



Preparation of catalytic films of platinum on Au substrates modified by self-assembled PAMAM dendrimer monolayers

Sheela Berchmans^{a,*}, Paulraj Arunkumar^a, Shrikanth Lalitha^a, Venkatraman Yegnaraman^a, Santanu Bera^b

^a Central Electrochemical Research Institute, Karaikudi-630 006, Tamilnadu, India

^b Water & Steam Chemistry Laboratory, IGCAR, Kalpakkam-603 102, Tamilnadu, India

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ABSTRACT

In this work we demonstrate the preparation of highly catalytically active Pt formed by the galvanic replacement of the copper adlayer on Au substrates, modified by the self-assembly of fourth generation amine terminated PAMAM dendrimer (G4NH₂). The copper adlayer was formed on the dendrimer-modified gold substrate by chemical preconcentration of copper ions followed by electrochemical reduction. The Pt overlayer was characterized by SEM, XPS and by cyclic voltammetry. The catalytic efficiency of the modified film thus prepared through soft route was evaluated by the electro catalytic oxidation of methanol using cyclic voltammetry, chronoamperometry and AC impedance techniques. This work also demonstrates that the copper adlayer formed on the dendrimer-modified electrode can undergo galvanic replacement by nobler metals like Au and Ag, besides Pt. An elegant soft route involving a new three-step protocol to build the concentration of active Pt on the Au surface has been developed. Concentration of the same metal (Pt) or two different metals (Pt–Au) can be built at the interface in a stepwise manner at ambient temperature.

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1. Introduction

Synthesis of highly dispersed, high surface area catalysts is of very high importance, because of their unique properties and a number of impressive applications in catalysis, fuel cells and chemical sensors. The operating principle for direct methanol fuel cells (DMFCs) involves the oxidation of methanol and the reduction of oxygen over precious metal catalysts such as Pt–Ru alloy dispersed over a carbon support [1–3]. Consequently, the biggest barrier to commercialization of such catalysts is the cost of the precious metals involved in the catalyst preparation and the need exists therefore to reduce the amount of catalyst [4,5].

In most cases, such a reduction in the amount of metal catalyst can be achieved by increasing the amount of metal that is actually utilized on an electrode surface. One way to achieve this goal is by using high surface area materials. High surface area carbon supports, generally enable higher utilization of the metal catalyst [6–12]. Carbon nanostructures such as single-walled carbon nanotubes (SWCNTs) [13,14] and fullerenes [15] present themselves as potentially useful candidates for such applications. Most of the Pt

catalyst preparations involve relatively higher temperatures which involve wet impregnation of the metal precursors on a suitable support followed by chemical reduction [16]. Then the colloids are calcined to remove the templates. Alternately methods like micro emulsion [17], sonochemistry [18,19], microwave irradiation [20–24] and catalytic organic reactions [25,26] are employed to get Pt nanocolloids. Present method involves a soft route employing self-assembly of PAMAM dendrimers which acts as a base layer to build the loading of Pt in a stepwise manner using galvanic replacement procedure at ambient temperature. We have advantageously used the multidentate interactions of PAMAM dendrimer molecules with metal ions to get a higher loading of catalytically active Pt sites on the electrode surface. Dendrimers are highly branched, three-dimensional macromolecules with well-defined structures constructed around a central core [27]. The special architecture arises due to their extraordinary symmetry, high branching and maximized terminal functionality density. Their special architecture has led to a number of applications for the dendrimer molecules, viz., resonance imaging agents, catalysts, gene vectors, photon transduction, antioxidant and antimicrobial activity etc [28–33]. The preparation of dendrimer encapsulated metal nanoparticles (Pt, Au, Ag) and bimetallic nanoparticles through chemical reduction by borohydride is now well known [34–37] and this method yields nanoparticles which are monodisperse and are passivated against aggregation and they

* Corresponding author. Tel.: +91 4565 227551; fax: +91 4565 227779.

E-mail address: sheelaberchmans@yahoo.com (S. Berchmans).

are shown to be active for chemical and electrochemical catalysis [38–47]. There are reports where researchers prepare metal nanoparticles of Au and Pt stabilised by dendrimers and subsequently adhere them on silica or titania support after removing the template by calcination. Then these nanoparticles have been evaluated for chemical catalysis [48–50].

In this paper, we prepare a Cu adlayer on a gold substrate modified by the self-assembly of fourth generation amine terminated PAMAM dendrimer, which has been well characterized in our previous work [51]. It is further shown in this work that the copper adlayers can be galvanically replaced by metals like Au, Ag and Pt. The Pt overlayer prepared by this method exhibited very high catalytic activity.

