CuCrO₄ Nanoparticles Composite Modified Carbon Paste Electrodes for Sensitive Detection of Paracetamol: A Cyclic Voltammetric Study

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Abstract

An electrochemical sensor containing carbon paste electrode (CPE) for paracetamol is developed and modified with the CuCrO₄ Nanocomposites. The synthesised CuCrO₄ Nanocomposites was discussed with X-Ray Diffraction studies. Experimental studies such as scan rate, concentration and pH was studied by using cyclic voltammetric method. The CuCrO₄ Nanocomposites modified CPE (CuCrO₄ Nanocomposites MCPE) exhibited excellent electrocatalytic response towards the oxidation of paracetamol (PC). Over potential for oxidation of PC was minimised which considerably enhance the current response on the CuCrO₄ Nanocomposites MCPE when compared with bare carbon paste electrode (BCPE). Scan rate study for PC discuss the process of the electrode. Linear calibration curve was obtained with the range of 2 μM to 14 μM having the detection limit and quantification limit value of PC is discussed with CuCrO₄ Nanocomposites MCPE. This study shows that electrochemical oxidation of PC at CuCrO₄ Nanocomposites MCPE is pH dependent process.
Keywords: CuCrO₄ Nanocomposites, MCPE, Paracetamol, Hydrothermal method, Copper chromate

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1. Introduction

Nanocomposites have wide applications in various fields [1] such as semiconductors [2], catalyst, pigment, drug [3] in the area of electronic and magnetic materials [4-7], and development of electrochemical sensors [8]. From the past two decades the influence of nanocomposites is immense on sensing applications and devices. Sensor is a transducer, which detects/sense some specific vicinities of substances. Numerous active materials have wide range of applications in the field of sensors. The material which includes metals, metal oxides, metal sulphides, metal chromates, composite nanoparticles and many more in their nano (10⁻⁹) dimension. Different methods were discussed for the preparation of metal chromates those were wet chemical, micro emulsion, and sol–gel processes [9]. Ceramic and co-precipitation methods [10]. Electrochemical methods [11] have discussed a variety of applications and synthetic approaches of copper chromite nanocomposites [12]. In the present research work, the most significant stable Copper Chromate nanocomposites (CuCrO₄ nanocomposites) is prepared through hydrothermal method, which is characterized through XRD. These CuCrO₄ nanocomposites being used for the modification of CPE, which is CuCrO₄ Nanocomposites MCPE was used as an electrochemical sensor for PC.
Paracetamol (acetaminophen) (PC) is widely used as a pain reliever and a fever reducer. Many analytical techniques have been used for PC analysis including titrimetry [13-14], HPLC [15-17], fluorometry [18], Uv-visible spectrophotometric methods [19], colorimetry [20] and various modes of electrochemistry [21-24]. Since the results of above approaches are not accurate and the techniques involved are tedious and expensive, researchers have shown interest to detect the PC through nanocomposites modified carbon paste electrode. These modified electrodes are inexpensive and showed high sensitivity, minimum detection limit, high accuracy and response. These approaches are simple method to detect the PC through electrochemically. The electrochemical oxidation of PC at nanoparticles modified carbon paste electrode was reported in the earlier work [25]. Recently, the voltammetric behaviour of PC and some other drugs at various conducting polymers were studied [26]. Among all analytical methods, electrochemical methods are best. Electrochemical approaches are effective to quantify the biomarker levels in the blood as they are economic, provide rapid diagnosis and cause less pain in patients. Various electrochemical sensors like norepinephrine (NE), epinephrine (Ep) and Tryptophan (Trp) which are electroactive substances have been reported. Hence electrochemical technique like cyclic voltammetry (CV) technique used under physiological conditions can sensitively detect PC.

CuCrO$_4$ composites show enhanced ionic-conductivity especially for O$_2$ ions; thus, it is generally employed as fuel cells at high temperatures and oxygen sensors [27-28]. This composite also behaves as insulator at moderate temperatures, but it will turn into super ionic conductor at very high temperature. As of its good high hardness, biocompatibility and strength, hence it is frequently used as orthopaedic implants, such as dental implants and femoral head component in hip implants. As deliberated above, it is thermally and chemically firm, joint with its inimitable amphoteric characteristic, making it an idyllic candidate for
catalyst. For instance, the decomposition of \( \text{N}_2\text{O}_2 \), hydrogenation of aromatic carboxylic acids, the isomerization of alkanes, and countless other reactions. \( \text{CuCrO}_4 \) Nanocomposites is a familiar catalyst, holds both the common advantages of transition metal compound catalysts and its own unique merits.

