Synthesis of polypyrrole coated manganese nanowires and their application in hydrogen peroxide detection

M.R. Mahmoudian a,b,*, Y. Alias a, W.J. Basirun a,c, A. Moradi Golsheikh d, Farid Jamali-Sheini e

a Department of Chemistry, University of Malaya, Kuala Lumpur 50603, Malaysia
b Department of Chemistry, Shahid Sherafat, University of Farhangian, 15916 Tehran, Iran
c Nanotechnology & Catalysis Research Centre (NanoCat), Institute of Postgraduate Studies, University Malaya, 50603 Kuala Lumpur, Malaysia
d Low Dimensional Materials Research Centre (LDMRC), Physics Department, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia
e Department of Physics, Ahwaz Branch, Islamic Azad University, Ahwaz, Iran

**HIGHLIGHTS**
- Polypyrrole coated Manganese nanowires (Mn/PPy NWs) were prepared.
- The Mn/PPy NWs provided a high available surface area to react with H2O2.
- The calibration curve showed two linear segments of H2O2 concentration.
- The sensitivity of the low concentration was 0.4762 \( \mu \text{A M}^{-1} \).
- The LOD of low and high concentration was 2.12 \( \mu \text{M} \) and 22.3 \( \mu \text{M} \) respectively.

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*Corresponding author. Department of Chemistry, Shahid Sherafat, University of Farhangian, 15916 Tehran, Iran. Tel.: +98 610173928320.
E-mail address: M_R_mahmoudian@yahoo.com (M.R. Mahmoudian).

This study focuses on the synthesis and application of polypyrrole coated manganese nanowires (Mn/PPy NWs) as an enzyme-less sensor for the detection of hydrogen peroxide (H2O2). The X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) results confirm a core–shell structure with the Mn nanowires encapsulated by the PPy. An electrochemical sensor based on the Mn/PPy NWs for amperometric determination of H2O2 is prepared. The electrochemical behaviour of H2O2 is investigated by cyclic voltammetry with the use of modified glassy carbon electrode (GCE) with Mn/PPy NWs film. The modified glassy carbon electrode (GCE) with Mn/PPy NWs shows enhanced amperometric response for the detection of H2O2. This is due to the high available surface area of Mn/PPy NWs which can provide a suitable area for the reaction of H2O2. The detection limit and limit of quantification (S/N = 3) for two linear segments (low and high concentration of H2O2) are estimated to be 2.12 \( \mu \text{mol L}^{-1} \), 7.07 \( \mu \text{mol L}^{-1} \) and 22.3 \( \mu \text{mol L}^{-1} \), 74.5 \( \mu \text{mol L}^{-1} \) respectively. In addition, the sensitivity for these two linear segments is 0.4762 \( \mu \text{A mM}^{-1} \) and 0.0452 \( \mu \text{A mM}^{-1} \) respectively.

