# Electrochemical sensing of environment chlorophenol using $SnO_2$@graphene modified Glassy carbon electrode

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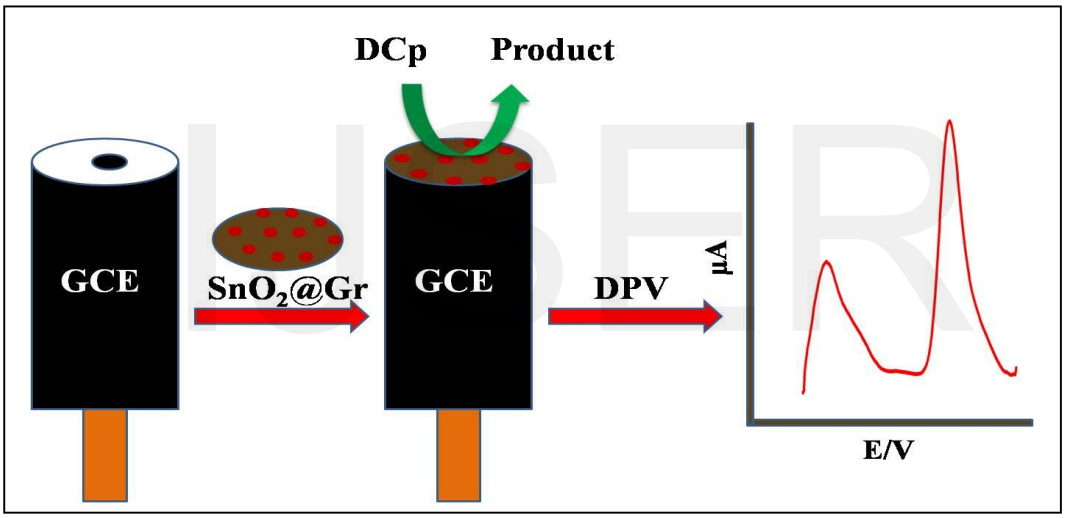
**Abstract:** We demonstrate a simple way to synthesize $SnO_2$@graphene ($SnO_2$@Gr) by heating the graphene oxide (GO) and $SnCl_2$ precursor. The synthesized composite was thoroughly characterized by X-ray diffraction analysis (XRD) and Field emmision scanning electron microscopy (FE-SEM). These results show that the spherical $SnO_2$ particles are uniformly distributed on the graphene sheets through electrostatic adsorption. Further, the $SnO_2$@Gr modified Glassy carbon electrode ($SnO_2$@Gr/GCE) was applied for electrochemical sensing of 3,5 dichlorophenol (DCp) under optimized experimental conditions. The $SnO_2$@Gr/GC-modified electrode showed enhanced electrochemical performance towards 3,5 Di-Chlorophenol determination. The linear calibration plot was obtained over the concentration range of 200 nM to 3.2 µM ($R^2$ =0.996) and the detection limit (S/N=3) was found to be 8 nM. The nanocomposite modified GC electrode showed good sensitivity aswell.




**Keywords:** Graphene, $SnO_2$, X-ray diffraction, 3,5 di-chlorophenol, cyclic voltammetry.

## 1 INTRODUCTION

Chlorophenol (Cp) is an organochloride of phenol, that contains one or more covalently bonded chlorine atoms. Cps are naturally produced by soils via fungi-derived enzymes utilizing harmful chlorinated phenols. Cps are extensively produced in many industries for agricultural and clinical devalopment purposes such as pesticides, herbicides, coal and petrochemicals, [1].etc. However, most of the chlorophenols are considered as high priority pollutants even at low levels. Commonly 2-Chlorophenol (2Cp), 4-Chlorophenol (4Cp), 2,4,6Tri-Chlorophenol (TCp) and 3,5 Di-Cholorophenol (DCp) especially 3,5 di-chlorophenol (DCp) exceed high wastage limits. These contaminates when exceed high wastage level in environment, produce acute toxicity [2]. A growing interest has been focused to quantification of various methods described for the determination of Cp's such as Solid-phase extraction (SPE) liquid chromatography (LC), Mass spectrometry (MS) High performance liquid chromatography (HPLC) and electro analytical (EA) methods.

Among the methods the electrochemical method has proved to be capable of sensing the environmental pollutants due to its high sensitivity, selectivity, operational simplicity and fast response [3]. In electroanalytical technique devolopment of various electrode materials are described for the de-

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tection of environment harmful chlorophenols. Furthermore the electrode materials such as transition metals and metal oxides, conducting polymer, graphene based nanohybrids and metal phthalocyanine have been tested for the detection of environmentally harmful compounds. Among these, the graphene based metal / metal oxide play vital role in electro analytical chemistry [4].

