Electrochemical polymerization of aniline over tetracyanoquinodimethane encapsulated ormosil matrix: application in the electrocatalytic oxidation of ascorbic acid and acetylthiocholine

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Organically modified sol–gel glass (ormosil) matrix is utilized as a template for the electrochemical polymerization of aniline. The ormosil matrix is further modulated by encapsulation of: (a) tetracyanoquinodimethane (TCNQ), and (b) tetracyanoquinodimethane together with palladium (Pd). The presence of tetracyanoquinodimethane within ormosil matrix considerably influences the polymerization process of aniline and the same is significantly enhanced as compared to that of control. The presence of palladium within ormosil network further influence the polymerization process as compared to that of TCNQ only. The polyaniline obtained as PAni–TCNQ and PAni–TCNQ–Pd composites has been utilized for fabricating the modified electrodes. These modified electrodes are used to study the electrochemical sensing of ascorbic acid and acetylthiocholine. The results based on cyclic voltammetry, differential pulse voltammetry and amperometry justify that the electrode material exhibits excellent electrocatalytic activity for the oxidation of ascorbic acid and acetylthiocholine with major findings as compared to the control: (1) a negative shift to the order of ~340 mV vs. Ag/AgCl in the anodic overpotential for the electro-oxidation of ascorbic acid, (2) a significant increase in the anodic peak current for the oxidation of ascorbic acid, (3) an increase in the sensitivity of ascorbic acid analysis to the order of 7-fold for the modified electrodes, (4) acetylthiocholine undergoes direct oxidation with considerable increase in both anodic and cathodic peak currents and (5) an increase in the sensitivity of acetylthiocholine analysis to the order of 5-fold for the modified electrodes.

1. Introduction

Polyaniline (PAni) has been attracting significant interest due to its high conductivity, ease of preparation, good environmental stability, and large variety of applications in electrorheological fluids, sensors, electrostatic discharge, anticorrosion coatings and electrocatalysis. Accordingly, several routes of aniline polymerization in both aqueous and non-aqueous solvents with varying media compositions are available. From the past few years, efforts have been made to combine the physical strength, chemical stability, and optical properties of certain sol–gels with the electrical properties of conducting polymers for a wide range of electrochemical applications. Additionally, encapsulation of electron transfer mediators having reversible redox electrochemistry within ormosil films might facilitate the charge-transfer process required for probing chemical/biochemical interactions taking place within or outside the nano-structured domains of the solid-state and may prove as a potential template for the electropolymerization of aniline. Earlier studies on the formation of PAni together with sol–gel glasses have been reported by Cox et al. and others following three different approaches. In the first one, chemically prepared polymers were dissolved and mixed with a sol that was subsequently processed into a solid material. Second, the silica precursor was organically modified with a monomer, subsequent to the gelation, then polymerization was performed electrochemically. The third general method was to form a thin film of silica on an indium tin oxide electrode, immerse the film in a solution that contains the monomer, and perform the polymerization electrochemically. The third method represents the template synthesis of PAni and has been performed to yield interpenetrating ordered polymer–silica composites along with electron transfer relay and a metal catalyst. In template synthesis, reactions are carried out within nanometric void spaces of the ormosil matrix and, thus, provide the control on the amount of polymer formed and also the morphology of the synthesized polymers could be manipulated by changing the pore size of the template. The polyaniline synthesized under these conditions introduces electrocatalysis when used in electrochemical sensor's design. Further, many amperometric electrochemical sensors incorporate the participation of a redox mediator for availing selective and sensitive detection of targeted analytes. Accordingly, the redox-mediated synthesis of PAni...
involving the participation of electron-transfer relays may lead to promising materials for electrochemical sensors development. Additionally, if the redox couple of the mediator has affinity toward the oxidation products of aniline, the resulting material may add facilitated electrocatalysis during the sensing process. Such an investigation has not been studied in sol-gel glasses manipulated with an electron transfer mediator together with a metal catalyst, which has been undertaken in this contribution. As an example the role of such material has been examined on the determination of two biologically important analytes like ascorbic acid and acetylthiocholine.

