Introduction
Lycurgus cup (4th AD), perhaps the oldest undamaged antique, represents special dichroic properties. The cup changes from opaque green to a shining translucent red upon exposure to light [1]. The color changing marvel of the cup is related to the presence of colloidal impurities of gold and silver in its manufacturing process. The Damascus sword is also a unique antique in the same context. The sword is known to cut silk as well as stones, retaining its sharpness [2, 3]. The sword’s strength is related to the presence of nanometer sized tubes and wires formed rather surprisingly during its manufacture [4]. The Wootz steel made in India from which the swords were forged contains transition metal impurities and these impurities have possibly catalyzed the growth of the nanometric structures from carbon provided by burning wood. As can be seen from these examples, nanostructured material synthesis started centuries ago, but rather accidentally. But once the importance of nano-sized material synthesis was realized, its potential applications had a far reaching impact on all fields of natural science. Nanocomposite materials are multiphase solid materials where one of the solid phases has one, two or three dimensions of less than 100 nm or structures possessing nanoscale distances between different phases.

This chapter begins with general introduction to nanoparticles (NPs) and their use in catalysis. The second portion of this chapter deals with the physical and chemical properties of NPs and their nanocomposites. The chapter also presents an introduction to various experimental techniques that have been used in this thesis for understanding more about these NPs and its composites. This chapter ends with a chapter wise summary that gives an overview of the several topics presented in this thesis.

1. NPs and Nanocatalysis

More than 90% of the industrial processes involve the use of catalysts for achieving enhancement in their product yields together with catalyst selectivity and recovery. In this context, homogeneous and heterogeneous catalysis are the two paths based on which a catalyst is tailored and designed.

In homogeneous catalysis, the catalysts as well as the reactants are in the same phase and all the catalytic sites are accessible because of the solubility of the catalyst in the solvent. Greater tuning of stereo, regio and enantioselectivity is thereby possible. The advantage of homogeneous catalysis lies not only in better yields but also in high selectivity engineered by modifying the ligands around the metal complex. Hence these catalysts find themselves in a number of commercial applications, but the catalyst recovery is difficult on an account of which, their impact is restricted. The presence of even trace quantities of the catalyst in the final product is
strictly screened for in several industries, particularly the pharmaceutical industry, limiting their usage.

Under this context, heterogeneous catalysts present myriad benefits that homogeneous catalysts fail to offer. The former are those that are not in the same phase as that of the reactants and have the inherent ease of separation from the reaction mixture. There are a plethora of scaffolds in this regard for supporting the catalysts. Though catalyst separation is easy in this case, a compromise has been sought in terms of catalytic efficiency due to phase differentiality between the catalyst and the reactants. Inspite of repeated efforts by researchers across the world to make materials that have all the sites over the support active for the catalytic process and to allow the catalytic rates and efficiencies comparable to that of homogeneous catalysts, only those sites present on the surface are active. On account of this, there has been a decrease in the overall reactivity of the catalyst framework.

In this context, catalysis using NPs has been widely explored in different frontier areas of science since the past 3 decades. The importance of metal NPs in catalysis is mainly due to its high surface to volume ratio [5]. Metal NPs are known to catalyze many reactions of academic as well as industrial importance [6]. NPs hold accessible surface area that not only provides greater contact between the reactants and the catalysts but also mimics the homogeneous catalysts. Moreover their colloidal nature in the reaction system makes them analogous to heterogeneous catalysts. Hence the usage of NPs in catalysis results in the creation of the nanocatalysis domain that serves as a bridge between homogeneous and heterogeneous catalysis, offering the advantages from both the worlds.

**Scheme 1. Schematic representation of the limitations overcome by Nanocatalysis**
NPs have drawn wide attention for a plethora of catalytic as well as electro-catalytic applications [7-10] and their synthesis has gained more prominence [11, 12]. The typical dimensions of the NPs lie in the range of 1-100 nm. In this regard, capping agents have been used to achieve a precise control over the size and shape of NPs [13, 14]. There are wide variety of capping agents ranging from small citrate ions to large entities such as polyvinylpyrrolidone, sodium dodecyl sulfate, cetyltrimethylammonium bromide, octadecylamine, to name a few. Exploring greener ways to synthesize NPs, a variety of reports suggest the use of plant extracts as natural capping agents [15, 16]. All these agents strongly bind to the planar surfaces of NPs thereby effectively preventing their agglomeration [17]. In catalysis, most of the reactions occur on the NPs surface. The presence of these capping agents however results in decreased electron transfer rate [18]. The capping agents block the active catalytic sites on the NPs, decreasing their activity [19-21]. Apart from the inhibition effects, the intermediates produced during the course of the chemical reactions tend to poison the active catalytic sites, accelerating the loss of catalytic activity [22, 23]. Clearly, there has been a lack of understanding over the ambiguous role of capping agents in creating an unfavorable catalytic turnover owing to the accumulation of the reaction intermediates over the NPs surface. These inhibitory and poisoning effects have resulted in an abysmal efficiency of the catalysts leading to a large scale loss in the commercial sector [24]. Besides these, the excessive use of capping and reducing agents has increased the cost associated in the mass production of these NPs based catalysts [25] and also resulting in large scale environmental pollution. This necessitates the use NPs without any linkers/binders/capping agents resulting in unmasked catalytic activity and paves the way for the next generation approach of ‘Spot-free catalysis’. The long standing problem of pristine NPs aggregation, however hinders the advance of spot-free catalysts.

