

## Role of Palladium in the Redox Electrochemistry of Ferrocene Monocarboxylic Acid Encapsulated Within ORMOSIL Networks

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**Abstract:** We report herein the effect of palladium on the redox electrochemistry of ferrocene monocarboxylic acid encapsulated within an organically modified sol-gel glass network (ORMOSIL). It has been found that amount of palladium and its geometrical distribution significantly alter the redox electrochemistry of FcMCA. The geometrical distribution of palladium has been controlled by two methods: (i) palladium is allowed to link within nanostructured network of the ORMOSIL which was subsequently availed from the reactivity of palladium chloride and trimethoxysilane; (ii) palladium powder is encapsulated together FcMCA thus allowing the presence of palladium within the nanoporous domain. The content of palladium is varied by controlling the reaction dynamics of palladium chloride and trimethoxysilane interaction. For this we initially allowed to trigger hydrolysis, condensation and poly-condensation of trimethoxysilane and dimethyldiethoxysilane in acidic medium and subsequently partially dried ORMOSIL film was allowed to interact with palladium chloride. Even with partially dried ORMOSIL derived from trimethoxysilane and dimethyldiethoxysilane undergoes rapid interaction with palladium chloride and the transparent color of ORMOSIL changed to a black colour due to the formation of palladium silicon linkage. The palladium-silicon linkage has been identified by NMR, UV-VIS and transmission electron spectroscopy. The electrochemistry of FcMCA encapsulated within such an ORMOSIL matrix has been studied. Excellent redox electrochemistry of ferrocene monocarboxylic acid having peak potential separation tending to 0 for a multilayered electrode was investigated. The palladium content has been found to affect the redox electrochemistry of ferrocene as well as electrocatalytic efficiency of new ORMOSIL

material. The electroanalysis of NADH is reported. The modified electrode is very sensitive to NADH with lowest detection limit of  $< 1 \mu\text{M}$ .

**Keywords:** ORMOSIL, Metallocene Palladium-linked ormosil-modified electrode, Electrocatalysis, Cyclic voltammetry, Electrochemistry of ferrocene monocarboxylic acid.

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## Introduction

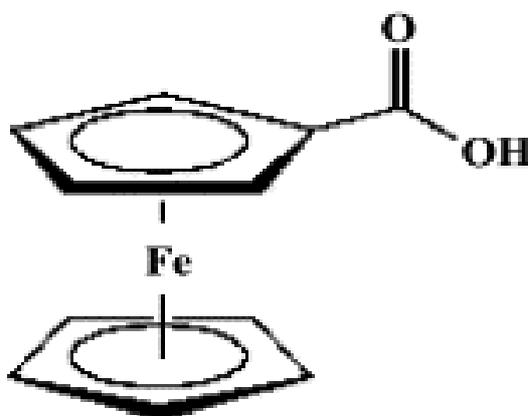
Modification of electrodes by porous matrix membranes, such as ceramic materials, has been a very active research area [1-10]. The properties of the silica materials, such as ionic interchange capacity, good catalytic support, great surface area, mechanical stability, low cost, etc., make them suitable as electrode surface modifiers [8-10], despite their low electrical conductivity. Further, such matrices provide the option of manipulating several targeted reacting species within their porous domain and generate the feasibility of several new devices of commercial significance. One of such species is ferrocene and its derivatives, which act as efficient and uniform electron transfer mediators [11-15] for regenerating the redox activity of several biological molecules. Accordingly, extensive investigations on the synthesis of ferrocene derivatives have been conducted, with particular attention paid to: (i) variations in hydrophobic property, (ii) heterogeneous second order rate constants for the reactions between mediator and redox biomolecules, (iii) electrocatalytic efficiency and (iv) biocompatibility. Ferrocene monocarboxylic acid (FcMCA) is one of the most widely used mediators because of its better efficiency and compatibility for regenerating the redox bio-molecules both in homogeneous and heterogeneous systems. Electrochemical sensors based on ferrocene as mediators have been widely studied [11-18]. The majority of ferrocene derivatives meet the conditions for ideal redox mediators, e.g (a) relatively low molecular mass, (b) reversibility, (c) regeneration at low potentials, (d) insensitivity to pH, (e) stability of each form of the redox couple, (f) insensitivity of its redox couple to physiological oxygen. When such a mediator is incorporated within the nano-structured domain of silica materials, the electrochemical communication between mediator and targeted redox molecule is restricted and accordingly the practical usability of devices could not be realized [19]. One route for facilitating electrochemical communication within such host matrices is to introduce electro-catalytic properties. Since metal-ceramic composites have shown electro-catalytic efficiency in many chemical systems and further, the application of palladium in facilitating catalytic properties is also very well known, we have worked in this area by introducing palladium within nano-structured domains of silica networks [18], since the use of palladium as an electro-catalyst is known [20-21]. Such introduction is possible while using the alkoxysilane precursors having functional reactivity leading to the formation of an organically modified sol gel glass (ORMOSIL). Fortunately the glycidoxy-group present in one of the alkoxysilane precursors was found to be sensitive to palladium chloride, which opened the possibility of attaching palladium within a nano-structured network. The redox electrochemistry of ORMOSIL encapsulated ferrocene monocarboxylic acid after palladium linkage, not only communicated bio-electrochemically but the redox electrochemistry of the mediator was observed to be even better than that observed in homogeneous solution [18]. We have made investigations in this direction using two alkoxysilanes, namely 3-glycidoxypropyltrimethoxysilane and 2-(3,4-epoxycyclohexyl)ethyl-trimethoxysilane, which contains valuable

