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A hydrogen peroxide sensor based on Ag nanoparticles electrodeposited on natural nano-structure attapulgite modified glassy carbon electrode

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ABSTRACT

A novel strategy to fabricate hydrogen peroxide (H_2O_2) sensor was developed by electrodepositing Ag nanoparticles (NPs) on a glassy carbon electrode modified with natural nano-structure attapulgite (ATP). The result of electrochemical experiments showed that such constructed sensor had a favorable catalytic ability to reduce H_2O_2. The good catalytic activity of the sensor was ascribed to the ATP that facilitated the formation and homogenous distribution of small Ag NPs. The resulted sensor achieved 95% of the steady-state current within 2 s and had a 2.4 μM detection limit of H_2O_2.

1. Introduction

Detection of hydrogen peroxide (H_2O_2) has become extremely important in recent years because of its wide and varied applications. These include uses in the textile, paper, cleaning product, and food industries [1,2]. Therefore, many techniques including titrimetry, spectrometry and chemiluminescence [3,4] have been employed in the determination of H_2O_2.

Electrochemical technique which is also a fine detecting method has attracted much attention recently based on low cost and high sensitivity. It has been proved to be an inexpensive and effective way to examine substances. Some inorganic materials modified electrode in determination of H_2O_2 is attracting more and more attention owing to its stability and convenience of electron transfer. The materials include nickel hexacyanoferrate [5] and perovskite-type oxide (such as $La_{0.6}Ca_{0.4}Ni_{0.7}Fe_{0.3}O_3$ and $La_{0.6}Ca_{0.4}MnO_3$) [6], some inorganic–organic composite materials [7], some inorganic-incorporated biology complex membranes [8,9]. Meanwhile, nanoparticles (NPs) can play an important role in improving sensor performance, due to their large specific surface areas, excellent conductivities and biocompatibilities. As nanotechnology becomes increasingly prevalent, more people are beginning to pay attention to NPs, especially metal NPs. The metal NPs used to construct H_2O_2 sensor include Au NPs [10], Pt NPs [11–14], and Ag NPs [15–17]. Recent studies [15–17] have showed that Ag NPs exhibited catalytic activity for H_2O_2. The shape and the distribution of Ag NPs played a vital role in the catalytic ability for H_2O_2, and the matrix for the preparation of Ag NPs is also very important.

Attapulgite (ATP) as a natural nano-structure material can be used as a matrix [18,19], which is a crystalline hydrated magnesium aluminum silicate with formula $Si_8O_{20}(Mg, Al, Fe)_5(OH)_2(OH_2)_4 \cdot 4H_2O$ [20]. The distinguishing feature of its structure is that the Si–O tetrahedra form long strips, each an amphibole unit wide, on alternate sides of the oxygen sheet in a manner which confers a regular corrugated Si–O structure [21]. The structure of the mineral results in zeolite-like channels, which are approximately 3.7 Å × 6.0 Å and 5.6 Å × 11.0 Å wide, respectively [22]. ATP has advantages of specific features in dispersion, high temperature endurance, salt and alkali resistance, high adsorption and penetrability due to its regular structure and large specific surface area. Because of those unique properties and stable structures, ATP was selected in this work as a matrix for the preparation of Ag NPs, which could supply a stable matrix for the formation of Ag NPs and facilitate the homogenous distribution of small Ag NPs with high activity. In this paper, ATP was used for the first time for electrochemical preparation of the Ag–ATP hybrid NPs for sensing purpose. This work presented a new simple and direct method for preparation of Ag NPs-attached functional surface by electrodeposition of Ag cations on an ATP modified glassy carbon (GC) electrode to fabricate a H_2O_2 sensor. Thus formed Ag NPs/ATP electrode

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showed excellent electrocatalytic activity to reduction of H_2O_2 at relatively low overpotentials. In comparison with other Ag NPs modified electrodes, this Ag NPs/ATP modified electrode has some advantages: (I) ATP, as a matrix of electrochemical sensor, is inexpensive and easy to obtain and does not need further treatment because ATP has natural nano-structure and some unique properties as mentioned above which make ATP suitable to be a fine matrix; (II) the preparation of Ag NPs is simple and quick, and the formed Ag NPs are roughly spherical in shape and could be uniformly distributed all over the substrate. Therefore, this Ag NPs/ATP modified electrode shows low expense of fabrication and operation simplicity, and meanwhile is easy to achieve fine catalytic effect, fine stability and reproducibility.

