Chapter II: Theory and Experimental Procedures
2. Theory and Experimental Procedures

In this chapter we have given an account of the preparation methods and different characterization techniques employed to explore the physicochemical properties of the materials. Preparation methods control physical, textural, optical and electronic properties of catalysts, thus control materials activity, selectivity in a catalytic process [1]. We have used solution combustion method for fast and simple synthesis of disordered mesoporous materials for unique catalytic properties, such as V doped titanium dioxide for partial oxidation reactions [2]. Incipient wet impregnation method, for preparation of 5% manganese oxide on titania was employed [3]. We have also used high temperature, high pressure reduction method to prepare H-TiO$_2$ materials for solar light harvesting application experiments [4]. Materials are analyzed for their textural properties using N$_2$ physisorption, structural features were studied using PXRD, Raman spectroscopy, and DRIFTs methods, electronic properties were explored using XPS and DRS, elemental composition analysis were made by SEM-EDAX studies, morphological analysis using HRTEM techniques. These techniques help us to explain the nature of Mn, V doped into rutile TiO$_2$. Also selected spent catalysts were analyzed to understand the active material under reaction condition.

2.1 Catalyst Preparation Method

2.1.1 Solution Combustion Method

The synthesis of solids having desired structures, composition and properties continues to be a major challenge to chemists, material scientists and engineers [5]. Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) is an effective, low-cost method for synthesis of various industrially useful materials, for synthesizing single phase solid solutions, nanomaterials, porous materials, crystalline oxides, composites as well as complex mixed oxide phases and homogenous doping in metal oxides. The term ‘combustion’ covers flaming (gas-phase), smoldering (heterogeneous) as well as explosive reactions. The strategy of the technique adopts a self-persistent reaction between an oxidizer and fuels that are dissolved in water medium. The process makes use of extremely exothermic redox chemical reactions between metals and nonmetals, the metathetical (exchange) reaction between reactive compounds or reactions involves redox compounds/mixtures. The combustion method has been successfully used in the preparation of a large number of technologically
useful oxide (refractory oxides, catalysts, magnetic, semiconducting, insulators, dielectric, sensors, phosphors etc.) and nonoxide (carbides, nitrides, borides, silicides etc.) materials [6]. It was understood that the conventional solid state SHS being a gasless combustion process typically yields much coarser particles than solution combustion approach. Combustion synthesis is broadly classified into three types based on the nature of the initial reaction medium:

- Conventional SHS of nanoscale materials, i.e. initial reactants are in solid state (condensed phase combustion).
- Solution combustion synthesis (SCS) of nanosized powders, i.e. initial reaction medium is aqueous solution.
- Synthesis of nanoparticles in flame, i.e. gas-phase combustion.

Solution combustion synthesis (SCS) is a simple, rapid and versatile process, which allows effective synthesis of a variety of nanosize materials [7]. The solution processes have been increasingly used due to their peculiar and unique characteristics. This process not only yields nanosize oxide materials but also allows uniform (homogeneous) doping of trace amounts of metal ions in a single step. In recent years, there has been remarkable interest in the combustion synthesis of materials because of its simple, fast, energetically economic and yields high purity products compared to the conventional routes to prepare these materials.

SCS is a method based on the principle that once are action is initiated under heating, an exothermic reaction occurs that becomes self-sustaining within a certain time interval, resulting in a powder as final product. As it is a high-temperature process, only thermodynamically stable phases can be prepared. Solution combustion synthesis process involves a self-sustained reaction in homogeneous solution by use of salts, such as nitrates, metal sulfates and carbonates, as oxidants and, reducing reagents, fuels such as glycine, sucrose, urea, hydrazides or other water soluble carbohydrates. Nitrate acts as an oxidizer for the fuel during the combustion reaction. The powder can be a pyrolyzed product of a single phase, but usually it is a combination of metal oxides and in some cases it needs subsequent heat treatment to form single phase products, which are usually the results required in this process. The exothermic reaction begins at the ignition temperature and generates a certain amount of heat that is manifested in the maximum temperature or temperature of combustion. Solution combustion synthesis has the advantage of rapidly producing fine and
homogeneous powders. Since it is an exothermic, auto-propagated process, and with a high heat release rate, it can be explosive and should be undertaken with extra precautions. Depending on the type of the precursors, as well as the conditions used for the process organization, the SCS may occur as either volume or layer-by-layer propagating combustion modes.

