CHAPTER 3

Potential Dependent Morphological Evolution of Platinum Mesostructures: Comparison of their Electrocatalytic Activity for Fuel Cells*

Present chapter demonstrates potential-dependent morphological evolution of platinum mesostructures in the form of multipods, discs and hexagons prepared using a porous alumina membrane (PAM) template potentiostatically at -0.7, -0.5 and -0.3 V, respectively. These structures reveal unique shape-dependent electrocatalytic activity towards formic acid, methanol and ethanol oxidation reactions. A comparison of the electrooxidation kinetics of these structures illustrates that hexagons show better performance towards formic acid and methanol oxidation whereas, for ethanol oxidation, multipods show significantly enhanced activity. Interestingly, the enhancement factor ($R$) for these mesostructures with respect to that of commercial platinized carbon toward formic acid oxidation ranges up to 2000% for hexagons whereas for multipods and discs they are about 700% and 300% respectively. Similarly, for ethanol oxidation, $R$ varies up to 600% for multipods while for discs and hexagons these values are 500% and 200% respectively. For methanol oxidation, $R$ is about 750% for hexagons and 450% and 350% respectively for multipods and discs. Thus, present results demonstrate the importance of precise control of morphology by electric field and their potential benefits especially for fuel cell applications since designing a better electrocatalyst continues to be an important challenge.

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3.1. Introduction

Materials in mesoscales are known to exhibit a wide range of electrical, optical, and mechanical properties that depend sensitively on both size and shape, and hence their investigation is of fundamental and technological importance. As a result, a plethora of research progress has been accomplished in the past few years on the synthesis, characterization, and applications of many metallic and semiconducting mesostructures in various sizes and shapes often with subnanometer resolution. Various methods including template synthesis, chemical vapor deposition, and colloidal synthesis using several capping agents/surfactants have been successfully demonstrated to generate many nano to meso level architectures with a remarkable shape control. Nevertheless, only limited success has been achieved in synthesizing mesoscale materials with precise morphological control and better shape distribution, despite the use of different types of surfactants. Although the presence of these external agents may alter their intrinsic surface properties, which in turn could hamper some of their technological applications, their presence is essential for long-term stability. For example, certain sensing applications making use of surface enhanced Raman scattering require analyte adsorption to the metallic nanoparticle surface as an essential prerequisite, and consequently the presence of surfactant/capping agents reveals significant interference. In order to obviate this problem, morphological control by electrochemical methods has been identified as a more convenient and reliable approach owing to its sensitivity and ease of handling. More significantly, the shape control accomplished by the modulation of an electric field without using any surfactant/capping molecule provides important advantages in terms of both purity of the systems (no surface contamination) and the flexibility to tune many intrinsic properties.

Further, there has been a great deal of interest in studying the shape-dependent catalytic activity of various nanomaterials because both the reactivity and selectivity of these structures in catalytic reactions are dependent on the morphology and therefore on
the crystallographic planes exposed on the surface. For example, El-Sayed's group has recently carried out extensive studies on the shape-dependent catalytic activity of Pt, where tetrahedral Pt is more active than spherical or cubic ones for electron-transfer reaction between hexacyanoferrate(III) ions and thiosulfate ions especially because they contain more catalytically active atoms on the surface. Also, Li et al. have studied the catalytic activity of different shaped silver nanoparticles for the oxidation of styrene to demonstrate that silver nanocubes are more active compared to nanoplates and near-spherical nanoparticles. This is explained on the basis of crystallographic planes, where Ag nanocubes have (100) crystal face as the basal plane whereas, the truncated triangular nanoplates and near spherical nanoparticles predominantly expose their most stable (111) plane. Further, the effect of particle size (ca. 2-9 nm) in methanol, formic acid, and formaldehyde electrooxidation has been explored by Weaver et al. for platinum nanoparticles. These studies clearly indicate that the rate of methanol oxidation decreases for Pt nanoparticle diameters below 4 nm. However, formic acid oxidation exhibits the opposite behaviour while formaldehyde oxidation displays little such sensitivity to size. This size-dependent electrocatalytic activity has been discussed in terms of the availability of Pt terrace sites for the reaction. Although the particle size effect on electrooxidation has been studied, these deal only with spherical particles and hence it is extremely important to carry out similar investigations for various other shapes.

In Chapter 2, we have demonstrated the fabrication of PAM template with linear as well as hierarchically branched nanopore arrays and the control of various factors influencing the pore dimensions. In this chapter, we demonstrate the utility of those linear PAM for the synthesis of different shaped platinum mesostructures through a potentiostatic route followed by a comparison of their electrooxidation activity. To our knowledge, there is no report on the synthesis of different morphology of platinum mesostructures using such a templated electrochemical approach and this mode of confined potentiostatic growth is relevant to the preparation of many other similar mesostructures of Rh, Pd, Ru etc., for their catalytic and other applications. More
Interestingly, these differently shaped mesostructures show unique variation in electrocatalytic activity for formic acid, methanol, and ethanol oxidations (three important reactions for portable fuel cell applications) in comparison with that of commercial platinized carbon. Analysis of the exchange current density ($j_0$) using Tafel plot suggests that the hexagons of Pt show better electrocatalytic activity for formic acid oxidation (ca. $3 \times 10^{-5}$ A/cm$^2$) compared to that of multipods, discs, and commercial platinized carbon (ca. $8 \times 10^{-6}$ A/cm$^2$) whereas, for ethanol oxidation, multipods show significantly enhanced electrocatalytic activity (ca. $2 \times 10^{-6}$ A/cm$^2$) compared to that of disc, hexagons, and commercial platinized carbon (ca. $4 \times 10^{-7}$ A/cm$^2$). Interestingly, for methanol oxidation, hexagons show better performance (ca. $7.76 \times 10^{-7}$ A/cm$^2$) compared to that of multipods, discs, and commercial platinized carbon (1.02 x $10^{-8}$ A/cm$^2$). All these observations are rationalized with the help of a tentative mechanism based on experimental evidences using a combination of both electrochemical and spectroscopic techniques.

