



Short communication

A novel non-enzymatic hydrogen peroxide sensor based on Mn-nitrilotriacetate acid (Mn-NTA) nanowires

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ABSTRACT

A novel non-enzymatic hydrogen peroxide sensor was realized from Mn-nitrilotriacetate acid (Mn-NTA) nanowires, which were successfully fabricated via a facile hydrothermal route. Cyclic voltammetry (CV) revealed that the Mn-NTA nanowires exhibited direct electrocatalytic activity for the oxidation of H_2O_2 in phosphate buffer solution. The sensor showed linear response to H_2O_2 at the concentrations range from 5×10^{-6} M to 2.5×10^{-3} M with a detection limit of 2×10^{-7} M. The sensitivity was up to $78.9 \mu\text{A mM}^{-1} \text{cm}^{-2}$. These results indicated that the Mn-NTA nanowires were promising in realizing non-enzymatic H_2O_2 detection.

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1. Introduction

Highly sensitive and selective detection of H_2O_2 is of greatly practical importance in chemical, biological, clinical, environmental and many other fields. Many traditional techniques have been employed for this purpose, such as chemiluminescence [1], titrimetry [2] and electrochemistry [3]. Among these methods, electrochemistry biosensors [4–11] based on electrocatalysis of immobilized enzymes towards H_2O_2 are useful due to their simplicity, high sensitivity and selectivity. However, optimal operational conditions of the enzyme electrodes are generally limited by the properties of native enzymes. The enzymes being biological macromolecules obviously cannot provide a complete long-term stability of the sensor due to their inherent instability causing denaturation. In addition, native enzymes gradually lose their catalytic activity after repeated measurements. Therefore, a development of novel electrocatalyst which overcomes the disadvantages of native enzymes is desired.

In recent years, with the development of nanotechnology, nanomaterials have become excellent substitutes for peroxidase. The manganese oxide (MnO_2) nanomaterials have been widely used in catalyst, ion-exchangers, sorbents, and energy storage in sec-

ondary batteries [12–16]. To date, there were some reports by employing MnO_2 nanomaterials as electrochemical sensor for the detection of H_2O_2 , which exhibited good sensitivity and selectivity [17–21]. Many other nanomaterials, such as copper oxide [22–24], cobalt oxide [25,26], iron oxide [27–29], silver [30,31], prussian blue [32–34], carbon nanotubes [35–37] and their complexes [38–41] which are capable of cyclic oxidation-reduction on an electrode, have also been used as electrochemical sensor. However, there are few reports by using manganese based compounds as electrocatalysts in H_2O_2 detection. In order to obtain more support for potential using manganese contained nanomaterials as artificial peroxidases to prepare biosensors and biocatalysts, this work describes the design of Mn-NTA nanowires by a hydrothermal route. A novel functional hybrid film of nanowires Mn-NTA and Nafion on a glassy carbon electrode (labeled as nanowires Mn-NTA/Nafion/GCE) has been constructed as a catalytic layer for H_2O_2 detection. To our best known, Mn-NTA nanowires have never been reported to be used for H_2O_2 detection. Tests show that Mn-NTA nanowires are an excellent sensing material towards the oxidation of H_2O_2 . It is believed that the Mn-NTA nanowires will be a promising material for biosensor application.

2. Experimental

2.1. Reagents and apparatus

H_2O_2 solution (30%) was purchased from Changsha Chemical Reagent Factory (Changsha, China). Nafion was obtained from

