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## Electrochemical rectification at electrode surface modified with poly (acrylic acid) and decane thiol

Received: 16 November 2005 / Revised: 19 December 2005 / Accepted: 4 January 2006 / Published online: 29 March 2006  
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**Abstract** Gold surface modified with a two-component system consisting of poly (acrylic acid) (PAA) by electropolymerizing acrylic acid (AA) and decane thiol (DT), further functionalized with ferrocene monocarboxylic acid (FMC) through covalent linkage, was used to demonstrate mediated electron transfer resulting in a unidirectional flow of current. The electrode surface was modified using two different configurations. In Configuration 1 (Config. 1), electrode surface modified with FMC showed rectification behavior when contacted with a solution containing methylene blue (MB). In Configuration 2, redox-active bilayer was constructed using polyvinyl pyrrolidone (PVP) and hexaamineruthenium (II) chloride  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  showed rectification characteristics. The continuous rectification property of the redox-active bilayer is achieved by releasing the trapped  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  in the outer layer using a reductant (ascorbic acid). Spectroelectrochemical measurements were made to study the reduction property of the ascorbic acid. Atomic force microscopic images and impedance measurements were also made on the modified electrode surfaces to explore the compactness of the first layer (PAA and PAA/DT).

**Keywords** Two-component system · Electropolymerization · Redox-active bilayer · Mediated electron transfer · Continuous rectification

### Introduction

In recent years, the field of molecular electronics [1] has attracted many scientists. Currently, a lot of efforts have been put forward towards the miniaturization of electronic devices [2] such as wires [3, 4], gates [5, 6], rectifiers [7, 8], etc. to nanoscale dimension. The rectifier is a simple electronic device, which allows electron flow in one direction. Aviram and Ratner [9], pioneers of rectifiers, had constructed rectifying interface consisting of electron donor and acceptor molecules connected by alkyl bridge. Martin and Sambles [10] used several monolayers of zwitterionic molecules to construct rectifiers and these experiments were further extended by Metzger et al. [11].

Murray et al. [12, 13] had first constructed electrochemical rectifier by modifying electrode surface with a redox-active bilayer of polymer derivatives of Ru and Os complexes. The electron transfer from the outer layer redox species (in the bilayer assembly) were mediated through first layer redox species. Rectifiers using biomolecules [14, 15], dendrimers [16], and pH dependent rectifiers [17, 18] have also been reported in the recent past.

To construct an electrochemical rectifying interface, the electrode surface should be modified with redox-active thin layers or thin films, which exhibit excellent blocking properties [19, 20]. Hence, with the evolution of self-assembled monolayers (SAMs) of thiol, which forms an organized and compact monolayer [21, 22] on the noble metals, rectifiers using the thiol monolayers [23, 24] have been widely reported. We have already demonstrated mediated electron transfer studies through electrode surface modified with functionalized self-assembled monolayer of thiol [25].

Efficiency of rectifying interfaces constructed using redox-active polymer layers depends on the thickness of the polymer layer constructed. Pinholes or pits present in the polymer layer and very thin polymer layer are not compact. Hence, the pinholes limit the rectifying characteristics of the redox-active layers. Increasing the thickness of the polymer layer may overcome the above problems. However, the speed of the device is decreased.

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Hence, in this work, we have attempted to construct rectifying interface using polymer layer of less thickness, and it was made perfect and compact by the adsorption of decane thiol (DT) on pinholes or pits. This two-component system consisting of poly (acrylic acid) (PAA) and DT serves as a perfect blocking layer preventing the direct electron transfer from the redox species present in the solution or in the bilayer.

Although rectifiers have been constructed using thiol or redox-active polymer layers [19, 26] individually, fabrication of rectifying interface using the thiol and redox-active polymeric mixed layers has not been reported, so far, to the best of our knowledge. Recently, we have carried out charge trapping studies through electrode surface modified with mixed self-assembled monolayer of thiocetic acid and thiophenol as the first layer and redox-active polymer layer as the second layer [27].

