Preparation of ultra-thin polypyrrole nanosheets decorated with Ag nanoparticles and their application in hydrogen peroxide detection

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This study examines the preparation of ultra-thin polypyrrole nanosheets decorated with Ag nanoparticles (Ag-UTPNSs) and their application in the enzyme-less detection of hydrogen peroxide (H2O2) detection. The X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) results confirmed that Ag nanoparticles (NPs) were deposited onto the surface of the UTPNSs. The increase of the H2O2 reduction current peak to 120 μA was in the presence of the Ag-UTPNS/glasy carbon electrode (GCE) as compared to the UTPNS/GCE indicates that the sensitivity of the electrode to H2O2 is significant. This observation can be explained by the larger surface area of the UTPNSs, which can increase the interactions between the polymer and the AgNO3 solution during the deposition of the Ag NPs, and by the small size of the deposited Ag NPs, which can produce a surface area of Ag that is suitable for the reaction with H2O2. The amperometric responses show that the limit of detection, the limit of quantification (S/N ~ 3) and the sensitivity are estimated to be 0.57 μM, 1.53 μM and 4.477 μA mM−1, respectively, for the linear segment. The results of the reproducibility experiments show that the use of Ag-UTPNS/GCE is feasible for the quantitative detection of certain concentration ranges of H2O2.

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1. Introduction

In recent years, there have been a large number of studies examining conducting polymers because of their unique properties [1–6]. These compounds are organic materials that generally possess an extended conjugated π-electron system along a polymer backbone, such as polypyrrole (PPy), polyaniline (PAn) and polystyrene. Additionally, nanoscale conducting polymers have attracted considerable attention for sensor fabrication because they can recognize certain analytes through their inherent signal transduction mechanisms [7–10]. Recent research efforts have also demonstrated that the hydroxyl groups of the nanostructures that consist of both conducting polymers and nanoparticles of noble metals, such as silver, gold, can be used as electrochemical sensors [11–13]. The electrochemical techniques, when compared to the traditional techniques, can be used to construct suitable sensors and biosensors that have high sensitivity and good selectivity.

The detection of hydrogen peroxide (H2O2) is of great importance because of its application in a wide range of enzymatic reactions, biology and clinical control. Recent reports show that composite materials of PPy or PAn with noble metal nanoparticles are promising candidates for the detection of H2O2 [14–18]. Recent investigations have shown that the catalytic activity of the nanocomposites is affected not only by the type of noble metal nanoparticles but also by the type of morphology of the conductive polymers [14,19]. Therefore, investigations examining the effects of polymer morphology on the performance of the nanocomposite as a sensor for the detection of H2O2 are of interest. PPy is the best choice among the conductive polymers because of its good conductivity, simple synthesis and controllable morphology.

In this work, we report on the synthesis of ultra-thin PPy nanosheets (UTPNSs) that are decorated with Ag nanoparticles (NPs). The UTPNSs were first prepared in the presence of sodium dodecyl sulfate (SDS), and the Ag NPs were then deposited onto the surface of UTPNSs from the in situ reduction of AgNO3. The application of the Ag/ultra-thin PPy nanosheets (Ag-UTPNSs) as a sensor for the detection of H2O2 was examined.

2. Experimental

2.1. Synthesis of ultra-thin PPy nanosheets

All chemicals used were from Sigma–Aldrich (ST LOUIS, MO, USA). Ferric chloride was used as the oxidant, and the pure pyrrole
that was used in the experiment was always stored in the dark prior to synthesis. The preparation of the UTPNSs is reported in the literature [20], but in this work, SDS was replaced with sodium decylsulfonate. The chemical polymerization was performed by dissolving 2.88 g of SDS in 100 ml of distilled water in a reaction vessel; the reaction was maintained at 30 °C while continuously stirring at 800 rpm with a mechanical stirrer. After 30 min, the solution was cooled to 0 °C. During this step, 20 mmol of the pyrrole monomer was added to the above solution, and the stirring was continued for another 30 min while the temperature was maintained at 0 °C. A pre-cooled solution containing 45 mmol ferric chloride (20 ml) was added to the prepared solution drop-wise. The stirring was continued for 3 h at 0 °C to completely polymerize the UTPNSs. The resulting product was filtered and repeatedly washed with distilled water, followed by drying in a vacuum oven at 40 °C for 24 h.

2.2. Synthesis of Ag-ultra-thin PPy nanosheets

An amount of 0.05 g of the synthesized ultra-thin PPy was dispersed into 20 ml of distilled water using the ultrasonication method. Following this step, 20 ml of a 0.02 M AgNO₃ solution was added to the dispersed UTPNSs solution, and the stirring was continued for 2 h at room temperature. The composite was then filtered and repeatedly washed with distilled water, followed by drying in a vacuum oven at 60 °C for 24 h.