2. Experimental

2.1 Apparatus and Reagents

Cyclic voltammetry was achieved in CHI-660c potentiostat an analytical system model (Electrochemical workstation, USA). The conventional three electrode electrochemical cell consist of a saturated calomel electrode (SCE) which act as reference electrode while platinum wire as a counter electrode and bare Carbon Paste Electrode \( \text{CuCrO}_4 \) composites modified Carbon Paste Electrode as working electrode. A digital pH meter MK VI (Systronics) employed for the pH measurements. All potentials were given against SCE at 25±0.5°C. PC was procured from Himedia and the stock solution of PC (2.5 mM), and they were prepared in doubly distilled water. Graphite powder was bought from Lobo and silicon oil (as binder) was bought from sigma Aldrich. All chemicals were of AR grade. For buffer solution preparation, the chemicals were bought from Merck. 0.2M PBS was prepared by adding standard stock solutions \( \text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O} \) (0.2M) and \( \text{Na}_2\text{HPO}_4 \) (0.2M). All the solutions were prepared freshly prior to be analysis.

2.2 Preparation of bare carbon paste electrode (BCPE)

BCPE was prepared by adding graphite powder (70%) and silicone oil (30%) and hand mixing this mixture in a agate mortar for 45mins till to get a uniform paste. Then paste
is poured to Poly Vinyl Chloride tube cavity and made smooth on a rubbing paper. A copper wire was used at the end of tube for the electrical connection.

2.3 Preparation of Copper (II) Chromate nanoparticles (CuCrO$_4$ NPs)

The CuCrO$_4$ NPs were prepared through hydrothermal approach. For that, the copper chloride (CuCl$_2$) and potassium chromate (K$_2$CrO$_4$) taken in the ration 1:1 and dissolved in deionized water (50 mL). Then, 0.7 g NaOH was added and sonicated for 3 hrs consequently, later mixture was poured to Teflon-autoclave and maintained at 210 °C for 20hrs. Final products were parted using centrifugation and allowed for drying at 60 °C. Further, centrifugation removes powders from solution and washed with deionised water and methanol and dried at 100 °C for 24 hrs to obtain CuCrO$_4$ NPs.

2.4 Preparation of CuCrO$_4$ NPs composite MCPE

The CuCrO$_4$ NPs MCPE were synthesized by adding 30% silicon oil and 70% graphite powder and different amounts of CuCrO$_4$ NPs from 2mg to 8mg in an agate mortar till it results a uniform paste. Resulted paste was crammed firmly to electrode cavity and then refined the surface by tissue paper.

3. Results and Discussion

3.1 The XRD pattern of Carbon/ CuCrO$_4$ NPs

The XRD patterns of Carbon/ CuCrO$_4$ powders are presented in Fig. 1. It shows that the typical peaks of CuCrO$_4$, corresponding to the (211), (202), (112), (200), (303), (400) and (224) faces of the hexagonal structure appear in both patterns at 35.31, 37.91, 31.31, 29.81, 56.41, 61.71 and 65.01, respectively
3.2 Effect of CuCrO$_4$ NPs as a modifier towards the detection of PC

CuCrO$_4$ NPs have been used as a modifier in the preparation of CuCrO$_4$ NPs composite MCPE. The CuCrO$_4$ NPs composite MCPE was characterized by using cyclic voltammetric technique. CuCrO$_4$ NPs composite MCPE were synthesized by adding few mgs of CuCrO$_4$ NPs. By increasing the amount of CuCrO$_4$ NPs from 2 to 6 mgs in the CPE, the electrochemical redox peak current ($I_{\text{peak}}$) of Potassium ferrocyanide ($K_4[\text{Fe(CN)}_6]$) (1mM) goes on increasing in Potassium Chloride (KCl)(1M) as supporting electrolyte. Further increase of CuCrO$_4$ NPs in CPE decreased the current signal of Potassium ferrocyanide. The Cyclic voltammograms shows different quantity of CuCrO$_4$ NPs in CPE showed maximum anodic current signal noticed in 6 mg CuCrO$_4$ NPs-MCPE as shown in fig.2, therefore 6 mg CuCrO$_4$ NPs composite MCPE was chosen as optimum for all other parameters.
Fig. 2- Cyclic Voltammograms of K₄[Fe(CN)₆] (1mM) in 1M KCl at different amount of CuCrO₄ NPs composite MCPE at scan rate of 0.1V/s.