epoxides and offers the possibility of selective ring opening reactions with nucleophiles and radicals in the presence of Lewis acids or Lewis bases and investigated the interactions of palladium chloride with such alkoxy silanes containing epoxide rings and indeed developed good materials for electrocatalytic applications [16-19]. We examined the interaction of palladium with 3-glycidoxypropyltrimethoxysilane and subsequently made ORMOSIL in acidic media containing either trimethoxysilane [18] or 3-aminopropyltrimethoxysilane. The hydrolysis, condensation and polycondensation are subsequent steps leading to a nano-structured ORMOSIL network where the contribution of alkoxy-groups, i.e.  $\text{OCH}_3$  or  $\text{OC}_2\text{H}_5$ , are kinetically remarkable and were studied in detail. Amongst the various silanes *trimethoxysilane* is highly reactive and a kinetically faster alkoxy silane. We have used this silane for initiating ORMOSIL formation of palladium linked 3-glycidoxypropyltrimethoxysilanes. Linkage of palladium to the ORMOSIL network provided good electrocatalytic properties for practical applications [18] followed by facilitating redox electrochemistry of ferrocene derivatives. The interaction of palladium chloride with 3-glycidoxypropyltrimethoxysilane took place through the epoxide group and a palladium-carbon bond was established within the ORMOSIL network. In the present investigation we observed very interesting findings on the interactions of palladium chloride and trimethoxysilane leading to the formation of a new palladium-silicon linkage which is entirely different than that of earlier reports [18]. Accordingly, we have developed an ORMOSIL material having palladium-silicon linkages useful in bioelectrocatalysis. The material facilitates the reversible redox electrochemistry of ferrocene monocarboxylic acid with a peak separation tending to zero. The results were based on NMR, transmission electron microscopy and cyclic voltammetry data, as reported in this communication.

## Results and Discussion

### *Chemistry of the palladium chloride and trimethoxysilane interaction*

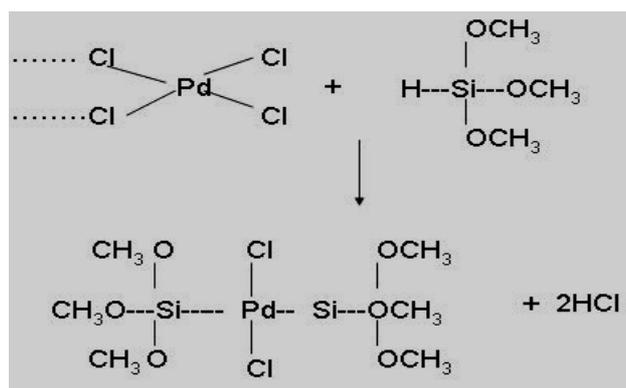
Ferrocene monocarboxylic acid, the structure of which is given below, has been used as a mediator in a variety of electrochemical systems [22],



