Catechol encapsulated surfactant film modified glassy carbon electrode to detect thiourea at 10^{-7} M level

Rimki Bhattacharjya & Diganta Kumar Das*
Department of Chemistry, Gauhati University, Guwahati, 781 014, India

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Glassy carbon electrode surface has been modified with catechol encapsulated in cetyltrimethylammonium bromide (CTAB) or sodium dodecyl sulphate (SDS) surfactant film. The modified electrodes show quasi reversible cyclic voltammograms in tris buffer at pH 7.0 with redox potential values + 0.250 V and + 0.185 V respectively, using Ag-AgCl (3M NaCl) as reference. Addition of thiourea into the electrolytic medium increases the cathodic and anodic currents of the modified electrodes. Anodic current of CTAB film modified electrode is increased by 18 times while cathodic current increased by 1.8 times. However, SDS film modified electrode shows an increase in anodic current by 5.5 times and that in cathodic current by 8.0 times at 3×10^{-7} M concentration of thiourea compared to that at zero thiourea concentration in electrolytic medium.

Keywords: Catechol, Cetyltrimethylammonium bromide, Cyclic voltammetry, Glassy carbon electrode, Sodium dodecyl sulphate, Thiourea

Thiourea is extensively used in rubber industry, photography and agriculture. It is a good spectrophotometric reagent for detection/determination of a number of metal ions. Thiourea is toxic due to its influence on the metabolism of carbohydrates and has carcinogenic activity.

Film modified electrode as voltammetric sensors has gained importance due to easy preparation, easy application and low cost. There are reports of a number of different materials impregnated with a suitable redox probe as film modifying agent. Few examples are clay film modified electrode for catechol detection, surfactant didodecyldimethylammonium bromide film modified electrode for simultaneous determination of dopamine and ascorbic acid, nano-ZnO/polymer modified electrode for ascorbic acid, aluminium electrode modified with nickel complex for dopamine, nanostructured copper-salen film modified electrode for sulfite ion, etc.

Surfactants often in combination with others are also quite extensively used as modifying agent of electrodes in order to sense a number of species voltametrically. Montmorillonite clay with surfactant cetyltrimethylammonium bromide (CTAB) modified glassy carbon (GC) electrode is found to act as voltammetric sensor of pesticides, sodium dodecyl sulphate (SDS) modified carbon paste electrode is reported for selective detection of dopamine over ascorbic acid, and neutral surfactant modified electrode is used for direct electrochemistry of heme proteins. Bhattacharjya & Das have already developed surfactant and polymer modified electrodes as voltammetric sensor for ascorbic acid and thiourea, and caffeine. CTAB and carbon nanotube modified GC electrode have been developed to detect Zn^{2+} ion over a number of other metal ions.

There are very few reported papers on electrochemical determination of thiourea. Potentiometric determination of thiourea in strong acid solution using ion selective electrode with membrane containing Ag^{+} ion is known. Oxidative method of thiourea determination using alumina modified platinum electrode using cyclic voltammetry is reported. Copperoxide-copper electrode is designed by Manea et al. for electrochemical detection of thiourea. Bhattacharjya & Das reported a ferrocene encapsulated lipid and surfactant film modified glassy carbon electrode to voltammetrically detect thiourea at the level of 2 µM and the original electrode could be recovered by simple chemical treatment.

In this study, a new pyrocatechol encapsulated surfactant film modified glassy carbon electrode has been developed which can detect thiourea at a...
concentration level of $10^{-7}$ M in aqueous medium. This modified electrode can further distinguish thiourea from urea.

**Experimental Procedure**

All the chemicals were obtained from Loba Chemie and used without further purification. CHI 660B Electrochemical Analyzer (USA) with a three electrode cell assembly was used for the electrochemical studies. Electrochemical experiments were carried out under a blanket of nitrogen gas after passing the gas through the solution for 10 min. The working electrode used is glassy carbon (GC) disc, reference electrode is Ag-AgCl and sodium nitrate (0.1M) is the supporting electrolyte. In Osteryoung Square wave voltammetry (OSWV) experiments, the square wave amplitude was 25 mV. The working electrode was cleaned by polishing with 0.05 micron alumina powder using a polishing kit (CHI) Followed by sonication.

**Preparation of modified electrode**

Catechol/CTAB/GC or Catechol/SDS/GC electrode was prepared using the following procedure. Catechol (0.02 g) was dissolved in 10 mL of chloroform. To this solution, 0.2g of sodiumdodecyl sulphate (SDS) or cetyltrimethylammonium bromide (CTAB) was added. 20 µL of the appropriate solution was then placed on the tip of the glassy carbon electrode using Hamilton micro syringe and chloroform was allowed to evaporate under nitrogen environment, resulting in the formation of catechol encapsulated film. Cyclic voltammogram was recorded by dipping the tip of this modified electrode into 0.1 M tris buffer at pH 7.0 and containing 0.1 M NaNO$_3$.