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1. Introduction

Conducting polymers has been studied as a new class of materials for the corrosion protection of metals. They are readily formed...
in aqueous solutions on various substrates [1–6]. These compounds are organic materials that generally possess an extended conjugated π-electron system along a polymer backbone. Recent reports confirmed that polypyrrole (PPy) coating has good protective property for corrosion control [7,8]. PPy among the group of conducting polymers has been the most widely used material due to its good electrical conductivity and environmental stability [7,9]. Moreover, the metal oxide/PPy core–shell structure has been proven to show better electronic properties compared to the pure substrate material [10]. Recent reports show that the composite of PPy or polyaniline with noble metal nanoparticles are good candidates for the detection of hydrogen peroxide (H₂O₂) [11–13]. H₂O₂ is one of the most important universal oxidants because of its wide applications in industrial process. Moreover, H₂O₂ has an intermediate role in environmental and biological reactions [14,15] and it is an important by-product of the oxygen reduction reaction, which has important effects in the operation of electrochemical devices such as fuel cells [16,17]. Recent investigations have shown that not only the noble metal nanoparticles can effect the catalytic activity of nanocomposites, but their morphology and structure also have an effective role on the catalytic activity of the sensor [18,19]. Therefore, investigations on the effect of polymer morphology, metal nanoparticles shape and the type of metal on the nanocomposite performance as a sensor for H₂O₂ detection will always be interesting. The detection of H₂O₂ with a reliable, rapid and economic method is important for many processes. Several methods such as titrimetry [20] spectrophotometry [21,22], fluorometric [23,24] and chemiluminescence [25] have been applied for this purpose. Electrochemical methods attracted considerable interest in the development of sensors for H₂O₂ determination because of high sensitivity, low cost and effectiveness. On the other hand, the slow electrode kinetics and high over-potentials required for redox reactions of H₂O₂ on many electrodes materials severely limit the application of these electrochemical methods. Due to these limitations, redox mediators have been widely used. For instance, a built-in three-in-one screen-printed electrode assembly containing nano-bismuth species deposited silver as working, pre-oxidized silver as reference and plated silver as counter electrode were prepared for the FESEM and EDX characterisations by dropping the suspension onto the ITO surface, which were then dried at room temperature. X-ray diffraction (Siemens D5000) with Cu Kα radiation measurements was used to analyse the structures and surface morphologies of the synthesised Mn/PPy NWs and the Mn in the absence of PPy. Transmission electron microscopy (TEM) (Philips CM200 with an operating voltage of 200 kV) was used to confirm the in situ polymerisation of PPy onto the surface Mn nanowires and to obtain more details about the Mn/PPy NWs. FT-IR spectra of the samples were obtained using a Spectrum 400 (FT/IR–FT–FIR spectrometer). Elemental CHN analysis (Mikro Kemi AB, Uppsala, Sweden) was used to determine the PPy content of the composite. The PPy content was estimated from the nitrogen content measured in the CHN analysis, as PPy was the only nitrogen-containing substance in the composite. A potentiostat/galvanostat, model PGSTAT-302N from Autolab controlled by a USB_IF030 (Metrohm Autolab) interface card connected to a computer was used to study the electrical properties of the Mn/PPy NWs/GCE in 0.1 M phosphate buffer solution. The Ag/AgCl (3 M) electrode was used as the reference electrode while a platinum foil was used as the counter electrode.

### 2. Experimental

#### 2.1. Synthesis of PPy coated manganese nanowires

Analytical grade manganese (III) acetate•dihydrat (97%) (C₉H₈MnO₆•2H₂O) was purchased from Merck (Schuchardt OHG) while other chemical including; Na₂HPO₄, NaH₂PO₄, H₂O₂ (30%) were from Sigma–Aldrich (St. Louis, Mo, USA). The pure pyrrole that was used in the experiments was always stored in the dark prior to synthesis. The synthetic method is based on the previous report described in the reference [27]. In a typical process, 1 mL 0.1 M Mn(CH₃COO)₂•2H₂O solution was added into 30 mL 7 M NaOH solution in a reaction vessel; the reaction was maintained at room temperature while continuously stirred at 500 rpm with a mechanical stirrer. After 15 min, 0.5 mL pyrrole monomer was added and the solution turned from light brown to dark brown colour. The polymerisation of PPy was completed after 30 min. Then the solvothermal reduction was performed by injecting 0.01 mL hydrazine monohydrate into the reaction mixture and the reaction temperature was increased to 60 °C by 1.5 °C min⁻¹. This process was maintained for another 60 min and finally the reaction mixture became transparent and light brown, which was the evidence for the reaction completion. The reaction mixture was centrifuged at 4000 rpm for 10 min to separate the Mn/PPy NWs from the solution, followed by drying in a vacuum oven at 60 °C for 24 h. In addition, to understand the effect of PPy, the whole procedure was repeated in the absence of the pyrrole monomers.

#### 2.2. Preparation of the H₂O₂ sensor

The prepared Mn/PPy NWs (1 mg) were dispersed into DMF (1 mL) using ultra-sonication for 1 h to obtain a homogenous suspension. Then, 5 μL of the homogenous suspension was dropped onto the surface of polished glassy carbon electrode (GCE) and dried at room temperature.