The determination of ascorbic acid (AA) in biological fluids using electrochemical sensors is of wide interest, but is hampered by the high overpotentials seen for ascorbic acid oxidation at inert electrodes. Modified electrodes containing electrogenerated polymers provide a promising method to lower the overpotential. At the same time determination of acetylthiocholine (ATC) is of great interest since one of the products of acetylcholinesterase (AChE) mediated hydrolysis of acetylthiocholine is choline and its detection can be used to assess the activity of AChE, a biomarker of the effect of pesticides (organophosphates (OPs) and carbamates) which inhibit cholinesterases. Analysis of acetylthiocholine is, therefore, of great importance, particularly in the development of electrochemical sensors for detection of environmental pollutants such as OPs and carbamates.

In the present article, we report the electropolymerization of aniline within an organically modified sol-gel glass (ormosil) matrix derived through a sol–gel process. It has been observed that the rate of electropolymerization was very slow within such a matrix with poor electroactivity of the resulting polymer. Accordingly, it was planned to incorporate redox mediator tetracyanoquinodimethane (TCNQ) within the ormosil matrix to enhance the rate charge transfer process during electropolymerization. The reasons for such prediction originate from the fact that TCNQ is a strong acceptor ligand and has the capability to coordinate with metal ions and polymers both as neutral molecules and radical anions thus forming a stable charge transfer complex. Additionally, palladium, was also introduced within the solid-state network of ormosils to investigate the role of the electrocatalyst on the polymerization of aniline and finally utilizes the electrocatalytic properties of these materials in the electrochemical detection of ascorbic acid and acetylthiocholine.

2. Experimental

2.1. Materials

Aniline, 3-aminopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, tetracyanoquinodimethane (TCNQ), palladium chloride, graphite powder (particle size 1–2 μm) and Nujol oil (density 0.838) were obtained from Aldrich Chemical Co. 2-(3,4-Epoxycyclohexyl)ethyltrimethoxysilane was obtained from Fluka. Ascorbic acid, dopamine and uric acid were obtained from SRL Chemical India and acetylthiocholine was purchased from Sigma. All other chemicals employed were of analytical grade. Aniline was distilled under vacuum prior to use. The aqueous solutions of ascorbic acid and acetylthiocholine were freshly prepared in triply-distilled water before each experiment. Experiments were performed at room temperature.

2.2. Preparation of mediator encapsulated ormosil films

A typical ormosil film was prepared by adding alkoxysilane precursors, TCNQ, hydrochloric acid and distilled water in the composition shown in Table 1. The mixture was vigorously stirred for 5 min. An aliquot of 10 μl of the suspension was layered on the indium tin oxide (ITO, with surface resistance ~30 Ω) electrodes, and the electrodes were air-dried for 8–10 h to ensure complete hydrolysis and gelation resulting in the ormosil film.

2.3. Electrochemical synthesis of polyaniline over ormosil films

Poylanine was synthesized electrochemically using a single compartment cell equipped with three electrodes, viz. ITO plate as working electrode, Ag/AgCl (Orion, Beverly, MA, USA) as reference electrode and Pt plate as the counter electrode. All the electrochemical work was done with an Electrochemical Workstation Model 660B, CH Instruments Inc., TX, USA. Polyaniline was deposited potentiodynamically over ormosil modified ITO electrodes from 1 M HCl with typical concentration of 0.1 M aniline by cycling the potential between ~0.2 and 1.0 V versus Ag/AgCl. Electrochemical characterization of PAni films deposited over ITO electrodes was performed through cyclic voltammetry by cycling the potential between ~0.2 and 1.0 V versus Ag/AgCl in 1 M HCl at various scan rates, viz. 0.01, 0.02, 0.05, 0.10 and 0.20 V s⁻¹. SEM studies of PAni films were performed using an FEI Quanta 200F Scanning electron microscope.

2.4. Preparation of modified graphite paste electrodes

Polyaniline synthesized within TCNQ and TCNQ–Pd encapsulated ormosil matrix was extracted from ITO electrodes and suspended in tetrahydrofuran (5 mg in 1 ml THF) followed by sonication for 15 min. Then the resulting solution was then kept in an oven at 60 °C for 1 h. After complete evaporation of THF the dried material was used to modify graphite paste electrodes. The electrode body used for the construction of modified electrode was obtained from Bioanalytical Systems (West Lafayette, IN; (MF 2010)). The well was filled with active paste of composition given in Table 2 (paste-1, paste-2 and paste-3). The desired amount of PAni–TCNQ and PAni–TCNQ–Pd composites was thoroughly mixed with graphite powder (particle size 1–2 μm) in a blender followed by addition of Nujol oil. After

