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# A Simple Fabrication of Co (II)-phthalocyanine Modified Disposable Activated Screen Printed Carbon Electrode for the Effective Determination of L-cysteine

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An amperometric electrochemical sensor for the sensitive detection of L–Cysteine was constructed using cobalt (II) tetrasulfonated phthalocyanine (CoTsPc) and activated screen printed carbon electrode (ASPCE) through a simple approach. The fabricated electrode was confirmed by field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX) and cyclic voltammetry (CV). The sensitivity and selectivity of our modified electrode towards L–Cysteine were higher when compared to the performance of unmodified electrode. The experimental conditions for the electro–oxidation of L–Cysteine were optimized and the good electrocatalytic ability of our sensor was shown from the evaluated values of linear range (5 to 220  $\mu$ M), LOD (0.22  $\mu$ M) and sensitivity (953.8 $\mu$ A/mM cm<sup>-2</sup>). In addition, our fabricated electrode selectively detects the L–Cysteine even in the presence of interfering other biomolecules. The satisfactory results for the demonstration of practical feasibility were also achieved with our modified electrode in human serum samples. An appreciable repeatability and reproducibility were attained by our fabricated electrode.

**Keywords:** cobalt (II) tetrasulfonated phthalocyanine, activated screen printed carbon electrode, L–Cysteine and sensitivity, practicality.

# **1. INTRODUCTION**

L-Cysteine (L-Cys) is a vital non-essential amino acid which contains sulfur. It involves the biological functions including protein folding, cell protection from the free radicals in anti-oxidant defense system, etc [1, 2]. The deficiency of L-Cys in biological system causes heart diseases,

depigmentation of hair, liver damage, lethargy and skin lesions[3]. On the other hand, it may also result in L–cystinuria, Parkinson's disease, and AIDS when present in excess. At present, L–Cys can also be seen in foods and pharmaceuticals[4]. Thus, a sensitive method for the detection of L–Cys is more important. Although, several methods such as UV–Vis spectroscopy[5], chromatography[6], mass spectrometry[7] and fluorometry[8] have been developed for the detection of L–Cys, electrochemical methods provide a simple, economic, highly sensitive and selective approach to detect L–Cys. Furthermore, electrochemical methods of detection offer better repeatability and reproducibility compared to other methods[9].

In contrast, the unmodified (bare) carbon electrodes used in electrochemical methods suffer high over potential, electrode fouling and poor electron transfer kinetic process in the determination of L–Cys. In order to overcome these demerits, various conducting polymers, metal–metal oxide nanoparticles and metallophthalocyanines were utilized to chemically modify the bare electrode. Remarkably, metallophthalocyanines display a good electrocatalytic activity in various applications including fuel cells[10], solar cells[11], electrochromic devices [12], sensors [13] and biosensors[14] as they have unique chemical structures and physico-chemical properties. Relative to other metallophthalocyanines, cobalt(II) tetrasulfonated phthalocyanine (CoTsPc) complex has been widely used by the researchers for the detection of both biologically and environmentally important compounds such as glucose, ascorbic acid, cysteine, oxalic acid, amino phenol, nitrite and etc. [13, 15-19]. However, complex leaching from the electrode surface, high over potential and low conductance are the main difficulties in using CoTsPc. In an attempt to minimize these key issues and to attain an efficient immobilization of CoTsPc on the electrode surface, physical adsorption, layer by layer and electro polymerization [15, 20] methods have been developed.

Since CoTsPc is a highly negative charged metal complex, some of the positively charged polymers such as poly lysine, poly aniline, poly pyrrole, poly allylamine hydrochloride and poly amidoamine [21-24] have been used to make it as a more stable complex in recent years. Electrochemical anodic activation of bare carbon electrode has been done so as to create more porosity and hydrated surface layers in or on its surface. This activated carbon electrode gives more number of catalytic sites and high conductance compared to only bare carbon electrode [25, 26]. Recently, graphene and cobalt phthalocyanine were immobilized on the surface of anodically activated carbon electrode by Xingquan He *et. al.* The resultant fabricated electrode showed a good electrocatalytic activity towards the detection of nitrite[15].

