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An Amperometric Hydrogen Peroxide Sensor Based on Reduced Graphene Oxide/Carbon Nanotubes/Pt NPs Modified Glassy Carbon Electrode

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An enzyme-free hydrogen peroxide (H₂O₂) electrochemical sensor was constructed through building carbon nanotubes (CNTs), reduced graphene oxide (RGO) and platinum nanoparticles (Pt NPs) nanocomposite with a 3D structure modified glassy carbon electrode (GCE). Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) analysis were used to characterize the morphology and element distribution of the modified electrodes RGO/CNTs-Pt/GCE. The electrocatalytic reduction performance of RGO/CNTs-Pt on H₂O₂ was investigated by cyclic voltammetry (CV) and chronoamperometry (i-t). Because of the synergistic effect of enhanced conductivity and catalytic ability of the carbon based nanocomposites (RGO/CNTs) and Pt NPs implanted 3D interfaces, the sensor shows excellent electrocatalytic property on H₂O₂ reduction. Under the optimized conditions, a high sensitivity (347 ± 5 μ A mM⁻¹ cm⁻², *n* = 3) and a linear range (0.0003 – 0.018 mM and 0.01 – 4.0 mM) with a low detection limit (~ 0.31 μ M) operated at the working voltage of -0.2 V (*vs.* Ag/AgCl) are achieved by RGO/CNTs-Pt/GCE. In addition, the sensor is resistant to interference and maintains long-term stability and has been successfully used to detect the spiked H₂O₂ in milk samples, which has important significance for monitoring the abuse of H₂O₂ in milk.

Keywords: Amperometric sensor; 3D structure; Hydrogen peroxide; Electrocatalytic property; Real sample analysis

1. INTRODUCTION

Hydrogen peroxide (H_2O_2) is an excellent oxidant, bleach and disinfectant with the properties of high efficiency of sterilization, low residue, easy decomposition and good bleaching effect, which has prompted many food manufacturers to use hydrogen peroxide in food production and processing. It can be used to kill harmful microorganisms in production equipment, packaging materials and food to improve the preservation period, anti-corrosion and deodorization, and bleach food to increase the aesthetics etc [1, 2]. As one of the world's high-consumption foods, milk is rich in nutrients, and microbes are easily multiplied. If the preservation method is improper or there is no refrigeration facility during storage and transportation, the microorganisms in the milk will multiply and the milk will be damaged [3-5]. Therefore, in order to inhibit the growth of microorganisms in milk and prevent the number of bacteria in the milk from exceeding the standard, some preservatives will be added to the milk. H₂O₂, as a kind of preservative, is colorless, odorless and easy to obtain, and does not affect the smell of milk after a small amount of addition. Therefore, dairy farmers often incorporate H_2O_2 into the milk to prevent corrosion. However, the addition of H_2O_2 (especially the low-cost industrial grade H₂O₂) will directly affect the quality of the finished milk, greatly harming the economic interests of consumers and seriously threatening the health of consumers [6]. In China and many other countries, food grade H₂O₂ is allowed to be used as a processing aid in food production, but it should be removed before it is finished or strictly controlled within the specified range if not completely cleaned. However, due to the many performance advantages of H₂O₂ in the process of use, some manufacturers excessively or illegally add H₂O₂ in the production process and thus the food poisoning incident often occurs. In addition, excessive H_2O_2 can cause diseases related to oxidative stress, such as cancer, cardiovascular disease, and Alzheimer's disease [4, 7, 8]. Therefore, it is very important to detect residual H₂O₂ in foods, especially high-consumption milk, which is important in food safety and human health.

At present, the detection of H_2O_2 is mainly carried out by various techniques such as chemical titration [9], spectrophotometry [10], chemiluminescence [11], high performance liquid chromatography [12], fluorescence spectrometry [13] and electrochemical analysis [2, 14, 15]. Among these methods, the electrochemical method is a rapid and efficient detection strategy with low cost and simple preparation steps. At present, the construction of electrochemical sensors is inseparable from the development of nanomaterials [2, 16-18]. Especially, carbon-based nanomaterials such as graphene, carbon nanotubes, etc. can improve the detection sensitivity of electrochemical sensors. Nanomaterials such as gold, platinum, palladium, and alloys can replace the catalytic properties of certain biological enzymes. Therefore, the selection of suitable nanomaterials for efficient construction is critical to improve the performance of electrochemical sensors.