3.3 Electrochemical characterization of CuCrO₄ NPs composite MCPE using standard K₄[Fe(CN)₆]

The supporting electrolyte (i.e., newly prepared K₄[Fe(CN)₆] solution (1mM) in 1M KCl took in an electrochemical cell. The Fig. 3 represents the voltammograms of K₄[Fe(CN)₆] at both BCPE (i.e., dashed line) and CuCrO₄ NPs composite MCPE (i.e., solid line). Owing to the lethargic electron transfer kinetics, low redox I_peak response was observed at BCPE. Nevertheless, under same conditions, the CuCrO₄ NPs composite MCPE revealed a static rise in redox peak currents, which is due to improvisation of electron transfer kinetics. It indicates that the the modified electrode has brought considerable change in the surface properties as reflected in the results of electrocatalytic activity of CuCrO₄ NPs composite MCPE. The Randles-Sevcik equation (1) could be used to calculate the available surface area for species reaction in solution [29-31].
\[ I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C_0 V^{1/2} \]  \hspace{1cm} (1)

where, \( I_p \); peak current, \( C_0 \); electroactive species concentration, \( n \); number of electrons, \( D \); diffusion coefficient, \( v \); scan rate and \( A \); electroactive surface area. For CuCrO\(_4\) NPs composite MCPE the electroactive surface area was found to be maximum (i.e., 0.03522 cm\(^2\)) when compared to BCPE (i.e., 0.02829 cm\(^2\)).

Fig. 3 Voltammograms of 1.0mM \( K_4[Fe(CN)_6] \) in 1M KCl solution at BCPE (dashed line) and CuCrO\(_4\) NPs composite MCPE (solid line) at scan rate of 0.05 V/s.

3.4 Electrochemical response of PC at CuCrO\(_4\) NPs composite MCPE

Fig.4 represents voltammograms for the oxidation of 10\( \mu \)M PC at BCPE (dotted line) and CuCrO\(_4\) NPs composite MCPE (solid line) in 0.2M PBS. At BCPE, redox \( I_{\text{peak}} \) response of PC was observed to be very poor with \( E_{\text{pa}} = 349\text{mV} \) (anodic peak potential) and \( E_{\text{pc}} = 174\text{mV} \) (cathodic peak potential). The CuCrO\(_4\) composite NPs MCPE depicts significant enhanced response of \( I_{\text{peak}} \) for PC with (\( E_{\text{pa}}=333\text{mV} \)) and (\( E_{\text{pc}}=177\text{mV} \)). Therefore, PC
departs reversible process with improvement of $I_{\text{peak}}$ and sharp peak potential observed at CuCrO$_4$ NPs composite MCPE.

![Voltammogram](image)

Fig. 4- Voltammograms of 10µM PC in 0.2M PBS of pH 7.4 at BCPE (dotted line) and CuCrO$_4$ NPs composite MCPE (solid line) at scan rate of 0.05 V/s.

3.5 Effect of scan rate on peak current of PC

The scan rate effect for 10µM PC in 0.2 M PBS was examined by cyclic voltammetry at CuCrO$_4$ NPs composite MCPE depicted in Fig. 5. The changed scan rate displays a reflective effect on the redox $I_{\text{peak}}$, shows that the redox $I_{\text{peak}}$ regularly enhances with increment in the scan rate i.e., from 0.05 to 0.5V/s and proportional to each other according to Randles Sevcik eqn. The $\text{E}_{p\text{a}}$ changed partly towards positive direction while $\text{E}_{c\text{a}}$ towards negative direction. The graph of log $I_{\text{pa}}$ of PC v/s log$\upsilon$ was plotted for CuCrO$_4$ NPs composite MCPE and the slope obtained was 0.55 therefore the electrode process was controlled by diffusion [32] as shown in Fig.6. From the graph, it shows a good linearity between anodic
I_{peak} \text{ and scan rates. It showed an excellent linearity for CuCrO}_4 \text{ NPs composite MCPE i.e., } \log (I_{pa}) = 0.55940 \log (\nu) + 4.8669 \text{ with } (r^2 = 0.9991).