In this work, we have tried to modify the electrode surface with poly (acrylic acid) by electropolymerization of acrylic acid, and it was made compact by dipping in decane thiol solution. We have also investigated the following with a view to current interest and stimulate further studies:

- (1) the role of SAM of thiol in the electropolymerization of acrylic acid in the presence and absence of thiol,
- (2) the time or number of cycles of polymerization was also optimized and
- (3) the above layer was functionalized with ferrocene monocarboxylic acid so that the modifying surface performs the function of a rectifier when it comes in contact with the second redox species kept either in solution or in the redox- active bilayer assembly.

Releasing the trapped outer redox species in the second layer ensures the efficiency of the redox-active bilayer. Abruna et al. [19] have discussed several methods in releasing the trapped species; one of them is using strong reductants. In this work, ascorbic acid, a strong reductant, has been used to release the trapped  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  species.

## Experimental

### Materials and methods

Decanethiol(DT),*N,N*,dicylohexylcarbodiimide (DCC), hexaamineruthenium(II)chloride, poly (vinyl pyrrolidone) (PVP) and ferrocene monocarboxylic acid (FMC) were purchased from Sigma-Aldrich. Sulfuric acid and sodium sulfate were obtained from Rankem, India. Methylene blue, sodium hydroxide and zinc chloride were obtained from SRL, India. FMC was recrystallized from 95% ethanol. Potassium ferrocyanide and potassium ferricyanide were obtained from BDH. All other chemicals were used as such without further purification.

A gold disc of area  $0.0314 \text{ cm}^2$ , embedded in an epoxy resin coating, served as the working electrode. A Pt foil and an Hg/Hg<sub>2</sub>SO<sub>4</sub> were used as the counter and reference electrodes, respectively. Potential values mentioned in this study are against this reference electrode. Cyclic voltam-

metric (CV) experiments were carried out using an electrochemical analyzer, Model 620B, CH instruments, USA. Pico SPM Atomic Force Microscopy (Molecular Imaging, USA) operated in contact mode. Cantilever material: 1–10 Ohm, phosphorous n-doped Si with radius of curvature of the probe tip being  $\sim 10 \text{ nm}$ .

Before modifying the electrode surface, it was thoroughly polished with emery sheets of grade (4/0) and (5/0) using alumina slurry. The polished electrode was cleaned and then cycled in 0.5 M sulfuric acid solution for 5 min in the potential range  $-0.2$  to  $+1.2 \text{ V}$  at  $50 \text{ mV/s}$  scan rate [28]. The cleanliness of the electrode surface was ensured by obtaining a reproducible and reversible cyclic voltammogram with  $\Delta E_p = 60 \text{ mV}$  in 0.5 M sodium sulphate solution containing 10 mM potassium ferrocyanide. Electrodes standardized as above were used for modification and subsequent voltammetric experiments.

### Modification of the electrode surface

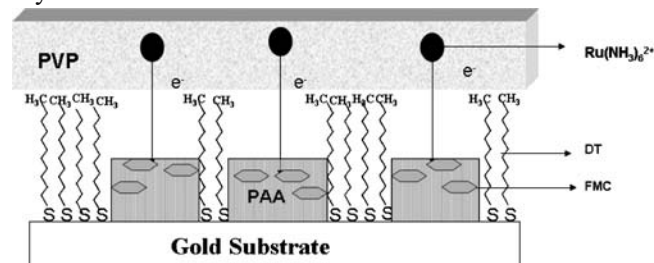
The electrode surface was modified by two different configurations. The difference between the two configurations is as follows: In Config. 1, the second redox species is kept in the solution, whereas, in Config. 2, the second redox species is immobilized on a polymer layer. In both the configurations, the first layer is a mixed layer comprising of polymer and a self-assembled monolayer of DT, further functionalized with redox species.

#### Configuration 1

The electrode surface was modified with poly (acrylic acid) by electropolymerizing acrylic acid as reported by Katz et al. [29] for a) 15 min and b) 30 min. The polymeric layer of PAA was made redox-active by dipping the electrode first in 0.2 mM solution of DCC followed by dipping the solution in 20 mM ethanolic solution of FMC. After this treatment, the electrode was rinsed with ethanol and dried in N<sub>2</sub> atmosphere, followed by dipping in DT solution for 20 min.

