A Nanocomposite of Graphitic Carbon Nitride and Carbon Dots as a Platform for Sensitive Voltammetric Determination of 2-chlorophenol in Water

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Received: 20 December 2020 / Accepted: 8 February 2021 / Published: 31 March 2021

Herein, we report the preparation, characterisation and application of graphitic carbon nitride/carbon nanodots nanocomposite (g-C₃N₄/CDs) as a platform for the sensing of 2-chlorophenol in water. The g-C₃N₄/CDs was prepared via microwave irradiation and characterised by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The electrochemical properties of modified glassy carbon electrodes were studied using cyclic voltammetry (CV). In comparison to unmodified GCE, there was a marked enhancement of the oxidation peak of the analyte when GCE modified with the nanocomposite material was used. The composite modifier also performed better than the single-component modifiers. The oxidation peak currents varied linearly with the concentrations in the range 0.5 to 2.5 μM with a detection limit of 0.67 μM. The sensor was used to determine the analyte in real water samples with good recoveries.

Keywords: Graphitic carbon nitride, Carbon nanodots, 2-Chlorophenol, Electrode modifiers, Electroanalysis.

1. INTRODUCTION

The presence of organic pollutants such as phenols and substituted phenols in water can pose health risks to humans and animal populations [1; 2]. Chlorophenols (CPs), for instance, are widely used in industries to manufacture chemical substances for the control of weeds, pests, insects and so on. They are also produced during the disinfection of municipal water using chlorination method [3]. CPs often
find their way into the aquatic environments via various routes. Consequently, CPs such as 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol have been detected in tap water and environmental waters [4; 5]. Owing to their potential to induce debilitating biological effects, CPs are classified as priority organic pollutants and maximum permissible amounts in drinking water have been set by many countries and organisations including the United States Environmental Protection Agency (EPA) and the European Union [6]. It is thus necessary to monitor their presence in environmental waters. Due to the low contamination level and severe toxicity of 2-chlorophenol, the development of sensitive, simple and reliable analytical method is required. Various methods such as high performance liquid chromatography (HPLC), gas chromatography, gas chromatography-microwave-induced plasma atomic emission spectroscopy (GC-MIP-AES) and gas chromatography-tandem mass spectroscopy are commonly used to monitor organic pollutants including chlorophenols. [7-9]. These methods can be very sensitive and accurate. However, they do have some drawbacks which include high cost and complexity of analytical equipment, non-portability of the equipment and tedious sample preparation process amongst others [10]. As a result, it is necessary to develop alternative methods in which these drawbacks are circumvented. In this regard, electrochemical devices offer simple, inexpensive and rapid means for the determination of electrochemically active organic pollutants in aqueous media. It is worth mention that electrochemical sensors are also well suited for onsite analysis because of their small sizes. In fabricating an electrochemical sensor, the sensing platform (i.e. the electrode surface) can be designed to maximise communication between the analyte and the sensor. In this way, high sensitivity and considerable selectivity can be achieved [11]. The modification of the surface of commercial electrode such as the glassy carbon electrode (GCE) to obtain enhanced signal when used to analyse organic pollutants has been the subject many scientific reports. Materials possessing nanometric dimensions have been used as modifiers to achieve this goal. The choice of nanomaterials is often informed by their beneficial properties including electrical conductivity, high surface area, catalytic activity, and so on. Some of the materials also have functionalities that promote interaction between the target pollutant and the modified electrode. Carbon nanomaterials, metal and metal oxide nanoparticles [12], nanofibres, etc. have been explored as electrode modifiers to detect and quantify various analytes in water.

Recently, graphitic carbon nitride (g-C_3N_4), a polymeric material comprising mainly carbon and nitrogen atoms, has been receiving attention as a promising material for electrochemical applications. It has been indicated to have sites that may mediate redox processes [13; 14]. Liu et al. reported the non-enzymatic determination of glucose using a composite electrode modifier containing g-C_3N_4 [15]. The authors suggested that the presence of g-C_3N_4 promotes the accumulation of the glucose molecules on the surface of the electrode. This accumulation can lead to improved electrochemical signal. Tia et al. also prepared a bi-component electrode modifier with g-C_3N_4 and reported that the sensing platform exhibited considerable catalytic activity for H_2O_2 [16]. The stability of g-C_3N_4 in aggressive media and high adsorption capacity are beneficial for electroanalysis. The abundant pi bonds in the polymeric material may also offer benefits in the determination of aromatic compounds such as phenols. Its low conductivity, however, is a disadvantage [17]. Thus, most electrochemical investigations in which g-C_3N_4 is used as electrode material/modifier incorporated other materials which can enhance conductivity [18; 19].
In this study, a composite of g-C$_3$N$_4$ and carbon dots was prepared and used as an electrode modifier. Carbon dots are a stable and electrically conductive carbon materials whose sizes are below 10 nm. They have been indicated as having excellent electrocatalytic properties and thus have been employed in a variety of electrochemical studies [20; 21]. It is thought that a sensing platform consisting of g-C$_3$N$_4$ and carbon dots (CDs) would be markedly sensitive to phenolic compounds in aqueous solutions, and produce reproducible current signals which could be correlated to the amounts of the analytes in solution. Studies on the use of g-C$_3$N$_4$ as electrode modifier for monitoring organic pollutants in water are still sparse and this is the first report to investigate the voltammetric determination of 2-chlorophenol using a nanocomposite of g-C$_3$N$_4$ and carbon nanodots.

