

RESEARCH ARTICLE

In situ Immobilization of Copper Nanoparticles on Polydopamine Coated Graphene Oxide for H₂O₂ Determination

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Citation: Liu Y, Han Y, Chen R, Zhang H, Liu S, Liang F (2016) *In situ* Immobilization of Copper Nanoparticles on Polydopamine Coated Graphene Oxide for H₂O₂ Determination. PLoS ONE 11(7): e0157926. doi:10.1371/journal.pone.0157926

Editor: Nikolai Lebedev, US Naval Research Laboratory, UNITED STATES

Received: March 23, 2016

Accepted: June 7, 2016

Published: July 5, 2016

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Data Availability Statement: All relevant data are within the paper.

Funding: R.S.C. acknowledges support by the National Natural Science Foundation of China under award number 21105077, the Open Funds of Key Laboratory of Analytical Chemistry for Biology and Medicine of Ministry of Education under contract number ACBM2014001, and the Open Funds of Key Laboratory of Inorganic Coating Materials of Chinese Academy of Sciences KLICM-2013-05. F.L. thanks the National Natural Science Foundation of China under award number 21372183, Hubei Provincial Natural Science Foundation of China 2013CFB328,

Abstract

Nanostructured electrochemical sensors often suffer from irreversible aggregation and poor adhesion to the supporting materials, resulting in reduced sensitivity and selectivity over time. We describe a versatile method for fabrication of a H₂O₂ sensor by immobilizing copper nanoparticles (Cu NPs; 20 nm) on graphene oxide (GO) sheets *via in-situ* reduction of copper(II) on a polydopamine (PDA) coating on a glassy carbon electrode. The PDA film with its amino groups and catechol groups acts as both a reductant and an adhesive that warrants tight bonding between the Cu NPs and the support. The modified electrode, best operated at a working voltage of −0.4 V (vs. Ag/AgCl), has a linear response to H₂O₂ in the 5 μM to 12 mM concentration range, a sensitivity of 141.54 μA·mM^{−1}·cm², a response time of 4 s, and a 1.4 μM detection limit (at an S/N ratio of 3). The sensor is highly reproducible and selective (with minimal interference to ascorbic acid and uric acid). The method was applied to the determination of H₂O₂ in sterilant by the standard addition method and gave recoveries between 97% and 99%.

Introduction

Rapid, low-cost and reliable detection of hydrogen peroxide (H₂O₂) is of particular significance due to its wide application in food industry, environmental protection, and medical field [1–4]. Most previous studies indicate that H₂O₂ is actually a universal metabolic intermediate in organism and is closely associated with the metabolic function of human body [5, 6]. Moreover, bioaccumulation of H₂O₂ produces oxidative stress and results in severely detrimental damage to cells [7]. Nowadays many analytical methods have been employed for the determination of hydrogen peroxide, such as chemiluminescence, spectrophotometry, titrimetry and electrochemistry [8–11]. Among them, electrochemical sensors are attracted much attention

Wuhan Applied Basic Research Programs of China 2015060101010069, and the Open Funds of the State Key Laboratory of Electroanalytical Chemistry SKLEAC201609. S.M.L. acknowledges support by the Thousand Youth Talents Program.

Competing Interests: The authors have declared that no competing interests exist.

due to its excellent properties of low-cost, simplicity, high sensitivity and handling convenience [12].

Hydrogen peroxide sensors based on the nanoparticles of metal or metal oxides have been intensively explored recently [13–15]. The electrocatalytic activities of the nanoparticles can produce remarkable voltammetric responses towards H₂O₂. But the irreversible aggregation will occur due to the high surface energy of free nanoparticles and will significantly decrease the analytical performance [16, 17]. A variety of supporting materials have been employed to disperse the nanoparticles. And graphene is the most frequently employed substrate to integrate the nanoparticles by procedures such as hydrothermal deposition and chemical vapor deposition [18, 19]. The sensitivity and selectivity of H₂O₂ determination depend on the immobilized nanoparticles. Therefore, the adhesion of the immobilized nanoparticles to the substrate is a key issue for H₂O₂ sensors in practical applications.