In this present work, we have prepared a more stable CoTsPc/ASPCE and employed it for the detection of L–Cys. The screen printed carbon electrode (SPCE) has been activated at a potential of +2.0 V for 100s prior to drop–casting of CoTsPc. This activation step is done to nullify the drawbacks of CoTsPc: (i) instability of material physically adsorbed on the electrode surface and (ii) low conductivity of CoTsPc leading to reduced electrocatalytic activity of the electrode. The modified electrocatalytic activity towards the determination of L–Cys in terms of low over potential, wide linear range, low limits of detection and high sensitivity.

# 2. EXPERIMENTAL

#### 2.1. Reagents and apparatus

CoTsPc was purchased from Porphyrin Products Inc, Utah, U.S. and all other chemicals were purchased from Sigma-Aldrich. All the chemicals used were of analytical grade and used without further purification. 0.05 M phosphate buffer (PB) solution was prepared using Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>. All the experiments were performed using double distilled water with conductivity  $\geq$ 18 MΩ. A stock solution of L-Cys was prepared in 0.05 M PB solution (pH 7). Electrochemical measurements were carried out using CHI 6171D work station in a conventional three electrode cell with modified SPCE as working electrode (area 0.071 cm<sup>2</sup>), saturated Ag|AgCl (saturated KCl) as reference electrode and Pt wire as counter electrode. All the electrochemical experiments were carried out at ambient temperature. Amperometric measurements were performed with analytical rotator AFMSRX (PINE instruments, USA). Field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX) spectra were performed using Hitachi S4700 and HORIBA EMAX X-ACT, respectively.

# 2.2. Fabrication of CoTsPc modified activated screen printed carbon electrode

The anodic activation of SPCE was done through simple electrochemical potentiostatic method. The potential applied for the above mentioned activation was 2.0 V. Later, 15  $\mu$ L of CoTsPc was drop–cast on the activated surface of screen printed carbon electrode (ASPCE) and dried at ambient conditions. The modified CoTsPc/ ASPCE was washed several times with water to remove the unbounded CoTsPc on the surface of ASPCE. As control, other modified electrodes such as SPCE, CoTsPc/SPCE (without activation) were also fabricated. All the electrochemical experiments were carried out at room temperature of 25°C. A schematic illustration for the fabrication of CoTsPc/ASPCE was given in Scheme 1.



Scheme 1. A schematic illustration for the fabrication of CoTsPc/ASPCE

# **3. RESULT AND DISCUSSION**

# 3.1 The study of surface morphology and elemental composition of fabricated electrodes

Scanning electron microscopy (SEM) was chosen for knowing the morphologies of fabricated screen printed electrode. Fig1 shows the SEM images of ASPCE (A) and CoTsPc/ASPCE (B). The image of ASPCE shows the highly porous and hydrated surface layers on/in its surface while, the SEM image of CoTsPc/ASPCE shows the surface of the ASPCE was fully covered by the CoTsPc. Moreover, the EDX spectrum of CoTsPc/ASPCE (Fig1C) portray the signals of carbon oxygen, sulfur and cobalt with the weight percentage of 31.2, 48.81, 13.42 and 6.55. The presence of cobalt and sulfur validates the successful interaction of the positive charged activated carbon and negative charged CoTsPc.



Figure 1. FESEM images of ASPCE (A) and CoTsPc/ASPCE (B). EDX spectrum of CoTsPc/ASPCE (C).