$SnO_2$ is a low cost and non-toxic material. It is a n-type transparent semiconductor with high thermal stability. A facile synthetic route, applicable to Gas sensors ($CH_4$, CO, $CO_2$, $H_2S$, $NO_2$, $H_2$, $O_2$, $NH_3$ ), photo-catalytic activity, Lithium-ion batteries, dye-sensitized solar cells is adopted. Also the ability to tune the physical and chemical properties with impurities is made possible. we demonstrate the simple thermal decomposition method for the preparation of $SnO_2$@Gr nanocomposite material further the $SnO_2$@Gr modified GC electrode was utilized for the electrochemical determination of chlorophenol. These results shows an enhanced the electrocatalytic activity towards the determination of 3,5 dichlorophenol with high sensitivity, selectivity and low concentration level detection.

## 2 EXPERIMENTAL

### 2.1 Synthesis of $SnO_2$@graphene

GO was synthesised from graphite powder by improved Hummers method [5]. Then, $SnO_2$@Gr was synthesised by a typical procedure: 100 mg of GO was dispersed in 100 mL of distilled water and sonicated for 30 min ,then about 0.948 g of $SnCl_2$ in ethanol medium was added. After that, reaction mixture was refluxed at 95 °C for 1 h on oil bath. The resulting suspension was centrifuged for 30 min at 4000 rpm and then washed several times with ethanol. The reidue was transferred in to silica crucible and calcinated at 450 °C for 2 h. Cool down to room temperature, $SnO_2$@Gr nanocomposites were collected and used for characterization.

### 2.2 Fabrication of SnO2@Gr/GC electrode:

Glassy carbon electrode was polished with 0.3 and 0.05 μm alumina slurry and then pre-treated in $H_2SO_4$ medium in -0.2 V to 1.0 V then washed with distilled water. To fabricate the $SnO_2$@Gr/GC electrode, 1 mg of $SnO_2$@Gr dispersed in 2 mL of ethanol was sonicated for 30 min, then 5 μL of composite was drop casted on the GCE surface and dried (graphical abstract). The Pt wire and saturated calomel electrode are used as counter and reference electrodes respectively.About 1mM of 3,5 DCp stock solution was prepared and diluted to further lower concentrations for the electrochemical analysis .

## 3 RESULTS AND DISCUSSION

3.1 stuctural and morphological studies: Fig.1A shows the XRD pattern of the pepared sample after calcination at 450 °C. The diffraction pattern of $SnO_2$@Gr shows the major peaks indexed at (110) (101) (200) (211) (220) and (002) lattice planes. All the diffraction peaks of confirms the tetragonal structure with rutile phase of $SnO_2$ particles along with lower intense of 002 plane of graphene at $2\theta$ = 24.6 °. This may be attributed to the electrostatic attraction between $SnO_2$ and Gr sheets. These results match well with JCPDS No. 41-1445 file [6]. The morphology of sample was analysed by field emission scanning microscope (FESEM). The photograph as Fig.1B reveals the spherical $SnO_2$ nanoparticles uniformly distributed over the graphene surface via the $Sn^{2+}$ ion electrostatic adsorption on the negatively charged graphene oxide sheet. Raman spectra of graphene oxide and $SnO_2$@Gr are shown in Fig.2A GO exhibits characteristic D 1342 $cm^{-1}$ and G 1582 $cm^{-1}$ bands due to $sp^2$ and $sp^3$ hybridised carbon atoms respectively [7] However $SnO_2$@Gr obtained shifted D and G band to lower regions, 1328 and 1551 $cm^{-1}$ with decreased intensity of $SnO_2$@Gr. This is due to the most of the hydroxyl and carbonyl functional groups that are intracted by $Sn^{2+}$ during calcination at 450 °C.