3.2. Experimental Details

3.2.1. Materials

H$_2$PtCl$_6$.6H$_2$O (99.98%) was purchased from Aldrich chemicals while boric acid (99.5 %) was purchased from Loba Chemie. Solvents like ethanol (99.9 %), methanol (99.5 %) and formic acid (98 %) were purchased from Merck. All reagents were used without further purification and deionized water (18 MΩ) from milli-Q system was used in all experiments.

3.2.2. Preparation of Different Shaped Platinum Mesostructures

Free-standing linear PAM templates fabricated via a two-step anodization (for details see Chapter 2, section 2.4.2) was served as working electrode for templated electrodeposition, after sputtering Au film (200 nm) onto one side of the membrane. (Sputter coating was performed using JEOL JFC-1100E Ion Sputter with a double-pole
horizontal electrode discharge system). Electrodeposition was carried out in an aqueous solution of 5 mM H₂PtCl₆ as the platinum precursor and boric acid, as a buffer (1 mM) at a pH of 2.5. After a pretreatment of the Au film-supported PAM template in ethanol by sonication to drive out trapped air inside the holes, electrodeposition was potentiostatically carried out at -0.3, -0.5, and -0.7 V vs SCE, for 15 min. After electrodeposition, the mesostructures were released from the PAM by dissolving the template in 0.1 M NaOH and then washing several times with deionized water till a neutral pH, followed by a final washing with ethanol. Different structures were subsequently separated from nanorods by centrifugation at 2000 rpm and for each case, almost 90% purity was obtained by this way.

3.2.3. Procedure for the Investigation of Electrocatalytic Activity

In order to investigate the electrocatalytic activity of Pt mesostructures, the working electrode was prepared as follows: 20 wt % Pt mesostructured sample was dispersed well in Vulcan XC -72 carbon (C) using isopropyl alcohol and dropcast to form a thin film on a glassy carbon electrode (ca. 3 mm diameter) using 0.5 wt% Nafion binder and was dried well. A similar procedure was adopted to prepare the electrode of commercial platinized carbon (20 % Pt on Vulcan XC-72 carbon from Arora Matthey Ltd.; diameter = 8 nm) with the same amount.

Cyclic voltammogram (CV) of Pt mesostructures dispersed in Vulcan carbon (Pt/C-mesostructure) was first recorded in 0.5 M H₂SO₄, and the electroactive area (Aₑ) was determined from the adsorption/desorption charge of hydrogen measured from CV (ca. 210 μC/cm² for a polycrystalline surface). Further, to measure the electrocatalytic activity of these structures toward formic acid oxidation, the following procedure was adopted: Cyclic voltammogram and transient current-time curve for formic acid oxidation were recorded in a mixture of 0.25 M HCOOH and 0.5 M H₂SO₄ and the response was studied at various potentials ranging from -0.44 V to +0.16 V vs Hg-Hg₂SO₄ at an interval of 0.05 V for a period of 60 s. Further, the current density (j) was obtained after
normalizing the current to $A_{Pt}$. Before recording the current transients, sufficient care was taken to oxidize any existing adsorbate on the electrode surface so as to obtain a clean surface. Similarly, methanol oxidation was performed in a mixture of 0.5 M CH$_3$OH and 0.5 M H$_2$SO$_4$ whereas, ethanol oxidation was studied in a mixture of 0.1 M C$_2$H$_5$OH and 0.1 M HClO$_4$ using a similar procedure. All experiments were also repeated using commercial platinized carbon (Pt/C).

3.2.4. Structural and Morphological Characterization

3.2.4.1. X-ray Diffraction (XRD)

XRD studies were performed in order to understand the crystallinity and also to evaluate the orientation of mesostructures using CuK$_\alpha$ ($\lambda = 1.5405$ Å) radiation on a Panalytical XPert Pro diffractometer. Diffraction patterns were collected at a step of 0.02° (2$\theta$) and the background was subtracted with the linear interpolation method. Samples were prepared by making thin films on glass substrates.

3.2.4.2. X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were carried out on a VG MicroTech ESCA 3000 instrument at a pressure of $>1 \times 10^{-9}$ Torr (pass energy of 50 eV, electron takeoff angle 60°, and overall resolution ~1 eV) using monochromatic Mg K$\alpha$ (source, $h\nu = 1253.6$ eV). The core level spectrum of the Pt 4f orbital was recorded with an overall instrumental resolution of ~1 eV and the binding energies (BE) were aligned taking the adventitious carbon BE as 285 eV. The spectra were fitted using a combined polynomial and Shirley type background function.

3.2.4.3. Scanning Electron Microscopy (SEM)

The morphology of platinum mesostructures was examined using a scanning electron microscope and the instrumentation details have already been discussed in Chapter 2,
A little amount of sample was dispersed in ethanol and drop-casted on Cu substrate and dried at room temperature.

### 3.2.4.4. Electrochemical Measurements

All electrochemical experiments were performed on an Autolab PGSTAT30 (Ecochemie) instrument. For electrodeposition, a saturated calomel electrode (SCE) and a Pt foil were used as reference and counter electrodes respectively. For the electrocatalytic study, a glassy carbon electrode modified with mesostructure/C (mesostructure dispersed in Vulcan carbon) was used as the working electrode (section 3.2.3). Also, Hg-Hg$_2$SO$_4$ and a platinum foil served as the reference and counter electrodes, respectively.

### 3.3. Results and Discussion

#### 3.3.1. SEM Analysis

A comparison of the scanning electron micrographs of different shaped Pt mesostructures prepared at various potentials after complete removal of the template is shown in figure 3.1. Interestingly, the image of potentiostatically formed platinum structures at -0.7 V (corresponding to diffusion-limited region in the current-potential curves) shows a distribution of multipods as revealed in figure 3.1a, where the number of arms of each multipod is more than 6, having a common origin with almost the same length (ca. 500 nm). Most of the arms have uniform width (ca. 100 nm), whereas some of the branches are formed by the assembly of nanometer sized rods. It is instructive to compare the present electrochemical route for the formation of Pt multipods with those reported by Yang et al. from organometallic precursors like Pt 2,4-pentanedionate in the presence of a trace amount of Ag acetylacetonate at around 200 °C.\^3 External nucleating agents (Ag salt) has been used here to trigger the formation of platinum multipods of much smaller size, in contrast to our case, where the formation of multipods is achieved exclusively by templated electrodeposition without the assistance of any additive.
Figure 3.1. (a) - (c) SEM images of platinum mesostructures revealing multipods of platinum prepared potentiostatically at -0.7 V (a), disc shaped structure at -0.5 V (b) and hexagonal structure at -0.3 V (c), after etching the alumina membrane in 0.1 M NaOH; scale bar 1 µm.