2. Experimental

2.1. Preparation of copper–dendrimer nanocomposite and subsequent galvanic replacement of Cu by nobler metals

Gold substrate is immersed in a 60 μl of 5% solution of fourth generation PAMAM dendrimer (G4NH_2) (Aldrich) in 5 ml ethanol for overnight (28–30 h). It is withdrawn, washed with ethanol, air-dried and then immersed in a 1 mM solution of copper sulphate [Central Drug House Ltd., Mumbai] in water for 25 min. (A time period of 25 min was sufficient to get the maximum loading of Cu^{2+} ions in the dendrimer-modified gold substrate. This time was fixed by doing an independent experiment measuring the copper loading with respect to preconcentration time.) After preconcentration, the substrate is taken out from the solution, washed with water and then introduced in a cell containing 0.5 M sulphuric acid [Merck (India) Ltd.] for electrochemically reducing the Cu^{2+} ions trapped inside the dendrimer monolayer. Pt and $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode served as counter and reference electrodes, respectively. The working electrode is clamped at a potential of -600 mV sufficient to reduce the copper ions. The preconcentrated copper ions in the dendrimer-modified substrate were reduced to copper by applying a reduction potential of -600 mV for 10 min.

The copper film modified gold substrate is then washed with water and immersed in the salt solution of the metal, which has to replace copper for 20 min. Typically, AgNO_3 (1 mg/ml), K_2PtCl_4 [Merck (India) Ltd.] (1 mg/ml) and HAuCl_4 [Merck (India) Ltd.] (1 mg/ml Au) solutions were used to obtain overlayers of Ag, Pt and Au, respectively. A control experiment was also carried out in the absence of dendrimer film on gold substrate. The bare gold substrate was taken in an electrochemical cell containing deaerated solution of 0.5 M H_2SO_4 and 1 mM CuSO_4 and Cu ions are deposited by applying a potential of -600 mV for 10 min. The electrode is washed with distilled water. Then the response was recorded after transferring the electrode to an electrochemical cell containing 0.5 M H_2SO_4 only.

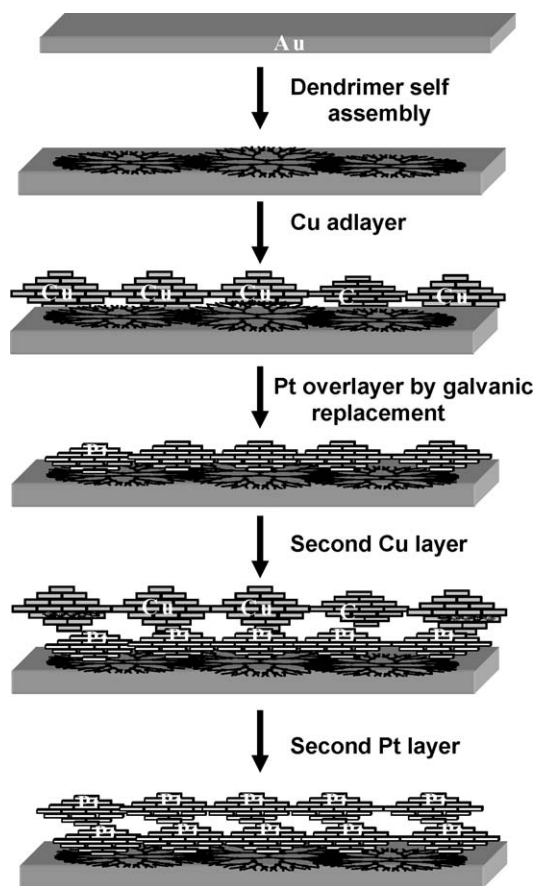
2.2. Stepwise protocol to build the concentration of Pt at the gold surface

First step: Copper adlayers on Au substrate modified by self-assembled monolayer of PAMAM dendrimer were prepared by the procedure mentioned in the previous section

Second step: Cu adlayer is galvanically replaced by Pt.

Third step: The Pt layer is electrochemically cycled once in 0.5 M H_2SO_4 between the limits -0.8 and 0.8 V at 50 mV/s. This step aids in the formation of adsorbed hydrogen on the Pt film.

Fourth step: The cycled Pt film is dipped in 1 mM CuSO_4 for 20 minutes when Cu is deposited on the Pt film by the adsorbed hydrogen on the Pt film.



Scheme 1. Scheme of the stepwise procedure developed to build the concentration of catalytically active Pt on Au substrate modified by a self-assembled monolayer of PAMAM dendrimer.

Repeat steps 2–4 to build Pt concentration at the gold surface

The steps 2–4 form one cycle and it will be referred to as one loading cycle. Increasing the loading cycle number increases the concentration of Pt on the surface. This method has resulted in the formation of nano- to mesostructured films of Pt on the gold substrate (Scheme 1).

