Chapter - III
EXPERIMENTAL DETAILS

This chapter describes the materials and reagents used for synthetic procedure and the characterization methods which were used in this research work.

3.1 MATERIALS

The precursors of ZrOCl\(_2\), MnSO\(_4\), ZnSO\(_4\), CuCl\(_2\), CoCl\(_2\) NiSO\(_4\), H\(_2\)SO\(_4\), NaOH and safranin O dye (C.I name: Basic Red 2, C\(_{20}\)H\(_{19}\)ClN\(_4\)) are purchased from Himedia and used without further purification. All solutions are made up with deionised water.

3.2 SYNTHESIS

3.2.1 Synthesis of Metal Oxide nanoparticles

50ml of 1M NaOH was added drop wise to an aqueous solution of MnSO\(_4\) (50mL, 0.1M), making a final volume of 100mL. The mixture was stirred well and refluxed at an elevated temperature for two hours. The MnO\(_2\) nanoparticles were collected by centrifugation, washed with water and dried over for a period of one day at room temperature. Similarly ZnO, CuO, Co\(_3\)O\(_4\) and NiO nanoparticles were also prepared using the precursors such as 0.1M ZnSO\(_4\), 0.1M CuCl\(_2\), 0.1M CoCl\(_2\) and 0.1M NiSO\(_4\).

3.2.2 Synthesis of Mixed Nanooxides

Nano MnO\(_2\)-ZrO\(_2\) mixed oxide was prepared by wet chemical method. The aqueous solution of 50ml of 1M NaOH was added to the solution of 25ml of 0.05M MnSO\(_4\) and stirred well. To this mixture 25ml of 0.05M zirconiumoxychloride was added making a final volume of 100mL. The resulting mixture was stirred well and refluxed at an elevated temperature for 2 hours. The sample was collected by
centrifugation, washed with distilled water to remove anions and dried over for a period of one day at room temperature. The same procedure was carried out to prepare different concentrations of MnO$_2$-ZrO$_2$ mixed metal oxide nanoparticles by varying the concentrations of both MnSO$_4$ and Zirconiumoxychloride in the range of 0.15M-0.45M. Similar procedure was adopted to prepare ZnO-ZrO$_2$, CuO-ZrO$_2$, Co$_3$O$_4$-ZrO$_2$ and NiO-ZrO$_2$ mixed oxide nanoparticles using the precursors as Zirconiumoxychloride and ZnSO$_4$,CuCl$_2$, CoCl$_2$, NiSO$_4$.

3.3 PHOTOCATALYTIC MEASUREMENT:

The photocatalytic activity of metal oxide and mixed oxide nanoparticles were examined by studying the degradation of Safranin O (SO) dye aqueous solution under UV-Visible spectrophotometer. In this photocatalytic experiment, 0.1g of the synthesized nanoparticles was added to 100 ml of 10 mg of aqueous solution of safranin dye. The aqueous suspension was put under constant stirring in dark for 1hr so that the SO dye atoms is adsorbed on the surface of nanoparticles. The stable suspension was then exposed to the UV irradiation with continuous magnetic stirring. The UV-Visible Spectra of the degraded solution were recorded at various time intervals after centrifugation and filtration.

3.4 ELECTROCHEMICAL WORKSTATION

The electrochemical workstation (mode650C),CH-Instrument Inc.,Tx USA was employed for the various electrochemical studies performed. The system contains a fast digital function generator, high speed data acquisition circuitry and potentiostat. The potential control range is +10V and the current range is +250mA. This instrument has the latest analog and microcomputer design to provide high performance, better
precision and greater versatility in electrochemical measurements. This instrument was employed for performing voltammetric studies, Impedance and capacitance studies.

3.5 ELECTROCHEMICAL CELL SETUP

The cell was made of glass, having a capacity of 25 ml. The cell top was made of Teflon and comprised of three separate holes for the insertion of electrodes viz. working electrode, counter electrode and reference electrode. The cell top also has the purging and blanketing of nitrogen gas facility with separate tubes to remove oxygen gas. This setup enables to maintain an inert atmosphere in and above the sample solution throughout the experiment. These functions are controlled through CHI 650C software.

3.6 WORKING ELECTRODES

3.6.1 Glassy Carbon Electrode (GCE)

In the case of cyclic voltammetric studies metal oxide and mixed oxide nanoparticles were coated on a glassy carbon electrode by pasting a pinch of the metal oxide and mixed oxide nanoparticles sample in dimethyl sulfoxide.