#### Configuration 2

For fabricating a bilayer redox-active assembly, the first layer was modified as described above, and a second redox-active layer was constructed by spreading a few drops of 3% PVP + hexaamineruthenium (II) chloride and allowed to dry.



In Config. 1, FMC is covalently linked to  $-\text{COOH}$  group of PAA. In the direct oxidation of second redox species, methylene blue (MB) kept in the solution is prohibited and hence, undergoes oxidation through mediated fashion. However, in Config. 2, the electron transfer from  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  takes place through FMC in the first layer, exhibiting the property of unidirectional flow of current.

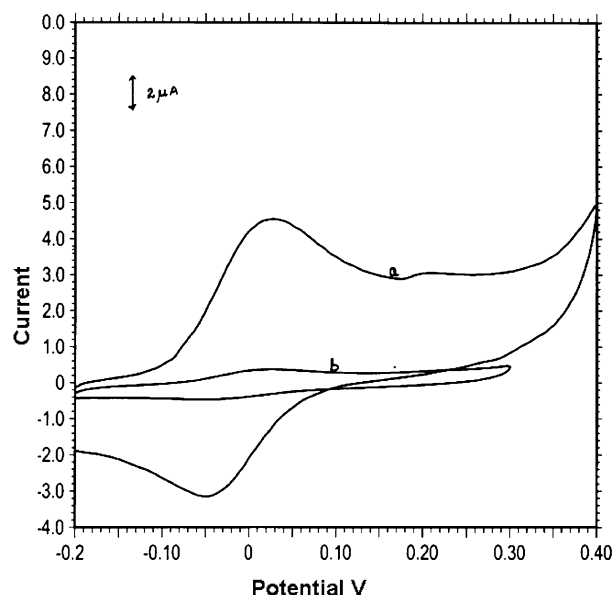
### Characterization of the electrode surface

CV experiments were carried out with the electrodes modified with PAA and PAA/DT to investigate the blocking properties or the compactness of the modified interface in the presence of MB in solution Scheme 1.

## Results and discussion

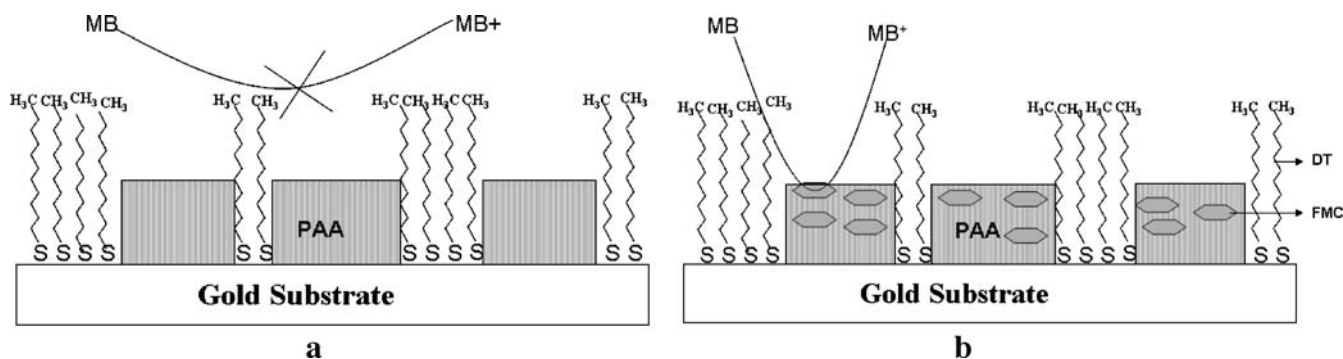
### Characterization of the first redox-active layer