When templated electrodeposition is carried out at a moderate overpotential (mainly corresponding to the activation polarization region of the current-potential curve) different shapes of Pt structures arise. For example, accurate maintenance of potential at -0.5 V generates disc-shaped mesostructures (diameter ca. 2 µm) as illustrated in figure 3.1b. A close examination of the image, however, reveals that the surface of the disc is not uniform, perhaps because of some involvement of mass transfer effects since the overpotential is about ca. -0.4 V ($E_{eq}$ is -0.1 V). In comparison, electrodeposition at -0.3 V (close to equilibrium potential) predominantly gives hexagons, as shown in figure 3.1c, where the edge length varies from 0.5 µm to 1 µm. In addition to these mesostructures, nanorods of platinum are also obtained, as usually expected from template synthesis. Thus we could observe multipods of Pt at potential regions far away from the equilibrium, hexagonal shaped structures at regions close to equilibrium, and disc-like
structures at intermediate potential regions along with Pt nanorods in all cases, thus illustrating the importance of competition between charge transfer and diffusion. Thus it could be surmised that diffusion limited aggregation favours multipod/fractal formation while kinetic control generates hexagons and discs.

3.3.2. Current–time Transients

To understand the nucleation and growth mechanism of such uniquely shaped mesostructures we have analyzed the current transients after polarizing the electrode at various potentials as shown in figure 3.2(a-f). Current-time response is measured after stepping the potential from the equilibrium value to -0.3 (a), -0.5 (c), and -0.7 V (e) respectively. On stepping the potential from the equilibrium value, the current first increases instantaneously to a maximum ($I_{\text{max}}$), followed by a slow exponential decay. Further, a comparison of $I_{\text{max}}$ at three different overpotential shows a direct correlation of the magnitude of $I_{\text{max}}$ thus establishing a vital link in controlling the morphology of Pt mesostructures during electrodeposition.
Figure 3.2. Current transients for different potential steps -0.3, -0.5 and -0.7 V revealed in figure (a), (c) and (e) and the inset shows the corresponding I vs t^{1/2} plots; three different zones involved during current transients are clearly shown in (b), (d) and (f) respectively.

For the convenience of analysis, three different zones can be distinguished in all these I-t transients as illustrated in figure (b), (d), and (f). For example, zone 1 reveals an exponential decrease (in few seconds) after an instantaneous rise in current which is
attributed to the effect of double layer charging while zone II corresponds to the
deposition of the metal into the pores of the template since the current variation is less
prominent. Here, soon after the initial nuclei formation on the bottom of the pore (i.e., on
the cathode surface which in our case is gold), the growth proceeds via a two-
dimensional nucleation involving a layer-by-layer growth mode.\(^{34}\)

I-t transients in zone III result from an increase in the deposition area that occurs
when the pores are completely filled with the metal and the deposition begins on the
surface of the membrane. It is this region which is extremely critical to regulate various
shapes depending on the overpotential variation. Finally, almost a steady-state behavior is
achieved when the deposition of metal saturates the surface where the limiting current is
achieved by the increased overpotential. We have analyzed the rising part of the transient
curve (zone III) at three different potentials to check whether the nucleation process
occurs by an instantaneous or a progressive mechanism (inset of Figure a, c, and e). The
linearity observed using the experimental data for I vs \(t^{1/2}\) suggests that an instantaneous
nucleation mechanism is valid in all cases.\(^{35}\) However, there is a slight deviation from
linearity, perhaps arising from the presence of pores responsible for changes from ideal
Cottrell diffusion (valid mainly for planar surfaces with linear semi-infinite diffusion
conditions); shape asymmetry and edge effects could also possibly contribute to this
deviation.

3.3.3. XRD Analysis

To understand the crystal structure and preferential growth direction of these
mesostructures, powder XRD is very helpful and accordingly figure 3.3 shows a
comparison of XRD pattern of Pt/C-hexagons, Pt/C-discs, Pt/C-multipods and Pt/C which
reveals the formation of a cubic structure with high crystallinity. All diffraction peaks,
(111), (200), and (220) match well with Bragg reflections of the standard and phase-pure
face centered cubic (fcc) structure of Pt. Also the XRD pattern reveals no change in the
peak position for three different mesostructures as compared to that of Pt multipods
reported by Yang et al.\textsuperscript{36} A comparison of the intensity ratio of $I_{(111)}/I_{(200)}$ and $I_{(200)}/I_{(220)}$ reveals that the intensity ratio of the former is higher for hexagons whereas the latter one is higher for multipods (vide infra). Apart from the response corresponding to Pt, a broad peak at $2\theta = 25^\circ$ is associated with the (002) planes of Vulcan XC-72 carbon, which is the support.

![XRD pattern comparison](image)

**Figure 3.3.** A comparison of XRD pattern of different morphology platinum mesostructures dispersed in vulcan carbon; all these diffraction peaks match well with the corresponding peaks of fcc structure of bulk platinum; figure also includes XRD pattern of commercial platinized carbon (Pt/C).

### 3.3.4. XPS Analysis

Information on the oxidation state of different shaped platinum mesostructures is provided by the XPS analysis, and accordingly a comparison of the XP spectra of Pt-multipods, Pt-disc, and Pt-hexagon is shown in figure 3.4(a-c). Figure (a) shows the Pt 4f region of Pt-multipods, where, deconvolution of the peak reveals two signals at 71.1 eV and 74.3 eV (after carbon correction) corresponding to Pt 4f\textsubscript{7/2} and 4f\textsubscript{5/2} respectively.\textsuperscript{37} These values confirm that platinum multipod exists in metallic state with a typical peak to
peak separation of ca. 3 eV, in agreement with that of bulk platinum metal. In addition, XP spectra of Pt-disc and Pt-hexagon (figure b, and c), also reveal similar binding energy values as observed for Pt-multipods, which again supports the existence of Pt(0) oxidation state.

