A Voltammetric Sensor for the Determination of Hydroxylamine Using a Polypyrrole Nanotubes-Modified Electrode

Peyman Mohammadzadeh Jahani, Hadi Beitollahi, and Antonio Di Bartolomeo

Abstract: In this work, we develop an electrochemical sensor using a polypyrrole nanotubes-modified graphite screen-printed electrode (PPy NTs/GSPE) for sensing hydroxylamine. The PPy NTs/GSPE-supported sensor has an appreciable electrocatalytic performance and great stability for hydroxylamine oxidation. Compared to a bare graphite screen-printed electrode, we demonstrate that using the PPy NTs/GSPE leads to a significant reduction in the oxidation potential of hydroxylamine. The standard curve shows a linear relationship ranging from 0.005 to 290.0 µM (R² = 0.9998), with a high sensitivity (0.1349 µA/µM) and a narrow limit of detection (LOD) of 0.001 µM. In addition, the PPy NTs/GSPE has satisfactory outcomes for hydroxylamine detection in real specimens.

Keywords: hydroxylamine; polypyrrole nanotubes; electrochemical sensor; voltammetry

1. Introduction

Hydroxylamine, NH₂OH, is derived from ammonium as an intermediate during the two primary microbial nitrogen processes of anaerobic ammonium oxidation and nitrification. Hydroxylamine has a variety of industrial and pharmaceutical applications as a raw material [1,2]. The characteristics of hydroxylamine were recently detected following two major events; one involved the deaths of five people in the United States (February 1999), and the other involved the deaths of four people in Japan (June 2000). Moreover, hydroxylamine is a mutagenic, toxic, and harmful agent for living organisms that produces reversible and irreversible physiological alterations [3–5]. Accordingly, from environmental, health, and industrial viewpoints, the achievement of a sensitive analytical method for the detection of trace amounts of hydroxylamine is of remarkable importance.

Various techniques for the detection of hydroxylamine content have been developed, such as spectrophotometric methods [6], high performance liquid chromatography [7], gas chromatography [8], and polarography [9]. In spite of their many advantages, all these methods present some challenges, such as their complexity, expensiveness, the need for advanced equipment, and prolonged execution times [10].

For these reasons, electrochemical techniques are promising candidates for the construction of cost-effective and portable electrochemical sensing systems because of their high stability, lengthy linearity, possibility of miniaturization, simple instrumentation, quick response, and higher sensitivity and selectivity [11–20].

Disposable electrochemical graphite screen-printed electrodes (GSPEs) possess special features, such as low background current, capacity for mass production, cost-effectiveness, and disposability that can compensate for the numerous shortcomings of glassy carbon electrodes and carbon paste electrodes, including difficult cleaning procedures and memory impacts [21–25].
Most bare electrodes used for the electrochemical determination of analyte have multiple restrictions (e.g., low selectivity, high overpotential, and negligible stability in a broad spectrum of solution compositions). Hence, electrode modification can bypass these barriers [26–30]. The mass transfer kinetics can be improved by chemically modified electrodes (CMEs) at low overpotential, which reduces the impacts of interferants and inhibits surface fouling [31–36].

In recent years, nanomaterials have been investigated extensively in various fields, owing to their small size, impressive porosity, large specific surface area, and special physicochemical traits [37–41]. Several advances in the field of nanomaterials have been made to improve the performance of the sensors [42–45].

Conducting polymer nanomaterials have many applications in the fields of optoelectronics, electronics, (bio)sensing systems, and energy storage [46]. Polypyrrole (PPy) nanomaterials are popular polymers because of their admirable electronic conductivity, high stability, ease of construction, and appreciable biocompatibility. In addition, their outstanding electrical properties are related to the resonance of the delocalized π electrons present in the entire carbon chain of the polymer structure [47,48].

It should be noted that conductive polymers such as the PPy nanomaterials can be employed in various types of electrochemical equipment, such as voltammetric and corrosion sensors, because of their great electrical and electrochemical windows. In addition, the morphology of polypyrrole nanomaterials affects the catalytic properties. In particular, the PPy NTs are of unparalleled utility for sensing systems owing to their appreciable electron transduction, large surface areas, huge surface functionalities and porous structure [49–51].

In this paper, a graphite screen-printed electrode modified with polypyrrole nanotubes was fabricated for the determination of hydroxylamine. Such an electrode has not been tested for this purpose before. The fabricated sensor exhibited an enhanced catalytic performance for hydroxylamine oxidation.