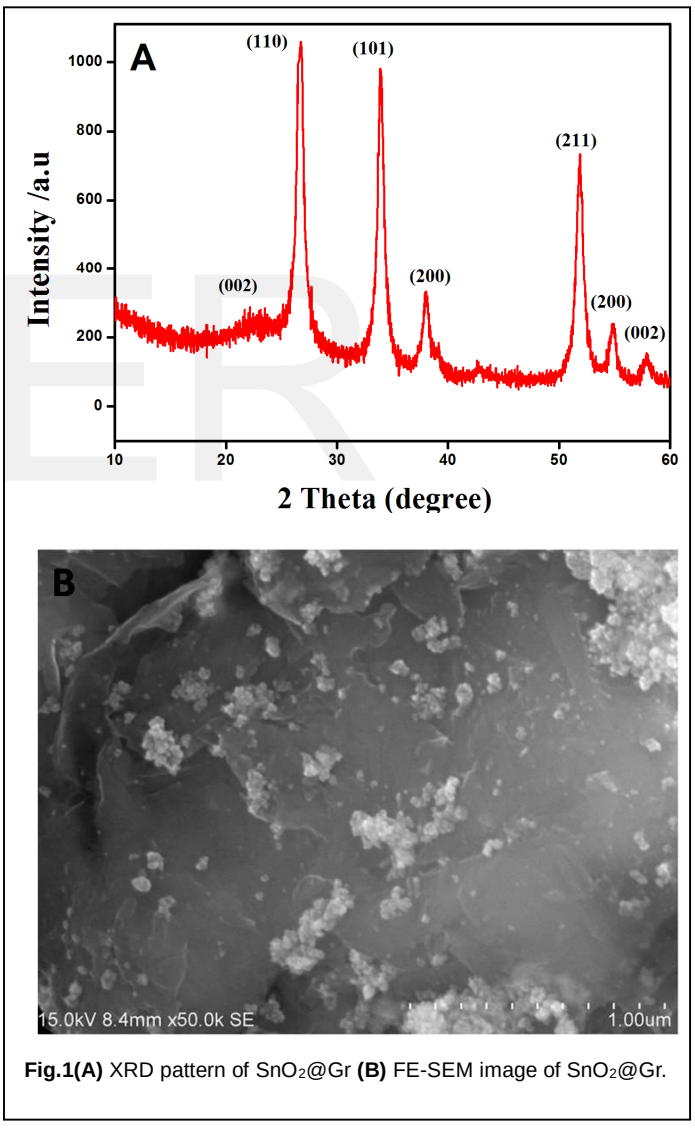


**Fig.1(A)** XRD pattern of $SnO_2$@Gr **(B)** FE-SEM image of $SnO_2$@Gr.

### 3.2 Electrochemical sensing of DCp

Fig.2B shows the cyclic voltammograms of bare GCE, GO/GCE and Gr@$SnO_2$/GCE, in the presence of 0.1 mM DCp in 0.1M PBS at pH 7 in the scan rate of 50mV $s^{-1}$. For oxidation

of DCp, bare GCE gives small and broad oxidation peak at 0.75 V while the Gr/GCE shows well-defined oxidation peak current at the same potential. Furthermore the $SnO_2$@Gr/GC electrode shows enhanced anodic peak current and lower oxidation potential of 81.7 μA and 0.74 V respectively. This may be due to the unique electronic properties of the $SnO_2$@Gr which accelerates the fast electron transfer rate. This suggests that the $SnO_2$@Gr/GC electrode is a more effective mediator for the electrochemical oxidation of DCp and there is no corresponding reduction peak appearance. This indicates that the electrochemical reaction is totally irreversible.