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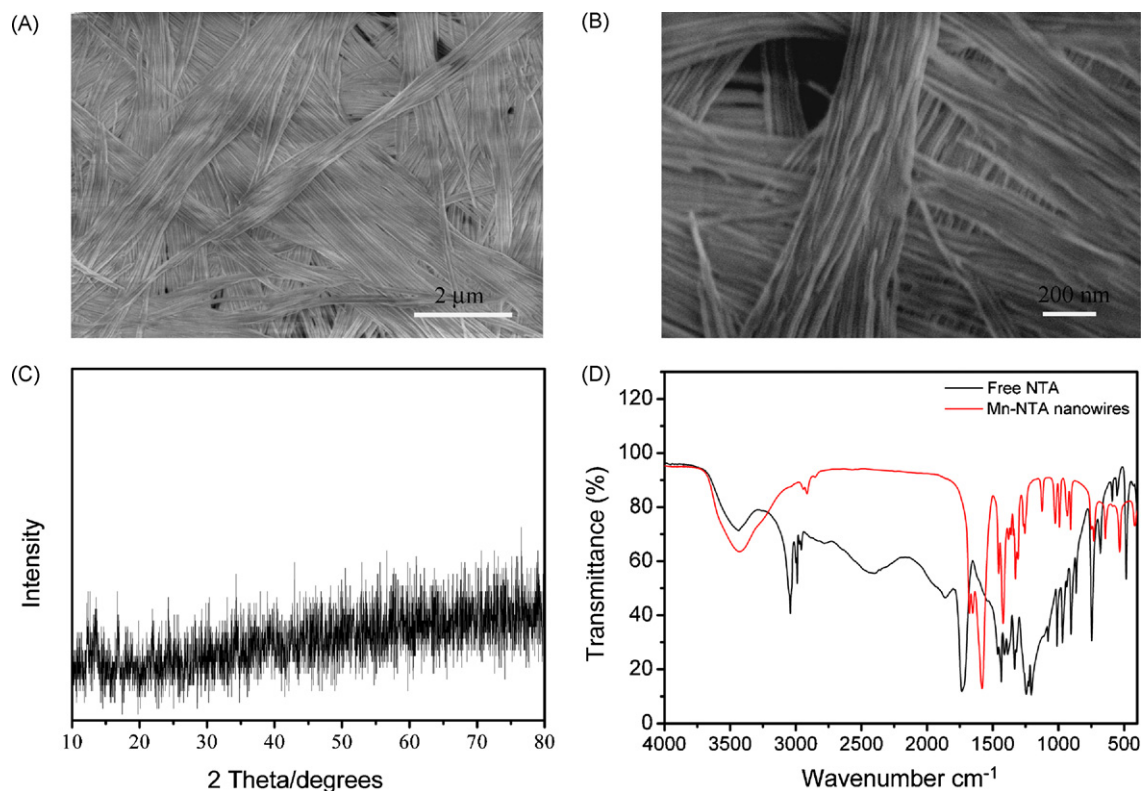


Fig. 1. (A) Low-magnification and (B) high-magnification SEM images and (C) XRD pattern of the as-prepared products, and (D) Fourier transform infrared spectra of free NTA and Mn-NTA nanowires.

Aldrich. All chemicals used were analytical grade. Double-distilled water was used for preparation of buffer and standard solutions. H_2O_2 solution was freshly prepared daily before the electrochemical measurements.

Mn-NTA nanowires were prepared by a facile hydrothermal route. Typically, 5 mmol nitrilotriacetate acid (NTA) and 5 mmol $\text{Mn}(\text{Ac})_2$ were dissolved in 100 mL water. Then, the suspension was transferred into a 130 mL Teflon-lined stainless steel autoclave and maintained at 453 K for 6 h. After that the autoclave was cooled down to room temperature, the white products were centrifuged, and sequentially washed with ethanol and distilled water several times and then dried in air at 353 K for 8 h.

Scanning electron microscopy (SEM) characterization was performed on Hitachi S-4800. Powder X-ray diffraction (XRD) patterns were collected using a SHIMADZU, XRD-6000 with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Fourier transform infrared (FT-IR) spectra were recorded for a KBr diluted sample using a Bruker Vertex 70 spectrometer with a resolution of 2 cm^{-1} .

Electrochemical experiments were performed with CHI 660 B electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China) with a conventional three electrode cell. The working electrode was a nanowires Mn-NTA/Nafion/GCE. A saturated calomel electrode (SCE) and a platinum electrode were used as the reference and the auxiliary electrodes, respectively. Experiments were carried out at room temperature.

2.2. Electrode modification

The Mn-NTA nanowires on the electrode were fabricated by the following way: Firstly, The GCE was successfully polished by 0.3 and 0.05 μm aluminum slurries, and then was cleaned by dipping into 1:1 (v/v) aqueous solution of deionized water and ethanol with the assistance of ultrasonication prior to the experiment. 10 mg Mn-NTA was dispersed in 2 mL Nafion solution. Next, 8 μL of Mn-

NTA/Nafion solution (5 mg mL^{-1}) was cast on the surface of GCE and dried in air. Thus nanowires Mn-NTA/Nafion/GCE was obtained.