#### 3.2 Different film comparison towards oxidation of L-cysteine

Cyclic voltammetry was used to study the electrochemical performance of fabricated electrode and its voltommograms are presented in Fig 2. Fig 2 shows the voltammograms of SPCE, CoTsPc/SPCE and CoTsPc/ASPCE in the presence of 1 mM L-Cys at the scan rate of 50 mVs<sup>-1</sup>. The electrochemical performance of all the fabricated electrodes towards the oxidation of 1 mM L-Cys exhibit the order: SPCE< CoTsPc/SPCE <CoTsPc/ASPCE. Only SPCE attained a large overpotential at 0.607 V (Ag|AgCl) and very small anodic current ( $I_p$ ) at 25 µA which indicates the poor electrocatalytic activity of SPCE. Whereas, the obvious electro-oxidation peak for 1 mM L-Cys at the anodic potential of 0.317 V with current intensity as 50.4 µA was observed at CoTsPc/SPCE, indicating the better catalytic activity of CoTsPc in the electro oxidation of cysteine than that of only SPCE. However, the obtained anodic peaks were broad which may be due to the poor stability and conductivity of CoTsPc. The highly reduced overpotential and subsequently sharp increased anodic peak current were observed to be 0.264 V and 90.1 µA for the electrooxidation of 1 mM L-Cys at CoTsPc/ASPCE. The obtained response at CoTsPc/ASPCE exhibited many folds higher performance than bare SPCE and two folds higher than that of CoTsPc/SPCE. The outstanding ability of CoTsPc/ASPCE can be due to the large surface area, porous and conductivity ASPCE and good catalytic activity of CoTsPc. Moreover, ASPCE provides more surface sites for the maximum anchoring of CoTsPc on its surface and therby it produces larger catalytic sites towards the electrooxidation of L-Cysteine. Moreover, the obtained peak was quasi reversible redox indicating the one electron electrooxidation peak of cobalt and phthalocyanine. The possible mechanism for the electro-oxdiation of cysteine at CoTsPc/ASPCE is given in equations 1&2 [27].



**Figure 2.** CVs obtained at SPCE, CoTsPc/SPCE and CoTsPc/ASPCE in PBS (pH 7) in the presence of 1 mM L-Cys (b) at the scan rate of 50 mVs<sup>-1</sup>

#### 3.2 Various pHs and scan rates towards electro-oxidation of L-cysteine

In order to study the influence of pH at CoTsPc/ASPCE towards the electrochemical reactions of L-Cys, various PB pH solutions from 3 to 11 were chosen and their consecutive results are presented in Fig 3. The obtained pH results apparently displayed that the anodic peak current of L-Cys was increased with decrease in pH from 11 to 3. Moreover, the peak potentials were shifted positively from pH 11 to 3. The potential shifting of cysteine in pH 9 and 11 were identical and the peak current of pH 9 and 11 were smaller, reveals the oxidation of L-Cys at CoTsPc/ASPCE is lower effect in the basic medium. From the literature survey, the electrochemical oxidation of L-Cys vs pH was difficult to predict and it is highly dependent on the electrode and L-Cys [28, 29]. In our case, the maximum peak current was observed in pH 3. However, to achieve the practical feasibility of CoTsPc/ASPCE, pH 7 was chosen as the supporting electrolyte for the further studies. In addition, the calibration plot

[Fig.3B] between the pH vs  $E_p$  showed a linear relationship which indicate the oxidation L-Cys peak is strongly affected by different pH solutions. The obtained slope values are 69 mVs<sup>-1</sup>/pH which closely in agreement with theoretical value of 59 mVs<sup>-1</sup>/ pH, confirms that the equal number of proton and electron ( $n_p = n_e$ ) involved during the electrochemical oxidation of cysteine [22].



**Figure 3A.** CVs obtained at CoTsPc/ASPCE in various phosphate buffer pH solutions (pH 3–11) containing 1 mM L–Cys at the scan rate of 50 mVs<sup>-1</sup>. B. Calibration plot between  $I_p$  and  $v^{1/2}$ 

Fig.4A presents the influence of scan rate on the oxidation of L–Cys at CoTsPc/ASPCE in 0.05 M PBS (pH 7). The scan rate was varied from 0.1 to 1 V/s. A linear increase in the anodic peak current was observed for the increase scan rate from 0.1 to 1 V/s. In addition, a positive shift in the peak potential was seen with the increase of scan rate. The linearity between the square root of scan rate  $(v^{1/2})$  and the anodic peak current in the calibration plot (Fig 4B) proves the oxidation of L–Cys at CoTsPc/ASPCE is a diffusion controlled process[22].



