IJCPS Vol. 2, No. 4, July-Aug 2013 ISSN:2319-6602
www.ijcps.org International Journal of Chemical and Physical Sciences

Preparation and Characterization of 4-hydroxybenzylidencarbamide-CTAB modified Glassy Carbon Electrode by using $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ redox system

N.RAMALAKSHMI*, S.MUTHUKUMAR, B.MARICHAMY

Post-Graduate and Research Department of Chemistry,
Presidency College, Chennai-05, Tamil Nadu, India. e-mail: rrama_subhar@yahoo.co.in

Abstract

4-hydroxybenzylidenecarbamide (ligand) has been synthesized by combination of 4-hydroxybenzaldehyde and urea. The ligand containing hydroxyl, imine and amide functional groups were characterized using IR, NMR spectroscopic techniques. The co-immobilization of cetyltrimethylammoniumbromide (CTAB) and ligand on glassy carbon electrode is achieved by drop coating technique. The ligand-CTAB modified glassy carbon electrode is characterized by using ferro/ferricyanide redox system via electrochemical techniques such as cyclic voltammetry, chronoamperometry and chronocolumetry. Adsorption of these compounds onto glassy carbon electrode gives rise to stable redox probe for ferro/ferricyanide system. Active surface areas of bare GCE, CTAB/GCE, ligand/GCE and ligand-CTAB/GCE are calculated by using cyclic voltammetry and chronoamperometry techniques. The surface concentration of electroactive molecules on the different types of electrodes is calculated by using chronocoloumetry technique.

Key words: Schiff base, Cyclic Voltammetry, Chronoamperometry, Chronocoloumetry, Active Surface Area

Introduction

The synthesis of tridendate Schiff base ligands by reaction between diamines and the corresponding salicylaldehyde derivative is an important reaction in organic chemistry due to the great number of molecules that can be generated and the well know ability of these tridentate ligands to form stable complexes with different metal cations [1].

Although electrochemical methods have traditionally focused on the analysis of species in solution, the use of chemically modified electrodes provides highly sensitive methods for determining micro quantities of sparingly soluble compounds. Modified electrodes provide surfaces capable of preferentially preconcentrating target analytes from solutions on the basis of coordination reactions and electrostatic interactions by using appropriate ligand or ion-exchanger.

Self assembled monolayers(SAMs) have been described as a spontaneous, coordinated chemical interaction of individual molecular building blocks to create a stable, highly ordered and densely packed single layer of molecules from a solution or a gas phase onto a substrate[2]. Over the past two decades, SAMs have received extensive attention due to their stability, simple formation and potentiality of application in many fields such as sensor and biosensor construction [3, 4], studies of charge transfer kinetics [5] and trace ion determination [6]. Thus characterization of the modified electrodes is necessary for analysis of the electroactive species in the solution

This work is investigated the preparation and characterization of 4-hydroxybenzylidene-CTAB modified glassy carbon electrode by using ferro/ferricyanide redox system via electrochemical techniques such as cyclic voltammetry, chronoamperometry and chronocoloumetry.

Reagents

CTAB (HIMEDIA), potassium ferrocyanide (sd fine limited) p-hydroxybenzaldehyde(HIMEDIA), urea(Rankem), alcohol, chloroform (Fisher Scientific).

Materials and Methods

Electrochemical workstations of CHI. USA: Model 600D with potentiostate driven by electroanalytical measuring softwares was connected to PC computer to perform cyclic voltammetry (CV), chronocoloumetry (CC), and chronoamperometry (CA). An Ag/AgCl (3M KCl) and platinum wire are used as a reference and counter electrode respectively. The working electrodes used in this study are GCE, ligand/GCE, CTAB/GCE and ligand-CTAB/GCE obtained by evaporated ligand and CTAB on GCE using chloroform as a solvent.

Polishing of Glassy Carbon Electrode

The glassy carbon electrode is polished with fine alumina powder (0.3micron) on a wet polishing cloth. To do so a part of the cloth is mode wet with deionized water and alumina powder is sprinkled on it. The glassy carbon electrode is then polished on this surface by pressing softly the electrode against the polishing surface in the end for 3-5 minutes. The electrode is then thoroughly washed with deionized water. At this point the electrode surface would look like a shiny black mirror.