To overcome this caveat and also to improve the catalyst separation, in this thesis work, spot-free catalysts have been supported on low-dimensional carbon substrates such as carbon nanotubes and few layered graphene. These substrates not only impart high surface area to support the pristine NPs but also exhibit exceptional conducting properties. This in turn enhances the electronic relay between the substrates and the spot-free catalysts further boosting the catalytic turnover. These supports also improve the catalyst separation from the reaction mixture. The application of these spot-free catalysts is not only limited to catalysis but also can be extended to sensing, opto-electronic devices and as materials for environmental remediation.

The metal NPs, especially, gold, palladium and platinum have been extensively studied over the past decade due to their exceptional catalytic behavior. The catalytic property of NPs is strongly
dependent on the size, shape and the nature of the capping agent. The chemical stability of the particles is associated with their ability not to aggregate and undergo partial oxidation. The insufficient stability of the nanomaterials has led to impedance in the development of these materials for real world applications. Among the noble metal NPs, nano gold plays a crucial role in nanoscience and nanotechnology with its fascinating physical, chemical and catalytic properties. The relative stability of nano gold colloid in both dispersion and dry particulate matter is of importance. These remarkable properties of gold NPs have led to its application as sensors, nano devices and as catalysts in both homogeneous and heterogeneous catalysis.

In the present thesis work, nanomaterials have been synthesized and used for homogeneous and heterogeneous catalysis. During the course of this work, a number of experimental techniques and methods have been used. These have essentially been classified into 3 types for convenience, namely:

- Catalytic material synthesis and characterization techniques.
- Electrochemical techniques used in catalytic applications.
- Electrocatalysis for fuel cell applications (this is the translational application of this thesis).

2. Catalytic material synthesis and characterization techniques

The experimental approach used predominantly for nanomaterial synthesis in this thesis is by laser ablation mediated synthesis (LAMS). The LAMS technique has been elaborated in detail, in chapter 2 of the thesis. The experimental technique used for the characterization of the catalytic material has been discussed in detail below.

2.1. Electron microscopy

The limitation of light microscopes is its magnification and resolution which has in turn led to the development of electron microscopes. In an electron microscope, a beam of highly energetic electrons are used to image the sample, to get an insight into the topography, morphology along with its structure and composition. There are two kinds of electron microscopes: Transmission electron microscope (TEM) and Scanning electron microscope (SEM) that are most frequently used in nanoscience and technology. In the present study, SEM has been used to characterize the surface topography of the laser ablated materials.

SEM consists of electromagnets that are used to bend the electron beam to furnish the required image on the screen. The use of electromagnets in SEM gives us an edge in terms of the magnification, while the electron beam gives an improved clarity of the produced image. SEM
potentially has very large depth of field that allows for an increased focus onto the sample and makes it possible to examine rougher surfaces and at much higher magnifications.

The advantages of SEM in terms of the ease of sample preparation, higher magnification, increased resolution and large depth of focus has resulted in its use in a plethora of applications. The electron gun having the tungsten tip causes the generation of the electron beam. This electron beam is attracted towards the anode and in due course condensed by the magnetic lens and further focused onto the sample at a very fine point using the objective lens. The electron beam can be deflected back and forth from the sample in a controlled fashion, by varying the scan generator voltage that energizes the scan coils. The striking of the electron beam onto the sample surface generates secondary electrons from the sample that are collected by a secondary electron detector called as the backscatter detector. The obtained signal is immediately converted into a topographic image of the sample. In SEM studies, the selected sample must be electrically conductive because electrostatic charge accumulation takes place at the surface. Non-conducting samples tend to get charged during the electron beam scanning especially during the secondary electron imaging mode. This causes image artifacts as well as scanning faults in the image. Due to this reason the non-conducting samples are usually coated with an electrically conducting material by low vacuum sputter coating or by high vacuum evaporation.

In TEM, a beam of electrons are usually transmitted through an ultra-thin sample and interacts with the sample as and when it passes through. An image is formed upon the interaction of the transmitted electrons through the sample. The image is magnified and focused onto a fluorescent screen or a photographic film or is detected by a sensor such as a camera. Due to the small de Broglie electronic wavelength, TEM’s are capable of imaging at a higher resolution than the light microscopes. This gives the user an edge to proceed to fine magnification of a single atomic column that is tens of thousand times smaller than the smallest resolvable object observed using a common light microscope. In this thesis work, TEM has been used to characterize the gold NPs as well as its carbon composites.
2.2. Fourier Transform Infrared Spectroscopy

The spectroscopy that deals with the interaction of infrared (IR) radiation with a liquid/solid and the subsequent measurement of their frequencies, where the sample absorbs the radiation is known as infrared (IR) spectroscopy. The IR spectrometer records the absorption or transmittance intensities over a wide range of wavenumbers (4000-400 cm\(^{-1}\)) and is expressed in wavenumber units. The major components of the instrument are the source, interferometer and the detector.

