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Ferrocene-functionalized polydopamine as a novel redox matrix for H_2O_2 oxidation

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Abstract:

We describe a simple approach for the synthesis of the ferrocene-derivative of dopamine by reacting ferrocene dicarboxylic acid with the amine functional groups present in dopamine *via* amide linkage. Polymerization of this derivative was effected at room temperature under mild alkaline conditions (pH ~8.5). The formation of covalent amide linkage between polydopamine (polyDA) and ferrocene (Fc) units was confirmed by FTIR and NMR spectra. Electrochemical characterization of the poly(DA-Fc)-modified glassy carbon electrodes shows a reversible response at E_{pa} = 0.40 V and E_{pc} = 0.28 V pertaining to the ferrocene/ferrocenium redox, in addition to polyDA redox peaks at E_{pa} = 0.63 V and E_{pc} = 0.57V. Furthermore, the poly(DA-Fc) film displays excellent electrocatalytic oxidation of H_2O_2 in phosphate buffer solutions (pH~7.4). A Fenton-type reaction mechanism is proposed to explain the electrocatalytic oxidation, in which oxidation of ferrocene occurs along with the hydroxyl groups in the forward anodic scan, yielding a polymer film with Fc^+ and hydroxyl radicals and also a polymer radical, upon reaction with H_2O_2 gives out oxyhydroxy radicals and ferrocene-polydopamine polymer. During the reverse scan, charge neutralization among the radicals takes place taking the polymer back to its original state. A linear relationship between the anodic current and [H_2O_2] allows quantitative determination of the latter with a detection limit and sensitivity of 5 μM and 0.7μA/μM respectively. Also, the poly(DA-Fc) film shows no interference from other small organic molecules such as glucose and ascorbic acid.

Keywords: Polydopamine, Ferrocene, electrochemical sensing, redox mediator, H_2O_2.

Introduction:

Mussel-inspired polydopamine and its derivatives have attracted significant research interest in chemical, biological and medical applications due to their exceptional physico-chemical properties[1]. Messersmith and co-workers demonstrated the ability of polydopamine to form extraordinarily adherent films of a few nm-thicknesses on diverse substrates[2]. The versatility of the polydopamine has been traced to the presence of catechol, amine and imine functional groups. The functional groups can readily coordinate or form a covalent bond with metals, metal oxides and organic molecules. Nevertheless, the structure of the polydopamine obtained by self-polymerization under alkaline conditions (pH~8.5) is still obscure. But there are a few reports which elucidate the mechanism of polymer formation *via* the C-C linkages, charge transfer, π-π stacking and hydrogen bond interactions between the monomers[3,4]. The presence of free amine and imine groups in the polydopamine matrix permits various types of organic molecules to be attached to the polydopamine depending on the synthetic requirements. Reactions of this type will eventually lead to the pre-determined functionalization of the polydopamine chain for specific applications and are of great significance because they pave new and versatile ways of modification of diverse substrates with specific functionalities, and provide an important platform for the construction of hybrid materials[1,5]. The chemically modified polyDA composites have been used in sensitive and selective detection of small organic molecules, bio-imaging, drug delivery, catalysis and as membranes in separation techniques[6,7].

PolyDA is evolving as a natural choice for achieving adhesion of the modifying layers to the substrate, for example in the fabrication of electrochemical biosensors. In addition, polyDA film can assist in the immobilization of highly dense biomolecules which in turn can enhance selectivity, sensitivity and stability of the sensor[7,8]. Xie et al fabricated a biosensor based on polyDA-laccase-CNT composite materials for the detection of phenolic compounds[9]. Here, laccase enzyme acts as a catalyst for the polymerization of dopamine. The polyDA network in turn helps in improving the enzyme stability and activity. Electropolymerized polyDA films grown on the surface of a bilayer lipid membrane, pre-immobilized with horseradish peroxidise (HRP) was used for fast, reliable and sensitive detection of H_2O_2 at sub-micro level[10]. The polyDA film plays a crucial role in retaining the structure of the bilayer lipid membrane and also protects the HRP enzyme from leakage and deactivation. Gao et al fabricated another type of H_2O_2 electrochemical sensor by entrapping G-quadruplex hemin in polyDA which was found to have a detection limit of 2.2 μM[11]. The above procedures for fabricating biosensors employ either enzymes or noble metals that involve tedious synthetic steps and high costs. PolyDA not only serves as a network for immobilization of organic molecules, but also serves as a reducing and capping agent in the synthesis of metal nanoparticles.[12] PolyDA-capped metal nanoparticles are widely employed in detecting small organic molecules.[13,14] For example, polyDA-derived Au and Pt nanoparticles on a conducting matrix such as conducting polymer and carbonaceous materials (carbon nanotubes, graphene) are used for the detection of ascorbic acid, dopamine and uric acid.[13,15] Wang et al reported a synthetic procedure for the preparation of monodisperse polyDA-Ag hybrid hollow microspheres with ZnO as sacrificial templates.[16] The polyDA-Ag hybrid hollow microspheres showed H_2O_2 electrocatalytic response with a detection limit of 1.97μM. A novel enzymeless H_2O_2 sensor has been reported based on the in-situ polymerization of dopamine in the 3-D graphene scaffolds. Further modification with thionine molecules was found necessary to effectively mediate the reduction of H_2O_2 near the electrode surface.[17] These examples, though not exhaustive prove that there is tremendous interest in using the catechol chemistry for surface-derivatization[1] which warrant attachment of various chemical functionalities to dopamine before its polymerization. Redox-functionalization of polydopamine is very important in the context of mediated chemical reactions, chemical sensing and functional materials for device fabrication.[5]

As a natural consequence of the oxidation of the dopamine to quinone form, a permanent redox moiety is present on the polydopamine chains. However, the redox activity of the quinone is discernible only under acidic conditions. As quinone-hydroquinone conversion is pH-dependent, its utility as a redox mediator in an electron-transfer reaction is limited. Hence, there is a need to introduce an outer-sphere type redox group such as ferrocene whose redox is pH independent.[18] In this context, one may recall a well-known redox mediator, ferrocene that finds wide application in chemical sensing when incorporated in a conducting matrix.[19,20] It is also known that Fc/Fc^+ can induce modifications to surface properties such as wettability[21,22], conductivity[23] etc. As ferrocene and its derivatives poorly adsorb on the electrode surfaces, it becomes necessary to either immobilize them in a matrix or link to an adherent polymeric modifier, like polydopamine. Electrochemical biosensors based on ferrocene-modified carbon nanotubes[24] and graphene[25] electrodes for amperometric H_2O_2 sensing have been reported with detection limits as low as 5μM.