Cyclic voltammograms were recorded using PARSTAT 2263. A conventional three electrode cell was used with a gold slide (0.5 cm^2 area unless otherwise specified), $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{H}_2\text{SO}_4$ (0.5 M) (MSE) and a Pt wire as working, reference and counter electrodes respectively. Gold slides (1000 Å Au coating on Si wafers with an intermediate adhesion layer of 100 Å thick Ti, procured from Lance Goddard Associates, USA) of size 1 cm \times 1 cm were used in XPS and SEM measurements for the characterization of the metallic films. The performance of the catalytic layers was compared with that of two commercial catalysts E Tek (10% Pt loading) and HiMedia (10% Pt loading). The amount of Pt loading comparable to that of the film prepared by our method was incorporated onto a similar gold substrate and the experiments were carried out under the same conditions for comparison.

The VG ESCA MK200X was used for XPS analysis. Al $\text{K}\alpha$ X-ray (1486.6 eV) with 300 W power was used as the exciting source and pass energy of 20 eV was used for data collection. The energy analyzer employed was a hemispherical analyzer of 150 mm diameter. Vacuum maintained during the experiment was 1.2×10^{-9} mbar. SEM images were taken using Hitachi S3000-H model microscope.

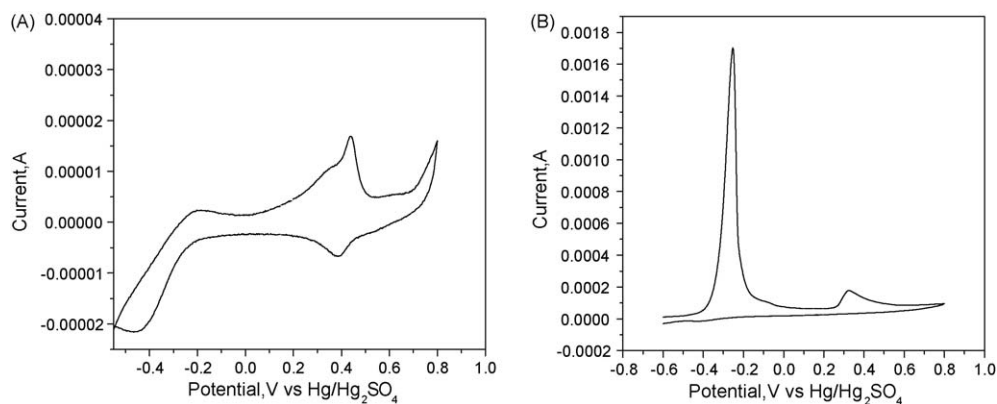


Fig. 1. Cyclic voltammogram representing the response of copper film formed on (A) bare Au substrate. (B) Au substrate modified by the self-assembly of the dendrimer; scan rate 50 mV/s.

3. Results and discussion

Fig. 1 explains the multidentate interactions of PAMAM dendrimer molecules leading to higher loading of Cu on dendrimer-modified gold substrates when compared with bare gold substrates. Fig. 1A represents the control experiment carried out in the absence of dendrimer film on the gold substrate as explained in Section 2. In this case during the anodic scan only one peak is observed at 0.45 V and the corresponding cathodic peak appears at 0.37 V. This peak corresponds to the under potentially deposited Cu. The response due to bulk deposit of Cu is irreversible. Fig. 1B shows a representative cyclic voltammogram for an Au substrate modified by dendrimer film which is subsequently loaded with Cu and it is recorded at 50 mV/s in 0.5 M sulphuric acid. During the anodic scan two main anodic peaks are observed at about -0.25 and 0.30 V, respectively. The anodic peak appearing at the more positive potential corresponds to that of the copper under potential deposition (upd) while the second peak corresponds to bulk copper deposition. In the reverse scan only negligible cathodic currents are observed which suggests that the copper ions are complexed or entrapped by the dendrimer molecules. The charges associated with the anodic peaks for bulk-deposited and under potential-deposited Cu correspond to $8200 \mu\text{C}/\text{cm}^2$ and $550 \mu\text{C}/\text{cm}^2$ respectively. upd layer is associated with a charge of $550 \mu\text{C}/\text{cm}^2$, nearly 1.1 times that expected for a monolayer. The theoretically expected coverage [52] for a complete monolayer of upd corresponds to $480 \mu\text{C}/\text{cm}^2$. The upd process requires direct

contact of the Cu(II) ions with the electrode surface resulting in the formation of Cu adatoms, over which multilayer deposit or bulk deposit of Cu takes place. It is interesting to note that the peaks are not observed in the cathodic scan in the presence of dendrimer film which indicates dendrimer–Cu interactions.

