Nonenzymatic electrochemical assay for hydrogen peroxide detection based on green synthesized MnO$_2$ nanosheets

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Abstract

In this study, manganese oxide (MnO$_2$) nanosheets were successfully prepared with a green and cost-effective method by using Gum Arabic as they both reduce agent and template in the absence of other additives. The composition, crystalline structure and morphology of the synthesized MnO$_2$ nanosheets were studied using different characterization methods. The TEM and FESEM images show that the prepared MnO$_2$ exhibits wrinkle-like nanolayer morphology. Then, the performance of the synthesized MnO$_2$ was investigated for electrochemical detection of hydrogen peroxide (H$_2$O$_2$). The electrochemical sensing of H$_2$O$_2$ based on MnO$_2$ nanosheets modified carbon ionic liquid electrode (MnO$_2$/CILE) was constructed by a pasting method and its electrocatalytic performance was studied using cyclic voltammetry and amperometry. Compared with the bare CILE, the MnO$_2$/CILE electrode exhibited good electrocatalytic behavior for H$_2$O$_2$ reduction in alkaline solutions. The fabricated nonenzymatic H$_2$O$_2$ sensor also showed a linear relationship over an extensive concentration range of 5.0 μM to 10.0 mM ($r^2 = 0.998$) with a LOD of 1.0 μM and a response time of fewer than 5 s. In addition, the developed electrochemical sensor displayed excellent anti-interfering ability, good recovery and also good reproducibility on the H$_2$O$_2$ detection in urine samples. The simple synthesis of MnO$_2$ nanosheets and good electrocatalytic activity reveal the promising usefulness of the fabricated sensor for detection of H$_2$O$_2$.

1. Introduction

Manganese oxide (MnO$_2$) nanostructures have been regarded as one of the most favorable inorganic materials due to its abundance, low cost, and fascinating catalytic properties [1]. Manganese oxide is among the strongest oxidants and has numerous polymorphic shapes such as α, β and γ type which show distinctive physical and chemical properties [2]. According to literature, synthesis methods such as hydrothermal synthesis [3], sol gel process [4], electrodeposition method [5] and template method [6] have been developed to obtain MnO$_2$ with a desired morphology. So far, MnO$_2$ nanostructures with various morphologies like nanorods [7], nanoflowers [8], nanosheets [9], nanospheres [10] and so on have been successfully synthesized. MnO$_2$ nanoparticles have been employed in various domains including catalysis [11], energy storage [9, 12], electrochemical study [13], and biological applications [14]. In recent years, MnO$_2$ nanostructures have been extensively explored for biological applications such as biosensing [15], cell imaging [16], and drug delivery [16, 17]. Also they have been widely studied in photocatalysis [18] and the oxidative degradation of organic/inorganic contaminants [19].

Due to good electrocatalytic properties and wide potential window, MnO$_2$ nanostructures have been extremely applied in the field of electrochemical sensing of various analytes like dopamine [20], glucose [21], hydrazine [22] and hydrogen peroxide [23–25]. However, the restrictions such as low electrical conductivity and mechanical instability severely hinder their applications as electrode materials [26]. Hence, conductive materials such as graphene nanosheets [27], graphite nanofibers [7] and carbon nanotube [28] have been hybridized with
MnO₂ in order to maximize their electrochemical performance. This helps form hybrid or composite nanostructures, reduce the electrical resistance, and improve sensing performance.

Hydrogen peroxide (H₂O₂) is a prominent biomolecule that shows a crucial role in pharmaceutical, environmental, textile, and food industries. H₂O₂ is most frequently used as a universal oxidizing factor in different areas such as the degradation and elimination of pollutants from waste water [29]. It has also been considered as an important reactive oxygen species (ROS) which is generated as a by-product from most oxidases in cell and plays a vital role in different cellular signaling transductions [30]. Moreover, excess of H₂O₂ in cell leads to damage in the DNA, cytokines, and defective cell growth [31]. In spite of other applications, H₂O₂ is utilized as disinfectant agent in food industry such as a milk treatment [32]. Therefore, the selective and sensitive determination of H₂O₂ with a simple, green and rapid analytical method has aroused considerable concerns in numerous applications. H₂O₂ is also produced in most enzymatic reactions; thus, its measurement is necessary for the evolution of biosensors. Among various techniques for the accurate determination of H₂O₂, electrochemical methods have been accepted as an efficient quantification system with high selectivity and sensitivity and fast response reliability. The electrochemical sensing of H₂O₂ were developed based on enzymatic [33] and nonenzymatic [23–25] sensors. However, enzymatic-based sensors such as horseradish peroxidase and hemoglobin are unstable, high cost and require complex immobilization processes that limit their application [33, 34]. In order to overcome those obstacles, the developments of nanostructure materials for nonenzymatic detection of H₂O₂ have gained growing attention. As one of the most applied metal oxide nanostructures, MnO₂ has received significant attention for H₂O₂ determination [35–38]. Other functionalized MnO₂ nanoparticles with Ag nanoparticles have been demonstrated to be appropriate for electrochemical sensing of H₂O₂ [39, 40].

