Chapter 2

2. MATERIALS AND METHODS

This chapter covers the details of all chemicals and experimental techniques that have been used in the study. The typical procedures for preparation of samples and details of their characterization techniques are described herein. The chemical reactions performed to evaluate the activity of the samples are also described in detail.

2.1 Materials

The chemicals used in this study along with their supplier's name are listed in Table 2.1. All the reagents are employed without further purification and distilled water is employed throughout the experiments.

Table 2.1 List of chemicals.

Chemicals	Supplier
Zinc Acetate Dihydrate ($Zn(CH_3COO)_2.2H_2O$), Stannous Chloride Dihydrate ($SnCl_2.2H_2O$), Copper Chloride Dihydrate ($CuCl_2{\cdot}2H_2O$), Urea (H_2NCONH_2), Sodium Hydroxide ($NaOH$), Tetraethyl Orthosilicate (TEOS), Pluronic P123, Cetyl Trimethyl Ammonium Bromide (CTAB), Graphite Powder, Ethanol (C_2H_5OH), Hydrochloric Acid (HCl), 30% Hydrogen Peroxide (H_2O_2), *n*-Butylamine ($CH_3(CH_2)_3NH_2$), Sodium Nitrate ($NaNO_3$), Potassium Permanganate ($KMnO_4$), Sulfuric Acid (H_2SO_4), Sodium Bicarbonate ($NaHCO_3$), Sodium Sulfate Anhydrous (Na_2SO_4), Silica Gel 60-120 Mesh, Acetyl Chloride (CH_3COCl), Benzoyl Chloride (C_6H_5COCl), Anisole ($C_6H_5OCH_3$), Chlorobenzene (C_6H_5Cl), Dichloromethane (CH_2Cl_2), Acetonitrile (CH_3CN), Tetrahydrofuran (C_4H_8O)	Merck
Toluene ($C_6H_5CH_3$), Veratrole ($C_6H_4(OCH_3)_2$), 1,3-Dimethoxybenzene ($C_6H_4(OCH_3)_2$), Mesitylene ($C_6H_3(CH_3)_3$), Benzene (C_6H_6), Thiophene (C_4H_4S), Phenylacetyl Chloride ($C_6H_5CH_2COCl$), Benzoic Anhydride ($(C_6H_5CO)_2O$)	Alfa Aesar
Ethyl Acetate ($CH_3COOC_2H_5$), Hexane (C_6H_{14})	RANKEM
Congo Red (CR), Rhodamine B (RhB), Methylene Blue (MB)	SRL Chemicals
Nitromethane (CH_3NO_2)	HiMedia

2.2 Synthesis of metal oxide nanostructures

2.2.1 Synthesis of zinc oxide hierarchical nanostructures

Zinc oxide hierarchical nanostructures are synthesized using a template-free hydrothermal method For synthesis, a 1:1 molar ratio of zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and urea ($H_2NCONH_2$) is separately dissolved in 40 mL of distilled water to create homogeneous solutions. The urea solution is then added dropwise to the $Zn(CH_3COO)_2{\cdot}2H_2O$ solution under stirring. After 1 h of continuous stirring, the resultant mixture is transferred to a 150 mL Teflon-lined autoclave, sealed and maintained at a temperature of 100 °C for required time (Table 2.2). The autoclave is then naturally cooled to room temperature. The as-formed white precipitate (precursor) is separated by centrifugation and washed several times with distilled water and ethanol, followed by drying in an oven at 80 °C for 12 h. The precursor is calcined at 400 °C for 4 h in an air environment to produce ZnO hierarchical nanostructures. The final products are labelled as ZO-5, ZO-10 and ZO-15.

Table 2.2 Synthesis of zinc oxide hierarchical nanostructures by hydrothermal method

Entry	Time (h)	ZnO Precursor	ZnO
1	5	ZP-5	ZO-5
2	10	ZP-10	ZO-10
3	15	ZP-15	ZO-15

2.2.2 Synthesis of tin dioxide nanoparticles

Tin dioxide nanoparticles (NPs) are synthesized by using a one-step solvothermal method using ethanol as solvent. In a typical synthesis of tin dioxide (SnO_2) NPs, 22.5 gL^{-1} of tin chloride dihydrate ($SnCl_2.2H_2O$) is dissolved in a 60 mL mixed solution of ethanol and distilled water (in 3:1 ratio) under magnetic stirring to form a homogeneous solution. The pH of this solution is kept at 12 by adding 1M NaOH solution to it and stirred for 1 h. The final mixture is put into a Teflon-lined autoclave, sealed, and heated for 5 h to 100 °C. After the autoclave naturally cooled to room temperature, the resultant precipitate is collected by centrifugation, washed several times with distilled water and ethanol, and finally dried in an oven at 50°C for 48 h. The obtained product is labelled as SnO_2 NPs.

