Y-junction Nanostructures of Platinum and Palladium
Using Hierarchically Designed Alumina Templates*

The utility of hierarchically designed alumina templates for the shape-selective preparation of platinum Y-junction nanostructures through electrodeposition is demonstrated in this chapter. Although these Y-junctions have typical diameters of the stem and branches as 100 nm and 50 nm respectively, it is indeed, possible to tune both these parameters by controlling the template design strategies. This chapter also describes our efforts using similarly designed alumina templates for the formation of Y-junction nanostructure of palladium possessing stem and branches having diameter 200 and 110 nm, respectively through a chemical vapour deposition. When the electrocatalytic performance of Pt Y-nanostructures is compared with that of commercial platinized carbon, towards formic acid oxidation, these junctions exhibit enhanced activity (up to 270 %), whereas for methanol and ethanol oxidation, the enhancement is up to 680 % and 180 % respectively. With respect to Pt nanowires, however, these Y-junctions show 200 % enhancement for formic acid oxidation while 400 % and 130 % are seen for methanol and ethanol oxidations respectively. In the end of this chapter we also demonstrate the usefulness of Pd Y-junctions as an alternative catalyst to Pt for formic acid oxidation where, about 1000 % better relative activity is seen. Apart from the obvious applications in developing electrocatalytic anodes for micro-fuel cells, these Y-junction nanostructures have several other promising applications such as interconnects in many molecular scale electronic devices like single electron transistors, resonant tunnelling diodes, and molecular rectifiers.

*A part of the work discussed in this chapter has been published in “Chem. Mater. 2008, 20, 601”.
5.1. Introduction

Recently, much effort has been directed towards the fabrication of shape selective nanostructures because of their exquisite size and shape dependent properties and also their technological relevance in diverse areas such as catalysis, photochemistry, chemical sensors and optoelectronics. These nanostructures are generally synthesized in many forms including highly monodispersed spherical nanoparticles on one hand, to several anisotropic nanostructures such as wires/rods, tubes and ribbons. It is generally accepted that the morphology of a nanostructure could be remarkably tuned during the synthesis by controlling pertinent parameters such as temperature, nature of surfactant, metal ion to capping molecule ratio, and the concentration of other additives in order to control the physical and chemical properties of these materials. As a result, various methods have been developed to generate many of these nano level architectures with relatively good shape control. Among these, the template-assisted route has been one of the widely investigated and exploited approaches, because it provides several distinct advantages over other approaches. More importantly, it offers a convenient route to control precisely the dimension of the nanostructures and these structures can be released easily from the support. Templates that can be used include soft (such as micelles) as well as hard (such as porous polymeric or ceramic membranes) templates. In particular, hard templates, like porous alumina membranes (PAM) have been extensively used due to many desirable characteristics, including tunable pore dimensions and lengths, good mechanical and thermal stability, and well developed fabrication methods. Even though, processing inside these type of porous templates is ideal to produce uniform morphologies, this route has been accomplished to date successfully, only for linear structures.

Interestingly, the fabrication of three terminal morphology like Y-junctions has drawn widespread attention considering their technological importance in advanced molecular-scale electronic devices and prospective applications in catalysis.
example, electron transport across multi-terminal junctions like Y, T, and X nanostructures is non-linear revealing interesting rectifying behavior at room temperature which, could be used for many efficient nanoelectronic devices. For example, Papadopoulos et al. have investigated the electron transport behavior of carbon nanotube Y-junctions to demonstrate intrinsic non-linear transport facilitating rectifying behavior at room temperature. However, the fabrication of these junctions is difficult using conventional methods because these linear structures cannot be controllably altered along their length. Although, much effort has been devoted to the fabrication of junction type nanostructures, the main attention, to date, has been focused mainly on Y-junctions of carbon nanotubes. For example, Rao et al. and others have synthesized Y-junctions of carbon nanotubes by a chemical vapor deposition route using a suitable metal catalyst, which facilitates the nucleation of junctions/branches. However, no metallic Y junction has been reported for metals such as Pt and Pd despite their theoretical and practical importance.

In chapter four, we have discussed the potentiostatic synthesis of nanoneedles of RuO$_2$ using linear PAM to indicate their unique electron transport behaviour. In comparison, here we demonstrate the utility of hierarchically designed PAM templates for the fabrication of Y-shaped platinum nanostructures through a similar electrodeposition route. Platinum has been selected because of its outstanding role as multifunctional catalysts in many industrial applications, particularly in fuel cells. Apart from this, the fabrication of Y-branched nanostructures of other catalytically active metals such as palladium is also discussed by extending a similar template-assisted approach, although chemical vapour deposition is used instead of electrodeposition. The utility of these structures for the electrocatalytic activity towards methanol, ethanol, and formic acid oxidations has been demonstrated which could be of immense relevance to portable fuel cell technology, since designing a better electrocatalysts continues to pose daunting challenges.
5.2. Experimental Details

5.2.1. Materials

H₂PtCl₆·6H₂O (99.98%) and PdCl₂ (99 %) were 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.