Figure 1a and b show the voltammograms of the electrode surface modified with PAA by electropolymerization of AA for 15 min (a) and 30 min (b), respectively, and further functionalized with FMC as described above. Voltammograms representing the electropolymerization of AA are not shown here. Figure 1a is a cyclic voltammetric response of gold electrode (a) modified with PAA/FMC, showing reversible behavior of FMC with the formal potential value of  $-0.04$  V. Figure 1b is the CV of gold electrode (b) modified with PAA/FMC, showing a very slight response for FMC. Although both the electrode surfaces were modified with PAA/FMC, the difference in the redox behavior of the FMC [in electrode (b)] is due to the electropolymerization carried out for a longer time in electrode (b), which resulted in a fairly thick polymer layer over the surface inhibiting the electron transfer from the FMC molecules. Hence, Fig. 1b with gold electrode (b) shows very slight redox response for FMC. For construction of rectifying interface, the first layer should be essentially redox-active. Hence, for further studies, the gold electrode surface was modified with PAA electro-polymerizing AA for 15 min.

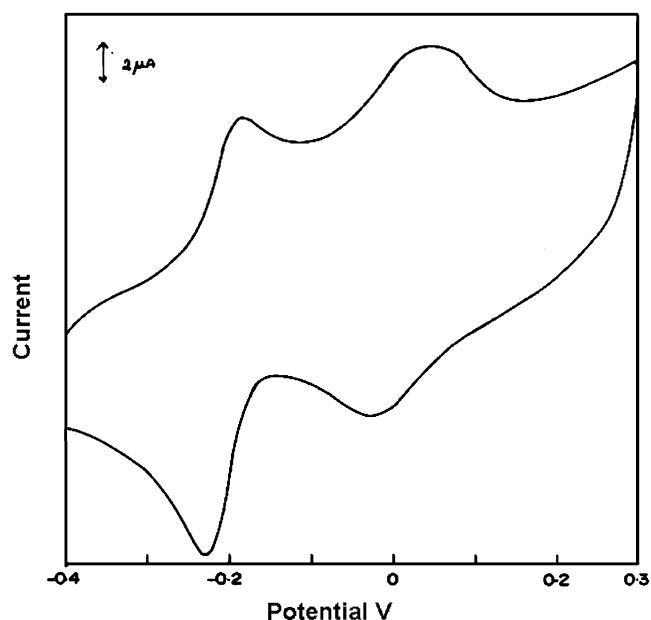


**Fig. 1** Cyclic voltammogram in 0.5 M of sulfuric acid of Au electrode modified with **a**PAA (for 15 min), **b**PAA (for 30 min) and further functionalized with FMC by Scheme 1 at the scan rate of 50 mV/s

To investigate the blocking characteristics, the CV experiments were carried out with the modified surface (PAA/FMC) in 2 mM MB solution in the potential range  $-0.4$  to  $+0.4$  V. In Fig. 2, CV showed redox responses for both FMC and MB indicating that the layer of PAA/FMC was not compact enough to prevent the electron transfer from MB. The formal potential value of MB is  $-170$  mV. Hence, to make the above PAA/FMC layer compact (which is one of the essential criteria for the modified surface to behave as a rectifying interface), electrode surface modified with PAA/FMC was dipped in ethanolic solution of DT for 20 min. Atomic force microscopy (AFM) image for surface modified with PAA (Fig. 3a) shows pits or pinholes, which is responsible for the electron transfer from both the redox species. In Fig. 3b, AFM image for the electrode surface modified with PAA/DT clearly indicates that most of the pits or pinholes are covered by DT making the first layer compact enough to prevent the direct electron transfer from the redox moiety and the electrode surface.