2.2.3 Synthesis of tin dioxide nanosheets

The tin dioxide nanosheets are synthesized using identical procedure as mentioned in the section 2.2.2 by varying the hydrothermal time to 20 h. The obtained product is labelled as SnO_2 NSs.

2.3 Synthesis of modified SBA-15 supported ZnO and SnO_2 nanocatalysts

2.3.1 Synthesis of modified SBA-15

Modified SBA-15 is synthesized using a reported procedure by Zhao *et al.* [1]. In a typical synthesis, 4 g of Pluronic P123 is dissolved in 144 mL of 1.7 M HCl solution at 40 °C. To this mixture, 3 g of 1,3,5-trimethyl-benzene (TMB) is added as swelling agent and stirred for 1 h. Thereafter, 9.2 mL of tetraethyl orthosilicate (TEOS) is added to the above mixture under vigorous stirring and further stirred at 40 °C for 24 h. The resultant mixture is transferred to a Teflon-lined autoclave and heated at 100 °C for 24 h. After natural cooling of the autoclave, the suspension mixture is filtered, washed with distilled water until neutral (pH = 6-7) and dried for 24 h at 100 °C. The resultant white powder is calcined at 550 °C for 6 h to obtain the modified SBA-15.

2.3.2 Synthesis of modified SBA-15 supported ZnO

Modified SBA-15 supported ZnO is synthesized by a wet impregnation method. Typically, 0.4 g of modified SBA-15 is contacted with 2.4 cm^3 of aqueous solution containing 0.107 g of $Zn(CH_3COO)_2.2H_2O$ as metal precursor. Following a 20 min treatment in an ultrasonic bath, the mixture is filtered to recover the solid which is then washed and dried at 40 °C overnight. The dried mixture is calcined at 500 °C for 2 h and the resultant samples are collected and labelled as ZS.

2.3.3 Synthesis of modified SBA-15 supported SnO_2

Modified SBA-15 supported SnO_2 is synthesized using a similar procedure as mentioned in section 2.3.2. In this case, 0.060 g of $SnCl_2.2H_2O$ is employed as the metal precursor. The resultant product is labelled as TS.

2.4 Synthesis of reduced graphene oxide supported Cu-doped ZnO

2.4.1 Synthesis of graphene oxide

Graphene oxide is synthesized from graphite powder by using the modified Hummer's method [2]. Typically, 5 g of graphite powder, 2.5 g of sodium nitrate are added in 100 mL of concentrated sulphuric acid and the solution is cooled to 0 ºC for 20 min in ice bath. 15 g of potassium permanganate is then added dropwise in the solution with stirring at 0 ºC. The mixture is heated at 40 ºC for 2 h with vigorous stirring till the colour of the slurry turned to dark green. In the obtained dark green sample, 250 mL of distilled water is added dropwise at temperature below 50 ºC followed by adding 20 mL of hydrogen peroxide (30%) dropwise and the colour of the solution became yellowish brown. The obtained product is centrifuged for 10 min, cleaned with 10% HCl to remove impurities and washed with distilled water until the pH reaches 7. The obtained dark brown paste is dried overnight and a black graphene oxide solid is formed. The black solid is then grounded in mortar and dispersed in distilled water, centrifuged and dried overnight to attain the graphene oxide sample which was labelled as GO.

2.4.2 Synthesis of reduced graphene oxide supported ZnO

Reduced graphene oxide supported ZnO is prepared by hydrothermal method. At first, 0.674 g of zinc acetate dihydrate ($Zn\ (CH_3COO)_2H_2O$) is dissolved in 40 mL of distilled water to form a homogeneous solution. In a separate round bottom flask, 0.1 g of graphene oxide (GO) is dissolved in 40 mL distilled water and sonicated for 30 min. The dissolved GO is then added dropwise in the salt solution under continuous stirring and sonicated for 10 min. The pH of this solution is sustained at 10-12 by adding NaOH solution (1 M). The solution is then shifted to a 150 mL autoclave with a Teflon-liner, sealed and heated at 150 °C for 6 h. After the autoclave is cooled to ambient temperature naturally, the resultant precipitate is recovered by centrifugation, washed with distilled water and ethanol for 5 times, and dried in an oven at 50 °C for 48 h. The final product is labelled as ZnO/rGO.

