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Electrochemistry of Surface Confined Metal Phthalocyanine: Tuning of Redoxpotential and Axial Coordination

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Abstract - The redox processes of iron containing macrocycles play an important role in biological electron transfer. Porphyrins are commonly occuring biological tetrapyrrole macrocyclic ligands. Studies on the redox chemistry of macrocyclic metal complexes received considerable interest to understand the electron transfer process in the biological system. Inner-sphere coordination of exogeneous ligand has great control over the redox potential of metalloredox proteins [1]. The binding of exogeneous ligands to a superstructured metal porphyrin or phthalocyanine provide important information on the metalloenzyme substrate binding. In the present investigation,

***Keywords*: Electrocatalysis, iron(III) macrocyclic complexes, carbon nanotubes.**

INTRODUCTION

Metallo-macrocycles and their derivatives exhibit many outstanding chemical and physical properties, they have always been target molecules used for nonlinear optical materials [2], optical data storage [3], electrochemical microsensors or optical sensors [4]. Electrodes modified with adsorbed metallo-macrocycles have received considerable attention in the literature due to the great variety of electrochemical reactions that are catalysed by these metal-macrocycles [5-10]. The CNT modified electrodes are known to promote the electron transfer kinetics of the redox reaction of different redox proteins [11]. CNT has been chosen to confine Fe(III) phthalocyanines, as it has excellent electrical, chemical and mechanical properties [12].

As a part of our continuing effort to develop an efficient transducer, we explore the possible utilization of Fe(III) phthalocyanines confined on the nanostructured carbon, carbon nanotube (CNT) for the study of the influence of axial binding of ligand on the redox potential.

REAGENTS AND MATERIALS.

MWCNTs (≥ 95% purity), iron(III) phthalocyanine chloride, Dimethyl sulphoxide (DMSO) were purchased from Sigma-Aldrich. All other chemicals used in this investigation were of analytical grade. All solutions were prepared using Millipore water.

INSTRUMENTATION.

Electrochemical measurements were performed using two-compartment three-electrode cell with a glassy carbon (GC) working electrode, a Pt wire auxiliary electrode and Ag/AgCl (3 M KCl) reference electrode. Cyclic voltammograms were recorded using a computer controlled CHI643B electrochemical analyzer connected to a Picoamp Booster-Faraday cage.

PREPARATION OF CNT-FE MACROCYCLE COMPOSITE THIN FILM.

The GC electrodes (0.07 cm^2) were used as substrate for making CNT-Fe macrocycle thin film. Before modification, the GC electrodes were polished well with fine emery paper and alumina (0.05 µm) slurry and then sonicated in Millipore water for 10-15 min. Finally the electrode was thoroughly rinsed with Millipore water and used for modification. A 0.4 mg of purified CNT was dispersed in 200 µL DMSO containing 5.7 mM of iron (III) phthalocyanine. The mixture was stirred in a magnetic stirrer vigorously for 30 min to obtain a homogeneous suspension. An aliquot of 10 µL of the suspension was uniformly coated on the clean GC electrode and allowed to dry at room temperature for 30 min.

RESULTS AND DISCUSSION

Fe(III) phthalocyanine confined on the CNTs (Scheme 1) exhibit reversible voltametric response characteristic of a surface confined species at 0.21 V corresponding to the redox reaction of Fe(III)/Fe(II) couple. The surface coverage (Γ) was obtained by integrating the area under the cathodic peak and was 0.0052 x 10^{-6} mol/cm^2. Fig.1 illustrates the influence of the coordination of exogenous ligand on the redox potential of surface confined Fe(III) phthalocyanine. 20-25 mV positive shift in the redox potential of Fe(III) phthalocyanine was observed in the presence of pyridine and imidazole (10 mM). However, a 55 mV negative shift in the redox potential was noticed in the presence of dimethylaminopyridine. The shift in the redox potential depends on the nature of the axial ligand. The binding of these ligands have also been investigated by spectral measurement (Data not shown). The tuning of redox potential by the axial coordination of the ligands is in progress.

CONCLUSIONS

We have investigated the effect of ligand environment iron(III) macrocyclic complexes on CNT based electrode in aqueous solution in electrochemical properties of for the first time for the study of the influence of axial binding of ligand on the redox potential.

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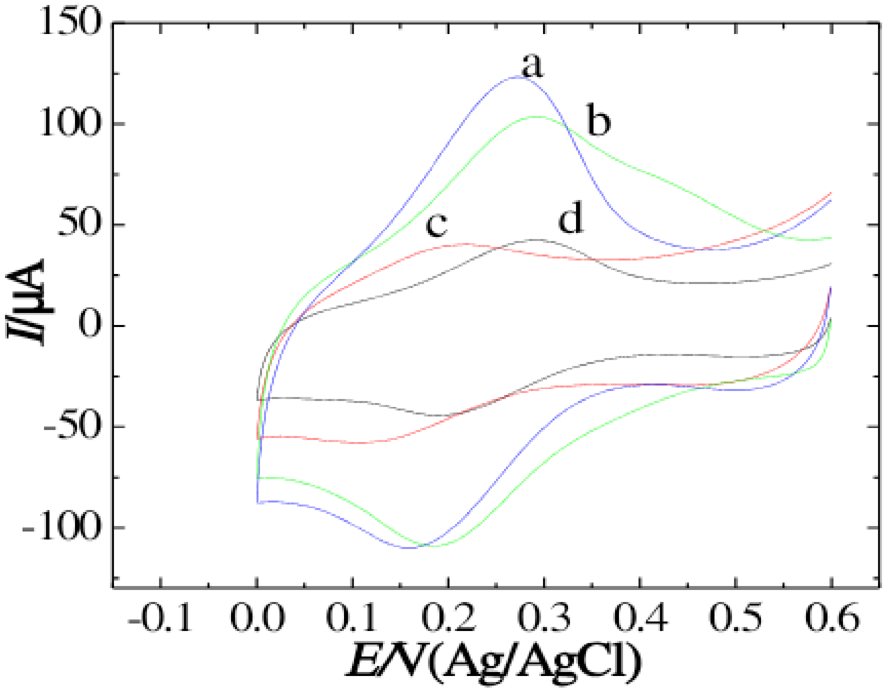
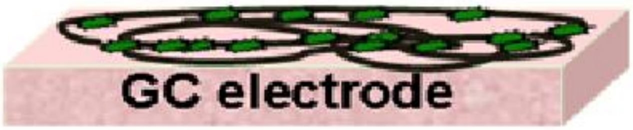


Fig.1 Cyclic Voltammograms of CNT-phthalocyanine electrode in 0.1 M PBS (pH 7.2) (a) in absence and (b,c,d) in presence of 10 mM imidazole, dimethylaminopyridine and Pyridine, respectively. Scan rate: 100 mV/s



Scheme-1: Schemetic representation of **CNT-phthalocyanine electrode.**

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