Herein, we present a versatile approach to immobilize nanoparticles on graphene sheets *via in situ* reduction of metal ions on the polydopamine (PDA) coating that can provide a tight bonding between the nanoparticles and the supporting materials. Graphene oxide (GO) was coated with a PDA film through simple dip-coating in an aqueous solution of dopamine, which can generate a nanofilm on most inorganic and organic materials in alkaline media by self-polymerization [20–23]. Dopamine is a chemical agent that contains catechol and amine groups. The PDA film composed of cross-linking with amine and catechol groups can serve as a reductant as well as an adhesive agent [24–28]. Copper nanoparticles (Cu NPs) were produced on the PDA film by *in situ* chemical reduction of copper ions and were integrated to the graphene sheets by the adhesive PDA coating. The GO/PDA/Cu NPs composite was characterized by transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS). The electrochemical behaviors were studied by cyclic voltammetry (CV) and amperometric *i-t* curve. The electrochemical sensor fabricated by GO/PDA/Cu NPs exhibited high sensitivity towards H₂O₂ determination with excellent reproducibility. The sensor also displayed good selectivity with minimal interference from the coexisting species such as ascorbic acid (AA) and uric acid (UA) in biological fluids and can be applied to real sample analysis.

Materials and Methods

Reagents

Hydrogen peroxide (H₂O₂, 30%) was purchased from Nanjing Chemical Reagent. Dopamine hydrochloride, tris(hydroxymethyl)aminomethane (Tris, 99%), ascorbic acid (AA), uric acid (UA) and polyvinylpyrrolidone (PVP, MW = 5000) were purchased from Sigma-Aldrich and used without further purification. Graphene oxide (GO, 1 mg/mL) was obtained from Institute of Coal Chemistry of Chinese Academy of Science. Other analytical grade chemicals were purchased from Sinopharm Group Co. Ltd. and also used without further purification. All aqueous solutions were prepared with deionized (DI) water and prepared just prior to use.

Instruments

The microstructure and composition of GO/PDA and GO/PDA/Cu NPs were characterized by TEM (JEM-2010 UHR, JEOL) and XPS (ESCALAB 250, Thermo Fisher Scientific) using the Al K α radiation (1486.6 eV, 15 kV, 150 W) at a vacuum of 2×10^{-9} mbar. Electrochemical measurement was performed at room temperature in phosphate buffer (PBS) on the CHI 660e potentiostat (CH Instruments Inc., Shanghai, China). A simple three-electrode configuration used in the measurement consisted of an Ag/AgCl electrode as the reference electrode, a Pt wire as the counter electrode, and a glassy carbon electrode (GCE, 3 mm in diameter) modified with GO/PDA/Cu NPs composite as the working electrode.

Preparation of GO/PDA and GO/PDA/Cu NPs

GO powder was obtained by drying the purchased GO aqueous solution (1 mg/mL) at 80°C under vacuum. An amount of 20 mg GO powder was dispersed in 4 mL Tris buffer (10 mM, pH = 8.5) and ultra-sonicated in ice bath for 5 min. Then added 16 mL Tris buffer in the GO solution and continued ultra-sonicated for 5 min to obtain a homogeneous dispersion of GO. The GO solution was separated by centrifugation before washing with Tris buffer for three times, and then dispersed in 2 mg/mL dopamine solution under stirring for 24 h at room temperature. GO/PDA composite was obtained by centrifugation and dried in vacuum at 60°C. An amount of 10 mg of GO/PDA composite was added into the fresh prepared 10 mM copper sulfate solution, followed by addition of sodium citrate (0.1 M) and PVP (1 wt.%) under stirring for 12 h. After centrifugation, the GO/PDA/Cu NPs sediment was washed with DI water and dried in vacuum [29]. The fabrication procedures can be depicted in Fig 1.

The GCE was polished with 0.05 μm α-Al₂O₃ power, and then sonicated in ethanol and DI water for several times to obtain a clean surface. The GO/PDA/Cu NPs composite was dripped onto the cleaned GCE surface. For comparison, GO/PDA composite was also dripped onto the GCE surface. The electrodes were dried at room temperature prior to electrochemical test.

Results and Discussion

Morphology and composition of GO/PDA/Cu NPs composite

The morphology of GO/PDA and GO/PDA/Cu NPs was investigated by TEM. The TEM images revealed multilayer structures of GO/PDA composite without any particles (Fig 2a). Spherical nanoparticles with an average diameter of 20±4 nm (estimation from 100 nanoparticles) uniformly deposited on the surface of GO/PDA were observed in Fig 2b. As can be seen from HR-TEM images (inset in Fig 2c), the spacing of the lattice fringes (0.1810 nm) corresponds to the lattice planes Cu (1, 1, 1) [30], suggesting the deposition of Cu NPs on the GO/PDA sheets. Chemical composition of the nanoparticles was also analyzed by XPS (Fig 2d). The Cu 2p_{3/2} single peak for Cu NPs at 934.92 eV should be attributed to copper zero or copper (I). The O 1s peak at 532.67 eV for Cu NPs indicates the existence of copper oxide [31]. The results further confirm that the formation of the GO/PDA/Cu NPs composite.