Fig. 2 represents the loading of Cu^{2+} ions on the gold substrate, in the presence and absence of PAMAM dendrimer film with respect to time. The time variation in the amount of charge associated with the Cu upd is marginal on bare Au substrate (Fig. 2A). In the case of dendrimer-modified Au substrate, the total charge corresponding to the two peaks increases and reaches saturation after 25 min (see Fig. 2B). The multidentate nature of the dendrimer molecules is able to complex more Cu ions on the electrode surface and the Cu loading is nearly 45 times of that corresponding to bare gold substrate. Hence the presence of dendrimer has enabled us to increase the surface concentration of Cu ions by 45 times. The formation of Cu^0 by electrochemical reduction and subsequent replacement by noble metals like Pt, Ag and Au have been confirmed by X-ray photo electron spectroscopy (see Supporting information).

Fig. 3 demonstrates how an overlayer of metal can be formed on the dendrimer-modified gold substrate. The presence of the different metal layers is identified by their voltammetric behaviour. Fig. 3A shows the Pt overlayer formed by the galvanic replacement of Cu adlayer on dendrimer-modified electrode. The Pt layer formed exhibits the characteristic hydrogen adsorption–desorption region and oxide formation and reduction peaks, which are characteristics of a Pt film. The substrate modified by the Pt overlayer was again immersed in a 1 mM solution of CuSO_4 for 20 min. The adsorbed hydrogen on the Pt overlayer aids in the deposition of the non-noble metal layer of Cu (curve B) on to the Pt overlayer, which is already present. The formation of the Cu layer is shown by the characteristic copper stripping peaks (Fig. 3B). Then the substrate was immersed in a solution of auric chloride (1 mg of Au/ml of water) for 20 min, which resulted in the formation of gold layer (Fig. 3C), which exhibits the characteristics of gold oxide formation and reduction. It may be understood that the Cu layer has been galvanically replaced by a layer of gold. Thus, by using a repetition of these steps, a layer-by-layer assembly of metals can be formed on the dendrimer-modified gold substrate.

Several methods have been reported in the literature to modify electrode substrates with metallic films. Upd adlayers have often been used for the modification of electrodeposition processes [52–54]. For example, in the case of gold electrodeposition, the upd adlayers of several metals greatly improve the morphology of the Au deposits. Most recently, epitaxial Ag single crystal thin films were electrochemically grown on Au(1 1 1) using a Pb upd adlayer

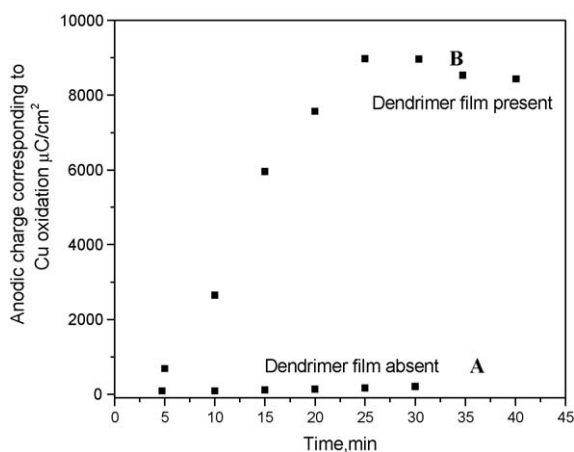


Fig. 2. Variation of Cu loading with time in the presence and absence of dendrimer film on Au substrate.

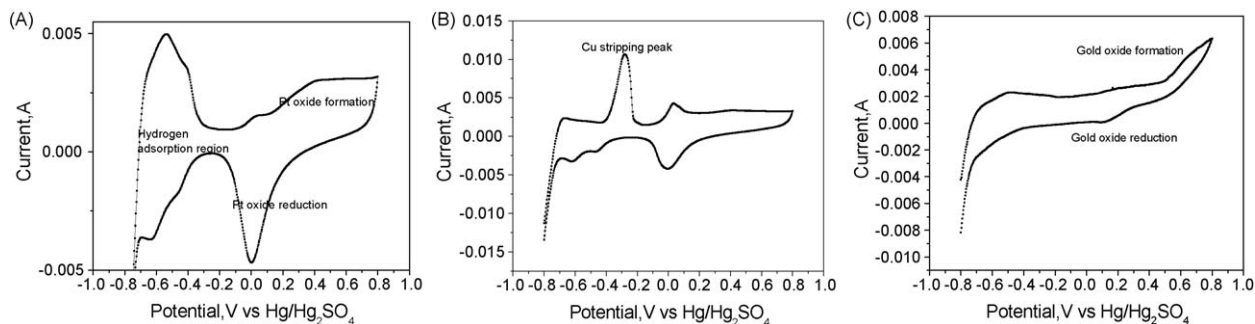


Fig. 3. Cyclic voltammogram showing the response of (A) Pt overlayer formed by replacement of Cu monolayer, (B) Cu layer deposited on Pt over layer and (C) Au layer formed by redox replacement of Cu.