#### 2.3. Apparatus and characterisations

The morphology and weight percentage of the Mn/PPy NWs and synthesised Mn in the absence of pyrrole monomers were investigated using field emission scanning electron microscopy (FESEM, Quanta 200F) and energy dispersive X-ray (EDX) spectroscopy. The samples were prepared for the FESEM and EDX characterisations by dropping the suspension onto the ITO surface, which were then dried at room temperature. X-ray diffraction (Siemens D5000) with Cu Kα radiation measurements was used to analyse the structures and surface morphologies of the synthesised Mn/PPy NWs and the Mn in the absence of PPy. Transmission electron microscopy (TEM) (Philips CM200 with an operating voltage of 200 kV) was used to confirm the in situ polymerisation of PPy onto the surface Mn nanowires and to obtain more details about the Mn/PPy NWs. FT-IR spectra of the samples were obtained using a Spectrum 400 (FT/IR–FT–FIR spectrometer). Elemental CHN analysis (Mikro Kemi AB, Uppsala, Sweden) was used to determine the PPy content of the composite. The PPy content was estimated from the nitrogen content measured in the CHN analysis, as PPy was the only nitrogen-containing substance in the composite. A potentiostat/galvanostat, model PGSTAT-302N from Autolab controlled by a USB_IF030 (Metrohm Autolab) interface card connected to a computer was used to study the electrical properties of the Mn/PPy NWs/GCE in 0.1 M phosphate buffer solution. The Ag/AgCl (3 M) electrode was used as the reference electrode while a platinum foil was used as the counter electrode.

#### 3. Results and discussion

Fig 1(a) shows an overview of FESEM image of synthesised Mn/PPy NWs. The FESEM result confirms homogenous synthesised Mn/PPy NWs with 140 ± 19 nm in width. A higher magnification FESEM image of the synthesised Mn/PPy NWs is shown in Fig. 1(b). The result clearly demonstrates PPy coating onto the surface of the nanowires. The effect of pyrrole monomers on the synthesis of nanowires can be confirmed by the FESEM result in Fig. 1(c). The result shows the presence of bulk powders in the absence of the pyrrole monomers. The FESEM results can be confirmed by the TEM results in Fig. 1(d). The TEM result in Fig. 1(d) confirms that the Mn/PPy NWs are a core–shell nanostructure. As can be seen, the TEM image of the Mn/PPy NWs shows a rough surface of the
polymerised PPy encapsulated onto the surface of the nanowires. Additionally, the long length of the Mn nanowires as the core and a large rough surface area of polymerised PPy as the shell can produce a highly available surface area of the Mn/PPy NWs core—shell nanostructure.

Fig. 2(a) and (b) show the XRD pattern for the Mn/PPy NWs and H₂MnO₂ particles synthesised in the absence of pyrrole monomers respectively. The XRD pattern in Fig. 2(a) shows the intensity for the (330) and (422) peaks of Mn (Ref. code: 00-003-0991). The XRD results confirm that Mn³⁺ (manganese (III) acetate) is reduced to Mn in the presence of the pyrrole monomers and protected by the PPy shell. A broad, amorphous diffraction peak, which appears in the range of 2θ = 12–35° in the XRD pattern can be attributed to the scattering of the interplanar spacing between the bare polymer chains [10,28]. X. Zhang et al. [27] has suggested that a synergistic crystal growth and polymerisation process has induced the formation of the PPy-metal nanowires. The growth of Mn depends on the reduction of Mn³⁺ in the presence of the pyrrole monomer. The PPy polymerisation can act as a protector and it create the first PPy-capped Mn particles as seeds for the nanowire growth, via the Ostwald ripening process [29,30]. Other researcher believes that surface energy and the capping effect are major driving factors for the nanowires formation [31]. The TEM result clearly shows that the nanowires are coated with PPy. The formation of a coordination bond between the synthesised PPy in the solution and seeds can be considered as a hypothesis for the formation of the PPy-Mn NWs.