**a. Self-propagation mode**: The reaction initiates locally and propagates a wave-like pattern throughout the medium. This type of mode takes longer time for completion. The slow but stepwise heating favors the growth of nanoparticles. The steady evolution of reactant gases produces wormhole mesoporous materials that are acclaimed for having the property of fast diffusion of charge carriers from the bulk to the surface. For an example, mesoporous V-doped TiO$_2$ is prepared by combustion synthesis via self propagation mode.

**b. Voluminous combustion mode**: There is uniform heating and concurrent reaction occurs throughout the reaction mixture. This mode is advantageous for producing crystalline materials. The feature of crystallinity in photocatalysts is one of the important factors for reducing recombination centers and in particular catalysts that are involved in water splitting reaction are expected to have good crystallinity. This is a fascinating preparation for wide variety of materials with excellent catalytic activities. The most attractive feature of this preparation method is that there is no need of any purification treatment required as well as high thermally stable catalysts. High thermal stability arises due to its preparation at high temperatures and generally they withstand harsh high temperature as well as pressure conditions adopted in real-world catalysis.

Relatively speaking combustion synthesis takes place at rapid kinetics. Due to the fast kinetics some disadvantages are also present, such as particle size, textural properties may not be controlled to the fullest desired extent. However, by varying the preparation parameters such as, different starting materials with same cations, different fuels, one is able to tune the material characteristics within a certain range. The combustion synthesis is an energy efficient process and requires simple instrumental facility of muffle furnace. The reaction takes place in a furnace chamber.
that is preheated to the desired high temperature sufficient for the complete combustion of reactant mixture [8].

At elevated temperature, the water was evaporated first and the mixture becomes compact followed by a self-ignition route. After the combustion process takes place, the precursor materials are converted into fine crystallites accompanied with the evolution of plenty of gases. The reaction time and mode takes major role in deciding the growth of the crystallites either into bulk form or nanoparticles form. Also as the synthesis procedure is growing material particle from solution state, thus foreign atoms are easily incorporated into lattice. We introduced vanadium and manganese into the TiO_2 lattice positions. Same size cations with similar charge, as that of host cation, can only be introduced into the lattice. Similar charge makes the resulting material suitable for redox reactions, often encountered in catalysis. Also synthesis procedure is also growing material particle from solution state [9, 10].

2.1.2 Reduction Method
Hydrogen is a very small molecule, under high temperature and high pressure conditions when materials are treated with hydrogen gas, they are incorporated into the lattice, reduce the native lattice ions (cations). Because of reducing nature hydrogen atoms will create O vacancies, dangling bonds on the surface, hydrogen bond on surface. Surface of a perfectly crystalline material will get affected after hydrogen treatment [11]. We prepared materials by reducing under hydrogen atmosphere, reduction conditions were varied i.e. temperature and pressure of gas inside the autoclave. Catalysts are prepared at higher temperatures of 250, 300, and 400 °C under ambient hydrogen pressure and they are given codes of 25AP, 30AP and 40AP, respectively. 20 bar pressure was applied at 200 °C to understand the influence of high pressure treatment and it is termed as 20B. Reduction of some amount of Ti^{4+} to Ti^{3+} is advantageous in terms of different catalyst and hence catalysis. When activities are evaluated, reduced catalyst shows better values than the pristine virgin catalyst [12]. Color of the materials changed drastically after treatment, indicating the generation of new species. Best methods for self doping i.e. Ti^{3+} species generation, materials were analyzed via other techniques also. Reduced materials show long term stability, and no change in color was observed even after six months.
2.1.3 Incipient Wet Impregnation Method

The impregnation method is useful to physically bind two materials. One of the components is taken as major constituent and act as support. There are two types of impregnation methods, namely dry impregnation method and incipient wet impregnation method. The dry method is that the gaseous vapor of minor component is sprayed over the major component. This method is very fast method and require small amount of components. The disadvantage associated with the method is that the nanomaterials are generally not dispersed well and the clusters are agglomerated. The interaction between the components remains poor due to poorly embedded minor components on the surface of major component [13].

The wet impregnation method is that the support material is suspended in aqueous solution of minor component. The selection of solvent is based in such a way that support is to be in the suspended state and the minor component is to be in well dissolved state. This method is advantageous for better dispersion of nanomaterial over the support and that is expected to help the photocatalysis for easy light penetration. The nanoparticle of the minor constituent is nucleating and growing into clusters on the support and thus, the nanoparticles is deeply buried into the matrix creating composites with fairly bound components. We prepared catalysts for ODH analysis by incipient wet impregnation, 5% Mn3O4 over TiO2 [14].