2. EXPERIMENTAL

2.1 Reagents and materials

Thiourea, 2-chlorophenol, dimethylformamide (DMF), potassium chloride (KCl), sodium chloride (NaCl), sodium hydrogen phosphate (Na$_2$HPO$_4$), potassium dihydrogen phosphate (KH$_2$PO$_4$), bisphenol, 4-nitrophenol, phenol, 4-chloro-3-methyl-phenol were purchased from Sigma Aldrich (South Africa). The pine cones (from which carbon dots were obtained) were collected from pine trees in Vanderbijlpark (26°42'37.91"S 27°51'39.35"E), South Africa.

2.2. Characterisations

The electron images of the pristine and composite materials were obtained on transmission electron microscope (JEOL JEM-2100) at 200 kV. The X-ray diffraction patterns were recorded using the Shimadzu-XRD 700 diffractometer with Cu K$_\alpha$ radiation ($\lambda$ = 1.54056 Å), at a scan rate of 1° per min and a current and a voltage of 30 mA and 40 kV respectively. Electrochemical experiments were conducted on a Bio-Logic SP-240 potentiostat electrochemical workstation. Unmodified and modified glassy carbon electrodes were used as the working electrodes, while a platinum wire and Ag/AgCl (3.0 M KCl) were used as the counter electrode and the reference electrode respectively. FTIR spectra were recorded on Perkin Elmer 400 spectrophotometer in the range of 600 - 4000 cm$^{-1}$.

2.3. Synthesis of g-C$_3$N$_4$

Approximately 10 g of thiourea was weighed and transferred into an alumina crucible, 5 mL of distilled water was added, and the mixture was heated in a microwave oven at 600 W for 15 min. The resulting material was calcined in air in a tube furnace at a heating rate of 5 °C/min. The furnace was maintained at 550 ºC for 1 h. The yellow powder obtained after calcination was kept for use.
2.4. Synthesis of Carbon dots

CDs was prepared by a facile one-pot hydrothermal method using pine cone as the carbon source. Exactly 10 g of pine cone weighed into 50 mL ultra-pure water and the dispersion was placed in a 100 mL Teflon-lined stainless steel autoclave. The autoclave was subsequently maintained at a temperature of 180 °C for 24 h in an air oven. The dispersion was filtered and the residue obtained was dried for 48 h.

2.5. Synthesis of g-C₃N₄/CDs

About 10 g of thiourea was weighed and mixed with 5 mL of carbon dots dispersion in an alumina crucible. The crucible was then transferred into a microwave oven and heated at 600 W for 15 min. The resulting solid material was calcined in a tube furnace under atmospheric condition at a heating rate of 5 °C/min to 550 °C for 1 h.

2.6. Preparation of the working electrode

Prior to modification, the bare GCE was polished with alumina slurries (0.05 and 1 microns), followed by sonication with anhydrous alcohol and distilled water for 1 min. For electrochemical studies, 15 μL of the g-C₃N₄/CDs dispersion (dispersed in dimethylformamide) was placed on the surface of GCE and left to dry. This new modified GCE was denoted as g-C₃N₄/CDs electrode. The dispersions of g-C₃N₄ and CDs were used to modify GCE electrodes following the same procedure.

2.7. Electrochemical detection of 2-chlorophenol

Different concentrations of the analytes were prepared in 0.1M phosphate buffer solution (pH = 7.6), and 10.0 mL of the analyte solution was transferred into an electrochemical cell and the electrodes were dipped in the cell to record all electrochemical signals using differential pulse voltammetry (DPV).

