown in Figure 2. The strong intensity of the diffraction peaks indicates that the synthesized $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposites have a well-ordered structure. The results prove the formation of the ternary heterojunction structure of $\text{Cu}_2\text{O}/\text{Ag-rGO}$. No other impurities are found in the figure, which demonstrates that the synthesized $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposite is relatively pure.

The chemical composition and valence distribution of $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposites were characterized by XPS, as shown in Figure 3. C 1s, O 1s, Ag 3d, and Cu 2p in the full spectrum prove the existence of C, O, Ag, and Cu elements, respectively (Figure 3a). In Figure 3b, the binding energy peaks at 374.15 and 368.15 eV correspond to Ag 3d_{3/2} and Ag 3d_{5/2}, respectively [35,36]. The binding energy peaks at 288.1, 285.95, 284.8, and 284.3 eV in the C 1s spectrum indicate that the structure contains C=O, C–O, C–C, and C=C [37], as shown in Figure 3c. In Figure 3d, the binding energy peaks at 532.95, 531.45, and 530.25 eV in the O 1s spectrum indicate that the structure contains C=O, C–OH, and Cu–O [38]. In Figure 3e, the binding energy peaks at 952.1 and 932.3 eV correspond to Cu 2p_{1/2} and Cu 2p_{3/2}, respectively

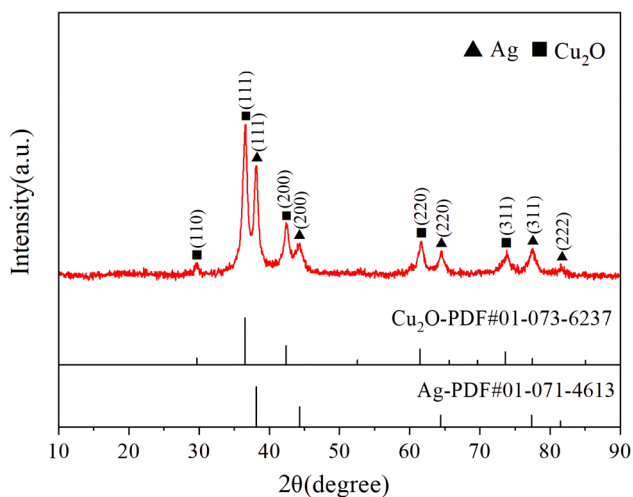


Figure 2: XRD diffraction patterns of $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposites.

[39]. The results prove the formation of $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposites.

3.2 Optimization of H_2O_2 catalytic conditions

In order to explore the optimal conditions for the obtained $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposites to catalyze H_2O_2 , control experiments were carried out. The catalytic performance of the nanocomposites was adjusted by controlling the amount of $\text{Cu}(\text{NO}_3)_2$ added into the reaction. Under the working potential of -0.4 V , H_2O_2 with different concentrations was added slowly into the working system to observe the current response. It can be seen from Figure 4 that the nanocomposites prepared with the addition of 0.04 M $\text{Cu}(\text{NO}_3)_2$ have the best catalytic effect on H_2O_2 .

To prove that the prepared nanocomposites have good electrocatalytic activity, the catalytic behaviors of unmodified GCE, rGO-modified GCE, and the $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposite-modified GCE for H_2O_2 were compared, as shown in Figure 5. It can be seen that the unmodified GCE has no obvious oxidation–reduction process after adding $10\text{ }\mu\text{M}$ H_2O_2 , while the diffusion current of GCE increased after rGO modification. In contrast, the current of the GCE modified by $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposites is significantly increased, indicating that the nanocomposites have reduced H_2O_2 on the electrode surface and form an amplified current signal. These results show that the $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposites have obvious electrocatalytic reduction activity for H_2O_2 . The introduction of Cu_2O makes the local energy level in the nanocomposite change correspondingly, which is conducive to the transfer of electrons. The synergistic effect between Cu_2O and Ag could enhance the electrical conductivity of the electrode. Additionally, $\text{Cu}_2\text{O}/\text{Ag}$ nanoparticles can disperse rGO and make it difficult to agglomerate, which increases the active surface areas of the modified electrode.