5.2.2. Preparation of Y-junction Platinum Nanostructures

A free-standing Y-PAM template, fabricated via an extended two-step anodization route (for details see Chapter II, section 2.4.3) was used as the working electrode for electrodeposition, after evaporating Au film (200 nm) on one side of the membrane. Electrodeposition was carried out using this working electrode in an aqueous solution of 5 mM H₂PtCl₆ 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, the membrane was kept at 80 °C in a mixture of H₂PtCl₆ (5 mM) and boric acid (1 mM) for 30 min and subsequently electrodeposition was carried out at a potential of -0.7 V vs SCE, for 15 min. In addition, electrodeposition was carried out at 60 °C and also without any prior heat treatment. Finally, the nanostructures 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 to yield almost 80 % of pure structures. A schematic representation of different stages involved during the formation of Pt Y-junction is shown in scheme 5.1, which includes evaporation of Au film on one side of the free standing Y-PAM and followed by electrodeposition of Pt.
5.2.3. Preparation of Platinum Nanowires

A free-standing linear PAM template fabricated via a two-step anodization route (for details see Chapter II, section 2.4.2) was used as working electrode, after evaporating Au film (200 nm) onto one side of the membrane for electrical contact. Similar electrodeposition procedure as discussed above was adopted for the formation of Pt nanowires.

5.2.4. Preparation of Y-junction Palladium Nanostructures

Monolayer protected gold nanoclusters, AuMPCs (capped by tridecylamine, prepared via a modified Brust synthesis route; diameter ca. 6 nm) was vacuum (10^{-3} torr) filtered through the Y-branched alumina membrane, in order to deposit the nanoparticles.
at the bottom of these membrane. These nanoparticles could act as catalysts for the growth of Y-junction Pd inside the membrane. After filtration, the membrane was washed thoroughly in dichloromethane to remove particles adhered on the external surface of the membrane. An indigenously fabricated CVD set-up capable of attaining 1000°C comprising a single zone furnace was used for the synthesis of Pd Y-junction nanostructures. CVD set-up for the deposition of Pd inside the Y-PAM is shown in figure 5.1. It consists of a tubular furnace, in which the above membrane was placed (face down) on the top of the alumina boat containing 25 mg of PdCl₂ at the centre of the furnace. The reaction was carried out at 850 °C under N₂ atmosphere for 4 h. After the reaction, the temperature of the furnace was cooled to room temperature with uninterrupted N₂ flow. Subsequently, the membrane was dissolved in 0.1 M NaOH and the sample was washed several times with deionized water till neutral pH, followed by a final washing with ethanol to yield almost 90 % pure structures. A cartoon, representing different stages involved during the formation of Pd Y-junction nanostructure is shown in scheme 5.2, where incorporation of AuMPCs at the pore bottom and subsequent deposition of Pd inside the branched alumina membrane are shown.

![Diagram of CVD set-up](image)

**Figure 5.1.** CVD set-up used for the deposition of palladium inside the Y-PAM; reaction was performed at 850°C for 4h under N₂ atmosphere; various components including single zone furnace, carrier gas and precursors are shown.
Scheme 5.2 Different steps involved in the preparation of Pd Y-junction nanostructure through chemical vapour deposition: deposition of AuMPCs at the bottom of the porous membrane was followed by Pd deposition through CVD at 850 °C under N₂ atmosphere; finally the structures were released after dissolving the membrane in NaOH.

5.2.5. Investigation of electrocatalytic activity

To investigate the electrocatalytic activity of Pt Y-junction nanostructures, the working electrode was prepared by dispersing 20 wt % Pt Y-nanostructures in Vulcan XC-72 carbon (C) using isopropyl alcohol followed by drop casting to form a thin film on a glassy carbon electrode (ca. 3 mm diameter) using 0.5 wt% Teflon binder. A similar procedure was adopted to prepare the electrode of Pt nanowires, Pd Y-junctions and commercial platinized carbon (20 % Pt on Vulcan XC-72 carbon from Arora Matthey Limited; diameter 8 nm) always using identical amounts.

Cyclic voltammogram (CV) of Pt Y-junction nanostructure was first recorded in 0.5 M H₂SO₄, and the electroactive area (Aₚ) was determined from the adsorption/desorption charge of hydrogen atoms from this (ca. 210 μC/cm² for a
polycrystalline surface). 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 at various potentials ranging from -0.44 V to +0.16 V vs Hg-Hg2SO4 at an interval of 0.05 V. Further, the current density (j) was obtained after normalizing the current to APt. Before recording the current transients, sufficient care was taken to oxidize any adsorbate on the electrode surface so as to obtain a clean surface. Similarly, the electrocatalytic activity of Pt Y-junctions towards ethanol oxidation was studied in a mixture of 0.1 M CH3CH2OH and 0.1 M HClO4, whereas the mixture of 0.5 M H2SO4 and 0.5 CH3OH was used for methanol oxidation, following similar procedures. All experiments were repeated using commercial platinized carbon and nanowires of Platinum.