Electrochemical behaviors of the GO/PDA/Cu NP sensor

Cyclic voltammograms (CV) were measured to investigate the electrocatalytic property of the GO/PDA/Cu NPs composite in PBS buffer, as shown in Fig 3a. No obvious current response

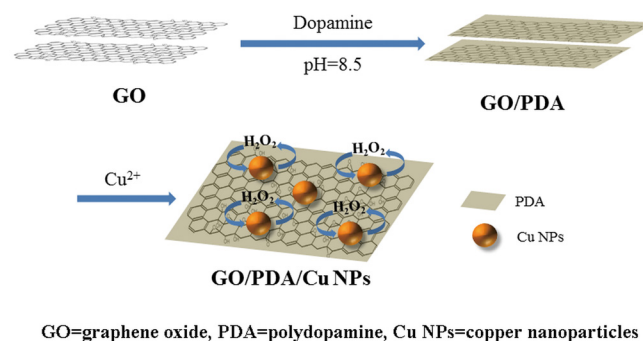


Fig 1. Scheme of the GO/PDA/Cu NPs sensor fabricated by immobilizing Cu NPs on GO sheets via *in-situ* reduction of copper(II) on a PDA coating.

doi:10.1371/journal.pone.0157926.g001

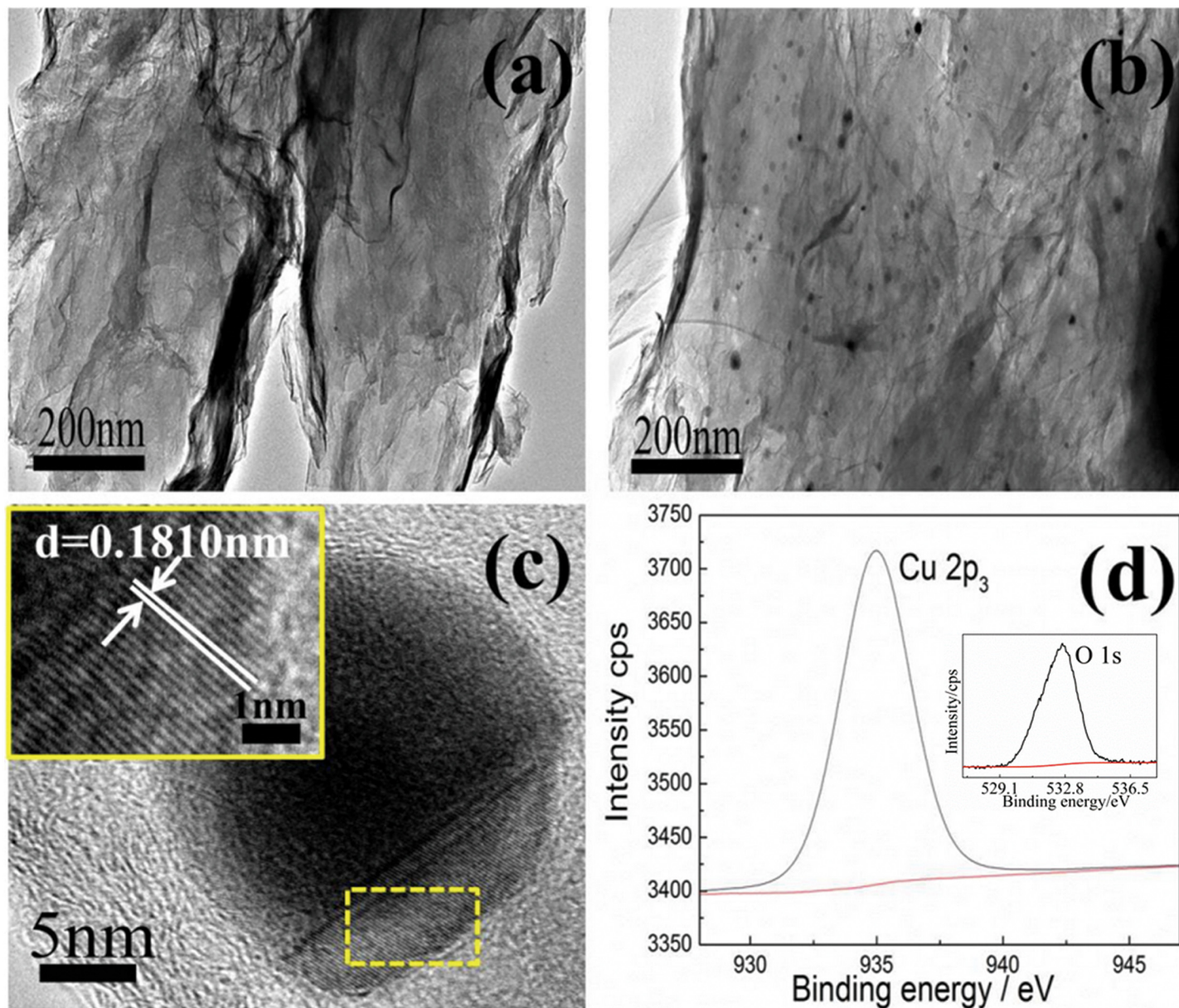


Fig 2. TEM images of GO/PDA (a), GO/PDA/Cu NPs (b), HR-TEM images of GO/PDA/Cu NPs (c) and the Cu2p and O 1s (inset) XPS spectra of GO/PDA/Cu NPs (d).

doi:10.1371/journal.pone.0157926.g002

changes can be observed between the CV of GO/PDA in the absence (a) and presence (b) of 10 mM H₂O₂. Compared the GO/PDA/Cu NPs without H₂O₂ (c), the GO/PDA/Cu NPs with H₂O₂ (d) shows a steep increase of current response. There are no obvious current peaks associated with CuNPs or PDA, as can be seen from Fig 3a in the absence of H₂O₂. While in the presence of H₂O₂, a peak current at -0.65 V associated with the reduction of H₂O₂ was observed at the GO/PDA/Cu NPs sensor. The odd shape of the CVs should be attributed to the impedance of the PDA film that produced an ohmic shape when the current was significantly enhanced in the presence of H₂O₂ at the GO/PDA/Cu NPs sensor [32–33]. These results indicate that the GO/PDA/Cu NPs composite exhibits good electrocatalytic performance for the