3.3 Sensitivity analysis of the detection system

Figure 6a shows a typical $i\text{--}t$ curve with the $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposite-modified GCE on successive additions of H_2O_2 into the 0.1 M of PBS solution. It is clear that the addition of $1\text{ }\mu\text{M}$ H_2O_2 causes a rapid and stable current response as a result of the reduction of H_2O_2 . The

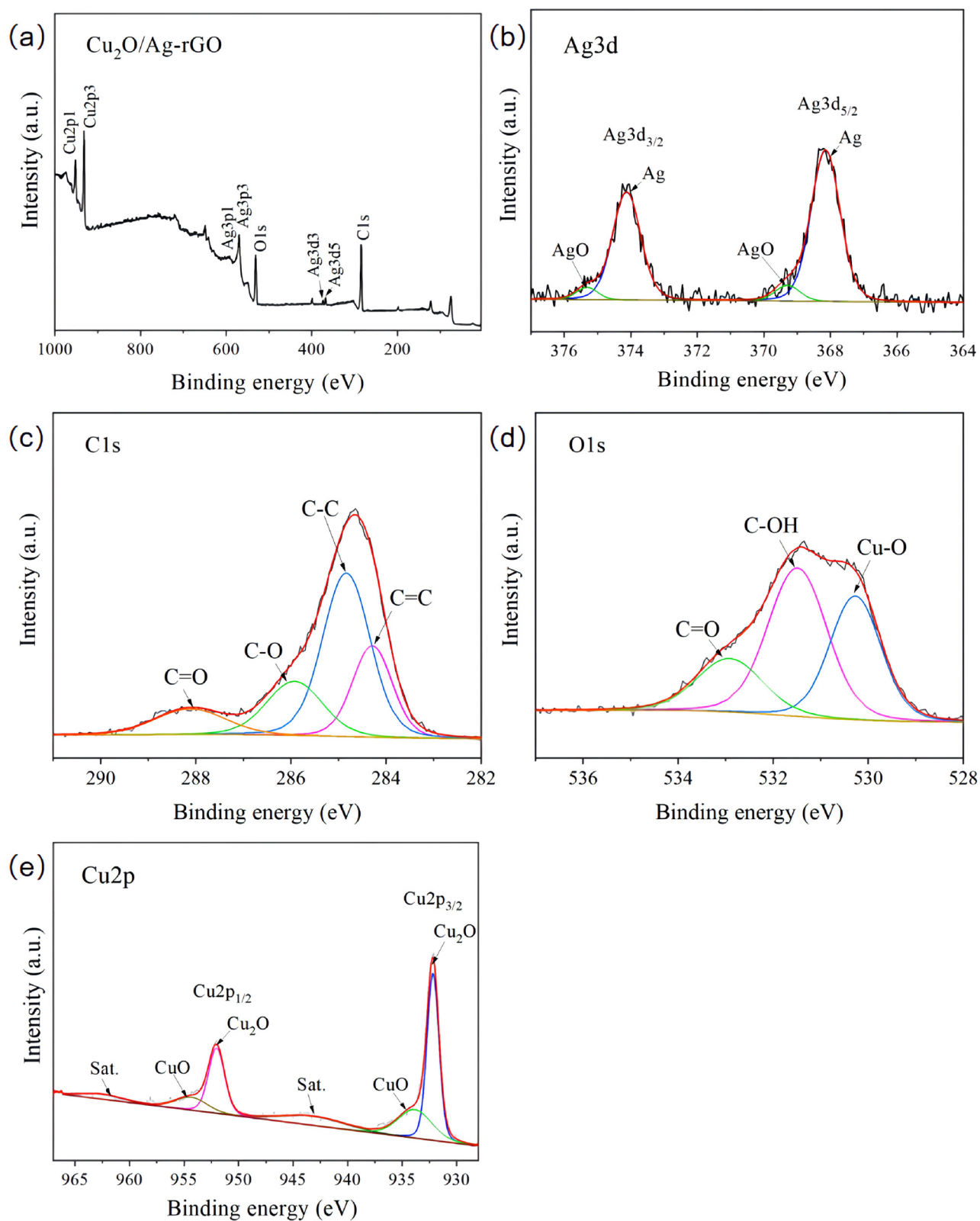


Figure 3: (a) XPS full spectrum of $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposites. High-resolution XPS spectra of (b) $\text{Ag}3\text{d}$, (c) $\text{C}1\text{s}$, (d) $\text{O}1\text{s}$, and (e) $\text{Cu}2\text{p}$.

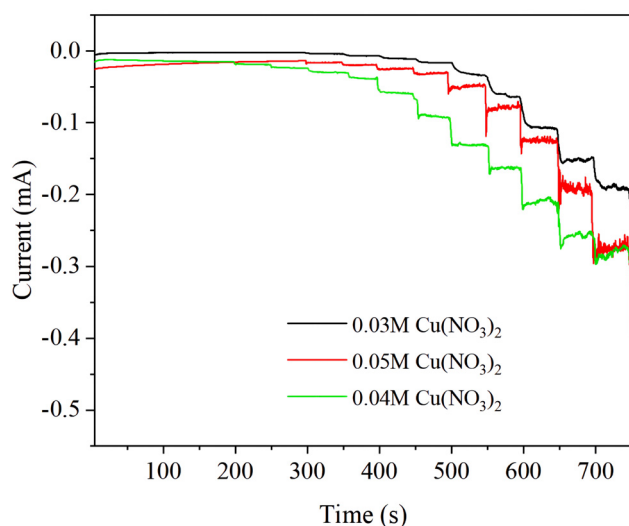