2.4.3 Synthesis of reduced graphene oxide supported Cu-doped ZnO

The synthesis procedure for reduced graphene oxide supported Cu-doped ZnO is similar to that of section 2.4.2 keeping other conditions unaltered and only adding copper dichloride dihydrate ($CuCl_2.2H_2O$) as dopant source to obtain 0.5 at% Cu-doped ZnO/rGO. The final product is labelled as Cu -doped ZnO/rGO.

2.5 Characterization techniques

2.5.1 Thermogravimetric analysis (TGA)

The thermogravimetric analysis is a technique which provides information on the thermal stability of materials. TGA measures the gain or loss in weight of a sample as a function of increasing temperature, in an atmosphere of air, nitrogen, helium, other gas, or in vacuum. When a substance is heated and cooled in a controlled manner, it typically experiences physical, chemical, or mechanical changes. Most physical, chemical or physicochemical changes are characterized by fluctuations in the mass of the concerned substance after subjecting to different environments, such as temperature, pressure, vacuum, and atmosphere [3, 4]. Since temperature is often the main parameter, the common name for this technique is thermogravimetry. The measuring instrument comprises of an ultra-sensitive weighing device. The variations in mass of the sample clearly imply release or uptake of matter by the sample [5]. All the TGA curves presented in this thesis are collected on a Thermal Analyzer (Model: TGA-50, Shimadzu, Japan) instrument. The samples are heated from room temperature to 600 °C under N_2 atmosphere with a heating rate of 10 °C min^{-1}.

2.5.2 Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy is an important analytical technique for the identification of chemical bonds in a molecule by producing an infrared absorption spectrum. The infrared (IR) region of the electromagnetic spectrum is typically divided into three categories: near-, mid- and far-IR, based on their relation to the visible region. Near-IR radiation with high energy (~14000–4000 cm^{-1}) can excite overtone or harmonic vibrations. The mid-IR range (~4000–400 cm^{-1}) can be utilized to investigate the fundamental vibrations and associated rotational-vibrational structure. The low energy far-IR (~400–10 cm^{-1}) may be used for rotational spectroscopy [6]. FTIR spectra in the present work are recorded on FTIR spectrophotometer (Model: Nicolet Impact I-410, USA). All the FTIR measurements are done in the mid-IR region by pelletizing the samples using KBr.

2.5.3 X-ray diffraction (XRD)

X-ray diffraction is an analytical technique for the identification of crystalline nature of a material along with its crystal structure and phase composition. It also provides information on the atomic arrangements within the crystal and unit cell dimensions. The wavelengths of X-rays are on par with the interatomic distances in solids and their energy is sufficient to penetrate the substance. Therefore, in accordance with Bragg's law, the crystalline phases of the sample diffract a collimated beam of X-rays [7]. By measuring the angles (θ) at which an X-ray beam of wavelength λ is diffracted by the sample, powder XRD profiles are generated. Information about the material can be gleaned from the position, intensity, shape and width of the diffraction lines. The powder X-ray diffractograms are recorded on an X-ray diffractometer (Model: Bruker AXS, Germany) using nickel-filtered CuKα (λ = 0.15418 nm) radiation source and a scintillation counter detector. The intensity data are collected over a 2θ range of 10−80°.

The crystallite size is calculated using the Scherrer equation 2.1 as mentioned below:

$$D = K\lambda/\beta\cos\theta \qquad \ldots\ldots \quad (2.1)$$

where,

D is the average crystallite size,

K is the Scherrer's constant,

λ is the wavelength of the X-ray beam,

β is the full width at half maximum (FWHM) of the diffraction peak, and

θ is the diffraction angle.

2.5.4 Raman spectroscopy

Raman spectroscopy is a commonly used analytical technique based on inelastic scattering of monochromatic light, generally a laser source. Inelastic scattering implies that the photons of laser light lose or gain energy during the scattering process upon interaction with the sample, which provides information on vibrational, rotational and other low frequency modes in molecules [8]. Each molecule has a unique Raman spectrum that can be linked to a molecular fingerprint. Raman spectra are collected in

Raman spectrometer (Model: LabRam HR, Horiba Jobin Yvon, France and Renishaw Basis Series, Renishaw, UK) equipped with integral microscopes using 488 nm and 514 nm lasers as excitation sources under ambient conditions.

