

# Preparation of Manganese Dioxide Nanozyme as Catalyst for Electrochemical Sensing of Hydrogen Peroxide

Na Zou<sup>1,2,\*</sup>, Xianyong Wei<sup>1,3,\*</sup>, Zhimin Zong<sup>1</sup>, Xin Li<sup>2</sup>, Funa Meng<sup>2</sup>, Zhaoxia Wang<sup>2</sup>

<sup>1</sup> Key Laboratory of Coal Processing and Efficient Utilization, Ministry of Education, China University of Mining & Technology, Xuzhou 221116, Jiangsu, China

<sup>2</sup> Department of Chemistry and Chemical Engineering, Heze University, Heze 274015, Shandong, China

<sup>3</sup> State Key Laboratory of High-efficiency Coal Utilization and Green Chemical Engineering, Ningxia University, Yinchuan 750021, Ningxia, China

\*E-mail: [wei\\_xianyong@163.com](mailto:wei_xianyong@163.com) (X. Wei), [zgdytzn@126.com](mailto:zgdytzn@126.com) (N. Zou)

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The two-dimensional manganese dioxide nanoflakes (MnO<sub>2</sub> NFs) with peroxidase-like activity was synthesized by a biomineralization method using bovine serum albumin (BSA) as a template. After then MnO<sub>2</sub> NFs was hybridized with reduced graphene oxide (rGO) for electrochemical sensing of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The composition and structure of MnO<sub>2</sub> NFs were characterized by Energy Dispersive X-ray Spectrometer (EDX) and Transmission Electron Microscope (TEM), and the morphology of hybridized material were characterized by Scanning Electron Microscopy (SEM). Electrochemical experiments showed that the hybridized material exhibited good sensing performance toward the reduction of H<sub>2</sub>O<sub>2</sub> with broad linear ranges of 20 nM to 5 μM and 5 μM to 800 μM. The limit of detection is 14.92 nM (S/N=3). The good sensing performance is ascribed to the synergistic effects of the special morphology of MnO<sub>2</sub> NFs and good conductivity of the reduced graphene oxide (rGO). The proposed sensor can be used for monitoring the H<sub>2</sub>O<sub>2</sub> content in real biological environments with good stability, repeatability and selectivity.

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**Keywords:** MnO<sub>2</sub> NFs, enzyme-like, H<sub>2</sub>O<sub>2</sub> sensing, ultrasensitive

## 1. INTRODUCTION

Nanozyme is a kind of nanomaterials with enzymatic catalytic properties. Preparation of catalytically active nanomaterials has become an emerging field in biomimetic chemistry, which aimed at designing functional nanomaterials to mimic various intrinsic properties of natural enzymes [1, 2]. Nanozyme materials can be used as the substitutes of natural enzymes in the field of analytical sensing [3-6], environmental protection [7-9] and cancer treatment [10-13], because they are easier to be

prepared, more stable, and more widely used.

H<sub>2</sub>O<sub>2</sub> is the most abundant active oxygen species in the body. Excessive H<sub>2</sub>O<sub>2</sub> is considered to be a marker of oxidative stress, and it is associated with the occurrence and development of many diseases [14, 15]. In order to deeply understand the relationship of the oxidative stress with diseases, quantitative detection of H<sub>2</sub>O<sub>2</sub> is necessary. The electrochemical sensor is one of the most suitable tools for detection of H<sub>2</sub>O<sub>2</sub> in biological environments due to its intrinsic advantages, such as high sensitivity and selectivity, fast response, simplicity, low-cost and convenient operation. Many electrochemical H<sub>2</sub>O<sub>2</sub> sensors have been designed to actualize the accurate and sensitive detection of H<sub>2</sub>O<sub>2</sub>. In these sensors, two main strategies were usually adopted, they are enzymatic catalysis (including natural enzymes and nanozymes materials) [16-18] and non-enzymatic nanomaterials catalysis [19-23]. Natural enzymes have high catalytic activity and substrate specificity, but they need expensive preparation and tedious purification, and they are easy to denature or degrade. Non-enzymatic nanomaterials have wider range of applications and more stable performance, but they suffered from the poor selectivity and sensitivity. Therefore, the use of nanozyme materials to construct H<sub>2</sub>O<sub>2</sub> electrochemical sensors is a good selection.