3.7 REFERENCE AND COUNTER ELECTRODES

Ag/Ag+ was used as reference electrode for electrochemical investigation. A platinum foil of (1 x 1) cm² was used as counter electrode for electrochemical studies. Pt electrode was cleaned successively with a dilute detergent solution, isopropanol and sodium hydroxide solution. Finally, it was rinsed in distilled water.
3.8 INSTRUMENTATION

The metal oxides and mixed oxide nanoparticles were characterized by various instrumental techniques. Computer controlled JASCO V-530 was used to study UV-VIS spectral behavior. The FT-IR spectra were recorded by SHIMADZU instrument. The X-ray diffraction (XRD) patterns were recorded for the powdered materials using a BRUKER (D8 ADVANCE) X-ray diffract to meter in the scanning range of 20-80°(2θ) using Cu Kα radiation having wavelength of 1.5405Å. EDAX and SEM measurements were carried out through JEOL JSM-6700F field emission scanning electron microscope. The cyclic voltammetry, polarization and impedance studies were carried out using electrochemical workstation (mode 650C), CH-Instrument Inc., TX, USA. TGA/DTA analysis was carried out using Perkin Elmer model and DSC analysis using METTLER TOLEDO model. TEM images were taken using PHILIPS model CM 200 operating at voltages 20-200kV and with a resolution of 2.4Å.

3.9 EXPERIMENTAL PROCEDURES

3.9.1 UV-VIS Spectroscopy

The nature of the material that absorbs the light of particular wavelength is termed as absorption. The intrinsic absorption in a semiconductor occurs in the vicinity of its energy band gap. The absorbent in an absorbing medium obeys the Lamberts law given as T = T₀ e⁻αt, where α is the absorption coefficient, T is the instantaneous transmission, T₀ is the transmission at time t = 0 and t is the thickness of the medium. In this part electronic transitions occurred from the upper part of the valence band to the lower part of the conduction band. The low absorption can be reconciled with the high dc conductivity of the material in terms of the recent electrical transport theories.
in heavily doped wide band gap semiconductors. Most of the electrical applications require the film to have low absorption in the visible region and high dc conductivity. The method is most often used in a quantitative way to determine concentrations of an absorbing species in solution, using the beer-lamberts law as given in equation.1

\[ A = \varepsilon cl \quad \ldots (1) \]

Where A is the measured absorbance, ε is the intensity of the incident light at a given wavelength, l the path length through the sample, and c the concentration of the absorbing species. For each species and wavelength, ε is a constant known as the molar absorptive or extinction coefficient. The absorbance and extinction ε are sometimes defined in terms of the natural logarithm instead of the base-10 logarithm. UV/Vis Spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied.

3.9.2 FT-IR

The interferogram in practice consists of a set of intensities measured for discrete values of retardation. The difference between successive retardation values is constant. Thus, a discrete Fourier transform is needed. The fast Fourier transform (FFT) algorithm is used. The first FTIR spectrometers were developed for far-infrared range. The reason for this has to do with the mechanical tolerance needed for good optical performance, which is related to the wavelength of the light being used. For the relatively long wavelengths of the far infrared (~10 μm), tolerances are adequate, whereas for the rock-salt region tolerances have to be better than 1 μm. It uses a stepper motor to drive the moving mirror, recording the detector response after each step was
completed. The near-infrared region spans the wavelength range between the rock-salt region and the start of the visible region at about 750 nm. Overtones of fundamental vibrations can be observed in this region. It is used mainly in industrial applications such as process control and chemical imaging.

### 3.9.3 X-RAY Diffraction (XRD)

XRD permits the identification of crystalline structures in samples. The analysis of the patterns can lead to the determination of other structural parameters such as strain state, crystallite size, phase composition and preferential growth of the crystals. In XRD, a filtered X-ray beam is directed on the sample and the beam is diffracted when it interacts with a plane in the crystalline structure. To detect diffracted beams of different planes it is necessary that the diffracted beam should be in phase with respect to another one. Otherwise the beams will disappear. The figure given below shows the basic aspects involved with a diffraction experiment. The interplanar distance ‘d’ can be calculated using Bragg’s equation and the average crystallite size by using Scherrer’s equation.

\[
n\lambda = 2d \sin (\theta) \quad \ldots (2)
\]

\[
t = \frac{0.95\lambda}{\beta \cos \theta_m} \quad \ldots (3)
\]

Equation 2 is the so-called Bragg’s equation for inter planar distance calculation whereas equation 3 is the Scherrer’s relationship used for crystallite size calculations. \( \lambda \) is the wavelength of the X-ray beam, \( d \) corresponds to inter planar space, \( \theta \) is the diffraction angle and ‘\( n \)’ is a integer number relationship with the constructive interference for the X-ray beams travel at different pats, ‘\( \beta \)’ is the width in radians of the diffraction peak at half of the highest intensity.
X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology.