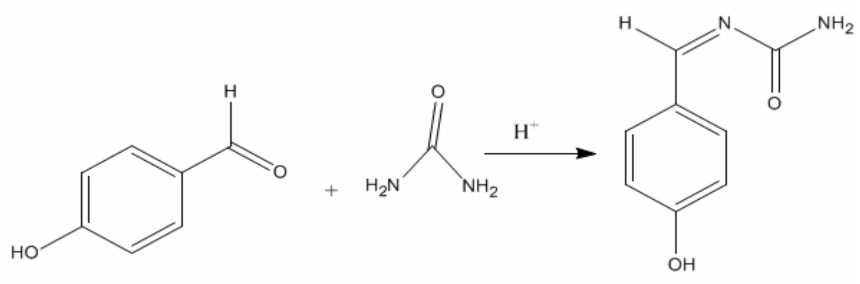
Experimental procedure

First of all, the cell and the Teflon top (with the counter electrode) are cleaned with deionized water; any excess water is wiped off with a tissue paper. A small magnetic stir-bar is put in the cell. The cell is filled with desired volume of the analyte solution and the Teflon cap is placed on the cell. The reference electrode and the purging tube are inserted through the holes. The purging tube should be halfway inside the solution. A range of redox ion concentration (1mM to 5mM) is used.

Results and discussion

Synthesis of Schiff base

The Schiff base used is prepared by mixing an ethanolic solution (30ml of 1.22g 0.01mol) of p-hydroxybenzaldehyde (0.60g, 0.01mol) of urea in the same volume of ethanol. Few drops of dil HCl is added to adjust pH 4 and the obtained mixture then refluxes with stirring for 2h. The precipitate is collected by filtration through Buchner funnel, recrystallized from ethyl alcohol and derived at ambient temperature. The synthetic scheme is shown in below



Sheme.1 Synthesis of 4-hydroxybenzilidene carbamide

Chracterization of ligand

IR spectral data (KBr disc, γ/cm^{-1}): Usual broad band in the region around 3826 due to the NH_2 stretching frequency of the amide group of the ligand. The band at 1597 due to the □(C=N) stretching frequency. The band at 1667 due to the presence of carbonyl group. (C=O). The band at 3167 due to the phenolic OH group.

^1H NMR data (δ ppm in $CDCl_3$): A singlet at 3.5 equivalent to 1H indicates Ar-OH, A multiplet centered at 6.9 and 7.7 equivalent to 4H is due to aromatic protons. A singlet at 9.7 is due to amide NH resonances. A broad peak at 10.5 is due to -CH=N-.

Mass spectrum data: m/z, 164.25. Molecular formula: $C_8H_8N_2O_2$

Preparation of ligand-CTAB/GCE modified glassy carbon electrode

The surfactant is added to control and keep the size of the particles small so that the surface area is higher and diffusion of counter ions is more facile. CTAB is a commonly used surfactant for obtaining small and uniform sized ligand particles. Hence in the present study we have used this surfactant and soft template as it possesses long chains. The soft CTAB is easily removed by wasing with water.

A solution evaporation technique was employed [7,8]. It is done by evaporating a certain quantity of ligand and CTAB solution onto the clean GCE surface. The solution of 1mM CTAB is prepared by dissolving CTAB in chloroform to form a colourless solution. The solution of 0.1% of ligand is prepared by dissolving ligand in chloroform to form a colourless solution. A 10µL solution of CTAB is then deposited onto GCE by successive fast drying of the CTAB droplets to produce thin film of CTAB. A 10µL solution of ligand is then deposited onto CTAB/GCE by successive fast drying of the ligand droplets to produce ligand-CTAB film on GCE. In a similar manner, ligand/GCE is prepared by drop coating of 10µL of ligand solution on the GCE and kept to dry in air at room temperature.