In recent years, scientists have synthesized many kinds of peroxidase nanozyme materials by optimizing the synthesis conditions and changing the morphology and structure of the materials, and applied them to the colorimetric sensing of H<sub>2</sub>O<sub>2</sub> [24-30]. For example, Kang and co-workers synthesized Mn<sub>2</sub>O<sub>3</sub> hollow nanoparticles were by calcination and used them as a highly efficient sensing nanozyme for hydrogen peroxide and glucose [25]. Lei Huang et al synthesized VO<sub>x</sub> quantum dots using VO<sub>2</sub> as a precursor. The VO<sub>x</sub> quantum dots exhibit oxidase and peroxide-like activity and produce three different colors under three different concentrations of H<sub>2</sub>O<sub>2</sub> [26]. Lei Han and colleagues [30] synthesized MnO<sub>2</sub> NFs and used them as a tandem nanozyme for the colorimetric detection of glucose and H<sub>2</sub>O<sub>2</sub>.

In this work, MnO<sub>2</sub> NFs nanozyme was synthesized using BSA as a biomineralization template [30-31] and then hybridized with rGO. The rGO is two-dimensional sheet with good physical and chemical properties, and it is easy to hybridize with MnO<sub>2</sub> NFs to form a stable dispersion. The hybridized material was used as a sensing platform to amplify the electrical signal and to decrease the reduction potential of H<sub>2</sub>O<sub>2</sub>. Based on this, the ultra-sensitive electrochemical detection of H<sub>2</sub>O<sub>2</sub> molecules in biological environment was realized. Relative to colorimetric sensing, the use of substrates and large instruments is avoided, and it is more sensitive and more specific than non-enzymatic H<sub>2</sub>O<sub>2</sub> sensing.

## 2. EXPERIMENTAL

### 2.1 Reagents and chemicals

Manganese acetate (MnAc<sub>2</sub>) and BSA were purchased from Sigma Co. Ltd (USA), rGO powder was purchased from Nanjing XFNANO Materials Tech Co., Ltd (Nanjing, China), H<sub>2</sub>O<sub>2</sub> (30%), sodium hydroxide (NaOH), ethyl alcohol, disodium hydrogen phosphate dodecahydrate

( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ) and monobasic sodium phosphate dihydrate ( $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ) were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). The phosphate buffer solution was prepared from 0.2 M  $\text{NaH}_2\text{PO}_4$  solution and 0.2 M  $\text{Na}_2\text{HPO}_4$  solution. Ultrapure water ( $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ) was obtained from a Milli-Q ultrapure system (Qingdao, China). All reagents were of analytical grade and used without any further purification.

## 2.2 Synthesis of $\text{MnO}_2$ NFs nanozyme

$\text{MnO}_2$  NFs nanozyme was synthesized by chemical precipitation of  $\text{MnAc}_2$  crystals in an alkaline solution containing BSA, the same with the method reported in the literature [11]. And the peroxidase-like activity of  $\text{MnO}_2$  NFs had been strongly confirmed by colorimetric assay of  $\text{H}_2\text{O}_2$  according to the paper. The specific steps are as follows: First of all, add 1 mg of BSA into a stirred solution of  $\text{MnAc}_2$  (10 mL,  $2 \times 10^{-3}$  M), and keep stirring for 1 hour at room temperature. After BSA and  $\text{Mn}^{2+}$  were incubated for one hour, adjust the pH of the mixture solution to about 10 using NaOH solution (0.2 M) and  $\text{H}_3\text{PO}_4$  solution (0.2 M). Keep stirring and 7 hours later, obvious nanoparticles were formed in the mixture solution. And then the obtained product was transferred to a centrifuge tube, and centrifuged at 5000 r/min for 5 min. After several times of washing and centrifugation, the obtained product is transferred out of the centrifuge tube and stored for future use.

