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Synthesis, characterization of manganese(II) Schiff base complex and its electrocatalytic sensing of hydroquinone

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The Schiff base metal complexes exhibit excellent catalytic activity in various chemical reactions. The manganese(II) Schiff base complexes have good electrochemical redox activity due its various oxidation states. It will be utilized as an electrocatalytic sensor for detection of hydroquinone (HQ). HQ is widely used in several fields, such as dye, photography, pharmaceutical, antioxidant etc. Due to high toxicity to human and low degradation ability in ecological system HQ is considered as a serious environmental pollutant. Based on the environmental factor it is necessity to develop a simple quantification technique for HQ. The Mn^{II} Schiff base complex modified GCE exhibits better electrochemical sensing ability to determine HQ at low detection limits with lower potential than bare GCE.

Keywords: Manganese(II) Schiff base complex, hydroquinone, electrocatalytic sensor, electrochemical polymerization.

Introduction

The chemistry of Schiff base metal complex is undergoing rapid development due to their essential roles in biological systems and chemical industries. Schiff base ligands are most common in coordination chemistry because of it's simple synthesis procedure and wide range of applications. The Schiff base ligands form more stable complexes with almost all transition metal ions. These transition metal complexes exhibit excellent catalytic activity in various chemical reactions. Although, many reports are available in the Schiff base complexes with good efficiency in different fields, remarkable effort is still carried out in designing a new Schiff base ligands and studying their stability. Manganese is an important trace element in living systems because of its role in many enzymes, such as in catalase, superoxidase dismutase and in the photosynthetic oxygen evolving complex (OEC). Due to its rich redox behavior, the manganese Schiff base complexes are deeply studied with different applications. The manganese(II) Schiff base complexes have good electrochemical redox activity, due to its various stable oxidation states. Because of its better electrochemical redox nature, it can be polymerized by electrochemical method on the surface of glassy carbon electrode (GCE). The modified electrode was utilized for the electrocatalytic sensing of hydroquinone (HQ). HQ is a small and important organic compound, which is widely used in different fields, such as dye, photography, pharmaceutical, antioxidant, reducing agent, polymerization inhibitor and cosmetic industries. Due to high toxicity to human and low degradation ability in ecological system HQ is considered as a serious environmental pollutant. The US Environmental Protection Agency (EPA) and the European Union (EU) has announced that HQ is a serious environmental pollutant. Hence there is a necessity for the quantification of HQ. There are several analytical methods available for the determination of HQ, such as spectrophotometry, HPLC and electroanalysis. Among the available methods electrochemical determination has some merits, it give better sensitivity, selectivity, cost effective, simple procedure and rapid response. In the present work a manganese(II) Schiff base complex was synthesized by microwave irradiation method and characterized with the aid of different spectral techniques then utilized for sensing of HQ[1–3].

Experimental

Chemical and reagents:

5-Bromosalicylaldehyde (AR), diethylenetriamine, and hydroquinone were purchased from Sigma Aldrich, manganese(II) chloride (AR) was purchased from Alfa Aesar, tetrabutylammonium perchlorate (AR) was purchased from Fluka and recrystallized by using hot ethanol, sodium dihydrogen phosphate (AR), disodium hydrogen phosphate (AR) were purchased from SRL Chemicals. The solvents were purchased from Qualiogens and used without further purification

Synthesis of manganese(II) Schiff base complex:

An absolute methanolic solution of 1 mmol, 5-bromoaldehyde (0.402 g) was taken in a beaker, to this aldehydic solution, 1 mmol methanolic solution of diethylenetriamine (0.1 ml) was added under stirring condition. After the addition of amine solution, 1 mmol of manganese(II) chloride (0.198 g) was added in the reaction mixture. It was continuously stirred for about 2 h. Then finally it was employed for the microwave irradiation at 320 W, for 5 min. A brown colour precipitate was obtained, it was collected and washed with methanol several times and it was recrystallized by using hot methanol[4].

Results and discussion

Characterization of Mn^{II} Schiff base complex:

The synthesized cobalt(II) Schiff base complex was characterized by UV-Visible, FT-IR, emission, EPR spectral techniques and electrochemical studies. The UV-Visible spectrum exhibits three absorption peaks at 221, 315 and 540 nm due to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ electronic transfer transition and d-d transition of the Mn^{II} ion respectively. The FT-IR spectrum conforms the formation of Mn^{II} Schiff base complex based on the following important characteristic bands. A band at 1658 cm^{-1} is due to the imine (C=N) functional group, 827 cm^{-1} is corresponds to the stretching vibration of phenyl ring, the metal nitrogen bond exhibit a band at 547 cm^{-1} and the metal oxygen bond shows its vibration band at 446 cm^{-1}. These peaks conform the complex formation between Schiff base ligand and Mn^{II} metal ion[5]. The Mn^{II} complex has emission property which clears by the emission spectrum, its shows emission at 520 nm for the irradiation of 310 nm wave length. The electronic transition in d-orbitals of the Mn^{II} ions may arises the emission. The EPR spectrum shows five splitting it conforms the Mn^{II} oxidation state. The electrochemical studies of Mn^{II} complex was tested using three electrode system of cyclic voltammetry (CV) at the potential range of –1 V to 1 V, it shows an anodic peak at 0.6 V and two cathodic peaks at 0.16 V and –0.9 V, it shows the complex has electrochemical activity[6,7].