![Figure 3.4. X-ray photoelectron spectra of Pt (a) multipod, (b) disc, and (c) hexagon where, Pt 4f core level is deconvoluted using Shirley software; circles represent the raw data while triangles represent the fitted data for the overall signal; dash lines indicate the background, whereas the solid lines represent the deconvoluted individual peaks.](image)

All the above results indicate the importance of electric field modulation through the pores of PAM as a primary reason for the shape variation for these electrodeposited Pt particles after the template removal. This, of course, assumes that template removal by leaching has no effect on the shape of these Pt particles. Accordingly, Scheme 3.1 conveniently depicts a comparison of the shape modulation during the potentiostatic
electrodeposition of these structures followed by the release after a complete dissolution of the PAM membrane with sodium hydroxide. Similar shape modulation accomplished by various capping agents in colloidal synthesis suggests that the electric field plays a key role in tuning the shape similar to perhaps the role of concentration of capping agents.\textsuperscript{38,39,13} For example, hexagonal shaped mesostructures with the lowest specific surface energy appear at a low overpotential (-0.3 V) whereas multipods with high specific surface energy require high overpotential (-0.7 V) for their formation. Hence, by changing the applied potential of the cathode, it is possible to tune different shapes of electrodeposited mesostructures as illustrated in this case. Observation of these various shapes at different applied potentials is in close agreement with the results of Xiao et al., where different morphological particles at applied potentials close to the equilibrium value and high aspect ratio structures, such as nanowires, nanobrushes, and multipods at high overpotentials, have been obtained on HOPG surfaces.\textsuperscript{26}

\begin{scheme}
\centering
\includegraphics[width=\textwidth]{scheme3.1.png}
\caption{Electric field dependent, morphological evolution of platinum mesostructures using PAM. (i) PAM with one side evaporated with Au film for electrical contact; (ii) formation of hexagonal, disc and multipod structures of Pt over alumina membrane at potentials -0.3, -0.5 and -0.7 V respectively; (iii) desolution of the membrane in 0.1 M NaOH and the release of different morphology platinum mesostructures along with the nanorods.}
\end{scheme}
3.3.5. Electrocatalytic Activity of Platinum Mesostructures toward Formic acid, Ethanol, and Methanol Oxidation Reactions

While hydrogen as a primary fuel in a polymer electrolyte membrane fuel cell (PEMFC) allows higher energy efficiency to be obtained, its production and storage are expensive since it require either on-site H₂ storage or an onboard reformer to extract H₂ from organic fuels. As a result, extensive research has been launched into the development of direct liquid fuel cells. In liquid fuels, mainly methanol, ethanol, and formic acid are employed, since they are abundant, inexpensive and can be easily handled, stored, transported. Their theoretical mass energy density is also high (for example energy density of methanol and ethanol are 6.1 and 8.0 kWh/kg respectively). However, the electrooxidation kinetics of these organic molecules is very subtle and greatly sensitive to the surface structure leading to a dramatic variation with size, shape and nature of the electrode material. In the following section, we report the results of a comparative study of the electrocatalytic performance of different shaped platinum mesostructures such as multipods, discs and hexagons toward the electrooxidation of formic acid, ethanol, and methanol which, are promising reactions for microfuel cells.

3.3.5.1. Formic Acid Oxidation

The overall reaction involved in the irreversible electrooxidation of formic acid to CO₂ on Pt surface could be written as

\[
HCOOH \rightarrow CO_2 + 2H^+ + 2e^- \quad \text{(3.1)}
\]

\[E^0 = -0.25 \text{ V vs NHE}\]

The electrooxidation of HCOOH to CO₂ on a Pt surface proceeds via a dual path mechanism, which involves a reactive intermediate (main path, dehydrogenation) and adsorbed CO as a poisoning species (parallel path, dehydration). The reactive intermediate during the main path is adsorbed formate, which has been confirmed using surface enhanced infrared reflection absorption spectroscopy (SEIRAS).\(^\text{40}\)
Figure 3.5 compares cyclic voltammetric response of different shaped platinum mesostructures toward formic acid oxidation at 50 mV/s in a mixture of 0.5 M H₂SO₄ and 0.25 M HCOOH where all samples reveal the characteristic features of formic acid oxidation. Because of the substrate effect (initial effects) variations in the first cycle, we show here only the second cycle, as a representative example although current corresponding to CO oxidation progressively increases with the cycle. The voltammetric response of Pt/C is also shown in figure 3.5. The voltammograms show two peaks during the anodic scan (at -0.07 and 0.72 V for Pt/C-hexagon) while only one peak (-0.15 V for Pt/C-hexagon) is observed during the reverse (cathodic) scan. A slight change in peak position is observed for different electrodes, as obvious from the voltammogram.

It has been widely accepted that formic acid is oxidized to CO₂ via a dual path mechanism, which involves a reactive intermediate (main path, dehydrogenation) and adsorbed CO as the poisoning species (parallel path, dehydration). Hence, all the noticeable current can be attributed to the oxidation of formic acid and/or CO to CO₂. The first anodic peak is due to oxidation of HCOOH to CO₂ on unblocked surface sites whereas the second anodic peak corresponds to the oxidation of adsorbed CO (peak current slightly increases on cycling). During the cathodic sweep, a peak is observed after the partial reduction of irreversibly formed surface oxides, which represents the real catalytic activity of the Pt surface. Interestingly, a close examination of the ratio of area under the first and second anodic peak reveals that charge consumed due to the oxidation of HCOOH to CO₂ is higher compared to that for CO to CO₂, in contrast to the earlier reports. We have calculated this ratio for different shapes of Pt structures, which shows the following order: Pt/C-hexagon > Pt/C-multipod > Pt/C-disc > Pt/C. Hence, it is clear that compared to Pt/C our Pt mesostructures show higher activity for HCOOH oxidation to CO₂ than that to CO₂, perhaps due to significantly less CO poisoning on Pt mesostructures. In addition, the peak during the cathodic sweep corresponding to the real catalytic activity of the Pt surface almost retraces the first anodic peak as seen from the voltammogram, which clearly confirms less CO adsorption. Interestingly, a comparison of the peak currents of these different electrodes reveal significant change as follows:
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Pt/C-hexagon > Pt/C-multipod > Pt/C-disc > Pt/C. (Current has been normalized to the electroactive Pt surface area, $A_{Pt}$). In addition to the above observed features, a comparison of the voltammetric response of Pt/C and mesostructures/C reveals that the hydrogen adsorption/desorption features of the latter are significantly smaller than that of the former. This is presumed to be due to the blocking of some of the active sites for hydrogen adsorption by carbon or may be due to the poor dispersion of the mesostructures in carbon.