**Scheme 1** Schematic representations of the electrode surfaces modified with **a**PAA/DT and **b** (PAA/DT)+FMC and the mediated electron transfer through FMC

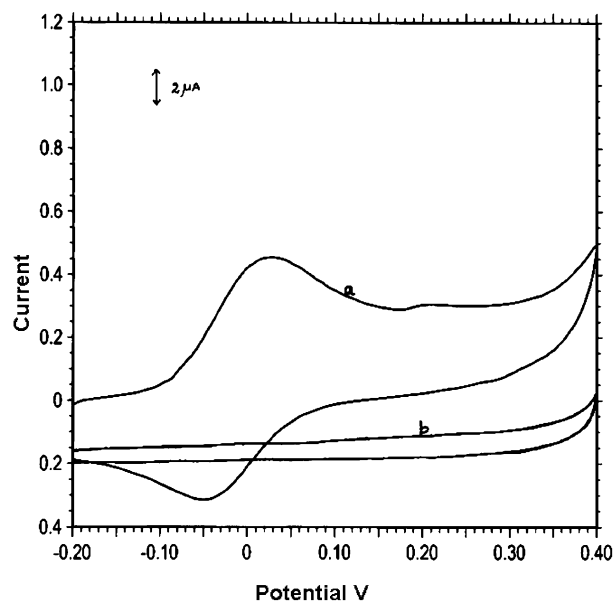
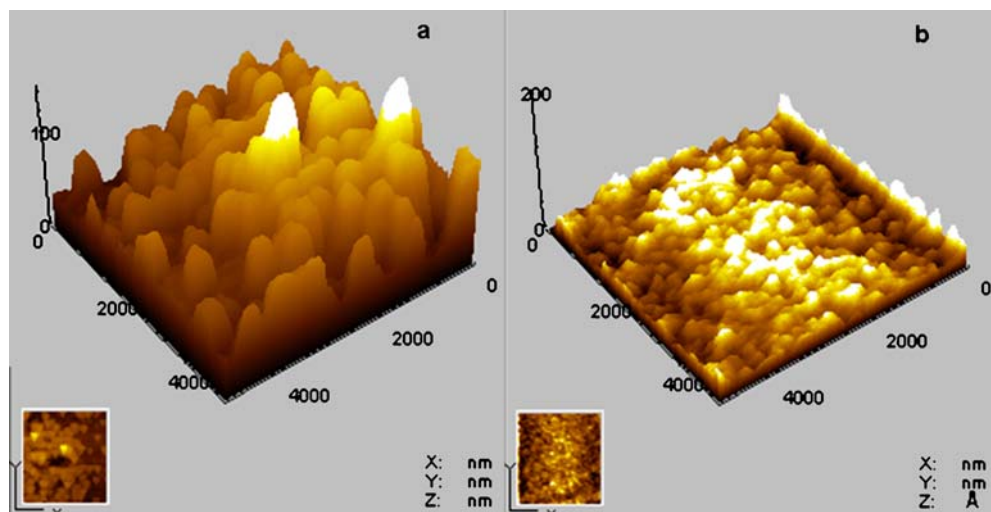


**Fig. 2** Cyclic voltammogram in 0.5 M of sulfuric acid of Au electrode modified with PAA (15 min)/FMC in 2 mM MB solution at the scan rate of 50 mV/s

Figure 4a shows the redox response of modified surface with (PAA+DT)/FMC in 0.5 M sulfuric acid indicating that FMC is covalently linked to the  $-\text{COOH}$  group of PAA and this covalent linkage is not disturbed even after dipping in DT solution. The formal potential value of FMC is  $-0.04$  V and  $\Delta E_p$  is not equal to zero due to the repulsion of  $-\text{COO}^-$  ionic groups of PAA [29]. The charge corresponding to the FMC is  $3.8 \times 10^{-7}$  mol/cm<sup>2</sup>.

To investigate the role of SAM of thiol in the kinetics of electropolymerization of AA, the electrode surface was also modified in the other way viz. by reversing the order of modification. That means, the electrode surface was first modified with DT for 20 min and then modified with PAA by electropolymerizing AA for 15 min followed by functionalizing with FMC (cf. Fig. 4b). The cyclic voltammogram of gold electrode modified in the reverse

**Fig. 3** AFM images for the electrode surface modified with PAA (a) and PAA/DT (b), respectively.  $T=1.5\text{--}2.5$   $\mu\text{m}$ ,  $L=515\text{--}525$   $\mu\text{m}$ ,  $W=25\text{--}35$   $\mu\text{m}$ ,  $f_0=5\text{--}15$  kHz,  $K=0.05\text{--}3$  N/m,  $L$  Length,  $W$  width,  $T$  thickness,  $f_0$  frequency,  $K$  force constant



**Fig. 4** Cyclic voltammogram in 0.5 M of sulfuric acid of Au electrode modified with a) PAA (for 15 min)+DT (for 20 min), b) DT for 20 min+PAA (for 15 min) and further functionalized with FMC by Scheme 1 at the scan rate of 50 mV/s

order (DT/PAA/FMC) is featureless as self-assembled monolayer of DT on the gold surface inhibits the polymerization of AA. Therefore, a further modification step with FMC is not materialized.