Electrochemical characterization of modified Glassy Carbon Electrodes

Cyclic Voltammetry study

The electrochemical probe molecules, $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ are chosen to characterize the modified electrodes. The bare GCE, CTAB/GCE, ligand/GCE and ligand-CTAB/GCE have been used as the working electrodes. The CVs of 0.1 x 10^{-3}molL^{-1} $K_4[Fe(CN)_6]$ in 0.1molL^{-1} KCl solution are shown in Fig.(1) and its parameters are tabulated in table.1. The ratio of anodic peak current to cathodic peak current (Ipa/Ipc) is very close to unity. $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox redox system exhibit good reversible redox behavior in all kinds of electrodes. As compared with bare GCE, ΔEp values are lower in other modified electrodes. These results suggest that, at the modified electrodes, the reaction of ferrocyanide is a surface-confined redox process, evidencing its non-adsorption onto the glassy carbon electrode surface.

Oxidation potential is shifted towards lower values in CTAB/GCE and ligand/GCE. Based on literature information, the actual adsorption interactions should be very complex. Two main theories [9, 10] were suggested: 1) negatively charged pores at electrode surface take up cations and positively charged take up anions when micropore structures were developed from electrochemical activation. Or 2) the surface interactions involve electron-donor-acceptor, hydrogen bonding, dispersive and solvophobic interactions. These theories are still debated since some authors reported also a compact oxide layer formed as a consequence of the electrochemical activation of the GCE, blocking negatively charged species from reaching the electrode surface[11, 12]. Compared to bare GCE redox peak currents of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ on CTAB/GCE, ligand/GCE and ligand-CTAB/GCE decreased significantly. The active surface area of the electrodes is in the order: bare GCE > CTAB/GCE > ligand/GCE > ligand-CTAB/GCE. This is due to the negative charge of $[Fe(CN)_6]^{4-}$ and ligand immobilized on the electrode surface resulted in the static repulsive force and weakend the electrochemical reaction of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ on the electrode, which lead to the decrease of the redox peak currents and active surface area.

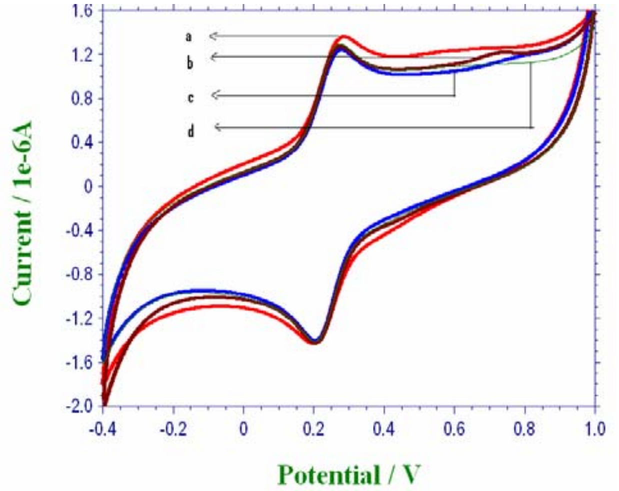


Fig.1 Cyclic Voltammogram for 0.1mM $K_4[Fe(CN)_6]$ on
a) bare GCE; b) CTAB/GCE; c) ligand/GCE; d) ligand-CTAB/GCE. at 40mV/s in 0.1M KCl medium.

Table:1 Cyclic Voltammetric parameters for 0.1mM $K_4[Fe(CN)_6]$
on different electrodes at 40mV/s in 0.1M KCl medium.

Types of electrodes	Ipc x 10^6 (A)	Epc (V)	Ipa x 10^6 (A)	Epa (V)	ΔEp (V)	Active surface area (cm^2)	Γ x 10^3 (cm^2mol^{-1})
Bare GCE	-1.470	0.2013	1.390	0.2858	0.0845	0.0035	3.193
CTAB/GCE	-1.450	0.2057	1.296	0.2698	0.0641	0.00343	3.242
Ligand/GCE	-1.433	0.2080	1.317	0.2720	0.0640	0.0034	3.204
Ligand-CTAB/GCE	-1.424	0.2057	1.201	0.2813	0.0756	0.00336	3.222

An approximate estimate of the electrode surface coverage was made using the following equation [13].

$$Ip = n^2F^2A.\Gamma\ v/ 4RT \qquad (1)$$

Where the peak current (Ip) is related to the surface concentration of electroactive species (Γ), n is the number of electrons involved in the redox reaction, A is the electrode surface area and the other symbols have the usual meaning. The values of surface concentration of electroactive species are in the order of CTAB/GCE > ligand-CTAB/GCE > ligand/GCE. Thus CTAB molecules restrict the adsorption of the ligand molecules on GCE.