Gum Arabic (GA) is known as a natural, high soluble, nontoxic and highly branched polysaccharides which are derived from exudates of Acacia Senegal tree. GA as a natural polymer has various applications in the food, cosmetic and pharmaceutical productions. GA is a highly heterogeneous material which is composed of carbohydrate moieties consisting of galactose, rhamose, arabinose, gluconic acid, 4-0-methylglucuronic acid and small fraction of arabinogalactan protein (AGP, 10.4% of total), and glycoprotein (≥1% of total) [41]. Due to the multiple functional groups such as amine and carboxylate in GA and its good steric stabilization effect, it has been extensively applied as a stabilizing and reducing factor in the synthesis of nanoparticles. Typically, GA is used in the synthesis of various nanoparticles such as gold [42], CuO/Cu₂O [43], silver [44], and ZnS [45] nanoparticles. In addition, GA can be used as a magnetic nanoparticles coating to prevent destabilization and agglomeration and produce reactive functions on the surface of nanoparticles [46]. In this study, ultrathin MnO₂ nanosheets were successfully prepared via a simple and green process with Gum Arabic as a both reactive template and reducing agent. The synthesis strategy developed here provides a simple and facile method to prepare MnO₂ nanosheets in large scale.

In previous reports carbon ionic liquid electrode (CILE) was introduced as a high performance electrode with special properties such as high rate of electron transfer [47]. Furthermore, CILE modified with various nanoparticles such as gold [48], palladium [49], copper hydroxide [50] nanoparticles and so on showed superior electrochemical properties and has been mainly used in the detection of different analytes. However, CILE electrode shows a weak response towards H₂O₂ reduction. Therefore, MnO₂ nanosheets-modified carbon ionic liquid electrode was constructed as an electrochemical sensor. The performance of MnO₂ nanosheets modified with carbon ionic liquid electrode (MnO₂/CILE) was investigated for nonenzymatic H₂O₂ detection in alkaline solution. The proposed sensor gave a fast current response, good sensitivity, wide linear range, and eligible selectivity.

2. Experimental

2.1. Materials

Hydrogen peroxide (H₂O₂), potassium permanganate (KMnO₄), sodium hydroxide (NaOH), glucose, sodium chloride (NaCl), 1-iodooctane, ethanol, pyridine, diethyl ether and ascorbic acid (AA) were purchased from Merck. Ammonium hexafluorophosphate, graphite powder, dopamine (DA), uric acid (UA) and Gum Arabic (GA) were obtained from Sigma Aldrich. Octyl pyridinium hexafluorophosphate ionic liquid (OPyPF₆) was prepared as described previously [47]. All chemicals were used as received. All solutions were prepared with deionized water.

2.2. Apparatus

The surface morphology characterization of the nanomaterials was studied using field emission electron microscopy ((Hitachi S-4160 FESEM) and high resolution transmission electron microscopy (JEOL, JEM-2100T, 200 KV). The semi-quantitative chemical analysis of as-prepared nanomaterials was conducted by energy-dispersive x-ray spectroscopy (EDX). The structure and crystalline phase of the nanoparticles was
analyzed by x-ray diffraction pattern (XRD, D8, Advance, Bruker, AXS diffractometer) with Cu Kα irradiation ($\lambda = 1.5418$ Å) in the range 20–80. A particle size analyzer (Horiba LB-550) was used to investigate the size distribution of the nanoparticles. The study of electrochemical behavior was performed on Autolab PGSTAT204-Compact and modular potentiostat/galvanostat system equipped with NOVA software. Cyclic voltammetry and amperometric experiments were carried out using a conventional three electrode system in 0.1 M NaOH solution. CILE and MnO$_2$/CILE (1.8 mm in diameter) were used as the working electrodes, a platinum disk as the counter electrode and Ag/AgCl as the reference electrode at ambient conditions.