Herein, we report a bio-inspired approach for the synthesis of redox-functionalized polydopamine thin film, viz., ferrocene-polydopamine. Primarily, ferrocene dicarboxylic acid is covalently linked to dopamine using carbodiimide chemistry at room temperature, followed by dopamine self-polymerization under mild alkaline conditions (pH ~8.5) thus leading to a ferrocene-grafted polydopamine. PolyDA provides a very simple polymeric modifier to achieve nanometer thickness of the redox-functionalized polymer film, with scope to reversibly effect Fc/Fc^+ electron transfer within the polymer film. The dip-coated poly(DA-Fc) film shows electrocatalytic oxidation of H_2O_2 in the phosphate buffer solutions (pH

~7.4). Incidentally, its sensitivity to H_2O_2 oxidation is reflected in its ability to show current jumps upon gradual addition of the analyte in amperometry. The sensitivity of this modified electrode to H_2O_2 oxidation is examined in the presence of commonly interfering molecules like glucose and ascorbic acid.

Experimental:

Materials and Methods:

1,1'-ferrocenedicarboxylic acid and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) were purchased from Sigma Aldrich. Dopamine hydrochloride, N-hydroxysuccinimide (NHS) and Tris(hydroxyl methyl)aminomethane (TRIS) used as received from Alfa Aesar. 2-(*N*-morpholino) ethanesulfonic acid (MES) were purchased from SISCO Research Laboratory. 30% hydrogen peroxide solutions were purchased from the Merck pvt ltd. All aqueous solutions were prepared using MilliQ water (18.2 MΩ.cm).

Synthesis of Ferrocene-derivative of polydopamine:

A simple two-step synthesis was carried out by activating ferrocene carboxylic acid using MES buffer solution at pH~6.The buffered solution consisting of 2 mM ferrocene carboxylic acid, 25 mM each of EDC and NHS were kept at room temperature for about 4 hours for activation of carboxylic acid groups in ferrocene moiety. To the buffer solution, an aliquot of 5 mM dopamine hydrochloride was added and left aside at room temperature for 2 hours. The dispersion was freeze-dried to obtain a solid product of dopamine linked ferrocene (DA-Fc). Further, the polymerization of dopamine was carried out using the known procedure[26] that utilizes a TRIS buffer solution at pH ~8.5 at room temperature for 8 hours. A well-cleaned and -polished glassy carbon electrode (GC) with 0.03, 0.05µ sized alumina powder was kept immersed in the polymerization solution to find a thin film of polydopamine-ferrocene (poly(DA-Fc)) formed on the electrode surface after 8 hours.

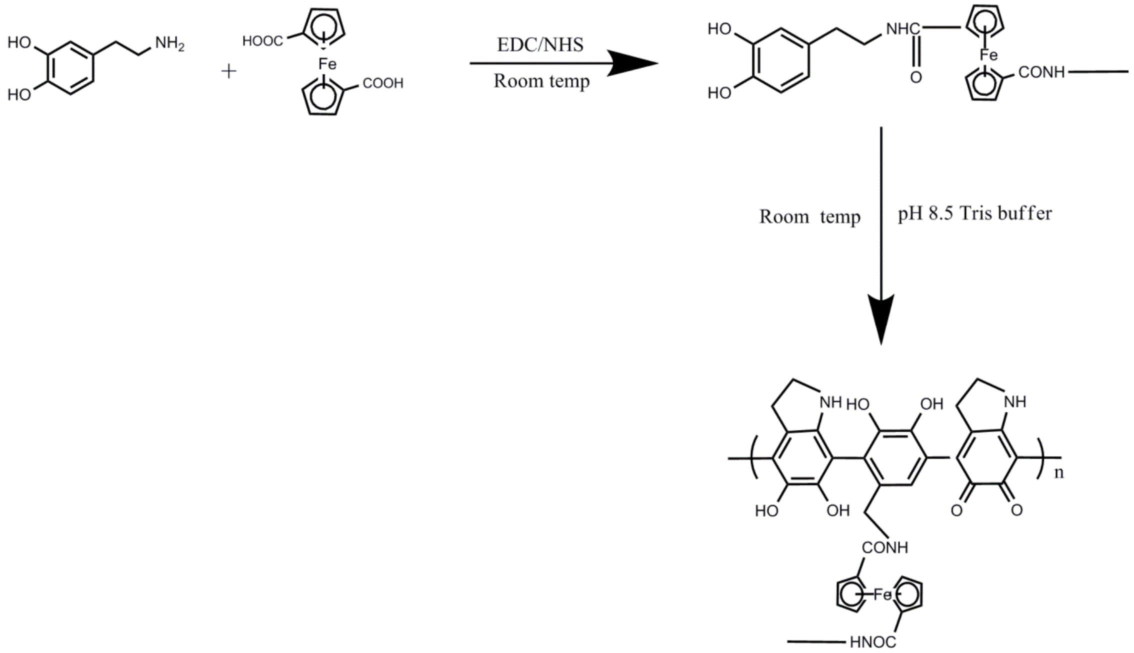
Characterization methods:

FT-IR spectra were recorded using FT-IR (Thermo Nicolet Model 670) equipped with a DTGS detector. NMR spectra were recorded with a Bruker instrument (400 MHz). AFM characterization was done using Agilent (Model 5500). All the AFM images were taken in the contact mode. Electrochemical characterization was carried out on a BASi100B workstation using Ag/AgCl as reference and platinum foil as counter electrodes. 0.5 M sulfuric acid was used as supporting electrolyte. 0.1 M phosphate buffer solution (pH~7.4) was used for studying H_2O_2 oxidation.