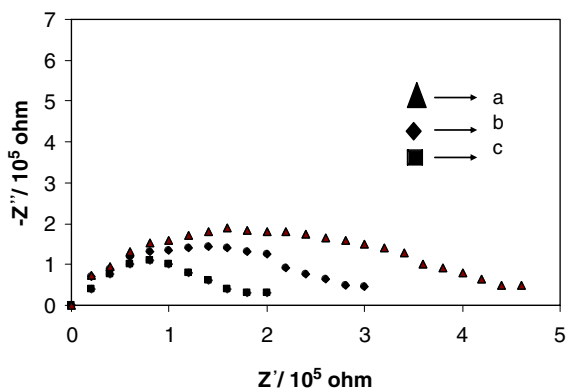
Electrochemical impedance measurements were made with the electrodes modified with PAA, DT, and PAA+DT to explore the compactness of the modified surface [30, 31]. The measurements were carried out with 0.5 M sulfuric acid containing 1 mM of  $\text{K}_4[\text{Fe}(\text{CN})_6] + \text{K}_3[\text{Fe}(\text{CN})_6]$  in the frequency range 10 Hz to 1 MHz. Figure 5 shows the Nyquist plots for the electrode surface modified with PAA, DT, and PAA+DT, respectively. Comparison of heterogeneous electron transfer resistance,  $R_{ct}$  values of the electrode surface modified with DT ( $2.6 \times 10^5$  ohm), PAA ( $1.6 \times 10^5$  ohm), and PAA+DT ( $4.6 \times 10^5$  ohm) show that the electrode surface modified with PAA+DT offered higher

interfacial electron resistance, which clearly indicates that the modified surface with PAA+DT obstructs the direct electron transfer across the PAA/DT interface [31]. Therefore, for carrying out charge transfer studies, gold electrodes were modified first by PAA and then dipped in DT solution.

