Major highlights of the work are summarized in the present chapter, outlining the potential utility of linear as well as hierarchically branched porous alumina templates for the formation of uniform and well-aligned high aspect ratio metallic nanostructures of Pt, Pd and RuO$_2$. Several advantages of template-assisted approach over other available routes along with some of their limitations are also demonstrated. Moreover, the prospective applications of such high aspect ratio nanostructures formed in the absence of surface passivating agents especially in fuel cell electrocatalysis are also reviewed. Related promising developments and daunting challenges in the broad area are also discussed to extend the applications of these fascinating metallic nanomaterials in view of their fundamental and technological interest by physicists, chemists, biologists and engineers. Finally, some of the future prospects and precautions for processing these nanomaterials are also explained within the broad perspective of nanotechnology and its societal impact.
Preparation and characterization of one dimensional nanomaterials have emerged as a major theme in contemporary nanotechnology due to its immense application possibilities. These are the smallest dimensional structures that can be used for efficient transport of electrons/phonons and optical excitations, and are thus expected to be critical to the function and integration of nanoscale devices. Their unique and outstanding physical and chemical properties which could be controlled remarkably by tuning their morphology, have captured amazing attention (even from general public). However, the ultimate potential of these nanostructures is strongly dependent upon the ability to precisely control their morphology (which include size, shape and dimensionality), composition, crystal structure and phase purity. Despite immense knowledge in this area, the synthesis of these nanostructures with high selectivity and their applications are still in an early stage of development. A number of challenges such as difficulty of precisely controlling the aspect ratio, lack of selectivity and uniformity in size distribution, difficulties of scale-up and cost effectiveness remain to be addressed before these materials will find viable applications. In this regard, a thorough understanding of the growth mechanism is a key step towards achieving selective growth of nanostructures, which is of particular significance both for the creation of new materials as well as for the fabrication of devices using these structures.

Various methods including the template-assisted approach, electrochemical route and reduction using several capping molecule/surfactants have been demonstrated to generate these nanostructures as discussed in Chapter 1. Nevertheless, only limited progress has been achieved in synthesizing these materials with precise morphological control and better shape distribution, that too often in the presence of different types of capping molecule/surfactants and in some cases foreign species. Although these external agents are essential for the shape-selective evolution of nanostructures, their presence could drastically hamper their potential benefits. Accordingly, through the present investigation we demonstrate the potential utility of hard templates such as porous alumina membrane (PAM) to synthesize metallic high aspect ratio and other non-
spherical nanostructures. These porous templates, including both linear and branched
types are fabricated through an anodization route as discussed in Chapter 2.

PAM templates are beneficial for shape controlled synthesis of not only high aspect
nanostructures but also other non-spherical shapes without the assistance of any capping
molecule/surfactants or any other foreign species. However, till date these templates have
been accomplished successfully only for high aspect ratio structures and no reports are
available on the synthesis of non-spherical nanostructures. As a consequence, we have
successfully utilized these porous templates for the synthesis of nanorods as well as other
non-spherical shapes such as multipods, discs and hexagons of platinum as illustrated in
Chapter 3. One of the important characteristics of these structures is their unique
electrocatalytic performance which depends highly on their shape/structure. Accordingly,
we have compared the electrocatalytic performance of different shapes of platinum
towards reactions such as formic acid, methanol, and ethanol oxidation, which are
relevant for fuel cell technology. Further, we have extended this template-assisted
strategy for the synthesis of bundles of RuO2 nanoneedles through a potentiostatic route
as mentioned in Chapter 4. More importantly, electrical transport measurement reveals a
transition from metallic to semiconducting behavior especially at low temperature, in
contrast to that of bulk commercial RuO2. The application of scanning electrochemical
microscopy for mapping the electroactivity of these nanoneedles has also been explored
in the end.

Synthesis of Y, T and other junction type nanostructures are potentially promising
for the development of molecular-scale electronic devices. However, this is difficult to
achieve using conventional methods because the linear structures cannot be controllably
altered along its length. Consequently, Y-junctions of carbon nanotubes have been
recently fabricated successfully through different routes such as template-assisted route
and chemical vapour deposition using a suitable catalyst. However, only a limited
progress has been made on the synthesis of metallic Y-junctions due to the lack of
flexibility in controlling the rigid structures. Accordingly, in Chapter 5 we demonstrate
the utility of Y-branched alumina nanochannels for the formation of platinum Y-junction
nanostructures through electrodeposition. These structures reveal enhanced
electrocatalytic activity for the oxidation of formic acid, methanol and ethanol compared
to that of commercial platinized carbon and Pt nanowires.

In addition to the Y-junction nanostructures of platinum, we also discuss the
formation of Pd Y-junction using the Y-branched alumina nanochannels through
chemical vapour deposition (Chapter 5). Palladium has been selected as an alternative
catalyst for platinum because it is known to facilitate formic acid oxidation through a
direct CO2 pathway without the formation of CO intermediate. Consequently, we have
compared the electrocatalytic performance of Pd Y-junction in relation to that of Pt Y-
junction nanostructure in order to demonstrate enhanced performance of the former
towards formic acid oxidation.