## 2.3 Characterization

The morphology of materials was observed by SEM. Samples were prepared by drying a drop of aqueous solution of materials on a glass sheet and observed by SEM SU8010 (Hitachi, Japan). The composition and structure of materials were characterized by TEM (Tecnai G2 F20, FEI, USA, operation voltage 120 kV). A combined energy-dispersive X-ray spectroscopy and elements mapping analysis system attached to the TEM were used for elemental analysis.

All electrochemical measurements were performed at room temperature on a CHI 920C electrochemical workstation. Electrochemical experiments were conducted with a three-electrode unit structure. The modified GCE was used as the working electrode, the saturated calomel electrode was used as the reference electrode, and platinum wire was used as the counter electrode. The 0.2 M phosphate buffer purified by  $\text{N}_2$  was used as the electrolyte for  $\text{H}_2\text{O}_2$  sensing.

## 2.4 Construction of the sensor and $\text{H}_2\text{O}_2$ Sensing

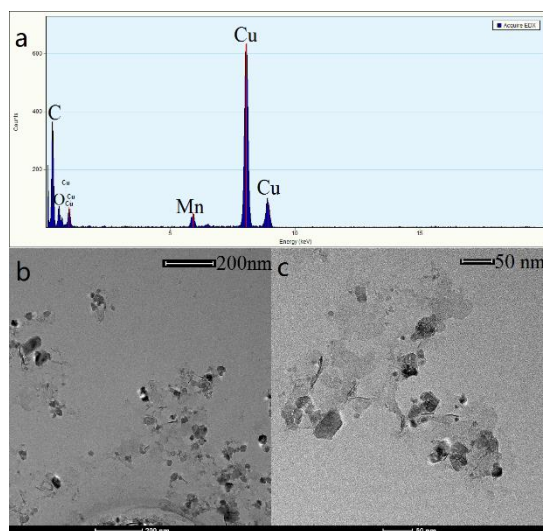
The experiment steps of construction of the sensor and  $\text{H}_2\text{O}_2$  Sensing are as followed: Firstly, the glassy carbon electrode (GCE) (diameter 3 mm) is polished on the suede board with  $\text{Al}_2\text{O}_3$  (0.03  $\mu\text{m}$ ) powder until it is a mirror surface. And then monitor it by cyclic voltammetry in 5 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  solution. The voltammetric characteristic curve of GCE is observed, and the negative and positive peaks of the voltammetric characteristic curve are obtained. If  $\Delta E_p < 0.08 \text{ V}$ , the surface of GCE has been well activated. Rinse the activated GCE with ultra-pure water to make sure the electrode surface

is clean, and dried naturally at room temperature. The prepared rGO solution should be ultra-sonicated for 10 minutes before use, in order to destroy the agglomeration of nanomaterials, and ensure the uniform dispersion of the modified solution. After the surface of GCE is completely dry, 5  $\mu\text{L}$  of rGO mixture is casted to the surface of GCE by using a pipette gun, and then it is dried again at room temperature. The modified electrode is recorded as rGO/GCE. Then the prepared  $\text{MnO}_2$  NFs were covered on the rGO/GCE and recorded as  $\text{MnO}_2$  NFs/rGO/GCE. After that, it is stored in cold for further use. The modified electrode is used as the working electrode in the next experiment.

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization of $\text{MnO}_2$ NFs

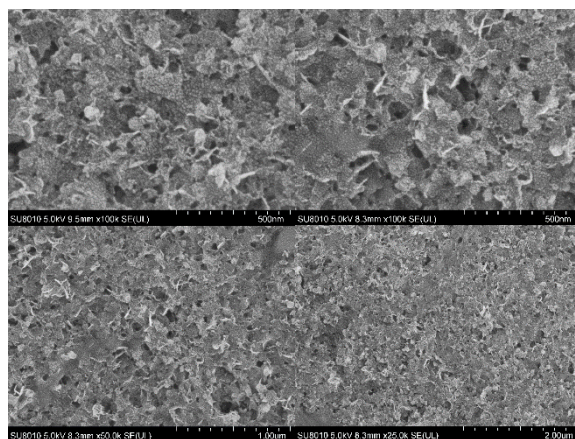
From the analysis on the EDX spectrum (Figure 1a), it was found that manganese and oxygen are present in the spectrum, which means  $\text{MnO}_2$  was obtained by chemical precipitation under basic conditions. The appearance of copper and carbon is due to the use of ultra-thin carbon film copper mesh substrate. The EDX result is consistent with a literature reports which synthesized  $\text{MnO}_2$  nanoparticles under acidic conditions [32].