3.9.4 Scanning Electron Microscopy

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity.

3.9.5 Principle of SEM & EDAX

SEM is essentially a high magnification microscope, which uses a focused scanned electron beam to produce images of the sample, both top-down and, with the necessary sample preparation, cross-sections. The primary electron beam interacts with the sample in a number of key ways:-

- Primary electrons generate low energy secondary electrons, which tend to emphasize the topographic nature of the specimen.
- Primary electrons can be backscattered which produces images with a high degree of atomic number (Z) contrast.
- Ionized atoms can relax by electron shell-to-shell transitions, which lead to either X-ray emission or auger electron ejection. The X-rays emitted are characteristic of the elements
- In the top few ml of the sample are measured by the EDAX detector.
The SEM is also widely used to identify hashes based on qualitative chemical analysis and/or crystalline structure. Precise measurement of very small features and objects down to 50 nm in size is also accomplished using the SEM.

Energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS), sometimes called energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA), is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray emission spectrum. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.
3.9.6 TEM

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; The image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

TEM images are formed using transmitted electrons (instead of the visible light) which can produce magnification details up to 1,000,000 xs with resolution better than 10 Å. Furthermore, the analysis of the X-ray produced by the interaction between the accelerated electrons with the sample allows determining the elemental composition of the sample with high spatial resolution. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. TEM finds application in cancer research, virology, materials science as well as pollution, nanotechnology, and semiconductor research.

3.9.7 Electrochemical Measurements

The electrochemical performances of the pseudocapacitors were measured by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) using CH Instruments 650 electrochemical analyzer. Electrochemical measurements were carried out in a three-electrode cell with a silver-silver chloride electrode, a counter electrode of platinum sheet, and aqueous 0.1 M H₂SO₄ as the electrolyte. CVs were recorded between 0 and 0.8 V versus silver–silver chloride electrode at a scan rate varied from 100 to 500 mV/s. The values of the capacitance (F) were estimated from cyclic voltammetric curve by using the following equation.4
\( Q = CE \) \( \ldots (4) \)

For a simple parallel plate capacitor, charge on the capacitor, \( Q \), is proportional to the voltage drop across the capacitor, \( E \), as shown in the above equation. The proportionality constant \( C \) is the capacitance of the medium. Capacitance is a crucial factor in electrochemical experiments because it gives rise to current during the charging of the capacitor. To calculate the magnitude of this current, we differentiate the above equation with respect to time \( (t) \) and assume that the capacitance is constant.

\[
\frac{dQ}{dt} = C \frac{dE}{dt}, \quad \ldots (5)
\]

Recognizing that \( \frac{dQ}{dt} \) is an expression for current and \( \frac{dE}{dt} \) is the potential scan rate \( \nu \), we obtain:

\[
i = C \nu \quad \ldots (6)
\]

From this very simple derivation, we have an expression for the charging current at steady state when applying a ramping voltage. Thus by measuring the charging current at a given scan rate, we can determine the capacitance of the system. If there is no possibility for electron transfer between the solution and the electrode (we don’t add a redox couple) this is the only current that we will observe.

### 3.9.7.1 Cyclic Voltammetry

![Cyclic Voltammetry Image](image_url)

**Fig. 3.1 : CH Instrumentation Electrochemical workstation**
Cyclic voltammetry is perhaps the most versatile electro analytical technique for the study of electro active species and for the determination of mechanisms and rates of oxidation / reduction reactions. Cyclic Voltammograms trace the transfer of electrons during an oxidation-reduction (redox) reaction. The potential of an electrode in solution is linearly cycled from a starting potential to the final potential and back to the starting potential. Here, the current is measured as a function of potential. This process, in turn, cycles the redox reaction. Multiple cycles can take place. The system starts off with an initial potential at which no redox can take place. At a critical potential during the forward scan, the electroactive species will begin to be reduced. After reversal of potential scan direction and depletion of the oxidized species, the reverse reaction, oxidation takes place. The commonly used working electrodes are glassy carbon, planar platinum disks, platinum wires, hanging mercury drops and carbon paste electrode.