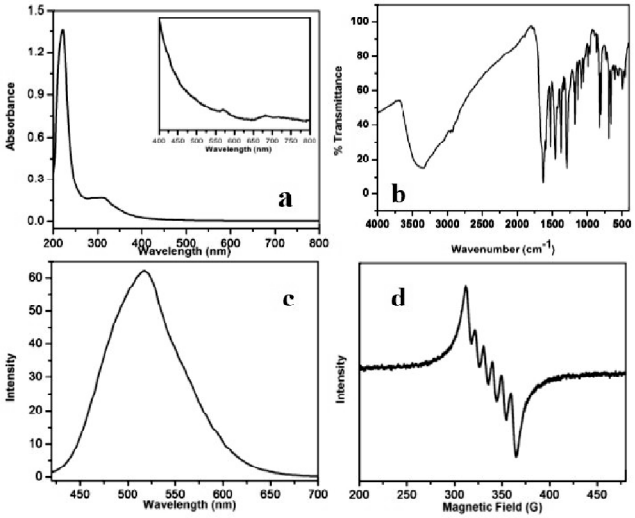

Fig. 1. (a) UV-Vis, (b) FT-IR, (c) emission spectra and (d) EPR spectrum of Mn^{II} complex.

Then the complex was electrochemically polymerized on the GCE working electrode surface then used for the quantification of HQ.

Electrocatalytic sensing of HQ:

Cyclic voltammograms were recorded to examine the electrocatalytic determination of HQ at Mn^{II} Schiff base complex modified GCE and bare GCE in 0.1 *M* PBS buffer (pH 7). The electrocatalytic sensing of Mn^{II} Schiff base complex modified GCE and bare GCE towards HQ at 50 mV s^{-1} were shown in Fig. 2b**.** The Fig. 2b, depicts that the bare GCE exhibits poor electrochemical response towards HQ, it gives the anodic peak at 0.236 V, with 2.54 μA current and its corresponding cathodic peak at –0.128 V with –1.95 μA current and the electrode process was irreversible in nature[8].

But, the Mn^{II} Schiff base complex modified GCE shows better electrocatalytic sensing ability for HQ, it has the anodic peak at 0.173 V, with 8.33 μA current and its corresponding cathodic peak at –0.077 V with –6.79 μA current and the electrode process was reversible in nature. These results indicated that Mn^{II} Schiff base complex modified GCE

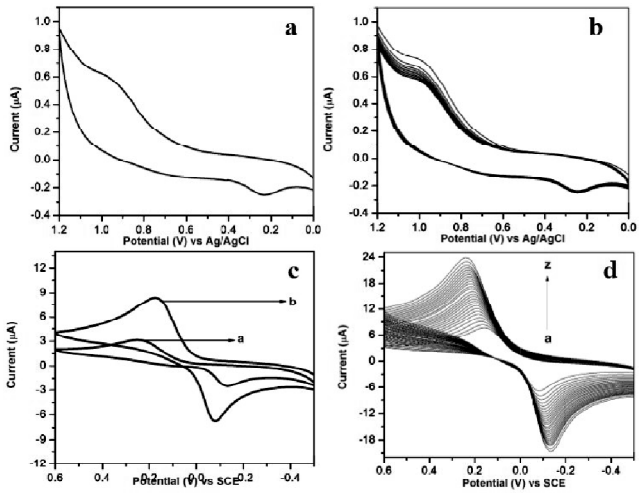

Fig. 2. (a) Electrochemical studies of Mn^{II} complex, (b) polymerization of Mn^{II} complex and (c) sensing of HQ at (a) bare GCE, (b) modified GCE presence of 0.1 mM HQ in 0.1 *M* PBS and (d) scan rate effect.

has an excellent selectivity towards HQ, and the fabricated modified electrode might be applied to determine HQ in real samples[9].

Conclusion

To conclude, Mn^{II} Schiff base complex was synthesized by microwave irradiation method. The synthesized Mn^{II} complex was characterized by different spectral techniques such as UV-Vis, FT-IR, emission and EPR, all the spectrums were confirmed the complex formation between Mn^{II} ion and the Schiff base ligand. The electrochemical activity of Mn^{II} Schiff base complex was studies by cyclic voltammetry, it confirms the Mn^{II} complex has redox property. Further, we developed poly-Mn^{II} complex/GCE as a HQ sensor by electrochemical polymerization method. The proposed poly-Mn^{II}-complex/GCE exhibited high electrocatalytic activity towards HQ.

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