![Figure 3.5. Cyclic voltammetric response (2nd cycle data) of Pt/C-multipod, Pt/C-disc, Pt/C-hexagon and Pt/C towards formic acid oxidation at 50 mV/s in a mixture of 0.25 M HCOOH and 0.5 M $\text{H}_2\text{SO}_4$ is shown.](image)

Figure 3.5. Cyclic voltammetric response (2nd cycle data) of Pt/C-multipod, Pt/C-disc, Pt/C-hexagon and Pt/C towards formic acid oxidation at 50 mV/s in a mixture of 0.25 M HCOOH and 0.5 M $\text{H}_2\text{SO}_4$ is shown.

Figure 3.6a-d shows the voltammogram of Pt/C-multipod, Pt/C-disc, Pt/C-hexagon, and Pt/C at different scan rates where a shift in peak position with scan rate is observed, as expected for an irreversible charge transfer process. However, the variation
of peak current with scan rate reveals a slight deviation from linearity. This type of non-
linearity in the variation of peak current with scan rate was reported by Matsuda et al.\textsuperscript{43} for an irreversible systems, and explained in terms of a parameter ‘\( \Lambda \)’, which is a quantitative measure of reversibility, being effectively the ratio of the kinetics of charge transfer to the mass transfer. For an irreversible reactions, the value of ‘\( \Lambda \)’ is rather smaller as compared to that of a reversible one.

Figure 3.6. Superimposed cyclic voltammetric response of (a) Pt/C-multipod, (b) Pt/C-disc, (c) Pt/C-hexagon and (d) Pt/C toward formic acid oxidation at different scan rates; inset shows the plot of \( I_p \) vs \( \sqrt{v} \) of the respective electrodes.
Figure 3.7 shows a comparison of current–time transients of formic acid oxidation at -0.09 V (potential selected from cyclic voltammogram) on the Pt/C, Pt/C-multipod, Pt/C-disc, and Pt/C-hexagon at room temperature after normalizing the current with respect to the electroactive Pt surface area (Ap). Interestingly, the current density on Pt/C-hexagon is significantly higher compared to that on other structures and the order is as follows: Pt/C-hexagon > Pt/C-multipod > Pt/C-disc > Pt/C. The enhancement factor $R$, which is defined as the ratio of the current density on Pt/C-hexagon versus that acquired on Pt/C, ranges up to 2000% whereas for Pt/C-multipods versus Pt/C it is up to 700% and for Pt/C-disc versus Pt/C the value ranges up to 300% respectively, depending upon the electrode potential. Similar shape dependent studies carried out Wang et al. for tetrahedral platinum nanocrystals towards formic acid oxidation reveals only 400% and 310% enhancement respectively for Pt nanospheres and Pt/C catalyst.\textsuperscript{44}

![Figure 3.7](image_url)

Figure 3.7. A Comparison of the catalytic activity of Pt/C-multipod, Pt/C-disc, Pt/C-hexagon and Pt/C towards formic acid oxidation as revealed in the current-time transients at a potential of -0.09 V for 60 s.
Steady-state current density from the I-t transients (corresponding to various potentials, -0.44 V to +0.16 V) for formic acid oxidation is plotted against each respective potential in figure 3.8 in order to compare their current density (j). A comparison of the j at a given potential (-0.1 V) for different mesostructures of Pt and Pt/C clearly illustrates superior electrocatalytic properties of Pt hexagons. For example, the current density on Pt/C-hexagon, Pt/C-multipod, Pt/C-disc, and Pt/C structures for formic acid oxidation at -0.1 V are $3.62 \times 10^3$, $1.35 \times 10^3$, $6 \times 10^2$, and $1.9 \times 10^2$ A/cm$^2$, respectively. In each case, a well-defined volcanic plot is observed, with a maximum near -0.04 V and with decrease in the current density successively at both sides of this potential. The drop in the catalytic performance at lower potentials, may be ascribed to the decrease in the electrochemical driving force that favours the oxidation reaction whereas the deactivation at potentials higher than the platinum oxidation threshold should be attributed to the (bi)sulphate interactions and also due to the oxide formation.\textsuperscript{31}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.8.png}
\caption{Potential-dependent steady state current density of formic acid oxidation on Pt/C-multipod, Pt/C-disc, Pt/C-hexagon and Pt/C, where all the electrodes show maximum activity at -0.04 V.}
\end{figure}
In order to measure the exchange current density \( j_0 \) towards formic acid oxidation, Tafel polarization studies have been carried out in acid electrolytes using these mesostructures dispersed in C as working electrodes. Accordingly, a plot of log \( j \) versus overpotential (\( \eta \)) for three different Pt structures and for Pt/C is shown in figure 3.9a-d, facilitating the estimation of exchange current density from the intercept. Since \( j_0 \) is a direct measure of the electron-transfer kinetics at the interface at equilibrium conditions a summary of these values in Table 3.1 is very useful to compare the electrocatalytic properties. For example, \( j_0 \) is slightly higher for the Pt/C-hexagon electrode than that of the Pt/C-multipod, and Pt/C-disc electrodes and Pt/C which could be explained based on the results of other studies.