2.5.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy is a surface sensitive analytical technique based on photoelectric effect [9]. This technique provides information about the chemical composition and oxidation states of the elements present in the material. When the surface of a substance is irradiated with an X-ray beam, the core electrons of the surface atoms completely absorb the X-ray photon energy. If the energy of X-ray photon is high enough, the core electrons will be ejected from the surface atoms with specific kinetic energies, which are called as photoelectrons. The kinetic energies of the photoelectrons are related to their respective binding energies (BE) as follows:

$$\mathrm{E_K} = \mathrm{h}\vartheta - \mathrm{E_b} - \phi \quad \ldots\ldots \quad (2.2)$$

$$\mathrm{E_b} = \mathrm{h}\vartheta - \mathrm{E_K} - \phi \quad \ldots\ldots \quad (2.3)$$

where,

E_K is the kinetic energy of the photoelectron,
$h\nu$ is the X-ray photon energy,
E_b is the BE of electron, and
ϕ is the work function induced by the analyzer.

The BE of photoelectrons are characteristic of the atoms from which they are ejected and can be used to analyze surface elements. Moreover, small shifts in the elemental BE deliver information about their chemical states. For our investigation, XPS measurements are performed using X-ray photoelectron spectrometer (Model: ESCALAB Xi$^+$, Thermo Fisher Scientific Pvt. Ltd., U.K. and PHI 5000 Versa Probe II, FEI Inc., Japan). Binding energies of the sample are charge-corrected with respect to the adventitious carbon (C 1s) peak at 284.6 eV.

2.5.6 Scanning electron microscopy (SEM)

Scanning electron microscopy is an analytical technique used for studying the surface topography of materials. In SEM, a focused high-energy beam of electrons is scanned over the surface of the material in a raster scan pattern. The electron beam’s interaction with the material produces a variety of signals such as secondary electrons, backscattered electrons, X-rays, photons, and so on, which can be used to characterize specific properties of the material [10]. To study the surface topography, SEM analyses are carried out with a scanning electron microscope (Model: JSM 6390 LV, JEOL, Japan) operating at an accelerating voltage of 15 kV.

2.5.7 Transmission electron microscopy (TEM)

Transmission electron microscopy is a powerful characterization technique which uses high-energy beam of electrons (typically 100-400 keV) for direct observation of morphology, particle size and crystallographic analyses of a specimen by lattice imaging and micro diffraction techniques [11]. TEM provides a much higher spatial resolution than SEM. With the aid of an objective aperture for axial illumination, the high-resolution transmission electron microscopy (HRTEM) approach combines multiple diffracted beams with the axial transmitted beam to create the image [12, 13]. The atomic structure of the material can be directly inferred from the HRTEM images. It is possible to gather information from the images about the shape and size of particles belonging to active phases as well as supports and unravels their distribution with respect to each other [14]. The TEM investigations are carried out on transmission electron microscope (Model: TECNAI G^2 20 S-TWIN, FEI Company, USA and JEE-2100, JEOL, Japan) equipped with slow-scan CCD camera at an accelerating voltage of 200 kV.

2.5.8 Energy-dispersive X-ray spectroscopy (EDS or EDX)

The energy dispersive X-ray spectroscopy is a chemical microanalysis technique employed in conjunction with SEM and TEM. This method detects the X-rays emitted from a sample upon bombardment with an electron beam to determine the elemental composition of the analyzed volume. The EDX/EDS measurements in this study are carried out in the same instruments mentioned in sections 2.5.6 and 2.5.7.

2.5.9 Field emission scanning electron microscopy (FESEM)

Field emission scanning electron microscopy is a microscopic technique that provides information on the topographies of specimens at very high magnifications (×10 to ×1000,000). In FESEM, a fine beam of electrons is used to scan back and forth across the surface of the specimen. A scintillator collects the generated low-energy secondary electrons which turns each electron hit into a flash of light. A photo multiplier tube then amplifies each of these light flashes to create the final image of the specimen on a fluorescent screen [15]. In this study, FESEM images are recorded using FESEM instrument (Model: JSM-7200F, JEOL, Japan and Sigma, Zeiss, Germany) with maximum accelerating voltage of 30 kV.

2.5.10 Atomic force microscopy (AFM)

Atomic force microscopy is an advanced microscopic technique that can be utilized to study the topography of materials with nanometer resolution [16]. In AFM, the sample is scanned under a tip which is mounted at the free end of a cantilever. Deflection of the cantilever due to the forces of interaction between the tip and sample surface is measured by a detector and utilized in generating an accurate topographic map of the surface features. AFM images for this study were recorded on an atomic force microscope (Model: SPA400, AFM, Seiko Instruments, Japan). All AFM images are taken in dynamic force mode at optimal force. The thickness of the sample is estimated by spectroscopic ellipsometry (M-2000X, J.A. Woollam).