The FT-IR spectra of the Mn/PPy NWs, H₂MnO₂ nanoparticles and PPy are shown in Fig. 3(a), (b) and (c) respectively. The FT-IR spectrum of the Mn/PPy NWs shows the characteristic peaks of PPy, but these peaks have a shift compared to the pure PPy FT-IR (Fig. 3(c)), which indicates an interaction between the polymer backbone and the Mn nanowires has occurred [32]. A large, descending baseline appears in the spectral region of 1600–
2200 cm\(^{-1}\), which is attributed to the free-electron conduction in the conducting polymers [33]. In the FT-IR spectrum of the synthesised Mn/PPy NWs, the peaks at 3114.54 cm\(^{-1}\) can be attributed to the N–H bond. Peaks at 1650.28 cm\(^{-1}\) is related to the C–N=C bond in the Mn/PPy NWs spectrum. The strong bands at 2880.21 cm\(^{-1}\) can be attributed to the aliphatic C–H in the Mn/PPy NWs spectrum. Additionally, peaks at 1390.24 cm\(^{-1}\) is characteristic of a typical PPy ring vibrations. Peaks at 1016.40 cm\(^{-1}\) is a special peak which belong to C–N stretching vibration and the C=H out-of-plane vibration. The FTIR spectrum of the H\(_2\)MnO\(_2\) is shown in Fig. 3(b). The peak at 571.45 cm\(^{-1}\) is attributed to the vibrations of the Mn–O bond. The peaks above 3000 cm\(^{-1}\) are assigned to traces of water absorbed on the nanoparticles and O–H vibration (the peak height decreased with heating of the synthesised powder sample). The peak at 1643 cm\(^{-1}\) is attributed to C=O vibration which is due to CO\(_2\) absorption of the H\(_2\)MnO\(_2\) nanoparticles.

CHN microanalysis was used to determine the amount of PPy in the composite. This analysis indicated that the composite consists of (0.46 ± 0.03)% PPy which is in good agreement with the TEM image and confirm that PPy covers the surface of Mn nanowires as a thin layer. When pyrrole was added to a solution of Mn(CH\(_3\)COO)\(_3\)\(\cdot\)2H\(_2\)O and NaOH, the light brown colour of the solution turned dark brown. This is the major evidence for the occurrence of pyrrole polymerisation. FT-IR spectroscopy and CHN elemental analysis proved the existence and estimated the amount of polymer in the composite.

The electrocatalytic activity of Mn/PPy NWs/GCE towards H\(_2\)O\(_2\) reduction was investigated by cyclic voltammetry. Fig. 4 shows the cyclic voltammograms of the bare GCE, the Mn/PPy NWs/GCE and the H\(_2\)MnO\(_2\) particles synthesised in the absence of pyrrole monomers/GCE. The voltammograms were performed in a 0.2 M phosphate buffer solution (Na\(_2\)HPO\(_4\) and NaH\(_2\)PO\(_4\)) with a pH of 6.5 and in the presence of 1.0 mM H\(_2\)O\(_2\). The Mn/PPy NWs/GCE show better electrical response for the reduction of H\(_2\)O\(_2\), where the H\(_2\)O\(_2\) reduction starts at −0.06 V and an obvious catalytic reduction peak appears at −0.35 V Fig. 4 also shows that the cathodic peak current is greatly increased and the oxidation peak current is decreased in the presence of H\(_2\)O\(_2\), suggesting a typically excellent electrocatalytic reduction process of the H\(_2\)O\(_2\). For the reduction of H\(_2\)O\(_2\), the Mn/PPy NWs/GCE shows a 0.52 V positive shift of the peak.
potential compared to the $\text{H}_2\text{MnO}_2$ particles synthesised in the absence of pyrrole monomers/GCE. The reasons for this observation can be explained by the different oxidation states of Mn and different available surface area of the Mn nanowire and synthesised $\text{H}_2\text{MnO}_2$ in the absence of the pyrrole monomers. From these results the following catalytic reactions (1) and (2) describes the reaction sequence for the reduction of $\text{H}_2\text{O}_2$ by the Mn/PPy NWs.