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Table 1: Composition of different ormosil-modified electrodes*

<table>
<thead>
<tr>
<th>System</th>
<th>A*/µl</th>
<th>B*/µl</th>
<th>C*/µl</th>
<th>D*/µl</th>
<th>E*/µl</th>
<th>F*/µl</th>
<th>G*/µl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank sol–gel</td>
<td>70</td>
<td>10</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>5</td>
<td>300</td>
</tr>
<tr>
<td>TCNQ</td>
<td>—</td>
<td>10</td>
<td>70</td>
<td>—</td>
<td>—</td>
<td>5</td>
<td>300</td>
</tr>
<tr>
<td>TCNQ–Pd</td>
<td>—</td>
<td>10</td>
<td>70</td>
<td>10</td>
<td>10</td>
<td>5</td>
<td>280</td>
</tr>
</tbody>
</table>

* A* = 3-Aminopropyltrimethoxysilane, B* = 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, C* = TCNQ in 3-aminopropyltrimethoxysilane (45 mM), D* = 3-glycidoxypropyltrimethoxysilane, E* = palladium chloride (3 mg ml⁻¹), F* = 0.1 M HCl, G* = distilled water.
homogenization the mixture was stored in a stoppered glass vial at room temperature when not in use. The paste surface was manually smoothed on a clean butter paper.

3. Results and discussion

3.1. Role of nano-structured network during electropolymerization of aniline

The objective of the present work concerns the study of the role of the nano-structured network during the electropolymerization of aniline. At first, the electropolymerization was performed on the bare ITO surface and over a sol–gel modified ITO electrode in the absence of redox mediator under similar experimental conditions. The results of polymerization are shown in Fig. 1(a) and (b). The number of cycles required for polymerization of aniline over bare ITO is very less as compared to that of ormosil modified ITO. However, the electrochemical behavior of PANi over ormosil modified electrode was considerably better than the bare ITO and that reported earlier on sol–gel modified electrodes. This is due to the generation of a patterned nano-structured network resulting in controlled growth of PANi. This finding suggested the requirement for further manipulation of the ormosil network to understand the role of the redox mediator during the electropolymerization of aniline.

3.2. Role of redox-mediator and electrocatalyst in the electropolymerization of aniline

Pолyaniline was grown within ormosil matrix encapsulating TCNQ to understand the interaction between redox mediator and different chemical states of PANi. The purpose of incorporating TCNQ and palladium within the sol–gel is to enhance the rate of polymerization of aniline within ormosil matrix and to study the effect of electrocatalysis on polymerization. The glycidyl group of 3-glycidoxypropyltrimethoxysilane is highly reactive. When an aqueous solution of palladium chloride, which acts as a Lewis acid, is added, it opens the epoxide ring of the glycidyl moieties and in turn palladium is reduced. The reduced palladium was found coordinated with carbon atoms of glycidyl residues which were initially bonded to the epoxide linkages. This reduced palladium acts as an electrocatalyst in the process of the electropolymerization of aniline. To obtain the polymer with good redox behavior, the number of cycles required in the case of blank sol–gel is about 100 and for the same in the case of TCNQ and TCNQ–Pd are about 30, which justifies the role of TCNQ and TCNQ–Pd during the polymerization process. The results recorded on electropolymerization of aniline for 30 cycles in the absence and in the presence of palladium within ormosil network are shown in Fig. 2(a) and (b). The polymerization of aniline in the presence of palladium shows higher anodic and cathodic peak currents in the same number of cycles as compared to that in the absence of palladium. This difference is possibly due to the hydrophobicity and anionic behavior of TCNQ that might lead to the formation of a charge transfer complex with palladium. This leads to the following observations: (i) the anodic and cathodic currents are increased after the addition of palladium within the ormosil network, and (ii) the redox electrochemistry of PANi after adding palladium content is much better as compared to that in the absence of palladium within the ormosil network.

Four redox couples were observed in the TCNQ–Pd system whereas in the case of the TCNQ system three redox couples were observed. The 2nd and 3rd redox couples merged together in single broad peak in the case of TCNQ. The low potential redox peak at 0.2 V can be attributed to a quasi-reversible reaction of leucoemeraldine oxidation to protoemeraldine, and the 2nd and 3rd redox peaks are attributed to oxidation of the latter to emeraldine and subsequent oxidation to nigraniline respectively.

