Electrochemical Synthesis of a Binary Mn-Co Oxides Decorated Graphene Nanocomposites for Application in Nonenzymatic H\textsubscript{2}O\textsubscript{2} Sensing

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In this work, binary metallic oxides of MnO\textsubscript{2}-Co\textsubscript{3}O\textsubscript{4} nanocomposite was electrodeposited on graphene oxide (GO) modified electrode by a facile and one-step electrochemical method. The resultant MnO\textsubscript{2}-Co\textsubscript{3}O\textsubscript{4}/graphene (MnO\textsubscript{2}-Co\textsubscript{3}O\textsubscript{4}/GP) electrode was characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) to study its morphology and element composition. The as-prepared MnO\textsubscript{2}-Co\textsubscript{3}O\textsubscript{4}/GP modified electrode was employed in fabricating a nonenzymatic H\textsubscript{2}O\textsubscript{2} electrochemical sensor. The cyclic voltammetry (CV) and amperometric experiments demonstrated that the MnO\textsubscript{2}-Co\textsubscript{3}O\textsubscript{4}/GP composites exhibited superior electrocatalytic activities toward oxidation of H\textsubscript{2}O\textsubscript{2} to the monometallic oxide decorated graphene materials (MnO\textsubscript{2}/GP and Co\textsubscript{3}O\textsubscript{4}/GP). The developed nonenzymatic H\textsubscript{2}O\textsubscript{2} sensor showed a high sensitivity of 53.65 \( \mu \)A mM\textsuperscript{-1} cm\textsuperscript{2}, a wide linear range of 5 \( \mu \)M-1.2 mM, and a detection limit of 0.8 \( \mu \)M (S/N = 3). In addition, good selectivity, high detection accuracy and acceptable stability were also obtained for the present sensor. Therefore, this work will open an avenue to construct high-performance electrode materials and expand their applications in various fields such as catalysis and biosensor.

Keywords: Electrochemical; Graphene; binary metallic oxides; Hydrogen peroxide

1. INTRODUCTION

In recent years, growing research interest has been paid to the design and preparation of bimetallic or bimetallic oxides/hydroxides nanomaterials due to the fact that diverse properties and even better performance than their corresponding monometallic counterparts can be generated under the coordination effect of these two nanobuilding blocks. It was currently demonstrated that the
hybrids of Cu-Co alloy dendrites [1], Ni-Co nanostructures [2], Ni-Cu-oxide nanowire arrays [3] and NiOx/MnOx nanoparticles [4] exhibited superior performance to both their corresponding individual components toward oxidation of glucose or hydrogen peroxide (H2O2) in terms of excellent electrocatalytic activities and high detection sensitivity. The nanohybrid of Co3O4@MnO2 [5] has been reported to display a significant increase (4-10 times) in areal capacitance compared to single Co3O4 nanomaterials. Ni5Co2x(OH)6x/graphene hybrids [6] have been demonstrated to exhibit improved specific capacitance along with rate capability in comparison with those of Ni(OH)2 or Co(OH)2 materials on graphene support. In addition, for electrochemical biosensor application, the Ni5Co2x(OH)6x/graphene nanohybrid electrode exhibits excellent performance towards the nonenzymatic detection of H2O2.

As important transition metal oxides materials, MnO2 and Co3O4 have been extensively explored as electrochemical H2O2 sensors [7-13], driven by their distinct electrocatalytic activity to oxidation of H2O2, and the characteristic properties of these materials with high abundance, environmental friendly and low cost. However, MnO2 suffers from poor electric conductivity (10^{-5}–10^{-6} S cm^{-1}) [14,15], which limits its electron transfer capability and thus its electrochemical performance. Through integration of MnO2 with higher conducive Co3O4, the improved electrical conductivity along with electrochemical activity is expected to demonstrate. Importantly, the attributes of MnO2 and Co3O4 in this binary composites can be combined together to form highly efficient electrocatalyst. To further enhance the electric conductivity of this MnO2-Co3O4-based electrochemical sensing material, the effective strategy is to introduction of various carbon materials like carbon foam [15], graphene or its derivatives [16-19], carbon nanotube [20-23] and ordered mesoporous carbon (OMC) [24] as support materials. Among these carbon materials, graphene (GP), with a single layer of sp² hybridized carbon atoms, has arisen widespread interest in electrochemical applications [25,26]. Accordingly, a binary Mn-Co oxides decorated graphene (MnO2-Co3O4/GP) composite is expected to exhibit high electrocatalytic activities and shows prospects for application in fabricating highly efficient H2O2 sensors.