\[
\text{Mn/PPy (s) + H}_2\text{O}_2 (l) + 2\text{H}^+ (aq) \rightarrow \text{Mn}^{2+}/\text{PPy (s) + 2H}_2\text{O (l)} \quad (1)
\]

\[
\text{Mn}^{2+}/\text{PPy (s) + 2e} \rightarrow \text{Mn/PPy (s)} \quad (2)
\]

The increase of the reduction peak current with the Mn/PPy NWs/GCE compared to the $\text{H}_2\text{MnO}_2$ particles synthesised in the absence of pyrrole monomers/GCE, shows that the sensitivity of the electrode to $\text{H}_2\text{O}_2$ is significant and the coated Mn nanowires with PPy can increase the rate of reaction for the reduction of $\text{H}_2\text{O}_2$. There are two reasons which can be given for the improvement of catalytic performance of the Mn/PPy NWs compared to the $\text{H}_2\text{MnO}_2$ particles synthesised in the absence of the pyrrole monomers. Firstly, the Mn nanowire morphology can create a large surface area for the interaction of $\text{H}_2\text{O}_2$ during the reduction, and secondly, previous reports show that the over-oxidation phenomena can also occur for the PPy during the reduction of $\text{H}_2\text{O}_2$ and this is another reason for the direct reduction of $\text{H}_2\text{O}_2$ in the presence of PPy (3 and 4) [34]. Therefore it is reasonable that reactions (3) and (4) could be increased with the increase of the PPy surface area. The TEM result of Mn/PPy NWs (Fig. 1(d)) shows a specific morphology of PPy on the surface of Mn nanowire with high surface area.

\[
2\text{PPy (s) + H}_2\text{O}_2 (l) \rightarrow 2\text{OH}^- (aq) + 2\text{PPy}^{+} (s) \quad (3)
\]

\[
\text{PPy}^{+} (s) + e \text{ (from applied negative potential)} \rightarrow \text{PPy (s)} \quad (4)
\]

The dependency of the amperometric response on the applied potential of the Mn/PPy NWs/GCE under batch conditions was evaluated over a range of $-0.15$ to $-0.5$ V (Fig. 5) using a solution of 0.1 M $\text{H}_2\text{O}_2$ in 0.2 M phosphate buffer solution (Na$_2$HPO$_4$ and NaH$_2$PO$_4$) at pH 6.5. The plot of the steady-state current versus potential shows a significant increase for potentials higher than $-0.2$ V. A suitable working potential should be chosen based on the least negative potential to achieve good selectivity, along with a potential value that shows a high analyte-dependent current. Fig. 5 show that the potential value of $-0.2$ V fulfils these conditions; therefore, it was selected as the working potential.

The amperometric responses of the Mn/PPy NWs/GCE to the addition of $\text{H}_2\text{O}_2$ aliquots from a stock solution of 0.2 M phosphate buffer (Na$_2$HPO$_4$ and NaH$_2$PO$_4$) at pH 6.5 was carried out and shown in Fig. 6. The responses were rapid, in less than 5 s. The currents increase linearly with the concentration of $\text{H}_2\text{O}_2$ between 0.005 and 8 mmol L$^{-1}$. The calibration curve for the Mn/PPy NWs/GCE shows two linear segments: the first linear segment increases from 0.005 to 0.090 mmol L$^{-1}$ with a linear regression equation of $I = 0.4762 (\mu\text{A} \text{mM}^{-1}) + 5.8152 (R^2 = 0.9919)$, and the second linear segment increases up to 8 mmol L$^{-1}$ with a linear regression equation of $I = 0.0452 (\mu\text{A} \text{mM}^{-1}) + 53.762 (R^2 = 0.9966)$. The limit of detection (LOD) and the limit of quantification (LOQ) of the Mn/PPy NWs/GCE were calculated using the following equations [35]:

\[
\text{LOD} = \frac{3.3sd}{m} \quad \text{LOQ} = \frac{10sd}{m}
\]