**Results and Discussion**

Cyclic voltammogram of catechol encapsulated SDS film modified glassy carbon electrode was recorded at various added concentrations of thiourea in the electrolytic medium, the cathodic and anodic currents are found to increase. Fig. 1 shows the cyclic voltammogram of catechol encapsulated CTAB film modified GC electrode at zero and at different added concentrations of thiourea. Inset of Fig. 1 shows the plot of anodic currents of the cyclic voltammograms of the modified electrodes versus thiourea concentration. The slope of the current versus concentration plot is found to be $8 \times 10^2$ A/M

![Fig. 1—Cyclic voltammetric response of catechol/CTAB/GC electrode at different added concentration of thiourea in the electrolytic medium [Inset plot of reduction current versus thiourea concentration in electrolytic medium]](image-url)

The cyclic voltammogram is due to the redox process involving one electron, as shown in following equation:

$$\text{QH} + \text{H}^+ + e \leftrightarrow \text{QH}_2$$  \hspace{1cm} (1)

where QH is the catechol.

Formation of QH free radical on one electron oxidation of QH$_2$ on carbon electrode at pH 7.0 is well established$^{17}$. Due to electrostatic reason the catechol free radical (QH) is likely to be unstable in negative SDS film compared to that in positive CTAB film compared to that in negative SDS film. Hence, in CTAB film the reduction process is comparatively easier and therefore leads to a positive shift of 0.065 V compared to that in SDS film.
From the figures it is clear that the modified electrodes respond to thiourea in near nanomolar concentration.

It is reported that thiourea undergoes easy oxidation into c,c‘-dithiodiformamidinium ion due to the formation of S-S single bond. The potential of the modified electrode is cycled between +1.000 V and -0.600 V. At the applied positive potential, thiourea present in electrolytic medium undergoes easy oxidation into c,c‘- dithioformamidinium ion. The formed dithioformamidinium ion which has two positive charges will react with catechol forming catecholate free radical and itself will convert into thiourea. Thus, catecholate free radical will be formed both due to electrode process by reacting with c,c‘ - dithioformamidinium ion. This results in increased cathodic and anodic currents with added thiourea in the electrolytic medium. This reaction mechanism is shown in Scheme 1.

If the proposed mechanism is correct then replacement of thiourea by urea, which has an oxygen atom in place of sulfur, in the electrolytic medium, should not be able to increase the current of the modified electrode due to the lack of formation of S-S bond. Indeed it has been observed that the current of the modified electrode decreases when cathodic and anodic currents are measured as a function of urea.

Figure 2 compares the oxidation and reduction currents for the two modified electrodes, when thiourea concentration is zero and 3×10⁻⁷ M in the electrolytic medium. In catechol/SDS/GC electrode the reduction current increases by 18.5 times while the oxidation current increases only by 1.5 times. The reduction process in the reversible reaction \( \text{QH} + \text{H}^+ + \text{e} \leftrightarrow \text{QH}_2 \) is obviously favorable one as it replenishes free radicals. Further, presence of cationic CTAB molecules favor formation of free radical by chemical path as described in Scheme 1. In case of catechol/SDS/GC film the reduction current increases by about five times while oxidation current increases by eight times. This implies that in anionic SDS film the relative concentration of catecholate free radical is less than that of catechol. This is quite possible because anionic SDS molecules will not favor formation of free radicals due to electrostatic reason. From above discussion, it is clear that catechol/SDS/GC electrode is best for determination of thiourea in solution.

Analytical applications

The voltammetric sensor developed was tested in the determination of thiourea in real samples using catechol/SDS/GC electrode. Bleaching solution, washing solution and toning solution used in photography or electroplating were prepared as per reported procedure. 1.0 mL of each of the solutions were diluted 100 times with double distilled water and a definite amount of thiourea was added. The recoveries from the samples spiked with different amounts of thiourea are shown in Table 1. From the table it is clear that the maximum deviation in recovery is 2.5% and the maximum relative error is 0.6%, hence the method is applicable for determination of thiourea in real solutions.
It has been shown that GC electrode modified in a very simple way with catechol encapsulated surfactant film can sense thiourea at $10^{-8}$ M concentration in aqueous medium. Urea does not increase the currents of cyclic voltammograms of the modified electrode and hence this electrode could distinguish between thiourea and urea.

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**Table 1—Recovery of thiourea using catechol/SDS/GC electrode**

<table>
<thead>
<tr>
<th>Sample solution</th>
<th>Thiourea added $\times 10^{-7}$, M</th>
<th>Thiourea found $\times 10^{-7}$, M</th>
<th>Average recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bleaching</td>
<td>6.9</td>
<td>7.10±0.020</td>
<td>102.8</td>
</tr>
<tr>
<td>Washing</td>
<td>0.42</td>
<td>0.43±0.002</td>
<td>102.4</td>
</tr>
<tr>
<td>Toning</td>
<td>0.50</td>
<td>0.515±0.003</td>
<td>103.0</td>
</tr>
</tbody>
</table>

* Average value of four determinations and SD.

**References**