The interferometer measures all of the frequencies simultaneously by controlling the intensity of individual radiation frequencies prior to the detector picking up the output signal. The output signal from the interferometer is called as an interferogram that is a plot of intensity over the mirror position. Using a mathematical method called as the Fourier transform (FT), a computer translates the interferogram into an IR spectrum. Hence the IR spectroscopy using this technique is called as Fourier transform infrared spectroscopy (FT-IR). The presence of different kinds of functional groups in the spectrum can be identified due to their characteristic signature absorption at specific frequency zones. This in turn can be used to determine the unknown structure of a chemical compound along with the data from other characterization techniques.

2.3. Ultraviolet-visible (UV-vis) spectroscopy

UV-vis spectroscopy is an absorption technique where the sample absorbs in the ultraviolet and visible region of the electromagnetic radiation. The molecules usually undergo electronic transitions in this region of the electromagnetic spectrum. UV-vis spectroscopy is analogous to
fluorescence spectroscopy in a way that the latter deals with transitions from the excited state to the ground state, whereas the former measures transitions from the ground state to the excited state. The gold NPs give a characteristic peak in the visible region, called as the surface plasmon resonance peak (SPR). It is possible to predict the size and shape of the NPs based on the position and shape of the SPR peak. In this thesis work, we have used UV-vis spectroscopy to study the electronic transitions of the NPs and their composite materials.

2.4. Raman Spectroscopy
One of the most effective methods to characterize carbon materials is Raman spectroscopy. This is a rapid, non-destructive and high resolution technique that offers unique signature peaks for carbon nanotubes and graphene materials. The information that pertains to the electronic structure can be obtained with the use of the Raman spectroscopy, through electron phonon coupling. Even the deposition of different metals on carbon substrates such as graphene or carbon nanotubes can be studied by monitoring the Raman peak shifts (of carbon materials) before and after metal deposition. The Raman shift gives us an insight into the predominant mode of interaction, i.e. charge transfer or strain between the metal and the low-dimensional carbon substrate. In this thesis work, Raman spectroscopy has been used to understand the mode of interaction between gold NPs and the low-dimensional carbon substrates.

2.5. Powder X-ray Diffraction (XRD)
This technique gives us an insight into the type of the crystallographic planes present in the material along with their characteristic d-spacing. Using powdered XRD the average bulk composition of finely grounded homogenized material is determined. The diffraction pattern is a constructive interference of crystalline sample and monochromatic X-rays, when the conditions satisfy Bragg’s law. The Bragg’s equation is nλ=2d sinθ, where n is number of planes of crystalline material, λ is the wavelength of incident light, d is the distance between the 2 crystalline planes of the sample, θ is the diffraction angle. The Bragg’s law relates the electromagnetic radiation’s wavelength to diffraction angle and lattice spacing of the crystalline sample. The X-rays that are diffracted are then detected, processed further, before counting them. The sample is scanned by a range of 2θ angles and all possible directions of diffraction are obtained, due to random orientations of the powdered sample. The conversion of diffraction peaks to d-spacing gives the materials identification. Each material has unique set of d-spacings and the identification is achieved by comparing the d-spacings with standard reference patterns. In this thesis work, XRD has been used to characterize the gold composite materials.
3. Electrochemical techniques used in catalytic applications

Electrochemistry is the back bone of various applications pertaining to energy conversion and energy storage. The fundamental electrochemical techniques used in this thesis work, have been discussed below.

3.1. Potential sweep techniques

Among all electrochemical voltage sweep techniques, cyclic voltammetry is the most utilized technique and is also known as CV. In CV, the waveform is applied as a closed loop shuttling between two sets of potentials. The other commonly used technique is the linear sweep voltammetry (LSV). In LSV, the potentials starts from one and reaches another potential value, thus it is a unidirectional waveform. In CV, there is a forward scan from potential $V_1$ to potential $V_2$ at particular scan rate, similarly after reaching $V_2$ the scan reverses to $V_1$, measuring the electrochemical current in the cell as shown in scheme 3.

![Scheme 3. Potential-time profile for CV.](attachment:image)

The measured electrochemical current can be faradaic due to the redox properties of the chemical species or non-faradaic/capacitive current due to the double layer charging. The resultant plot between the current and the potential values is called as the cyclic voltammogram. Different redox events have different electrochemical potential windows in the broad electrochemical spectrum. Several events such as homogenous reactions, adsorptions, heterogeneous reactions at the interface of the electrode are studied using the CV technique. The shape of the CV curve varies for different reactions. The potential at which the maximum/peak current has been witnessed is called as the peak potential and the potential at which the redox current starts increasing/decreasing leading to the peak current is called as the onset potential. A typical CV curve for a 1 electron reversible redox process is shown below. The mass transfer rate is always slower than the rate of charge transfer and the reaction is hence governed by the
The diffusion of the electro-active species. The concentration ratios of the oxidant to reductant, in a reversible reaction are governed by the Nernst equation and the concentration gradient at the region close to the electrode interface is called as Nernst diffusion layer. In this layer, the concentration gradient of the electro-active species is linear. At all the potentials, the nernstian equilibrium is maintained at the electrode surface.