2.3. Synthesis of MnO$_2$ nanosheets

MnO$_2$ nanosheets were synthesized through a simple and green method as follows: firstly, 100 mg of Gum Arabic was dispersed at 20 ml of deionized water and the solution was stirred for 10 min. Then, 30 mg of KMnO$_4$ was dissolved in 20 ml of water and was added to the above solution under constant stirring. The mixture was heated at 60 °C for 5 h. After the completion of reaction, the color of solution changed from purple into dark brown. The as-prepared MnO$_2$ nanosheets were collected and washed for several times by centrifugation using deionized water and ethanol. Then, they were dried at 50 °C.

2.4. Preparation of electrode

CILE electrode was made by hand-mixing of graphite powder with ionic liquid (OPyPF$_6$) with ratio of 50:50 [47]. The MnO$_2$/CILE electrode was constructed by mixing MnO$_2$ nanosheets: ionic liquid: graphite powder with a ratio of 5%: 45%: 50% w/w ratio, respectively. The paste was packed into the Teflon holder with the diameter of 1.8 mm and copper wire was used to prepare the electrical contact. The electrode surface was renewed mechanically by polishing the electrode on the surface of smooth paper.

3. Results and discussion

3.1. Characterization of nanosheets

In this study, MnO$_2$ nanosheets were produced with reduction of potassium permanganate by GA. The product was characterized by EDX, XRD, FESEM, TEM and DLS methods. To study the effect of GA on the generation of MnO$_2$ nanosheets, the synthesis process was performed in the presence and absence of GA (2.5 g l$^{-1}$) at 60 °C. In the presence of GA, the color of solution changed from purple into dark brown and the reaction was completed after 5 h but in the absence of GA, no color change was observed even after 24 h and the reduction of permanganate was not occurred. Thus, ultrathin MnO$_2$ nanosheets were efficiently synthesized in the presence of Gum Arabic as a both reactive template and reducing agent. The formation of MnO$_2$ nanosheets was found to be dependent on the appropriate concentration of the KMnO$_4$. The effect of the different amounts of KMnO$_4$ (10, 20, 30, 50 and 100 mg) was investigated in the presence of 2.5 mg l$^{-1}$ of GA. At low concentrations of KMnO$_4$ (0.25, 0.50 and 0.75 g l$^{-1}$) a brown colloidal stable MnO$_2$ nanosheets were obtained but at higher concentrations of KMnO$_4$ (1.25 and 2.50 g l$^{-1}$) the nanosheets were aggregated and finally a brown precipitate was formed. Therefore, the amount of 30 mg of KMnO$_4$ was selected for synthesis of MnO$_2$ nanosheets.

Also, the effect of temperature on the synthesis process of MnO$_2$ nanosheets was examined by changing the temperature from 25 to 60 °C. The rate of the reaction are strongly dependent on the temperature. At 25 °C, the process was completed after 72 h. By increasing the temperature, the reduction reaction rate increased sharply and at 60 °C the color of the solution changed from purple to brown after 5 h. Therefore, synthesis of MnO$_2$ nanosheets was performed at 60 °C. Higher temperatures were not tested due to higher evaporation rates.

TEM images (figures 1(A)–(C)) were employed at different magnification to identify the morphology of the synthesized MnO$_2$ nanostructures. The TEM images clearly displayed 2D MnO$_2$ layered nanosheets with uniform morphology. The obtained MnO$_2$ nanosheets exhibited extra thin wrinkle-like nanolayer with only a few nanometers in thickness. XRD technique was utilized to identify the crystalline phase of MnO$_2$ nanosheets under our synthesis condition. Figure 1(D) exhibits the broad and weak diffraction peaks at 12.2, 25.2, 37.2 and 65.7 of MnO$_2$ nanosheets represent the (001), (002), (−111) and (020) significant reflection planes, respectively. The diffraction peaks of nanosheets could be perfectly categorized to the birnessite type MnO$_2$ (JCPDS 80–1098). The XRD pattern of birnessite type MnO$_2$ with broad and weak diffraction peaks also were recorded in previous reports [23, 51]. The XRD pattern with broad peaks and no other characteristic reflections confirms the formation of MnO$_2$ nanostructures with high purity.

Furthermore, DLS was exploited to analyze the size distribution of MnO$_2$ nanosheets (figure 2(A)). DLS analysis indicate that the average particle size of MnO$_2$ nanosheets is about 70 nm and a size distribution of nanoparticles is lower than 100 nm. The composition of as-synthesized nanosheets was confirmed by EDX analysis and the obtained EDX pattern is shown in figure 2(B). The EDX spectrum revealed the existence of manganese, oxygen, and carbon element in the structure of nanosheets. The FESEM image and elemental
Figure 1. (A)–(C) HRTEM images and (D) XRD pattern of synthesized MnO₂ nanosheets.