as a surfactant or as a mediator metal. An alternative approach to electrodeposition is the spontaneous deposition of metals, obtained by the immersion of a clean Pt electrode in a solution of non-noble metal cations leading to a monolayer deposit [55–58]. In this work, a new method is presented for metal deposition in which the first step is the formation of Cu adlayer, which, in the second step, is galvanically replaced by a more noble metal, Pt. The replacement of metal Pt occurs via an irreversible and spontaneous redox process. In the third step, a deposit of non-noble metal, Cu is formed by the immersion of the substrate, already having a Pt overlayer, in an aqueous solution of CuSO₄ (1 mM). The deposition of Cu was driven by the reduction of Cu by the hydrogen adsorbed on Pt overlayers. The Cu layer thus formed is galvanically replaced by gold in the fourth step. It is now well known that the modification of metal surfaces by deliberate addition of another metal component can lead to selective improvement or degradation in catalytic activity, selectivity and resistance to poisoning of such surfaces in both gas phase and liquid phase environments and this method will be a suitable approach to achieve the qualities mentioned.

By following the above procedure, Pt loading was increased four times in a stepwise manner on the dendrimer-modified gold substrate. The currents due to hydrogen adsorption/desorption and oxide formation/reduction currents increased with increase in the number of steps (see Fig. 4). The charge corresponding to hydrogen adsorption–desorption and the corresponding increase in surface area of Pt, in terms of coverage calculated according to Ref. [59] are listed in Table 1 for the four steps.

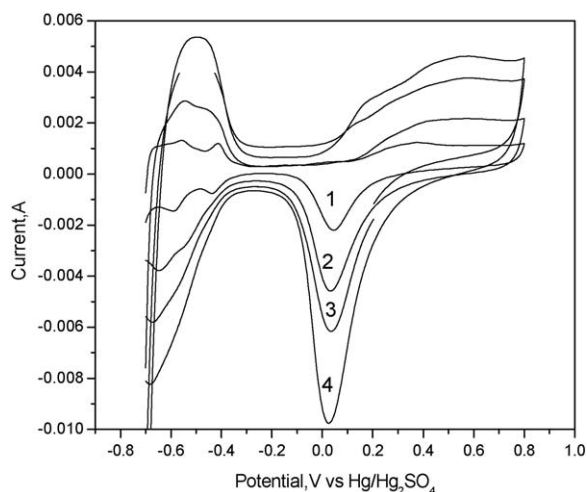
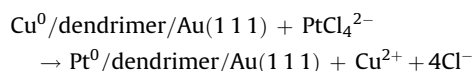


Fig. 4. Cyclic voltammogram showing the response of four Pt over layer in 0.5 M sulphuric acid. Scan rate: 50 mV/s. Electrode area: 0.5 cm².

Fig. 4 represents Pt overlayers formed by galvanic replacement of copper. The typical response for Pt along with hydrogen adsorption/desorption features is seen in the voltammogram. The peaks corresponding to the weak and strong hydrogen adsorption are distinctly resolved in the case of first and the second layer. The charge corresponding to the adsorption and desorption are 7.54 mC/cm² and 9.32 mC/cm² respectively for the first step. In electro analytical measurements, calculation of true area of any electrode surface is important. Often, it is estimated by measuring the coverage due to hydrogen adsorption. The charge under hydrogen adsorption is calculated to determine active surface area of the Pt electrode. Compared to bulk Pt metal which exhibits monolayer coverage of 210 μC/cm² [59] the surface produced by our present method shows 44 times higher coverage, which obviously contributes to the enhanced catalytic activity.

Fig. 5 represents the SEM picture of Pt and Au layers formed by galvanic replacement. The size of the Pt particles is in the range 100–500 nm whereas in the case of gold layers the size is of the order of 50–150 nm. Few particles are bigger and they vary between 250 and 450 nm. On a closer examination, it is observed that the Pt particles are arranged along a straight line. In the case of Ag, the morphology looks different. The Ag deposit appears to be made up of bigger chunks whereas the deposits of Pt and Au are particulate in nature.

The spontaneous deposition of Pt on an Au surface at open circuit potential is not known, so the only possibility is that the Pt deposition on Au was induced via the Cu upd adlayer on Au surface in contact with PtCl₄²⁻ ions. The process occurs as a spontaneous irreversible redox reaction in which one Pt²⁺ ion from the solution oxidizes two Cu upd adatoms while it is simultaneously reduced to Pt⁰ and deposited on Au.



The amount of Pt deposited by replacement of a full monolayer of Cu is stoichiometrically equivalent to Pt⁰ formed, because Cu oxidation can supply only two electrons per adatom, and two electrons are necessary for the reduction of one Pt²⁺ ion. In the case

Table 1
Hydrogen adsorption–desorption charge values for the Pt films formed by our protocol: The loading procedure was repeated four times.