Fig. 5- Voltammograms of 10µM PC in 0.2M PBS of pH 7.4 at CuCrO_4 \text{ NPs composite MCPE at different scan rate from 0.05V/s to 0.5V/s.)}
3.5 Effect of concentration

Fig. 7 shows voltammograms at different concentrations of PC. The PC concentration diverse from 2 to 12µL in PBS (0.2M) at scan rate of 0.05V/s for CuCrO$_4$ NPs composite MCPE. It is comprehensible that as PC concentration increases, the $I_{pa}$ and $I_{pc}$ also increases with shift in $E_{pa}$ and $E_{pc}$ towards less negative potential and positive potential, respectively. Graph of $I_{pa}$ of PC v/s PC concentration, displays enhancement in redox Ipeak at CuCrO$_4$ NPs composite MCPE. It is almost good linearity with straight line shows in Fig.8. Linear regression equation for PC at CuCrO$_4$ NPs composite MCPE gives $I_{pa}(\mu A) = 0.1562 \times (C_0 \mu M/L) + 2.698 \times 10^{-7}$ and correlation co-efficient ($r^2$) value is 0.9953. This revealed that good linearity and quantification limit (LQ). The detection limit (LD) was computed using the equations (2 & 3) [33-36].
LQ = 10* (S / M) -------- (2)

LD = 3* (S / M) -------- (3)

Where, S; standard deviation and M; slope from the graph. The LD and LQ values for PC were 1.21 µM and 4.04 µM, respectively at CuCrO₄ NPs composite MCPE. It is clear that the prepared CuCrO₄ NPs composite MCPE observed good linearity and low LD and LQ values.

Fig. 7 - Voltammograms of PC in 0.2M PBS of pH 7.4 at CuCrO₄ NPs composite MCPE with different concentration from 2 to 12 µL.
3.6 Effect of solution pH

PC is an easily oxidizable electroactive drug. The CV studies were carried out to examine the supporting electrolyte effect on electrochemical oxidation of PC at CuCrO$_4$ NPs composite MCPE. The Fig.9 represents the voltammograms of 10µM PC in 0.2 M PBS at various pH (6.2 to 7.8) at scan rate of 0.05V/s at CuCrO$_4$ NPs composite MCPE. $I_{pa}$ and $I_{ca}$ initially from 6.2 to 7.0 decreases, then from 7.0 to 7.4 increases after words it decreases with increases from 7.4 to 7.8. The $I_{pa}$ and $I_{ca}$ were shifted towards negative direction with increment in pH from 6.2 to 7.8. A shift in $E_{pa}$ 0.45 V to 0.35V was observed for PC oxidation at CuCrO$_4$ NPs composite MCPE with pH from 6.2 to 7.8. But the pH 7.4 was the physiological pH therefore it was chosen for all the studies. The potential figure was put up by the plot of $E_{pa}$ v/s different values pH (Fig.10). The results afford from linear equation with the slope of 43mV/pH ($r^2 = 0.998$) at CuCrO$_4$ NPs composite MCPE [37]. All this
indicates that during electrochemical reaction of PC, the process of electrode where, exchange of electron is considerably affected by protons and electrons. From the slope, it is confirmed that the number of exchanged electrons and protons were same. This study exposes that electrochemical oxidation of PC at CuCrO$_4$ NPs composite MCPE was pH dependent process and CuCrO$_4$ NPs composite MCPE represents good enhancement of redox $I_{peak}$ and minimize the over potential.

Fig. 9-Cyclic voltammograms of oxidation of 10µM PC in 0.2M PBS of different pH at CuCrO$_4$ NPs composite MCPE
Fig. 10 - Graph of anodic peak potential versus pH

4. Conclusion

An electrochemical sensor for PC finding was established based on the CuCrO$_4$ NPs composite MCPE. The CuCrO$_4$-NPs homogeneously dispensed confirmed that large surface area, good conductivity and exhibited excellent catalytic activity towards the electrochemical oxidation of paracetamol. The CuCrO$_4$-NPs composite MCPE based electrochemical sensor displayed wide linear range and significant sensitivity and it also attained a very low LD of just 1.21µM. The CuCrO$_4$ nanoparticle composite MCPE process of the electrode was controlled by diffusion. The pH studies shows equal number of electrons and protans engaged in the electrochemical oxidation of paracetamol.
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