**Table 1**

<table>
<thead>
<tr>
<th>Type of electrode</th>
<th>LOD/μmol L$^{-1}$</th>
<th>Linear range/mmol L$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-UTPNs/GCE</td>
<td>0.57</td>
<td>0.1–90</td>
<td>[34]</td>
</tr>
<tr>
<td>AgNP-PPyCs</td>
<td>1.05</td>
<td>0.1–90</td>
<td>[37]</td>
</tr>
<tr>
<td>PQ11-AgNPs/GCE</td>
<td>33.7</td>
<td>0.1–180</td>
<td>[38]</td>
</tr>
<tr>
<td>MnO$_2$ nanoparticles</td>
<td>0.08</td>
<td>0.002–2</td>
<td>[39]</td>
</tr>
<tr>
<td>AgNP/GO/GCE</td>
<td>31.3</td>
<td>0.1–100</td>
<td>[35]</td>
</tr>
<tr>
<td>GO/MnO$_2$</td>
<td>0.8</td>
<td>0.005–0.6</td>
<td>[40]</td>
</tr>
<tr>
<td>SPAGE-Bi$_{14}$nano</td>
<td>56.59</td>
<td>0.1–0.5</td>
<td>[26]</td>
</tr>
<tr>
<td>Cytochrome c/macroporous active carbon</td>
<td>14.6</td>
<td>0.02–0.24</td>
<td>[36]</td>
</tr>
<tr>
<td>MnO$_2$ nanorod</td>
<td>7.5</td>
<td>–</td>
<td>[41]</td>
</tr>
<tr>
<td>PPy/Mn bone like</td>
<td>2.12</td>
<td>0.005–0.09</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>22.3</td>
<td>0.1–8</td>
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</tr>
</tbody>
</table>
where $S_b$ is the standard deviation of the blank solution and $b$ is the slope of the analytical curve, as shown in Fig. 6(b and c). The LOD and LOQ ($S/N = 3$) is estimated to be 2.12 $\mu$mol L$^{-1}$, 7.07 $\mu$mol L$^{-1}$ and 22.3 $\mu$mol L$^{-1}$, 74.5 $\mu$mol L$^{-1}$ for the two linear segments respectively. In addition, the sensitivity is 0.4762 $\mu$A mM$^{-1}$ and 0.0452 $\mu$A mM$^{-1}$ for two linear segments respectively. As can be seen from Table 1, the LOD for $H_2O_2$ at the PPy-Mn nanowires/GCE is lower than those obtained on SPAgE-B$^{nano}$ 56.59 $\mu$mol L$^{-1}$ [26] and AgNP/rGO/GCE 31.3 $\mu$mol L$^{-1}$ [35] and is comparable to that of Cytochrome c/macroporous active carbon (14.6 $\mu$mol L$^{-1}$) [36] indicating a favourable analytical performance of this electrochemical sensor.

For analysis applications, a recovery experiment was conducted to examine the potential use of the Mn/PPy NWs/GCE. Three different concentrations of $H_2O_2$ (30, 90 and 1000 $\mu$mol L$^{-1}$) were added into a 0.2 M phosphate buffer solution at pH 6.5 under the optimum applied potential of 0.2 V. All of the measurements were performed four times ($n = 4$) and the average recoveries are listed in Table 2. The observation of acceptable recoveries and the relative standard deviation (RSD) suggests the feasibility of the proposed method for the quantitative detection of certain concentration ranges of $H_2O_2$.

4. Conclusions

In summary, Mn/PPy NWs were prepared and applied as electrochemical sensing interface for $H_2O_2$. The electrochemical behaviour of $H_2O_2$ was studied by cyclic voltammetry with the use of modified glassy carbon electrode (GCE) coated with the Mn/PPy nanowire film. The X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) results confirmed a core shell structure for the Mn/PPy NWs. The results also showed that the Mn/PPy NWs can provide a favourable micro-environment for the electrochemical detection of $H_2O_2$, resulting in an enhanced amperometric response. The reason can be explained from the highly available surface area of the Mn/PPy NWs that can provide a substantial area for the detection of $H_2O_2$. This Mn/PPy NWs based electrochemical sensor possess a low detection limit, suitable sensitivity and long-term stability for the determination of $H_2O_2$. The Mn/PPy NWs may offer a new approach for the development of electroactive polymer-based electrochemical sensors and biosensors.

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