Carbon-based nanomaterials (fullerene, carbon nanotubes, graphene, etc.) have attracted extensive attention of scientists due to their special physical, chemical and electrical properties. They have displayed good application prospects in the area of biomedicine, biosensor, information science, material chemistry, energy and so on [19]. Graphene is a two-dimensional (2D) carbon nanomaterial with a single atom thickness. In addition to its small size effect, surface effect, self-assembly effect, and surface functionalization that generally exhibits in nanomaterials, it is important that the electron transfer performance is high and the 2D structure is very suitable for covalent or non-covalent bonding with other nanomaterials [15]. On the other hand, its properties such as good electrical conductivity (64 mS/cm), large surface area (2630 m²/g), wide potential window, low charge transfer resistance, fast transfer speed between electrons, and excellent electrochemical activity, provide a broader perspective in the area of biosensing [15, 18]. Similarly, carbon nanotubes (CNTs) are one-dimensional nanomaterials with a special structure. It has the characteristics of high aspect ratio, large

specific surface area, favorable probe molecule loading, and large loading capacity. Its ultra-high conductivity plays a catalytic role in electrochemical sensing detection, thus improving the sensitivity of analysis [20-22]. 2D graphene and one-dimensional carbon nanotubes can form novel three-dimensional carbon nanomaterials. Particularly, sheet-like graphene can be bridged by long and tortuous CNTs to significantly reduce the aggregation of graphene, and the conductivity of both is improved by the synergistic effect of conductivity [23, 24]. For example, Woo et al. [25] have synthesized a graphene–multiwalled carbon nanotube (MWCNT) composite material, which displayed a large electrochemical surface area and fast electron transfer speed in $[Fe(CN)_6]^{3-/4-}$ redox species. The electrode modified with graphene–MWCNT composite exhibits favorable performance on the electrocatalytic reduction of H₂O₂.

In order to further enhance the properties of electrochemical sensors, such as the sensitivity, linear range, stability and selectivity, electrocatalytically active metal nanoparticles, such as Pt [26-28], Au [29, 30], Ag [31-33], Pb [34], are usually added in the production process of the highly conductive substances of carbon-based nanomaterial. Platinum nanoparticles (Pt NPs) have superior electrocatalytic properties and are widely used in the construction of electrochemical sensors. Pt NPs decorated on carbon nanomaterials has been shown to increase electrochemical active surface areas and significantly accelerate the electron transfer between the electrode and the detection molecule, resulting in a fast and sensitive current signal response [35]. Recent years, many strategies have been exploited to construct Pt NPs/carbon nanomaterials related composites, such as photochemical reduction, chemical synthesis, electro-deposition, etc [36, 37]. Mani et al. [38] synthesized an ovel RGO-MWCNT-Pt composite using a wet chemical approach, and then obtained RGO-MWCNT-Pt/Mb composite by adsorbing Mb molecule. The results indicate that the large surface area and favorable affinity of the RGO-MWCNT-Pt composite allowed an aboundant of Mb encapsulated. For the composite materials, Pt nanoparticles not only display excellent electrocatalytic activity, but also effectively prevent the accumulation and stacking of graphene and CNTs. Liu et al. [39] put forward a simple method to realize the adsorption of highly dispersed PtAu nanoparticles on graphene (PtAuNPs-CTAB-GR) using cetyltrimethylammoniumbromide (CTAB). Electrochemical tests proved that the prepared PtAu NPs-CTAB-GR composite has excellent catalytic activity on H₂O₂ reduction. In summary, the combination of carbon-based nanomaterials and Pt nanoparticles to construct a synergistic composite material for the preparation of a H₂O₂ sensor will bring excellent performance.