2. Experimental Procedure

2.1. Instrumentation

A Tescan Field Emission Scanning Electron Microscope (FE-SEM, Mira3-Xum, Brno, Czech Republic) was used to capture FE-SEM images of the polypyrrole nanotubes. A PAN analytical instrument (x,pert3, Almelo, The Netherlands) was applied to obtain the X-ray diffraction (XRD) pattern of the polypyrrole nanotubes. Moreover, Fourier transform infrared spectroscopy (FT-IR) was carried out on a Bruker spectrometer with KBr pellets (Tensor-2, Bruker Corporation, Hanau, Germany) and was applied to obtain the functional groups of the polypyrrole nanotubes. An Autolab electrochemical instrument (Metrohm-PGSTAT302N, Metrohm Autolab B.V., 3526 KM, Utrecht, The Netherlands) was used for the voltammetric measurements. The experimental settings were explored using General Purpose Electrochemical System (GPES) software. The three-component DropSens screen-printed electrode (DRP-110, DropSens, Oviedo, Spain) consisted of a graphite working electrode, a silver pseudo-reference electrode, and a graphite counter electrode. All pH adjustments were performed using a Metrohm 710 pH meter (Metrohm Autolab B.V., 3526 KM, Utrecht, The Netherlands).

2.2. Materials

All chemicals and reagents were in a state of analytical purity, with no need for further purification. Hydroxylamine, methyl orange, iron (III) chloride (FeCl₃), pyrrole, and ethanol were obtained from Sigma-Aldrich (St. Louis, MO, USA).

The preparation of a 0.1 M phosphate buffer solution (PBS) was carried out using orthophosphoric acid and the respective salts in a pH range between 2 and 9.

2.3. Synthesis of the PPy NTs

The preparation of the PPy NTs was performed through pyrrole monomer oxidation with iron (III) chloride in exposure to methyl orange as a structure-guiding agent [52].
Thus, FeCl$_3$ (3.888 g; 23 mmol) with methyl orange (0.784 g; 2.3 mmol) were dissolved in deionized water (480 mL) followed by the addition of pyrrole (0.84 mL; 12.1 mmol), and the solution was stirred at an ambient temperature for 24 h. Then, the deionized water/ethanol (with proportions of 70:30) was used to thoroughly wash the attained PPy NTs precipitate until the filtrate was colorless and neutral, followed by vacuum-drying at 65 °C for 20 h.

2.4. Modified Electrode Fabrication

The modification of the GSPEs with the PPy NTs was performed using the drop-casting method. Briefly, 1 mg of the synthesized PPy NTs was poured into 1 mL of pure water under ultra-sonication for one hour. Then, 4 µL of the PPy NTs suspension was placed onto the working electrode surface of the GSPE. After solvent evaporation at an ambient temperature, the electrode was stored for future use.

2.5. Real Sample

The real river and well water specimens were filtered (with a 0.45 µm filter) prior to analysis using the standard addition method, and the variable hydroxylamine contents were spiked in the specimens.

3. Results and Discussion

3.1. Characterization of the PPy NTs

The FE-SEM image captured of the PPy NTs is shown in Figure 1, illustrating a one-dimensional nanotube structure of the PPy that is 87–150 nm in diameter and several micrometers in length, which is consistent with that reported in the previous literature [53].

![Figure 1. FE-SEM image of the PPy NTs.](image)

The FT-IR spectrum of the PPy NTs ranged from 400 to 4000 cm$^{-1}$ (Figure 2). The peaks at 1552 and 1450 cm$^{-1}$ can be related to symmetric and asymmetric polypyrrole ring stretching bonds, sequentially. Moreover, the peak at 1038, 1333, 1110, and 1603 cm$^{-1}$ corresponds to C-H deformation vibrations, C-N stretching vibrations, C-C stretching, and C=C stretching, sequentially. A broad peak at 3446 cm$^{-1}$ can also be related to the N-H stretching vibrations of the pyrrole ring. The successful PPy polymer formation is evident based on the FT-IR patterns [52,54].
The FT-IR spectrum of the PPy NTs ranged from 400 to 4000 cm$^{-1}$ (Figure 2). The peak at the 2θ value of 24.8° (Figure 3). The wide peak indicates the amorphous polymer and intramolecular stacking structure [55].

Figure 2. The FT-IR spectrum obtained of the PPy NTs.

Figure 3. XRD pattern of the PPy NTs.