Inspired by the unique properties of MnO2-Co3O4/GP composites, herein, a new type of a binary Mn-Co oxides decorated graphene nanocomposite was fabricated by a facile and green one-step electrochemical method and utilized directly as nonenzymatic sensors for H2O2 detection. The MnO2-Co3O4/GP composite was firstly prepared by solution-casting of graphene oxide (GO) nanosheets on surface of glassy carbon electrode (GCE), followed by simultaneous electrochemical reduction of GO and electrodeposition of MnO2-Co3O4 nanoparticles on it. To our best knowledge, it is the first successful attempt to synthesize MnO2-Co3O4/GP composite by means of one-step electrochemical reduction method. The MnO2-Co3O4/GP composite exhibited excellent electrocatalytic activities toward oxidation of H2O2, thus the resultant sensors presented low detection limit, high sensitivity, wide linear range and rapid response towards the detection of H2O2. Consequently, the proposed strategy for the fabrication of binary metal oxide/graphene composites in this work will provide new insights on designing facile and highly efficient electrode materials for various applications.
2. EXPERIMENTAL SECTION

2.1. Reagents and materials

GO was supplied by Nanjing XFNANO Materials Tech Co., Ltd. Mn(CH$_3$COO)$_2$·4H$_2$O, glucose, H$_2$O$_2$, ascorbic acid (AA), dopamine (DA), uric acid (UA), L-tyrosine were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) without the further purification. K$_2$HPO$_4$ and NaH$_2$PO$_4$ were used to prepare the supporting electrolyte of 0.1 M phosphate buffer solution (PBS, pH 7.0). Deionized water (18.2 MΩ cm) was prepared by a Milli-Q water purification system.

2.2. Apparatus

The surface morphology and the element component of synthesized modified electrode was characterized by field emission scanning electron microscopy with EDX equipped (FESEM, JSM-6701F, Japan). Electrochemical measurements were performed on a CHI 660D electrochemical analyzer (CHI Instruments Shanghai, China) with a conventional three-electrode system. The MnO$_2$-Co$_3$O$_4$/GP composite modified glassy carbon electrode (MnO$_2$-Co$_3$O$_4$/GP/GCE) was used as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a Pt wire as counter electrode.

2.3. Electrochemical preparation of MnO$_2$-Co$_3$O$_4$/GP composite modified electrode

Prior to modification, a bare glassy carbon electrode (diameter of 3 mm) was carefully polished with 1.0, 0.3 and 0.05 μm alumina slurries respectively to obtain a mirror-like surface. The polished electrode was ultrasonicated in ethanol and deionized water in sequence. Then, 10 μL 1 mg/mL GO aqueous solution was coated onto electrode surface, and allowed to dry to obtain GO modified electrode (GO/GCE). The obtained GO/GCE was subsequently immersed into deposition solutions containing with 0.1 M Na$_2$SO$_4$+5 mM CoCl$_2$+5 mM Mn(CH$_3$COO)$_2$, and cycled under the potential window from -1.5 V to 0 V for 10 cycles. Through this electrochemical process, GO was electrochemically reduced to GP, meanwhile, Mn-Co oxides was electrodeposited on GP surface to form MnO$_2$-Co$_3$O$_4$/GP composites modified electrode (MnO$_2$-Co$_3$O$_4$/GP/GCE). For comparison, The electrodes modified with GP, and monometallic Co or Mn oxides decorated GP were separately prepared by immersing the GO/GCE into deposition solutions of 0.1 M Na$_2$SO$_4$ without (for GP/GCE) and with only 5 mM CoCl$_2$ (for Co$_3$O$_4$/GP/GCE) or 5 mM Mn(CH$_3$COO)$_2$ (for MnO$_2$/GP/GCE) involved, respectively, according to the same electrochemical method described above.

2.4 Electrochemical sensing of H$_2$O$_2$

The electrochemical behavior of H$_2$O$_2$ was investigated by cyclic voltammetry (CV) technique in the potential range of -0.4~0.8 V. The amperometric sensing of H$_2$O$_2$ was performed at an applied potential of +0.5 V by adding various aliquots of H$_2$O$_2$ stock solution into electrochemical cell with 10
mL 0.1 M PBS (pH 7.0) contained. The PBS solution was kept continuously stirred to make the concentration of added H₂O₂ uniform. Current-time curve was performed to record the steady state current response with interval of 50 s for every addition of H₂O₂.