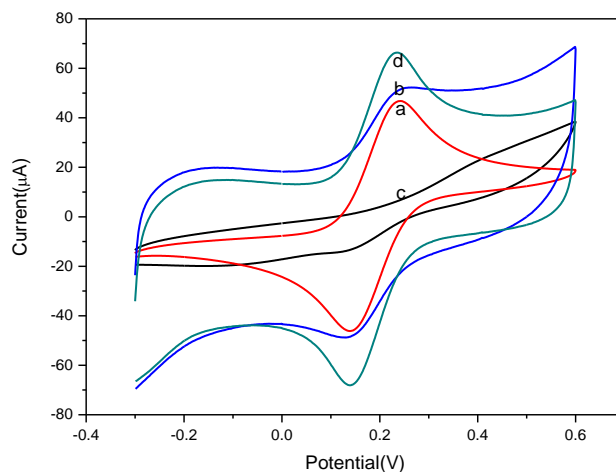
**Figure 1.** The morphology and composition of  $\text{MnO}_2$  NFs. (a) TEM-EDX pattern spectra of  $\text{MnO}_2$  NFs. (b, c) TEM images of  $\text{MnO}_2$  NFs with different magnifications.

In order to investigate the nanostructure of  $\text{MnO}_2$ , TEM was measured with different magnification (Figure 1b, 1c). Most of the morphology is two-dimensional thin thickness, and the material is recorded as  $\text{MnO}_2$  NFs. It is proved that we have successfully synthesized flaky  $\text{MnO}_2$  nanomaterials under the given experimental conditions using biomineralization methods. The obtained material was then modified on GCE with rGO, and the surface morphology of the deposited material was scanned using SEM (Figure 2). It is found that the size of the material is about 100 nm, and the morphology of the material is sheet stacked. Compared with other literatures, the  $\text{MnO}_2$  NFs

synthesized in this paper has a two-dimensional nanometer morphology, it is different from flower-like or sphere MnO<sub>2</sub> which was synthesized by one step acidification [32, 33].



**Figure 2.** SEM images of MnO<sub>2</sub> NFs/rGO/GCE with different magnifications.



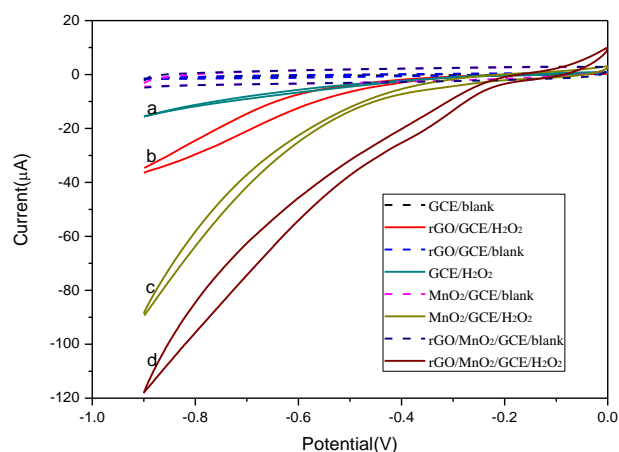
**Figure 3.** Cyclic Voltammograms obtained in 1 mM [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> solution containing 0.1 M KCl at bare GCE (curve a), rGO/GCE (curve b), MnO<sub>2</sub> NFs/ GCE (curve c) and MnO<sub>2</sub> NFs/rGO/GCE (curve d).