2. Experimental

2.1. Reagents

ATP was obtained from Jiangsu Junda AT Material Co., Ltd. (Jiangsu, China). Other chemicals were purchased from Beijing Chemical Reagent (Beijing, China). The solution of hydrogen peroxide was prepared daily by dilution from a stock solution obtained from Aldrich (30%, w/w in water, 99% purity) to avoid excessive decomposition of the hydrogen peroxide to water and oxygen. Phosphate buffer solutions (PBS) were prepared by mixing stock standard solutions of Na_2HPO_4 and NaH_2PO_4. Pure water obtained by Milli-Q water purification set was used throughout.

2.2. Preparation of the H_2O_2 sensor

A GC electrode (3 mm in diameter) was polished to a mirror-like with fine emery papers and 1.0, 0.3 and 0.05 μm alumina slurry followed by rinsing thoroughly with Milli-Q water, then 10 μL purified ATP suspension [23] was directly dropped onto the GC electrode and dried at room temperature for 4 h to obtain ATP/GC electrode. And then the electrode was immersed in 0.1 M KNO_3 solution containing 3.0 mM $AgNO_3$ and electrodeposited to obtain Ag NPs/ATP modified electrode.

2.3. Measurements and apparatus

All electrochemical experiments were performed by a CHI 660 (USA) electrochemical workstation with a conventional three-electrode system. A GC electrode was used as working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as the reference and the auxiliary electrodes, respectively. Electrolyte solutions were purged with high purity nitrogen prior to experiments and blanketed with nitrogen during electrochemical experiments. During the amperometric experiments, a magnetic stirring bar was used.

Atomic force microscopy (AFM) measurements were performed on the ITO with ATP and Ag NPs/ATP separately with a SPI3800N microscope (Seiko Instruments, Japan) in tapping mode. Standard cantilevers NSG-11 (Veeco, USA, B:k = 5.5 N m^{-1}) were used under its resonance frequency (typically, 150 kHz). All experiments were carried out at the room temperature.

3. Results and discussion

3.1. Electrodeposition of Ag NPs

Cyclic voltammetry (CV) was utilized to monitor the redox behaviors of Ag^+ at bare and ATP modified GC electrode. As shown in Fig. 1a, in the solution containing 3.0 mM $AgNO_3$ and 0.1 M KNO_3, a bare GC electrode showed a cathodic peak at 0.295 V and a sharp anodic peak at 0.497 V. The cathodic peak was ascribed to the reduction of Ag^+ to form Ag NPs and the anodic peak was attributed to the stripping of the electrodeposited Ag NPs [24]. However, when the ATP modified electrode was scanned in the same solution, the redox peak currents were depressed and the peak potentials shifted in negative direction (Fig. 1b). The decrease of the redox peak current might result from the blocking effect of the ATP on the electron transfer. According to the above redox behaviors, the GC electrode was electrodeposited in the solution containing 3.0 mM $AgNO_3$ and 0.1 M KNO_3 for 75 s at −0.2 V to obtain Ag NPs modified electrode.