3. RESULTS AND DISCUSSION

3.1. CV responses for the formation of the modified electrodes and the morphology characterization

Fig. 1 exhibits the CV responses for the formation processes of thus fabricated GP, Co₃O₄/GP, MnO₂/GP, and MnO₂-Co₃O₄/GP modified electrode. As seen from Fig. 1a, at a scanning potential range from 0 to -1.5 V, the CVs of GO/GCE in solutions of 0.1 M Na₂SO₄ present a large cathodic peak current at around −1.3 V vs. SCE in the first cycle. In the subsequent cycles, the cathodic peak current significantly decreases and even disappears, which indicates that the surface-oxygenated groups of GO have been quickly reduced to form graphene. This phenomenon is consistent with previous results [27,28]. When the GO/GCE was immersed into 0.1 M Na₂SO₄ solution with 5 mM CoCl₂ involved, a new cathodic peak at -1.0 V corresponding to reduction of Co²⁺ was observed in the CVs of Fig. 1b, apart from the cathodic peak at -1.3 V related to GO reduction. In the presence of dissolved oxygen, the deposited Co was oxidized to Co₃O₄. By using this CV method, the previous works also demonstrates the successful formation of Co₃O₄ on electrode surface [11,29-31]. Recently, the electrochemical method, such as CV or constant applied potentials, has also been widely used for electrodeposition of MnO₂ materials from precursor of Mn²⁺ [19,20,24]. Here, the CV method was used. As can be seen from Fig. 1c, another new cathodic peak at about -0.9 V corresponding to reduction of Mn²⁺ appeared in the CVs of GO/GCE with deposition solutions of 0.1 M Na₂SO₄+5 mM Mn(Ac)₂, apart from the cathodic peak at -1.3 V corresponding to GO reduction. The obtained CV curves are in good agreement with that of Dong’s work in which the one-step electrochemical approach is developed for synthesis of graphene/MnO₂ nanowall hybrids [32]. Therefore, the hybrids of MnO₂/GP are estimated to be formed on electrode surface. Interestingly, with the GO/GCE immersed into the deposition solutions of 0.1 M Na₂SO₄+5 mM CoCl₂+5 mM Mn(Ac)₂, the obtained CV curves (Fig. 1d) integrate the feature of the respective CV curves of Fig. 1b and c.
Figure 1. The CV responses of GO/GCE in deposition solutions of (a) 0.1 M Na$_2$SO$_4$, (b) 0.1 M Na$_2$SO$_4$+5 mM CoCl$_2$, (c) 0.1 M Na$_2$SO$_4$+5 mM Mn(Ac)$_2$ and (d) 0.1 M Na$_2$SO$_4$+5 mM CoCl$_2$+5 mM Mn(Ac)$_2$ for 10 cycles to prepare the GP/GCE, Co$_3$O$_4$/GP/GCE, MnO$_2$/GP/GCE and MnO$_2$-Co$_3$O$_4$/GP/GCE, respectively.

Figure 2. FESEM images of the prepared MnO$_2$/GP/GCE (a), Co$_3$O$_4$/GP/GCE (b), MnO$_2$-Co$_3$O$_4$/GP/GCE (c) and the EDX spectra of MnO$_2$-Co$_3$O$_4$/GP/GCE.

Three distinct cathodic peaks at −1.3, −1.0 and −0.9 V correspond to the reduction of GO, Co$^{2+}$ and Mn$^{2+}$, respectively, to obtain the resulting MnO$_2$-Co$_3$O$_4$/GP modified electrode. The above results suggest that the proposed one-step electrochemical method is feasible for preparation of binary Mn-Co oxides decorated graphene nanocomposites. The surface morphology of the prepared MnO$_2$/GP/GCE,
Co$_3$O$_4$/GP/GCE, MnO$_2$-Co$_3$O$_4$/GP/GCE was characterized by FESEM images, the results of which were displayed in Fig. 2.

As can be seen from Fig. 2a, the wrinkled surface of the RGO film is decorated with flower-like MnO$_2$ nanoparticles with diameters ranging from 50 to 100 nm. For Co$_3$O$_4$/GP/GCE (Fig. 2b), about 20-30 nm Co$_3$O$_4$ nanoparticles were decorated onto RGO surface. However, for MnO$_2$-Co$_3$O$_4$/GP/GCE, more densely and aggregated nanoparticles with diameters of about several tens nanometer sized nanoparticles were electrodeposited onto RGO surface. From the EDX result presented in Fig. 2d, the elements of C, O, Mn and Co were all observed, indicating that the MnO$_2$-Co$_3$O$_4$/GP nanocomposites have been successfully synthesized on electrode surface.