3.2. Electrochemical Behavior of Hydroxylamine on the PPy NTs/GSPE

Since the selected analyte oxidation depends on the pH, the influence of the pH on the hydroxylamine oxidation was determined for the optimization of the operational conditions to reach the highest response. The electrochemical behavior of hydroxylamine on the PPy NTs/GSPE was examined in 0.1 M PBS at variable pHs of 2.0–9.0 using cyclic voltammetry (CV) (Figure 4). Reportedly, the hydroxylamine electro-oxidation on the PPy NTs/GSPE surface was higher in neutral conditions than in an alkaline medium or acidic medium (Figure 4A). Consequently, a pH of 7.0 was chosen as optimal for the hydroxylamine electro-oxidation on the PPy NTs/GSPE surface. In addition, it was discovered that the values of the peak potential shift to lower values with increasing pH, as shown in Figure 4B. Thus, the peak potential is linearly dependent on the pH, according to the following equation:

$$Ep (mV) = -59.786 \times pH + 1208.6 \quad (R^2 = 0.9997).$$

The value of the slope ($-59.786 \text{ mV/pH}$) was very close to the theoretical value ($-59 \text{ mV/pH}$), indicating that the same electron and proton numbers participate in the electrochemical oxidation process.

The electrochemical behavior of 100.0 µM hydroxylamine in the buffer solution (pH 7.0) was illustrated by using differential pulse voltammetry (DPV) techniques on the surfaces of bare GSPE (Figure 5, curve b) and the PPy NTs/GSPE (Figure 5, curve a). The anodic peak potential was approximately 1000 mV for the hydroxylamine oxidation on the bare GSPE, while it was approximately 790 mV on the PPy NTs/GSPE. On other hand, the GSPE exhibited a minimal current (4.0 µA), and the PPy NTs/GSPE exhibited an elevation in the oxidation current (14.5 µA). Accordingly, the greatest electrocatalytic impact on hydroxylamine oxidation was on the surface of the PPy NTs/GSPE as opposed to the bare GSPE, which was caused by increasing the simplification of the electron transfer process.
Figure 4. CV response of 100.0 μM hydroxylamine on the PPy NTs/GSPE in 0.1 M PBS at different pH values (2.0–9.0). (A) Plot of the oxidation peak current of hydroxylamine as a function of the pH solution. (B) Plot of the oxidation peak potential of hydroxylamine as a function of the pH solution.

Figure 5. DPV recorded for (a) the PPy NTs/GSPE and (b) the un-modified GSPE in 0.1 M PBS at pH = 7 with 100.0 μM hydroxylamine at a 50-mV/s scan rate.
3.3. Scan Rate Exploration

The influence of the scan rate (v) on the hydroxylamine (100.0 µM) electrochemical response in 0.1 M PBS at pH = 7.0 on the PPy NTs/GSPE was determined via linear sweep voltammetry (LSV). The corresponding data are shown in Figure 6. The hydroxylamine oxidation peak current (Ipa) was enhanced with an increasing scan rate from 10 to 500 mV/s and the peak potential shifted towards a more negative value, confirming the irreversibility of the oxidation reaction of hydroxylamine on the PPy NTs/GSPE. The peak current of the hydroxylamine oxidation was proportional to the scan rate square root ($\nu^{1/2}$) (Figure 6, inset), highlighting that the oxidation of hydroxylamine on the PPy NTs/GSPE was a typical diffusion-controlled electrode process, and the peak potential shifted towards a more negative value, confirming the irreversibility of the oxidation reaction of hydroxylamine on the PPy NTs/GSPE.

The rate-determining step was explored via the Tafel plot (Figure 7) according to the rising domain of the current–voltage curve at a scan rate of 10 mV/s. This section of the voltammogram (or the Tafel region) is influenced by electron transfer kinetics between the hydroxylamine and the PPy NTs/GSPE surface. The Tafel slope was 0.2555 and the charge transfer coefficient ($\alpha$) was 0.77; thus, a two-electron transfer procedure can be discerned in the rate-determining step for the electro-oxidation of hydroxylamine.