The chief strengths of cyclic voltammetry are

- Applicability to a wide range of electrode materials.
- A range of five orders of magnitude in scan rates.
- Great flexibility in setting up scan limits and reversal conditions.
- An intrinsic facility for highlighting the chemical conditions between various electroactive species present in the voltammogram.
- Highly developed theory.

The shape of the voltammogram depends on the mechanism of the electrode process. The number of electrons transferred in each peak can be determined by cyclic voltammetry.
3.9.7.2 Impedance Measurements

The technique is actually a combination of two methods. a) The FFT (Fast Fourier Transform) technique measurements from 0.0001 to 10Hz and b) phase-sensitive lock in amplification for measurements from 1 to 20 KHz.

In this way the optimum method can be applied to both high and low frequency experiments. Since the system includes a microcomputer with dedicated software, it is possible to measure the data from Lock-in and FFT measurements and display the impedance data over a wide range of frequencies.

The FFT excitation waveform is applied to the test system via the potentiostat and interface module. The interface also functions as a response measurement device. In the FFT mode, it transmits the raw data in digital form to the Apple Rlle for subsequent reduction and display. In the lock in mode, the total cell response signal is routed to the lock in amplifier where it is resolved into its real and imaginary components. The lock-in system then transmits this information to the microcomputer for reduction and display. The entire experiment form definition to data display and evaluation by the model CHI 660C dedicated software package, which has been written in convenient menu driven format. The three electrode-polarization cell was used in this technique. GCE was used as the working electrode. The working electrode dipped in the electrolyte was allowed for 5-10 minutes time interval for the system to attain a steady state open circuit potential. Then the experiment is started with the help of micro computer key board. After the experiment was over, the real part of impedance ($Z'$) in ohms and the imaginary part of impedance ($Z''$) in ohms were plotted on a recorder as $Z''$ Versus $Z'$. 
3.9.8 Differential Scanning Calorimeter

The Differential Scanning Calorimeter (DSC) measures the constant pressure heat capacity \( (C_p) \) by monitoring the difference in the amount of heat absorbed by the sample solution and an equal amount of a matching buffer as the temperature of both solutions is slowly changed. If the sample undergoes a thermally induced transition, this method directly identifies the transition temperature \( (T_m) \) and the excess heat capacity which allows the determination of the enthalpy associated with this transition \( (\Delta H_{\text{cal}}) \). Unlike optical approaches (CD, fluorescence, UV/Vis), DSC is used to study stability and melting behavior of molecules and it permits characterization of multiple transitions in a single run. Furthermore, it is not constrained to the two-state data analysis model, which is the common assumption when calculating van’t Hoff enthalpy \( (\Delta H_{\text{vH}}) \) from data obtained by optical methods.

Typical applications of DSC include:

- Studies of protein stability and folding.
- Assessment of the effects of mutation on protein stability.
- Characterization of nucleic acids, lipids, membranes, and micellar systems.

3.9.9 TGA/DTA

Thermogravimetry (TG) is the branch of thermal analysis which examines the mass change of a sample as a function of temperature in the scanning mode or as a function of time in the isothermal mode. Not all thermal events bring about a change in the mass of the sample (for example melting, crystallization or glass transition), but there are some very important exceptions which include desorption, absorption, sublimation, vaporization, oxidation, reduction and decomposition. TG is used to characterize the decomposition and thermal stability of materials under a variety of
conditions and to examine the kinetics of the physicochemical processes occurring in
the sample.

Simultaneous DTA/TGA is a powerful thermo analytical technique that combines a DTA and a TGA into one instrument that performs both DTA and TGA on the same sample at the same time. This instrument or testing technique is sometimes referred to as Simultaneous Thermal Analysis, or STA, or simply ST. The resulting DTA and TGA curves are simultaneously plotted on a dual Y-axis graph so the DTA’s fingerprint and the TGA’s weight loss/gain characteristics are directly compared as the test sample is heated and cooled. Simultaneous DTA/TGA System which includes the furnace, differential thermocouple, analytical balance, and furnace control console with user-programmable controller. Although not shown, the system includes Windows 98/2000 compatible data acquisition/analysis software and an analog to digital interface card for the user supplied personal computer system. The included software displays the test progress on the monitor, stores the data and enables the user to perform the standard DTA and TGA analyses on the data after the test is completed. The DTA identifies the temperature regions and the magnitude of critical events during a drying or firing process such as drying, binder burnout, carbon oxidation, sulfur oxidation, structural clay collapse, cristobalite transitions, alpha-beta quartz transitions, carbonate decompositions, recrystallizations, and melting.