**Figure 1. Typical CV profile for a single electron reversible process**

The chemical equation for these kinds of redox events is as shown in Eq. 1.

\[
O + ne^- \rightarrow \text{R} \quad \text{.........................Eq. 1}
\]

For a single electron reversible redox event, the shape of the CV characteristic profile shown in Fig. 1 can be explained as follows. When the electrodic potential is swept to negative potentials, the reactant’s (O) surface concentration decreases, as a result of this the concentration gradient is increased and thereby the current increases. The increment in the concentration gradient during this process is due to the reduction of ‘O’ at the interface than in the bulk. Hence to satisfy the nernstian equilibrium, a concentration gradient is set up. Consequently, a proportional current to the established concentration gradient flows at the electrode surface. Because of the ionic diffusion, the concentration gradient decreases and does not continue to be constant. The surface concentration of ‘O’ decreases owing to a change in the electrode potential until it reaches a zero value. As the concentration of ‘O’ becomes zero, the concentration gradient of the accumulated reduced species at the electrode surface also decreases (relaxation effect), as a result of this the current flow also drops down. On account of these events, we notice a peak shaped CV profile as seen in Fig. 1. Similarly it is possible to explain the peak response that appears exactly in the opposite direction during the reverse scan. On increasing the scan rate, apart from the increase in
the concentration gradient and the current, we also have a shorter experimental time frame that leads to a lesser relaxation effect. The current density at the peak of the CV is associated with several parameters by the following relationship in Eq. 2

\[ j_p = -0.4463 \text{ nF \ [nF/RT]}^{1/2} c_0^\infty D^{1/2} v^{1/2} \]  

…………………Eq. 2

where, \( j_p \) is the peak current density in A/cm\(^2\), \( n \) is the number of electrons participating in the redox event, \( F \) is the Faraday constant, \( R \) is the gas constant, \( T \) is the absolute temperature, \( C_0 \) is the concentration of the reactant ‘O’ in mol/cm\(^3\), \( D \) is the diffusion coefficient in cm\(^2\)/s, \( v \) is the sweep rate in V/s. The above Randles-Sevick equation at 25°C gets simplified to, as shown in Eq. 3.

\[ j_p = -(2.69 \times 10^5) n^{3/2} c_0^\infty D^{1/2} v^{1/2} \]  

…………………Eq. 3

The above equation indicates that the peak current density is directly proportional to the concentration of the electro-active species, square root of the scan rate and square root of the diffusion coefficient. The negative convention denotes the process is cathodic in nature.

The reversibility of the electrochemical process can be measured by plotting \((j_p \text{ Vs. } v^{1/2})\). The linearity or constancy of the plot reflects the reversible nature of the system. Additional diagnostic tests to check the reversible nature of the electrode are as follows:

1. \( \Delta E_p = |E_p^A - E_p^C| = 59/n \text{ mV} \).
2. \( |E_p - E_{p/2}| = 59/n \text{ mV} \).
3. \( |j_p^A - j_p^C| = 1 \).
4. \( j_p \) is proportional to \( v^{1/2} \).
5. \( E_p \) is independent of \( v \).
6. At potentials beyond \( E_p \), \( I^2 \) is proportional to \( t \).

There are electrochemical diagnostic tests that verify quasi-reversibility and irreversibility of given systems. The CV technique has been widely used in the present thesis work, to study the electron transfer reactions and to measure the electrochemically active surface area (or true surface area) of the nanocomposite modified electrodes.

3.2. Real surface area determination for metallic electrodes

A modification in CV can be tailored for determining the real surface area of the metallic electrodes based on the adsorption/stripping from the solution. This method is applicable mainly to Pt, Rh and Ir electrodes based on the H atom adsorption in the potential region, before the
profuse evolution of hydrogen [26]. In a typical real surface area determination, the charge measured under the H atom adsorption/desorption peak, after correcting the double layer charging current is presumed to correspond to single H atom adsorption on every metal atom and symbolized by $Q_H$.

For a unit surface area, the charge related with one to one M-H occurrence is denoted by $Q_{S_H}^S$ and the charge is calculated based on the distribution of the metallic atoms on the surface. In such a case the true surface area is given by Eq. 4.

$$\text{True surface area} = \frac{Q_H}{Q_{S_H}^S} \quad \text{Eq. 4}$$

With respect to polycrystalline Pt surface, by calculating the density of atoms at the Pt surface to be $1.31 \times 10^{15} \text{ cm}^{-2}$, the charge related with H adsorption is $210 \mu\text{C cm}^{-2}$ [27].

For example the charge for the anodic curve between -0.3V to -0.2V is measured, highlighted in black in Fig. 2. This charge $Q_H$ of the sample is then divided with $210 \mu\text{C \ cm}^{-2}$ to determine the ECSA of the material.

![Figure 2. CV profile of a Pt based material in 0.1 N HClO4, to measure ECSA.](image)

For metals such as gold, this method is based on the adsorption of oxygen, causing the formation of oxide/hydroxide on the metal surface and their subsequent reduction. Oxygen is presumed to be chemisorbed on a one to one basis on the surface metal atoms, as a monoatomic layer prior to
the oxygen evolution reaction. The charge pertaining to the formation or reduction of the mono-
layered oxide is given by Eq. 5

\[ Q_o = 2e N_A \Gamma_o A \] …………………………………………………………Eq. 5

\( N_A \) is the Avogadro number, \( \Gamma_o \) is the atomic oxygen’s surface concentration, that is presumed to be equal to \( N_M \) the metal atom’s surface density and \( A \) is the geometric area of the electrode. The reference charge value \( Q_o \) can be obtained from the value of \( N_M \) per unit area. The charge associated with desorption of monolayer gold oxide for polycrystalline gold is calculated to be 390 \( \mu \text{C cm}^{-2} \). The electrochemical active surface area (true surface area) is obtained from the charge of the modified gold electrodes in acidic or alkaline solutions and by dividing it with the actual charge value.