2.5.11 Surface area, pore size and pore volume analysis (BET and BJH method)

The Brunauer-Emmett-Teller (BET) method is the most acceptable procedure for measurement of surface areas of materials by physical adsorption of non-corrosive inert gases like nitrogen, argon etc. at their boiling temperatures [17]. In principle, the amount of adsorbate (usually nitrogen) required for monolayer formation over the surface of adsorbent (sample) is represented by the following BET equation 2.4:

$$\frac{P}{V_a(P_0-P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\frac{P}{P_0} \qquad \ldots\ldots \quad (2.4)$$

where,

P is the pressure,
P_0 is the saturation vapor pressure,
V_a is the amount of gas adsorbed at the relative pressure P/P_0,
V_m is the monolayer capacity, and
C is the BET constant.

A plot of $\frac{P}{V_a(P_0-P)}$ versus relative pressure of $\frac{P}{P_0}$ is a straight line with a slope of $\frac{C-1}{V_mC}$ and intercept of $\frac{1}{V_mC}$, respectively. V_m can be calculated from the slope and intercept. Subsequently, the specific surface area of the material can be obtained by applying the following equation 2.5:

$$\text{Specific Surface Area } (m^2g^{-1}) = \frac{V_m \times N_A \times A_m}{W \times V_0} \ldots\ldots \quad (2.5)$$

where,

N_A is the Avagodro constant (6.023×10^{23} molecules mol^{-1}),

A_m is cross sectional area of adsorbate molecule (N_2), 0.162 nm^2 at 77 K,

W is weight of the sample, and

V_0 is 22414 mL mol^{-1}.

The BET surface areas in this study are determined by N_2 adsorption-desorption using a BET surface pore size analyser (Model: NOVA 1000e, Quantachrome Instruments, USA). All the BET values are measured within the precision of ± 5%. The pore size and pore volume are determined using the Barrett-Joyner-Halenda (BJH) method in the same instrument.

2.5.12 Temperature programmed desorption of ammonia (NH_3-TPD)

NH_3-TPD is one of the versatile techniques for the determination of total acidity present in a material. This method is based on the measurement of desorption profile of pre-adsorbed NH_3 during controlled heating [18]. In this study, NH_3-TPD is performed using a Chemisorption Analyzer (Model: ChemBET Pulsar TPR/TPD Automated Chemisorption Analyzer, Quantachrome Instruments, USA). For NH_3-TPD experiment, 50 mg of sample is loaded in U-shaped quartz tube and preheated at 200 °C under He flow for 1 h to remove adsorbed H_2O. After cooling, the sample is exposed to 10% NH_3/He at a flow rate of 80 mL min^{-1} for 45 min. To obtain the NH_3-TPD profile, the gas flow is switched to He and the temperature is raised to 550 °C at a ramping rate of 10 °C min^{-1}. The effluent gas stream is analyzed by a dual-filament diffusion type thermal conductivity detector (TCD).

2.5.13 Pyridine adsorbed FTIR spectroscopy (Py-FTIR)

Pyridine adsorbed FTIR spectroscopy is a useful method for the identification of the nature of acid (Lewis or Brönsted) sites in solid materials. Brönsted acidic sites are due to acidic hydroxyls in the structure and Lewis acidic sites are the cations exposed to the reactants. Pyridine as a weak base often binds to these acidic sites and gives characteristic IR absorption peak [19]. Py-FTIR spectra for the samples in this study are collected using an FTIR spectrometer (Model: Nicolet iS50FT-IR, Thermo Scientific, USA). Before analysis, the samples are preheated under N_2 atmosphere at 150 °C for 2 h. Subsequently, the preheated samples are cooled to room temperature and pyridine vapour is introduced into the sample. Finally, FTIR spectra are collected by evacuating the sample at different temperatures.

2.5.14 Hammett indicator-amine titration

Qualitative determination of strength of acid sites of samples are performed by Hammett indicator method reported by a standard literature method [20]. The Hammett indicators used are: methyl red (pKa = 4.8), bromothymol blue (pKa = 3.85), methyl orange (pKa =3.4), and p-nitroaniline (pKa = 1.1). In the procedure, 1 mL of indicator solution (0.1 % in methanol) is added to 25 mg of catalyst at first. The mixture is shaken well, allowed to equilibrate for 2 h and then the colour of the catalysts is noted. The acid strengths have been reported as stronger compared to the weakest indicator that exhibits a colour change and weaker than the strongest indicator which exhibit no colour change.

The total amount of acid sites for the samples is measured by neutralization titration with *n*-butyl amine [21]. The samples (0.05 g) were dispersed in 2 mL of ethanol under sonication. The suspension is titrated with 0.1 M *n*-butylamine using methyl red as an indicator. Finally, the amount of *n*-butylamine consumed by the catalyst is determined and represented as acidity of the catalyst in terms of mmolg^{-1} of catalyst.