2.2 Catalytic Activity Studies

Catalytic studies of material for various thermal conversions, photocatalytic processes were evaluated. Sulfide oxidation, ethylbenzene oxidative dehydrogenation, hydrogen evolution were analyzed and solar conversion techniques. The descriptions on the reactor designs followed by the details on reaction conditions of catalytic studies are given.

2.2.1 Sulfide Oxidation

Sulfide oxidation to sulfoxides was carried out in a batch reactor under continuous stirring. Liquid phase sulfoxidation was carried out in a round bottom flask (RBF), attached with a condenser. Fresh catalyst (50 mg), 30% H2O2 (1.5 mmol) used as oxidant for supplying oxygen, at 1.5 equivalent to substrates, different sulfide
substrates (1 mmol) were added into the RBF. Reactions were carried out at different temperatures, including sub-ambient temperatures. Reaction mixtures were collected after 6 h and analyzed via Agilent gas chromatograph (6890 N) equipped with an HP 5.5\% phenyl methyl siloxane column and a flame ionization detector (FID). Products were also analyzed by using GC–MS. Acetonitrile was the solvent employed in all reactions [15].

2.2.2 Oxidative Dehydrogenation

The catalytic activity was evaluated using a continuous flow fixed bed reactor (FBR) having two furnace zones over a temperature range of 430–570 \(^\circ\)C at atmospheric pressure (atm.). An inconel reactor tube with 13mm internal diameter and 510 mm length was used to pack the catalyst. Reactor system was prepared via settling a column of ceramic beads where sieved catalysts bed (1 mL or 0.76±0.04 g) is placed in the middle of reactor with quartz wool packed in the spaces on either side of the bed. Prepared catalysts pellet of 0.8 mm mesh size was filled into the reactor. The reactant flow was configured to operate in up-flow mode and the products were condensed using a chiller. The temperature on the wall of the reactor and in the catalyst bed was measured using a K-type coaxially centered thermocouple. EB flow was controlled using a high precision isocratic pump (Lab Alliance Series II) and the oxygen flow was controlled using a Brooks-make mass flow controller (5890 E series). Samples of reaction mixture were collected at regular interval via cold trap into vials; collected samples were then analyzed using an Agilent 6890N gas chromatograph with a BP-5 (5.5\% phenyl methylsiloxane) column along with an FID detector. The optimized conditions for the reactions were: 500 – 530 \(^\circ\)C, atmospheric pressure, LHSV (liquid hourly space velocity) of 1.8 h\(^{-1}\) with respect to EB, and air flow at GHSV (gas hourly space velocity) 10800 h\(^{-1}\), i.e. \(\text{O}_2/\text{EB}\) molar ratio of 2.0. Liquid and gaseous products analysis was carried out separately. EB conversion, styrene selectivity and yield has been calculated from the GC analysis results and discussed in chapter 4, all data points were obtained in duplicate with an error of ±2\% [16].
2.2.3 Hydrogen Production via Water Splitting

Hydrogen production was studied for evaluation of photocatalytic activity of prepared H-TiO$_2$ materials. Catalysts were used under different light sources such as UV-Vis., and AM1.5. 20 mg catalyst was taken in quartz RB followed by sonication and degassing in argon gas to remove any dissolved oxygen; after this treatment, the solution was irradiated with required wavelength range photons. Water and methanol mixtures were used for hydrogen production [17]. Reactions were carried out via stirring the solution and collecting the hydrogen produced via water reduction in the presence of methanol electron donor. Gases were collected periodically via gas tight syringe over a reaction period of 6 h, and were analyzed by Agilent gas chromatograph (7890 N) equipped with a Carbo Sieve S-II packed column and a thermal conductivity detector.