The roughness factor can be determined by dividing the true surface area with the geometric area as shown in Eq. 6.

Roughness factor = True surface area / geometric area ……………Eq. 6

The typical CV profile of Au electrode, showing the characteristic peaks of gold oxide formation and its subsequent stripping in dilute HClO\(_4\) solution has been presented in Fig. 3.

![Graph](image)

**Figure 3. CV of Au electrode in dilute HClO\(_4\) solution**

The true surface area in the case of gold modified electrodes can be obtained by dividing the area measured under the gold oxide stripping peak with 390 \( \mu \text{C cm}^{-2} \).
3.3. Electrochemical impedance spectroscopy (EIS)

EIS is an AC technique unlike CV which is a DC technique. Here the electrochemical system is perturbed close to the steady state equilibrium unlike far from equilibrium as in the case of CV. EIS involves small perturbation of the electrode potential, by the application of a sinusoidal signal with amplitude of 10 mV from the equilibrium potential. Subsequently the electrochemical response from the system is measured. Generally the signal response differs in current and amplitude from the applied signal. The sinusoidal perturbation signals and their subsequent response from the electrochemical system are shown in Fig. 4.

![Sinusoidal signal of perturbation and response output from EIS.](image)

**Figure 4.** *Sinusoidal signal of perturbation and response output from EIS.*

With respect to analysis of different kinds of electrode process such as double layer charging, kinetics, electron transfer (heterogeneous and homogeneous) and diffusion, the measurement of amplitude (impedance) and phase difference over a broad range of the frequency is crucial. EIS has been widely used to study batteries, membranes, corrosion, ionic liquids, solid electrolytes, porous electrodes and chemically modified electrodes, to name a few.

To study the rate determining step in a fast electron transfer process, it is necessary to obtain the information in a very short time scale. The AC techniques come in handy to determine the rate constant of fast redox process. The advantage with a small perturbation is that it becomes linear and it is easy to treat the measured response theoretically using the linear current voltage characteristics. As the working window is very close to the equilibrium, an in depth knowledge of current voltage characteristics is not required. As a result of this, there is no need for the
application of equations related to kinetics and diffusion. High precision measurements can be made because the response is steady and consequently averaged over a long run. Comparisons are usually drawn between the electrochemical cell and equivalent circuits that contain capacitance and resistance and behave like an electrochemical cell. The benefit of circuit fitting is to explain the values generated out of the fitting to an interfacial phenomenon taking place at the electrode interface. The frequent use of the impedance technique is to evaluate the heterogeneous charge transfer process and the double layer structure. The two frequently encountered impedance plots are the Nyquist and Bode plots, shown in Fig. 5 and Fig. 6 respectively.

**Figure 5. Typical nyquist plot**

![Nyquist plot](image1)

The Nyquist plot is essentially between the real $Z'$ part and imaginary part $Z''$ of the impedance at different frequencies, whereas, the Bode plot is between total impedance and the frequency.

**Figure 6. Typical Bode plots**
For any charge transfer controlled process, a semicircle alone is obtained and the diameter of the semicircle gives the charge transfer resistance ($R_{ct}$). In case of a diffusion controlled reaction, Warburg impedance is an additional parameter. At a low frequency region, it becomes inversely varied with frequency and as one proceeds further to very low frequency, it increases and shoots out as a straight line with a phase angle of 45°. For Bode plot, the y value at the low frequency region of x axis gives the total impedance value. Both the $R_{ct}$ value and the total impedance value give an estimate of the impedance at the studied potential.

A typical circuit for a diffusion controlled electron transfer reaction is Randles equivalent circuit as represented in Fig. 7. It is indicated with the double layer capacitance ($C_{dl}$), the charge transfer resistance, ($R_{ct}$), Warburg impedance ($W$) and the solution resistance, ($R_s$).

![Randles equivalent circuit](image)

**Figure 7. Typical Randles equivalent circuit for an electrochemical reaction**

In the present thesis work, EIS has been used to dynamically observe the electron transfer kinetics during Hydrogen evolution reaction for various modified electrodes.

### 3.4. Chrono-amperometry

This technique falls under the category of the potential step experiment, where the working potential of the electrode is varied instantaneously and the current-time response of the electrochemical system is recorded. The plot between the current and time is called as chronoamperogram (CA) and the method is called as chronoamperometry. Fig. 8 represents the typical chronoamperogram response of an electrochemical system.
From Fig. 8, it is clearly evident that as soon as the potential is applied, there is a large flow of current at the electrode surface due to the reaction taking place. Initially, the surface of the electrode is fully covered by reductant species and once the potential has been applied the formation of oxidant species occurs. This current, however, decreases with time because of its dependence on the concentration gradient. In the present thesis work, this technique has been utilized to derive the Tafel plots.