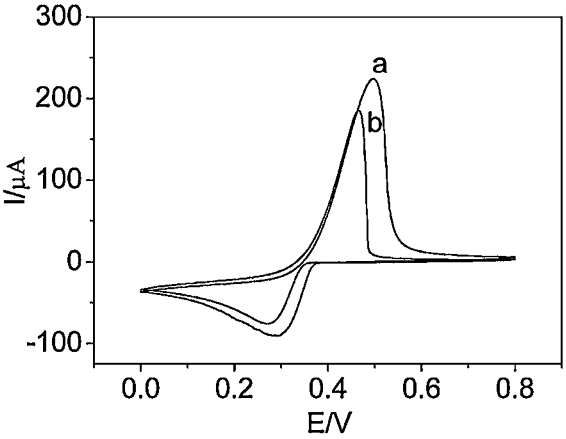


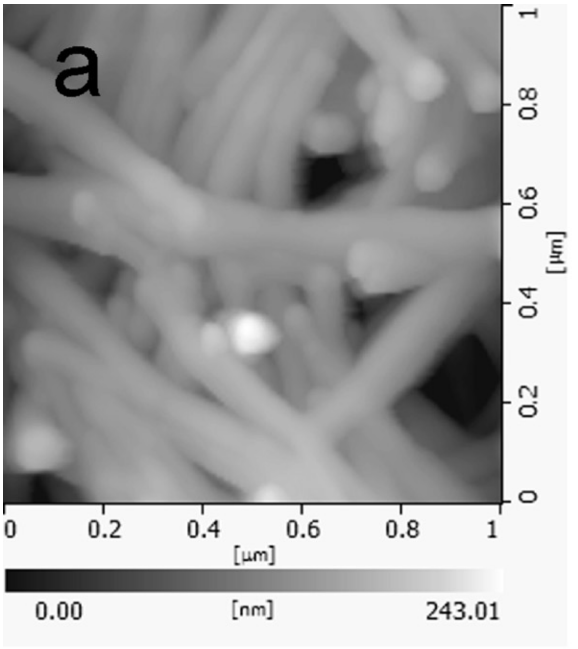
Fig. 1. Cyclic voltammograms of (a) GC and (b) ATP/GC electrode in the solution containing 3.0 mM $AgNO_3$ and 0.1 M KNO_3. Scan rate: 100 mV s^{-1}.

3.2. AFM characterization of the immobilization of Ag NPs on ATP

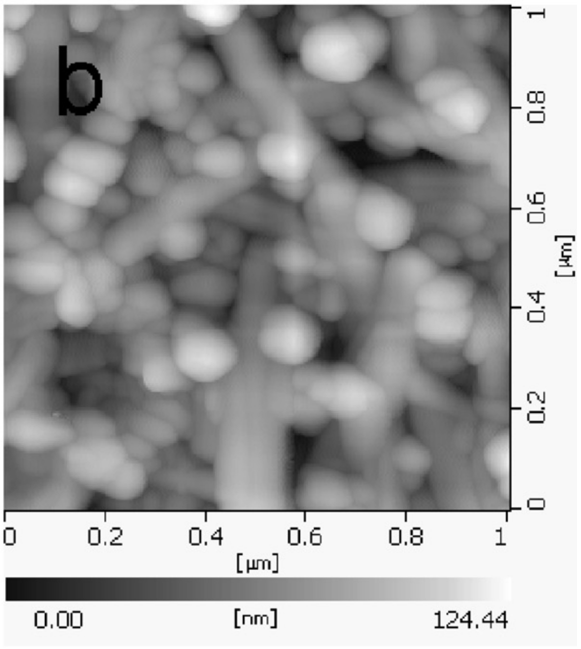
Morphological characterization was conducted by AFM on ATP and Ag NPs/ATP. Fig. 2a showed that ATP immobilized on the ITO substrate emerged as rods or fibers and dispersed very well in water with an average diameter of about 50 nm, which provided a three-dimensional medium and formed net-like structure to facilitate the homogenous distribution of Ag NPs (Fig. 2b). The particles are roughly spherical in shape and uniformly distributed all over the substrate, which implied Ag NPs were quite easy to be assembled on the ATP. We speculate that the structure of the mineral results in zeolite-like channels and the gaps of ATP could supply a template for Ag NPs.

3.3. Amperometric response to H_2O_2

Cyclic voltammograms for the ATP/GC electrode and the bare GC electrode were shown in Fig. 3b and c in the presence of 1.0 mM H_2O_2, respectively. It can be seen that the electrochemical responses of those two electrodes are almost same, which indicates the ATP/GC electrode has no catalytic activity to H_2O_2. Fig. 3a and e exhibited the electrochemical behaviors of the Ag NPs/ATP/GC electrode without and with 1.0 mM H_2O_2. Drastic enhancement in the reduction current at about −0.42 V shows the electrode can efficiently catalyze H_2O_2. In comparison with the direct reduction of H_2O_2 at Ag NPs/GC electrode (Fig. 3d), the cathodic overpotential is reduced by about 80 mV and the catalytic current is enhanced. The increase of current and decrease of potential are both considered as the enhancement of electrocatalysis [25]. These results showed that the Ag NPs/ATP/GC electrode possessed the relatively remarkable catalytic ability to H_2O_2 reduction, and the catalytic current mainly resulted from the Ag NPs on the electrocatalytic reduction of H_2O_2.