Figure 2. (A) DLS diagram, (B) EDX spectra and (C) elemental mapping analysis of synthesized MnO₂ nanosheets.
mapping analysis of as prepared MnO₂ nanosheets were shown in figure 2(C). The elemental analysis shows the uniform distribution of the elemental constituents throughout the nanostructure.

3.2. The study of electrocatalytic performance of MnO₂ nanosheets

The electrocatalytic performance of MnO₂ nanosheets modified with carbon ionic liquid electrode (MnO₂/CILE) was examined by cyclic voltammetry at the scan rate of 50 mV s⁻¹ in 0.1 M NaOH solution. Figure 3(A) displays the typical cyclic voltammograms of bare CILE and MnO₂/CILE (MnO₂ 5%) in N₂-saturated NaOH solution with and without of H₂O₂. In the absence of H₂O₂, no apparent reduction peak was monitored for both electrodes (figure 3(A), Curve a, c). The background current of MnO₂/CILE (figure 3(A), curve c) was higher than that of bare CILE, demonstrating that MnO₂ nanosheets improve the electroactive surface area. When 1.0 mM H₂O₂ was added to the solution, MnO₂/CILE (figure 3(A), curve d) displayed a high reduction peak current at −0.3 V while at bare CILE (figure 3(A), curve b), the current slightly increased. This result suggests that the MnO₂/CILE has efficient electrocatalytic properties toward H₂O₂ reduction. The amount of MnO₂ nanosheets in the construction of modified carbon ionic liquid electrode was optimized. Figure 3(A) (curve d) exhibits the cyclic voltammogram of MnO₂/CILE that contain of 5% of MnO₂ nanosheets. Figure 3(B) shows the cyclic voltammograms of MnO₂/CILE with different amounts of MnO₂ nanosheets (MnO₂ 10% and 20%) in NaOH solution with and without of 1.0 mM H₂O₂. By increasing the amount of MnO₂ nanosheets, both the reduction current of H₂O₂ and the background current increased and the

![Graph](image-url)
net current for reduction of H2O2 was not changed dramatically. Therefore, the amount of 5% of MnO2 nanosheets was selected as the optimum ratio for determination of H2O2 with good sensitivity.

According to the previous studies, it seems that the reduction of MnO2 to Mn(OH)2 compounds with H2O2 and then oxidation of Mn(OH)2 to MnO2 is the possible mechanism of electrocatalytic reduction of H2O2 at MnO2 modified electrodes [39].

\[
\text{MnO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{Mn(OH)}_2 + \text{O}_2
\]

(1)

\[
\text{Mn(OH)}_2 + 2\text{OH}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O} + 2\text{e}^-
\]

(2)

The influence of scan rate on the current of H2O2 reduction peak at MnO2/CILE was studied by cyclic voltammetry in the 5–500 mVs\(^{-1}\) interval. As can be observed from figure 4, with increasing the scan rate, the reduction current increased linearly with the square root of scan rate with the high correlation coefficient of \(r^2 = 0.993\) (figure 4 inset). The reduction of H2O2 at MnO2/CILE involves a diffusion controlled process.

In order to examine the sensitivity of the MnO2/CILE toward H2O2 detection, the amperometric analysis was used to evaluate the linearity between the current responses of fabricated electrode and H2O2 concentrations. Figure 5 displays the amperometric response of the MnO2/CILE with consecutive addition of H2O2 in 0.1 M NaOH under a practical potential of −0.4 V. The addition of H2O2 resulted in a clear increase of the reduction current. In each addition of H2O2, the time required to achieve the steady-state current is fewer than 5 s, representing the rapid amperometric response of the MnO2/CILE. The H2O2 concentrations and their corresponding current responses show an excellent linear relationship in the wide range from 5.0 \(\mu\text{M}\) to 10.0 mM with a correlation coefficient of 0.998 (figure 5 inset). The reduction of H2O2 at MnO2/CILE involves a diffusion controlled process.

In biological fluids, there are several types of interfering compounds that coexist with H2O2. For the nonenzymatic sensors, detecting the electrochemical signals from the interfering compounds has important role in the practical analysis. The selectivity of MnO2/CILE was investigated by sequential addition of H2O2 and interference species such as glucose, uric acid, dopamine and ascorbic acid and comparing their current response in N2-saturated 0.1 M NaOH. The amperometric response in figure 6 reveals that the sequential augmentation of each interfering compounds exhibited the negligible current response at the MnO2/CILE while an apparent current response was observed toward H2O2. This suggests the high selectivity of MnO2/CILE for H2O2 detection.