3.5. Tafel plot analysis

In corrosion studies and catalysis (hydrogen evolving cathodes), Tafel plots have been extensively used. In the present thesis work, Tafel slopes have been used to study the property of the nanocomposite modified electrodes towards the electrocatalytic oxidation of small molecules such as ethanol, glycerol, and ethylene glycol. The use of these plots is even extrapolated to study the mechanistic aspects in hydrogen evolution reaction. The typical representation of the Tafel equation for a cathodic reaction is as shown in Eq. 7.

$$\log |j| = \log j_o - \alpha C n F \eta / 2.303 RT$$  \hspace{1cm} Eq. 7

Whereas for an anodic reaction the equation is given by Eq. 8.

$$\log |j| = \log j_o + \alpha A n F \eta / 2.303 RT$$  \hspace{1cm} Eq. 8

The equation parameters are as follows:

- $j$ is the total current density,
\[ j_o \] is the exchange current density,

\[ \alpha_C \] and \( \alpha_A \) are the Tafel slopes of anodic and cathodic process

\( \eta \) is the overpotential, that is described as the deviation of the applied potential from the equilibrium potential as in literature. A plot of \( \log |j| \) versus \( \eta \) is known as the Tafel plot. The slope and the intercept of the plots are used to determine the \( \alpha_C \), \( \alpha_A \) and the exchange current density \( j_o \).

**3.6. Tafel slope to study alcohol electrooxidation**

The deviation of the Tafel slopes from linearity in certain experiments has a special implication. The values of these slopes with respect to the electrooxidation of alcohols is dependent on the activities on the electrode surface, such as adsorption of intermediates and surface poisoning that affects the availability of catalytically active sites.

Unlike fundamental electrode processes where linear plots are common, Tafel slopes that have been used to arrive at the mechanistic understanding of redox processes are nonlinear. The nonlinearity is on account of the intermediates generated during the course of the electrochemical reaction that tend to block the catalytic surface to varying extents at different potentials.

In the present thesis work, two slopes have been obtained for a predominant number of electrooxidation reactions involving alcohols. The slope at the higher overpotential is always larger than the slope at the low overpotential region. This particular occurrence is not uncommon as it has already been reported in earlier studies pertaining to alcohol electrooxidation. A low value of the Tafel slope is always desirable, so as to achieve high current density at low overpotentials. In the past, studies have also reported using Tafel plots at various temperatures. Till date, the Tafel slope values have increased with increasing temperature, indicating surface fouling due to intermediates generated during alcohol electrooxidation. In the present work, we have accounted for this occurrence as a result of the interaction of the capping agents (on the NPs) with the intermediates, leading to enhanced blocking of the surface active sites of the metal catalyst. On account of this, in the present work we could clearly observe anti-fouling behavior with NPs devoid of any capping agents.
4. Electro catalysis for fuel cell applications

The importance of electrocatalysis in the context of energy conversion and storage is remarkable. For scientists across academia and industries, the electrocatalysis phenomenon in fuel cell reactions is an important frontier area of research. The definition of electrocatalysis in simple words is “it expresses the enhancement of electrochemical reaction rates by surface modifications of various kinds at the electrochemical active surface”. An electrocatalyst essentially takes part in an electrochemical reaction and enhances the rate of the reaction without being consumed in the electrochemical process. Technically, an electrocatalyst reduces the overpotential of an electrochemical reaction by getting it closer to the thermodynamic equilibrium potential. The applied voltage across an electrolytic cell (V) for any kind of electrochemical reaction can be represented by Eq. 9.

\[ \Delta V = \Delta E + \eta + \Delta \Omega \]  

………………..Eq. 9

Where \( \Delta E \) is the thermodynamic voltage of the cell (depending on the characteristics of the electrode), \( \eta \) is the total overpotential (additional energy) required to carry out the reaction at a normal rate and \( \Omega \) is the cell circuit’s ohmic drop. The required overpotential for the electrochemical reaction can be brought down using an electrocatalyst.

A true electrocatalytic effect is the increase in the reaction’s rate by modifying the nature of the surface active sites rather than increasing the surface area. The two factors that determine the reaction rate for any given electrocatalyst is its geometric and electronic structure. Of the two, the former dictates how the geometry of the catalyst increases the catalytic activity of the material. Additionally, the catalytic activity is also affected, if a metal is used in combination with another metal, as there is a change in the surface structure.

The electronic factor dictates how the electronic structure i.e. electronic orbitals of the catalyst atoms (especially the outer or valence electrons) affect the catalytic properties. The noble metals are the most predominantly preferred catalytic material for fuel cells. These metal catalysts include Pt, Ir, Ru, Pd, Au and Ag. Apart from these, non-noble elements such as Ni, Fe, Co, Cr, V, Mo, Sn, W and few other elements have also demonstrated excellent electrocatalytic activity in conjunction with the noble metals. Platinum metal is the element of choice on account of its ability to catalyze the reaction close to its thermodynamic potential. The focus of frontier research in the recent past has been to identify cost-effective and relatively abundant materials for electrocatalysis. To realize the electrocatalytic properties of any material,
Volcano plots have been studied. These plots display the maximum catalytic activity for a series of catalytic materials for any given property. As an example, these plots can be obtained for a property such as heat of adsorption of an element on the electrode surface and for such a case, a linear decrease on either side of these obtained plots, resembles a volcano. A typical volcano plot of electrocatalysis for hydrogen evolution reaction (HER) has been presented in Fig 9. and the property that has been studied here is the enthalpy associated with the adsorption of hydrogen. It is noteworthy to highlight the significance of Pt group metals that have an intermediate value of enthalpy for hydrogen adsorption and a high degree of activity. This also indicates that an intermediate value of enthalpy for hydrogen adsorption is required for accomplishing high electrocatalytic activity [28-30].