### 3.2 Electrochemical behavior of different modified electrodes

In the constructing process the sensor, the electrochemical behavior of GCE was studied by cyclic voltammetry (CV). The CV scan was carried out in a 1 mM [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> solution containing 0.1 M KCl. The current response of the modified electrode to [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> can reflect the status of modified electrode. Many literatures have used this method to characterize the electron transfer of the electrode. Similar to some literatures [21-23], this experiment also obtained similar expected results. As shown in figure 3, a couple of expectedly reversible redox peaks were obtained on the GCE. After a

layer of rGO was modified on bare GCE, the redox peak potentials were almost unchanged, and the peak current is increased significantly, indicating that the rGO provided large specific surface area and excellent electrical conductivity for electron transfer. However, on the MnO<sub>2</sub> NFs/GCE, [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> showed irreversible electrochemical behavior and no obvious redox peaks were obtained. The results showed that the MnO<sub>2</sub> NFs is not a good electrode surface modifier for improving the conductivity of electrode. Therefore, it is necessary to hybridize it with rGO to compensate the shortcoming of its poor conductivity. As we expected, on the MnO<sub>2</sub> NFs/rGO/GCE electrode, a large peak current response was obtained.

The excellent electrochemical properties of the MnO<sub>2</sub> NFs/rGO nanocomposites for electrochemical response of H<sub>2</sub>O<sub>2</sub> were showed by for recording the CV of different modified electrodes in pH 7.4 PBS solution containing 20 mM H<sub>2</sub>O<sub>2</sub> with a scanning rate of 0.08 V s<sup>-1</sup> (Figure 4). It was found that, on the bare GCE, rGO/GCE, MnO<sub>2</sub> NFs/GCE and MnO<sub>2</sub> NFs/rGO/GCE, no obvious current response was obtained in pH 7.4 PBS solution without of H<sub>2</sub>O<sub>2</sub>. As we add H<sub>2</sub>O<sub>2</sub> in the pH 7.4 PBS solution, the current increased significantly as the sequence of bare GCE, rGO/GCE, MnO<sub>2</sub> NFs/GCE and MnO<sub>2</sub> NFs/rGO/GCE, indicating that H<sub>2</sub>O<sub>2</sub> had no obvious electrochemical response on the bare GCE and the MnO<sub>2</sub> NFs have excellent electrocatalytic activity for the reduction of H<sub>2</sub>O<sub>2</sub>. After the MnO<sub>2</sub> NFs hybridized with rGO, the biggest electrochemical response of H<sub>2</sub>O<sub>2</sub> was obtained on the MnO<sub>2</sub> NFs/rGO/GCE, indicating that they played synergistic effect for the H<sub>2</sub>O<sub>2</sub> sensing. The rGO can increase the electrical conductivity and also prevent the aggregation of the MnO<sub>2</sub> NFs, thus providing more electrical sites for the H<sub>2</sub>O<sub>2</sub> reaction.

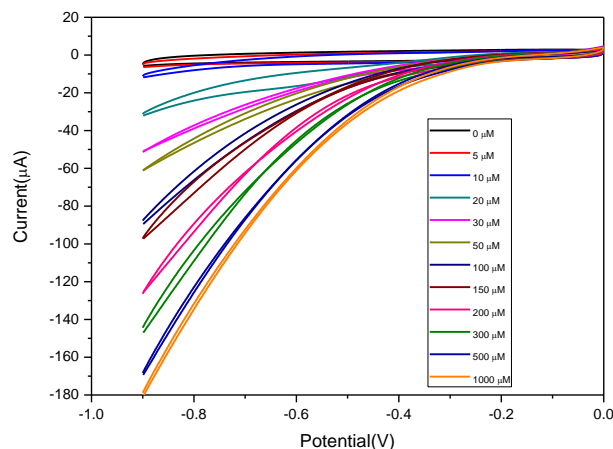


**Figure 4.** Cyclic Voltammograms obtained in 0.1 M pH 7.4 PBS solution at bare GCE (curve a), rGO/GCE (curve b), MnO<sub>2</sub> NFs/ GCE (curve c) and MnO<sub>2</sub> NFs/rGO/GCE (curve d) with (solid line) and without (dash line) 1 mM H<sub>2</sub>O<sub>2</sub>.