3. RESULTS AND DISCUSSION

3.1 Characterisations of the CDs, g-C₃N₄, and g-C₃N₄/CDs

3.1.1 Morphology

The morphologies of CDs, g-C₃N₄ and g-C₃N₄/CDs were investigated by TEM. The electron images of CDs (Figure 1(a)) show well-dispersed particles, while the image of g-C₃N₄/CDs (Figure 1(b)) reveal sheets with many voids and pores, but CDs cannot be distinguishably observed on the g-C₃N₄ nanosheet.
3.1.2 XRD

Figure 2 shows the XRD patterns of CDs, g-C₃N₄ and g-C₃N₄/CDs. In the pattern for CDs, a broad peak at around $2\theta = 20.96^\circ$ which corresponds to (002) lattice spacing of carbon can be observed. The broadness of the peak indicates that the carbon material is amorphous. The g-C₃N₄ sample exhibits one pronounced peak at $27.75^\circ$ which corresponds to the diffraction signal of graphitic carbon materials, and results from the interlayer stacking of aromatic segments, (JCPDS card no.066-0813) [22]. From the XRD pattern of g-C₃N₄/CDs nanocomposite, the characteristic peak of g-C₃N₄ is observed and left...
shifted to 27.61° with less intensity, while the characteristic band of CDs is much less prominent. This may be because of its relatively small quantity in the nanocomposite.

3.1.3 Electrochemical characterisations

As displayed in Figure 3, a well-defined pair of redox peaks on g-C₃N₄/CDs/GCE could be observed with higher peak currents in comparison with other electrodes (g-C₃N₄/GCE and CDs/GCE). The higher peak current recorded on the g-C₃N₄/GCE indicates that the composite material provided more redox sites for the probe and the electron transfer was enhanced. This suggests a good synergy between CDs and g-C₃N₄. The electro-active surface areas of the electrodes were calculated using the Randles-Sevcik equation:

\[ i_p = 2.69 \times 10^5 n^{3/2} v^{1/2} D^{1/2} AC \]

Where \( n \) is the number of electrons, \( v \) (mV/s) is the scan rate, \( A \) (cm²) the area of the electrode, \( C \) is the concentration in mol/L and \( D \) (cm²/s) is the diffusion coefficient of \([Fe(CN)₆]^{3-/4-}\) in KCl at room temperature which has been reported to be \( 6.3 \times 10^{-6} \) cm²/s, and \( i_p \) (A) is the peak current. The g-C₃N₄/CDs/GCE exhibits the largest active surface area of 0.082 cm² compared to 0.072 cm² and 0.052 cm² for g-C₃N₄/GCE and bare GCE respectively. High electroactive surface area is expected to offer benefits for electroanalysis of compounds.

![Figure 3](image_url)

**Figure 3.** CVs of GCE, g-C₃N₄/GCE and g-C₃N₄/CDs/GCE in 5mM \([Fe(CN)₆]^{3-/4-}\) (prepared in 0.1 M KCl) at scan rate of 50 mV/s.

The kinetics of the redox probe on the surface of g-C₃N₄/CDs/GCE was studied. As shown in Figure 4(a), both anodic and cathodic peak currents were found to be proportional to the scan rate in the range 10 to 100 mV/s, suggesting a diffusion-controlled process. This implies that the quantitative analyses of the compound can be successfully achieved using the electrode [20].
Figure 4. (a) CV of g-C$_3$N$_4$/CDs/GCE in 5mM [Fe(CN)$_6$]$^{3-}/4^-$ (prepared 0.1 M KCl), (b) The linear plot of peak current vs square root of scan rate

3.2 Optimization of detection condition

3.2.1 Optimization of pH

pH is known to affect transfer of proton in redox processes, and the interaction between the analyte of interest and the electrode modifier [23]. As a result, the effect of pH on the electro-oxidation of 2-CP on g-C$_3$N$_4$/CDs/GCE was investigated from pH 3.0 to 9.0 using differential pulse voltammetry (DPV) in 0.1 M PBS (Figure 5). The peak current is most pronounced at near neutral pH values, with highest current value at pH 7.6. The current value decreased at pH > 7.6. Consequently, the analyte was prepared in PBS and the pH adjusted to 7.68 for all analyses.

Figure 5. The effect of pH value on the oxidation current of 2 mM 2-CP in 0.1 M in PBS on the g-C$_3$N$_4$/CDs/GCE
3.2.2 Effect of the amount of g-C₃N₄/CDs on the GC electrode

To determine the amount of the modifier on the surface of GCE that would give the highest peak current for 2-CP, 5 to 25 μL of the modifier suspension was pipetted onto the GCE. As can be seen in Figure 6, the oxidation peak current of 2-chlorophenol gradually increases with increasing amount of g-C₃N₄/CDs. The current response began to decline when the amount of the modifier was greater than 15 μL. Thus, the surface of GCE was modified with 15.0 μL of the nanocomposite for all analyses in this study.

![Figure 6](image)

**Figure 6.** Effect of the amount of the g-C₃N₄/CDs suspension on the oxidation peak current of 2mM 2-chlorophenol

3.3 Voltammetric determination of 2-chlorophenol

Owing to its better sensitivity and higher signal resolution than cyclic voltammetry, differential pulse voltammetry (DPV) was utilised for the analysis of 2-chlorophenol using the g-C₃N₄/CDs/GCE sensor under optimised conditions. It is evident in Figure 7 that the peak current of 2-chlorophenol exhibits linear increment with concentrations of the analyte, in the ranges 0.5 to 2.5 μM and 2 to 10 μM. The calibration graphs plotted for the two concentration ranges are shown in Figures 7(b) and 7(d).