**Figure 9.** Volcano plot for HER for different pure metals. (Source: Conway et al. [29])

With the Pt group metals, the electro-chemisorption of H atom on the metal surface can easily eliminate the adsorbed oxygen with the formation of water. These extraordinary properties of nanomaterials offer unique advantages when used as electrodes or electrolytes for fuel cell application.

Enhanced electrocatalytic properties are witnessed with nanomaterials that have high surface area coupled with small particle size, as the electronic structure of surface atoms changes significantly. Since Pt is expensive, nanomaterials of Pd, Au in combination with other low-cost materials have the potential to emerge as an alternative without compromising the catalytic activity. Essentially, a fuel cell is an electrochemical device that converts chemical energy to electrical energy. Contrary to batteries, fuel cells do not require charging/discharging, they run
as long as the fuel is supplied to generate electricity. Typically a fuel cell contains an electrolyte packed in between two electrodes. The two electrodes are an anode and cathode, where electrochemical oxidation of fuel takes place at the former and electrochemical reduction of oxidant takes place at the latter. The ions generated out of the anode activity permeate through a membrane that is ionically conducting but electronically insulating. The membrane is also a barrier to the fuel and the oxidant, but not only to the electrodes. The electrons generated in due course of electrochemical oxidation of fuel at anode have to pass through an external circuit before reaching the cathode to reduce the oxidant. Current is generated as a result of this continuous electronic movement. At any point there would not be mixing of the fuel and the oxidant and as a result of this there would be no combustion. Theoretically, fuel cells afford 100% efficiency as they are not restricted by the Carnot efficiency. Practically, there are a variety of physical and chemical issues such as the choice of electrolyte material, type of membrane and temperature, to name a few, that govern the efficiency. A typical fuel cell is Proton exchange membrane fuel cell (PEMFC) or hydrogen oxygen fuel cell. The two half reactions at the anode and cathode are as follows,

\[
\text{At the anode} \quad H_2 \rightarrow 2H^+ + 2e^- \quad E_o = 0 \text{V} \quad \text{Eq.10}
\]

\[
\text{At the cathode} \quad \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad E_o = 1.23 \text{V} \quad \text{Eq.11}
\]

\[
\text{Overall reaction} \quad H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad E = 1.23 \text{V} \quad \text{Eq.12}
\]

The factors that are associated with difficulty in attaining the theoretical efficiencies are the overpotentials due to activation, ohmic and mass transport phenomena.

4.1. Electrocatalysis of small organic molecules

The problems associated with hydrogen as the fuel are processability, transmission and storage as result of which small chain alcohols such as methanol, ethanol, ethylene glycol and glycerol that are liquids at normal temperatures have been used. If alcohols are used as fuel in fuel cell devices then they are called as direct alcohols fuel cells (DAFCs). Methanol is a liquid in the range of -97.0°C to 64.7°C, at atmospheric pressure that is good enough to be used as fuel under all conditions. Moreover, the energy density of methanol is larger than that of hydrogen which makes it an attractive fuel for fuel cell technology. The main caveat with methanol use however has been its poisonous nature. The electrooxidation of methanol always produces carbon monoxide that strongly poisons the catalytic surface of platinum and ultimately deteriorates the performance of the fuel cell. Research has subsequently shifted towards other alcohols such as ethanol, ethylene glycol and glycerol. Significant work on metal alloying that produces poison
tolerant catalysts have been pursued. Ru or Au metals have always been considered for their CO tolerant behavior. This behavior is due to the competitive binding of hydroxyl ions over the metal surface that covert CO to CO$_2$ [31-33]. The temperature effect on the electrocatalytic activity of the Pt-Ru alloy has also been studied [34]. Pandey et. al. have used Au and Pd modified conducting polymer combinations as plausible electrocatalysts for fuel cells [35-37]. Although significant research has gone into various issues related to the catalyst and fuel cell, there has been a clear lack of understanding on the effect of the capping agents (on NPs) on catalysis and in specific electrocatalysis. Capping agents are known to cause inhibition of the binding of the reactants on the metal surface and mask the inherent catalytic activity of the metal, called as inhibition effect. Capping agents also act as anchoring filaments to carbonaceous species generated during the course of the electrooxidation reaction and enhance their blocking of the metal active sites. This is referred to as electrode fouling effect due to intermediates accumulation on the surface. The present thesis explores the effect of capping agents on catalysis. Furthermore, it also develops a Tafel based approach to differentiate the catalysts with fouling effects to those without (Spot-free catalysts).

5. Objectives and chapter wise overview
Since the start of the nano revolution, nanocatalysis has drawn wide spread attention. It has become imminent to use capping agents to achieve a precise control and shape of the nanocatalysts. However, the capping agents mask the inherent true catalytic activity of the metal NPs. The objective of the present research work is to synthesize capping agent free metal carbon nanocomposites by laser ablation and their subsequent use as catalytic material. The study also highlights how the capping agents mask the catalytic activity, by comparing the catalytic rates between the capped and uncapped variants.