ATP/ITO



Ag-ATP/ITO

Fig. 2. AFM images of (a) ATP/ITO and (b) Ag NPs/ATP/ITO.

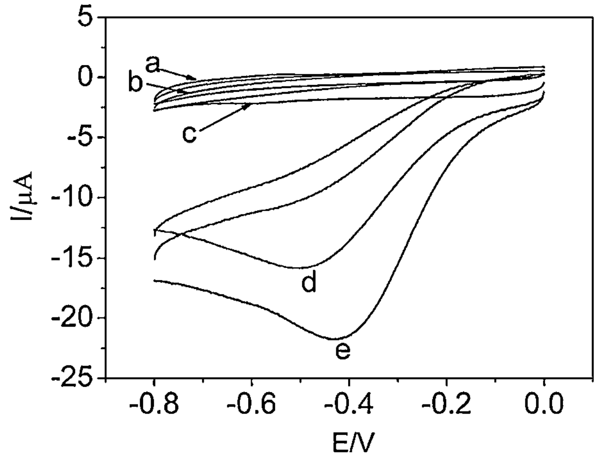


Fig. 3. Cyclic voltammograms of different electrodes in 0.1 M phosphate buffer (pH 7.0) containing 1.0 mM H_2O_2: (b) ATP/GC electrode; (c) bare GC electrode; (d) Ag NPs/GC electrode and (e) Ag NPs/ATP/GC electrode. (a) Cyclic voltammogram of Ag NPs/ATP/GC electrode in 0.1 M phosphate buffer (pH 7.0) without H_2O_2. Scan rate: 100 mV s^{-1}.

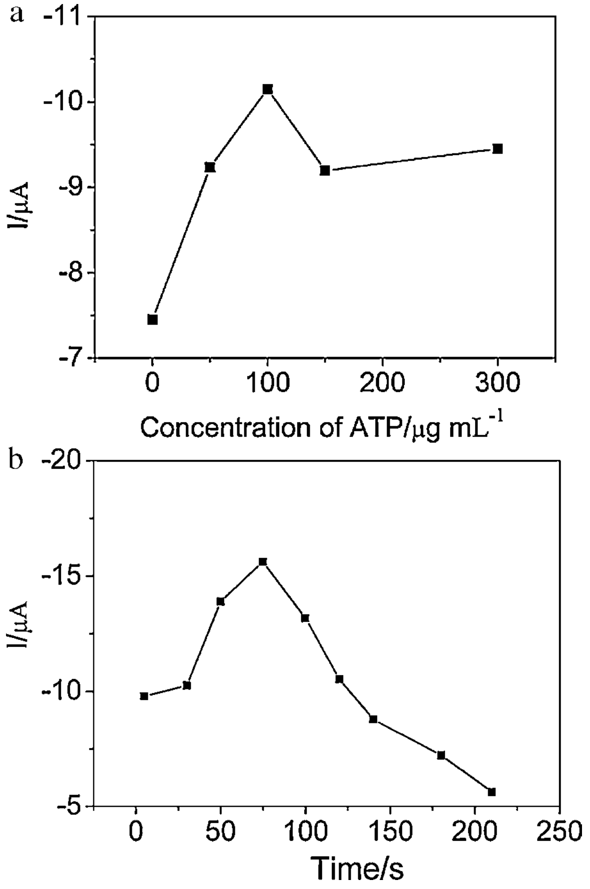


Fig. 4. Effects of (a) ATP concentration and (b) Ag NPs electrodeposition time on the amperometric responses in the presence of 1.0 mM H_2O_2 in 0.1 M phosphate buffer (pH 7.0).