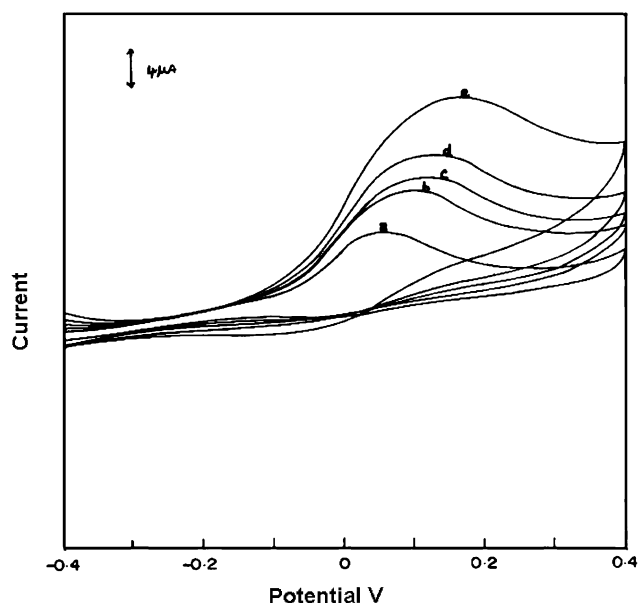
### Charge trapping studies

Figure 6 shows the CV of the modified interface (PAA+DT/FMC) in contact with different concentrations of MB in 0.5 M sulfuric acid in the potential range  $-0.4$  to  $0.4$  V. The formal potential value of MB and FMC are  $-170$  and  $-40$  mV, respectively. When the electrode potential is scanned from  $-0.4$  to  $+0.4$  V, the oxidation of MB at its formal potential value is not observed. An anodic peak of ferrocenium ion at  $+150$  mV (positively shifted to about  $100$  mV) alone is observed with the increase in the anodic current as the direct electron transfer from the MB to  $\text{MB}^+$  species is prevented; it undergoes oxidation through the ferrocenium ion present in the first layer through mediated fashion [19, 25]. The charge corresponding to the anodic peak in Fig. 6e is  $7 \times 10^{-7}$  mol/cm<sup>2</sup>. When the scan direction is reversed, the reduction peak for both the redox species were absent and this behavior corresponds to rectification of current. The absence of cathodic peaks of the redox species, increase in the anodic peak current, and increase in charge clearly show that the oxidation of MB is facilitated through FMC resulting in unidirectional flow of current. Comparing the formal potential values of both the redox species suggest that ferrocenium ion is a strong oxidant to oxidize the MB to  $\text{MB}^+$ , whereas reverse reaction is a thermodynamically unfavorable process [24] and does not take place. Hence, the current flow across the modified interface is unidirectional.

Figure 7a represents the CV of electrode surface modified with PAA+DT/FMC/PVP/[Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> in 0.5 M sulfuric acid. The formal potential value of [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> is  $-685$  mV. When the electrode potential is scanned positively with this redox-active bilayer assembly, an anodic peak starts at  $+200$  mV and the oxidation peak of



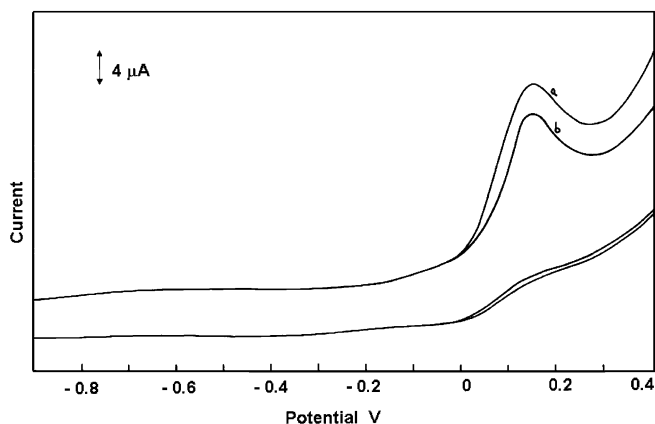
**Fig. 5** Nyquist plot of the electrodes modified with PAA (a), DT (b) and PAA+DT (c), respectively in 1 mM of  $\text{K}_4[\text{Fe}(\text{CN})_6] + \text{K}_3[\text{Fe}(\text{CN})_6]$



**Fig. 6** Cyclic voltammogram in 0.5 M of sulfuric acid of Au electrode modified with PAA+DT/FMC in different concentrations of MB at the scan rate of 50 mV/s. Curve nos. a-e:  $[\text{MB}] = 2, 3, 4, 5,$  and 7 mM, respectively

$[\text{Ru}(\text{NH}_3)_6]^{2+}$  species is not observed at its formal potential value. The formal potential of FMC is also shifted positively with the enhancement in its oxidation current. This clearly indicates that the oxidation of  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  takes place through oxidation of [32, 33] FMC and in the reverse scan, reductions of both the redox species are prevented, thereby, making electron flow across the modified interface unidirectional. The charge corresponding to the mediated oxidation peak is  $9.2 \times 10^{-7}$  mol/cm<sup>2</sup>. When the formal potential values of both the species are compared, the mediated electron transfer from  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  to FMC is a thermodynamically downhill process, whereas, when the scan direction is reversed, the energy levels are not favorable for the mediated reduction of the redox species [12, 34]. Hence, bilayer assembly exhibits the property of unidirectional flow of current analogous to an electrochemical rectifier. However, since the reduction of  $\text{Ru}^{3+}$  to  $\text{Ru}^{2+}$  is a thermodynamically forbidden process, the  $\text{Ru}^{3+}$  is trapped and this redox-active bilayer rectifies the current for one cycle. Hence, to make this redox-active bilayer work as a rectifier, the modified surface having the trapped species is dipped in 1 mM of ascorbic acid solution for 20 min. In Fig. 7b, voltammogram of redox-active bilayer after dipping in ascorbic acid solution shows rectification behavior, which indicates that ascorbic acid reduces  $\text{Ru}^{3+}$  to  $\text{Ru}^{2+}$ .