![Figure 3.9](image)

**Figure 3.9.** A comparison of Tafel Plot for formic acid oxidation on Pt/C-multipod, Pt/C-disc, Pt/C-hexagon and Pt/C under galvanostatic conditions in a mixture of 0.25 M HCOOH and 0.5 M H\(_2\)SO\(_4\).
Table 3.1. A summary of exchange current density of Pt/C-multipod, Pt/C-disc, Pt/C-hexagon and Pt/C toward formic acid, ethanol and methanol oxidation estimated from the intercept of Tafel plots based on Figure 3.9.

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>Exchange Current Density (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Formic acid oxidation</td>
</tr>
<tr>
<td>Pt/C</td>
<td>$8 \times 10^{-6}$</td>
</tr>
<tr>
<td>Pt/C-Multipod</td>
<td>$1.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>Pt/C-Disc</td>
<td>$10 \times 10^{-6}$</td>
</tr>
<tr>
<td>Pt/C-Hexagon</td>
<td>$3 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

It is clear that Pt/C-hexagon shows better catalytic activity compared to that of Pt/C-multipod, Pt/C-disc, and Pt/C, for formic acid oxidation. Increase in the rate of electrocatalytic activity has been well studied by means of foreign ad-atoms and anion effects. However, any increase in current density due to the presence of foreign ad-atoms could be neglected in our case since we have not used any foreign ad-atoms. Similarly since the electrocatalytic activity has been studied for all electrodes in the same electrolyte, it is unlikely that the contribution from anion effects is significant. More interestingly, our observation could be correlated with the structural data obtained from XRD results especially because all samples show higher intensity of the (111) crystallographic plane compared to that of the (200) and (220) planes. In addition, the structural effect on formic acid oxidation has been well studied to confirm less CO poisoning on (111) planes. Since for all our samples, (111) plane is highly intense, the oxidation of HCOOH to CO₂ is favored during the positive scan with poor CO adsorption features. Further, in close examination of the intensity ratio of Pt(111)/Pt(200), it is obvious that this ratio varies as follows: Pt/C-hexagon > Pt/C-multipod > Pt/C-disc > Pt/C. Thus,
the Pt/C-hexagon shows higher activity toward formic acid oxidation compared to that of Pt/C-multipod, Pt/C-disc, and Pt/C, respectively. This is in excellent agreement with other reports on the electrocatalytic activity of Pt\(_{(111)}\) planes for formic acid oxidation where the highest activity during the anodic scan is observed for the (111) plane.\(^{46}\) Hence, from the above observation, we conclude that one of the possible reasons for varying the reactivity of different shapes of platinum mesostructures is the difference in the intensity ratio of various crystallographic planes present in the sample.

3.3.5.2. Ethanol Oxidation

The overall reaction involved in the electro-oxidation of \(\text{C}_2\text{H}_5\text{OH}\) to \(\text{CO}_2\) on Pt electrode surface could be written as

\[
\text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \quad \ldots \quad (3.2)
\]

\(E^0 = 0.08\ \text{V vs NHE}\)

Electrooxidation of ethanol to \(\text{CO}_2\) is a very complex reaction associated with the cleavage of the C-C bond, which requires higher activation energy than C-H breaking. The reaction is known to proceed via a multistep mechanism, involving a number of adsorbed intermediates and by products resulting from incomplete ethanol oxidation such as adsorbed CO and C-1 and C-2 hydrocarbon residues. Since, the breaking of C-C bond for the total oxidation to \(\text{CO}_2\) is a difficult task, partial oxidation products such as \(\text{CH}_3\text{CHO}\) and \(\text{CH}_3\text{COOH}\) also form along with \(\text{CO}_2\). These intermediates and byproducts have been detected using differential electrochemical mass spectrometry (DEMS), infrared spectroscopy, ion chromatography, and liquid chromatography.\(^{47}\)

Figure 3.10 accordingly, shows the overlayed cyclic voltammetric response of different shaped platinum mesostructures (and also commercial Pt/C for comparison) for ethanol oxidation in a mixture of 0.1 M \(\text{C}_2\text{H}_5\text{OH}\) and 0.1 M \(\text{HClO}_4\) at 20 mV/s. These voltammograms show two peaks during the anodic scan (at 0.17 and 0.70 V respectively for Pt/C-multipods), while one peak (at -0.02 V for Pt/C-multipod) is observed during the cathodic scan. The first anodic peak corresponding to the -OH bond formation on Pt
surface, is presumed to play an important role in ethanol oxidation facilitating the cleavage of the C-C bond thus producing CO2 via the strongly adsorbed CO intermediate.\(^{48}\) Also, it is important to point out that not only the strongly adsorbed CO, intermediates with one or two carbon atoms also are formed on Pt surface.\(^{49}\) Further, the second anodic peak is caused by the formation of CO2 and other by-products such as acetic acid and acetaldehyde.\(^{50}\) Interestingly, in the negative-going potential sweep, only one anodic peak appears, which is attributed to renewed oxidation of ethanol. A close examination of these voltammogram reveals a remarkable variation of the peak current for different structures as follows: Pt/C-multipod > Pt/C-disc > Pt/C-hexagon > Pt/C.

![Cyclic Voltammetric response](image)

**Figure 3.10.** Cyclic Voltammetric response (2\(^{nd}\) cycle data) of Pt/C-multipod, Pt/C-disc, Pt/C-hexagon and Pt/C towards ethanol oxidation at 20 mV/s in a mixture of 0.1 M C\(_2\)H\(_5\)OH and 0.1 M HClO\(_4\).

Figure 3.11a-d shows the voltammogram of Pt/C-multipod, Pt/C-disc, Pt/C-hexagon, and Pt/C at different scan rates where a shift in peak position suggests an
irreversible charge transfer. As observed for formic acid oxidation, here also the variation of peak current with scan rate reveals a slight deviation from linearity.

Figure 3.11. Overlayed cyclic voltammetric response of (a) Pt/C-multipod, (b) Pt/C-disc, (c) Pt/C-hexagon and (d) Pt/C toward ethanol oxidation at different scan rates; inset shows the plot of \( I_p \) vs \( V^{1/2} \) of the respective electrodes.