For Pd Y-junctions, cyclic voltammogram was first recorded in 0.5 M H2SO4, and the electroactive area (APd) was determined from the charge required for the reduction of palladium oxide monolayer (i.e., 405 µC/cm²). Further, to measure the electrocatalytic activity of these structures towards formic acid oxidation, polarization experiment was performed in a mixture of 0.25 M HCOOH and 0.5 M H2SO4 using a similar procedure as discussed above.

5.2.6. Structural and Morphological Characterization

5.2.6.1. SEM and EDX

The morphology of the Y-junction nanostructures was characterized using three scanning electron microscopes, Lieca Stereoscan 440 Model, Hitachi S-4800 field emission scanning electron microscope and FEI Quanta 200 3D microscope equipped with tungsten filament. Energy dispersive point spectra were measured at 10 keV using an Oxford INCA x-sight energy dispersive X-ray microanalysis system connected with the Hitachi S-4800. For these, a little amount of sample was dispersed in ethanol and dropcast on Cu substrate and dried at room temperature.
5.2.6.2. TEM

TEM images were recorded on a JEOL model 1200 EX instrument operated at an accelerating voltage of 120 kV after placing a drop of the dispersed solution onto a carbon-coated Cu grid (3 nm thick, deposited on a commercial copper grid for electron microscope), which was dried in air and loaded into the electron microscopic chamber.

5.2.6.3. Electrochemical Measurements

All electrochemical experiments were performed on an Autolab PGSTAT30 (Ecochemie) instrument at room temperature. For electrodeposition, Au film supported linear PAM/Y-PAM was used as the working electrode whereas saturated calomel electrode (SCE) and two Pt foils were used as reference and counter electrodes respectively. Electrocatalytic study was performed using a glassy carbon (GC) electrode modified with nanostructure/C (nanostructure dispersed in Vulcan carbon) as explained in details in section 5.2.5. Also, a Hg-Hg_{2}SO_{4} and a platinum foil were used as the reference and counter electrodes, respectively.

5.2.6.4. Conducting Atomic Force Microscopy

Platinum nanowires and Y-junctions were characterized by using conducting AFM-built around Burleigh Metris-2000 AFM head. Prior to the measurements, Si (111) wafer was dipped for 30 s in hydrofluoric acid in order to remove the oxide layer. The conducting force sensing probe was connected to the virtual ground of the preamplifier. The sample was isolated from ground and connected to a bias voltage. n-type silicon cantilever (from nanosensors) of resistivity 0.01-0.02 Ωcm and spring constant of 40-50 Nm^{-1} was used after depositing platinum (thickness 10 nm) on the n-type Si cantilever to avoid oxidation of the tip. After dispersing the sample in chloroform, a drop was added onto the silicon wafer for measurements.

Other characterization details like XRD and XPS have already been described in Chapter 2, section 2.4.5.2 and Chapter 3, section 3.2.4.2 respectively.
5.3. Results and Discussion

5.3.1. SEM Analysis

A typical field-emission scanning electron micrograph (FESEM), (top view) of the Pt Y-junction (before dissolving the membrane) prepared using the above mentioned hierarchically designed alumina template is shown in figure 5.2a, revealing that almost all the pores are effectively filled with Pt. Similar FESEM images after dissolving the membrane in 0.1 M NaOH, however, in figure 5.2b-d, depict uniform Y-junctions with well defined branches and stems having diameter ca. 100 and 50 nm respectively, closely in agreement with those of the Y-branched alumina nanochannels. In addition, the angle between the branches is ca. 12°, slightly higher compared to that of the template, perhaps due to the tendency of the structure to release the strain involved at the junction after the dissolution of the membrane. Also, figure 5.2e shows image of some broken Y-junction nanostructures, presumably formed during the purification. In addition the energy dispersive x-ray analysis (EDX) spectrum (Figure 5.2f) confirms the complete removal of Al from the sample (Si peak seen in the spectrum, could be from the substrate).
Figure 5.2. FESEM images of Pt-Y junction nanostructures (a) before dissolving the membrane (top view; scale bar 300 nm); (b-d) after etching the alumina template in 0.1 M NaOH, where the diameter of the stem and branches are ca. 100 and 50 nm respectively (scale bar 200 nm, 100 nm and 100 nm); (e) some broken Y-junction nanostructures (scale bar 100 nm); (f) shows the EDX spectrum taken from the Pt Y-junction nanostructure.
Since these Y-junction nanostructures are obtained only after maintaining the electrolyte above a critical temperature (80 °C) for 30 min, it is important to understand systematically the influence of temperature on controlling the dimensional features of Y-junctions. Interestingly, at room temperature and also at 60 °C, scanning electron micrographs (SEM) reveal only tiny nanorods of Pt and low aspect ratio Y-junction with poor yield respectively, as shown in figure 5.3a,b and hence it is absolutely essential to maintain higher temperature like 80 °C to form Y-junctions. This is because the nanoporous structure of the template, due to its slow diffusion, (Knudsen diffusion) hinders the deposition rate, which in turn prevents uniformity and quality of the structure at low temperature. At higher temperatures, the mass-transfer resistance is reduced by decreasing the Nernst diffusion layer thickness, which facilitates the Y-junction formation. In contrast, reports are available on the utilization of ultrasonication during template-assisted electrodeposition to improve the mass-transfer resistance.