Results and Discussion:

Chemical and structural characterization:

In order to confirm the amide linkage formed between dopamine and $Fc(COOH)_2$ *via* mechanism (Scheme 1), FTIR spectra of dopamine, $Fc(COOH)_2$, DA-$Fc(COOH)_2$, poly(DA-$Fc(COOH)_2$) were recorded (Figure 1). FTIR spectra of dopamine show the characteristic ν(N-H), δ(N-H), δ(C=C), ν(C=N) at 3300, 1608, 1502, 1282 cm^{-1} respectively. As expected, $Fc(COOH)_2$ displays its characteristic ν(C=O), ν(C-O) and δ(N-H) vibrations at 1680, 1296, 915 cm^{-1} respectively that are due to the carboxylic acid functionalities while, a sharp peak at 1489 cm^{-1} corresponding to aromatic (C=C) and peaks at 513 cm^{-1} can be ascribed to ν(Fe-C) in the $Fc(COOH)_2$. In addition to peaks present in the spectra of DA and $Fc(COOH)_2$ after chemical linkage using carbodiimide chemistry, the appearance of sharp ν(C=O) and ν(N-H) vibrations at 1635 and 3454 cm^{-1} confirms the formation of amide linkage between DA and $Fc(COOH)_2$. Furthermore, the polymerization of DA-$Fc(COOH)_2$ was confirmed by the presence of ν(C=N), ν(C=C) vibrations at 1510 and 1443 cm^{-1} respectively from the dopamine units and ν(CNC) at 1366 cm^{-1} from the indole moieties present in the polydopamine film (in accordance with the structural analysis reported by Zangmeister et al.[27]



Scheme 1: Mechanism of formation of amide linkage between dopamine and ferrocene carboxylic acid followed by polymerization of dopamine

Figure 2 shows the ^{1}H NMR spectra of dopamine, Fc(COOH)$_2$ and poly(DA-Fc(COOH)$_2$). The spectrum of dopamine show signals at 2.7, 3.0 and 6.7 ppm characteristic of methylene, amine and aromatic species. The ^{1}H NMR spectra of Fc(COOH)$_2$ show two signals at 2.3 and 7.3 ppm pertaining to the aromatic and carboxylic units. In support of the FTIR spectra, the chemical linkage between the polyDA and Fc(COOH)$_2$ was confirmed in the ^{1}H NMR spectra by the appearance of a new resonance at 7.0 ppm ascribed to the formation of an amide linkage between polyDA and Fc(COOH)$_2$.

Morphology of polyDA, poly(DA-Fc) films:

The topography and surface roughness of the bare substrate, films of polyDA and poly(DA-Fc(COOH)$_2$) were characterized by atomic force microscopy (AFM) (Figure 3). Topographically, the polyDA films are made of granules of size in the order of 5-10 nm with features consistent with those observed in R.A.Zangmeister et al[27]. On the contrary, the poly(DA-Fc) films display larger granules with size in the range of 45-50 nm. AFM topography can be used to estimate film thickness in terms of the step height (z-axis) values. The thickness of the polyDA and poly(DA-Fc) films prepared under similar conditions are estimated to be 5.53 and 25.5 nm respectively. This difference in thickness values may arise from the distinctly different morphological features (Figure 4). Following a similar trend, the as-prepared polyDA films show a roughness factor (Rq) of 0.832 nm whereas the poly(DA-Fc) films display an increased Rq of 7.9 nm proving successful linkage of polyDA to $Fc(COOH)_2$ and increased active area of poly(DA-Fc) films (surface roughness of the bare GC was found to be 0.44 nm). The data collected at different deposition time durations (S1) show that the thickness initially increases sharply to start levelling off beyond 8 hours' duration at a thickness value of approx. 27 nm (Figure 4). This levelling off phenomenon was reported in the case of polydopamine, though its mechanism is not as yet understood. In parallel, ferrocene redox in the polymer chain can also provide approximate estimates of thickness, in which the same levelling off was observed (see below) after polymerization during the first 8 hours, in correspondence with the results of the characterization of polydopamine film formation.[27]

Electrochemical Characterization:

For electrochemical characterization, adherent films of polyDA and its derivative were obtained on the glassy carbon surface by dip-coating. The formation of polydopamine films on the glassy carbon surfaces takes place through non-covalent interactions like hydrogen-bonding or π-π stacking interactions between the functional groups present on the glassy carbon surface and hydroxyl groups present in the polydopamine units[5]. The molecular species present in the polyDA/GC and poly(DA-Fc)/GC films were probed using cyclic voltammetry in 0.5M H_2SO_4. As depicted in Figure 5a, the polyDA/GC film modified electrode shows its characteristic reversible redox peaks at $E_{pa} = 0.52V$ and $E_{pc} = 0.46V$ ($\Delta Ep = 60$ mV) associated with the quinone/hydroquinone moieties present in the polymer matrix.