Table 2 Composition of graphite paste electrodes

<table>
<thead>
<tr>
<th>Systems</th>
<th>PANi–TCNQ/TCNQ–Pd (% w/w)</th>
<th>Graphite powder (% w/w)</th>
<th>Mineral oil (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paste-1</td>
<td>—</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>Paste-2</td>
<td>1</td>
<td>69</td>
<td>30</td>
</tr>
<tr>
<td>Paste-3</td>
<td>1</td>
<td>69</td>
<td>30</td>
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Fig. 1 Potentiodynamic electropolymerization of 0.1 M aniline in 1.0 M HCl at the scan rate of 0.05 V s⁻¹ over ITO modified with (a) bare ITO; (b) blank sol–gel.

Fig. 2 Potentiodynamic electropolymerization of 0.1 M aniline in 1.0 M HCl at the scan rate of 0.05 V s⁻¹ over ITO modified with (a) TCNQ; (b) TCNQ–Pd.
These two peaks suggest the formation of a benzoquinone/hydroquinone couple in the acid electrolyte.41 The highest oxidation potential peak at 0.8 V is attributed to oxidation of nigraniline to pernigraniline and corresponding reduction of the latter at 0.7 V.22 All redox peaks were well resolved and defined in both systems, and the film formation was found to be best in the TCNQ–Pd system.

The charge accumulation results in the polymerization of aniline in TCNQ and TCNQ–Pd systems are shown in Fig. 3. The accumulation of charge during polymerization provides valuable information about the level of doping within the polymer films and increase in peak current during the growth of the polymer. It was observed that the accumulation of charge increases rapidly in the TCNQ–Pd system suggesting a high level of doping which subsequently increases the anodic and cathodic peak currents of PANi. In the case of the TCNQ system the accumulation of charge is less than in the previous case, suggesting a low level of doping and low peak current values. Being a strong π-acceptor ligand TCNQ has the capability to coordinate to metal ions and polymers both as neutral molecules and radical anions39,40 and thus forming a stable charge transfer complex. This special property of TCNQ might be responsible for all the anomaly observed during the electropolymerization of PANi over ormosil matrix.

### 3.3. Electrochemistry of PANi grown within ormosil matrix

Cyclic voltammetry of PANi prepared within the nano-structured matrix was performed in monomer free solution to investigate the difference in the electroactivity of PANi prepared in TCNQ and TCNQ–Pd systems. Voltammograms of PANi synthesized within ormosil matrices in the absence and in presence of palladium at the scan rates of 0.01 V s\(^{-1}\) and 0.20 V s\(^{-1}\) are shown in Fig. 4. It was observed that all the oxidation states of PANi were clearly visible at the lower scan rate in the case of the TCNQ–Pd system, while in the case of TCNQ alone, 2nd and 3rd redox states merged together. This may be attributed to the formation of a stable charge transfer complex between TCNQ and palladium that provides stability to all the oxidation states of PANi. Further, the presence of the TCNQ–Pd complex provided stability to PANi even at higher scan rates, whereas the redox behavior of PANi formed in the TCNQ system deteriorated rapidly with increase in scan rate. At higher scan rates, the PANi prepared by the TCNQ–Pd system showed sharp peaks without any shift in potential while in the case of PANi prepared by the TCNQ system this showed broad peaks with slight shift in potential values. This difference may be attributed to the higher level of doping in the former case due to the formation of a stable charge-transfer complex. It was found that the PANi formed within the TCNQ–Pd system shows excellent electroactivity as compared to that of PANi prepared by the TCNQ system.

The stability of modified ITO interfaces was examined in water, phosphate buffer (100 mM pH 7.0) and ethanol. The samples were immersed in the respective solution for more than two hours at room temperature and then dried in air for a few minutes. After these treatments, cyclic voltammetry was recorded in 1.0 M HCl at scan rates of 0.01 V s\(^{-1}\) and 0.2 V s\(^{-1}\). The results are similar to those presented in Fig. 4. Thus, suggesting the good chemical and mechanical stability of PANi film over ITO electrodes.