Pt loading step	Hydrogen adsorption (mC/cm ²)	Hydrogen desorption (mC/cm ²)	Surface coverage of Pt (mmol/cm ²)
1.	7.54	9.32	9.658 × 10 ⁻⁵
2	22.36	20.82	2.157 × 10 ⁻⁴
3	29.46	25.96	2.69 × 10 ⁻⁴
4	33.5	35.76	3.71 × 10 ⁻⁴

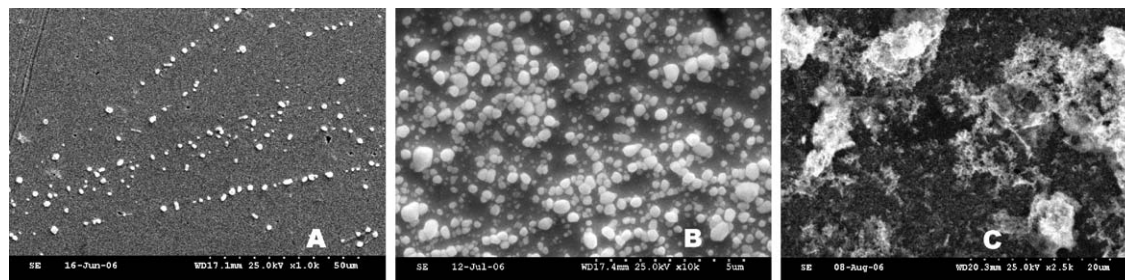


Fig. 5. SEM images of overlayers formed by the redox replacement of copper monolayer on gold (1 1 1) substrate modified by the self-assembly of dendrimer by (A) Pt, (B) Au and (C) Ag.

of galvanic replacement of Au, three electrons are required for the formation of Au^0 . Hence only two thirds of Au^0 will be formed on the surface. According to the stoichiometry of the redox reaction, the replacement of a Cu adlayer by Ag should result in the deposition of two Ag atoms for each Cu adatom. Hence, the Ag deposit is predominantly continuous and appears as bigger chunks and covers almost the entire surface.

Fig. 6A shows the cyclic voltammetric response for methanol oxidation (0.024 M) for the first overlayer of Pt modified electrode. Cyclic voltammogram shows that methanol gets oxidized at a very low overpotential of 0.1 V with a current density of 20 mA/cm^2 . In the case of single walled carbon nanotube electrodes, it is reported [60] that methanol (1.8 M) oxidation occurs at 0.4 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ with a current density of $50\text{--}69 \text{ mA/cm}^2$. In the case of bulk Pt electrode, a current density of $210 \mu\text{C/cm}^2$ is reported for a concentration of 0.25 M methanol and the oxidation occurs at 0.24 V in this case [60]. In the present work, the onset of methanol oxidation occurs at -0.188 V . The large surface area makes the electrode ideal for methanol oxidation. The methanol oxidation takes place at a lower potential of 0.1 V. The magnitude of the peak current is proportional to the amount of methanol oxidized at the electrode. The oxidation current is of the order of 20 mA/cm^2 even for a low concentration of methanol (0.024 M) which is really very high compared to literature reports [60,61]. The onset potential of oxidation is very low (nearly by an order of 200 mV compared to bulk Pt electrode). The reduction of the onset potential for the methanol oxidation reaction on this Pt overlayer electrode is comparable to the effect observed with a mixture of Pt and Ru. In the case of Pt–Ru mixture electrodes, usually, a low onset potential for methanol oxidation is observed. The shift in onset potential is attributed to the reduced work function of Ru compared to Pt ($\varphi_{\text{Pt}} = 5.36 \text{ eV}$, $\varphi_{\text{Ru}} = 4.52 \text{ eV}$). The substantial shift we observe here may be due to lower work function of the base gold substrate, which acts as the electron collector electrode ($\varphi_{\text{Pt}} = 5.36 \text{ eV}$, $\varphi_{\text{Au}} = 5.1 \text{ eV}$).

Fig. 6B represents the Nyquist plot for the impedance measurements recorded at a DC potential of 0.1 V. Very low charge transfer resistance (8.6Ω) is associated with the methanol oxidation reaction as represented by the diameter of the semi-circle. This indicates that the methanol oxidation reaction is associated with a very low charge transfer resistance and the reaction occurs in a very facile manner. From the R_{ct} values, the rate constant for methanol oxidation was calculated to be $7.25 \times 10^{-5} \text{ cm/s}$ using the expression $k_s = RT/n^2F^2AR_{\text{ct}}C$.

In the chronoamperometric experiment (Fig. 6C), the current value remains steady at 4 mA, which corresponds to 8 mA/cm^2 . Considering that a very low methanol concentration is employed in this study, the observed current is relatively very high compared to earlier literature reports [60,61]. A control experiment performed with Pt layers formed by the replacement of Cu upd layers in the absence of dendrimer film showed very poor electro catalytic activity for the oxidation of methanol. The oxidation occurred at nearly 400 mV higher overpotential (see supporting information).