On the other hand, the poly(DA-Fc)/GC shows an additional redox couple at E_{pa}= 0.40Vand E_{pc} = 0.28V corresponding to the ferrocene/ferrocenium couple, in addition to the polyDA redox at E_{pa}= 0.63V and E_{pc}= 0.57V. Inclusion of ferrocene in the polymer matrix was further confirmed from cyclic voltammetry carried out in a neutral buffer medium. The peak pair at 0.05 V and -0.05V due to polyDA is conspicuous by its absence under neutral pH conditions under which the quinone-hydroquinone redox shows very poor characteristic voltammetric responses.[28,29] But at the same time a quasi-reversible peak is observed at E_{pa} = 0.32V and E_{pc} = 0.10V as shown in Figure 5b. This peak arises due to the presence of ferrocene in the polymer. A considerable potential shift observed in both dopamine and ferrocene redox when they are linked in the polymer is suggestive of π-π interactions holding polyDA and ferrocene together in the chemically linked polymer.[30,31] The ΔEp ($|E_{pa} - E_{pc}|$) of ferrocene/ferrocenium redox couple in poly(DA-Fc) films was determined to be 120 mV which is considerably higher than the Nernstian value for a one-electron process. This tendency of ferrocene/ferrocenium redox transition becoming quasi-reversible is akin to the behaviour exhibited by the redox-polymers with limited number of redox sites for charge transport [32].

Figure 6a shows the effect of scan rate on the voltammetric behavior of poly(DA-Fc) electrode. The current was found to linearly increase with increasing scan rate pointing to surface confined nature of the process with anodic-to-cathodic peak separation (ΔE_p) of 120 mV (Figure 6b). However, the peak separation increases at higher scan rates showing that diffusion-control takes over the charge transport within the film, specifically electron hopping between the adjacent redox active sites. The E_{fwhm} value determined for the ferrocene redox was found to be 190 mV which is significantly much higher than the theoretically predicted value of 90.6 mV/n for a single electron reversible couple. This larger E_{fwhm} is likely due to the interactions between ferrocene molecules covalently stacked within the alternating polydopamine layers[25,33].

The surface coverage of the ferrocene on the film was calculated to be 7.4×10^{-9} mol cm^{-2} by using the Brown-Anson equation[34] (1). The charge transfer diffusion coefficient calculated from the Randles-Sevick equation (2) works out to be 4 $\times10^{-9}$ cm^2 s^{-1} which is considerably higher than the systems involving ferrocene immobilized on other matrices such as conducting polymers[35,36], hydrogels, etc[37]. The apparent heterogeneous rate constant was found to be $13s^{-1}$ by applying the Laviron's therotical formulation[38] (3).

$$\Gamma = \frac{tp4RT}{n^2F^2Av} \qquad \text{----------(1)}$$

$$i_p = 0.4463(nF)^{3/2}\, A\, D^{1/2}\, C\, \nu^{1/2}/RT \qquad \text{----------(2)}$$

$$k_s \;=\; \frac{nF\alpha\nu_c}{RT} \;=\; \frac{nF(1-\alpha)\nu_a}{RT} \qquad \text{-----------(3)}$$

where i_p is the anodic peak current, n, the number of electrons transferred, F, the Faraday's constant, D, the diffusion coefficient, C, the concentration of ferrocene redox centres in the film, ν, the scan rate, R, the universal gas constant, α, the transfer coefficient (~ 0.5), ν_a, the anodic scan rate, ν_c, the cathodic scan rate, and T, the temperature.

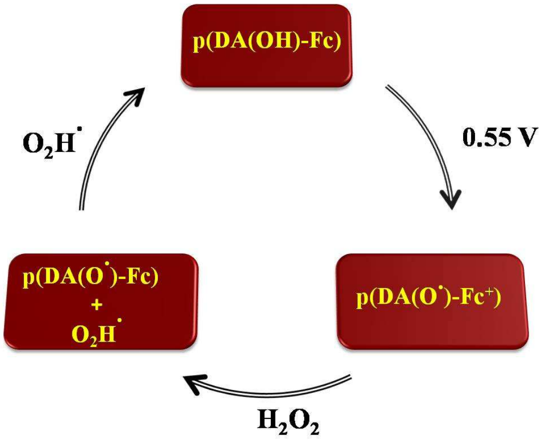
Ferrocene-mediated redox catalysis of H_2O_2 oxidation:

The electrocatalytic activity of poly(DA-Fc) towards oxidation of H_2O_2 was carried out by considering the following factors:

1) When the potential is swept anodically to 0.55 V, the abundant –OH groups present in polyDA can form $O^{\cdot}$ free radicals in turn helping oxidation of H_2O_2.[39]
2) The poly(DA-Fc) films can be immobilized on the electrode surface to form a thin film facilitating efficient mass transfer.

3) The ferrocene redox is surface-confined to the polyDA matrix that can mediate electron transfer between the modified surface and the analyte, i.e., H_2O_2 oxidation and in turn its quantitative detection.

Figure 7a shows the cyclic voltammograms of H_2O_2 oxidation on bare GC, polyDA/GC and poly(DA-Fc)/GC in 0.1M phosphate buffer solution (pH~7.4). As can be seen from the voltammograms, the anodic peak current at a potential of 0.55V vs. Ag/AgCl was found to increase with the addition of H_2O_2 explaining the tendency of poly(DA-Fc) to catalyse oxidation of H_2O_2. The bare GC and polyDA modified electrodes do not show any H_2O_2 oxidation current confirming the synergistic effect of polyDA and ferrocene towards oxidation of H_2O_2. A plausible mechanism of oxidation of H_2O_2 by poly(DA-Fc) films is given in Scheme 2.



Scheme 2: Mechanism of H_2O_2 oxidation by poly(DA-Fc)

At 0.55 V in the forward oxidative scan [Figure 7a], oxidation of ferrocene occurs along with the hydroxyl groups, yielding a polymer film with Fc^+ and hydroxyl radicals [Scheme 2]. According to the Fenton reaction,

$$Fc^+ + H_2O_2 \longrightarrow Fc + {}^{\cdot}OOH + H^+$$

and also a polymer radical, upon reaction with H_2O_2 gives out oxyhydroxy radicals and ferrocene-polydopamine polymer. During the reverse scan, charge neutralization among the radicals takes place taking the polymer back to its original state. A recent example of poly(aniline-aminophenol) in which hydroxyl radicals are produced from its electrochemical reaction with H_2O_2 , as in the present case, supports this mechanism[39]. Having observed a linear relationship between the oxidation current and concentration of H_2O_2, its quantitative determination will be interesting.