2.5.15 Ultraviolet-visible (UV-vis) spectroscopy

UV-vis spectroscopy is an analytical technique which refers to absorption of ultraviolet or visible light by chemical compounds due to electronic transitions [22]. The working principle of UV-vis spectroscopy is based on the Beer-Lambert law:

$$A = \varepsilon \mathrm{Cl} \qquad \ldots\ldots \quad (2.6)$$

where,

A is the absorbance,
ε is the molar absorption coefficient,
C is the concentration of sample solution, and
l is the path length of sample solution.

In the present work, UV-vis absorption spectra are measured on a UV-vis spectrophotometer (Model: UV-2550, Shimadzu, Japan).

2.5.16 Diffuse reflectance ultraviolet-visible (DRUV-vis) spectroscopy

DRUV-vis spectroscopy is a spectroscopic technique used to characterize materials in the powder form with the advantage of enhanced scattering phenomenon. This technique is closely related to UV-vis spectroscopy. The difference lies in the fact that UV-vis spectroscopy measures the relative change of absorbance/transmittance of light as it passes through a solution, whereas DRUV-vis measures the relative change in the amount of reflected light off from a surface [23]. The DRUV-vis spectra of the samples are collected on a UV-vis spectrophotometer (Model: UV–2450, Shimadzu, Japan).

2.5.17 Nuclear magnetic resonance (NMR) spectroscopy

NMR spectroscopy is a technique associated with the magnetic properties of certain atomic nuclei. This technique helps to investigate the structures of molecules by determining the differences in magnetic properties of various nuclei present within the molecule [24]. NMR spectroscopy also provides information on different kinds of environment within the molecule by detecting the presence of atoms in the neighboring groups. In this study, ^{1}H and ^{13}C NMR spectra are recorded on a 400 MHz NMR spectrometer (Model: JNM-ECS 400, JEOL, Japan) using $CDCl_3$ as solvent. Chemical shifts (δ) are reported in ppm with TMS as the internal standard. The coupling constant (J) is reported in hertz (Hz).

2.5.18 CHN analysis

The CHN elemental analysis determines the mass percentage of carbon, hydrogen and nitrogen in a sample based upon the direct weight of the material. Before analysis, the sample is broken down into its atomic components via combustion in an oxygen atmosphere at 1000 °C to form CO_2, H_2O, N_2, and oxides of nitrogen (N_xO_y) [25]. These gases are then carried via a stream of helium gas through a reduction chamber followed by a homogenization chamber to a thermal conductivity detector. CHN analysis of the products of Friedel-Crafts acylation reaction are performed using a CHN analyser (Model: 2400 Series II, Perkin Elmer, USA).

2.5.19 High Resolution Mass Spectrometry (HRMS)

High-resolution mass spectrometry (HRMS) is an analytical technique that determines the exact molecular masses of compounds present in a sample. In HRMS, ions from either inorganic or organic compounds are generated by any suitable method and these ions are separated by their mass-to-charge ratio (*m/z*) [26]. This technique provides the highest possible precision of *m/z* measurement using different analyzers to detect them qualitatively and quantitatively. HRMS spectra are recorded using a mass spectrometer (Model: Xevo XS QTof, Waters ACQUITY UHPLC, USA).

2.6 Typical procedures of catalytic reactions

2.6.1 Friedel-Crafts acylation reaction under classical condition

The catalytic reaction is carried out in a 50 mL round-bottom flask immersed in a constant temperature oil bath placed on a digital magnetic stirrer and connected to a spiral glass condenser. In this procedure, desired amount of catalyst, acid chloride/anhydride and solvent are mixed, followed by the addition of the aromatic substrate to the mixture. The whole mixture is stirred at a desired temperature for a certain period of time until the reaction is complete (monitored by thin layer chromatography). The reaction mixture is diluted with dichloromethane (DCM), and the catalyst is separated from the reaction mixture by filtration. The DCM extract is washed with aqueous solution of $NaHCO_3$, and the organic layer is dried over anhydrous sodium sulfate. The solvent is evaporated under reduced pressure and the product is purified by column chromatography. The isolated compound is identified and confirmed by different spectral analyses.

