# ABSTRACT

Nanotechnology is one of the rapidly emerging frontiers showcasing breakthroughs in almost every field of science and technology [1, 2]. Specifically, nanostructures have elicited significant research interest owing to their unique characteristics viz., high specific surface area, improved stability and surface permeability, well-defined interior voids, and so forth [3, 4]. The extraordinary physicochemical properties of nanostructured materials enable potential applications spanning from sensing, catalysis, adsorption, and photocatalysis to energy conversion devices [3]. The performance of the material in most of these applications relies on its morphology and crystalline properties [5]. Therefore, several methodologies have been developed for the synthesis of nanomaterials with controlled shape, size, and composition that trigger specific requirements [6].

Recently, metal oxide nanostructures have received tremendous attention due to their diverse properties and functionalities [7]. Among them, zinc oxide (ZnO) and tin dioxide ($SnO_2$) nanostructures have been widely studied because of their distinctive conductance properties, acid-base properties, and process flexibility. Owing to such fascinating properties, they have been extensively employed in various chemical transformations, energy conversion and storage devices, sensors, and photocatalytic applications [8, 9]. Again, unmodified metal oxide nanoparticles have high surface energy which results in their thermodynamic instability and agglomeration. The separation of nanoparticles from reaction mixtures also poses a major concern [10]. As such, metal oxide nanoparticles are supported onto solid supports such as $SiO_2$, $Al_2O_3$, $CeO_2$, reduced graphene oxide, graphitic carbon nitride, and so on. These supported metal oxides have been used as catalysts for various industrially important reactions [11]. For metal oxides to be applicable as effective catalysts in photocatalytic applications, modification of their properties by incorporation of optically active dopants, typically transition metal ions, inside the metal oxide lattice plays a major role [12].

Keeping these goals in mind, the present thesis aims at the synthesis, characterization, and evaluation of the activity of ZnO and $SnO_2$-based nanostructures for organic transformation and wastewater treatment. The main contents of this thesis have been broadly divided into seven chapters. **Chapter 1** includes the introduction part

and **Chapter 2** describes the details of materials, experimental methods, and characterization techniques used in this thesis. The results and discussion of the present investigations have been covered in **Chapter 3**, **Chapter 4**, **Chapter 5**, and **Chapter 6**. The conclusions and future scopes of this thesis are presented in **Chapter 7**.

**Chapter 1: Introduction**

This chapter provides a general introduction to the emergence and importance of nanoscience and technology and its remarkable applications in diverse areas of research. The chapter basically emphasizes the synthetic methodology and application of metal-oxide based nanostructures. More specifically, it provides an overview of the property and applications of ZnO and $SnO_2$-based nanostructures in two broad categories viz., organic transformation and wastewater treatment. The organic transformation that has been basically considered in this work is the Friedel-Crafts acylation reaction for furnishing aromatic ketones. Moreover, adsorption and photocatalytic process have been included for wastewater treatment. A general overview of organic pollutants along with their adverse effect on the environment has also been presented in this chapter. Furthermore, use of support plays a vital role in the activity of a material owing to its stability, large specific surface area, and high selectivity. Therefore, the importance of supported metal oxides has been discussed herein. This chapter also describes the significance of dopants in tuning the property of metal oxides for enhancing photocatalytic applications.

Finally, based on the literature review, we have set the objectives of the present investigation as follows:

(i) Synthesis and characterization of ZnO and $SnO_2$ nanocatalysts for Friedel-Crafts acylation reaction.

(ii) Synthesis and characterization of ZnO and $SnO_2$ supported on modified SBA-15 mesoporous silica for Friedel-Crafts acylation reaction.

(iii) Evaluation of the activity of $SnO_2$ nanostructures towards adsorptive removal of organic pollutants from aqueous solution.

(iv) Development of Cu-doped ZnO supported on reduced graphene oxide for photocatalytic degradation of organic pollutants.