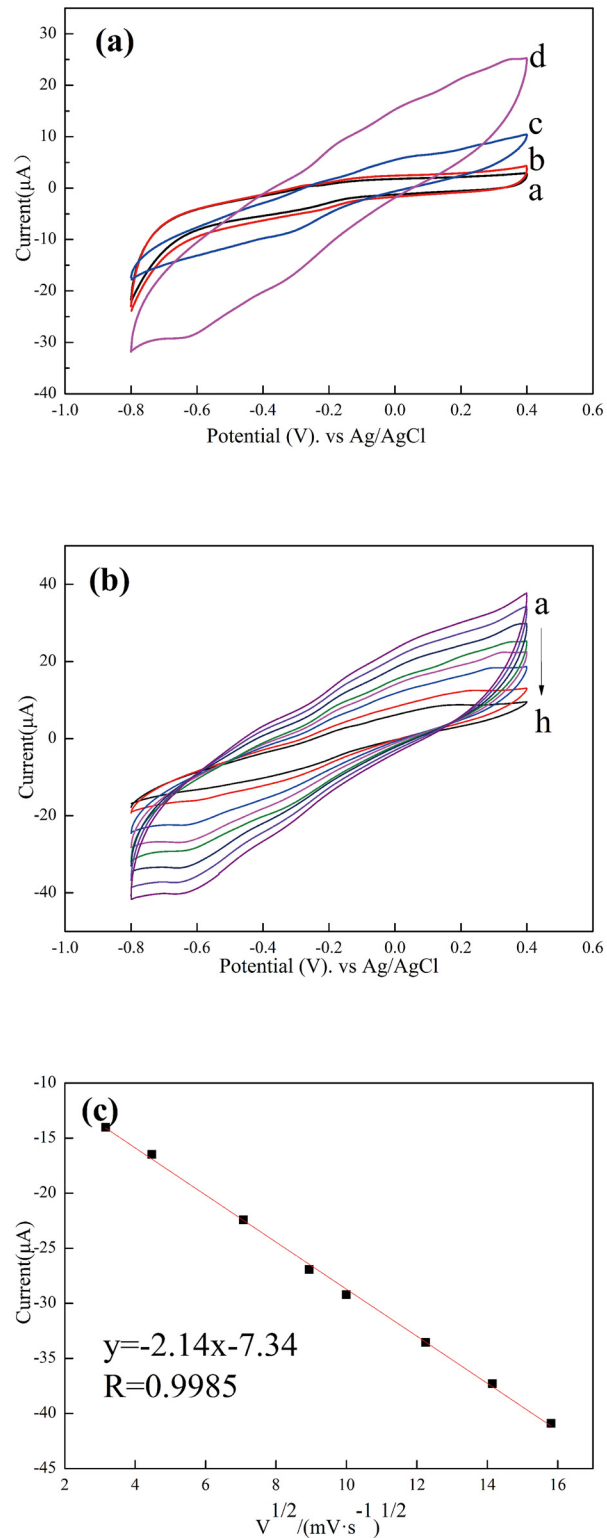


Fig 3. (a) Cyclic voltammograms of GO/PDA sensor (a and b) and GO/PDA/Cu NPs/GCE sensor (c and d) in the absence (a and c) and presence (b and d) of 10 mM H₂O₂ at a scanning rate of 100 mV/s in 0.1 M pH 7.2 PBS. (b) Cyclic voltammograms of the GO/PDA/Cu NP sensor in 0.1 M pH 7.2 PBS containing 10 mM H₂O₂ at different scan rates (V) of 10, 20, 50, 80, 100, 150, 200 and 250 mV/s (from a to h). (c) Plots of the response peak current vs. the square root of the scan rate (V^{1/2}). Results are presented as mean ±SD (error bar) of triplicate experiments.

doi:10.1371/journal.pone.0157926.g003

reduction of H₂O₂. Thus it can be considered as for a promising H₂O₂ sensor. The electrocatalytic detection of H₂O₂ should be attributed to the reduction of H₂O₂ on the GO/PDA/Cu NPs surface. The possible reaction can be summarized as the following equation [14, 34]:

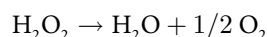


Fig 3b shows the cyclic voltammograms of GO/PDA/Cu NPs sensor in 0.1 M pH 7.2 PBS containing 10 mM H₂O₂ at different scan rates of 10~250 mV/s. As can be seen, the response currents are proportional to the square root of the scan rate with the correlation coefficient of 0.9985 (Fig 3c), indicating that the electrocatalytic reaction on the modified electrode is a diffusion-controlled process instead of a surface-controlled one [35].

Determination of H₂O₂ by the GO/PDA/Cu NP sensor

The pH value and applied potential are essential parameters to electrocatalytic process of GO/PDA/Cu NP sensor. Hence, effects of pH (Fig 4a) and applied potential (Fig 4b) on the response current of 10 mM H₂O₂ at GO/PDA/Cu NP sensor were studied. In Fig 4a, the current response increases when the pH increases from 5.1 to 7.2, and then begins to decrease when the pH is further increasing. It indicates that pH 7.2 is optimal condition for the electrocatalytic reaction, which is close to the pH in the environment of human body fluids. In Fig 4b, it is found that the current response increases with the increase of applied potential in the range of -0.1 V and -0.4 V. It suggests that the current response of the GO/PDA/Cu NP sensor has reached high electrocatalytic activity at the applied potential of -0.4 V. For a higher sensitivity, -0.4 V was chosen as the optimal applied potential for the detection of hydrogen peroxide.