In order to determine the detection limit, chronoamperometry was carried out at a constant potential of 0.55V in 0.1M phosphate buffer solution (pH ~7.4). As described earlier (Scheme 2), $O^{\cdot}$ radicals produced from poly (DA-Fc) assist oxidation of H_2O_2 thus showing a linear increase in current. With the addition of equal aliquots of H_2O_2 (10μM) to the electrolyte, current jumps occur building up a staircase of *i vs. t* with successive additions, in support of the cyclic voltammetric results obtained at different concentrations of H_2O_2 (Figure 7b). The detection limit and sensitivity of poly(DA-Fc) electrode for H_2O_2 sensing, found from chronoamperometry work out to be 5 μM and 0.7 μA/μM. Control experiments involving chronoamperometry and cyclic voltammetry performed using polyDA/GC films in the absence of ferrocene show H_2O_2 oxidation only at concentrations above 1 mM, which is significantly higher than that observed at the poly(DA-Fc) electrode. The data obtained by other workers [Table 1] concern systems wherein ferrocene is linked or immobilized in a matrix in the fabrication of an electrochemical sensor for H_2O_2, while the ferrocene-alone films were found to be unstable without a support. These control experiments clearly point to the existence of synergism between polyDA and ferrocene towards the efficient electrocatalytic oxidation of H_2O_2.

Table 1: Comparison of hydrogen peroxide oxidation on various modified electrodes

Materials	Potential (V)	Linear range	Detection limit
Fc@PANI	0.56	4-64µM	4µM[40]
Fc@CNT	0.50	5-500µM	5µM[24]
Fc@Graphene	0.50	5µM-4.75mM	4.15µM [25]
Fc@RTIL	0.90	-	50µM[41]
poly(DA-Fc)	0.55	10µM-20mM	5µM **(This work)**
Prussian blue	0.90	1µM-20mM	1µM[42]

According to the above table, ferrocene-functionalized conducting polymers and carbonaceous materials except Prussian blue shows similar detection limit with minimal change in the oxidation potential of H_2O_2. Poly (DA-Fc) modified electrodes reported in this work show much lower anodic potentials than the electrodes reported earlier, rendering them potential candidates for H_2O_2 sensing. The stability of the sensor plays a vital role in long-term operation of the sensing devices. The formation of OH^- affects the stability of H_2O_2 sensor by increasing the solution or interfacial pH in turn leading to the deterioration of the sensor. For example, the Prussian blue modified electrode is unstable in alkaline conditions leading to deterioration of the electrode towards H_2O_2 sensing.[43] But in the case of poly(DA-Fc), $O^\bullet$ radicals do not affect the poly(DA-Fc) film contributing to its stability.

The selectivity of poly(DA-Fc) electrode was evaluated with the most interfering molecules such as glucose, ascorbic acid and dopamine in addition to H_2O_2. The concentrations of all interfering molecules were taken above the normal levels in the human blood. As shown in Figure 8, only dopamine was found to interfere during H_2O_2 detection due to the catalytic activity of polyDA to oxidize dopamine[44], while glucose and ascorbic acid showed negligible interference during H_2O_2 detection which makes poly(DA-Fc) a highly selective material for H_2O_2 detection. It is reasonable to assume that glucose and ascorbic acid do not undergo oxidative interaction with the polydopamine matrix as the latter may resist fouling by biomolecules, as exemplified in various cases.[45–47] Further, poly(DA-Fc) films can be coupled with enzymes to yield enzymatic biosensors in order to guard against any other interferences that may arise in the biomedical context. We are currently pursuing approaches to immobilize enzymes in various redox-functionalized polydopamine matrices.

Conclusions:

In summary, we have demonstrated a simple synthetic route to covalently link ferrocene and dopamine by reacting ferrocene dicarboxylic acid and the amine functionalities in dopamine *via* amide linkage. Spectral studies such as FTIR and NMR confirm the formation of amide linkage. The surface roughness found from the film topography in AFM was found to be higher in the case of poly(DA-Fc) films confirming the successful linkage of polyDA to ferrocene. Voltammetric studies on the poly(DA-Fc) films show redox responses characteristic of polyDA and ferrocene. The poly(DA-Fc) film displayed excellent electrocatalytic oxidation of H_2O_2 in phosphate buffer solutions (by the formation of $O^{\cdot}$ radicals followed by the dissociation of H_2O_2 in a Fenton-type reaction) with a detection limit and sensitivity of 5 μM and 0.7 μA/μM respectively. The poly(DA-Fc) film was found to be selective to H_2O_2 with negligible interference from other small molecules such as ascorbic acid and glucose.