3. Results and discussion

Typical SEM images of as-prepared Mn-NTA nanowires are displayed in Fig. 1A. A great deal of uniform nanowires with an average length of 10–20 μm can be clearly seen. A high resolution SEM image is shown in Fig. 1B, it can be clearly seen that the diameter of nanowires is about 50 nm. Fig. 1C shows the XRD pattern of the as-synthesized Mn-NTA nanofibers. No obvious characteristic diffraction peaks are observed, indicating that the as-prepared nanowires are amorphous. The infrared spectrums of NTA and Mn-NTA nanowires are shown in Fig. 1D. It can be observed that one can discuss the structure of Mn-NTA in the light of the infrared spectra obtained for the carboxylate group both in NTA and in Mn-NTA nanowires. The strongest peak at 1764 cm^{-1} for the free acid can be attributed to the free carboxylic acid group [42]. There were three strong peaks at 1581, 1652 and 1677 cm^{-1} for the Mn-NTA nanowires, which were not observed in the spectrum of free NTA and can be assigned to the stretching vibration of the coordinated carboxylate group to Mn(II) [43]. Mn-NTA nanowires with peaks for C–O, CH_2 , C–N, and C–H groups appeared at 1326, 1307, 1254, and 1124 cm^{-1} , respectively. From these observations, it was clear that the formation of Mn-NTA nanowires can be ascribed to the coordination NTA to Mn(II).

Fig. 2A shows the CVs of the nanowires Mn-NTA/Nafion/GCE in 1/15 M PBS (pH 7.0) at a scan rate of 0.1 V/s. For the Nafion/GCE, no obvious oxidation and reduction peaks were observed in the potential range of 0–1.0 V (curve a). For the nanowires Mn-NTA/Nafion/GCE, a couple of obvious reduction peaks and oxidation peaks were observed (curve b) at around 0.4 and 0.7 V, which were assigned to the reduction of Mn(IV) to Mn(II) and oxidation of Mn(II) to Mn(IV). Fig. 2B shows the CVs of the nanowires

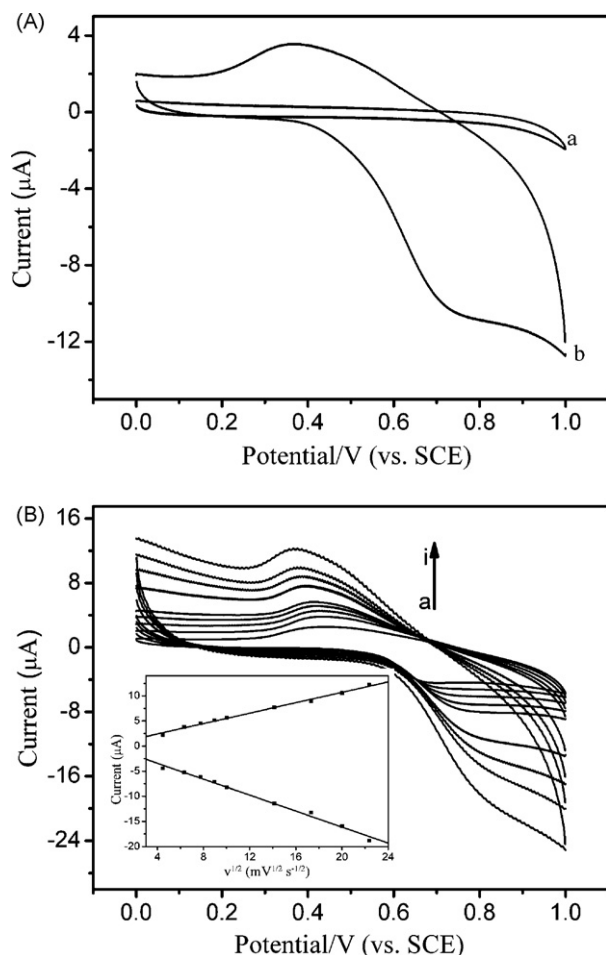
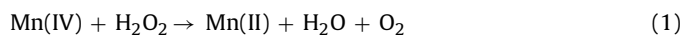


Fig. 2. (A) CVs of Nafion/GCE (a) and the nanowires Mn-NTA/Nafion/GCE (b) in deoxygenized 1/15 M PBS (pH 7.0) at scan rate 0.1 V/s. (B) CVs of the nanowires Mn-NTA/Nafion/GCE in deoxygenized 1/15 M PBS (pH 7.0) at different scan rates (a–i: 0.02, 0.04, 0.06, 0.08, 0.10, 0.20, 0.30, 0.40, and 0.50 V/s, respectively). Inset is the linear dependence of peak current with the square root of scan rate.