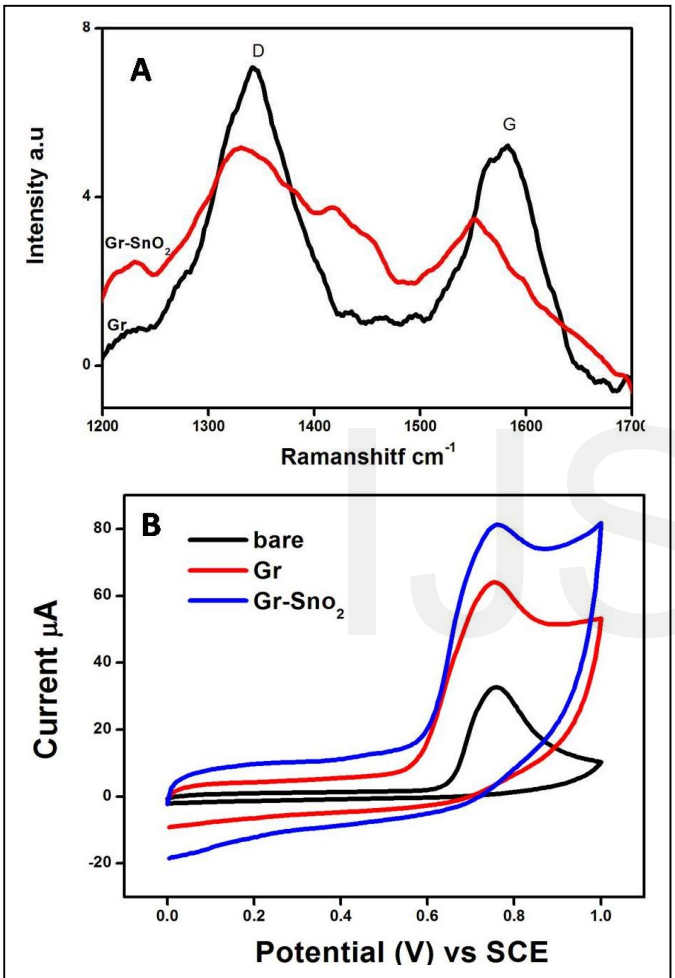


**Fig:2 (A)** Raman Spectrum of GO and $SnO_2$@Gr **(B)** Cyclic voltammograms of different modified electrodes presence of 0.1mM DCp in 0.1 M PBS (pH 7.0). scan rate at 50 mV $s^{-1}$.

### 3.3 Effect of Scan rate and pH

The cyclic voltammetric scan rate study was performed in the range, 10–500 $mVs^{-1}$, with the potential scan rates in PBS (pH= 7.0) containing 0.1 mM of DCp at $SnO_2$@Gr/GC (Fig. 3). The results showed that the peak current of DCp varies linearly with the scan rate (Ʊ). Insert Fig. 3 shows the plot of log Ʊ mV $s^{-1}$ vs log $i_{pa}$. the linear regression equation is expressed as

$$\log i_{pa} = 0.5755\ Ʊ\ mV\ s^{-1} - 6.042\ (R^2 = 0.990) \ldots\ldots\ldots (1)$$

The slope value confirms the adsorption-controlled process for the electrochemical oxidation of DCp on the $SnO_2$@Gr modified electrode surface and the concentration of electroactive species adsorbed on the $SnO_2$@Gr/GCE surface was calculated and found to be $6.20x10^{-8}$ mol/$cm^2$.

The influence of the pH range values of PBS on the electrochemical response of DCp at the $SnO_2$@Gr modified GC electrode was investigated in pH range from 4.0 to 8.0 with 0.1mM of DCp, Fig. 4.

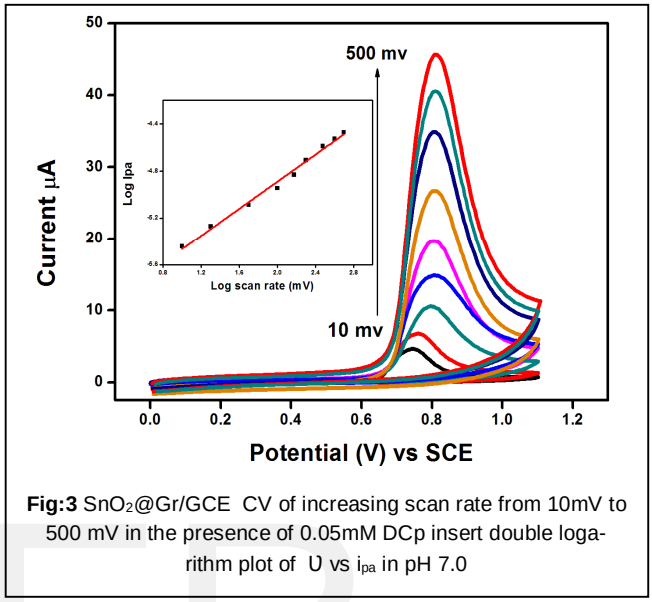


**Fig:3** $SnO_2$@Gr/GCE CV of increasing scan rate from 10mV to 500 mV in the presence of 0.05mM DCp insert double logarithm plot of Ʊ vs $i_{pa}$ in pH 7.0