Figure 4: Current-time (i - t) curves of the GCE modified by the $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposites prepared by adding different amounts of $\text{Cu}(\text{NO}_3)_2$ into the reaction solution.

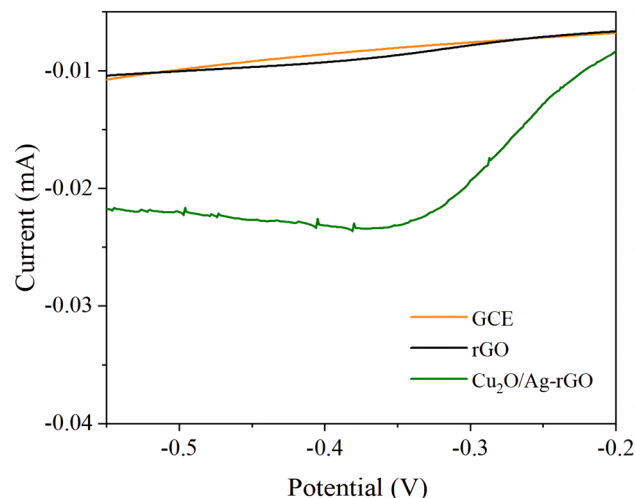


Figure 5: Cyclic voltammograms of bare GCE, rGO modified GCE, and $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposite-modified GCE toward the detection of H_2O_2 .

corresponding calibration of the i - t data indicates a regular response toward H_2O_2 with a linear detection range from 1 to 310 μM (Figure 6b). According to the linear fit, it can be concluded that the linear regression equation is $I \text{ (mA)} = -0.001c \text{ (}\mu\text{M)} - 0.036$. The calculated detection limit of this sensor is 0.34 μM ($S/N = 3$).