3.4. Optimization of experimental variables

The effect of ATP concentration on the response of the modified electrode was investigated. 10 µL ATP suspension of different concentrations was dropped onto the GC electrode and dried at room temperature to obtain different ATP/GC electrodes. These ATP/GC electrodes were immersed in 0.1 M KNO_3 solutions containing 3.0 mM $AgNO_3$ and electrodeposited for the same time to obtain Ag NPs/ATP modified electrodes. The effect of ATP concentration on the electrocatalytic reduction of H_2O_2 was illustrated in Fig. 4a, the current response of the sensor reaches the maximum value when the concentration of ATP is 100 µg mL^{-1}. Therefore, we used 100 µg mL^{-1} ATP to construct the sensor throughout this work.

The influence of Ag NPs electrodeposition time on the response of the sensor was also investigated. 10 µL ATP suspension of same concentration was dropped onto the GC electrode to obtain ATP/GC electrodes, then these ATP/GC electrodes were immersed in 0.1 M KNO_3 solutions containing 3.0 mM $AgNO_3$ and electrodeposited for

Table 1
Comparison of the performances of various hydrogen peroxide sensors.

Electrode	Linear range (μM)	Detection limit (μM)	Response time (s)	Reference
Hb/SA[a]-MWCNTs[b]/GC	40–200	16.41	10	[26]
Ti(III)-TNTs[c]/Hb	4.9–1100	1.5	<5	[27]
(PSS[d]/HRP)$_5$/ZnO/Au	5–1700	2.1	<5	[28]
(PDDA[e]/Fe_3O_4)$_5$/ITO[f]	4.18–800	1.4	3.5	[29]
HRP-Nafion-SPE[g]	5.98–35.36	0.48	–	[30]
ZnO/Au/Nafion/HRP/GC	15–1100	9	5	[31]
Cu_2S/OMCs[h]/Nafion/GC	1–3030	0.2	3.6	[32]
Ag NPs/ATP/GC	10–21,530	2.4	<2	This work

[a] Sodium alginate.
[b] Multiwall carbon nanotubes.
[c] TiO_2 nanotubes in situ self-doped with Ti(III).
[d] Poly(sodium 4-styrenesulfonate).
[e] Poly(diallyldimethylammonium chloride).
[f] Tin-doped indium oxide.
[g] Screen-printed electrode.
[h] Ordered mesoporous carbons.

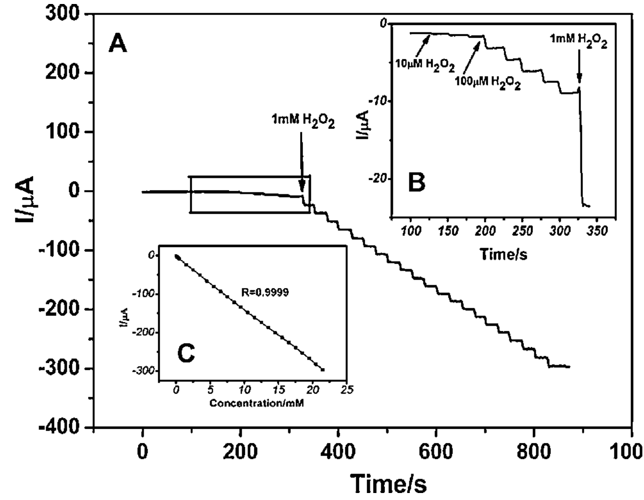


Fig. 5. (a) Typical steady-state response of the sensor to successive addition of H_2O_2. (b) Amplification of the marked rectangle region in (a). (c) Calibration curve of the sensor. Applied potential: −0.3 V and supporting electrolyte: 0.1 M phosphate buffer (pH 7.0).

different times to obtain Ag NPs/ATP modified electrodes. The influence of Ag NPs electrodeposition time on the reduction of H_2O_2 was shown in Fig. 4b, the amperometric response increased with increasing electrodeposition time and reached the maximum value at 75 s. Then the current response decreased gradually with further increased deposition time. This might be due to the fact that Ag NPs would become rather bigger with the excessive electrodeposition time, which might decrease its electrocatalytic sites on the Ag NPs [15]. So we selected 75 s as the optimum electrodeposition time to construct the sensor.