### 3.4. Morphology of PANi synthesized through different ormosil matrices

The electrochemical polymerization provides the possibility of controlling the thickness and homogeneity of the polymers. Fig. 5 shows the typical SEM images of PANi grown electrochemically within silica matrix encapsulating TCNQ and TCNQ–Pd. The images clearly depict that the nanostructure domains present in the matrix of ormosil acted as a template for the synthesis of polymer.30 In both the cases, a uniform inter-connected fibrillar network of PANi was seen but in the case of TCNQ–Pd, a more dense pattern and an ordered geometry of network of PANi was formed, again confirming the interaction of TCNQ with Pd leading to better growth of PANi.

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**Fig. 3** Plot between applied potential and charge accumulated during potentiodynamic electropolymerization of PANi over ITO modified with (a) TCNQ; (b) TCNQ–Pd.

**Fig. 4** Cyclic voltammogram of PANi in 1.0 M HCl over ITO modified with TCNQ (1) and TCNQ–Pd (2) at scan rates (a) 0.01 V s\(^{-1}\); (b) 0.2 V s\(^{-1}\).
3.5. Electrocatalytic oxidation of ascorbic acid over polymer modified electrodes

The oxidation of ascorbic acid (AA) was performed in a neutral condition, and herein phosphate buffer (100 mM, pH 7.0) was used as the electrolyte solution. The cyclic voltammograms for the oxidation of ascorbic acid over bare and modified electrodes are shown in Fig. 6. As can be seen, the irreversible oxidation of AA occurs at 0.34 V at the bare graphite paste electrode (Fig. 6a); while in the case of modified electrodes the oxidation starts before 0 V (Fig. 6b and 6c) which is almost 340 mV less negative than the oxidation of AA at the bare electrode. On the other hand, a well-defined pair of redox peaks of TCNQ in the composite material indicates that enhanced electron transfer occurs at the modified electrodes. Furthermore, the oxidation current of AA is greatly enhanced at the modified electrodes. The great negative shift in the anodic overpotential and the enhanced peak current for electro-oxidation of AA indicates the strong electrocatalytic function of modified electrodes as compared to that of bare electrodes; this might be attributed to the interaction of PAni chains with TCNQ and palladium which leads to the formation of electrocatalytic materials.

Fig. 7 (a), (b) and (c) represent the DPVs of different concentrations of AA (0.5 mM to 5 mM) at paste-1, paste-2 and paste-3 modified electrodes respectively in phosphate buffer solution. As it is very much clear from the results that in the case of modified electrodes one additional peak other than the mediator’s peak is also present which is due to the oxidation of PAni chains during the potential sweep from −0.2 to 1 V. The appearance of the peak suggests that the PAni synthesized through the sol–gel route exhibits some electroactivity in neutral medium. The oxidation of AA over the bare electrode occurs at 0.3 V with a peak current of 25 μA at the highest concentration of AA while in the case of the PAni–TCNQ modified electrode the oxidation takes place at around 0 V with a similar peak current to that of the bare electrode. However, in the case of PAni–TCNQ–Pd modified electrode the values of both oxidation potential (−0 V) and peak current (31 μA) for the oxidation of AA improve as compared to the other two systems. The evidently reduced overpotential over modified electrodes may be attributed to the improved electron transfer process due to the presence of two catalytic materials, i.e., PAni and TCNQ together in the composite. On the other hand, the increase in current value justifies the role of palladium in the composite material towards the oxidation of AA. It was also observed that with an increase in AA concentration (represented by the double headed arrow 2) the peak currents for all the three systems were also increased.

Amperometric determination of AA was obtained by successively adding AA (0.05 mM to 10 mM) to the continuously stirred solution with a working potential of 0.005 V. Fig. 8 shows the typical amperometric response curve for the three systems, where the expanded portion in the insets represents the response time which is calculated by taking the 95% value of the current when the response reaches a steady state. The lower value of the response time justifies the role of palladium in the composite material towards the oxidation of AA. It was also observed that with an increase in AA concentration (represented by the double headed arrow 2) the peak currents for all the three systems were also increased.

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of response currents on the concentration of AA was linear between 50 μM and 5mM (Fig. 9), indicating that the modified electrode can be applied to the quantitative analysis of AA. The sensitivities for paste-1, paste-2 and paste-3 modified electrodes are 0.11 μA / mM, 0.49 μA / mM and 0.83 μA / mM respectively.