3.4. Chronoamperometry

The hydroxylamine oxidation on the PPy NTs/GSPE was explored by chronoamperometry (Figure 8). Chronoamperometric determinations of the variable hydroxylamine contents on the PPy NTs/GSPE were performed at a working electrode potential of 840 mV. The obtained data were used to determine the diffusion coefficient (D) of the hydroxylamine. For the hydroxylamine as an electroactive material with a certain D value, Cottrell’s equation was used to describe the current for the electrochemical reaction at a mass-transport-limited rate:

$$I = \frac{nFAD^{1/2}}{C_b \pi^{1/2}} t^{-1/2}$$  \hspace{1cm} (1)
Figure 6. LSV recorded for the PPy NTs/GSPE in 0.1 M PBS at pH = 7 with 100.0 μM hydroxylamine at variable scan rates. Nos. a–g: 10, 25, 50, 75, 100, 300, and 500 mV/s, sequentially. Inset: variation of the anodic peak current versus $\nu^{1/2}$.

Figure 7. LSV recorded for the PPy NTs/GSPE at 10 mV/s in 0.1 M PBS at pH = 7 with 100.0 μM hydroxylamine. Points: data used in the Tafel plot. Inset: Tafel plot obtained from the LSV.

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$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2}$$

In this equation, I stands for the current (A), n for the number of transferred electrons, F for the Faraday’s constant, A for the electrode surface area (cm²), t for time (s), $C_b$ for the bulk concentration (mol/cm³), and D for the diffusion coefficient (cm²/s). The experimental data of the I plot versus $t^{-1/2}$ are shown in Figure 8A, with the optimal fits for the various hydroxylamine contents. The achieved slopes of the straight lines in Figure 8A were plotted versus the hydroxylamine content (Figure 8B). The average D value of $4.8 \times 10^{-5}$ cm²/s was based on the obtained slope and on Cottrell’s Equation (1).

Figure 8. Chronoamperograms recorded for the PPy NTs/GSPE in 0.1 M PBS at pH = 7 with variable hydroxylamine contents. Nos. a–f: 0.1, 0.25, 0.4, 0.8, 1.3, and 1.8 mM of hydroxylamine. Insets: (A) Plots of I versus $t^{-1/2}$ derived from chronoamperograms a–f. (B) Corresponding slopes from the chronoamperogram curves vs. the hydroxylamine concentration.

3.5. Linear Dynamic Range and Limit of Detection

The standard curves were obtained by preparing multiple hydroxylamine solutions with various concentrations in 0.1 M PBS and measuring them on the PPy NTs/GSPE. Figure 9 illustrates a voltammogram of the DPVs at variable hydroxylamine contents (0.005, 0.07, 1.0, 5.0, 15.0, 30.0, 75.0, 100.0, 150.0, 200.0, 250.0, and 290.0 μM of hydroxylamine). According to our findings, there was an elevation in the peak currents with increasing hydroxylamine content. The standard curve of the DPV peak current for the hydroxylamine oxidation versus hydroxylamine concentration (Inset, Figure 9) demonstrates admirable linearity over a broad range of concentrations (0.005–290.0 μM) at pH = 7, with a correlation coefficient of 0.9998. In addition, the detection limit at 3σ equaled 0.001 μM.

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3.6. Stability, Repeatability, and Reproducibility

The long-term stability test of the PPy NTs/GSPE using DPV was performed at room temperature. The results exhibited that the peak current of 50.0 µM hydroxylamine on the PPy NTs/GSPE remained at 92.7% of its primary current after seven days, 91.9% after 14 days, and 88.7% after 21 days, indicating the superior long-term stability of the proposed sensor.

Table 1. Comparing the analytical performance of the PPy NTs/GSPE with other modified electrodes used for hydroxylamine determination.

<table>
<thead>
<tr>
<th>Electrochemical Sensor Method</th>
<th>Linear Range</th>
<th>Limit of Detection</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene oxide/TiO₂/screen-printed electrode</td>
<td>Differential pulse voltammetry</td>
<td>0.1–300.0 µM</td>
<td>0.065 µM</td>
</tr>
<tr>
<td>Nickel(II)-morin complex modified multi-wall carbon nanotube paste electrode</td>
<td>Amperometry</td>
<td>2.5–400.0 µM</td>
<td>0.8 µM</td>
</tr>
<tr>
<td>Gold nanoparticle-polypyrrole nanowire/glassy carbon electrode</td>
<td>Differential pulse voltammetry</td>
<td>1.0–500.0 µM</td>
<td>0.21 µM</td>
</tr>
<tr>
<td>Gold nanoparticle-metal-metalloporphyrin frameworks/glassy carbon electrode</td>
<td>Differential pulse voltammetry</td>
<td>0.01–20.0 µM</td>
<td>0.004 µM</td>
</tr>
<tr>
<td>Cobalt(II) bis (benzoylacetone) ethylenediimino multi-wall carbon nanotube/carbon paste electrode</td>
<td>Square wave voltammetry</td>
<td>5.0–50.0 µM</td>
<td>12 µM</td>
</tr>
<tr>
<td>La₂O₃/Co₃O₄ nanocomposite/ionic liquid/carbon paste electrode</td>
<td>Differential pulse voltammetry</td>
<td>0.06–240.0 µM</td>
<td>3.0 nM</td>
</tr>
<tr>
<td>Polypyrrole nanotubes/graphite screen-printed electrode</td>
<td>Differential pulse voltammetry</td>
<td>0.005–290.0 µM</td>
<td>0.001 µM</td>
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</table>