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Figures

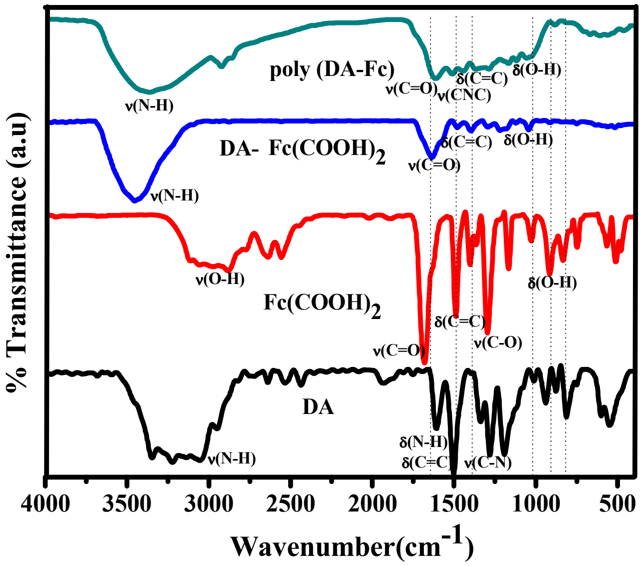

Figure 1. FTIR spectra of DA, Fc-COOH and poly(DA-Fc)

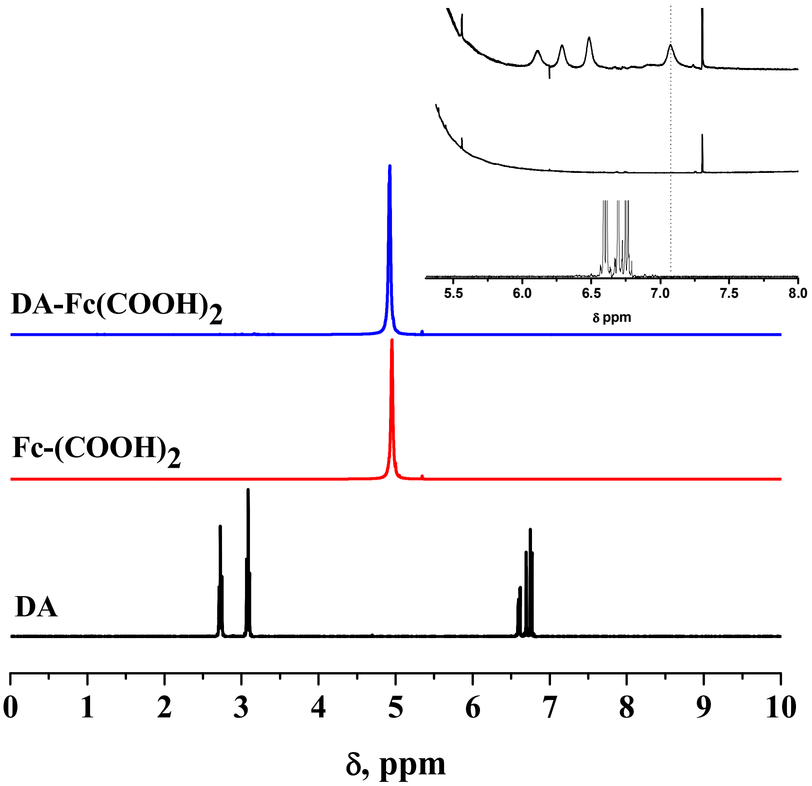

Figure 2: ^{1}H NMR spectra of DA, Fc-COOH and DA-Fc

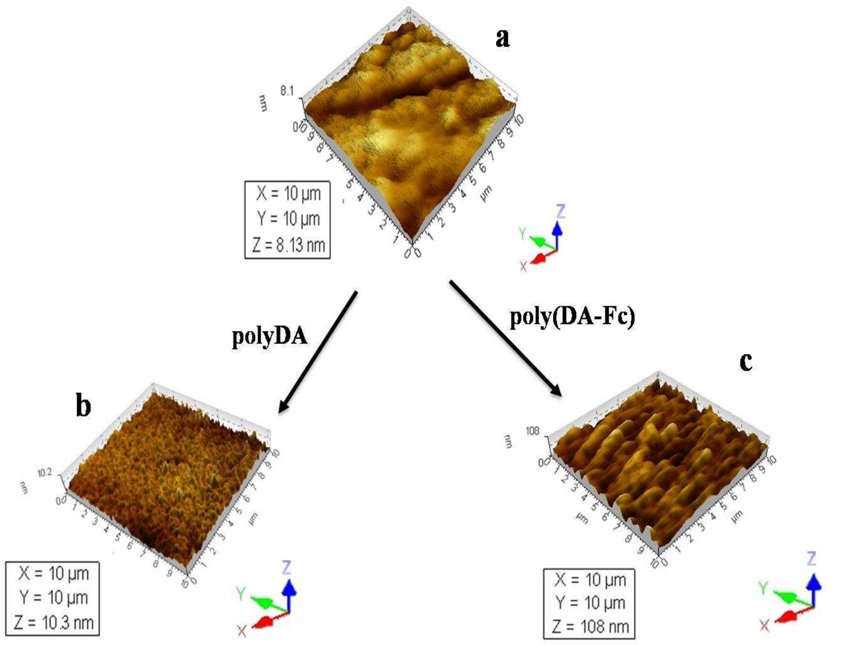

Figure 3. AFM images of (a) bare GC; (b) polyDA/GC; and (c) poly(DA-Fc)/GC

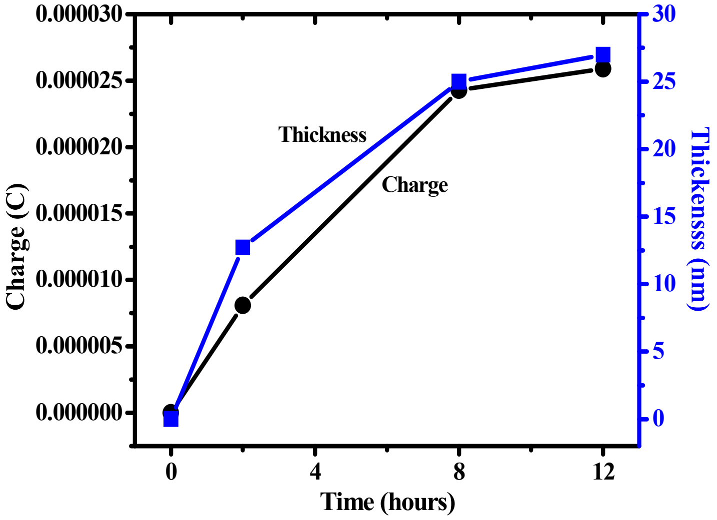

Figure 4: (a) AFM topographical step height (thickness) *versus* polymerization time (blue curve); (b) Charge consumed in the voltammetric redox response of ferrocene moiety in poly(DA-Fc) polymer *versus* polymerization time (black curve)