The selectivity and anti-interference of this electrochemical sensor were evaluated by adding glucose, AA, UA, and DA. Figure 7a shows that no interference is observed in the measured potential. Therefore, it can be concluded that this sensor has good anti-interference ability

and high selectivity. The reuse stability of $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposite-modified GCE was further investigated. Figure 7b shows that the fabricated sensor can be reused at least five times. The long-term stability of $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposite-modified GCE within 14 days was studied. The prepared electrodes were stored in a refrigerator at 4°C and measured once after 1, 2, 3, 7, and 14 days. Figure 7c shows that after 14 days, the reduction current response of 10 μM H_2O_2 remains at 85.4% of the initial value, revealing that the sensor based on $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposites has acceptable stability.

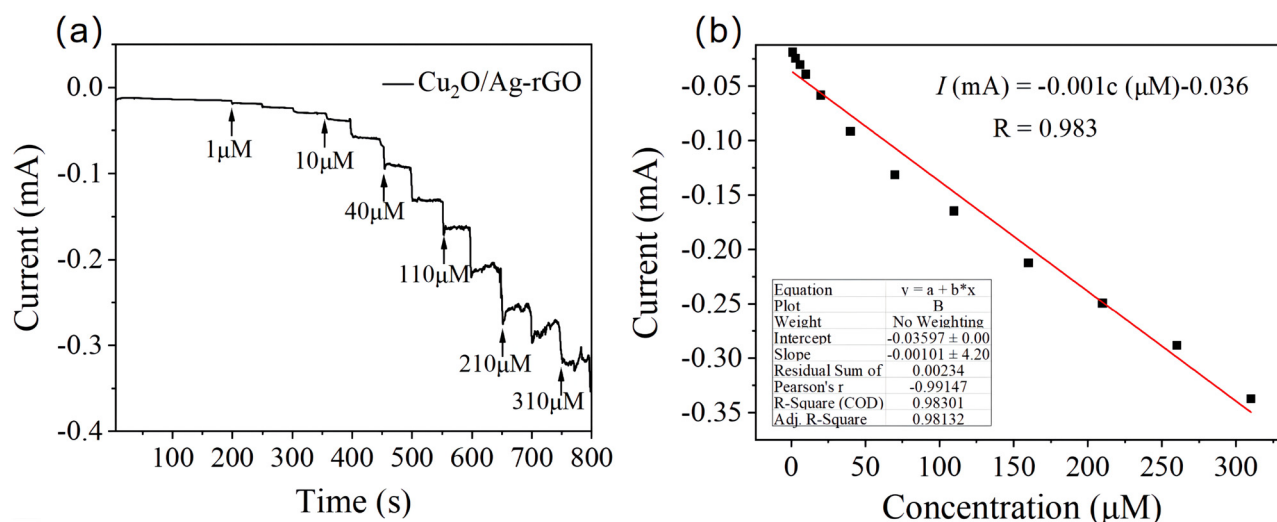


Figure 6: Electrochemical sensing H_2O_2 : (a) i - t response of the $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposite-modified GCE by adding H_2O_2 with various concentrations, and (b) corresponding calibration line of current against the concentration of H_2O_2 .