Electrooxidation of alcohols leave reaction intermediates during the course of catalysis and they tend to foul the electrode surface. One of the objectives of the present study is directed to study the interaction between the accumulated intermediates on a capped vis-à-vis uncapped metal nanoparticle surface. The study for the first time has highlighted the interaction between the capping agents and reaction intermediates that causes electrode fouling often termed as blocking effect. An electrochemical model based on Tafel plots for electrooxidation reactions has been developed as part of this thesis work to evaluate the fouling and antifouling behavior of the catalysts. A chapter wise summary has been presented in brief below to provide an overview of the complete thesis work.
Chapter 1: Introduction
In this chapter, an introduction to nanocatalysis as a bridge between homogeneous and heterogeneous catalysis has been presented. During the course of this research work, a number of experimental techniques and methods have been used. These have essentially been classified into 3 types for convenience, namely,

- Catalytic material synthesis and characterization techniques.
- Electrochemical techniques used in catalytic applications.
- Electrocatalysis for fuel cell applications.

Chapter 2: Novel synthesis and characterization of gold carbon nanotube and gold graphene composites
In this chapter, the novel synthesis of pristine gold NPs, gold carbon nanotube and gold graphene composites using LAMS has been presented along with detailed characterization. The LAMS technique offers several advantages such as: (i) Generation of the NPs in their pristine form. (ii) Simultaneously reduction/deoxygenation of the functionalized carbon surfaces. (iii) Controlled loading of NPs based on ablation time. (iv) Prevention of particle aggregation, as they are supported on the carbon substrates.

The as synthesized nanocomposites have been extensively characterized using TEM, ED, FESEM, EDAX, DLS, Powder XRD, Raman, FT-IR and UV-Vis spectroscopic techniques.

Chapter 3: Dye decolorization studies on gold graphene system
This work highlights the use of gold-graphene in the decolorization of dyes in comparison with other experimental controls. In this study, 4 different kinds of dyes have been chosen as model substrates for the decolorization process.

In case of Methylene blue alone, the reaction showed 17000 times better catalytic activity compared to the uncatalyzed reaction. In case of decolorization of Rhodamine B, the catalytic activity has nearly doubled with uncapped gold graphene composite compared to commercial citrate capped gold nanoparticles of similar size. This remarkable catalytic activity has been attributed to the unmasked, pristine catalyst surface of the gold graphene. This chapter summarizes the masking of catalysis due to the use of capping agents on the catalyst surface.
Chapter 4: Hydrogen evolution studies on gold graphene and gold carbon nanotube
In this chapter, the use of gold graphene and gold carbon nanotube composites for a detailed hydrogen evolution study has been presented. The carbon paste electrodes are modified with gold composites by a simple drop cast method to study the kinetics of proton reduction in acidic solution by CV, CA, Tafel plots and EIS.

This kinetic data comparison between uncapped gold carbon composites with other capped controls outlines the significance of the spot-free gold decorated on low-dimensional carbon frameworks. Briefly, the enhanced electro-catalytic performance of the clean (spot-free) gold decorated on low-dimensional carbon frameworks for an efficient electronic transfer at the interface of the electrode is on account of (i) clean surface of AuNPs, (ii) large surface area of carbon nanotube and graphene that provides a conducting 3-D framework for improved tethering of AuNPs, (iii) synergy of AuNPs and the carbon supports that provides an improved electronic relay during hydrogen evolution. The enhanced performance of these nanocomposites in the absence of the capping agents necessitates a deeper understanding on the requirement as well as the choice of these capping agents that leads to the discussion presented in chapter 5 of the thesis.

Chapter 5: Anti-fouling response of gold carbon nanotube system
This chapter deals with ethanol electrooxidation reaction on gold carbon nanotube composite. The catalyst has shown excellent stability towards electrooxidations even after 200 CVs. The kinetic study of electrooxidations in alkaline medium using the as-synthesized gold carbon nanotube, has resulted in significantly low Arrhenius energy of ~28 kJ mol⁻¹. Tafel studies indicate the improved efficiency of the catalyst with increasing temperature, on account of the reduced fouling of the modified electrode surface. This signifies the auto anti-fouling ability of the composite towards electrooxidation and also highlights it as a plausible contender for use as a catalyst material in fuel cells. This chapter concludes with the development of a Tafel based model to predict the fouling and anti-fouling abilities of any electrocatalyst. The testing of the model and fouling of the electrode surface due to reaction intermediates in the presence of capping agent has been discussed in chapter 6.

Chapter 6: Tafel based model for understanding fouling and anti-fouling behavior
In this chapter, the role of capping agent in electrocatalysis has been detailed by studying the Tafel based model developed as part of this thesis work. Four different catalysts have been chosen in a manner that provides a complete understanding of the Tafel slopes based model. The
conclusions drawn from the model relate for the first time that the presence of the capping agents could cause blocking on the catalyst surface due to its interaction with the reaction intermediates. The study also reveals poisoning of the metal surface due to the covalent binding of the reaction intermediates, as a capping agent independent phenomenon. This predictive outcome on the use of this model can be extended to study the nature of fouling behavior on any electrocatalyst surface and opens the door to next-generation electrocatalysis.

Chapter 7: Summary

- For the first time, we have synthesized gold graphene and gold carbon nanotubes using LAMS and the nanocomposites have been used for catalytic and electrocatalytic applications.
- This thesis work has developed the use of Tafel slopes as an indicator to measure fouling and anti-fouling effects that affect electrode behavior.
- The model has been tested for different metal composites synthesized by different techniques and has been used to understand electrooxidation reaction of different alcohols and polyols.
- Further development of this model would result in a deeper understanding on the requirement and role of capping agents.

REFERENCES