Fig. 7A shows the cyclic voltammetric response of methanol (0.024 M) oxidation in 0.5 M sulphuric acid for the electrode containing Pt film (loaded for four times with Pt by our protocol) on the dendrimer-modified gold substrate. Fig. 7B and C depicts the chronoamperometric and impedance response of the same electrode for methanol (0.049 M) oxidation in 0.5 M sulphuric acid.

It can be clearly observed from these figures, that the multilayered Pt film prepared by our new method exhibits superior electro catalytic properties. In the case of voltammetry, the peak current corresponds to 38 mA/cm^2 . The increase in the hydrogen adsorption–desorption coverage with the increase in the number of loadings is shown in Table 1. The stabilization current from the chrono amperometric response turns out to be nearly 12 mA/cm^2 . In the case of the impedance response a linear response is observed compared to the semicircular response for a single layer of Pt (see Fig. 6B). When the number of loading

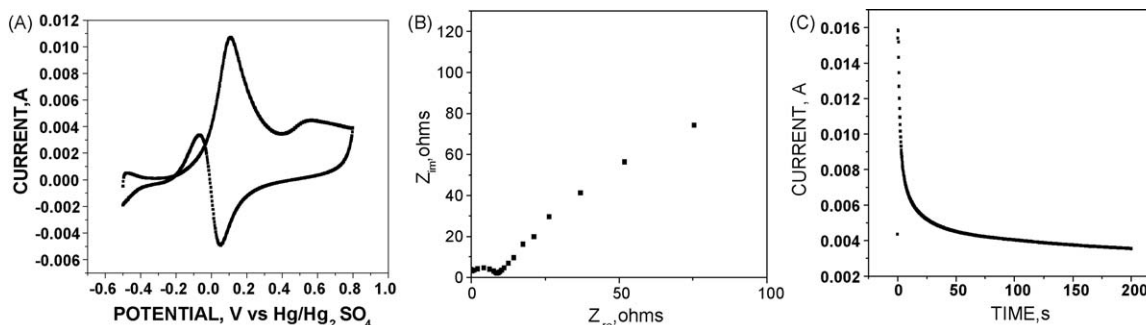


Fig. 6. Electro catalytic oxidation of 0.024 M methanol in 0.5 M sulphuric acid on the first Pt overlayer as shown by (A) cyclic voltammetry; scan rate 50 mV/s, (B) impedance technique and (C) chronoamperometry. Applied DC potential = 0.1 V for both (B) and (C). Electrode area: 0.5 cm^2 .

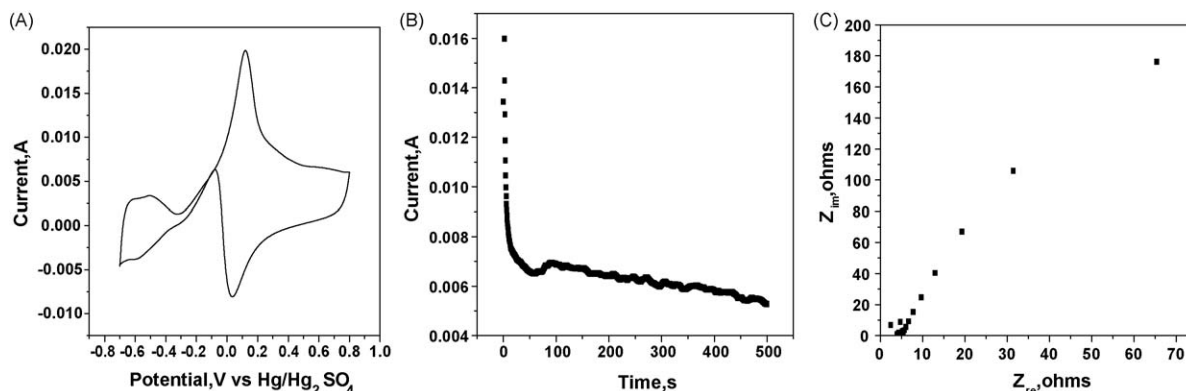


Fig. 7. Characterization of the dendrimer-modified gold substrate containing 4 layers of Pt in 0.5 M sulphuric acid; electrode area: 0.5 cm². (A) Cyclic voltammogram showing the response for methanol oxidation (0.049 M), scan rate: 50 mV/s. (B) Chronoamperometric response for 0.024 M methanol. (C) Impedance responses for 0.024 M methanol. Applied DC potential: 0.1 V for both (B) and (C).

Table 2

Performance characteristics of the prepared catalytic layers vs. commercial catalysts.