2.3. Preparation of the H₂O₂ sensor

The prepared Ag-UTPNSs (1 mg) were dispersed into DMF (1 ml) using ultrasonication 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.

2.4. Apparatuses and characterizations

The morphology and weight percentage of the Ag-UTPNSs was investigated using field emission scanning electron microscopy (FESEM, Quanta 200F) and energy dispersive X-ray (EDX) spectroscopy. The sample was prepared for the FESEM and EDX characterizations by dropping the prepared dispersion suspension onto the ITO surface, which was then dried at room temperature. X-ray diffraction (Siemens D5000), using Cu Kα radiation, and atomic force microscopy (AFM, PSIA XE-100) measurements were used to analyze the structures and surface morphologies, respectively, of the Ag-UTPNSs and the resulting UTPNSs. Transmission electron microscopy (TEM) (Philips CM200, at an operating voltage of 200 kV) was used to confirm the deposition of Ag NPs onto the surface of the UTPNSs and to obtain more details about the Ag-UTPNSs. FT-IR spectra were obtained from the samples using a Spectrum 400 (FT-IR/FT-FIR spectrometer). The electrical properties of the Ag-UTPNSs/GCE were investigated in a 0.1 M phosphate buffer solution using a Potentiostat/Galvanostat, Model PGSTAT-302N from Autolab that was controlled by a USB_JP030 (Metrohm Autolab) interface. The Ag/AgCl (3 M) electrode was used as the reference electrode, and all of the potential values were referenced to this electrode and platinum foil, which was used as the counter electrode.

3. Results and discussion

Fig. 1(a) shows a high-magnification FESEM image of the synthesized UTPNSs in the presence of SDS. The inset of Fig. 1(a) shows a single layer of the synthesized UTPNSs. Fig. 1(b) shows the UTPNSs that were deposited with Ag NPs. The FESEM images show that a high percentage of Ag was deposited onto the surface of the UTPNSs. Additionally, the results show that the size of the Ag NPs is small; therefore, the available surface area of Ag NPs that was deposited onto the surface of the UTPNSs is high. The results obtained using FESEM were confirmed from the TEM and elemental mapping analysis of the Ag-UTPNSs. Fig. 2(a) shows the UTPNSs with a nanosheet structure that has a large surface area that is capable of producing suitable interactions with the Ag⁺ ions. The results from the TEM analysis show that a considerable amount of Ag NPs was deposited onto the surface of the UTPNSs (Fig. 2(b)). As can be seen, the TEM image of the Ag-UTPNSs shows the presence of densely packed Ag NPs and that the surface of the UTPNSs became rough following the deposition of the Ag NPs. An AFM scan and the corresponding depth profiles of the UTPNSs are shown in Fig. 2(c1) and (c2). The combined thickness of the top and bottom of the UTPNSs was ~50 nm, which can confirm a nanosheet structure for the UTPNSs. Fig. 2(d1) and (d2) show a selected area of the Ag-UTPNSs and its elemental mapping, respectively. The elemental mapping clearly shows the surface coverage of UTPNSs by Ag, and it confirms the deposition of a large amount of Ag NPs onto the surface of the UTPNSs.

The weight percentage of each element in the composite was detected using EDX (Fig. 3). The EDX results, which were obtained from Fig. 3, show the existence of S and O (from SDS), Ag (from the deposited nanoparticles), Fe (from FeCl₃) and C (from PPy). The weight percentage of each element is provided in Table 1. The EDX
Table 1
EDX data of the deposited UTPNSs with Ag nanoparticles.

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>O</th>
<th>Fe</th>
<th>S</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Wt%)</td>
<td>43.90</td>
<td>12.98</td>
<td>17.65</td>
<td>10.54</td>
<td>14.93</td>
</tr>
</tbody>
</table>

Fig. 2. TEM image of (a) UTPNSs synthesized in the presence of SDS, (b) UTPNSs deposited with Ag nanoparticles, (c1) and (c2) an AFM scan and the corresponding depth profile of UTPNSs, respectively, and (d1) and (d2) a selected area of Ag-UTPNS and its elemental mapping, respectively.

