Chapter – 3

EXPERIMENTAL METHODS
3. EXPERIMENTAL SECTION

3.1. Preparation of photocatalysts

All the chemicals were obtained from Merck, India (Analytical grade). The commercially available TiO$_2$ (Degussa P-25) was obtained from Degussa Chemical, Germany. The typical synthesis procedure for pure and M-doped ZnO (M= Zr, La, Ce, Mg and Ba) is as follows: Zinc acetate dihydrate (Zn(Ac)$_2$·2H$_2$O) and metal nitrates such as zirconyl nitrate monohydrate (ZrO(NO$_3$)$_3$·H$_2$O), lanthanum nitrate hexahydrate (La(NO$_3$)$_3$·6H$_2$O), cerium nitrate hexahydrate (Ce(NO$_3$)$_2$·6H$_2$O), magnesium nitrate hexahydrate (Mg(NO$_3$)$_2$·6H$_2$O) and barium nitrate hexahydrate (Ba(NO$_3$)$_2$·6H$_2$O) were taken as the precursors of zinc and doped metal, respectively. Zn(Ac)$_2$·2H$_2$O and NaHCO$_3$ were dissolved separately in a double distilled water to obtain 0.1 mol/L solutions. Zinc acetate solution (250 mL of 0.1 mol/L) was slowly added into vigorously stirred NaHCO$_3$ (250 mL of 0.1 mol/L) and Triton-X 100 mixed solution. The Triton-X 100 concentrations in the mixed solutions differed within the range of 0–2 mmol/L, which correspond to the concentration for the structural changes of the surfactant from pre-micelle concentration (PMC) to critical micelle concentration (CMC), such as spherical micelle (CMC1), and rod-like micelle concentration (CMC2) [1]. Based on this, PMC, CMC1 and CMC2 in Triton X-100 aqueous solution were obtained. The values are respectively close to 2.1×10$^{-4}$ mol/L, 3.2×10$^{-4}$ mol/L and 1.3×10$^{-3}$ mol/L. Metal nitrates in the required stoichiometry was slowly added into the above solution, and a white precipitate was obtained. The precipitate was filtered, repeatedly rinsed with distilled water and then washed twice with ethanol. The resultant solid product was dried at 70°C for 2 h and calcined at 200°C for 3 h.
Pure ZnO was also prepared by the same procedure without the addition of metal nitrate solution. The doping concentrations of metals are expressed in wt%. The flow chart for the preparation of pure and M-doped ZnO (M = Zr, La, Ce, Mg and Ba) is shown in Figure 3.1

3.2. Characterization of the photocatalysts

This chapter covers the various experimental methods used for the characterization of the prepared photocatalysts. The physical, structural, morphological, optical and photocatalytic characteristics of all the photocatalysts are evaluated by various instrumental techniques as listed below.

3.2.1. X-Ray diffraction technique

Since the 1910s, X-ray crystallography has been a valuable tool for obtaining the structural parameters of the metal oxides. X-ray diffraction powder patterns come from the interference pattern of elastically dispersed X-ray beams by atom cores and, in case of materials with moderate to long-range order, contain information that arises from the atomic structure and the particle characteristics (for example, size, strain). The structural studies were carried out using a Philips X’pert diffractometer for 2θ values from diffraction angle 10 to 80°C using CuKα radiation at λ = 0.154 nm by applying Bragg’s law in the present study. The crystallite size of all the photocatalysts was calculated using the Scherrer formula [2],

$$L = \frac{0.89\lambda}{\beta \cos \theta}$$

where L is the crystallite size, \(\lambda\), the X-ray wavelength, \(\theta\), the Bragg diffraction angle and \(\beta\), the full width at half width maximum.
Fig. 3.1 Flow chart for the preparation of pure and M-doped ZnO
(M= Zr, La, Ce, Mg and Ba)
3.2.2. **High resolution scanning electron microscopy (HR-SEM)**

The particle size and surface morphology of the nanostructured photocatalysts, pure and M-doped ZnO (M= Zr, La, Ce, Mg and Ba), were observed using a high resolution scanning electron microscope (HR-SEM) (Stereo-scan LEO-JEOL 440) at the desired magnification in the present study.

3.2.3. **High resolution Transmission electron microscopy (HR-TEM)**

High resolution Transmission electron microscopy (HR-TEM) is one of the most powerful and versatile techniques for the characterization of nanostructured systems. As it is well known, the interaction of an electron beam with a solid specimen results in a number of elastic or inelastic scattering phenomena (backscattering or reflection, emission of secondary electrons, X-rays or optical photons, and transmission of the beam along with beams deviated as a consequence of elastic-single atom scattering, diffraction-or inelastic phenomena). The TEM technique is dedicated to the analysis of the transmitted or forward-scattered beam. Such a beam is passed through a series of lenses, among which the objective lens mainly determines the image resolution, to obtain the magnified image [3]. The particle size, morphology, lattice fringes and selected area electron diffraction (SAED) pattern were observed using a transmission electron microscope (HR-TEM) (JEOL JEM 3010).