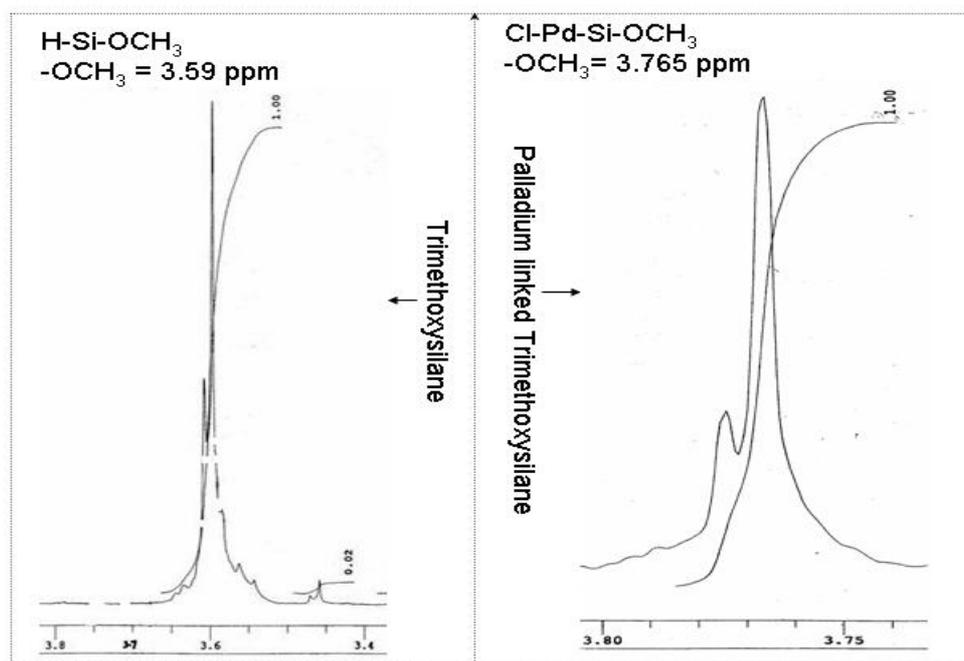
Although this mediator served to a greater extent in probing many enzymatic reactions however the solubility of redox couples in aqueous media caused leaching out of the mediator from the conventional microporous solid-state matrix. Accordingly, greater attention has been paid to

functionalizing the ferrocene chain or putting the mediator into a polymeric backbone. The functionalized ferrocene showed variable electrochemistry depending on the solid-state network. Since the ORMOSIL matrix provided a nanoporous domain, such small molecules could be encapsulated within such matrices and thus the problem of leaching out could be eliminated and the need for functionalized ferrocene may also be avoided. However, such encapsulation not only slowed down the redox electrochemistry of encapsulated un-functionalized ferrocene but also restricted the electrochemical communication between biomolecule and mediator within the nano-structured network. Accordingly, we attempted to facilitate both the electrochemistry of ORMOSIL-encapsulated ferrocene monocarboxylic and the electrochemical communication between mediator and redox biomolecules by introducing palladium within the nano-structured domain. Along these lines we carried out extensive investigations on the interaction of palladium chloride and 3-glycidoxypropyl-trimethoxysilane and subsequently developed ferrocene monocarboxylic acid encapsulated ORMOSIL. Dramatically the encapsulated ferrocene mono-carboxylic acid showed excellent redox electrochemistry [18], followed by better electrochemical communication with biomolecules in the solid-state. We concluded that the presence of palladium within the ORMOSIL network introduced electrocatalytic efficiency facilitating the electron hopping sites within the solid-state nano-structured network. The questions here raised were to find out the following: (i) the effect of palladium content on electrocatalysis, (ii) site directed requirements of palladium, if any, (iii) replacement of another alkoxy silane silane apart from 3-glycidoxypropyltrimethoxysilane since palladium was introduced through a Pd-C linkage [18]. Fortunately we found a better system and studied the interactions of palladium chloride and trimethoxysilane.