To substantiate the above studies, spectroelectrochemical studies have been carried out with  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  and ascorbic acid. Figure 8a represents the visible spectra of aqueous solution of Ru species showing two bands at 272 and 320 nm [35]. On controlled electrolysis at  $-0.5$  V (standard potential of Ru is  $-685$  mV),  $\text{Ru}^{2+}$  is oxidized to  $\text{Ru}^{3+}$  (Fig. 8b); the band at 320 nm is shifted to 385 nm, and the band at 272 nm is slightly shifted to 275 nm, which are

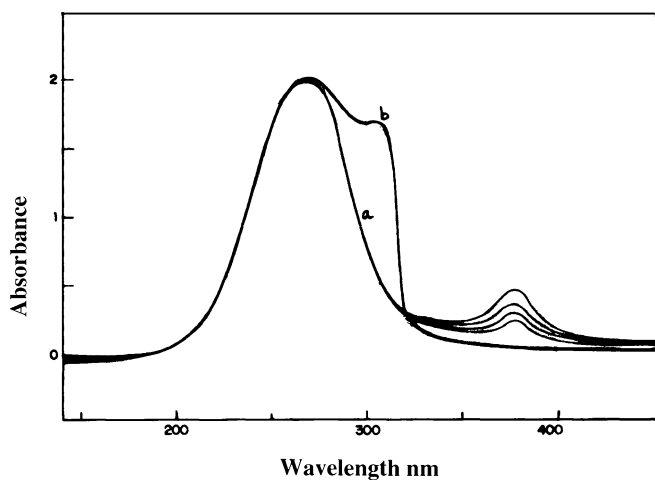


**Fig. 7 a** Cyclic voltammogram in 0.5 M sulfuric acid of Au electrode modified with *PAA+DT* further functionalized with *FMC*, initially and  $[\text{Ru}(\text{NH}_3)_6]^{2+}$ , subsequently, at the scan rate of 50 mV/s and **b** CV of redox-active bilayer electrode containing trapped and  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  after treating with 1 mM ascorbic acid at the scan rate of 50 mV/s

characteristics of  $\text{Ru}^{3+}$  species as reported earlier [35]. After the addition of 1 mM of ascorbic acid to the above solution, the bands at 275 nm is shifted again to 272 nm and the 385 nm is shifted back to 320 nm confirming the reduction of  $\text{Ru}^{3+}$  to  $\text{Ru}^{2+}$  species. Hence, by using ascorbic acid, the redox-active bilayer assembly can be used for current rectification analogous to a diode.

## Conclusion

This study investigated the modification of the electrode surface with polymer and thiol monolayer and functionalizing with redox species. We have demonstrated that the above modified surface can be used to dictate the mediated electron transfer, which results in unidirectional flow of current using second redox species present either in the solution or in the second layer. Moreover, a method for



**Fig. 8 a** UV-visible spectra for  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  species before bulk electrolysis and **b** UV-visible spectra for  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  generated on bulk electrolysis

releasing the trapped redox moiety in the second layer has also been suggested, which makes this study interesting. Furthermore, this study allows investigating the modification of the electrode surface with both thiol and polymer and also optimizing the conditions for the modification of the surface to meet the necessary applications. Although rectifying interfaces using two-component systems have been reported recently, our present result is interesting because we have constructed rectifying interface using simple molecules and techniques.

**Acknowledgements** The work described in this paper forms a part of the Ph.D. program of Chidambaram Ramalechume, and she is thankful to the Council of Scientific and Industrial Research (CSIR), Government of India, New Delhi, for financial support in the form of a senior research fellowship (SRF).

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