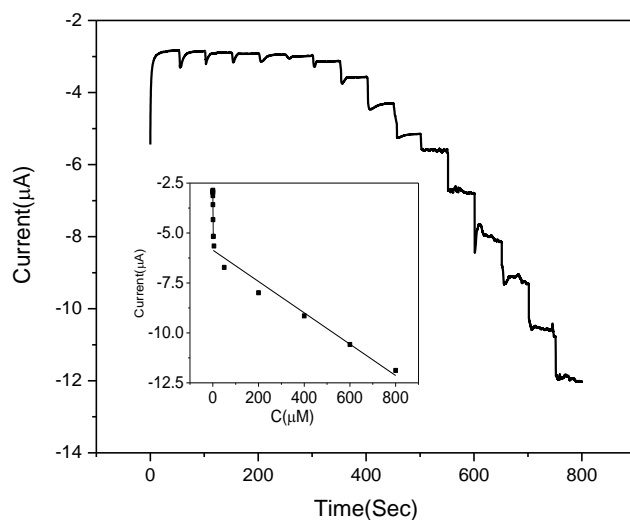
### 3.3 Working curve and linear relationship

In order to further verify the electrochemical sensing properties of the sensor, the redox properties of different concentrations of H<sub>2</sub>O<sub>2</sub> to MnO<sub>2</sub> NFs/rGO were investigated, and the optimal

potential for detecting  $\text{H}_2\text{O}_2$  were found. As shown in figure 5, the CV curve showed a regular change after adding equal amounts of  $\text{H}_2\text{O}_2$  (5-1000  $\mu\text{M}$ ). Obviously, the cathode current of the  $\text{MnO}_2$  NFs/rGO sensor increases with  $\text{H}_2\text{O}_2$  concentration increasing between -0.8 V and -0.3 V relative to the saturated calomel electrode.



**Figure 5.** Cyclic Voltammograms obtained in 0.1 M pH 7.4 PBS solution at  $\text{MnO}_2$  NFs/rGO/GCE sensor with different concentration of  $\text{H}_2\text{O}_2$  from 0-1000  $\mu\text{M}$ .



**Figure 6.** Amperometric  $i-t$  curve of  $\text{H}_2\text{O}_2$  at  $\text{MnO}_2$  NFs/rGO/GCE sensor at different concentrations from 20 nM to 800  $\mu\text{M}$  by continuous addition of  $\text{H}_2\text{O}_2$  in 0.1 M PBS (pH 7.4). Inset: plot of current,  $i$  vs.  $\text{H}_2\text{O}_2$  concentration.

The effectiveness of  $\text{MnO}_2$  NFs/rGO nanoparticles modified electrode for  $\text{H}_2\text{O}_2$  sensing was demonstrated in the next experiment, by the means of typical steady-state current response of synthetic materials. The effect of operating potential on the amperometric response of  $\text{MnO}_2$  NFs/rGO/GCE to 0.5 mM  $\text{H}_2\text{O}_2$  was investigated firstly.  $\text{H}_2\text{O}_2$  exhibits a stable current response at  $\text{MnO}_2$  NFs/rGO/GCE at different potentials, indicating that all potentials can be used for amperometric measurements.

However, the interference effect of dissolved oxygen will be significant at the polarization potential. Therefore, -0.3 V is suitable for further measurements.

Electrocatalytic reduction of H<sub>2</sub>O<sub>2</sub> current detection is an important detection method in electrochemical analysis, and the generated current is proportional to the concentration of the species produced. Figure 6 shows a typical amperometric response of MnO<sub>2</sub> NFs/rGO/GCE to -0.3 V for continuous addition of H<sub>2</sub>O<sub>2</sub> in 0.1 M PBS (pH 7.4). It can be clearly seen from the figure that when H<sub>2</sub>O<sub>2</sub> is added, the current response current increases and reaches a steady state within a few seconds. It shows that the MnO<sub>2</sub> NFs/rGO/GCE electrode has good electrocatalytic performance. The MnO<sub>2</sub> NFs/rGO/GCE electrode current response was linear with H<sub>2</sub>O<sub>2</sub> concentrations ranging from 20 nM to 5 μM and 5 μM to 800 μM with correlation coefficients of 0.983 and 0.969, respectively. In the range of 20 nM to 5 μM, the linear regression equation  $I_p (\mu A) = -2.886 + (-1.2095) \cdot C (\mu M)$  is obtained, and in the range of 5 μM to 800 μM, the linear regression equation is  $I_p (\mu A) = -5.857 + (-0.0079) \cdot C (\mu M)$ . The detection limit is 14.92 nM (S/N = 3). The outstanding value of this nanozyme H<sub>2</sub>O<sub>2</sub> sensor lies in its ultra-low detection linearity range compared with other sensors (Table 1). The improvement in H<sub>2</sub>O<sub>2</sub> detection performance of MnO<sub>2</sub> NFs/rGO/GCE can be attributed to the increasing conductivity by adding rGO and good nano-enzyme activity of MnO<sub>2</sub>.