Mn-NTA/Nafion/GCE in 1/15 M PBS (pH 7.0) at different scan rates. As can be seen, both the oxidation and reduction peak currents increased linearly with square root of the scan rates ($v^{1/2}$) from 0.01 to 1.0 V/s (inset of Fig. 2b). These results reveal that the electron transfer of nanowires Mn-NTA/Nafion complex on the GCE surface was a diffusion electrochemical process.

Fig. 3A shows the CVs of nanowires Mn-NTA/Nafion/GCE in the absence and presence of 0.5 mM H_2O_2 at the scan rate of 0.1 V/s in an oxygen-free 1/15 M PBS (pH 7.0). When the system did not contain any H_2O_2 (curve a), an oxidation peak at 0.7 V could be observed. When 0.5 mM H_2O_2 was added to the PBS (curve b), the oxidation peak current of Mn(II) to Mn(IV) was obviously enhanced in deoxygenized environment, which could be attributed to the parallel catalytic reaction. The catalyst Mn-NTA was chemical reduced to lower states (Mn(II)) by H_2O_2 (Eq. (1)) and at the same time was electro-oxidized back to Mn(IV) at the electrode surface (Eq. (2)) [18,44]:



Meanwhile, the increase of oxidation peaks was greater with the increase of H_2O_2 concentration from 1.0 to 2.0 mM (curves c and d). However, no obvious electrochemical oxidation peak was observed when the CV scan was performed at Nafion/GCE under the same conditions (shown in the inset).

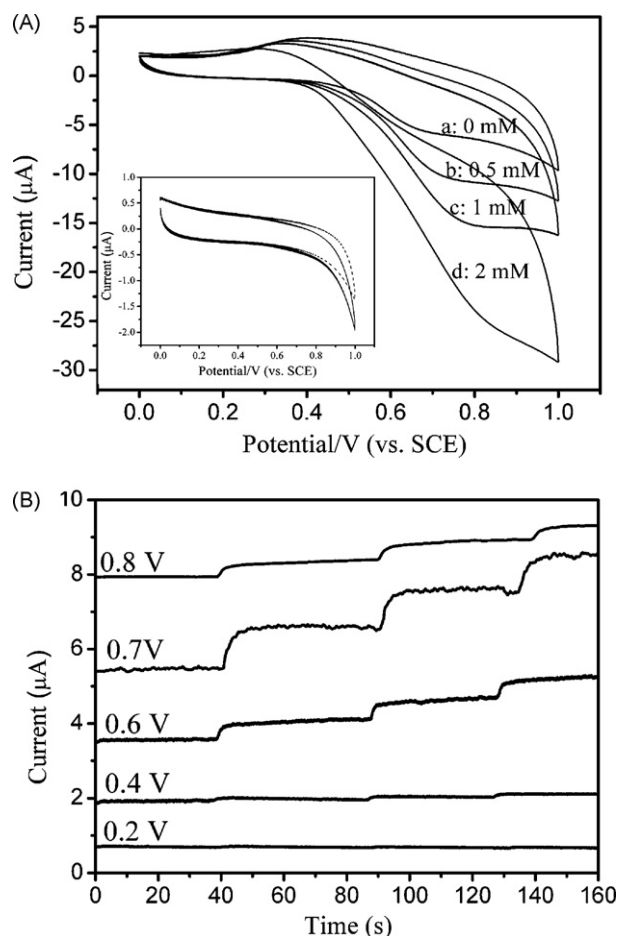


Fig. 3. (A) Nanowires Mn-NTA/Nafion/GCE in the absence (a) and presence (b–d) of 0.5, 1, and 2 mM H_2O_2 in deoxygenized 1/15 M PBS (pH 7.0). Scan rate: 0.1 V/s. Inset: Nafion/GCE in the absence (dash line) and presence (solid line) 2 mM H_2O_2 under the same condition. (B) Amperometric responses to three successive additions of 0.1 mM H_2O_2 at different applied potentials.