**Figure 4A.** CVs obtained CoTsPc/ASPCE in pH 7 containing 1 mM L-Cys at different scan rates from 0.1 to 1Vs<sup>-1</sup>. B. Calibration plot between different pH & *E*p.

#### 3.3 Effect of concentration: CV

Cyclic voltammograms taken in the potential range from -0.3 to 0.8 for the absence and presence of L–Cys (0.5 to 5 mM) at CoTsPc/ASPCE were shown in Figure 5A). The electrolyte used in this study is 0.05 M PBS (pH 7) and the scan rate was fixed to be 0.05 V/s. Up on each addition of 0.5 mM L–Cys, an increase in anodic peak current was observed. Thus, the good electrocatalytic ability of our modified electrode was evident from the linearly increasing anodic peak current for the electro–oxidation of L–Cys (Figure 5B).



Figure 5. CVs obtained at CoTsPc/ASPCE in the absence (0 mM) and presence of L–Cys (0.5 to 5 mM) in PB pH 7 solution at the scan rate 50 mVs<sup>-1</sup>. Calibration plot between  $I_p$  and [L-Cysteine].

#### 3.5 Amperometric i-t determination of L-Cys

The response for the amperometric (i-t) technique performed at CoTsPc/ASPCE on successive additions of 5  $\mu$ M L–Cys in to the PBS (pH 7) with continuous stirring was presented in Figure 6A. The applied potential and the rotating speed for this study was fixed to be +0.2 V (Ag|AgCl) and 1500 rpm. As a result, with in a time period of 4s 95% steady state current was reached showing the electrocatalytic oxidation of L–Cys at CoTsPc/ASPCE. The response current was linearly increased up on each addition of L–Cys with increasing concentration. The linear relationship between concentration of L–Cys and response current from the calibration plot (Figure 6B) gives the corresponding linear regression equation as  $I_p$  ( $\mu$ A) = 2.003[L-Cys] ( $\mu$ A/ $\mu$ M) + 27.919. The linear increase in the response current was observed in the linear range from 5 to 220  $\mu$ M. The limits of detection (LOD) and the sensitivity of CoTsPc/ASPCE were found to be LOD 0.22  $\mu$ M and 953.8 $\mu$ A/mM cm<sup>-2</sup>. The LOD was calculated using the formula LOD= 3s<sub>b</sub>/S, where s<sub>b</sub>= standard deviation of blank signal and S=sensitivity[30]. The calculated electroanalytical parameters of our sensor were fairly comparable with the performance of the previously reported metal complex based

cysteine sensors in the literatures (**Table.1**). Especially, the sensitivity of our fabricated sensor is higher compared to others.



**Figure 6.** (A) Amperometric i-t response of CoTsPc/ASPCE upon each addition of 5  $\mu$ M into continuously stirred pH 7 at the rotation speed of 1500 RPM. *E*app = 0.2 V. B. Calibration plot between  $I_p$  and [L-Cysteine]

Table 1. Comparison of electroanalytic	cal parameters for L-Cys	s determination at	CoTsPc/ASPCE with
other metal complex based mod	ified electrodes.		

Modified Electrode	Method	Linear	Sensitivity	LOD <sup>a</sup>	Ref
		range	$(\mu A m M^{-1} cm^{-2})$	(µM)	
		(µM)			
CoTsPc-poly(l-lysine)	$CA^{b}$	0.5-216	157	0.15	[22]
MWCNTs-iron (III) phthalocyanine	Amp <sup>c</sup>	10-200	176	1	[4]
Nitrogen doped graphene–CoPc	Amp	1-1600	-	1	[17]
Graphene oxide –CoPc	CA	0.03-200	_	0.005	[28]
Co(II) salophen	CA	3–770	_	0.5	[31]
poly N, N- dimethylaniline/ferrocyanide	CA	80-2250	_	61.7	[32]
iron (III) phthalocyanine-gold nanoparticles	$\mathrm{DPV}^{\mathrm{d}}$	50-1000	57.2	0.27	[33]
Co(II)-4-methylsalophen	DPV	0.5 - 100	_	0.2	[34]
Oxovanadium(IV)salen	CA	240-2300		170	[35]
CoPc-screen printed graphite electrode	SWV <sup>e</sup>	2.6-200	780	4	[3]
CoTsPc–ASPCE	Amp	5-240	953.8	0.22	This
					work

<sup>a</sup>LOD– limits of detection, <sup>b</sup>CA –Chronoamperometry, <sup>c</sup>Amp–Amperometry, <sup>d</sup>DPV–Different pulse voltammetry, <sup>e</sup>SWV–Square wave voltammetry.