2.6.2 Friedel-Crafts acylation reaction under microwave irradiation condition

The Friedel-Crafts acylation reaction under microwave irradiation condition are performed in "Catalyst system Scientific Microwave systems" scientific microwave reactor with output power of 700 Watt (2450 MHz), power levels from 140-700 Watt and automatic temperature sensors with flexible probe up to 600°C. For the synthesis, acid chloride (1 mmol) and catalyst (5 mol%) are added to aromatic substrate (1 mmol) in a long necked special microwave flask fitted with a reflux condenser at 425 Watt microwave power and at 70°C. The reaction progress is monitored by TLC and cooled to room temperature after the reaction is complete. Organic portion is then extracted with DCM, washed with aqueous solution of sodium bicarbonate, dried over anhydrous sodium sulfate and concentrated under vacuum to obtain the crude product. The products are purified by column chromatography and analyzed by ^{1}H and ^{13}C NMR techniques.

2.6.3 Selective adsorption of organic dye pollutants

Selective adsorption properties of the sample/catalyst are studied for mixtures of two different organic dyes, congo red (CR) and rhodamine B (RhB), using a batch adsorption experiment. A typical approach entails adding 3 mg of adsorbent to 20 mL of mixed solution with a 1:1 ratio of CR/RhB having 3 mgL^{-1} concentration of each dye, followed by magnetic stirring to bring the mixture to steady state. The solution is centrifuged to separate the adsorbent after adsorption and the concentration of the resultant dye solution is assessed at 497 and 554 nm wavelengths for CR and RhB, respectively, using a UV-vis spectrophotometer. The effect of pH on the adsorption process is investigated in a pH range of 2.0−11.0 using an initial dye concentration of 3 mgL^{-1}. A 0.1 M HCl or 0.1 M NaOH solution is used to adjust the pH of the mixed solution. The selective adsorption of CR and RhB for all other experiments are conducted under pH 3.0 and 7.0, respectively. Kinetic experiments are conducted at room temperature with an initial dye concentration of 3 mgL^{-1} for both dyes to determine the minimum time required for adsorption to reach steady state. The dye concentrations after adsorption are measured at regular time intervals. Adsorption isotherm tests are carried out by employing 3 mg of adsorbent in 20 mL of aqueous dye solution having initial dye concentrations of 2−5 mgL^{-1}. The adsorption capacity (q_e, mgg^{-1}) of the adsorbent and the removal percentage of dye by the adsorbent can be calculated by using equations 2.7 and 2.8, respectively

$$q_e = (C_0 - C_e)\frac{V}{m} \qquad \ldots\ldots \quad (2.7)$$

$$\%\ \text{Removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad \ldots\ldots \quad (2.8)$$

where,

C_0 is the initial concentration of dye solution,
C_e is the equilibrium concentration of dye solution,
V is the volume of the dye solution, and
m is the mass of the adsorbent.

Effect of amount of catalyst is investigated during the course of reaction. To test the recyclability, five successive cycles are carried out employing 3 mg of catalyst. After adsorption is completed, the adsorbent is recovered by centrifugation and stirred in 50 mL of ethanol for 60 min at pH 3.0 for CR and at pH 7.0 for RhB. The adsorbent is then collected by centrifugation, dried, and reused for another adsorption−desorption cycle. Similar procedure is repeated for the next five consecutive cycles.

2.6.4 Photocatalytic degradation of methylene blue

The photocatalytic activity of the synthesized catalyst is investigated for the degradation of methylene blue (MB) dye under both UV irradiation and direct sunlight. In a typical run, 5 mg of the photocatalyst is suspended to 20 mL dye solution of MB with initial dye concentration of 5 mgL^{-1} under light irradiation. The UV light source used is 125 Watt medium pressure Hg lamp and the reactions under sunlight are conducted during sunny days at Tezpur University between 10:00 a.m. to 14:00 p.m. Prior to light irradiation, the reaction mixtures are stirred in dark condition for 30 min to achieve adsorption-desorption equilibrium. Blank experiment is also performed under similar conditions without using catalyst. The samples are withdrawn at certain intervals of time and centrifuged to separate the catalyst. The concentration of the dye solution is monitored using a UV-visible spectrophotometer at maximum absorbance of 663 nm. The degradation percentage (D) of the dye solution was determined by using the following equation:

$$D = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad \ldots\ldots \quad (2.9)$$

where,

C_0 is initial concentration of dye solution, and

C_t is final concentration of dye solution.

The effect of various reaction parameters such as catalyst dosage, concentration of dye solution, and pH is also studied to get an optimized condition for the degradation process. All the experiments are conducted in duplicate for accuracy. For the recyclability test, the photocatalyst is collected via centrifugation after completion of the reaction, washed with water and ethanol, dried and applied for the next cycle.