The electrocatalytic responses of the GO/PDA/Cu NP sensor to hydrogen peroxide were further evaluated by amperometric current-time response upon successive addition of H₂O₂ into 0.1 M pH 7.2 PBS with an applied potential -0.4 V under a stirring condition (Fig 5a). By increasing the concentration of H₂O₂, the current response increases gradually as shown in Fig 5b. A linear relationship between hydrogen peroxide concentration (x) and current response (y) is obtained as a function of hydrogen peroxide in the concentration range of 5 μM to 12 mM with the calibration equation of $y = 20.106 + 0.010x$ ($R = 0.998$). The estimated sensitivity for the hydrogen peroxide sensor is $141.54 \mu\text{A}\cdot\text{cm}^{-2}\cdot\text{mM}^{-1}$, and the detection limit is calculated to be 1.4 μM at an S/N = 3 with a response time of 4 s.

Reproducibility, stability and selectivity

In order to investigate the reproducibility of the GO/PDA/Cu NP sensor, amperometric responses for successive injection of 1 mM H₂O₂ into 0.1 M pH 7.2 PBS with continuous stirring at an applied potential of -0.4 V were examined and the results are shown in Fig 6a. The inset of Fig 6a shows the amperometric response for different injections. The relative standard deviation (RSD) is calculated to be 2.5%, indicating good reproducibility of the GO/PDA/Cu NP sensor. Also, the stability of the GO/PDA/Cu NP sensor was evaluated by successive monitoring after storing in desiccator for 10 days, as seen in Fig 6b. It can be seen that only 2.3% of the current signal diminished from the original current response, indicating that the sensor is considerably stable. Thus, the GO/PDA/Cu NP sensor has good reproducibility and stability towards hydrogen peroxide determination.