Figure 9. DPVs recorded for the PPy NTs/GSPE in 0.1 M (pH 7.0) with variable hydroxylamine concentrations. Nos. a–I: 0.005, 0.07, 1.0, 5.0, 15.0, 30.0, 75.0, 100.0, 150.0, 200.0, 250.0, and 290.0 µM of hydroxylamine. Inset: Plot of the electrocatalytic peak current as a function of the variable hydroxylamine concentrations (0.005–290.0 µM).
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<td>[59]</td>
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<td>12 µM</td>
<td>[60]</td>
</tr>
<tr>
<td>La$_2$O$_3$/Co$_3$O$_4$ nanocomposite/onion liquid/carbon paste electrode</td>
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<td>0.005–290.0 µM</td>
<td>0.001 µM</td>
<td>This Work</td>
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</table>

The oxidation of hydroxylamine (50.0 µM) on the same PPy NTs/GSPE electrode was performed using ten repeated voltammetric measurements, the results of which confirmed the superior repeatability of the fabricated sensor, with a relative standard deviation (RSD) of 3.0%.

Similar conditions were provided for the measurement of the response currents of hydroxylamine (50.0 µM) on five PPy NTs/GSPEs, the results of which confirmed the excellent reproducibility of the fabricated sensor, with an RSD value of 3.7%.

3.7. Real Sample Analysis

The thus-fabricated sensor was examined for its applicability to the detection of hydroxylamine spiked in real specimens, including river (Halil, Jiroft, Iran) and well water (Graduate University of Advanced Technology, Kerman, Iran), by measuring via the standard addition method (Table 2). The spike recovery rate ranged from 96.7% to 104.3%, underlining the capacity of the modified electrodes for sensor applications in hydroxylamine determination in real specimens.

Table 2. Electrochemical determination of hydroxylamine in various water samples with the PPy NTs/GSPE. Concentrations are reported as µM (n = 3).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spiked Concentration</th>
<th>Found Concentration</th>
<th>Recovery (%)</th>
<th>R.S.D. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>River water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5.0</td>
<td>5.1</td>
<td>102.0</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>7.3</td>
<td>104.3</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Well water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6.0</td>
<td>5.8</td>
<td>96.7</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>7.1</td>
<td>101.4</td>
<td>2.0</td>
<td></td>
</tr>
</tbody>
</table>
4. Conclusions

We fabricated an ultra-sensitive electroanalytical sensor for hydroxylamine detection using the modification of a graphite screen-printed electrode based on polypyrrole nanotubes. The PPyNTs/GSPE was found to be a powerful platform for determining hydroxylamine in a range from 0.005 to 290.0 µM, voltammetrically. The limit of detection for hydroxylamine using the PPyNTs/GSPE was obtained as 0.001 µM. The recovery rate of 96.7% to 104.3% in real specimens verifies the appreciable potential of the newly developed sensor for sensing hydroxylamine in real specimens. As a result, it is evident that the PPyNTs/GSPE has an excellent electrochemical performance and potential for application as an electrochemical detection platform.

Author Contributions: Conceptualization, H.B. and A.D.B.; methodology, P.M.J. and H.B.; software, P.M.J.; validation, H.B. and A.D.B.; formal analysis, P.M.J., H.B. and A.D.B.; investigation, P.M.J. and H.B.; resources, P.M.J. and H.B.; data curation, A.D.B., P.M.J. and H.B.; writing—original draft preparation, P.M.J. and H.B.; writing—review and editing, A.D.B.; visualization, P.M.J.; supervision, H.B.; project administration, H.B. and A.D.B.; funding acquisition, P.M.J. and H.B. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available upon request from the corresponding authors.

Conflicts of Interest: The authors declare no conflict of interest.

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