The interaction of palladium chloride and trimethoxysilane was studied and found to be very sensitive and kinetically faster. After the addition of aqueous palladium chloride solution into trimethoxysilane, the site of palladium chloride solution become black solid followed by liberation of HCl as follows;



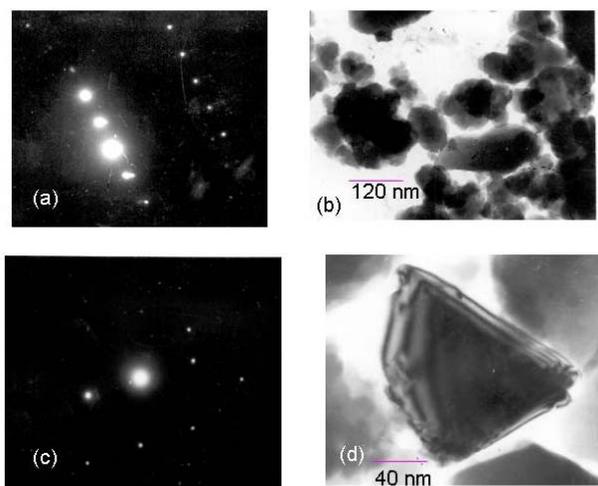
We investigated the formation of above palladium-silicon linkage based on NMR and UV-VIS spectroscopy. The results based on nuclear magnetic resonance spectroscopy before and after palladium linkage are given in Figure 1.

**Figure 1** NMR spectra of trimethoxysilane and palladium chloride treated trimethoxysilane

The position of the  $-\text{OCH}_3$  peak is highly dependent on the surrounding environment. The  $-\text{OCH}_3$  peak position in trimethoxysilane under the present conditions was found to be 3.59 ppm whereas when palladium is attached to silicon the same is shifted to 3.775 ppm. Such a large downfield shift may be only explained if chlorinated palladium is linked to silicon as in the present case.

We also investigated the linkage of palladium to silicon based on UV-VIS spectroscopy. Disappearance of absorption corresponding to 420 nm which is characteristic of light brown solution of palladium chloride justified the linkage of palladium to silicon. After identifying the linkage of palladium to silicon we subsequently moved to the preparation of ORMOSIL material. We used dimethyldiethoxysilane as one of the precursors to trigger the ORMOSIL formation. In order to control the interaction of palladium chloride with trimethoxysilane which is very rapid in homogeneous solution, we adopted two approaches to control such interaction. Initially we made a homogeneous solution of trimethoxysilane (30  $\mu\text{L}$ ), dimethyldiethoxysilane (30  $\mu\text{L}$ ) containing ferrocene monocarboxylic acid (2 mg/mL), methanol (70  $\mu\text{L}$ ), and HCl (5  $\mu\text{L}$ ) followed by pouring the suitable amount of the homogeneous solution onto desired substrate (glassy carbon electrode or glass slide). After 5-15 min of sol-gel processing, two approaches were adopted for carrying the interaction of palladium chloride to semi-processed ormosil's precursors; 1) the substrate was dipped overnight into aqueous solution of palladium chloride (2 mg/mL); 2) a drop of palladium chloride solution (2 mg/mL) was placed over the substrate containing semi-processed ORMOSIL's precursors. After overnight incubation black coloured ormosil was found over the substrate. The ormosils were characterized by transmission electron microscopy and electrochemical measurement. The results based on transmission electron microscopy are given in Figure 2.

**Figure 2.** Transmission electron microscopy of palladium-linked ormosil. Diffraction patterns (a) and (c) and their corresponding microstructure (b) and (d).