2.2.4 Inorganic Solar Cell Fabrication

TiO$_2$ paste was prepared for different titania powders samples following method in literature [18]. Anode electrodes were fabricated with H-TiO$_2$ materials for solar cells. FTO glass plates were cleaned in a detergent solution using an ultrasonic bath.
for 30 min and rinsed with water and ethanol. The FTO glass plates were immersed in 40mM TiCl₄ (aqueous) at 70°C for 30 min and washed with water and ethanol. The photoanode was prepared by doctor blade method using the TiO₂ paste on FTO plate. The TiO₂ electrodes were gradually heated under an air flow at 325°C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. A paste of TiO₂ for the scattering layer containing 400 nm sized anatase TiO₂ particles was deposited by doctor blade printing on photo anode and again gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The photo anodes were treated again by TiCl₄ at 70 °C for 30 min and sintered at 500 °C for 30 min. The working electrode was composed of a 12-13µm thick TiO₂ film (active area 0.16 cm²), composed of an 8-9 µm layer with H-TiO₂ particle and a 4-5 µm scattering layer composed of 400 nm sized TiO₂ particles. The dye solutions were prepared with N719 dye in methanol. 0.5 mM concentration of N719 dye in methanol was prepared. The photo anodes underwent dipping for different time interval to complete the loading with sensitizer. The dye-adsorbed TiO₂ electrode and Pt-counter electrode were assembled into a sealed sandwich-type cell by heating at 100 °C for 10 min. A drop of electrolyte solution (electrolyte of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.05 M I₂, 0.1 M LiI, and 0.5 M tert-butylpyridine in acetonitrile) was poured in to the counter electrode of the assembled cell [19-21]. Completed solar cells were kept under solar simulator and different analyses were done (JV plot, impedance measurement).

2.3 Physiochemical Characterization Methods

2.3.1 Introduction

To understand the material we have to analyze materials with various physiochemical techniques such as PXRD, surface area determination by BET method, UV-Visible spectroscopy (DRS), DRIFTs, X-Ray photoelectron spectroscopy(XPS), Raman spectroscopy, transmission electron microscopy, scanning electron microscopy (SEM), energy dispersive analysis of X-rays (EDAX), LSV, CV, NMR, thermo gravimetric analysis (TGA) etc. Instrumentation and experimental methods for these techniques are explained in detail below.
2.3.2.1 X-Ray Diffraction

Powder X-ray diffraction (PXRD) data were collected from PANalytical X’pert Pro dual goniometer diffractometer. A proportional counter detector was used for low angle experiments. The data point were collected with a step size of 0.02° and a scan rate of 0.5°/min. The sample was spun slowly throughout the scan for better counting statistics. The radiation used was Cu Kα (1.5418 Å) with Ni filter and the data collection was carried out using a sample holder in Bragg–Brentano geometry [22]. Scherrer equation is used to calculate particle sizes of crystallites. The equation is:

\[ \tau = \frac{K \lambda}{\beta \cos \theta} \]

where:

- \( \tau \) is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size;
- \( K \) is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite;
- \( \lambda \) is the X-ray wavelength;
- \( \beta \) is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. This quantity is also sometimes denoted as \( \Delta(2\theta) \);
- \( \theta \) is the Bragg angle.

2.3.2.2 Nitrogen Physisorption

Nitrogen adsorption/desorption isotherms for the materials were obtained from quantachrome autosorb automated gas sorption system (NOVA 1200). The Brunauer–Emmett–Teller (BET) equation was used to calculate the surface area from the adsorption branch. The pore size distribution was calculated by analyzing the adsorption branch of the nitrogen sorption isotherm using Barrett–Joyner–Halenda (BJH) method [23-24]. BET is based on the physical adsorption of gases on the material surface. The equation is:
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\[
\frac{1}{V_a(P_0/P - 1)} = \frac{C-1}{V_mC} \cdot \frac{P}{P_0} + \frac{1}{V_mC} \quad \ldots \ldots \quad \text{eq 1.}
\]

Where \(P\) and \(P_0\) are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, \(V\) is the adsorbed gas quantity (for example, in volume units), and \(V_m\) is the monolayer adsorbed gas quantity. \(C\) is the BET constant,

\[
C = \exp \left( \frac{E_1 - E_L}{RT} \right)
\]

Where \(E_1\) is the heat of adsorption for the first layer, and \(E_L\) is that for the second and higher layers and is equal to the heat of liquefaction.