3.2. Electrochemical behavior of H$_2$O$_2$ at the Mn-Co oxides/GP nanocomposites modified electrode

In order to verify the electrocatalytic activity of the synthesized materials for H$_2$O$_2$ oxidation, the CV experiments toward H$_2$O$_2$ was performed. Fig. 3a shows CV responses of different modified electrodes in 5 mM H$_2$O$_2$ at pH 7.0 PBS solution. As observed, the oxidation of H$_2$O$_2$ starts from a potential of +0.4 V at the three electrodes of GP/GCE, MnO$_2$/GP/GCE and Co$_3$O$_4$/GP/GCE, and the oxidation currents of H$_2$O$_2$ at MnO$_2$/GP/GCE and Co$_3$O$_4$/GP/GCE are obviously larger than that of GP/GCE, suggesting that the presence of MnO$_2$ and Co$_3$O$_4$ on GP surface play significant roles for electrocatalyzing the oxidation of H$_2$O$_2$. Therefore, cobalt and manganese oxide nanoparticles are both appropriate as mediators to shuttle electron between sensing electrode and analyte of H$_2$O$_2$. The similar results have been displayed in previous works [7-13]. However, at MnO$_2$-Co$_3$O$_4$/GP/GCE, the addition of H$_2$O$_2$ results in a significant current increase for oxidation of H$_2$O$_2$ with onset potential of +0.3 V, which is more negative than +0.4 V, meanwhile, the oxidation current increase prominently compared to the other three electrodes. These results demonstrate that the integration of MnO$_2$ and Co$_3$O$_4$ exhibits higher electrocatalytic activities toward oxidation of H$_2$O$_2$, and the electron exchange between modified electrode and H$_2$O$_2$ is thus further facilitated. This phenomenon is mainly ascribed to the synergistic effects of the MnO$_2$ and Co$_3$O$_4$ materials resulting in excellent electrocatalytic activities toward oxidation of H$_2$O$_2$. In addition, the good electrical conductivity of MnO$_2$-Co$_3$O$_4$/GP nanocomposites also enhanced its electrochemical performance.

The priority of MnO$_2$-Co$_3$O$_4$/GP nanocomposites modified electrode to electrodes modified with GP/GCE, MnO$_2$/GP/GCE and Co$_3$O$_4$/GP/GCE was further verified from amperometric results. Fig. 3b shows amperometric responses of various electrodes to successive additions of 100 µM H$_2$O$_2$ at an applied potential of +0.5 V. As observed, the current response of MnO$_2$-Co$_3$O$_4$/GP/GCE toward H$_2$O$_2$ is obviously higher than the other three modified electrodes, which further indicates that the synergistic effects between binary metallic oxides and the enhanced electrical conductivity by the introduction of graphene.
3.3. Amperometric detection of hydrogen peroxide

Amperometric technique was utilized to evaluate the electrochemical performance of the MnO$_2$-Co$_3$O$_4$/GP/GCE for determination of H$_2$O$_2$. The typical amperometric responses of the MnO$_2$-Co$_3$O$_4$/GP/GCE were presented in Fig. 4a upon dropwise additions of H$_2$O$_2$ into pH 7.0 PBS to increasing concentrations with an applied potential of +0.5 V. Immediately after the addition of H$_2$O$_2$, the oxidation current of the sensor responded rapidly and reached 95% of the steady-state current within 3 s, showing a fast response time for amperometric detection of H$_2$O$_2$. The calibration curve displayed in Fig. 4b indicates that the oxidation currents increase linearly with the increase of the H$_2$O$_2$ concentration. The linear range spans the concentration range from 5 µM to 1.2 mM with the linear regression equation of I (µA) = 0.30537 + 0.00379C (µM) (correlation coefficient of 0.9972). The amperometric sensitivity of the sensor was calculated to be 53.65 µA mM$^{-1}$ cm$^{-2}$ and the limit of detection (LOD) was estimated to be 0.8 µM based on a signal-to-noise ratio of 3.