Considering the synergistic effect of carbon nanomaterial and Pt nanoparticles as well as the increasing requirement for monitoring H_2O_2 , an electrochemical H_2O_2 sensor based on fluffy network 3D structure by electrodepositing Pt nanoparticles on RGO/CNTs modified GCE was constructed and the sensor was used to detect the spiked H_2O_2 in milk with good performance (Scheme 1). To the best of our knowledge, the sensor that integrates Pt nanoparticles and RGO/CNTs nanomaterials has not been reported to date for sensing applications. In addition, we have demonstrated the feasibility of this sensor for rapid detection of H_2O_2 in milk samples.



Scheme 1. Illustration of the preparation process of RGO/CNTs-Pt modified GCE for detecting H₂O₂ to assess the quality of milk.

2. EXPERIMENT PART

2.1. Materials and Instrumentation

 $K_2PtCl_6.6H_2O$ was purchased from Sigma–Aldrich. Hydrogen peroxide (H₂O₂), β -D (+) glucose (Glu), ascorbic acid (AA), fructose (Fru), cysteine (Cys), dopamine (DA), and glutathione (GSH) were bought from Sinopharm Chemical Reagent Co., Ltd. Single-walled carbon nanotube (CNTs) and reduced graphene oxide (rGO) were obtained from XF NANO, INC (China). Phosphate buffer (PB, 0.02 M, pH 7.4) was prepared from NaH₂PO₄ and Na₂HPO₄. All other chemicals were of analytical grade and used as received. Ultrapure water (18.2 M Ω ·cm) was used in all experiments.

All electrochemical measurements were performed on a CHI660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China) using a three-electrode system with a glassy carbon electrode (GCE) as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl electrode as the reference electrode. The JSM-7800F FESEM (JEOL, Japan) was used to obtain the morphological characterization of modified electrode.

2.2. The preparation of RGO/CNTs-Pt/GCE

A 2 mg/mL graphene suspension was prepared by using ultrapure water, and it was mixed for 2 hours under ultrasonic vibration. The same method was used to prepare a 2 mg/mL CNTs suspension. Then, the above two materials were ultrasonically mixed with a 0.1 wt% chitosan solution (1 mg

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chitosan solved in 1 mL 1 % acetic acid solution) at a volume ratio of 1:1:1 so as to obtain the carbon based nanocomposite material (RGO/CNTs). The glassy carbon electrode (GCE, diameter 3 mm) was polished on the suede coated with 0.3 μ m and 0.05 μ m alumina powder before use until the surface was mirror smooth, then washed with ultrapure water for 3 min before nitrogen drying. Immediately, a volume of RGO/CNTs was dropped onto the surface of the electrode. The modified electrode was obtained by drying at room temperature for about 3 hours, and was again wetted with ultrapure water and dried for twice before use to remove the nanomaterial which was not fixed on the surface of the modified electrode. Platinum nanoparticles (Pt NPs) were electrodeposited onto the RGO/CNTs/GCE using cyclic voltammetry (CV) techniques. Electrodeposited Pt NPs were scanned for a certain number of cycles in PB containing 2 mM K₂PtCl₆ and 20 mM KCl with a potential window of -0.4 V to +0.4 V and a scan rate of 50 mV/s. After electrodeposition, the RGO/CNTs-Pt/GCE was washed with a large amount of deionized water to remove the residual electrodeposition solution.

2.3. Electrochemical detection of H₂O₂ using RGO/CNTs-Pt/GCE

The catalytic reduction performance of RGO/CNTs-Pt/GCE on H_2O_2 was investigated by CV and chronoamperometry. CV study was conducted in a 0.02 M PB solution (pH 7.4) at a scan rate of 100 mV/s. The detection experiments of RGO/CNTs-Pt/GCE on H_2O_2 were determined by continuously dropping H_2O_2 into the PB solution (0.02 M, pH 7.4) at a potential of -0.2 V (*vs.* Ag/AgCl). The solution was bubbled with high purity (99.999%) nitrogen for 20 min before being used in the experiments. The electrochemical detection was performed under an inert atmosphere.

2.4. Electrochemical detection of H_2O_2 in milk samples

The detection of H_2O_2 in milk was carried out by i-t curve. First, adding certain volume of milk to PB (0.02 M, pH 7.4) to observe whether the milk contains H_2O_2 . Subsequently, a milk sample containing different concentrations of H_2O_2 was configured using standard dropping methods. The recovery of H_2O_2 in the milk sample was measured through the response current determined by the i-t curve, and combined with the fitted equation to calculate the recovery.