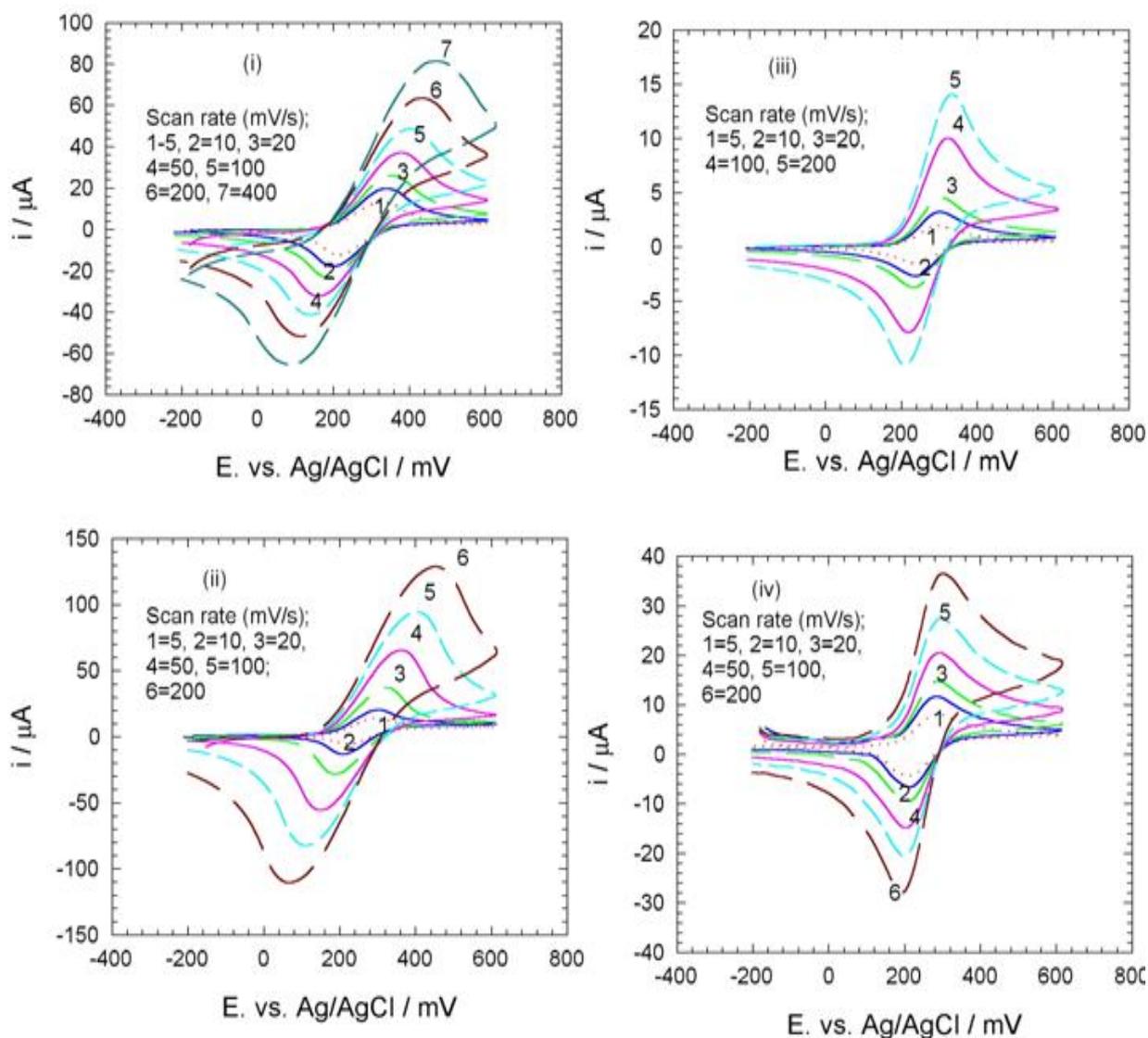


The TEM data was exploited to correlate the linkage of palladium with silicon if any. The  $dA^\circ$  calculated from diffraction pattern were found to be;  $1.78 A^\circ$ ,  $1.54 A^\circ$ ,  $1.00A^\circ$  that correspond to the reported values of palladium-silicon linkage[23]. The particle size calculated to be ranging from 60-190 nm.