To evaluate the selectivity of the GO/PDA/Cu NP sensor, UA and AA were employed as interfering species by successive addition of 1 mM H₂O₂, UA, AA and H₂O₂ into 0.1 M pH 7.2 phosphate buffer with an applied potential -0.4 V under a stirring condition (Fig 6c).

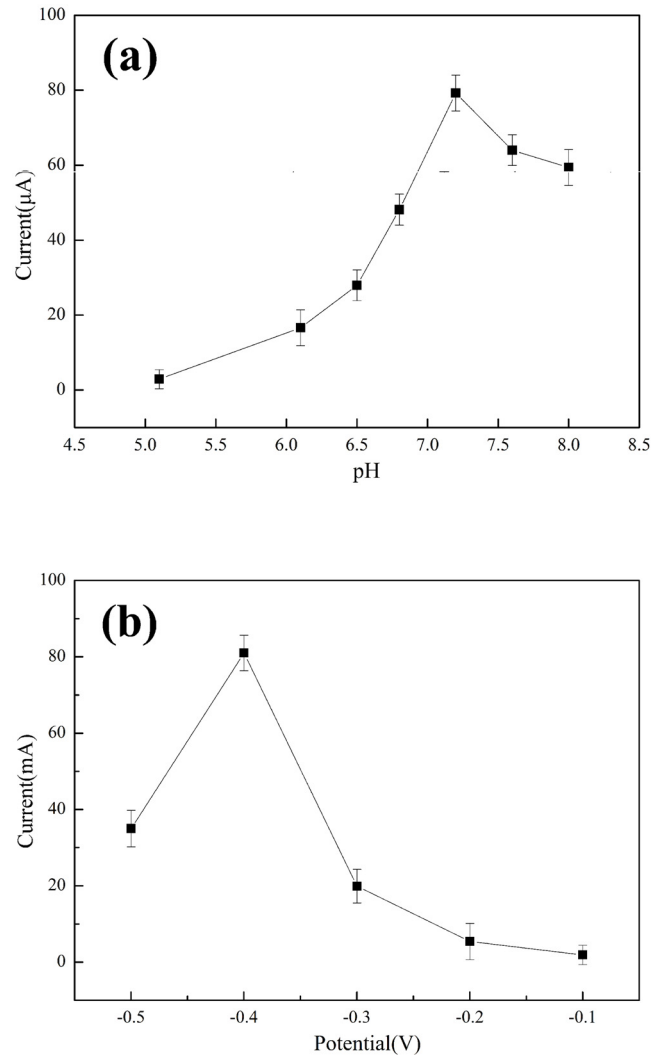


Fig 4. Effects of pH value at an applied potential -0.4 V (vs. Ag/AgCl) (a) and applied potential (b) on the response current of 10 mM H₂O₂ on the GO/PDA/Cu NP sensor. Results are presented as mean \pm SD (error bar) of triplicate experiments.

doi:10.1371/journal.pone.0157926.g004

Compared to the current response of H₂O₂, the current responses of UA and AA were negligible, revealing that these substances don't interfere the detection of hydrogen peroxide.

Real sample analysis

To test the reliability of the GO/PDA/Cu NP sensor as a non-enzymatic electrochemical hydrogen peroxide sensor, amperometric measurement of H₂O₂ in sterlant obtained from a local supermarket was carried out. Before measurement, the sterlant sample was diluted 10000-fold with phosphate buffer. In Fig 7, amperometric responses of the GO/PDA/Cu NP sensor upon the successive addition of 100 µM real sample, 50 µM H₂O₂, 100 µM H₂O₂, 150 µM H₂O₂ and 200 µM H₂O₂ into 0.1 M pH 7.2 PBS with an applied potential -0.4 V under a stirring condition are displayed. Then contact lens solution with 1000-fold dilution and milk sample with 50-fold dilution are also examined. The concentration of H₂O₂ was calculated by standard