The above experimental results indicated that the complex formed by nanowires Mn-NTA/Nafion film exhibited excellent electrocatalytic activity to H_2O_2 . The optimal constant potential for amperometry at the working electrode was chosen on the basis of the amperometric responses to three successive additions of 0.1 mM H_2O_2 , which were recorded with respect to different applied potentials (Fig. 3B). The steady-state current response increases obviously with the working potential from 0.2 to 0.7 V, and then decreases smoothly from 0.7 to 0.8 V. Therefore, 0.7 V is selected as the working potential for amperometric detection of H_2O_2 .

To examine the sensitivity of the as-prepared nanowires Mn-NTA/Nafion/GCE, we investigated the amperometric response of H_2O_2 in the stirring 1/15 M PBS solution. The applied potential was set at 0.7 V vs. SCE. Fig. 4A shows the typical current-time curves for the nanowires Mn-NTA/Nafion/GCE electrode with a successive addition of H_2O_2 . Upon the addition of H_2O_2 , the nanowires Mn-NTA/Nafion/GCE reaches the maximum steady-state response within 5 s, indicating a very rapid amperometric response. The linear relationship is obtained in the concentration range from 5×10^{-6} M to 2.5×10^{-3} M with a correlation coefficient of 0.998 (Fig. 4B) and a slope of $5.58 \mu\text{A mM}^{-1}$. The sensitivity of the biosensor to H_2O_2 is calculated to be $78.9 \mu\text{A mM}^{-1} \text{cm}^{-2}$. At a signal-to-noise ratio of 3, the detection limit of biosensor is 2×10^{-7} M. Various H_2O_2 sensors have been reported in literature. However, it is very difficult to compare one sensor to others because

Table 1
Comparison of various H₂O₂ sensors.

Electrode materials	Applied potential (V)	Detection limit (μM)	Sensitivity ($\mu\text{A mM}^{-1}$)	Reference
Mn-NTA nanowires/Nafion	0.7	0.2	5.58	This study
NanoAg/DNA networks	-0.4	1.7	-	[39]
NanoMnO ₂ /Na-montmorillonite	0.65	0.15	2.2 ^a	[17]
Fe ₂ O ₃ nanoparticles/Nafion	-0.37	1.5	-	[29]
Carbon nanotubes	0.95	20	0.8	[35]
Ag microspheres/Nafion	-0.5	1.2	-	[30]
Hemoglobin/silica sol-gel film	-0.2	0.86	4.58 ^a	[4]
Hemoglobin/kieselgubr film	-0.4	2.1	-	[5]
Horseradish peroxidase/nanoAu/chitosan	-0.4	0.65	0.176	[7]

^a Calculated from the data in paper.

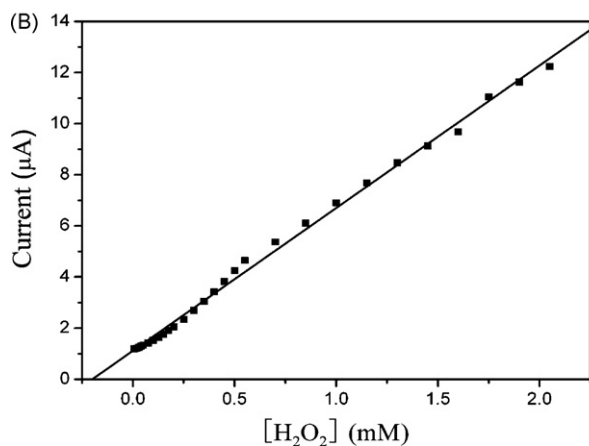
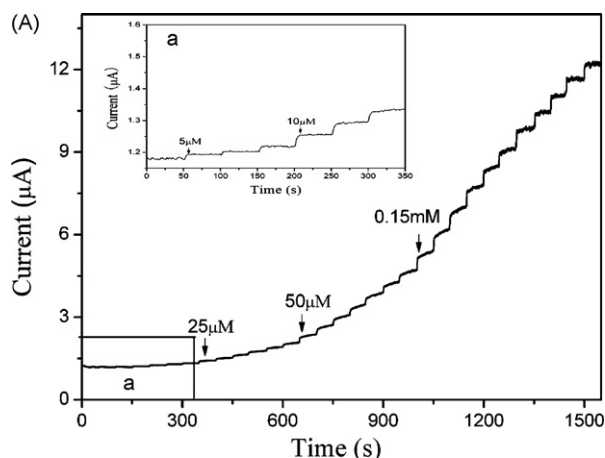