# 3.6 Interference study

The interference study at CoTsPc/ASPCE using the amperometric technique also revealed the better selectivity of our fabricated sensor. The biological species such as creatinine phenylalanine, methionine, L-tyrosine, glucose, uric acid, lucin, valin alanine, glycine and lactic acid were used in 200

fold excess concentration to examine the selectivity of CoTsPc coated ASPCE. Relative to other above mentioned interfering biomolecules, a notable high peak current response was obtained for each addition of 50  $\mu$ M L-Cys at CoTsPc/ASPCE in 0.05M PB solutions (pH 7). Thus, it is evident that our fabricated electrode is highly selective towards L-Cys even in presence of other biologically interfering molecules.

#### 3.7 Repeatability, Reproducibility and Stability

The examination for the repeatability and reproducibility of CoTsPc/ASPCE was done in 0.05 M PBS (pH 7) at the scan rate of 50 mV s<sup>-1</sup> using 1 mM L–Cys. An acceptable repeatability was attained accompanied by the relative standard deviation (RSD) of 3.6% for six measurements repeated with single electrode. CoTsPc/ASPCE showed a considerable reproducibility (RSD 3.9%) for six independent measurements done with six different electrodes. The storage stability of our modified electrode was tested through recording the electrocatalytic oxidation response for 0.5 mM L–Cys at CoTsPc/ASPCE and storing the electrode in 0.05 M PBS (pH 7) after the experiment at 4°C. CoTsPc film modified ASPCE displayed a good electrocatalytic response for the oxidation of L–Cys during the storage period of 30 days 96.3% of the initial response current was retained after 30 days resulting in an appreciable storage stability of CoTsPc/ASPCE. This experiment was carried out in the presence of 50  $\mu$ M L–Cys at the rotating speed of 1500 rpm. The obtained amperometric i-t response was stable and well–defined with only 5.2% decrease in the initial response current even after a time period of 1500s revealing an excellent operational stability of CoTsPc/ASPCE.

#### 3.8 Real sample analysis

Human serum samples were utilized to demonstrate the practicality of our modified electrode under the above mentioned experimental conditions for the lab sample analysis. A considerable electrocatalytic response was shown for the spiked concentrations (10, 20, 50 and 100  $\mu$ M) of L–Cys at CoTsPc/ASPCE (Table.2). The observed recovery results of L–Cys in the human serum samples were found to be 97, 98, 98.8 and 99.2%. Thus, CoTsPc film coated ASPCE can be exposed as a better platform for the detection of L–Cys in real samples.

Table 2. Determination of L-Cys at CoTsPc/ASPCE in human blood serum samples

Sample	Added (µM)	Found (µM)	Recovery (%)	RSD (%)
1	10	9.7	97	3.2
2	20	19.6	98	2.8
3	50	49.4	98.8	2.9
4	100	99.2	99.2	2.4

# 4. CONCLUSIONS

To conclude, we have electrochemically fabricated CoTsPc/ASPCE for the determination of L– Cys. The effective immobilization of CoTsPc on the surface of ASPCE was confirmed by scanning electron microscopy and energy-Dispersive X-ray spectroscopy. The outstanding electrocatalytic ability of our modified electrode towards electro–oxidation of L–Cys was evident from the evaluated electroanalytical parameters such as wide linear range (5 to 220  $\mu$ M), LOD (0.22  $\mu$ M) and sensitivity (953.8 $\mu$ A/mM cm<sup>-2</sup>). An acceptable repeatability, reproducibility and stability were attained by our fabricated modified electrode. The demonstrated practical feasibility of our sensor in human serum samples stand as a proof for the effective applications of CoTsPc/ASPCE in near–future.

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