Figure 3. The CV (a) and the amperometric (b) responses of GP/GCE, MnO$_2$/GP/GCE, Co$_3$O$_4$/GP/GCE and MnO$_2$-Co$_3$O$_4$/GP/GCE. The CVs of MnO$_2$-Co$_3$O$_4$/GP/GCE in 0.1 M PBS (pH 7.0) in the absence and presence of 5 mM H$_2$O$_2$ is shown in the inset of Fig. 3a.

Figure 4. Amperometric responses of the MnO$_2$-Co$_3$O$_4$/GP/GCE (holding at +0.5 V) upon addition of H$_2$O$_2$ to increasing concentrations (a) and the corresponding calibration curve (b).
To assess the anti-interference ability of the MnO$_2$-Co$_3$O$_4$/GP/GCE, the effect of potential interfering species including glucose, L-tyrosine, DA, AA and UA was examined, as shown in Fig. 5. There is a significant oxidation current response for the addition of 1 mM H$_2$O$_2$. In contrast, the current responses generated by addition of 1 mM glucose, L-tyrosine and UA can hardly be observed, and the current responses of 1 mM of DA and AA are also small. The amperometric response current ratios to H$_2$O$_2$ and the above interfering species on MnO$_2$-Co$_3$O$_4$/GP/GCE were shown in Fig. 5b. There are no significant interferences observed upon addition of those interfering species into analyte of H$_2$O$_2$, indicating a high selectivity for the present MnO$_2$-Co$_3$O$_4$/GP composites based H$_2$O$_2$ sensor. In addition, the reproducibility of the prepared MnO$_2$-Co$_3$O$_4$/GP/GCE was studied by preparing six electrodes separately under the same conditions. The oxidation current responses of these six electrodes toward 100 μM H$_2$O$_2$ yielded a relative standard deviation (RSD) of only 3.4%, which indicates an acceptable reproducibility. For one MnO$_2$-Co$_3$O$_4$/GP/GCE, it was stored in room temperature for 20 days and the current was periodically measured. It can be found that the current response retains 92% of its initial value after storage of 20 days. All of these results demonstrated that the prepared MnO$_2$-Co$_3$O$_4$/GP/GCE displayed an excellent electrocatalytic activity, good selectivity and stability toward H$_2$O$_2$ detection.

**Figure 5.** (a) Amperometric responses of the MnO$_2$-Co$_3$O$_4$/GP/GCE to successive additions of 1 mM H$_2$O$_2$, 1 mM DA, 1 mM H$_2$O$_2$, 1 mM AA, 1 mM L-tyrosine and 1 mM UA; (b) Amperometric current response ratio of the above interfering species on that of H$_2$O$_2$.

For comparison, the performance of our present MnO$_2$-Co$_3$O$_4$/GP composites with various MnO$_2$ and Co$_3$O$_4$ based materials to H$_2$O$_2$ sensing is listed in Table 1. Obviously, compared to several H$_2$O$_2$ sensors reported previously [9,16,33], the present MnO$_2$-Co$_3$O$_4$/GP composites possessed comparable and even better analytical parameters in terms of high detection sensitivity, appropriate linear range and low LOD, suggesting that the fabricated MnO$_2$-Co$_3$O$_4$/GP composites modified electrode might serve as a highly efficient and promising enzyme-free H$_2$O$_2$ sensor. Furthermore, the applied oxidation potential (+0.5 V) for detection of H$_2$O$_2$ in this work is much more negative than some of other materials, for example, MnO$_2$ microspheres [9], MnO$_2$/carbon fiber [33] and CoOxNPs/ERGO [13], which potentially reduce the possible interference of oxidative substances coexisting with H$_2$O$_2$. The good and acceptable performance of the present MnO$_2$-Co$_3$O$_4$/GP...
composites could be attributed to the following reasons. First, the MnO$_2$-Co$_3$O$_4$ binary composites exhibit high electrocatalytic activities toward H$_2$O$_2$ oxidation arising from their synergistic effects, which significantly enhanced the detection performance. Second, the introduction of graphene improves the electrical conductivity of the resultant MnO$_2$-Co$_3$O$_4$/GP composites, which favors the electron transfer and thus guarantees the full utilization of MnO$_2$-Co$_3$O$_4$ binary composites. It is also to point out that the proposed sensor is at the neutral biological conditions for detection of H$_2$O$_2$, which is different from other MnO$_2$ based sensors to carry out in strong alkaline media [16,21], thus, the present method has the potential prospect to direct and on-line analyze and determine H$_2$O$_2$ in biological samples.

**Table 1** Comparison of MnO$_2$-Co$_3$O$_4$/GP composites with various MnO$_2$ and Co$_3$O$_4$ based materials to H$_2$O$_2$ sensing.