Fig. 4. (A) Amperometric response of nanowires Mn-NTA/Nafion/GCE with successive addition of H₂O₂ at 0.7 V vs. SCE. Inset a: amplification of curve a. (B) The linear relationship between the catalytic current and the concentration.

the performance of the sensor is greatly dependent on the use of the applied potential, the supporting electrolyte, and the electrode material and its surface area. We have summarized various H₂O₂ sensors in Table 1 with respect to the operating conditions, sensitivity, and the detection limit. It can be seen that the performance

Table 2
Results of interfering experiment.

Interferent	Current ratio ^a
Cu ²⁺	0.45
Fe ³⁺	0.50
Ni ²⁺	0.85
Na ⁺	1
K ⁺	1
Cl ⁻	1
NO ₃ ⁻	1
Ac ⁻	1
SO ₄ ²⁻	1
Citric acid	0.98
Serum albumin	0.98
Glucose	0.97

^a Ratio of currents for mixtures of 0.5 mM interferents and 0.1 mM H₂O₂ compared to that for 0.1 mM H₂O₂ alone. Operating potential: 0.7 V vs. SCE. Electrolyte: 1/15 pH 7.0 phosphate buffer.

of the developed sensor is comparable to most of H₂O₂ sensors in literature in one or more categories.

The stability and reproducibility of the sensors have also been tested. When the electrode was stored at 4 °C for 1 week, the CV peak currents still retained 93%, and in the next 3 weeks the response still retained 90% of the initial value. For 10 repeated measurements of the same electrode, the relative standard deviation (R.S.D.) was 3.2%. Several cations, anions and molecules potentially existing in biological liquids were investigated for their interference with the amperometric determination of H₂O₂. The interference experiments were performed in PBS at optimal conditions by comparing the response current of 0.1 mM H₂O₂ plus 0.5 mM each interfering substance with that of 0.1 mM H₂O₂ alone. The results obtained are listed in Table 2. Na⁺ and K⁺ did not interfere in a 5-fold excess. Ni²⁺ interfered slightly, probably owing to its catalytic decomposition of H₂O₂ ability. This effect was even more pronounced for Cu²⁺, Fe³⁺, which can be assigned to their stronger catalytic ability to H₂O₂. Most anions such as nitrate, sulfate, acetate and chloride did not interfere. In addition, the serum albumin, glucose and citric acid, which were existed in biological sample, hardly interfered.

Two environment samples were selected to examine this H₂O₂ sensor in the feasibility of H₂O₂ detection. Both samples with 10-fold pre-dilution were used as the sample solutions in this experiment. By standard addition method, the results from pre-

Table 3
Determination of hydrogen peroxide in environment sample solutions ($n = 4$).

Sample	Value found in diluted sample (mM) ^a	Value found after H ₂ O ₂ addition (mM) ^b	R.S.D. (%)	Recovery (%)
Tap water	0.015	0.113	2.7	113
River water	0.02	0.118	2.2	118

^a 1:10 dilution with 1/15 pH 7.0 phosphate buffer.

^b The added H₂O₂ was controlled in 0.1 mM.

diluted sample solutions and the results of injection 0.1 mM H₂O₂ in both sample solutions are obtained. The calculated recovery values are shown in Table 3. These results proved that the sensor has potential applications in determination of H₂O₂ real samples.

4. Conclusion

Based on co-immobilizing Mn-NTA nanowires and Nafion on a glass carbon electrode, a new non-enzymatic H₂O₂ sensor was proposed. Tests showed that Mn-NTA nanowires exhibited remarkable electrocatalytic activity for the oxidation of H₂O₂. The high sensitivity, long-term stability and good reproducibility of the proposed sensor made it promising for providing a simple method for practical application. It should be noted that the main feature of this work was to propose a new non-enzymatic H₂O₂ sensor based on Mn-NTA nanowires, which was realized in a very economic and facile method.

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