Figure 3.12 shows a comparison of current–time transients of ethanol oxidation at -0.04 V (potential selected from the cyclic voltammogram) on the Pt/C, Pt/C-multipod, Pt/C-disc and Pt/C-hexagon at room temperature. The current density is higher for Pt multipods compared to that for other structures and the activity varies in the following order: Pt/C-multipod > Pt/C-disc > Pt/C-hexagon > Pt/C. This independently confirms the observed trend in the polarization plot. Interestingly, the enhancement factor \( R \),
(which is defined as the ratio of the current density measured on a specific shape versus that acquired on Pt/C spherical structures) varies up to 600% for multipod whereas for Pt/C-disc it is about 500% and for Pt/C-hexagon versus Pt/C about 200% respectively, depending on the electrode potential.

Figure 3.12. Comparison of the current-time transients of Pt/C-multipod, Pt/C-disc, Pt/C-hexagon and Pt/C towards ethanol oxidation at a potential of -0.04 V; inset shows the enlarged view.

A comparison of the steady state current density (obtained from the current transients recorded for 60 s) at different potential is shown in figure 3.13, where we observe that at a given potential, say +0.025 V, the corresponding current density on Pt/C-multipod, Pt/C-disc, Pt/C-hexagon and Pt/C are $2.4 \times 10^{-4}$, $1.7 \times 10^{-4}$, $8.33 \times 10^{-5}$ and $3.8 \times 10^{-5}$ A/cm² respectively.
Figure 3.13. Potential-dependent steady state current density for ethanol oxidation on Pt/C-multipod, Pt/C-disc, Pt/C-hexagon, and Pt/C in a mixture of 0.1 M C₂H₅OH and 0.1 M HClO₄.

Further, to evaluate \( j_o \) corresponding to the ethanol oxidation on these three mesostructures and also on commercial Pt dispersed in C, we have carried out Tafel polarization (figure 3.14 (a-d)), which enables a comparison of the \( j_o \) values as summarized in Table (3.1). The value of \( j_o \) is higher for the Pt/C-multipod electrode than that of the Pt/C-disc, Pt/C-hexagon, and Pt/C perhaps due to the change in the intrinsic rate constant of this reaction.
Thus from the above studies, it is clear that Pt/C-multipod shows better electrocatalytic activity for ethanol oxidation compared to that of Pt/C-disc, Pt/C-hexagon, and Pt/C respectively. Thus present observation could be further explained by the XRD results, using the higher intensity ratio of Pt(200)/Pt(220) for multipods than that for discs, hexagons, and commercial samples. This is in excellent agreement with other reports on the electrocatalytic activity of Pt_{(hkl)} planes for ethanol oxidation, where the activity of different (hkl) planes have been compared for the C-C cleavage involved during the ethanol oxidation and concluded that compared to Pt_{(111)} and Pt_{(220)}, Pt_{(200)} shows higher activity, while the Pt_{(111)} shows least activity.\(^5\)
3.3.5.3. Methanol Oxidation

The overall reaction involved in the electrooxidation of CH$_3$OH to CO$_2$ on Pt electrode surface could be written as

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad \text{.......................................... (3.3)}$$

$$E^0 = 0.02 \text{ V vs NHE}$$

Oxidation of methanol has been thoroughly studied for many years, so that the reaction mechanism is now well established. A variety of surface reactions combined with interfacial irreversible electron transfer occur when methanol decomposes on platinum in acidic media via a dual path mechanism that involves non-CO adsorbed intermediates such as (CH$_2$OH)$_{ads}$, (CHOH)$_{ads}$, (CHO)$_{ads}$ (main path) and adsorbed CO (parallel path). The formation of strongly bound CO$_{ads}$ species and other reactive intermediates have been well established by techniques such as electrochemically modulated infrared reflectance spectroscopy (EMIRS), fourier transform infrared reflectance spectroscopy and liquid or gas chromatography.

In order to explore the shape-dependent electrocatalytic activity of these Pt mesostructures towards methanol oxidation the corresponding cyclic voltammetric response in a mixture of 0.5 M CH$_3$OH and 0.5 M H$_2$SO$_4$ at 20 mV/s is shown in figure 3.15. The voltammetric response corresponding to Pt/C is also included for comparison. The voltammograms show two peaks during the anodic scan (at 0.14 and 0.75 V for Pt/C-hexagon), while one peak (at -0.01 V for Pt/C-hexagon) is observed in the cathodic scan. The first step in the reaction (peak 1) is the adsorption of the methanol molecule, immediately followed by its dissociation into several adsorbed species such as Pt(CH$_2$OH)$_{ads}$, Pt(CHOH)$_{ads}$, Pt(CHO)$_{ads}$ and Pt(CO)$_{ads}$. The second anodic process (peak 2) is caused by the oxidation of these adsorbed species by -OH generated from the dissociation of H$_2$O molecule. During the cathodic sweep, a peak is observed (peak 3) after partial reduction of irreversibly formed surface oxides, which represents the real catalytic activity of the Pt surface. Further, a close examination of these voltammogram
reveals an interesting variation of the peak current for different structures as follows: Pt/C-hexagon > Pt/C-multipod > Pt/C-disc > Pt/C.

![Cyclic Voltammetric response](image)

Figure 3.15. Cyclic Voltammetric response (2<sup>nd</sup> cycle data) of Pt/C-multipod, Pt/C-disc, Pt/C-hexagon and Pt/C towards methanol oxidation at 20 mV/s in a mixture of 0.5 M CH<sub>3</sub>OH and 0.5 M H<sub>2</sub>SO<sub>4</sub>.

A superimposed cyclic voltammogram of Pt/C-multipod, Pt/C-disc, Pt/C-hexagon, and Pt/C at different scan rates is shown in figure 3.16, where a shift in the peak position with scan rate is observed, as expected for an irreversible charge transfer process. As observed for the above two reactions, here also the variation of peak current with scan rate reveals a slight deviation from linearity.
Figure 3.16. Overlayed cyclic voltammetric response of (a) Pt/C-multipod, (b) Pt/C-disc, (c) Pt/C-hexagon and (d) Pt/C toward methanol oxidation at different scan rates; inset shows the plot of $I_p$ vs $\nu^{1/2}$ of the respective electrodes.