Equation 1 is an adsorption isotherm and can be plotted as a straight line with \(\frac{1}{V_a(P_0/P - 1)}\) on the y-axis and \(\phi = \frac{P}{P_0}\) on the x-axis according to experimental results. This plot is called a BET plot. The linear relationship of this equation is maintained only in the range of \(0.05 < \frac{P}{P_0} < 0.35\). The value of the slope \(A\) and the y-intercept \(I\) of the line are used to calculate the monolayer adsorbed gas quantity \(V_m\) and the BET constant \(C\). The following equations can be used:

\[
V_m = \frac{1}{A + I}
\]

\[
C = 1 + \frac{A}{I}
\]

The BET method is widely used in surface science for the calculation of surface area’s of solids by physical adsorption of gas molecules. The total surface area \(S_{total}\) and the specific surface area \(S_{BET}\) are given by

\[
S_{total} = \frac{(V_mN)s}{V},
\]

\[
S_{BET} = \frac{S_{total}}{a}
\]

where:

- \(V_m\) is in units of volume which are also the units of the molar volume of the adsorbate gas,
- \(N\) is Avogadro’s number,
- \(s\) the adsorption cross section of the adsorbing species,
- \(V\) the molar volume of the adsorbate gas, and
- \(a\) is the mass of the solid sample or adsorbent.
2.3.2.3 UV-Visible Spectroscopy (DRS)

UV-Visible Spectroscopy of powder materials doesn’t show specular reflection as shown in figure 2, thus uv-visible measurements were carried out in diffuse reflectance mode (DRS). UV visible reflectance measurements were carried out on Shimadzu spectrophotometer UV2700 [25].

![Figure 2 showing specular reflection and diffuse reflection over different surfaces.](image)

A Tauc plot is used to determine the optical gap, or Tauc gap, in semiconductors. The Tauc gap is often used to characterize practical optical properties of powder materials.

\[
ah v = A(hv - E_g)^{\frac{1}{n}}
\]

- \( h \): Planck's constant,
- \( v \): frequency of vibration,
- \( a \): absorption coefficient,
- \( E_g \): band gap,
- \( A \): proportional constant.

The value of the exponent \( n \) denotes the nature of the sample transition

- For direct allowed transition, \( n = 1/2 \)
- For direct forbidden transition, \( n = 3/2 \)
- For indirect allowed transition, \( n = 2 \)
- For indirect forbidden transition, \( n = 3 \)

2.3.2.4 DRIFTs

Diffuse Reflectance Infrared Fourier Transform spectroscopy means a special technique of infrared spectroscopy. DRIFTs powder materials doesn’t show specular reflection rather than diffuse reflection. DRIFT’S studies the surface chemistry of high surface area powders, notably for heterogeneous catalysis, where the temperature
and environment of the catalyst can be controlled in-situ in the DRIFTS cell. DRIFT measurements were carried out on Shimadzu make FTIR-8201PC [26]. The particle size should be smaller than the wavelength of the incident light, so this would infer that it should be less than 5 µm for mid-range infrared spectroscopy.

Alternative plots of Kubelka-Munk units can be used, which relate reflectance to concentration using a scaling factor, expressed in linear units Kubelka-Munk roughly correspond to absorbance in transmission KBr pellet technique.

\[ f(R) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{k}{s} \]

Where:

- \( f(R) \)… is called Kubelka-Munk function
- \( R_\infty \)… absolute reflectance of the sampled layer
- \( k \)… molar absorption coefficient
- \( a \)… absorbivity - proportional to the fraction of transmitted light
- \( s \)… diffusion (scattering) coefficient - proportional to the fraction of diffused light

2.3.2.5 Raman Spectroscopy

Raman spectra were recorded on a Horiba JY LabRAM HR 800 Raman spectrometer coupled with microscope in reflectance mode with 633 nm excitation laser source and a spectral resolution of 0.3 cm\(^{-1}\) [27].

2.3.2.6 X-ray Photoelectron Spectroscopy

XPS measurements were performed in a laboratory based custom built ambient pressure photoelectron spectrometer (APPES from Prevac, Poland) under UHV condition. XPS measurements were made with Mg Ka X ray source for X-ray generation and R3000HP (VG Scienta) analyzer for energy analysis [28].

\[ E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi) \]

Where:

- \( E_{\text{binding}} \) is the binding energy (BE) of the electron,
- \( E_{\text{photon}} \) is the energy of the X-ray photons being used,
- \( E_{\text{kinetic}} \) is the kinetic energy of the electron as measured by the instrument and \( \phi \) is the work function dependent on both the spectrometer and the material.

This equation is essentially a conservation of energy equation. The work function term \( \phi \) is an adjustable instrumental correction factor that accounts for the few eV of
kinetic energy given up by the photoelectron as it becomes absorbed by the instrument's detector. It is a constant that rarely needs to be adjusted in practice.