<table>
<thead>
<tr>
<th>Electrode materials</th>
<th>Potential (V)</th>
<th>Sensitivity (μA mM$^{-1}$ cm$^{-2}$)</th>
<th>Linear range</th>
<th>LOD (μM)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO$_2$ microspheres</td>
<td>+0.8</td>
<td>-</td>
<td>10 -150 μM</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>CoO$_2$NPs/ERGO</td>
<td>+0.75</td>
<td>148.6</td>
<td>5 μM–1 mM</td>
<td>0.2</td>
<td>13</td>
</tr>
<tr>
<td>MnO$_2$-carbon foam</td>
<td>-0.45 V</td>
<td>-</td>
<td>2.5 μM-2.055 mM</td>
<td>0.12</td>
<td>15</td>
</tr>
<tr>
<td>MnO$_2$/GO</td>
<td>-0.3 V</td>
<td>38.2</td>
<td>5 μM-0.6 mM</td>
<td>0.8</td>
<td>16</td>
</tr>
<tr>
<td>MnO$_2$-ERGO</td>
<td>-0.5</td>
<td>59.0</td>
<td>0.1-45.4 mM</td>
<td>10</td>
<td>19</td>
</tr>
<tr>
<td>MnO$_2$/VACN Ts</td>
<td>+0.45 V</td>
<td>1080</td>
<td>1.2 μM-1.8 mM</td>
<td>0.8</td>
<td>20</td>
</tr>
<tr>
<td>MnO$_2$/OMC</td>
<td>+0.45</td>
<td>806.8</td>
<td>0.5 μM-0.6 mM</td>
<td>0.07</td>
<td>24</td>
</tr>
<tr>
<td>MnO$_2$/carbon fiber</td>
<td>+0.58V</td>
<td>0.75 μA mM$^{-1}$</td>
<td>12-260 μM</td>
<td>5.4</td>
<td>33</td>
</tr>
<tr>
<td>MnO$_2$-Co$_3$O$_4$/GP</td>
<td>+0.5</td>
<td>53.65</td>
<td>5 μM-1.2 mM</td>
<td>0.8</td>
<td>This work</td>
</tr>
</tbody>
</table>

3.4. Real sample analysis

In order to verify the applicability of the MnO$_2$-Co$_3$O$_4$/GP composites based sensor, the content of H$_2$O$_2$ in real hydrogen peroxide samples that was stored at room temperature for 3 years was determined by the present method. The real samples were diluted with 0.1 M pH 7.0 PBS solution before determination. Another classical KMnO$_4$ titration method was also employed as a comparison to evaluate the confidence of the present electrochemical method. The determination results are displayed in Table 2. Obviously, the two results obtained from the different two methods for each sample are in good agreement, indicating that the proposed MnO$_2$-Co$_3$O$_4$/GP composites based sensor could be used for accurately determination of the H$_2$O$_2$ sample.
Table 2. Determination of H₂O₂ in real samples by the present electrochemical method and the KMnO₄ titration method.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>This method (mM)</th>
<th>RSD (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>KMnO₄ titration method (mM)</th>
<th>RSD (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.816</td>
<td>3.6</td>
<td>2.904</td>
<td>3.2</td>
</tr>
<tr>
<td>2</td>
<td>3.588</td>
<td>2.8</td>
<td>3.492</td>
<td>4.5</td>
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</table>

<sup>a</sup> Obtained from four successive measurements.

4. CONCLUSIONS

In summary, binary metallic oxides of MnO₂-Co₃O₄ were decorated on GP modified electrode through a facile and green one step electrodeposition method to form MnO₂-Co₃O₄/GP composites. MnO₂-Co₃O₄/GP electrode exhibited high electrocatalytic activity toward oxidation of H₂O₂, thus, a significant current response and low oxidation over-potential were obtained. Due to the synergistic effects of binary metallic oxides and the enhanced electrical conductivity by the introduction of graphene, MnO₂-Co₃O₄/GP electrode showed high performance towards the nonenzymatic determination of H₂O₂, including high detection sensitivity, good selectivity, high accuracy, and acceptable stability. In addition, the present electrochemical sensor can be successfully used for determination of H₂O₂ in real samples. Therefore, the proposed MnO₂-Co₃O₄/GP based sensor displayed excellent electrochemical response for H₂O₂ oxidation, demonstrating its potential application in routine analysis of H₂O₂.

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