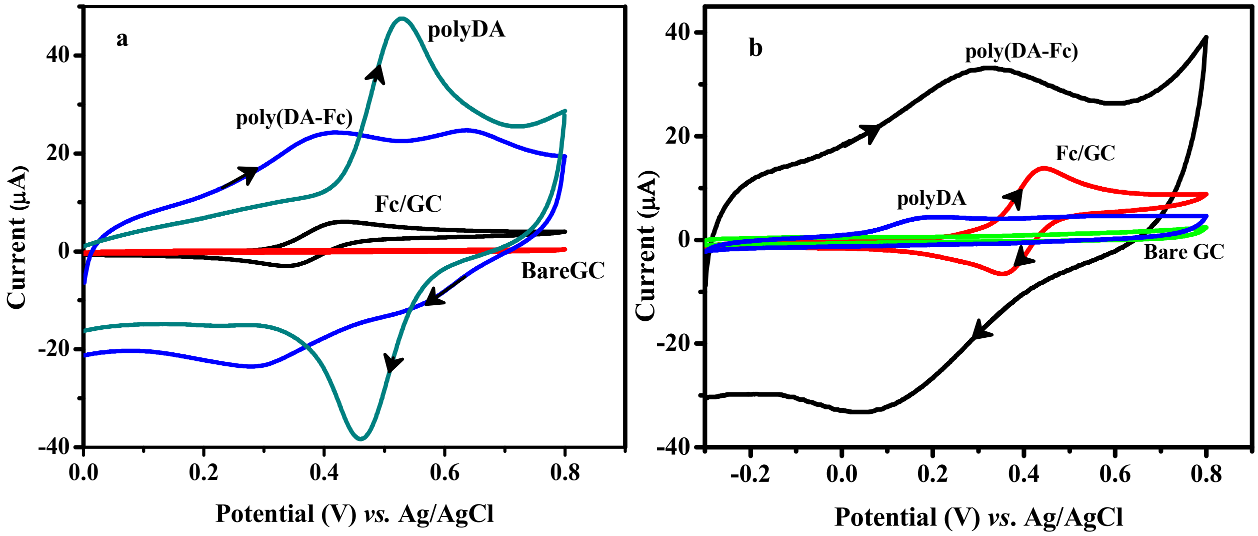

Figure 5. Cyclic voltammograms of bare GC, Fc/GC, polyDA and poly(DA-Fc) (a) 0.5M H_2SO_4; (b) 0.1M phosphate buffer solution (pH 7.4); Scan rate: 0.05V/s

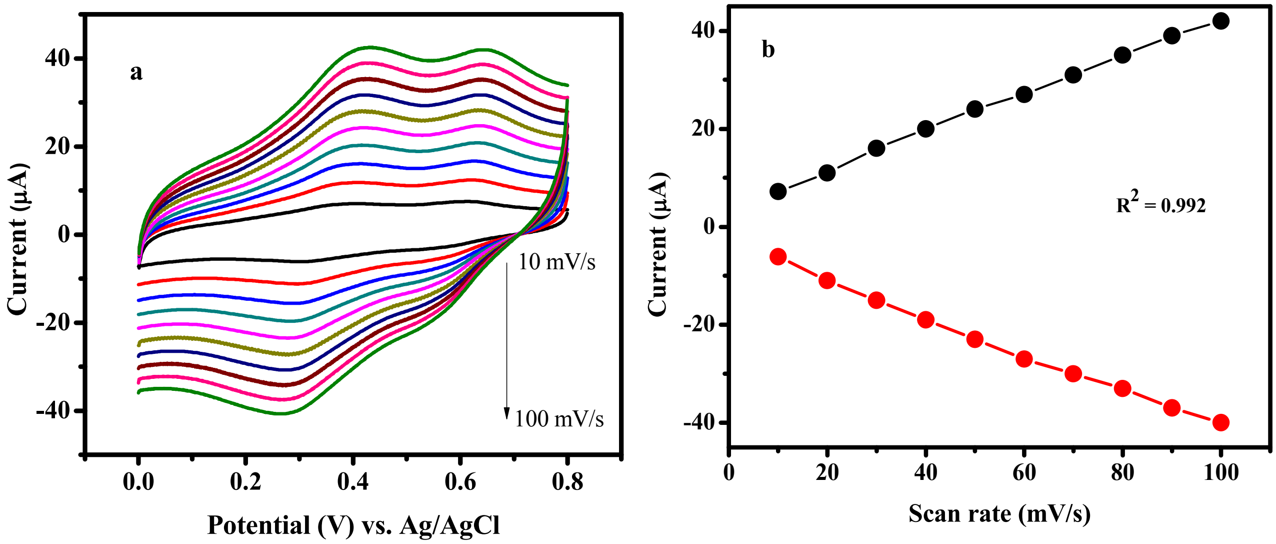

Figure 6. (a) Scan rate effect on the response of poly (DA-Fc) modified electrode; (b) scan rate dependence of poly(DA-Fc) current