**Table 1.** A comparison of proposed method of sensing H<sub>2</sub>O<sub>2</sub> with previous electrochemical studies.

Material/electrode	Linearity Range ( μ M)	LOD ( μ M)	Ref.
Au-MnO <sub>2</sub> -rGO nanocomposite	0.1–22 and 22–12600	0.05	34
flower-like MnO <sub>2</sub>	80-12780	20	35
f-MWCNTs/MnO <sub>2</sub>	5-4530	0.952	36
Mn <sub>2</sub> CuO <sub>4</sub>	0.036 -9300	0.013	37
Co <sub>3</sub> Mn-LDH	110-1200	86	38
COF <sub>ETTA-TPAL</sub> -Fc(COOH) <sub>2</sub>	1.1–500	0.009	39
rGO/MnO <sub>2</sub> nanozyme	0.02-5 and 5-800	0.015	This work

### 3.4 Repeatability, stability and selectivity

In order to evaluate the repeatability of the prepared sensor, the relative standard deviation (RSD) of the sensor for determination of 5 mM H<sub>2</sub>O<sub>2</sub> was calculated for 5 consecutive experiments in pH 7.4 phosphate buffer and RSD <3.84% (n = 4). This indicates that the modified electrode has good repeatability. Five electrodes were prepared using the same preparation process to evaluate the reproducibility of the sensor. The RSD current was 3.5% for 5 mM H<sub>2</sub>O<sub>2</sub>, showing acceptable reproducibility. The storage stability of the method is further studied. The MnO<sub>2</sub> NFs/rGO/GCE was stored at 4 °C and the current response was tested to maintain about 93.6% of the original signal over 30 days, indicating significant long-term stability. The anti-interference ability of the electrodes was demonstrated by amperometric method using L-cystine (L-cys), uric acid (UA) and ascorbic acid (AA). As expected, MnO<sub>2</sub> NFs/rGO modified GCE exhibited a low response when each interfering substance was continuously added, but a significant current was observed when 0.04 mM H<sub>2</sub>O<sub>2</sub> was added. These results indicate that the sensor has a unique selectivity for H<sub>2</sub>O<sub>2</sub>.



### 3.5 Real sample detection

The practicality of the developed sensor in the actual sample was verified by detecting H<sub>2</sub>O<sub>2</sub> in the urine (as real samples) using standard addition method under the optimal conditions. The urine was diluted with 0.1 M PBS (pH 7.4). The calibration curve was used to calculate the content of H<sub>2</sub>O<sub>2</sub> in the sample, and the recovery was between 98.66 and 101.48 %. The RSD was below 4.17% (n = 3).

## 4. CONCLUSIONS

The two-dimensional enzyme-like material MnO<sub>2</sub> NFs was synthesized by biomineralization method, and rGO was hybridized to improve the electron conduction performance of the electrode surface. Based on the hybridized material, a sensitive electrochemical sensor for H<sub>2</sub>O<sub>2</sub> was constructed. The sensor can directly and rapidly read the content of H<sub>2</sub>O<sub>2</sub> in a wide concentration range, and can be used in environmental monitoring and biological analysis. It is not only suitable for the detection of trace H<sub>2</sub>O<sub>2</sub> concentration in vivo and in vitro in biological environment, but also suitable for monitoring the inhibited enzymatic reaction when H<sub>2</sub>O<sub>2</sub> concentration is too high. In addition, the enzyme-like activity of MnO<sub>2</sub> NFs will be important for the design of enzymatic systems and for further potential application in anti-inflammatory, anti-tumor and maintenance of metabolic balance.

## ACKNOWLEDGEMENTS

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