#### *Electrochemistry of ferrocene monocarboxylic acid encapsulated ormosil-modified electrode based on palladium-silicon linkage*

The new material has been used to make modified electrodes in order to study the electrochemistry of ferrocene encapsulated within such ORMOSIL matrices. The material could be either casted on the surface of a glassy carbon electrode or could be incorporated within graphite paste after converting the material into a fine powder. In order to study the electrochemistry of ferrocene and to justify the contribution of palladium linked silicon we made the following types of electrodes; 1) ORMOSIL-modified electrode made in absence of palladium; 2) ORMOSIL-modified electrode in the presence of palladium powder thus avoiding the linkage of palladium to silicon; 3) ORMOSIL-modified electrode where the palladium chloride interaction with TMOS was conducted using drop of aqueous palladium solution over semi-processed ORMOSIL's precursors; and 4) ORMOSIL-modified electrode where the interaction of palladium chloride with TMOS was conducted by dipping the semi-processed ORMOSIL's precursors in aqueous solution of palladium chloride. The results based on cyclic voltammery on these four types of modified electrodes are recorded in Fig.3 as (i), (ii), (iii), and (iv) respectively at various scan rates.

**Figure 3.** Cyclic voltammograms of ormosil-modified electrodes in 0.1 M phosphate buffer pH 7 at different scan rates; (i) Ormosil-modified lectrode without palladium chloride treatment; (ii) Ormosil-modified electrode in the presence of palladium chloride and in absence of palladium chloride treatment; (iii) Ormosil-modified electrode with palladium chloride treatment using a drop of palladium chloride; (iv) Ormosil-modified electrode with palladium chloride treatment by dipping the electrode in palladium chloride.



Trace-(i) of the voltammograms show the electrochemistry of ORMOSIL-encapsulated ferrocene monocarboxylic acid in absence of any palladium content. In order to examine the contribution of palladium linkage we also made another electrode in the presence of palladium powder and the voltammograms of ORMOSIL-encapsulated ferrocene monocarboxylic acid is recorded in trace-(ii). In both these cases the peak separation is highly dependent of scan rate. Trace-(iii) and trace-(iv) show the voltammograms of ORMOSIL-encapsulated ferrocene where palladium is linked to the ORMOSIL network. Our experimental conditions predict relatively lower palladium content in case of trace-(iii) as compared to trace-(iv). Accordingly the redox electrochemistry of ORMOSIL-encapsulated ferrocene monocarboxylic acid as excellent as recorded in trace-(iv). The peak separation virtually

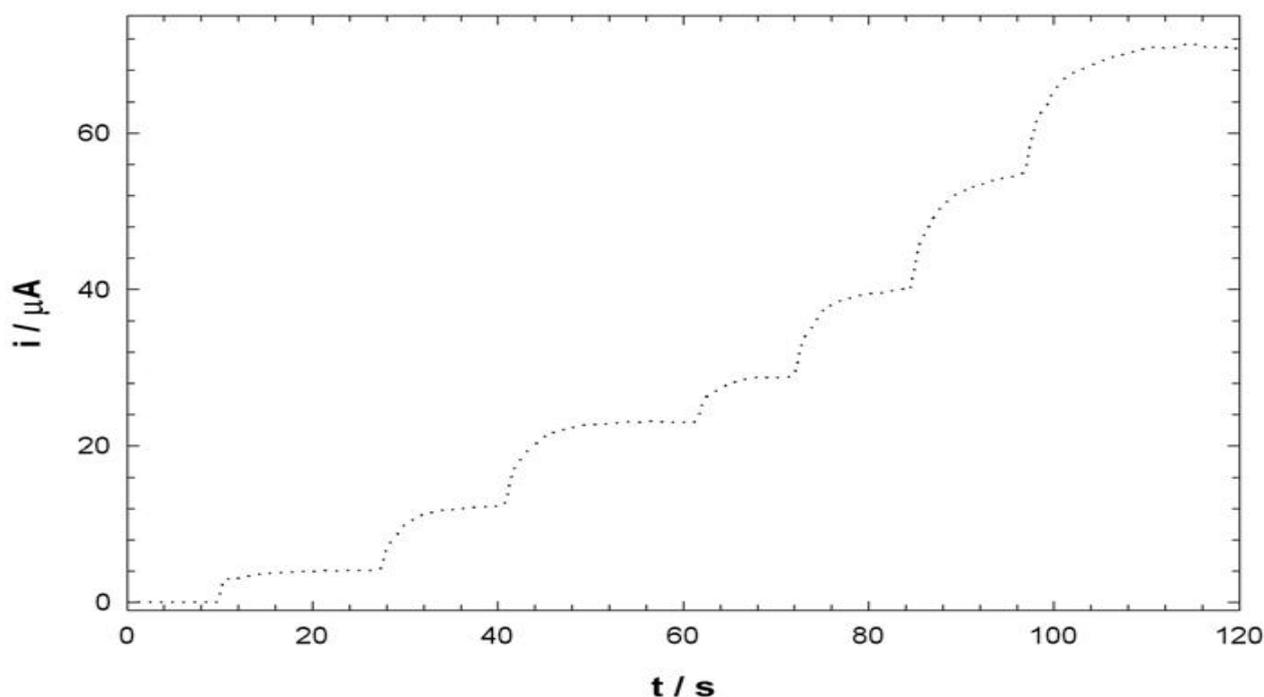
becomes independent on the scan rate justifying faster charge transport within matrix. We have also observed peak separation tending to '0' depending on the following factors; (1) decreasing to particle size of palladium below  $> 40$  nm; (2) increasing the palladium content and (3) reducing the thickness of ormosil on the electrode. Such investigations are under process.