Fig. 4 shows the XRD pattern for the Ag-UTPNSs. The XRD pattern in Fig. 4 shows the intensity for the (1 1 1) and (2 0 0) peaks of Ag (Ref. code: 01-087-0718). This result was confirmed from the FESEM analysis, where the Ag NPs were observed on the surface of the UTPNSs. Additionally, the XRD results can confirm that Ag⁺ from the AgNO₃ is reduced in the presence of the UTPNS colloids. A
broad, amorphous diffraction peak, which appears in the range of $2\theta = 17–25^\circ$ in the XRD pattern for the Ag-UTPNSs, is seen and can be attributed to the scattering from the interplanar spacing between the bare polymer chains [21,22]. Zhao et al. [23] have suggested that the deposition process of Ag onto the surface of PPy occurs in two steps. The first step is the formation of a coordination bond between Ag$^+$ and the imino groups in the PPy chains, and the second step is an in situ reduction of Ag$^+$ to Ag. It should be noted that the presence of Cl$^-$ and SO$_3^{2-}$ as dopant in the UTPNSs is another reason for the adsorption of Ag$^+$ on the surface of the UTPNSs.

The FT-IR spectra of the UTPNSs and the Ag-UTPNSs are shown in Fig. 5(a) and (b), respectively. A large, descending baseline appears in the spectral region of 1700–2800 cm$^{-1}$, which is attributed to the free-electron conduction in conducting polymers [24]. In the FT-IR spectra of the synthesized UTPNSs and the Ag-UTPNSs, the peaks at 3217.13 and 3159.50 cm$^{-1}$, respectively, can be attributed to the N–H bond. The FT-IR spectrum of the UTPNSs that were synthesized in the presence of SDS (Fig. 5(a)) exhibits the characteristic bands for SDS at 1188.33 cm$^{-1}$ (for SO$_3^-$) and 678.92 cm$^{-1}$ (both S=O stretch) [25,26]. In addition, the same characteristic bands for SO$_3$ and S=O can be seen in the FT-IR spectrum of the Ag-UTPNSs (Fig. 5(b)), but with a slight shift in the wavenumbers. The slight shift in the wavenumbers for the SO$_3$ and S=O stretches in the FT-IR spectrum of the Ag-UTPNSs, as compared to the UTPNSs spectrum, can account for the interaction between the Ag and the non-bonding electron pair, such as that from O (from SDS). Peaks at 1649.13 cm$^{-1}$ (Fig. 5(a)) and 1651.01 cm$^{-1}$ (Fig. 5(b)) are related to the C=N=C bond in the UTPNSs and the Ag-UTPNSs spectrum, respectively. The strong bands at 2849.93 cm$^{-1}$ (Fig. 5(a)) and 2849.24 cm$^{-1}$ (Fig. 5(b)) can be associated with the aliphatic C–H in the UTPNS and the Ag-UTPNS spectrum, respectively. Additionally, peaks at 1430.29 and 1454.24 cm$^{-1}$ are characteristic of typical PPy ring vibrations (Fig. 5(a) and (b), respectively).

The cyclic voltammograms of the bare GCE, the UTPNS/GCE and the Ag-UTPNS/GCE in a 0.2 M phosphate buffer solution (K$_2$HPO$_4$ and KH$_2$PO$_4$) with a pH of 6.5 in the presence of 1.0 mM H$_2$O$_2$ are shown in Fig. 6. The results show good electrical response of the
Ag-UTPNS/GCE for the reduction of H₂O₂ and an improved performance of the Ag-UTPNSs as compared to previous reports [9]. The increase to 120 μA of the reduction current peak shows that the sensitivity of the electrode to H₂O₂ is significant and that it can increase the rate of reaction for the reduction of H₂O₂. There are two reasons that can be given for the improvement of catalytic performance of the Ag-UTPNSs as compared to previous reports[9]. First, the morphology of the UTPNSs can create a large surface area for the interaction of Ag⁺ with the polymer nanosheets during the deposition of the Ag NPs, and second, the TEM results confirm that the large catalytic current of the Ag-UTPNSs could be attributed to the large amount of deposited Ag NPs onto the surface of the UTPNSs. Other researchers have reported an autocatalytic mechanism on the Ag electrode [28]. The mechanism for the direct reduction of H₂O₂ (1) can be explained from the formation of adsorbed OH⁻ ad species in a slightly acidic medium:

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} \]  (1)

The formation process, and the conversion of OH⁻ ad to OH⁻ is suggested with the diffusion of H₂O₂ from bulk to the electrode surface (2) followed by electron transfer steps ((3) and (4)) [28].

\[ \text{H}_2\text{O}_2(\text{bulk}) \rightarrow \text{H}_2\text{O}_2(\text{surface}) \]  (2)

\[ \text{H}_2\text{O}_2(\text{surface}) + \text{e}^- \rightarrow \text{OH}^{-}_{\text{ad}} + \text{OH}^{-} \]  (3)

\[ \text{OH}^{-}_{\text{ad}} + \text{e}^- \rightarrow \text{OH}^{-} \]  (4)