3. RESULTS AND DISCUSSION

3.1. Preparation optimization of RGO/CNTs-Pt

As shown in Fig. 1A, compared with the bare electrode, the current of each modified electrode was significantly increased after modifying RGO/CNTs. When the modification volume was 2.0 μ L, the current reached a maximum, which was 2.4 times larger than that of the bare electrode. Too much or too little modification of RGO/CNTs is not conducive to electron transport, so we determined that the optimal modification volume of RGO/CNTs nanocomposite is 2 μ L. According to the reports [5, 28], the catalytic efficiency is related to the amount of the Pt NPs deposited on the electrode. Therefore,

the deposition CV cycles of Pt NPs was invetigated using i–t curves. As shown in Fig. 1B, the detection sensitivity of the electrode to H_2O_2 was best when deposition CV for Pt NPs electrodeposition is 10 circles.



Figure 1. (A) CV curves of RGO/CNTs/GCE obtained in 1 mM K₃[Fe(CN)₆] solution containing 0.1 M KCl modified with different volume of RGO/CNTs nanocomposite. Inset: Histogram analysis of the increase of the redox current for different RGO/CNTs volume modified GCE. (B) The CV cycles for electrochemical deposition of Pt NPs on the RGO/CNTs/GCE evaluated by amperometric i–t curves in N₂-saturated PB (0.02 M, pH 7.4) at -0.2 V with adding H₂O₂ successively. Inset: Histogram analysis of the sensitivity of RGO/CNTs-Pt/GCE with different CV cycles of electrochemical deposition of Pt NPs. Error bars are the standard error of the mean (n = 3 electrodes).

According to our previous work, low dosage and severe aggregation happened under 3 and 15 CV scan circles respectively [5], which cause the reduction of the catalytic performance of RGO/CNTs-Pt/GCE on H₂O₂. Therefore, the volume of RGO/CNTs nanocomposites modified on GCE is 2.0 μ L and the CV scan times for Pt NPs electrodeposition are 10 circles in the next experiments.

3.2. Characterization of RGO/CNTs-Pt/GCE

Fig. 2A is a SEM of RGO/CNTs/GCE, in which we see that RGO exhibits a distinct twodimensional structure with a thin creped pattern. Single-walled CNTs and RGO combined with each other and alternately overlapped to form a 3D structure. Fig. 2B is a SEM characterization of RGO/CNTs-Pt/GCE. We can clearly see that the surface of RGO/CNTs electrodeposited Pt nanoparticles becomes rough, and the CNTs exhibit a floc distribution on the graphene. The surface and the gap can be seen to present a fluffy network structure with Pt nanoparticle embellishments. Further, EDS characterization indicates that the main element of RGO/CNTs/GCE is carbon, while the surface of RGO/CNTs-Pt/GCE has Pt in addition to carbon, indicating that Pt nanoparticles are successfully electrodeposited onto RGO/CNTs/GCE (Fig. 2C and D).



Figure 2. (A, B) FESEM images and EDS (C, D) of nanocomposites RGO/CNTs/GCE (A, C) and RGO/CNTs-Pt/GCE (B, D). The electrode was modified with 2.0 μL RGO/CNTs nanocomposites and 10 CV scan circles for Pt NPs electrodeposition.



Figure 3. EDS layered image of RGO/CNTs-Pt/GCE (A) and element mapping images of C (B), Pt(C), Cl(D) on RGO/CNTs-Pt/GCE.

The element mapping images of RGO/CNTs-Pt/GCE as shown in Fig. 3, the C and Pt elements are uniformly distributed on the modified electrode. Under a large field of view, RGO/CNTs-Pt is really evenly distributed on the surface of the electrode (Fig. S1). Therefore, and the single-walled carbon nanotubes and graphene are overlapped with each other, and the Pt nanoparticles are dotted thereon to form a unique three-dimensional structure. The characterizations indicated that RGO/CNTs-Pt is uniformly modified on the surface of the electrode with CNTs and RGO overlapped with each other and the Pt nanoparticles dotted thereon to form a unique fluffy 3D network structure.