Some other observations in support of the above finding are summarized below; (1) There is no interaction of palladium chloride with alkoxy silanes similar to trimethoxysilane where proton is replaced by other organic functionality i.e. phenyltrimethoxysilane, methyltrimethoxysilane, aminopropyltrimethoxysilane, and dimethyldimethoxysilane that support that  $-OCH_3$  is not involved in palladium chloride interaction, (2) Several other metal chloride such as Ruthenium chloride, Osmium chloride,  $FeCl_3$  and many more metal halides are not found sensitive to trimethoxysilane justifying requirement of divalent palladium site where co-ordination sites as described in reaction scheme is available.

#### *Electroanalysis of NADH*

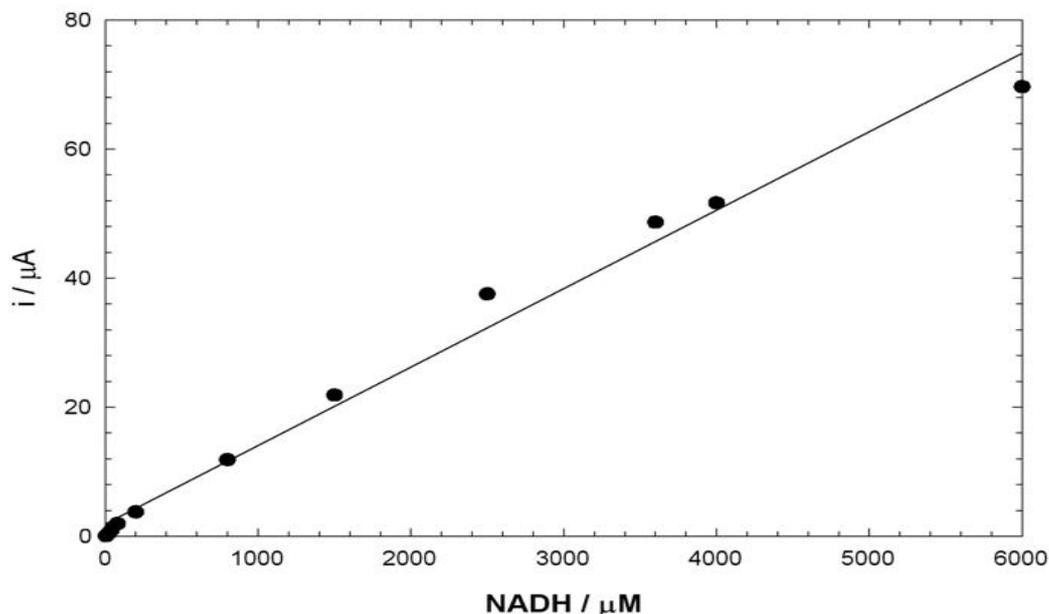
We have also examined the electrocatalytic behavior of these modified electrodes. The ferrocene monocarboxylic acid encapsulated within modified electrode without palladium and also in the presence of palladium powder, avoiding the palladium linkage to ormosil network, the electrode 1 and 2 neither electrocatalyze the electro-oxidation of NADH or other redox system nor mediate bioelectrochemically. On the other hand palladium-linked ormosil-modified electrode efficiently electrocatalyzes the regeneration of glucose oxidase, peroxidase, choline oxidase and cofactors like NADH [16]. The result on the electrocatalytic oxidation of NADH is shown in Figure 4.