2.3.2.7 Transmission Electron Microscopy
A FEI TECNAI 3010 electron microscope operating at 300 kV (Cs = 0.6 mm, resolution 1.7 Å) was used for recording high resolution transmission electron microscope (HRTEM) of all materials. Samples were crushed and dispersed in isopropanol before depositing onto a holey carbon grid [29]. Different X-rays and electrons generated by interaction with the matter are shown in the diagram.

2.3.2.8 Scanning Electron Microscope
SEM-Energy Dispersive Analysis of X-rays (EDAX) measurements were carried in SEM system (FEI, Model Quanta 200 3D) equipped with EDX attachment. EDX spectra were recorded in the spot-profile mode by focusing the electron beam onto specific regions of the sample [30].

![Diagram showing interaction of incident electron rays on matter, generating various x rays and electrons.](image)

Figure 3, Interaction of incident electron rays on matter, generating various x rays and electrons.

2.3.2.9 Thermo Gravimetric Analysis
TGA to understand the coke deposition or change in catalyst we have done gravimetric analysis. Thermal analyses of these adducts were conducted on Perkin–Elmer Diamond’s thermogravimetry (TG) and differential thermal analysis (DTA) using alumina as the internal standard [31].

2.3.2.10 Linear Sweep Voltammetry
LSV to monitor the change in current, this technique is used using the principle of voltammetric method in a conventional three electrode system immersed in the electrolyte bath. The current of the working electrode is measured while the potential between reference electrode and counter electrode are sweeping from positive potential to negative potential. Linear sweep voltammogram is the half the cycle of the cyclic voltammetry and redox potential of the elements in the catalyst can be identified. In case of photocurrent generation experiment, the catalyst should not be allowed to undergo both oxidation and reduction reactions because faradaic current should not be confused with the current generated by the conversion of light energy absorbed into excited electron/hole carriers. The window of the potential sweep is to maintain in the range that does not cause corrosion of the catalyst [32].

2.3.2.11 Chronoamperometry
This technique is used to analyze the sustainability of the current generation over a period of time. In case of electrochemical applications, the change concentration of electroactive species with respect to time or in other words, the reaction kinetics is monitored using chronoamperometry technique. However, in case of photocatalytic applications, the photocurrent generation is expected only due to the photofunctional behavior not the faradiac process. In that case, the plot of current Vs time is done along with the light irradiating shutter on/off operations. When the shutter for light irradiation is opened, current rises and maintains at the same value. The value of current generation drops on closing of the shutter [33]. Chronoamperometric studies were carried over Gamry 300 reference potensiostat.

2.3.2.12 Photoluminescence Spectroscopy
PL spectroscopy is a complimentary technique to UV-Visible spectroscopy that gives information on the electronic structure from the emission process (fluorescence) of the excited electron to the ground state [34]. Photoluminescence (PL) measurements
were performed using Horiba Jobin Yvon Fluorolog 3 spectrophotometer with a 450 W xenon lamp at room temperature under the excitation light of 330 nm. The conditions are maintained to compare the photocatalytic conditions.

2.3.2.13 JV plot

JV plot were measured on Photo emission technology inc. (PET) instruments solar simulator model #CT200AAA, Jsc and Voc shows the maximum current, maximum voltage that can be drawn from the cell at short circuit and open circuit condition respectively [35]. Series and shunt resistance were calculated correspondingly at Voc and Jsc. Maximum power output of the cell is denoted by Fill factor, which is ratio of actual power output to theoretical maximum power output of solar cell. Solar energy conversion efficiency of the cell is also calculated from the plot [36].

![IV curve of the solar cell](image)

**Figure 4.** Typical JV plot for solar cells, showing various characteristics parameters of the cell [37].

2.3.2.14 Electrochemical Impedance spectroscopy

EIS was done on Bio-Logic make SP-300 instrument to understand ionic and electronic processes in DSSC. Frequency response of the device is recorder. High frequency response is attributed to the charge transfer at the counter electrode while intermediate frequency response is attributed to electron transport in the mesoporous TiO$_2$ film and TiO$_2$/electrolyte interface. The low frequency region reflects for diffusion in the electrolyte. Electron transport rate and electron lifetime are measured.
for the device. Bias potential studies were done at 0.5, 0.6, and 0.7 V. to calculate the resistance at various barriers [38].

2.4 Conclusion

Characterization methods were summarized in this chapter. The aspects of preparation methods, reaction conditions, experimental reactor set up are explained in detail. The plausible mechanism for the formation of the product is also described with suitable illustration. The characterization methods which are adopted in thesis chapters are summarized along with instrumental conditions.

2.5 References