Figure 3.17 shows a comparison of the current–time transients of methanol oxidation at -0.09 V (potential selected from cyclic voltammogram) on the Pt/C, Pt/C-multipod, Pt/C-disc, and Pt/C-hexagon at room temperature after normalizing the current with respect to the electroactive Pt surface area ($A_{Pt}$). Interestingly, the current density on Pt/C-hexagon is significantly higher compared to that on other structures as per the order: Pt/C-hexagon > Pt/C-multipod > Pt/C-disc > Pt/C. The enhancement factor $R$, (which is defined as the ratio of the current density measured on a specific shape versus that
acquired on Pt/C spherical structures) is 750% for hexagons whereas for Pt/C-multipods and discs show 450% and 350% respectively, depending upon the electrode potential.

Figure 3.17. Comparison of the catalytic activity of Pt/C-multipod, Pt/C-disc, Pt/C-hexagon and Pt/C towards methanol oxidation in terms of current-time transients at a potential of -0.09 V for 60 s.

Steady-state current density (j) from the I-t transients (for various potentials, -0.2 V to +0.4 V) corresponding to methanol oxidation is plotted against respective potential in figure 3.18 which clearly illustrates superior electrocatalytic properties of Pt hexagons (at +0.1 V) than that of other structures of Pt and Pt/C. For example, the current density on Pt/C-hexagon, Pt/C-multipod, Pt/C-disc, and Pt/C structures for methanol oxidation at +0.1 V are 9 x 10^-4, 7 x 10^-4, 5 x 10^-4 and 1.8 x 10^-4 A/cm², respectively. Moreover, the exchange current density from Tafel polarization (figure 3.19) of these mesostructures dispersed in C toward methanol oxidation is summarized in Table 3.1, which reveals a slightly higher value for the Pt/C-hexagon electrode than that of the Pt/C-multipod, Pt/C-disc, and Pt/C respectively.
Figure 3.18. Potential-dependent steady state current density of methanol oxidation on Pt/C-multipod, Pt/C-disc, Pt/C-hexagon, and Pt/C.

Figure 3.19. Tafel Plots for the methanol oxidation on Pt/C-multipod, Pt/C-disc, Pt/C-hexagon and Pt/C electrodes in 0.5 M CH₃OH and 0.5 M H₂SO₄.
Thus from the above observations, it is clear that Pt/C-hexagons show better
electrocatalytic activity compared to that of Pt/C-multipod, Pt/C-disc, and Pt/C for
methanol oxidation. Similar to the case of formic acid and ethanol oxidations, the
reactivity order could be explained based on the XRD results, where the intensity ratio of
Pt\textsubscript{111}/Pt\textsubscript{200}, is higher for hexagon than that for multipod, disc, and commercial sample.
This is in excellent agreement with other reports on the electrocatalytic activity of Pt\textsubscript{(hkl)}
planes for methanol oxidation, where the activity increases in the sequence, Pt\textsubscript{200}<
Pt\textsubscript{220}< Pt\textsubscript{111}.\cite{46a,53} This could be attributed to the fact that during methanol oxidation,
the adsorbed OH from H\textsubscript{2}O molecule acts as the reactant necessary for the oxidation of
adsorbed species on the Pt surface. Tripkovic et al. have correlated the onset potential of
OH\textsubscript{ads} and CH\textsubscript{3}OH oxidation on different crystallographic planes of Pt and observed that
for (111) plane, the initials potentials of OH\textsubscript{ads} is close to the onset of methanol oxidation
compared to that of (220) and (200) planes and as a result, methanol oxidation
commences firstly on (111), then on (220) and finally on the (200) plane.\cite{53}

Present approach for the formation of different shapes of platinum mesostructures
has many intrinsic benefits over the earlier reported morphological control on planar
electrode surfaces\cite{26-28} because, in all these prior cases electric field has been applied on a
flat conducting substrate and hence the continuous field gradient existing at the electrode-
electrolyte interface (double layer) along with the mass transfer gradients in the diffusion
layer is presumably responsible for the morphology. However, if the electric field could
be confined in various regions due to the lateral surface heterogeneity rendered by filling
the pores of PAM with a metal and the presence of insulating barriers of the electrode
surface offers an anisotropic electric field. This anisotropic electric field would be more
useful to have a directional control of nucleation and growth and accordingly the use of
PAM is expected to cause a discontinuous distribution of electric field at the interface.
Also, the findings regarding the electrocatalytic activity of different shaped Pt
mesostructures towards both formic acid and ethanol oxidation would be important to
fuel cell development work, since the anchoring of different shaped mesostructures on
vulcan carbon can be used to control their electrocatalytic activity. In addition, the present approach is especially important because these structures are generated without the assistance of any surfactants/ capping agents, which could adversely affect the electrocatalytic activity for many reactions. However, since the template is usually a thin membrane, it is difficult to scale-up the nanostructure grown through this hard template method to macroscopic quantities. Moreover, the high cost and limited supply of Pt are still rather prohibitive for full exploitation of fuel cell technology and as a result efforts are concentrated on to replace it with less expensive metals, while retaining the activity at least equal to that of platinum.

### 3.4. Conclusions

Present chapter demonstrates a unique method for controlling the shape of platinum mesostructures by templated electrodeposition facilitating their potential dependent morphological evolution. Comparison of the electrocatalytic activity for formic acid and methanol oxidation of these structures reveal that the hexagons of platinum is a better electrocatalyst than multipods, disc and commercial platinized carbon, whereas for the ethanol oxidation the activity is higher for multipods compared to that of discs, hexagons and commercial platinized carbon, which is further strengthened by the XRD results. The approach developed in this work could serve as an efficient and reliable way of tuning the morphology (and hence shape-dependent properties) of platinum mesostructures facilitating their potential applications as multifunctional catalysts for many industrial processes, and most interestingly, it plays a central role for energy conversion, particularly in the polymer electrolyte fuel cells. More significantly since this method of shape tuning is very general, we believe that this could be extended to a variety of other metallic and semiconducting nanostructures using hard templates and suitable electrodeposition strategies.
3.5. References