Chronoamperometry study

The Cottrell plot for 0.1mM $K_4[Fe(CN)_6]$ in 0.1M KCl medium is presented in Fig.2 and its parameters are tabulated in table.2. In order to measure the electrochemically active surface areas of bare and modified electrodes, the chronoamperomogram of 0.1mM potassium ferrocyanide as the redox probe is recorded. In chronoamperometric studies, the current i, for the electrochemical reaction of ferrocyanide (at a mass-transfer limited rate) that diffuses to an electrode surface is described by the Cottrell equation [14].

$$I = nFAD^{1/2}C/\text{л}^{1/2}t^{1/2} \qquad (2)$$

Where A is the electrochemically active area, D is the diffusion coefficient; C is the bulk concentration of ferrocyanide while the remaining parameters have their usual meanings. Under diffusion control, a plot of I vs $t^{-1/2}$ (Fig.2) will be linear and from the slope, the value of A can be obtained, since the precise value of the diffusion coefficient of ferrocyanide is well known (6.20×10^{-6} cm^2/s). The electrochemically active surface areas of the different electrodes are shown in table.II. The active surface area of the different types of electrodes is in the order of bare GCE > CTAB/GCE > ligand/GCE > ligand-CTAB/GCE. This result suggests that remarkable stable intercalative binding is present between ferrocyanide and ligand molecules on ligand-CTAB/GCE.

Chronoamperometric method can be used to evaluate the catalytic rate constant. At intermediate time interval, the catalytic current (Icat) is dominated by the rate of electrocatalytic redox reaction of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$. On the basis of the equation presented follow it possible to calculate the rate constants of catalytic process. After measurement of the catalytic current, the electrode process is carried out the same conditions but in the absence of catalyst. The catalytic reaction then does not take place and it possible to determine the limiting current value I_L[14, 15]. So, the rate constant for the chemical reaction between ferrocyanide and ligand is determined according to the equation (3), described in the literature [14, 15].

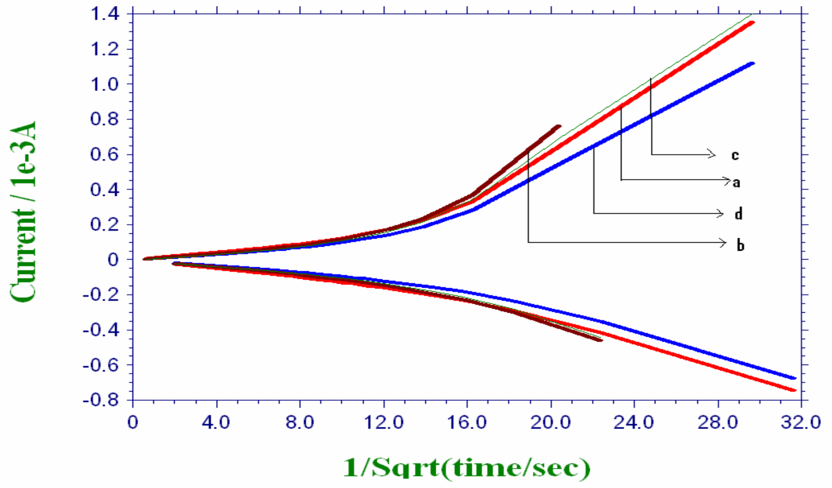


Fig.2 Cottrell plot for 0.1mM $K_4[Fe(CN)_6]$ in 0.1M KCl solution on
a) bare GCE; b) CTAB/GCE c) Ligand/GCE; d) ligand-CTAB/GCE.

Table.2 Chronoamperometric parameters for 0.1mM $K_4[Fe(CN)_6]$ in 0.1M KCl solution on different electrodes.