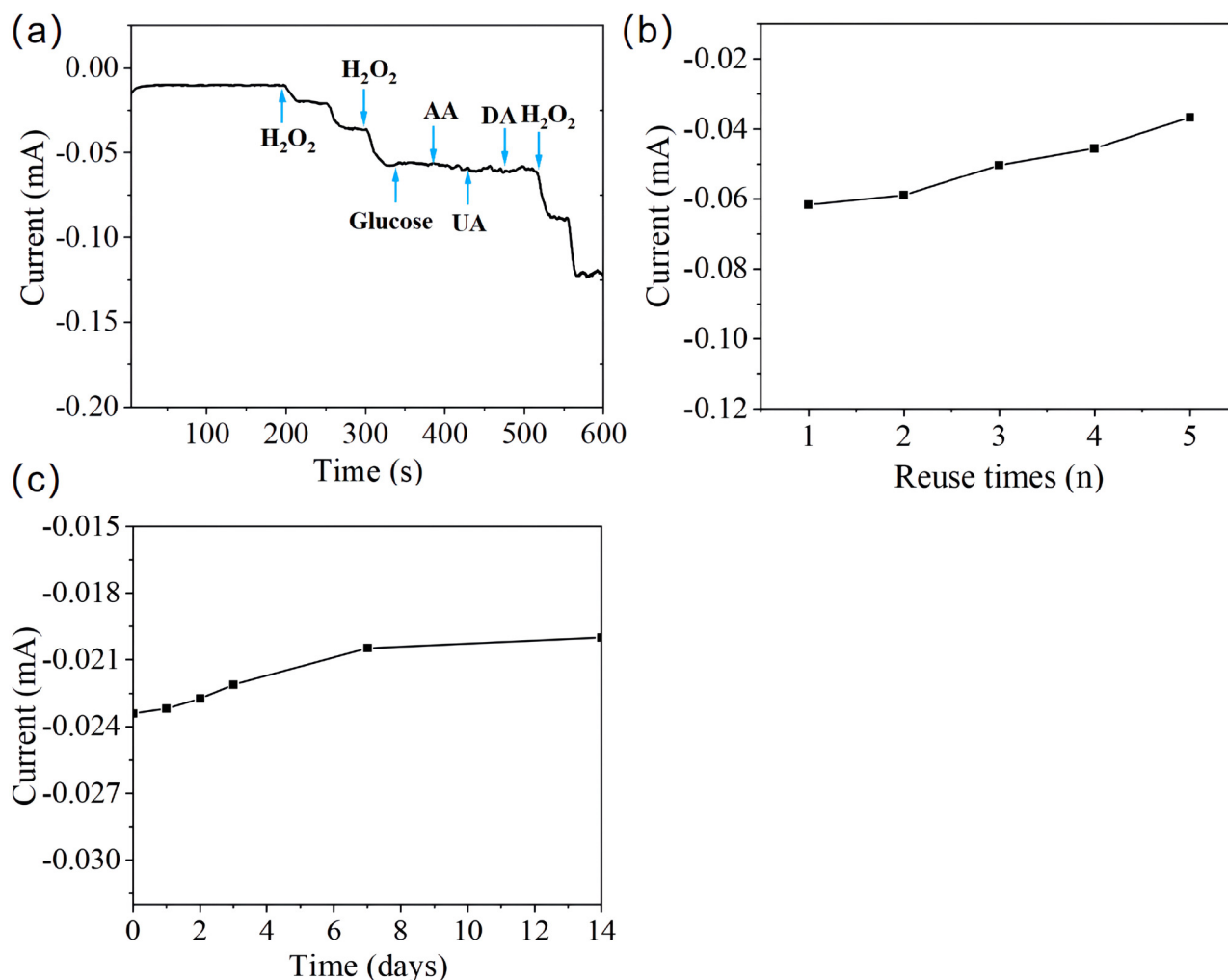


Figure 7: Performance of the H_2O_2 sensor based on the $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposites: (a) anti-interference capability, (b) reuse stability, and (c) long-term stability.

4 Conclusions

In this work, we proposed a method based on the $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposites to construct a nonenzymatic H_2O_2 sensor with high sensitivity and selectivity. We studied and analyzed the electrochemical performance of the sensor based on the $\text{Cu}_2\text{O}/\text{Ag-rGO}$ nanocomposites. The sensor exhibits a wide detection range of 1–310 μM and a relatively low detection limit of 0.34 μM . Compared with the traditional method, our method has the advantages of being a simple experimental process, using a simple instrument, and being environmentally friendly. Furthermore, this method provides a new idea for the construction of a fast, sensitive, economical, and highly selective non-enzymatic H_2O_2 sensor, which has theoretical and practical significance.

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Author contributions: Yuhong Qian: writing – original draft, methodology, data analysis; Yiting Wang: formal analysis; Li Wang: writing – original draft, writing – review and editing, project administration.

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