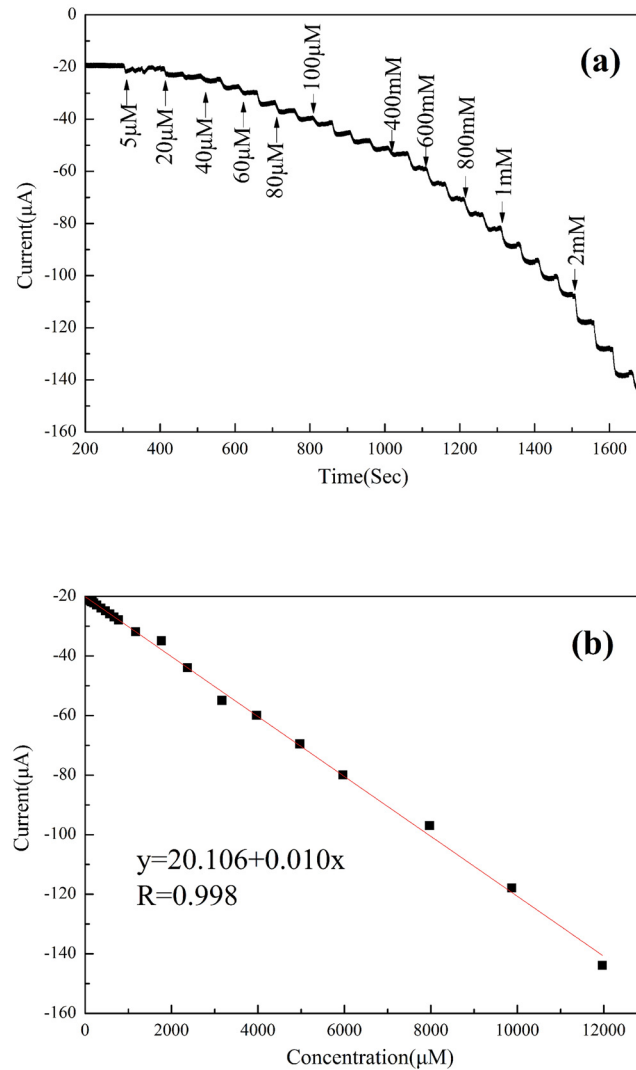


Fig 5. (a) Amperometric responses of the GO/PDA/Cu NP sensor upon successive addition of H₂O₂ into 0.1 M pH 7.2 PBS at an applied potential -0.4 V under a stirring condition. (b) Calibration curve of the GO/PDA/Cu NP sensor versus H₂O₂ concentration. Results are presented as mean ±SD (error bar) of triplicate experiments.

doi:10.1371/journal.pone.0157926.g005

addition method [36] and they are summarized in Table 1. The recovery values for the samples were 95%-99%. According to the obtained results, the GO/PDA/Cu NP sensor exhibits excellent electrocatalytic performance in practical analysis.

Conclusions

We present a versatile approach to fabricate H₂O₂ sensor by immobilization of Cu NPs on the sheets of GO *via in situ* reduction of copper ions on the PDA coating that can provide a tight bonding between the Cu NPs and GO. In this process, the PDA coating acts as a reductant as well as an adhesive agent. The GO/PDA/Cu NPs composite exhibits high sensitivity towards H₂O₂ determination with excellent reproducibility. The sensor also shows good selectivity with minimal interference from the coexisting species such as AA and UA in biological fluids. The