The reaction between the OH⁻ ion and the H⁺ ion leads to the formation of the final product (5).

\[ \text{OH}^{-} + \text{H}^+ \rightarrow \text{H}_2\text{O} \]  (5)

In addition, it is possible that the OH⁻ ad can simultaneously accept an electron and react with the H⁺ ion (6).

\[ \text{OH}^{-}_{\text{ad}} + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O} \]  (6)

Comparison of the responses of the citrate-protected Ag NP-modified GCE and the Ag-UTPNS/GCE shows that there is a 0.20 V positive shift of the peak potential for the reduction of H₂O₂. The TEM results confirmed the presence of densely packed Ag NPs. It is reported that the distance between the neighboring Ag NPs will change as the Ag NPs become more densely packed. In this case, the diffusion zones of the neighboring Ag NPs will greatly overlap such that the effect of the mass transport to the electrode surface would be greater than the size of the Ag NPs [14,27]. This effect will result in a shift of the peak potential. However, the results show an electrical response of the UTPNS/GCE in comparison with the bare GCE for the reduction of H₂O₂. Over-oxidation phenomena, which can occur for PPy during the reduction of H₂O₂, can be a reason for the direct reduction of H₂O₂ in the presence of PPy (Fig. 7). The high surface area of the UTPNS films can not only increase the interaction with the Ag⁺ ions but also can increase the direct reduction of H₂O₂ by PPy.

The dependence of the amperometric response of the Ag-UTPNS/GCE under batch conditions on the applied potential was evaluated over the range of −0.15 to −0.45 V (Fig. 8) using a solution of 0.1 M H₂O₂ in 0.2 M phosphate buffer solution (K₂HPO₄ and KH₂PO₄) at a pH of 6.5. The plot of the steady-state current versus potential shows a significant increase for potentials higher than −0.3 V. A suitable working potential should be chosen based on the least negative possible potential to achieve good selectivity, along with a potential value that allows for a high analyte-dependent current. Fig. 8 show that the potential value of −0.35 V fulfills these conditions; therefore, it was selected as the working potential.

The amperometric responses of the Ag-UTPNS/GCE to the addition of H₂O₂ aliquots from a stock solution in 0.2 M phosphate buffer solution (K₂HPO₄ and KH₂PO₄) with a pH of 6.5 is given in Fig. 9. The responses were rapid (less than 5 s). A typical calibration curve for the sensor can be prepared from the amperometric response (Fig. 9(a)). The low concentration region of a typical calibration curve is shown in the inset of Fig. 9(b). It can be clearly seen that the sensor electrode shows a linear steady-state amperometric response up to 90 mM of H₂O₂. The linear regression equation can be expressed as \( I = 4.477 \, (\mu\text{A}\, \text{mM}^{-1}) + 6.276 \) \( (r^2 = 0.9976) \). The limit of detection (LOD) and the limit of quantification (LOQ) of the Ag-UTPNS/GCE were calculated by using the equation given below [29]:

\[ \text{LOD} = \frac{3\sigma_b}{b} \]  (7)

![Fig. 7. A schematic of the direct reduction of H₂O₂ on UTPNS films.](image)

![Fig. 8. Effects of the applied potential on the current response of the Ag-UTPNS/GCE to 0.1 mM H₂O₂ in a 0.2 M phosphate buffer solution (K₂HPO₄ and KH₂PO₄) at a pH of 6.5.](image)

![Fig. 9. Steady-state response of the Ag-UTPNS/GCE to successive injections of H₂O₂ into a 0.2 M phosphate buffer solution (K₂HPO₄ and KH₂PO₄) at a pH of 6.5 with an applied potential: of −0.35 V (inset: the calibration curve).](image)
Table 2
The detection of H₂O₂ concentration in test samples (results based on four replicate determinations per sample).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Add (nmol L⁻¹)</th>
<th>(RSD, %) (n = 4)</th>
<th>Found (nmol L⁻¹)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>1.3508</td>
<td>0.4937</td>
<td>98.7536</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>1.6748</td>
<td>4.9303</td>
<td>98.6021</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>1.0806</td>
<td>9.6209</td>
<td>96.2097</td>
</tr>
</tbody>
</table>

Table 3
Summary and a comparison of the estimated LOD values of the present work and previous reports from different methods.