![Figure 5.3. SEM images of Pt nanostructure after dissolving the alumina membrane (a) Pt nanorods at room temperature; (b) low aspect ratio Pt Y-junction nanostructure at 60°C.](image)

Similarly FESEM image of Pt nanowires prepared through the same electrodeposition route, but using linear PAM is shown in figure 5.4 after releasing the structures form alumina template, where the nanowires are perfectly aligned possessing a uniform diameter of ca. 80 nm.
Figure 5.4. FESEM image of Pt nanowires after dissolving the alumina membrane in 0.1 M NaOH; the nanowires were prepared through an electrodeposition route after maintaining the electrolyte bath at 80°C; scale bar 100 nm.

Similarly, SEM images of Pd Y-junction nanostructures (after dissolving the membrane in 0.1 M NaOH) prepared using hierarchically designed alumina templates through a CVD route, are shown in figure 5.5. In contrast to electrodeposition route followed for Pt Y-junction nanostructure, CVD procedure is adopted basically due to the two reasons: (1) prior to electrodeposition, the membrane needs to be maintained at a particular temperature for efficient filling of the porous structure, and (2) relatively higher yield is obtained through CVD with respect to electrodeposition route. Here, figure 5.5a reveals an array of Pd Y-junctions, whereas individual Y-junctions are clearly shown in figure 5.5b revealing uniform and well defined branches and stems having a diameter of ca. 110 and 200 nm respectively. A close examination reveals that diameter of both the stem and branches are slightly higher compared to that of the template, presumed to be due to the expansion of the Y-branched nanochannels during the synthesis of the Pd Y-junction nanostructure at higher temperature. Furthermore, the angle between the branches is ca. 20°, slightly higher compared to that of the template, perhaps due to the tendency of the structure to release the strain involved at the junction.
after the dissolution of the membrane. This larger angle may also be due to the significantly higher reaction temperature (850°C).

![Figure 5.5](image)

**Figure 5.5.** SEM images of Y-branched Pd Y-junction nanostructure after dissolving the alumina membrane in 0.1 M NaOH, where (a) reveals an array of Y-junction palladium while individual Pd Y-junctions are clearly seen in (b); scale bar 10 μm and 1 μm, respectively.

### 5.3.2 TEM Analysis

Figure 5.6a shows the bright field transmission electron micrograph (TEM) of such a Y-junction nanostructure, after removing the structures from the template revealing the stem and branches having a diameter in complete agreement with the SEM results. Figure 5.6b shows the selected area electron diffraction (SAED) taken from a single Y-junction, where the diffractogram demonstrates that the structure is polycrystalline with (111), (200), and (220) preferred planes, corresponding to the face centered cubic (fcc) structure of Pt.\textsuperscript{17}
Figure 5.6. (a) TEM image of Y-junction platinum nanostructures after etching the alumina membrane, where the diameters of the stem and branches are consistent with the SEM images; the SAED pattern (b) taken from a single Y-junction revealing polycrystalline nature.

5.3.3. XRD Analysis

Information on the crystal structure and the crystallite size of these Y-junction nanostructures is also provided by powder XRD. Accordingly, figure 5.7a shows the XRD pattern of Pt-Y 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. Further, the crystallite size calculated using the Scherrer formula is ca. 9.2 nm, considering the (111) reflection. Also the XRD pattern reveals no change in the peak position for Pt-Y as compared to that of XRD pattern of Pt nanowires prepared using anodic alumina membrane. Apart from the response corresponding to Pt, a broad peak at $2\theta = 25^\circ$ associated with the (002) planes of Vulcan XC-72 carbon, is also seen due to the support.
Figure 5.7. Powder XRD pattern of (a) Pt Y-junction (b) Pd Y-junction dispersed in vulcan carbon; all these diffraction peaks match well with the corresponding peaks for the standard fcc structure of bulk Pt and Pd respectively; the spectrum also reveals a broad peak corresponding to the (002) planes of vulcan carbon.

Similarly, figure 5.7b shows the XRD pattern of Pd-Y/C which reveals the formation of a cubic structure with high crystallinity. All diffraction peaks for (111), (200) planes match well with Bragg reflections of the standard and phase pure face centered cubic (fcc) structure of Pd. Besides the response corresponding to Pd, a broad peak at 2θ = 25° is associated with the (002) planes of vulcan XC-72 carbon due to the support. Also the XRD pattern reveals no change in the peak position for Pd-Y as compared to that of Pd nanowires prepared using, anodic alumina membrane. The crystallite size of these Y-junction nanostructures calculated using the Scherrer formula is ca.15.8 nm, considering the reflection from (111) plane. Thus XRD results are in excellent agreement with the results obtained from TEM analysis.