**Chapter 2: Materials and methods**

This chapter provides the details of chemicals and solvents employed in this entire work. All the experimental methods for the synthesis of nanostructured metal oxide-based materials are described herein. This chapter also contains the details of different analytical tools and techniques that have been used throughout the thesis. The detailed reaction procedures for Friedel-Crafts acylation reaction, adsorption as well as photocatalytic reaction are also included in this chapter.

**Chapter 3: Bare zinc oxide (ZnO) and tin dioxide ($SnO_2$) nanocatalysts for regioselective Friedel-Crafts acylation reaction**

Chapter 3 describes the synthesis and characterization of bare zinc oxide (ZnO) and tin dioxide ($SnO_2$) nanocatalysts and their application for regioselective Friedel-Crafts acylation reaction of aromatic compounds. This chapter has been divided into four sections, viz., **Section 3A**, **Section 3B** and **Section 3C** as described below:

**Section 3A: Time-driven morphology evolution and catalytic activity of porous ZnO hierarchical nanostructures**

Hierarchically structured materials provide great potential for heterogeneous catalysis due to their abundant surface-active sites, high surface area, enhanced mass transport ability and easy separation compared to their nanosized counterparts. This section describes the synthesis of ZnO hierarchical nanostructures (HNs) via a template-free precursor mediated hydrothermal route by varying the reaction time with subsequent calcination at 400 °C for 4 h. The physicochemical properties of the synthesized precursors and ZnO nanostructures are investigated by various analytical and spectroscopic techniques. The results reveal that the morphology of the synthesized ZnO changes from rod-like HNs to two dimensional (2D) nanoflake assembled HNs at higher hydrothermal reaction time. The synthesized ZnO HNs are further employed for the Friedel-Crafts (FC) acylation reaction to evaluate the effect of different morphologies on their catalytic activity. The results imply that the nanoflake assembled ZnO HNs exhibit better catalytic activity towards the acylation reaction compared to the rod-like HNs, which is associated with the higher surface area and acidity of the nanostructures.

**Section 3B: $SnO_2$ nanoparticles as reusable catalyst for Friedel-Crafts benzoylation of anisole**

This section deals with the synthesis of $SnO_2$ nanoparticles (NPs) *via* a direct (one-step) solvothermal route in the presence of ethanol as a solvent. The as-synthesized $SnO_2$ NPs are well characterized by various analytical techniques. Powder X-ray diffraction study reveals that the synthesized oxide adopts orthorhombic $SnO_2$ crystal structure. Transmission electron microscopic investigation shows the formation of nanoparticles with an average size of 6.44 nm. The influence of the solvent on morphological and textural properties of as-synthesized $SnO_2$ is also explained herein. Further, the as-synthesized $SnO_2$ nanoparticles are employed for Friedel-Crafts benzoylation of anisole to furnish 4-methoxybenzophenone. Various reaction parameters viz. reaction temperature, catalyst dosage, solvent effect, and substrate ratio are also addressed for the acylation reaction. The $SnO_2$ NPs exhibit good catalytic activity (85% yield) for the acylation reaction of anisole. They also show high stability for the benzoylation with good recyclability up to five consecutive cycles.

**Section 3C: Regioselective Friedel-Crafts acylation reaction using single crystalline and ultrathin nanosheet assembly of scrutinyite-$SnO_2$**

In this section, a facile and general approach for the synthesis of single crystalline and ultrathin 2D nanosheet assembly of scrutinyite-$SnO_2$ through a simple solvothermal method has been reported. The structural and compositional characterization using various analytical techniques reveal that the as-synthesized 2D nanosheets are ultrathin and single crystallized in the scrutinyite-$SnO_2$ phase with high purity. The ultrathin $SnO_2$ nanosheets show predominant growth in the [011] direction on the main surface having a thickness of ca. 1.3 nm. The $SnO_2$ nanosheets are further employed for the regioselective Friedel−Crafts acylation to synthesize aromatic ketones that have potential significance in the chemical industry as synthetic intermediates of pharmaceuticals and fine chemicals. A series of aromatic substrates acylated over the $SnO_2$ nanosheets have afforded the corresponding aromatic ketones with up to 92% yield under solvent-free conditions. Comprehensive catalytic investigations display the $SnO_2$ nanosheet assembly as a better catalytic material compared to the heterogeneous metal oxide catalysts used so far in view of its activity and reusability in solvent-free reaction conditions.