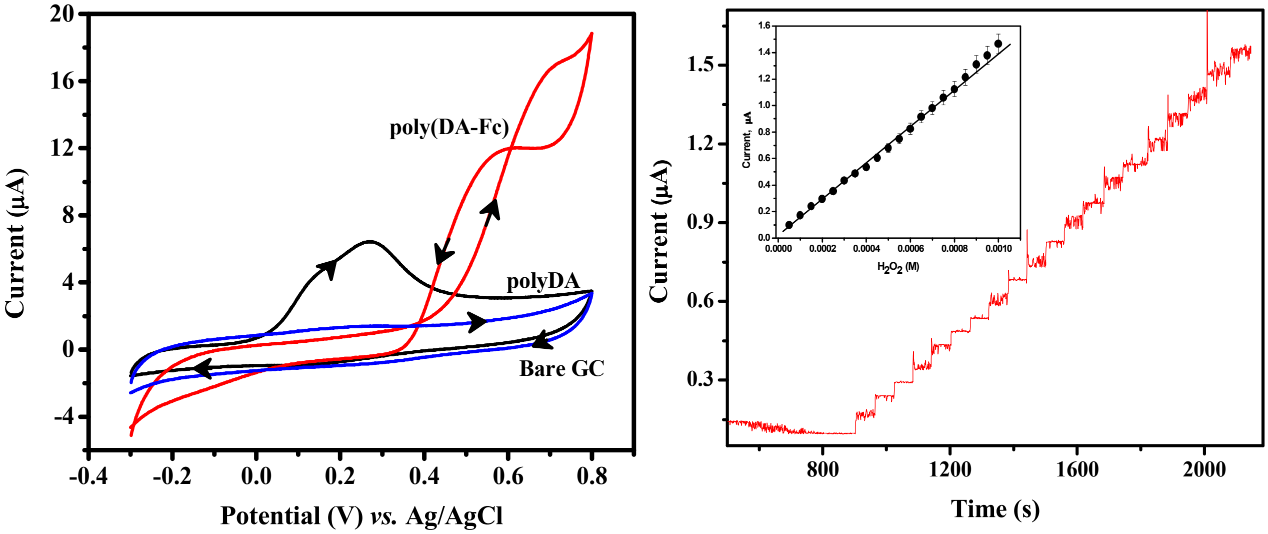

Figure 7. (a) H_2O_2 oxidation at GC, polyDA and poly(DA-Fc) modified electrodes at 5 mM concentration of H_2O_2; (b) Chronoamperometry for H_2O_2 oxidation. Electrolyte: phosphate buffer solution (pH 7.4) [Inset shows the linear curve for i vs. [H_2O_2]]

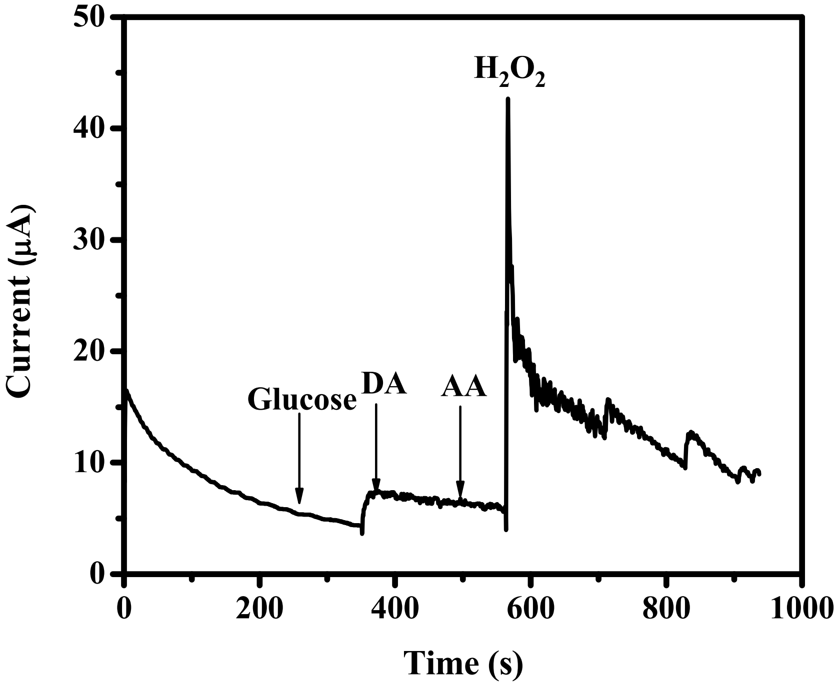

Figure 8. Selectivity of poly(DA-Fc) modified electrode towards H_2O_2 oxidation in presence of glucose, ascorbic acid and dopamine

Table of Contents

We describe a simple approach for the synthesis of the ferrocene-derivative of dopamine by reacting ferrocene dicarboxylic acid with the amine functional groups present in dopamine *via* amide linkage. Polymerization of this derivative was effected at room temperature under mild alkaline conditions (pH~8.5). The formation of covalent amide linkage between polydopamine (polyDA) and ferrocene (Fc) units was confirmed by FTIR and NMR spectra. Electrochemical characterization of the poly(DA-Fc)-modified glassy carbon electrodes shows a reversible response at $E_{pa} = 0.40$ V and $E_{pc} = 0.28$ V pertaining to the ferrocene/ferrocenium redox, in addition to polyDA redox peaks at $E_{pa} = 0.63$ V and $E_{pc} = 0.57$V. Furthermore, the poly(DA-Fc) film displays excellent electrocatalytic oxidation of H_2O_2 in phosphate buffer solutions (pH~7.4). A Fenton-type reaction mechanism is proposed to explain the electrocatalytic oxidation, in which oxidation of ferrocene occurs along with the hydroxyl groups in the forward anodic scan, yielding a polymer film with Fc^+ and hydroxyl radicals and also a polymer radical, upon reaction with H_2O_2 gives out oxyhydroxy radicals and ferrocene-polydopamine polymer. During the reverse scan, charge neutralization among the radicals takes place taking the polymer back to its original state. A linear relationship between the anodic current and $[H_2O_2]$ allows quantitative determination of the latter with a detection limit and sensitivity of 5μM and 0.7μA/μM respectively. Also, the poly(DA-Fc) film shows no interference from other small organic molecules such as glucose and ascorbic acid.