5.3.4. XPS Analysis

Since XPS analysis provides valuable information on the oxidation state of these Y-junctions, XP spectra of both Pt-Y and Pd-Y junction structures are shown in figure 5.8a and b respectively. Figure 5.8a shows the Pt 4f region where, deconvolution reveals two
peaks at 71.08 eV and 74.3 eV (after carbon correction) corresponding to Pt 4f_{7/2} and 4f_{5/2} respectively.\textsuperscript{20} These values confirm that Y-junctions are metallic with a typical peak to peak separation of ca. 3.2 eV, which is in excellent agreement with the bulk platinum metal. Similarly, XP spectrum of Pd Y-junctions shown in figure 5.8b reveals four peaks corresponding to Pd 3d_{3/2} and 3d_{5/2}, where peaks at 337.6 and 335.5 eV could be attributed to the Pd(0) state, with a peak to peak separation of 2.1 eV. In addition, the remaining two peaks at 343.4 and 340.7 eV could be assigned to 3d_{3/2} and 3d_{5/2} levels of Pd(II), representing perhaps un-reacted PdCl\textsubscript{2}.\textsuperscript{21}

Figure 5.8 X-ray photoelectron spectra of (a) Pt Y-junction showing Pt 4f core level; (b) Pd Y-junction showing 3d core level (here, Pd(0) and Pd(II) states are distinguished by superscripts 1 and 2 respectively) where, core levels are deconvoluted using Shirley software; the 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.

5.3.5. Electrocatalytic Performance of Pt Y-junctions, Nanowires and Commercial Platinized Carbon

5.3.5.1. Formic Acid Oxidation

Cyclic voltammetric response of Pt-Y/C and Pt-NW/C towards formic acid oxidation at 50 mV/s in a mixture of 0.5 M H\textsubscript{2}SO\textsubscript{4} and 0.25 M HCOOH are shown in figure 5.9, where both samples reveal the characteristic features of formic acid oxidation.
The voltammetric response of Pt/C is also shown in figure 5.9 where two peaks are clear during the anodic scan (at -0.07 V and +0.7 V for Pt-Y/C) while only one peak (-0.12 V for Pt-Y/C) is observed during the reverse (cathodic) scan. A considerable shift in peak position is observed for different electrodes, as obvious from the voltammogram. The first anodic peak is due to the oxidation of HCOOH to CO₂ on surface sites that remain unblocked by CO, whereas the second anodic peak corresponds to the oxidation of surface adsorbed CO. 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. [Reaction mechanism and different pathway involved during the formic acid oxidation has already been discussed in chapter III, section 3.3.5.1]

Furthermore, a closer look at the voltammogram reveals a substantial enhancement in peak current corresponding to Y-junction compared to that of other samples. (In all the cases oxidation current has been normalized to electroactive Pt surface area (\(A_{Pt}\)) so that the current density (\(j\)) can be directly used to compare the catalytic activity of all samples).

![Figure 5.9. Cyclic voltammetric response (2nd cycle data) of Pt-Y/C, Pt-NW/C and Pt/C toward formic acid oxidation in a mixture of 0.25 M HCOOH and 0.5 M H₂SO₄ at 50 mV/s.](attachment:image.png)
Figure 5.10 shows a comparison of transient current density of formic acid oxidation at -0.24 V (potential selected from the cyclic voltammogram, Figure 5.9) on Pt/C (commercial platinized carbon), Pt-Y/C (Y-junction Pt nanostructure in vulcan XC -72 carbon) and Pt-NW/C (Pt nanowires in vulcan XC -72 carbon) samples. Interestingly, the oxidation current density on Pt-Y/C is significantly higher compared to that on both Pt-NW/C and Pt/C and the enhancement factor $R$, (which is defined as the ratio of the current density measured on Pt-Y/C versus that acquired on Pt-NW/C or Pt/C) increases up to 270 % for Pt/C and up to 200 % for Pt-NW/C sample respectively, depending upon the electrode potential. Further, from the steady state I-V plot (where the steady state current density is obtained from the current transients recorded for 60 s for various potentials, -0.44 to +0.16 V), shown in figure 5.11, we observe that at a given current density, the corresponding potential on Pt-Y/C is much lower than that for Pt-NW/C and Pt/C. Further, the value is shifted negatively by ca. 90 mV at a current density of $9.5 \times 10^{-5}$ A/cm$^2$ with respect to that of Pt/C, whereas the shift is ca. 40 mV as compared with Pt-NW/C. Recently Wang et al. have seen for tetrahexahedral platinum nanocrystals that at a given oxidation current density, these tetrahexahedra show a negative shift in potential by 60 mV compared to that on Pt/C catalyst towards formic acid oxidation, which is indeed significantly lower compared to that of Pt-Y nanostructures. This shows that formic acid oxidation is thermodynamically more feasible on Pt Y-junctions compared to that on highly faceted structure such as tetrahexahedra.
Figure 5.10. Transient current density curves of Pt-Y/C, Pt-NW/C and Pt/C toward formic acid oxidation at -0.24 V for 60 s.