The selectivity of the composite modified electrodes for the detection of AA was also evaluated. Fig. 10 shows the amperometric response of the paste-3 electrode to electroactive dopamine (DA) and uric acid (UA). The concentration of DA and UA was kept constant, i.e., 1 mM each followed by additions of varying concentrations (1, 2 and 5 mM) of AA in the same medium (phosphate buffer, 100 mM, pH 7.0). As can be seen in Fig. 10, the amperometric response of DA and UA was negligible at the applied potential of 0.005 V as compared to that of AA. The detectable response on the electro-oxidation of AA, DA and UA over bare electrodes is observed at a potential greater than 0.2 V. The sensitive detection of AA at 0.005 V vs. Ag/AgCl eliminating the contribution of interferences justifies the potential usefulness of the present system in AA analysis.

It is now important to justify the significance of the present electrode design to those with earlier reported systems on AA detection. The electrocatalytic oxidation of ascorbic acid recorded earlier at the surface of other chemically modified electrodes is given in Table 3. Some of the authors (Table 3) have utilized an acidic medium for AA sensing over a PAni modified electrode which is not compatible with the biological systems. The data shown in Table 3 on the increased value of peak shift for AA detection within a biological pH range with comparable sensitivity justify the novelty of the present material.

3.6. Electrochemistry of acetylthiocholine over polymer modified electrodes

Acetylthiocholine (ATC) is electrochemically hydrolyzed into acetic acid and thiocholine amongst which thiocholine is electroactive. Direct hydrolysis of ATC over a graphite paste electrode was previously studied in detail. The cyclic voltammograms of different paste electrodes in the presence of 2 mM of ATC at the scan rate of 2 mV s⁻¹ in phosphate buffer (100 mM, pH = 7.0) are shown in Fig. 11. The corresponding anodic and cathodic peak currents, when the potential is in between −0.2 and 0.6 V versus Ag/AgCl, are found to be 14 μA /−9 μA, 25 μA /−12 μA and 37 μA /18 μA for paste-1, paste-2 and paste-3 modified electrodes respectively. The results show that both oxidation and reduction currents are greater in paste-2 and paste-3 as compares to paste-1, suggesting fast kinetics of spontaneous hydrolysis of ATC in the presence of electrocatalytic materials. In other words the process of hydrolysis is facilitated in the presence of PAni–TCNQ and PAni–TCNQ–Pd as compared to the bare graphite paste electrode.

Amperometric determination of ATC was obtained by addition of different concentrations (0.05 mM to 10 mM) of ATC in the phosphate buffer (100 mM, pH = 7.0) at a working potential of 0.4 V. Fig. 12 shows the typical amperometric response curves for the three systems. It is very much clear from the figure that...
the response was highest in the case of paste-3 followed by paste-2 and paste-1, again suggesting the excellent electrocatalytic behavior of the composite material towards the hydrolysis of ATC. The calibration curves for ATC detection by amperometry at graphite paste electrodes modified with paste-1, paste-2 and paste-3 were constructed using average currents recorded at three individual electrodes for each concentration point. Fig. 13 shows the calibration curves for ATC for paste-1 (curve a), for paste-2 (curve b) and for paste-3 (curve c). The sensitivities towards ATC were found to be 0.14 m\(A/C_6^3\)n\(M/C_0^1\) for paste-1 (curve a), 0.34 m\(A/C_6^6\)n\(M/C_0^1\) for paste-2 (curve b) and 0.67 m\(A/C_6^8\)n\(A_mM/C_0^1\) for paste-3 (curve c) modified electrodes. The inset of Fig. 13 shows the linear range for ATC detection from 50 \(mM\) to 3 \(mM\). A comparison on the performance of the present sensor with earlier reported analogous systems has been given in Table 4. Since acetylthiocholine is enzymatically hydrolyzed into electroactive material thiocholine accordingly, many of the authors have studied the acetylcholinesterase (AChE)-mediated detection of ATC. The non-enzymatic hydrolysis of ATC conducted in the present investigation at a relatively lower operating potential