Besides, for investigation of the the repeatability of the reduction current of fabricates sensor, the response current in seven successive determinations on one electrode was measured at a H2O2 concentration of 1 mM for MnO2/CILE. The relative standard division (RSD) was calculated to be 2.7%. The RSD value of the response current in seven successive determinations on one electrode was measured at a H2O2 concentration of 1 mM for MnO2/CILE.
Figure 5. (A) Amperometric response of the MnO2/CILE upon successive injection of hydrogen peroxide to 0.1 M N2-saturated NaOH solution at −0.4 V. Inset: the corresponding calibration plot of steady-state currents against concentrations of H2O2. (B) The magnification of the first part of the amperogram.

Table 1. Comparison of the electrocatalytic behavior of MnO2/CILE for hydrogen peroxide reduction with some of the MnO2 based reported electrodes.

| Electrode                        | Linear range    | Sensitivity (μA mM⁻¹ cm⁻²) | LOD (μM) | Potential (V) | References |
|----------------------------------|-----------------|-----------------------------|----------|---------------|------------|
| MnO2/MWCNTs/Ta                   | 3 μM–3025 μM    | 83.3                        | 0.04 μM | −0.75         | [37]       |
| Au/MnO2/ERGO/CF                 | 0.05 mM–14.2 mM | 0.167 mA cm⁻² mM⁻¹          | 2.0 μM  | −0.4          | [38]       |
| NGNF/MnO2                        | 0.1 mM–11 mM    | 1096                        | 1.25 μM | −0.6          | [7]        |
| MnO2/rGONRs                      | 0.25 μM–2455 μM| —                           | 0.071 μM| 0.78          | [3]        |
| PANI-MnO2/GCE                    | 5–50 μM, 0.05–10 mM | 403.3, 152.1 | 0.8 μM | −0.45         | [23]       |
| f-MWCNTs/MnO2                    | 5 μM–4530 μM   | 219.05 μA mM⁻¹             | 0.952 μM| −0.65         | [25]       |
| MnO2/nanosheets/GCE              | 0.025–2 μM, 10–454 μM | 3261 mAM⁻¹ cm⁻²          | 5 nM    | −0.6          | [24]       |
| Ag–MnO2–MWCNTs                  | 3 μM–10.4 mM    | 82.5                        | 1.7 μM  | −0.6          | [52]       |
| MnO2/ERGO                        | 5 μM–600 μM    | 36.2                        | 0.8 μM  | −0.4          | [53]       |
| MnO2–ERGO                       | 0.1 mM–45.4 mM | 59.0                        | 10 μM   | −0.4          | [54]       |
| Au–MnO2–rGO                     | 0.1–22 μM, 0.022–12.6 μM | 980, 101.6 | 0.05 μM | −0.2          | [55]       |
| MnO2/CILE                        | 5.0 μM–10 mM   | 162.8                       | 1.0 μM  | −0.3          | This work  |

a: Tantalum; ERGO/CF: Electrochemical reduced graphene oxide/carbon fiber; NGNF: Nitrogen doped graphite nanofibers; rGONRs: Reduced graphene oxide nanoribbons; PANI: Polyaniline; f-MWCNTs: functionalized multi-walled carbon nanotubes; NFs: Nanoflakes;
current in six modified electrodes, which were independently fabricated, was found to be about 3.5%, representing the excellent reproducibility of modified electrode. Furthermore, the stability of MnO₂/CILE was also investigated after one month. The results showed the current response to H₂O₂ remained 93% of its initial value, indicating the adequate stability of the prepared electrode.

The concentration of H₂O₂ in the urine samples were determined in order to examine the feasibility of the fabricated sensor based on MnO₂/CILE for practical analysis. 0.5 ml of the urine sample was diluted with 9.5 ml of 0.1 M NaOH solution and the known concentrations of H₂O₂ were regularly added and the reduction currents were obtained at −0.4 V by amperometry. The measurement results are summarized in table 2. The developed sensor displayed a good recovery in the range of 97%–106%, suggesting that the fabricated H₂O₂ sensor is reliable and has potential in the practical analysis of real samples.

4. Conclusion

In this study a green and reliable method was established for the synthesis of MnO₂ nanosheets and then the prepared nanosheets were applied to construct a nonenzymatic H₂O₂ sensor. MnO₂/CILE electrode has great ability in electrocatalyzing the reduction of H₂O₂ and can be utilized for amperometric detection of H₂O₂. It displays high sensitivity, extensive linearity and excellent selectivity against common interfering substances in H₂O₂ determination. Also, the fabrication method was simple and convenient. The suggested sensor was effectively used for the practical detection of H₂O₂ in the urine.

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Conflict of interest

The authors declare no conflict of interest, financial or otherwise, with regards to this paper.

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