Figure 5.11. Potential-dependent steady state current density curves of Pt-Y/C, Pt-NW/C and Pt/C toward formic acid oxidation; the corresponding shift in the potential at a particular current density is also shown.
In addition, the value of exchange current density ($j_o$) of these structures toward formic acid oxidation is calculated from the Tafel polarization studies as summarized in Table 5.1. The value of $j_o$ is slightly higher for Pt-Y/C than that of Pt-NW/C and Pt/C respectively highlighting the change in the intrinsic rate constant.

**Table 5.1.** Exchange current density values of Pt-Y/C, Pt-NW/C and Pt/C toward formic acid, methanol and ethanol oxidation; these values are obtained from the Tafel plots of the respective electrodes.

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<thead>
<tr>
<th>Electrodes</th>
<th>Exchange Current Density (A/cm²)</th>
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<tr>
<td></td>
<td>Formic acid oxidation</td>
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<td></td>
<td>Ethanol oxidation</td>
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<tr>
<td></td>
<td>Methanol oxidation</td>
</tr>
<tr>
<td>Pt-Y/C</td>
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<tr>
<td>Pt-NW/C</td>
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<tr>
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<td>$6.7 \times 10^{-7}$</td>
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**5.3.5.2. Methanol Oxidation**

Similar studies have also been explored for methanol oxidation and accordingly cyclic voltammetric response of Pt-Y/C, Pt-NW/C, and Pt/C in a mixture of 0.5 M CH$_3$OH and 0.5 M H$_2$SO$_4$ at 20 mV/s are shown in figure 5.12. The voltammogram shows two peaks during the anodic scan (at 0.13 and 0.73 V for Pt-Y/C), while one peak (at -0.01 V for Pt-Y/C) is observed during the reverse (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. [Details of the reaction mechanism have already been discussed in chapter III, section 3.3.5.3]. Similarly, as observed for formic acid oxidation, in the present case also, a considerable change in both the peak position and peak current are observed for all the three electrodes, as obvious from the voltammogram.

![Figure 5.12](image-url)

**Figure 5.12.** Cyclic voltammetric response (2nd cycle data) of Pt-Y/C, Pt-NW/C and Pt/C towards methanol oxidation in a mixture of 0.1 M CH₃OH and 0.5 M H₂SO₄ at 20 mV/s.

Figure 5.13 shows a comparison of current–time transients of methanol oxidation at +0.1 V (potential selected from cyclic voltammogram, Figure 5.12) on the Pt/C, Pt-Y/C, and Pt-NW/C. Interestingly, the current density on Pt-Y/C is significantly higher compared to that on Pt-NW/C and Pt/C. The enhancement factor $R$, (which is defined as the ratio of the current density measured on Pt-Y/C versus that acquired on Pt-NW/C or Pt/C,) varies up to 680 % for Pt/C whereas up to 400 % for Pt-NW/C depending upon the electrode potential.
Steady-state current density obtained from the I-t transients (at various potentials, -0.2 V to +0.4 V) is plotted against respective potential as shown in figure 5.14. Interestingly, it is observed that at a given current density, the corresponding potential on Pt-Y/C is much lower than that for Pt-NW/C and Pt/C. Further, the value is shifted negatively by ca. 90 mV at a current density of $1.6 \times 10^{-5}$ A/cm$^2$ with respect to that of Pt/C, whereas the shift is ca. 50 mV as compared with Pt-NW/C. Furthermore, the value of $j_0$ of these structures as calculated from the Tafel polarization studies is summarized in Table 5.1, where as observed for formic acid oxidation, a slightly higher value is observed for Pt-Y/C than that of Pt-NW/C and Pt/C respectively.
Figure 5.14. Potential-dependent steady state current density curves of Pt-Y/C, Pt-NW/C and Pt/C toward methanol oxidation; corresponding shift in the potential at a particular current density is also shown.

5.3.5.3. Ethanol Oxidation

Similar shape-dependent activity is also investigated for ethanol oxidation and the corresponding voltammetric response in a mixture of 0.1 M C₂H₅OH and 0.1 M HClO₄ at 50 mV/s is presented in figure 5.15 for comparison. The voltammograms show two peaks during the anodic scan (at +0.11 V and 0.61 V for Pt-Y/C), while one peak (at -0.05 V for Pt-Y/C) is observed in the cathodic scan where the first anodic peak corresponds to the -OH bond formation to the Pt surface, which plays an important role in ethanol oxidation. Further, the second anodic peak is caused by the formation of CO₂ and other by-products such as acetic acid and acetaldehyde. In the negative-going potential sweep only one peak appears and this is attributed to renewed oxidation of ethanol. [Details of the reaction mechanism have already been discussed in chapter III, section 3.3.5.2]. Similarly, as in the case of above two oxidation reactions, here also the respective voltammograms reveal a considerable change in both the peak position and peak current with shape.
Figure 5.15. Cyclic voltammetric response (2nd cycle data) of Pt-Y/C, Pt-NW/C and Pt/C towards ethanol oxidation in a mixture of 0.1 M CH₃CH₂OH and 0.1 M HClO₄ at 50 mV/s.