Catalyst	Loading cycle no.	Onset of oxidation potential (mV)	Methanol oxidation potential (mv)	I_f/I_b	Mass activity (mA/ μ g)	Current output from chrono amperometry (mA/cm ²)	Charge transfer resistance R_{ct} (Ω)
Dendrimer + Pt layers	1	−95.45	131.82	2.176	1.4610	8	8.6
	2	−200	84.21	3.165	1.1852	–	–
	4	−284	121.05	2.925	1.0182	12	Linear
Himedia (10% Pt)	–	−265.5	237.5	3.141	0.1531	1.2	Incomplete semicircle
E Tek (10% Pt)	–	−342.4	320	1.746	0.4336	1.2	99

cycle increases, diffusion becomes rate limiting rather than charge transfer. The catalytic current values as discussed in earlier sections are obviously very high compared to literature reports [60,61].

The poisoning effect is tested by holding the potential at methanol oxidation for 15 min and then recording the voltammogram. The current decreases nearly by 10% only. Thus, the poisoning effect is not significant in this film. The dendrimer layer present underneath prevents the species like CO from reaching the electrode surface and thereby avoids direct contact with the electrode surface and hence poisoning effect is not significant. When subjected to cycling the current decreases by only 8%. These experiments indicate that our method of preparation has yielded a very good catalytically active film, which is not subjected to the usual poisoning effects. The development of a highly efficient non-Pt catalyst, which can overcome the problem of poisoning, is a challenging task. It has been shown recently that the Au electrode does not undergo poisoning during methanol oxidation by the electro generated CO. It has been demonstrated by the use of time-resolved electrochemical impedance and surface plasmon resonance techniques that the Au surface is free from site poisoning by chemisorbed CO during methanol oxidation [62–65]. The ratio I_f/I_b further gives an idea about poisoning of the electrode by carbonaceous species. The anodic peak which appears in the reverse scan is attributed [66] to the removal of the incompletely oxidized carbonaceous species formed in the forward scan. These carbonaceous species are mostly in the form of linearly bonded Pt–CO. Hence the ratio of the forward anodic peak current density (I_f) to the reverse anodic peak current density (I_b), I_f/I_b , can be used to describe the catalyst tolerance to carbonaceous species accumulation. Low I_f/I_b ratio indicates poor oxidation of methanol to carbon dioxide during the anodic scan and excessive accumulation of carbonaceous residues on the catalyst

surface. The observed values are comparable with that of the commercial E Tek catalyst suggesting that the catalytic layers prepared by our new strategy possess catalytic properties equivalent to that of commercial catalyst. Further the superior catalytic activity is substantiated by the comparison of mass activity of the catalytic layers and the commercial catalyst (see Fig. 8). The current output obtained during chronoamperometric experiments can be considered as the real performance indicator of the fuel cell catalysts. From Table 2 it is very clear that the catalytic layer prepared through our new strategy performs outstandingly well compared to commercial catalysts.

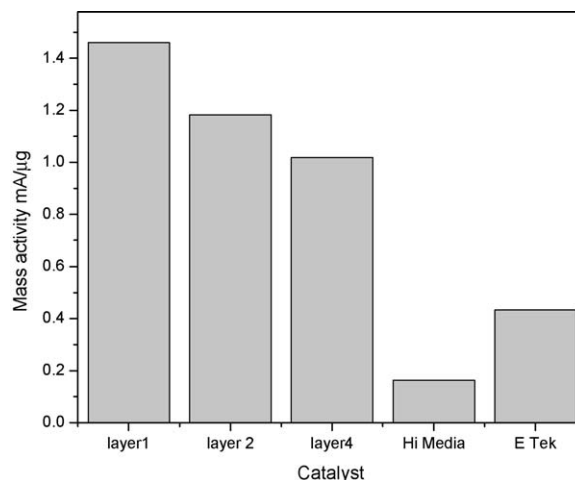


Fig. 8. Comparative performance of the commercial catalyst with that of the catalytic layers prepared from a dendrimer base layer.

4. Conclusions

The foregoing discussion reveals the formation of copper adlayer on dendrimer self-assembled on gold (1 1 1) substrate, which can be replaced by nobler metals like Au, Ag and Pt. The Pt overlayers exhibited high catalytic activity. For the first time, a novel protocol has been established for preparing highly catalytic multilayers of Pt by initially forming a Cu adlayer, which is galvanically replaced by Pt. Repetition of these two steps, will lead to the formation of multilayers of Pt. The superior catalytic activity has been evaluated using cyclic voltammetry, impedance technique and chronoamperometry. Such highly active catalytic films can be used for the fabrication of sensors for breath analysis, fuel cells, and waste water treatment and so on. Further, materials of high *surface-to-volume* ratios that can be generated using dendrimer templates by redox replacement are more suitable for miniaturized electrochemical systems, especially when platforms like *micro-total analytical system*, *micro-fuel cells* and *biofuel cells* are involved.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2008.10.003.

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