The peak current gradually increased when the pH of the electrolyte solution was increased from 4.0 to 7.0 At pH 8.0, the oxidation peak current conversely decreased. A maximum peak current was obtained at pH 7.0. So the optimal pH = 7 was chosen for electrochemical measurement. Fig.4 inset shows the relationship between ($E_{pa}$) vs pH. The Epa of the DCp oxidation shows linear relationship with the solution pH. The linear regression equation is expressed as

$$E_{pa}\ (V) = 0.0620\ pH + 1.1240\ (R^2 = 0.992) \ldots\ldots\ldots (2)$$

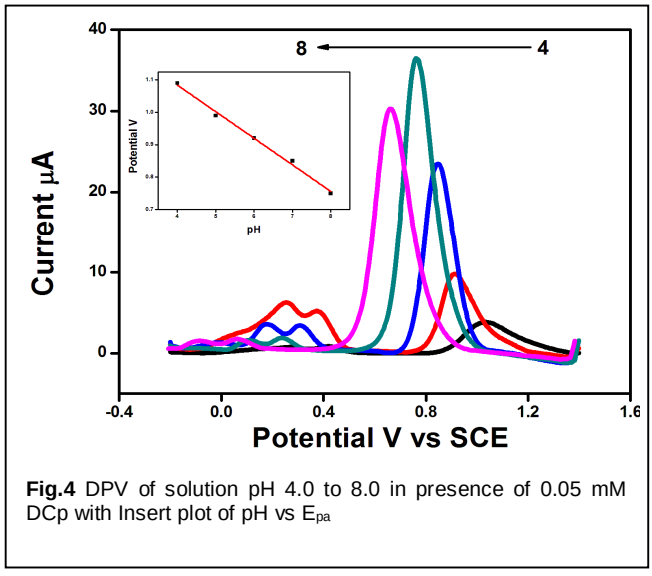


**Fig.4** DPV of solution pH 4.0 to 8.0 in presence of 0.05 mM DCp with Insert plot of pH vs $E_{pa}$

According to the Nernst equation [8], the slope of 62 mV/pH indicated that the equal number of electron and protons are transfered in the electrode interface.

### 3.4 Differential pulse voltammetry (DPV) detection of DCp

Considering the adsorption of DCp on the Gr-$SnO_2$/ GCE surface, the sensitive DPV technique was utilised for the detection of DCp as shown in graphical abstract. DPV measured potential range was from 0 V to 1.1 V. The $SnO_2$@Gr/ GC electrode shows the small peak at 0.15 V which was baseline corrected. The sensitive faraday current obtained at 0.74 V which is the analytical signal for DCp oxidation. As can be seen in Fig. 5, the anodic peak current responded to the oxidation of DCp. This suggested that the oxidation peak current was proportional to the DCp concentration in the range of 200.nM to 3.2μM [Fig. 5 (insert)], and the regression equation is

$$i_p(\mu A) = 0.9058\ \mu A + 1.2086\ \mu M\ (R^2 = 0.9961)\ \ldots.\ (3)$$

The sensitivity and limit of detection (LOD) of the modified electrode was found to be 0.905 μA/μM and 8nM (S/N = 3) respectively.

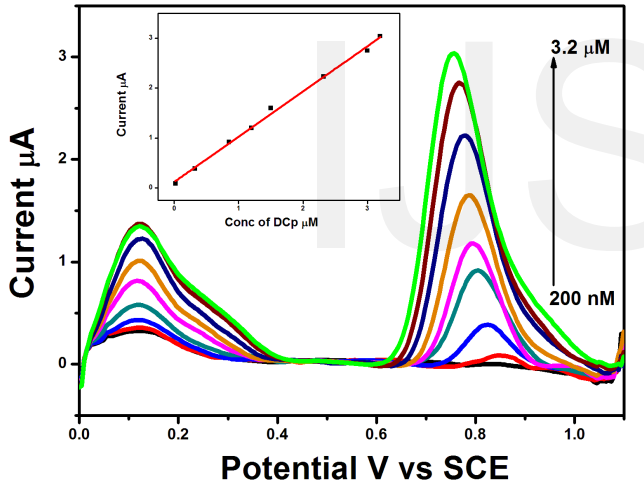


**Fig:5 (C)** DPV of 200 nM to 3.2 μM DCp insert Calibration plot of conc vs $i_{pa}$

## 4. Conclusion

In summary, we have successfully synthesized $SnO_2$ nanoparticles decorated on Gr by a simple method. The $SnO_2$@Gr composite was characterized. These results reveal that spherical $SnO_2$ particles are adsorbed on the graphene surface and also the GO was reduced by $Sn^{2+}$ under thermal condition. Furthermore $SnO_2$@Gr modified glassy carbon electrode enhances the electrochemical determination of 3,5DCp in environmentally minimiced sample. The proposed sensor show high sensitivity 0.905 μA/μM and the detection limit falls in the 8 nM.

## 5. Acknowledgments

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