Furthermore, the transient current density response of the three samples (Pt-Y/C, Pt-NW/C and Pt/C) at -0.04 V is shown in figure 5.16 for comparison. Interestingly, the enhancement factor of Pt-Y/C with respect to Pt-NW/C or Pt/C increases up to 180 % for Pt/C sample, whereas the factor varies up to 130 % for Pt-NW/C. Also from the potential-dependent current density curve (figure 5.17), it is obvious that the potential on Pt-Y/C is shifted negatively by 70 mV as compared to that of Pt/C, while 20 mV shift with respect to that of Pt-NW/C occurs at the same current density of 5.5 x μA/cm². Moreover, as observed for the above two reactions, the value of $j_o$ of these structures (Table 5.1) is slightly higher for Pt-Y/C than that of Pt-NW/C and Pt/C respectively.
Figure 5.16. Transient current density curves of Pt-Y/C, Pt-NW/C and Pt/C toward ethanol oxidation at -0.04 V for 60 s; inset shows the enlarged view.

Figure 5.17. Potential-dependent steady state current density curves of Pt-Y/C, Pt-NW/C and Pt/C toward ethanol oxidation; the corresponding shift in the potential at a particular current density is also shown.
Hence, form the above three electrooxidation reactions, it could be concluded that Pt-Y nanostructures exhibit enhanced catalytic activity per unit surface area for the oxidation of formic acid, methanol, and ethanol compared to that of Pt nanowires and commercial platinized carbon. This could be perhaps due to the high density of active sites on the surface of Y-junction Pt (large surface area is expected for these high aspect ratio nanostructures), and in addition it is presumed that the branched regions also enhance the activity due to large field gradient. This is clearly obvious on comparison of the performance of both Y-junctions and linear structures (nanowires) of Pt.

5.3.6. Electrocatalytic Performance of Pt Y-junction and Pd Y-junction Nanostructures toward Formic Acid Oxidation: A Comparative Study

From the above studies, especially on the electrocatalytic performance of Pt Y-junction nanostructures toward formic acid oxidation, it is obvious that Pt suffer from a major drawback such as poisoning by CO-like intermediate species. In order to obviate this problem, we have selected palladium as an alternative catalyst because it is known that this facilitates formic acid oxidation through a direct CO₂ pathway without the formation of poisonous CO intermediate and more importantly due to their relatively low cost. Accordingly, we have compared the electrocatalytic efficiency of these palladium Y-junction nanostructures with that of platinum Y-junctions. Figure 5.18 shows the cyclic voltammetric response of both Pd-Y/C and Pt-Y/C towards formic acid oxidation at 50 mV/s in a mixture of 0.5 M H₂SO₄ and 0.25 M HCOOH. As discussed earlier, the voltammogram corresponding to the Pt-Y/C shows two peaks during the anodic scan (at -0.025 V and 0.73 V), while only one peak (-0.12 V) is observed during the reverse (cathodic) scan. The first anodic peak is due to oxidation of HCOOH to CO₂ on surface sites that remain unblocked by CO, whereas the second anodic peak (shown by dotted arrow) corresponds to the oxidation of surface adsorbed CO (vide supra). Nevertheless, the voltammetric response corresponding to Pd-Y/C shows only one peak during the anodic scan (0.03 V) in contrast to the two peaks observed for Pt-Y/C. This could be attributed to the presence of palladium promoting the formic acid oxidation through a
dehydrogenation pathway wherein the reaction proceeds without any poisonous CO intermediate.\textsuperscript{24} Hence, in the case of Pd-Y/C no peak corresponding to the oxidation of CO is observed, whereas for Pt-Y/C due to the build-up of CO (since oxidation proceeds through a dual pathway, vide supra) on the electrode surface, a peak corresponding to the CO oxidation is observed. Further, the build-up of CO on the Pt electrode surface in turn decreases the availability of active sites for formic acid oxidation. Also, a comparison of the peak current density on both electrodes reveals a higher value for the Pd-Y/C than that for Pt-Y/C. Another factor which contributes to the enhanced performance of Pd-Y/C towards formic acid oxidation is the presence of Pd (II) species (confirmed from XPS studies, vide supra), which could also facilitate a direct CO\textsubscript{2} pathway without the formation of a poisonous CO intermediate.\textsuperscript{23b,c,25}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure518.png}
\caption{Superimposed cyclic voltammetric response of Pd-Y/C and Pt-Y/C toward formic acid oxidation in a mixture of 0.25 M HCOOH and 0.5 M H\textsubscript{2}SO\textsubscript{4} at 50 mV/s.}
\end{figure}

Figure 5.19 shows a comparison of the transient current density of formic acid oxidation at \(-0.09\) V (potential selected from cyclic voltammogram) on the Pd-Y/C and Pt-Y/C at room temperature. Interestingly, the oxidation current density on Pd-Y/C is
significantly higher compared to that on Pt-Y/C and the enhancement factor R (which is
defined as the ratio of the current density measured on Pd-Y/C versus that acquired on Pt-
Y/C) varies up to 1000% depending upon the electrode potential.