Figure 4 Typical response curve of new ormosil modified electrode on the addition of increasing concentrations of NADH.



The response is very sensitive to the lowest detection limit of  $< 1 \mu\text{M}$ . Fig.5 shows the calibration curve of NADH analysis. There has been wide linearity of NADH detection  $1 \mu\text{M}$  to  $10 \text{ mM}$  (Figure 5).

**Figure 5.** Calibration curve for NADH analysis.



## Conclusions

In summary, we have developed new ORMOSIL material having palladium silicon linkages based on sol-gel processing. The attachment of palladium to silicon is identified by NMR and transmission electron microscopy. The contribution of palladium linkage on the electrochemistry of ormosil-encapsulated ferrocene has been examined and has been concluded that palladium content significantly affect redox electrochemistry of ferrocene monocarboxylic acid.

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## Experimental

### General

Trimethoxysilane, dimethyldiethoxysilane (DMDEOS), ferrocene monocarboxylic acid, palladium chloride and palladium powder were obtained from Aldrich Chemical Co.

### Preparation of ORMOSIL having palladium-silicon linkages

Initially we made a homogeneous solution of trimethoxysilane ( $30 \mu\text{L}$ ), dimethyldiethoxysilane ( $30 \mu\text{L}$ ) containing ferrocene monocarboxylic acid ( $2 \text{ mg/mL}$ ), methanol ( $70 \mu\text{L}$ ), and HCl ( $5 \mu\text{L}$ )

followed by pouring the suitable amount of the homogeneous solution onto desired substrates (glassy carbon electrode or glass slide). After 5-15 min of sol-gel processing, two approaches were adopted for carrying the interaction of palladium chloride to semi-processed ormosil's precursors; 1) the substrate was dipped overnight into aqueous solution of palladium chloride (2 mg/ml); 2) a drop of palladium chloride solution (2 mg/mL) was placed over the substrate containing semi-processed ormosil's precursors. After overnight incubation black coloured ormosil was found over the substrate. Ormosil without palladium linkage was also made following same protocol as described above however the ormosil was not treated with palladium chloride. Another type of ormosil-modified electrode was made using palladium powder together with ormosil's precursors. Homogeneous solution of trimethoxysilane (30  $\mu$ L), dimethyldiethoxysilane (30  $\mu$ L) containing ferrocene monocarboxylic acid (2 mg/ml), methanol (70  $\mu$ L), palladium powder (2 mg) and HCl (5  $\mu$ L) followed by pouring the suitable amount of the homogeneous solution onto desired substrate (glassy carbon electrode or glass slide). Gelation was allowed to occur overnight at 30°C.

#### *Electrochemical measurements.*

The electrochemical measurements were performed with a Solartron Electrochemical Interface (Solartron 1287 Electrochemical Interface). A one-compartment cell with a working volume of 4 ml and the palladium-linked ormosil-modified electrode as working electrode, a Ag/AgCl reference electrode and a platinum foil auxiliary electrode were used for the measurements. The cyclic voltammetry was studied between  $-0.2$  and  $+0.6$  V vs. Ag/AgCl. The amperometric measurements using the modified electrode were obtained at the desired operating potential vs. Ag/AgCl in the presence and absence of NADH. The experiments were performed in phosphate buffer (0.1 M, pH 7.0) at 25°C. Before each set of measurements the working solution was degassed by purging nitrogen for 15 min.

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