Nanostructures of gold and rhodium have tremendous application potential in
many areas although their effective impact is especially in catalysis with respect to size
and shape-dependent selectivity. As a result, different morphologies of Au and Rh
including spherical particles, nanocubes, nanotriangles, nanorods/nanowires, nanotubes,
etc., have been synthesized successfully for their effective use as highly selective
heterogenous catalysts. However, no efforts have been made to couple these two metals
so as to form core-shell structures. Hence, in order to fill this lacuna, we demonstrate a
preliminary attempt to the synthesis of Rh@Au core-shell nanorods using PAM in
Chapter 6. These Rh@Au core-shell nanorods are promising as multifunctional catalysts
for a variety of reactions such as hydrogenation of unsaturated organic compounds,
electrooxidation of carbon monoxide and alcohols and for light-induced generation of H2
from water.

Thus main results of this thesis unravel few issues related to the synthesis and
applications of high aspect ratio metallic nanostructures. In the entire thesis, we have
focused mainly on platinum, palladium and ruthenium oxide because of their outstanding
role as multifunctional catalysts in many applications, particularly in fuel cells. We have
explored the uniqueness of template-assisted approach for the synthesis of these
nanostructures without the assistance of surfactants/capping molecule and foreign species, which is beneficial from their application point of view. More importantly, we have demonstrated how the properties unique to nanostructures vary with morphology by considering their application in electrocatalysis.

Thus the major accomplishments of the present investigations could be summarized as follows:

- Fabrication of both linear and hierarchically branched porous alumina membranes through anodization route.
- Precise control of different shapes of platinum mesostructures such as multipods, discs, and hexagons by mere tuning of the electric field using alumina templates.
- Shape-dependent electrocatalytic performance of platinum nanostructures for many oxidation reactions of interest to fuel cells.
- Synthesis of Y-junction nanostructures of platinum and palladium using hierarchically designed porous alumina template.
- Enhanced electrocatalytic performance of Pd Y-junction nanostructures for formic acid oxidation compared to that of Pt Y-junctions.
- Preparation of RuO₂ nanoneedles using porous alumina template and their transition from metallic to semiconducting behavior at low temperature.
- Synthesis of Rh@Au core-shell nanorods using templated approach.

However, there are a number of unsolved issues that remain to be urgently addressed before these materials could be exploited commercially. Even though, template-assisted approach allows a precise control of morphology without the aid of any surfactants/capping molecule, the nanostructures synthesized through reduction often proceeds through the mediation of these external species, which retards their reactivity. For example, in electrocatalysis, better performance of a catalyst requires the absence of surface passivating agents normally used during the synthesis often via the chemical reduction route. More importantly, the nanostructures which are used as catalysts should
have high uniformity in size and shape distribution to precisely quantify the catalytic influence. As a result, much more efforts are essential to resolve these issues before realizing the complete potential of these nanostructures. In addition, several existing gaps in our understanding need to be filled by important investigations focusing on structure property correlations. For example, to envisage the electronic application of these metallic linear as well as junction morphologies, understanding several fundamental and fascinating issues about the electronic properties such as the coherence of extended states, difficulty of having individually addressable electronic contacts, the role of finite size and symmetry breaking, and new phenomena at low energies is essential.

Furthermore, there are several daunting tasks like addressing the environmental concern and societal impact of these materials since very little is known about these materials especially how they behave inside living organisms. Based on previous studies on asbestos and chrysolite, we expect many of these nanostructures to be perhaps environmentally hazardous. Researchers dealing with these types of nanostructures should take great caution while handling these structures. In this regard, a systematic, but rigorous evaluation on how these nanostructures will impact our environment and health is urgently needed!

Our novel approach based on template-assisted route for the shape selective synthesis of nanostructures and its processing offers an unprecedented opportunity to obviate many limitations of currently employed materials, opening new possibilities of manipulating the properties and stability to give enhanced performance. However, several limitations need to be kept in mind before these results could commercially be exploited.

- Since the template is usually a thin membrane, it is difficult to scale-up the nanostructure and grow through this route to macroscopic quantities, although efforts in that direction are underway.
- The nanostructures synthesized through this template are often polycrystalline.
❖ Low mechanical stability and tendency to coalesce upon release from the template.
❖ The exact reason behind the metallic to semiconducting transition observed in the case of RuO$_2$ nanoneedles at low temperature has not been explored. This could have been possible by carrying out the measurement by varying the aspect ratio of nanoneedles and also experimental procedure.
❖ More details on both the preparation and characterization the core-shell rods are needed to prove their potential applications
❖ Recycling potential of these nanostructured electrocatalyst has not been pursued, which is important for exploiting their utility in practical applications.

Since, some of these disadvantages restrict the full potential of commercial applications of these structures, further work is desired to alleviate these problems. Despite these limitations, the present approach offers enough scope to design different shaped nanostructures through a simple route with better reproducibility. In addition to the shape-dependent electrocatalysis, the present approach is also believed to pave the way to understand several shape-dependent fundamental phenomena of these nanomaterials. More significantly since this method of shape tuning is very general, we believe that apart from linear and Y-junctions this could be extended to the synthesis of other potential multi-terminal junctions such as T and X of a variety of metallic and semiconducting nanostructures, and it is further hoped that more studies would contribute significantly in the years to come.