![Graph showing transient current density curves of Pd-Y/C and Pt-Y/C towards formic acid oxidation at -0.09 V.](image)

**Figure 5.19.** Transient current density curves of Pd-Y/C and Pt-Y/C toward formic acid oxidation at -0.09 V.

The steady state current density from the I-t transients (for various
potentials, in the range of -0.44 V to + 0.36 V) corresponding to formic acid oxidation is
plotted against each respective potential in figure 5.20, which clearly illustrates the
superior electrocatalytic performance of Pd-Y/C compared to that of Pt-Y/C. For
example, the value of current density (j) on Pd-Y/C and Pt-Y/C for formic acid oxidation
at -0.04 V are $1.5 \times 10^{-4}$ and $1.1 \times 10^{-4}$ A/cm$^2$ respectively.
Figure 5.20. Potential-dependent steady state current density plot of Pd-Y/C and Pt-Y/C samples towards formic acid oxidation; comparison of the current density reveals higher value for the Pd-Y/C compared to that of Pt-Y/C.

In order to estimate relative values of exchange current density, (which helps to compare electrocatalytic behaviour) $j_e$ towards formic acid oxidation on these nanostructures dispersed in Vulcan carbon, Tafel polarization offers several advantages. The value of $j_e$ obtained is considerably higher for the Pd-Y/C ($3 \times 10^{-6}$ A/cm$^2$) than that of the Pt-Y/C electrodes ($6.3 \times 10^{-7}$ A/cm$^2$) respectively, which further supports the above results. A cartoon representation showing the formic acid oxidation pathway on both Pt Y-junction and Pd Y-junction nanostructures is shown in scheme 5.3, where it is obvious that formic acid oxidation on platinum electrodes proceed either through CO or directly to CO$_2$. In contrast, the reaction proceeds directly to CO$_2$ without any poisonous intermediate on palladium, which is relevant for fuel cell applications.
Scheme 5.3. A cartoon representing different formic acid oxidation pathways on Pt Y-junction and Pd Y-junction electrodes; the oxidation reaction proceeds through a poisonous CO intermediate on Pt Y-junctions in contrast to that on palladium Y-junctions.

5.3.7. Electronic Transport in Y-junction Pt Nanostructures

In order to explain the enhanced electrocatalytic performance of Pt Y-junction nanostructures compared to that of nanowires the electron transport behaviour of these Y-junctions has been explored using conducting AFM (conducting AFM rather than STM has been used primarily because of the availability). Accordingly, figure 5.21a shows the I-V profile after positioning the tip on the junction as well as on the individual arms of the Y-junction, where an increase in current is almost linear for positive bias while nonlinear response is observed for negative bias. In contrast, the I-V profile corresponding to the Pt nanowires (figure 5.21c) reveals almost linear behaviour at both positive and negative bias. All measurements have been repeated after keeping the tip at different positions and these locations are indicated clearly in Fig. 5.21b,d where the contact mode AFM image of the both Pt Y-junctions and Pt nanowires are shown. However, more detailed studies are essential to pinpoint the exact reason for the non-linear behaviour of these Y-junctions, with respect to their fascinating electronic structure.
5.4. Conclusions

In summary, the use of hierarchically designed porous alumina membrane template is described in this chapter facilitating the fabrication of Y-junction nanostructures of Pt and Pd. These metallic Y-junctions are uniform with regard to the position of the junction and the diameter of the stem and arms. More importantly, a comparison of the electrooxidation activity of Y-junction nanostructures of platinum with that of nanowires and commercial platinized carbon reveals enhanced performance of the junction structures, which are relevant for designing new electrocatalysts for microfuel cells. These structures exhibit enhanced electrocatalytic activity for the oxidation of
formic acid (up to 270 %), methanol (up to 680 %) and ethanol (up to 180 %) compared to that of Pt/C, whereas with respect to Pt-NW/C the enhancement is up to 200 % for formic acid, up to 400 % and 130 % for methanol and ethanol oxidation respectively. Moreover, the potential on Y-junction platinum is shifted negatively by ca. 90 mV as compared with Pt/C whereas the shift is ca. 40 mV with respect to Pt-NW/C at the same current density for the case of formic acid oxidation. Similarly, for methanol oxidation the shift is 90 and 50 mV with respect to Pt/C and Pt-NW/C whereas in the case of ethanol oxidation, the Y-junction nanostructure shows a negative shift of 70 and 20 mV with respect to Pt/C and Pt-NW/C respectively.

We have also explored the utility of Y-junction nanostructures of palladium as an alternative catalyst with respect to platinum for formic acid oxidation reaction, where the former reveals a better performance compared to that of the latter, attributed to the direct oxidation pathway on Pd electrode and hence negligible CO poisoning. The present method of fabrication of Y-junction nanostructures using hierarchical alumina templates could be extended to other metallic/semiconducting systems, facilitating more opportunities for hierarchical designs in nanoelectronics.
5.5. References


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