Types of electrodes	Forward scan					Reverse scan				
	Slope values x 10^5	t x 10^4 (s)	I x 10^4 (A)	A (cm^2)	k x 10^{-2} mol s/cm^2	Slope values x 10^5	t x 10^1 (s)	I x 10^3 (A)	A (cm^2)	k x 10^{-2} mol s/cm^2
Bare GCE	-1.231	6.667	-7.542	0.907	-	1.154	2.507	1.363	0.851	-
CTAB/GCE	-0.965	6.667	-9.474	0.711	2.946	0.9070	2.507	1.654	0.669	0.6576
Ligand/GCE	-0.879	6.667	-8.749	0.648	2.831	0.8410	2.507	1.416	0.620	0.6084
Ligand-CTAB/GCE	-0.798	6.667	-6.792	0.589	2.495	0.7707	2.507	1.129	0.568	0.5433

$$I_{cat}/I_L = \gamma^{1/2} [\text{л}^{1/2} \operatorname{erf}(\gamma^{1/2}) + \exp(-\gamma)/\gamma^{1/2}] \quad (3)$$

Where I_{cat} and I_L are the currents of ferrocyanide redox system in the presence and absence of modifier respectively. $\gamma = KC_0t$ (C_0 is the bulk concentration of ferrocyanide in mol/cm^2), k is the catalytic rate constant ($mol^{-1}cm^2s^{-1}$) and t is time elapsed(s) and erf ($\gamma^{1/2}$) is the argument of error function. The second term in brackets in eq.1 then becomes negligible compared with $\text{л}^{1/2}$. Thus eq.(3) can be reduced to

$$I_{cat}/I_L = \gamma^{1/2}\text{л}^{1/2} = \text{л}^{1/2}(kC_0t)^{1/2} \quad (4)$$

From the table.II the catalytic rate constants of the modifier is in the order of CTAB > ligand > ligand-CTAB for the redox reaction of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ system. This result is also suggested that the intercalating binding is present between ferrocyanide molecule and ligand molecule on ligand-CTAB/GCE.

Chronocoloumetry study

Anson plot for 0.1mM $K_4[Fe(CN)_6]$ in 0.1M KCl solution on bare and modified electrode is shown in Fig.3 and its parameters are presented in table.3. In chronocoulometric studies, the charge (Q) for the electrochemical reaction of ferrocyanide (at a mass transfer limited rate) that diffuses to an electrode surface is described by the Anson equation.

$$Q = 2nFACD^{1/2}t^{1/2}/\text{л}^{1/2} \quad (5)$$

Under diffusion control, a plot of Q vs $t^{1/2}$ will be linear and from the slope, the value of A can be obtained, since the precise value of the diffusion coefficient of ferrocyanide is well known (6.20 x 10^{-6} cm^2s^{-1}). The electrochemically active surface areas of the different electrodes are shown in table.III. The active surface area of the different types of electrodes is in the order of bare GCE > CTAB/GCE > ligand/GCE > ligand-CTAB/GCE.

The surface concentration of the different types of electrode is calculated using the equation [16].

$$\Gamma = Q/nFA \qquad (6)$$

Where Q is the charge obtained during the redox process and other symbols have their usual meanings. The surface concentration of the electroactive species on the different modified electrode is in the order of bare GCE > CTAB/GCE > ligand/GCE > ligand-CTAB/GCE for both the oxidation and reduction reaction of the $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ redox system. These results suggest that the intercalating binding of ferrocyanide molecule with ligand molecule is charge dependent.