Table 3 Comparison on the performances of some modified electrodes used in the electroanalysis of ascorbic acid\(^{a,b}\)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Modifier</th>
<th>pH</th>
<th>(E_{p_b}/mV)</th>
<th>(E_{p_m}/mV)</th>
<th>Shift in peak potential/mV</th>
<th>Scan rate/(mV\ s^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt electrode</td>
<td>PA ni–CSA</td>
<td>7.0</td>
<td>630</td>
<td>340</td>
<td>290</td>
<td>50</td>
<td>42</td>
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<tr>
<td>Pt electrode</td>
<td>PA ni–polysulphone</td>
<td>0.1 M HClO(_4)</td>
<td>—</td>
<td>210</td>
<td>—</td>
<td>—</td>
<td>36</td>
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<tr>
<td>GC electrode</td>
<td>PA ni–Pd</td>
<td>0.1 M HClO(_4)</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<td>43</td>
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<td>(phosphate buffer)</td>
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<tr>
<td>CP electrode</td>
<td>PA ni–TCNQ and PA ni–TCNQ–Pd</td>
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<td>(phosphate buffer)</td>
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<td>~0</td>
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</table>

\(^{a}\) \(E_{p_b}\) = oxidation potential of AA over bare electrode. \(^{b}\) \(E_{p_m}\) = oxidation potential of AA over modified electrode.

Fig. 11 Cyclic voltammograms of graphite paste electrodes modified with (a) (1) paste-1, (b) (1) paste-2 and (c) (1) paste-3; (2) + 2 mM ATC in 100 mM phosphate buffer (pH 7.0) at the scan rate of 0.002 V s\(^{-1}\).

Fig. 12 Typical amperometric response curves on the addition of varying concentrations of ATC over graphite paste electrode made from (a) paste-1, (b) paste-2 and (c) paste-3 at 0.4 V vs. Ag/AgCl at 25°C in 100 mM phosphate buffer (pH 7.0).

Fig. 13 Calibration curve for the analysis of ATC over graphite paste modified electrode with (a) paste-1, (b) paste-2 and (c) paste-3. The inset shows the linear relationship between anodic current and concentration of ATC.
with comparable sensitivity justifies the advantage of the present system over earlier reports (Table 4).

4. Conclusions

Electropolymerization of aniline within a porous network of organically modified sol–gel glass (ormosil) matrix is reported. A well known redox mediator tetracyanoquinodimethane (TCNQ) and an electrocatalyst palladium were encapsulated within an ormosil film to investigate their role in the rate of polymerization and the electroactivity of PANi films formed over these modified electrodes. The resulting materials were characterized using cyclic voltammetry and SEM. Further, the application of these materials was investigated in the electrocatalytic oxidation of ascorbic acid and acetylthiocholine. Thus, it was concluded that the presence of redox mediator drastically enhances the rate of polymerization of PANi within ormosil films. Palladium acts as an electrocatalyst during polymerization and increases the anodic and cathodic currents and simultaneously provides excellent redox behavior to PANi films. The resulting composite materials of PANi with TCNQ and TCNQ–Pd show excellent electrocatalytic behavior towards the oxidation of ascorbic acid and acetylthiocholine.

Acknowledgements

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References

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Table 4 Comparison on the performance of some modified electrodes used in the electrocatalysis of acetyltiocholine

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Modifier</th>
<th>pH</th>
<th>Operating potential/mV</th>
<th>Stability</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au electrode</td>
<td>PANi with AChE</td>
<td>7.2 (phosphate buffer)</td>
<td>+400</td>
<td>Poor</td>
<td>49</td>
</tr>
<tr>
<td>CP electrode</td>
<td>AChE encapsulated ormosil</td>
<td>6 and 8 (Tris-HCl buffer)</td>
<td>+350</td>
<td>Good</td>
<td>18</td>
</tr>
<tr>
<td>Au electrode</td>
<td>AChE immobilized over AuNPs</td>
<td>8 (phosphate buffer)</td>
<td>+680</td>
<td>Poor</td>
<td>50</td>
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<tr>
<td>GC electrode</td>
<td>AChE covalently bonded with MWNT cross-linked chitosan composite</td>
<td>7 (phosphate buffer)</td>
<td>+800</td>
<td>Good</td>
<td>51</td>
</tr>
<tr>
<td>CP electrode</td>
<td>PANi–TCNQ and PANi–TCNQ–Pd (without enzyme)</td>
<td>7 (phosphate buffer)</td>
<td>+400</td>
<td>Good</td>
<td>Present work</td>
</tr>
</tbody>
</table>