3.5. *Chronoamperometric response and calibration curve*

The typical current–time curve of the sensor was shown in Fig. 5. The reduction current rose sharply and achieved 95% of the steady-state current within 2 s. The sensor displayed a linear range from 10.0 μM to 21.53 mM (r = 0.9999; n = 10), and the detection limit was estimated to be 2.4 μM based on the criterion of signal-to-noise ratio of 3. The reproducibility of the current signal (evaluated from the response for 10 μM H_2O_2) for the same electrode and for electrode-to-electrode was 2.57% and 4.60% (RSD, n = 10), respectively. When the electrode was stored in PBS (pH 7.0) for 2 weeks, there was no obvious change of current in the response to 1.0 mM H_2O_2.

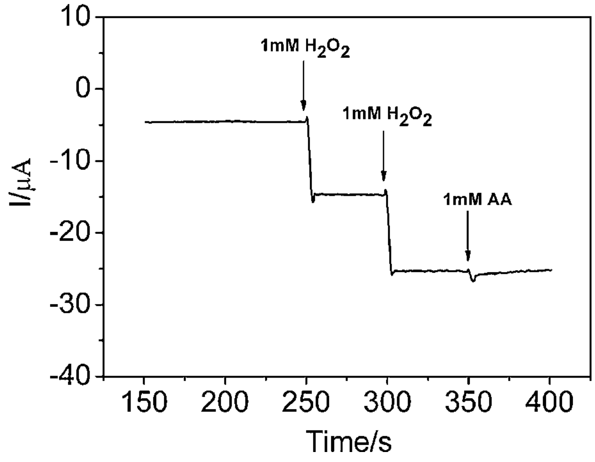


Fig. 6. Interfering effect of 1 mM ascorbic acid (AA) on the performance of Ag NPs/ATP/GC electrode. Applied potential: −0.3 V and supporting electrolyte: 0.1 M phosphate buffer (pH 7.0).

A comparison of linear range, detection limit, and response time for this Ag NPs/ATP modified electrode with other hydrogen peroxide sensors reported in the literature was shown in Table 1. All the data reveal the analytical performances for Ag NPs/ATP/GC electrode are comparable and even better than those obtained at several electrodes reported recently. Therefore, the Ag NPs/ATP/GC electrode could be used for the preparation of an amperometric sensor for hydrogen peroxide with prompt response and wide linear range.

3.6. *Interfering effect and real world sample analysis*

The influence of common interfering electroactive substances such as ascorbic acid (AA) was studied. 1.0 mM AA was added during the detection of H_2O_2, and the current responses of the sensor were shown in Fig. 6. It could be seen that the current response of AA was much lower than that of H_2O_2, which indicates that there is no obvious interference of AA in the detection of H_2O_2.

The analysis of real world sample was also performed. The sensor was used to determine the concentration of hydrogen peroxide in serum samples. The samples were diluted 100 times with 0.1 M phosphate buffer (pH 7.0). Using a standard addition method, the recoveries of hydrogen peroxide samples with concentrations of 0.5 mM (sample 1) and 1.0 mM (sample 2) were obtained as shown in Table 2. The results show that this sensor might have a potential use in detection of hydrogen peroxide.

Table 2
Determination of hydrogen peroxide in serum sample solutions.

	Found (mM)	Added (mM)	After added (mM)	Mean recovery (%)
Sample 1	0.023	0.5	0.558	106.7
Sample 2	0.041	1.0	1.029	98.8

4. Conclusion

This work developed a new H_2O_2 sensor based on Ag NPs electrodeposited on natural and inexpensive ATP modified GC electrode. Due to high surface area and fibrillar structure, ATP is an ideal template for preparing Ag NPs. Our experiments confirmed that when the ATP concentration was 100 $\mu g\,mL^{-1}$ and the electrodeposition time was 75 s, the sensor showed the maximal electrocatalytic ability for the reduction of H_2O_2. Meanwhile, the resulted sensor exhibited extremely fast amperometric response. The detection limit was down to 2.4 μM with a very wide linear range from 10.0 μM to 21.53 mM.

Acknowledgments

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