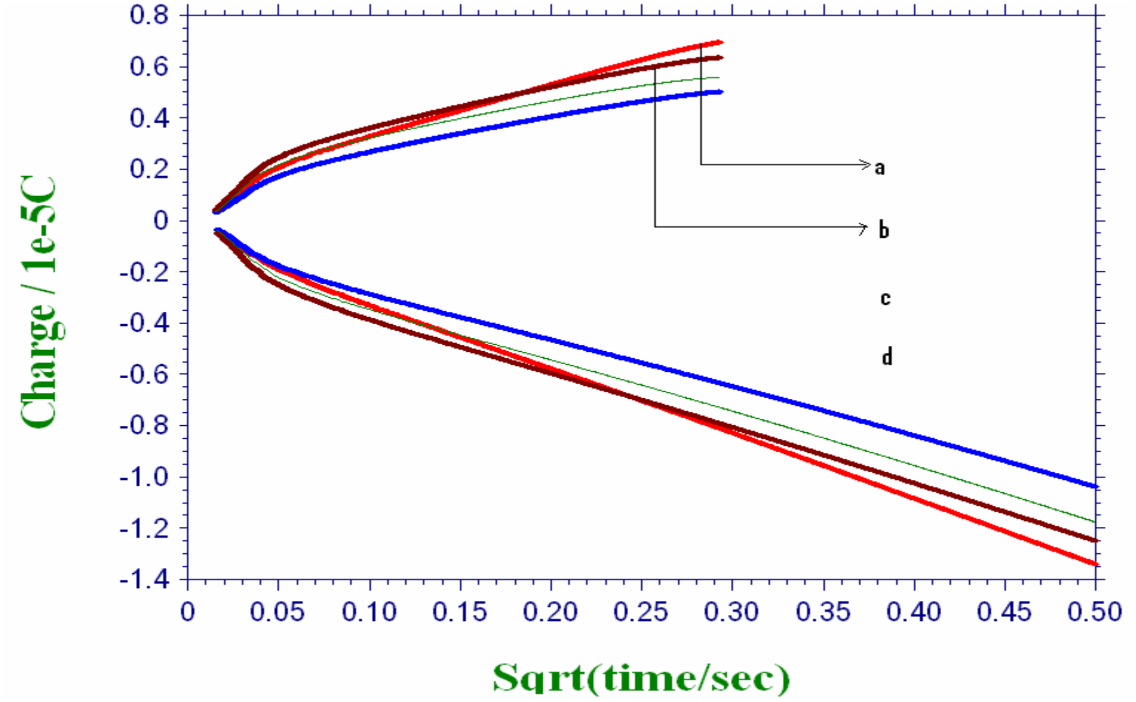


Fig.3 Anson plot for 0.1mM $K_4[Fe(CN)_6]$ in 0.1M KCl solution on
a) bare GCE; b) CTAB/GCE c) Ligand/GCE; d) ligand-CTAB/GCE.
b)

Table.3 Chronocoloumetric parameters for 0.1mM $K_4[Fe(CN)_6]$ in 0.1M KCl solution on different electrodes.

Types of electrodes	Forward scan				Reverse scan			
	Slope values x 10^5	Q x 10^6 (C)	A (cm^2)	Γ x 10^{11} cm^2mol^{-1}	Slope values x 10^5	Q x 10^5 (C)	A (cm^2)	Γ x 10^{10} (cm^2mol^{-1})
Bare GCE	-2.555	6.900	0.907	7.589	1.835	1.350	0.6766	2.068
CTAB/GCE	-2.196	6.395	0.711	8.184	1.282	1.249	0.4727	2.738
Ligand/GCE	-2.135	5.587	0.648	7.355	1.059	1.181	0.3905	3.134
Ligand-CTAB/GCE	-1.929	4.987	0.589	7.265	1.088	1.046	0.4012	2.702

Conclusion

The cyclic voltammogram of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ redox system gives both cathodic and anodic peaks and every step is single electron process in all types of electrodes. ΔEp value is nearly 60mV on ligand-CTAB/GCE which such as that ferrocyanide system exhibit reversible nature and undergoes a intercalative binding with ligand. The active surface area of the different types of electrodes is in the order of bare GCE > CTAB/GCE > ligand/GCE > ligand-CTAB/GCE. The surface concentration of electroactive species on the different types of electrodes is in the order of bare GCE > CTAB/GCE > ligand/GCE > ligand-CTAB/GCE. The catalytic rate constants of the modifier is in the order of CTAB > ligand > ligand-CTAB. These results suggest that ligand-CTAB molecule has crucial role in intercalating binding of ligand-CTAB and ferrocyanide molecules.

Acknowledgements

Authors are thankful to IIT Madras for providing instrumental facility.

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