3.3. Electrochemical performance of RGO/CNTs-Pt/GCE



Figure 4. (A) CV study of bare GCE, RGO/CNTs and RGO/CNTs-Pt nanocomposites modified GCE in potassium ferricyanide solution containing 0.1 M KCl and 1 mM K₃[Fe(CN)₆] at scan rate of 100 mV/s. (B) CV curves of RGO/CNTs-Pt/GCE in the absence and presence of H₂O₂ in 0.02 M PB, pH 7.4 at scan rate of 100 mV/s, where H₂O₂ concentrations are 0, 0.5, 1.5, 3.5, 5.5, and 7.5 mM, respectively.

As shown in Fig. 4A, the responses of the CV curve of the GCE modified with different materials in 1 mM K₃[Fe(CN)₆] solution all display a pair of clear redox peaks, indicating a reversible electron transfer process. The surface area of relevant electrodes is calculated according to the Randled-Sevcik equation [33] (The details of the equation are described in the Supporting information). Base on the equation, the electroactive surface areas of RGO/CNTs-Pt/GCE (0.4704 cm²), and RGO/CNTs/GCE (0.1612 cm²) are 5.92 and 2.03 times higher than that of bare GCE (0.0794 cm²), respectively. It shows that the surface area of the composite material is significantly improved after the combination of single-wall carbon nanotubes, graphene and Pt nanoparticles which can be attributed to the favorable electrical conductivity of the RGO/CNTs and the fluffy 3D network structure of the RGO/CNTs-Pt. Fig. 4B shows the CV curve of the RGO/CNTs-Pt/GCE sensor before and after the addition of H₂O₂ in deoxygenated PB (0.02 M, pH 7.4). With the increase of H₂O₂ concentration, the reduction current close to -0.2 V gradually increased, which indicates that RGO/CNTs-Pt/GCE has a reduction ability to H₂O₂ in the range of 0 to 7.5 mM.



Figure 5. (A) Amperometric response of RGO/CNTs-Pt/GCE, RGO/CNTs/GCE and Pt NPs/GCE in N₂-saturated 0.02 M PB (pH 7.4) at -0.2 V with successive addition of H₂O₂ 38.6 μ M, 77.3 μ M and 108.3 μ M. (B) The calibration plot of response current *vs.* H₂O₂ concentration for RGO/CNTs-Pt/GCE, RGO/CNTs/GCE and Pt NPs/GCE. Error bars are the standard error of the mean (*n* = 3 electrodes).

We investigated the electrochemical properties of RGO/CNTs-Pt/GCE, RGO/CNTs/GCE, and Pt/GCE. The same concentration of H₂O₂ was added dropwise to deoxygenated PB (0.02 M, pH 7.4), and the i-t curves were measured. It can be seen from Fig. 5A that the three electrodes RGO/CNTs-Pt/GCE, RGO/CNTs/GCE and Pt/GCE all have a current response when the same concentration of H₂O₂ is added, while the RGO/CNTs-Pt modified electrode is best. Fig. 5B shows that the detection sensitivities of RGO/CNTs-Pt/GCE and Pt/GCE to H₂O₂ are $347 \pm 5 \mu \text{A mM}^{-1} \text{ cm}^{-2}$ (*n* = 3), and $165 \pm$ 6 μ A mM⁻¹ cm⁻² (n = 3) respectively. The RGO/CNTs-Pt is much more sensitive to H₂O₂ than the two electrodes modified by RGO/CNTs and Pt alone. In fact, the excellent electrocatalytic activity of the RGO/CNTs-Pt modified electrode can be attributed to the good synergistic effect between the Pt nanoparticles and the RGO/CNTs nanomaterials. RGO/CNTs not only have excellent electrical conductivity, but also have good dispersion function for Pt nanoparticles. On the other hand, Pt nanoparticles dispersed on RGO/CNTs have better catalytic activity than Pt nanoparticles alone. It can be seen that the RGO/CNTs-Pt sensor prepared in this experiment has good catalytic performance on H₂O₂. There are two segments in the relevant linear range of RGO/CNTs-Pt/GCE for H₂O₂ detection: 0.0003 - 0.018 mM (correlation co-efficient $R^2 = 0.995$) and 0.01 - 4.0 mM ($R^2 = 0.995$) with the detection limit of ~ 0.31 μ M (S/N = 3) (Fig. 6). Table 1 shows the comparisons of our RGO/CNTs-Pt/GCE with reported H₂O₂ sensors in detection sensitivity, detection limit and linear range. The results show that our RGO/CNTs-Pt/GCE has similar or even better analytical parameters than the reported H₂O₂ sensors, indicating that RGO/CNTs-Pt has a great potential in the field of H₂O₂ sensors.