<table>
<thead>
<tr>
<th>Type of electrode</th>
<th>Performance</th>
<th>LOD (µmol L⁻¹)</th>
<th>Linear range (nmol L⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgNP–CNTNs</td>
<td></td>
<td>0.9</td>
<td>0.1–70</td>
<td>[12]</td>
</tr>
<tr>
<td>AgNP–PPyCs</td>
<td></td>
<td>1.05</td>
<td>0.1–90</td>
<td>[14]</td>
</tr>
<tr>
<td>PQ11–AgNPs/GCE</td>
<td></td>
<td>33.7</td>
<td>0.1–180</td>
<td>[15]</td>
</tr>
<tr>
<td>AgNPs/PANINFs</td>
<td></td>
<td>0.25</td>
<td>0.1–60</td>
<td>[19]</td>
</tr>
<tr>
<td>AgNPs/GO/GCE</td>
<td></td>
<td>31.3</td>
<td>0.1–100</td>
<td></td>
</tr>
<tr>
<td>AgNPs/collagen/GCE</td>
<td></td>
<td>0.7</td>
<td>0.005–40.6</td>
<td>[31]</td>
</tr>
<tr>
<td>HRP</td>
<td></td>
<td>0.03</td>
<td>0–0.8</td>
<td>[32]</td>
</tr>
<tr>
<td>SPAgE–Bi²⁺</td>
<td></td>
<td>56.59</td>
<td>0.1–5</td>
<td>[33]</td>
</tr>
<tr>
<td>3DOM GTD</td>
<td></td>
<td>0.2</td>
<td>0.0005–1.4</td>
<td>[34]</td>
</tr>
<tr>
<td>Roughed Ag electrode</td>
<td></td>
<td>6</td>
<td>0.01–22.5</td>
<td></td>
</tr>
<tr>
<td>Ag-UTPNSs/GCE</td>
<td></td>
<td>0.57</td>
<td>0.1–90</td>
<td>This work</td>
</tr>
</tbody>
</table>

LOQ = \frac{10S_B}{b} \quad (8)

where \( S_B \) is the standard deviation of the blank solution and \( b \) is the slope of the analytical curve, as shown in the inset of Fig. 9(b). The LOD and LOQ (S/N = 3) are estimated to be 0.57 \( \mu \)M and 1.93 \( \mu \)M, respectively. The sensitivity of the electrode, as calculated from the slope of the linear regression equation, is 4.477 \( \mu \)A M⁻¹ cm⁻².

To test the potential use of the Ag-UTPNSs/GCE for analytical applications, a recovery experiment was conducted using the modified electrode. Three different concentrations of H₂O₂ (0.5, 5, and 10 mM) were added into a 0.2 M phosphate buffer solution at a pH of 6.5 under the optimal applied potential (−0.35 V). All of the measurements were performed four times (n = 4). The average recoveries are listed in Table 2. Acceptable recoveries and the relative standard deviation (RSD) were obtained; this suggests that applying the proposed method for the quantitative detection of certain concentration ranges of H₂O₂ is feasible. As can be seen in Table 3, the LOD of H₂O₂ at the Ag-UTPNS/GCE is lower than those obtained on Ag NP-decorated PPy colloids (AgNP/rGO/GCE (1.05 \( \mu \)M) [14] and Ag NP/(reduced graphene oxide-modified GCE) rGO/GCE (31.30 \( \mu \)M) [30], and the results of the present work are comparable to the results of AgNP–decorated coordination polymer nanobelts (AgNP–CPNBs) (0.90 \( \mu \)M) [12], which indicates the favorable analytical performance of this electrochemical sensor.

4. Conclusions

UTPNSs decorated with Ag NPs were synthesized. The XRD, FESEM and TEM results confirmed that the Ag NPs were deposited on the surface of the UTPNSs. The XRD results confirmed that the Ag⁺ from AgNO₃ was reduced in the presence of UTPNSs colloids. The increase to 120 \( \mu \)A of the current peak for the reduction of H₂O₂ in the presence of the Ag-UTPNSs/GCE, in comparison to the UTPNS/GCE, showed that the sensitivity of the electrode to H₂O₂ is significant. The increase in the interaction between the polymer and Ag⁺ is due to the large surface area of the UTPNSs; furthermore, the small size of the Ag NPs can provide a suitable surface area of Ag that is available to react with H₂O₂. The amperometric responses showed that the LOD, LOQ (S/N = 3) and the sensitivity were estimated to be 0.57 \( \mu \)M, 1.93 \( \mu \)M and 4.477 \( \mu \)A M⁻¹ cm⁻² for the linear segment, respectively. The results of the reproducibility experiments showed that the use of Ag-UTPNSs/GCE for the quantitative detection of certain concentration ranges of H₂O₂ is feasible.

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