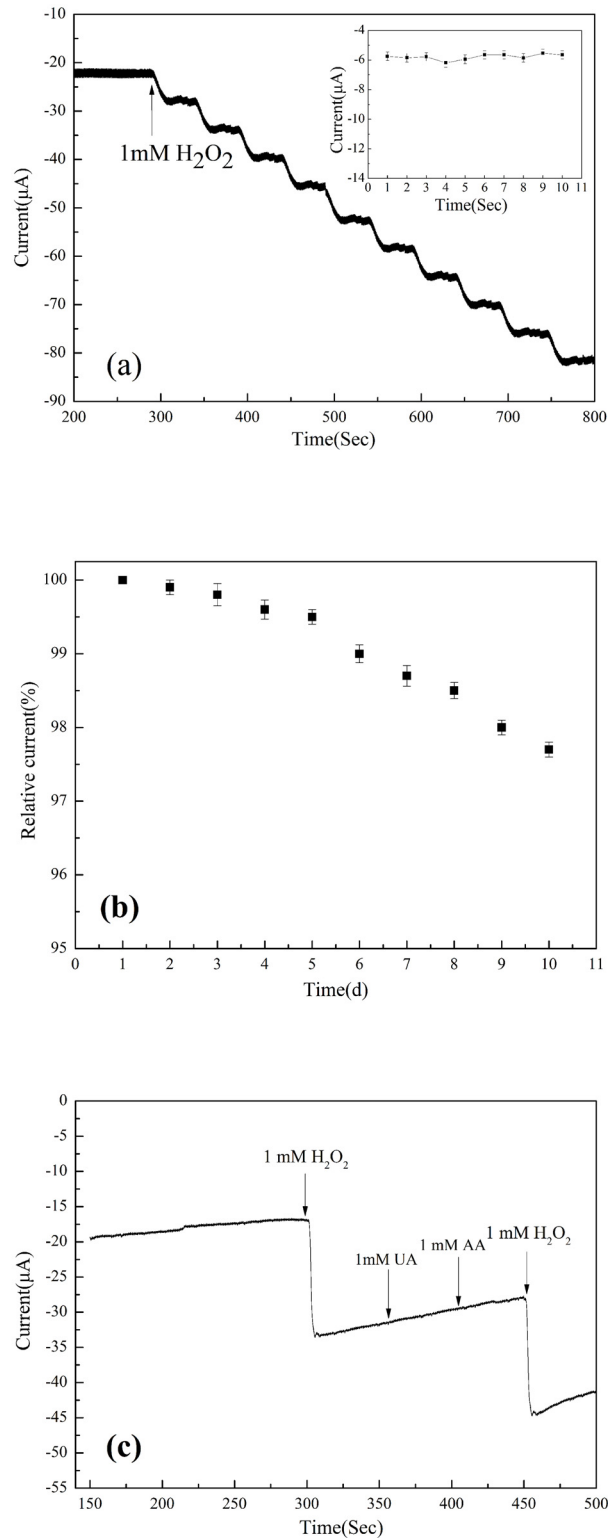


Fig 6. (a) Amperometric responses for successive injection of 1 mM H₂O₂ into 0.1 M pH 7.2 PBS with continuous stirring at an applied potential of -0.4 V with the inset showing the amperometric response for different injections. (b) Long-term stability of the sensor in 10 days. (c) Amperometric responses of the GO/PDA/Cu NP sensor upon the successive addition of 1 mM H₂O₂, UA, AA and H₂O₂ into 0.1 M pH 7.2 PBS at an applied potential -0.4 V under a stirring condition. Results are presented as mean ±SD (error bar) of triplicate experiments.

doi:10.1371/journal.pone.0157926.g006

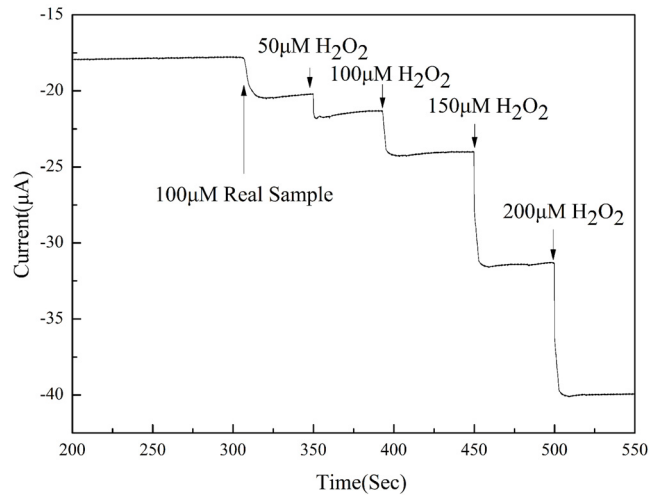


Fig 7. Amperometric responses of the GO/PDA/Cu NP sensor upon successive addition of 100 µM real sample, 50 µM H₂O₂, 100 µM H₂O₂, 150 µM H₂O₂ and 200 µM H₂O₂ into 0.1 M pH 7.2 PBS with an applied potential -0.4 V under a stirring condition.

doi:10.1371/journal.pone.0157926.g007

Table 1. Amperometric determination of H₂O₂ in sterilant (1), contact lens solution (2), and the milk sample (3).

Sample	Value found in real sample (µM)	Added H ₂ O ₂ (µM)	Found H ₂ O ₂ (µM)	Recovery (%)
1	100	-	-	-
-	-	50	49	98
-	-	100	99	99
-	-	150	146	97
-	-	200	198	99
2	150	-	-	-
-	-	50	49.5	99
-	-	100	97	97
-	-	150	147	98
-	-	200	192	96
3	10	-	-	-
-	-	20	19.6	98
-	-	50	48	96
-	-	70	66.5	95
-	-	100	97	97

doi:10.1371/journal.pone.0157926.t001

recovery values estimated from the standard addition method imply the potential applications of the GO/PDA/Cu NP sensor in practical analysis.

Acknowledgments

We acknowledge the help of Miss Zeng Y on material characterization.

Author Contributions

Conceived and designed the experiments: YZL RSC FL. Performed the experiments: YZL YWH. Analyzed the data: YZL RSC FL. Contributed reagents/materials/analysis tools: SML HJZ. Wrote the paper: YZL RSC FL.

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