Figure 6. (A) Amperometric response of RGO/CNTs-Pt/GCE in N₂-saturated 0.02 M PB, pH 7.4 at -0.2 V with successive addition of 9.375, 18.75, 37.5, 56.25, 75, 112.5, 150 and 240 μM H₂O₂ (adding at the points indicated by arrows). Inset: the current response of RGO/CNTs-Pt/GCE to H₂O₂ with successive addition of H₂O₂ 0.312, 0.937, and 2.812 μM. (B) The calibration line of the response current *vs*. H₂O₂ concentration ranging from 0.01 to 4.0 mM. Inset: Calibration line of the response current *vs*. H₂O₂ concentration ranging from 0.31 to 17.8 μM.

Sensors	Sensitivity	LOD	Linear range	References
	$(\mu A m M^{-1} cm^{-2})$	(µM)	(mM)	
graphene-MWCNT	32.91	9.4	0.02-2.1	[25]
Graphite-CS/PtNPs	465	0.066	0.00025-2.89	[26]
Pt/rGO-CNT paper	1410	0.01	0.0001-0.025	[27]
RGO-Pt	459	0.2	0.5-3.475	[28]
AuNBP/MWCNTs	170.6	1.5	0.005-47.3	[30]
AgNP-MWCNT-rGO	11790.5	0.9	0.1-100	[31]
RGO/Pt-AgNPs	699.6	0.04	0.005-1.5	[33]
Au-Pd/graphene	186.86	1.0	0.005-11.5	[34]
Pt-MWCNT	75.2	0.2	1-15	[40]
Pt nanoclusters/CNT	987.5	0.8	0.003-0.4	[41]
HRP/GO	118.9	1.6	0.002-0.5	[42]
SnS ₂ /MWCNTs	87.84	1.04	0.248 - 16.423	[43]
RGO/CNTs-Pt	347	0.31	0.0004-0.018	This work
			0.01-4.0	

Table 1. Comparison of the analytical performance of various electrodes for H₂O₂ detection

3.5. Selectivity, reproducibility, and stability of RGO/CNTs-Pt/GCE

In actual sample detection, there is inevitable interference, so the sensor is required to have anti-interference performance. As shown in Fig. 7, the prepared RGO/CNTs-Pt/GCE was tested for its response to H_2O_2 in the presence of interfering species. The amperometric current responses were measured by continuously adding 0.5 mM H₂O₂, DA, Cys, GSH, Fru, Glu, AA to PB (0.02 M, pH 7.4). It is found that the selected interference has no obvious current response and the interference is small. Within the allowable range of experimental error, we believe that the RGO/CNTs-Pt/GCE sensor has

good selectivity to H_2O_2 and strong anti-interference performance. Furthermore, reproducibility and long-term stability are also important parameters for H_2O_2 sensors, which are evaluated by using an amperometric method. Three independent RGO/CNTs-Pt/GCEs gave a relative standard deviation (RSD) of 3.68%, indicating that the sensor has a good reproducibility (Fig. S3). The as-prepared RGO/CNTs-Pt/GCE still showed a sensitivity response of ca. 98% to H_2O_2 after being stored at room temperature for 8 days, indicating that the sensor has a good long-term stability.



Figure 7. Amperometric response of RGO/CNTs-Pt/GCE upon addition of 0.5 mM H₂O₂, DA, Cys, GSH, Fru, Glu, AA and a second addition of 0.5 mM H₂O₂ in N₂-saturated 0.02 M PB, pH 7.4.