REFERENCES

[1] Zhao, D., Feng, J., Huo, Q., Melosh, N., Fredrickson, G. H., Chmelka, B. F., and Stucky, G. D. Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. *Science*, 279(5350):548–552, 1998.

[2] Al-Rawashdeh, N. A., Allabadi, O., and Aljarrah, M. T. Photocatalytic activity of graphene oxide/zinc oxide nanocomposites with embedded metal nanoparticles for the degradation of organic dyes. *ACS Omega*, 5(43):28046–28055, 2020.

[3] Coats, A. W. and Redfern, J. P. Thermogravimetric analysis. A review. *Analyst*, 88(1053):906–924, 1963.

[4] Horowitz, H. H. and Metzger, G. A new analysis of thermogravimetric traces. *Analytical Chemistry*, 35(10):1464−1468, 1963.

[5] Liu, X. and Yu, W. Evaluating the thermal stability of high performance fibers by TGA. *Journal of Applied Polymer Science*, 99:937–944, 2006.

[6] Chaudhuri, A. *Study of Nanostructured Iron Oxides*. PhD thesis, University of Calcutta, India, 2012.

[7] Clegg, W. *Crystal Structure Determination*. Oxford University Press, Oxford, 1998.

[8] Long, D. A. *Raman Spectroscopy*. McGraw-Hill, New York, 1977.

[9] Nolan, N. T. *Sol-Gel Synthesis and Characterisation of Novel Metal Oxide Nanomaterials for Photocatalytic Applications*. PhD thesis, Dublin Institute of Technology, Dublin, Ireland, 2010.

[10] McMullan, D. Scanning electron microscopy 1928–1965. *Scanning*, 17(3):175–185, 1995.

[11] O'connor, D. J., Sexton, B. A., and Smart, R. S. *Surface Analysis Methods in Materials Science*. Springer-Verlag Berlin, Heidelberg, New York, 1992.

[12] Carter, C. B. and Williams, D. B. *Transmission Electron Microscopy*. Springer, New York, USA, 2009.

[13] Egerton, R. *Physical Principles of Electron Microscopy*. Springer, New York, USA, 2005.

[14] Baram, M. and Kaplan, W. D. Quantitative HRTEM analysis of FIB prepared specimens. *Journal of Microscopy*, 232(3):395‒405, 2008.

[15] Brodusch, N., Demers, H., and Gauvin, R. *Field Emission Scanning Electron Microscopy: New Perspectives for Materials Characterization*. Springer, Singapore, 2018.

[16] Meyer, E. Atomic force microscopy. *Progress in Surface Science*, 41(1):3–49, 1992.

[17] Brunauer, S., Emmett, P. H., and Teller, E. Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, 60(2):309–319, 1938.

[18] Chen, L., Janssens, T. V., Skoglundh, M., and Grönbeck, H. Interpretation of NH_3-TPD profiles from Cu-CHA using first-principles calculations. *Topics in Catalysis*, 62(1):93–99, 2019.

[19] Parry, E. P. An infrared study of pyridine adsorbed on acidic solids. Characterization of surface acidity. *Journal of Catalysis*, 2(5):371–379, 1963.

[20] Tanabe, K. *Solid Acids and Bases: Their Catalytic Properties*. Elsevier, 2012.

[21] Toyama, N., Ogawa, R., Inoue, H., Ohki, S., Tansho, M., Shimizu, T., Umegaki, T., and Kojima, Y. Influence of morphology of hollow silica–alumina composite spheres on their activity for hydrolytic dehydrogenation of ammonia borane. *Journal of Advanced Ceramics*, 6(4):368–375, 2017.

[22] Rocha, F. S., Gomes, A. J., Lunardi, C. N., Kaliaguine, S., and Patience, G.S. Experimental methods in chemical engineering: Ultraviolet visible spectroscopy—UV-Vis. *The Canadian Journal of Chemical Engineering*, 96(12):2512–2517, 2018.

[23] Brittain, H. G. UV/Vis reflectance spectroscopy. In Brittain, H. G., editor, *Spectroscopy of Pharmaceutical Solids*, pages 141–170, CRC Press, 2006.

[24] Günther, H. *NMR Spectroscopy: Basic Principles, Concepts and Applications in Chemistry*. John Wiley & Sons, 2013.

[25] Wachberger, E., Dirscherl, A., and Pulver, K. Automatic procedure for the CHN-analysis of organic substances in the milligram range. *Microchemical Journal*, 16(2):318–328, 1971.

[26] Xian, F., Hendrickson, C. L., and Marshall, A. G. High resolution mass spectrometry. *Analytical Chemistry*, 84(2):708–719, 2012.