**Chapter 4: Modified SBA-15 supported ZnO and $SnO_2$ nanocatalysts for Friedel-Crafts acylation of anisole with benzoic anhydride**

This chapter describes the synthesis and characterization of ZnO and $SnO_2$ supported on mesoporous silica SBA-15 modified by using swelling agent trimethylbenzene (TMB). The metal oxides have been loaded into the SBA-15 via wet impregnation method followed by calcination. Elemental and spectroscopic study suggests that the dispersion of $SnO_2$ over the support is better as compared to ZnO. The catalytic activity of the synthesized materials has been evaluated for the Friedel-Crafts acylation of anisole using benzoic anhydride as the acylating agent. Effects of reaction parameters such as temperature, solvent, amount of catalyst and substrates ratio on the reaction have been explained. It has been observed that $SnO_2$ supported on modified SBA-15 is the better catalyst for this reaction than that of ZnO which is attributable to the better dispersion and redox property of the material.

**Chapter 5: Selective adsorption of dye pollutants from their mixture using $SnO_2$ nanostructures**

This chapter describes the application of $SnO_2$ nanostructures for the adsorptive removal of organic dye pollutants from aqueous solutions. The selective adsorption of dyes such as congo red (CR) and rhodamine B (RhB) from their mixture by pH modulation onto the synthesized $SnO_2$ nanostructures have been studied. The effects of various reaction parameters are also addressed on the adsorption of respective dyes. The $SnO_2$ nanostructures can efficiently remove the respective dyes depending upon the pH of the reaction solution. At pH 3.0, $SnO_2$ nanostructures can significantly remove CR due to the interactions between the acid hydroxyl group of tin oxide and $R-SO_3^-$ ions of CR from the mixture of CR−RhB solution, whereas at pH 7.0, it can selectively remove RhB due to the electrostatic interaction between the base hydroxyl group of tin oxide and $R-N^+$ ions of RhB. The results also indicate that the catalysts remain effective even after extended regeneration and reuse for adsorption-desorption cycles.

**Chapter 6: Reduced graphene oxide supported Cu-doped ZnO nanocatalysts for photocatalytic degradation of methylene blue**

This chapter deals with the synthesis and characterization of Cu-doped ZnO supported on reduced graphene oxide (rGO). The catalytic activity of the Cu-doped

ZnO/rGO has been evaluated for the photocatalytic degradation of methylene blue (MB) under both visible and UV light irradiations. The degradation study shows that efficient degradation (~98%) of MB is accomplished under UV light irradiation compared to that of visible light. A comparative study of the photocatalytic degradation of MB over Cu-doped ZnO/rGO has also been performed with ZnO and ZnO/rGO. A significant increase in photocatalytic degradation for MB over Cu doped-ZnO/rGO is achieved compared to ZnO and ZnO/rGO, which may be due to the combined effects of rGO and Cu doping into the ZnO crystal lattice. An increase in dye adsorption by adding GO with a high surface area and an improvement of charge transfer capacity through lowering the band gap energy of ZnO by doping results in increased photocatalytic activity. The effects of various parameters such as catalyst amount, initial dye concentration, and pH on the photodegradation process have also been studied in detail. The kinetics and possible mechanism of photocatalytic degradation of MB are also discussed herein. The recyclability of the catalyst has been studied and found to be active up to five cycles without any significant loss in activity.

**Chapter 7: Conclusion and future scopes**

This chapter provides a summary of the major findings of the experiments with significance of the work as well as describes the overall conclusion. The future scopes of the studied areas are also highlighted in this chapter.

**Keywords:** Metal Oxide, Nanostructure, Synthesis, Nanomaterial, Zinc oxide, Tin dioxide, Friedel-Crafts acylation, Photodegradation

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