3.6. Real sample detection

It is well known that in order to prevent milk from deteriorating, a small amount of H₂O₂ is added, but too much H₂O₂ may cause harm to human health. In order to investigate the practicality of the prepared H_2O_2 sensor, we used the sensor to determine whether H_2O_2 exceeds the standard in milk. Milk samples were bought from a local supermarket. Before analysis, the milk sample not spiked with H_2O_2 was detected to determine whether there is endogenous H_2O_2 . As shown in Fig. 8, the amperage current response did not change with the addition of milk, indicating that there is no residual H₂O₂ in the milk. Since the protein molecules contained in the milk interfere with the detection of the sensor, we have carefully corrected the linear range of the sensor in the milk sample. As shown in Fig. S4A, the i-t curves were obtained by gradually adding milk samples containing different concentrations of H₂O₂ into the N₂-saturated PB (0.02 M, pH 7.4). We can see that the RGO/CNTs-Pt/GCE had a good response to milk samples. As shown in Fig. S4B, amperometric calibration plots indicate a good correlation with three segments: 0.0063 - 0.031 mM (correlation co-efficient $R^2 = 0.997$), 0.075 - 2.13mM ($R^2 = 0.967$) and 2.58 – 20.46 mM ($R^2 = 0.971$). According to the corrected fitting equation, the recovery rate was calculated to be 96.1-109.5% for the spiked milk samples as shown in Table 2. The results show that the sensor is a practically useful tool for the detection of H₂O₂ doping in milk, especially in countries where H₂O₂ is prohibited to be a bactericide in milk.



Figure 8. Amperometric response of RGO/CNTs-Pt/GCE after continuous addition of commercially packaged aseptic milk at -0.2 V

Table 2. The recovery of H_2O_2 from commercial milk samples using the H_2O_2 sensor

Milk sample ^a	Concentration of $H_2O_2(\mu M)$			
	Original	Amount added	Amount detected ^b	Recovery (%)
1	ND ^c	32	31.6±0.8	98.7±2.5
2	ND^{c}	256	280.42 ± 5.6	109.5±2.2
3	ND^{c}	456	443.08 ± 3.4	97.2±0.7
4	ND ^c	1218	1170.12±12.3	96.1±1.0

^a Samples 1-4 were milk samples spiked with four different concentrations of H_2O_2 : 32, 256, 456, and 1218 μ M, respectively.

^b The results are the average values of three parallel assays.

^c ND: none detected.

4. CONCLUSIONS

An electrochemical H_2O_2 sensor was illustrated based on the synergistic effect of RGO/CNTs and Pt NPs to form a fluffy 3D network structure. The RGO/CNTs-Pt modified sensor showed high sensitivity and selectivity for H_2O_2 detection with a relevant detection limit of ~ 0.31 µM, a broad linear range of 0.0003 – 0.018 and 0.01 – 4.0 mM, and a high sensitivity of $347 \pm 5 \mu A mM^{-1} cm^{-2}$. In addition, the sensor has excellent immunity to interference and has been successfully used to detect H_2O_2 residues in milk samples with good reproducibility and long-term stability. Therefore, the sensor as an effective and reliable tool will have a broad applicable prospect in the field of H_2O_2 monitoring and sensing under complicated environmental conditions.

SUPPORTING INFORMATION



Figure S1. FESEM images of RGO/CNTs-Pt/GCE with magnification 200 times

The calculation of surface area of modified electrodes:

The surface area of relevant electrodes was calculated according to the Randled-Sevcik equation [1]:

 $I_p = 2.69 \times 10^5 AD^{1/2} n^{3/2} \gamma^{1/2} C$

where A is the electroactive surface area (cm²), here D is $(6.70 \pm 0.02) \times 10^{-6}$ cm² s⁻¹, representing the diffusion coefficient of K₃[Fe(CN)₆] in solution, n denotes the number of electrons involved in the redox reaction (for [Fe(CN)₆]^{3-/4-}, n = 1), γ is the scan rate(V s⁻¹), and C is the concentration of the redox probe (mol cm⁻³).



Figure S2. The reproducibility of RGO/CNTs-Pt/GCE stored in room temperature





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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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