The limit of detection (LOD) was calculated using the relation, LOD = 3σ/m [24], where σ is the standard deviation and m is the gradient of the linear calibration plot. The LOD was calculated as 0.67 μM.

The excellent performance of the g-C₃N₄/CDs modified GCE can be ascribed to the good conductivity of CDs and the high electroactive area of g-C₃N₄. The extensive π-conjugation bonds in g-C₃N₄ could also aid rapid electron transfer between the analyte and the electrode. The synergy between the two materials could also be beneficial for the electrochemical process. Compared to other electrochemical sensors in the table below (Table 1), the sensor proposed in this study exhibited...
considerably high sensitivity, and lower oxidation potential. The lower oxidation potential suggests that the composite modifier showed some electrocatalytic characteristic.

Figure 7. (a) Differential pulse voltammograms of 2-CP in 0.1 M PBS at pH 7.6 (\([2\text{-CP}] = 2 - 10 \text{ μM}\)) on g-C\(_3\)N\(_4\)/CDs/GCE (b) The linear plot of peak current vs concentration of 2-CP (2-10 μM) (c) Differential pulse voltammograms of 2-CP in 0.1 M PBS at pH 7.6 (\([2\text{-CP}] = 0.5 – 2.5 \text{ μM}\)) on g-C\(_3\)N\(_4\)/CDs/GCE (d) The linear plot of peak current vs concentration of 2-CP (0.5 – 2.5 μM)
3.4 Interference studies

A drawback of 2-chlorophenol detection using voltammetry or amperometric methods is that it could be susceptible to interference from various compounds which are oxidized at the same or almost the same potential with it. This leads to increase in the current signal of 2-chlorophenol. To study the effect of potential interfering compounds/species on the current signal of 2-chlorophenol, 2 µM of the analyte was used and a 5-fold higher concentration of each potentially interfering specie/molecule was added. A wide range of inorganic ions including Cd$^{2+}$, Hg$^{2+}$, Fe$^{2+}$, Pb$^{2+}$, As$^{3+}$, Zn$^{2+}$, Mn$^{2+}$, Fe$^{3+}$, Cd$^{2+}$, Ag$^{+}$, Na$^+$, Mg$^{2+}$ were found not to have significant effect on the current signal of 2-chlorophenol. The addition of 5-fold higher concentration of the ions did not cause up to 5% change in the signal of the analyte. Furthermore, phenol and some substituted phenols including bisphenol A, 4-nitrophenol and 4-chloro-3-methylphenol were also investigated for their influence on the oxidation current of 2-chlorophenol. It was found that 4-nitrophenol and bisphenol A showed no substantial interference on the oxidation signal of 2-chlorophenol, but phenol and 4-chloro-3-methylphenol caused signal changes of about +63 and +103% respectively.

3.5 Analysis of real water samples

To assess the suitability of the sensor for real life application, water samples were collected from a river in the Vanderbijlpark and from a water tap in the University. The results from the analysis of the water samples are shown in table 2. These results demonstrate that the sensor is promising for real analytical measurements.
Table 2. Recovery of 2-chlorophenol in water samples (n = 3)

<table>
<thead>
<tr>
<th>Water sample</th>
<th>Amount of analyte added (µM)</th>
<th>Amount of analyte found (µM)</th>
<th>Recovery (%)</th>
<th>Relative standard deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>River water</td>
<td>3.00</td>
<td>2.81</td>
<td>93.7</td>
<td>2.61</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>3.93</td>
<td>78.6</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>7.00</td>
<td>7.34</td>
<td>104.9</td>
<td>2.97</td>
</tr>
<tr>
<td>Tap water</td>
<td>3.00</td>
<td>3.80</td>
<td>126.7</td>
<td>3.94</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>6.32</td>
<td>126.4</td>
<td>3.95</td>
</tr>
<tr>
<td></td>
<td>7.00</td>
<td>7.47</td>
<td>106.7</td>
<td>2.28</td>
</tr>
</tbody>
</table>

4. CONCLUSION

An electrochemical sensor for the analysis of 2-chlorophenol in aqueous media was developed based on g-C₃N₄/CDs/CGE. The individual characteristics and the synergy between g-C₃N₄ and CDs were found to be beneficial for the detection and quantification of the analyte. Under optimised conditions, the analyte concentrations varied linearly with the current signals, and a relatively low limit of detection was obtained. This work provides a simple and sensitive device for monitoring 2-chlorophenol in water.

ACKNOWLEDGEMENT

The National Research Foundation, South Africa, is gratefully acknowledged for financial support (grant number 121191).

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