3.2.4. **Energy dispersive X-ray analysis (EDX)**

The quantitative elemental analysis of the photocatalysts was determined using a Leo-Jeol scanning electron microscope with parallel energy dispersive x-ray spectrophotometer. The EDX microanalysis was done at 15kV.
3.2.5. **Nitrogen adsorption-desorption studies**

The surface area and pore size distribution were derived from the nitrogen adsorption-desorption isotherms using liquid nitrogen at 77K. The nitrogen adsorption-desorption isotherms of the photocatalysts were measured using an automatic adsorption instrument (Quantachrome Corp. Nova-1000 gas sorption analyzer).

3.2.6. **Diffuse reflectance spectral studies (DRS)**

UV-Visible diffuse reflectance spectra of the samples were recorded by Cary100 UV-visible spectrophotometer between 350 and 800 nm wavelength region. Spectroscopically, pure barium sulphate was used as a reference. The band gap of the photocatalysts was estimated from the fundamental absorption edge or coefficient. The optical gap was calculated using the Tauc relation by plotting $(\alpha h\nu)^2$ against $h\nu$, where $\alpha$ and $h\nu$ denotes the absorption coefficient and photon energy respectively, and extrapolating the curve to the photon energy axis. The absorption coefficient is given by $\alpha = 2.303(A_b/t)$, where, $A_b$ is the absorbance, and $t$ the thickness of the sample [4].

3.2.7. **Photoluminescence studies (PL)**

Photoluminescence spectra of the samples were recorded using Varian Cary Eclipse Fluorescence spectrophotometer from 350 to 800 nm wavelength region. The optical properties of the samples were studied from the emission spectra of the samples.

3.3. **Photocatalytic reactor setup and photocatalytic degradation (PCD) procedure**

PCD experiments were carried out in a self-designed photocatalytic reactor as shown in Fig. 3.2. The cylindrical photocatalytic reactor tube was made up of quartz / borosilicate with a dimension of 36–1.6 cm (height-diameter). The top portion of the reactor tube has ports for sampling, gas purging and gas outlet.
Fig. 3.2. Schematic diagram of the photocatalytic reactor
The aqueous EDCs solution containing appropriate quantity of either pure ZnO or M-doped ZnO (M = Zr, La, Ce, Mg and Ba) was taken in the quartz/borosilicate tube and subjected to aeration for thorough mixing. This was then placed inside the reactor setup. The lamp housing has low pressure mercury lamps (8 × 8 W) emitting either 254 or 365 nm with polished anodized aluminum reflectors and black cover to prevent UV leakage.

The PCD was carried out by mixing 100 mL of aqueous EDCs solution and fixed weight of pure ZnO or M-doped ZnO photocatalysts. Prior to irradiation, the slurry was aerated for 30 min to reach adsorption equilibrium followed by UV irradiation. Aliquots were withdrawn from the suspension at specific time intervals and centrifuged immediately at 1500 rpm. The extent of EDCs degradation was monitored by using UV–Visible spectrophotometer (Perkin-Elmer, Lamda 25) and high performance liquid chromatograph (HPLC) (Shimadzu LC10 ATVP series equipped with UV–vis detector). The effect of pH of the solution was studied by adjusting the pH of EDCs solution containing the catalyst, using dilute HCl and NaOH (both from Merck, India). The pH of the solution was measured using HANNA Phep (Model H 198107, 0.2-0.5 pH unit accuracy) digital pH meter. The intermediates were identified using gas chromatograph coupled with mass spectrometer (GC–MS) (Perkin-Elmer Clarus 500). The temperature of the column was programmed as follows: initial column temperature was held for 2 min at 70 °C, ramped at 10 °C /min to 280 °C, with final hold for two minutes at 280 °C. The extent of mineralization was determined using a total organic carbon analyzer (TOC) (Shimadzu VCPN). The PCD efficiency (η) was calculated from the following expression [5],

\[ \eta = \frac{C_i - C_t}{C_i} \times 100 \text{ (or)} \eta = \frac{TOC_i - TOC_t}{TOC_i} \times 100 \]

where, \( C_i \) or \( TOC_i \) is the initial concentration of EDCs and \( C_t \) or \( TOC_t \), concentration of EDCs after “t” minutes.
REFERENCES


