# **Thesis abstract** (Index No. **56/17/Chem./25**)

Thesis Title: "***Development of some visible light active spinel and perovskite based novel nanocomposite photocatalysts for hazardous pollutants degradation and electrocatalytic application***"– Submitted by Kalyan Ghorai

Pure spinel and perovskite oxide materials alone are supposedly not an active member in the photocatalyst family due to their low band gap energy values and very high electron-hole pair recombination tendency, although they show a good visible light absorption activity. But surprisingly their combinations with other semiconductor materials forming a nanocomposite heterojunction system can act as a potential photocatalyst material with promising visible light absorption activity. In such nanocomposite photocatalysts, the catalytic performance is effectively increased due to improvement of charge separation via Type I, Type II, SER (surface plasma resonance), S-scheme, and Z-scheme mechanisms. Based on this background knowledge about the advantage of nanocomposite photocatalyst over single spinel oxide or single perovskite oxide, we have motivated to fabricate some spinel or perovskite oxide based nanocomposite photocatalyst materials for wastewater treatment and electrochemical oxygen evolution. The research work included in this thesis is based on the synthesis and development of some potential spinel and perovskite oxide based visible light active nanocomposite photocatalyst materials that are applied as an active photocatalyst for photocatalytic degradation of hazardous pollutants such as industrial colorful azo dyes like Rhodamine B (RhB), methylene blue (MB), methyl orange (MO), and reactive black 5 (RB5) as well as colorless antibiotics like tetracycline hydrochloride (TC-HCl), and norfloxacin (NORF) with the aid of visible light irradiation from a domestic light emitting diode (LED) light. These nanocomposite materials are also used as an active electrocatalyst for electrochemical oxygen evolution reaction (OER) under dark and light (visible) condition.

A general introduction on the basics of photocatalysis and its operation mechanism, photocatalyst, oxide based nanocomposite as photocatalyst and preparation methods of these materials, different types of charge transfer mechanisms in the nanocomposite heterojunction, and details of $CuCr_2O_4$ spinel and $LaNiO_3$ perovskite oxide systems which are the backbones of this research work is presented in **Chapter 1** that ends with the scope of the present investigation.

To achieve the targeted goal we have employed different synthetic routes for the preparation of pure components as well as their nanocomposite materials. The research methodology, the various types of characterization techniques and fabrication of photocatalytic reactor setup are discussed in **Chapter 2**.

In **Chapter 3,** we have discussed the findings on synthesis, characterization, and photocatalytic activity of $CuCr_2O_4$/BiOBr (CCO/BiOBr) nanocomposite photocatalyst for the degradation of RhB and TC-HCl using household LED light. In this nanocomposite system, sol-gel combustion made spherical shaped $CuCr_2O_4$ nanoparticles are decorated on BiOBr plates in a single step via coprecipitation method using cetyltrimethylammonium bromide (CTAB) as the Br-source as well as the template. The synthesized materials are subsequently characterized by employing several techniques such as powder X-ray diffraction (PXRD), Brunauer-Emmett-Teller (BET) surface area, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray (EDX) spectroscopy, elemental mapping, selective area electron diffraction (SAED), X-ray photoelectron spectroscopy (XPS), UV visible diffusion reflectance spectroscopy (UV–Vis DRS), photoluminescence (PL) spectroscopy and Raman spectroscopy. The 20%$CuCr_2O_4$/BiOBr composite exhibits high degradation efficiency for both RhB (96% in 15 min) and TC-HCl (96.7% in 300 min) in presence of LED light with good recycling behavior. Based on the band modification at the

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interface of the composite materials and radical trapping analyses a plausible mechanistic path of the photocatalytic degradation process is presented.

**Chapter 4** deals with the synthesis of $CuCr_2O_4/CeO_2$ (CCO/$CeO_2$) nanocomposite materials as a highly active heterogeneous Fenton like photocatalyst for the degradation of harmful azo dyes under domestic LED light irradiation. The catalysts have been synthesized via a simple co-precipitation method followed by heat treatment and is subsequently characterized thoroughly. The 10%CCO/$CeO_2$ nanocomposite sample exhibits high degradation activity and it could effectively degrade RhB (99% in 15 min), MB (98% in 20 min) and MO (96% in 30 min) with a very high rate. The radical trapping and coumarin based fluorescence probe methods suggest the generation of $^{\bullet}OH$ (hydroxyl radical) in the catalytic pathways and based on the reactive species trapping analysis, band positions and degradation results, we have established a detailed photocatalytic degradation mechanism. The recycling activity is also discussed.

**Chapter 5** is based on the studies on photocatalytic Fenton like activity of Anatase $TiO_2$ decorated $CuCr_2O_4$ nanocomposite material. In this chapter, we have discussed the surprising performance of $CuCr_2O_4$/anatase-$TiO_2$ (CCO/ $TiO_2$) nanocomposite as a Fenton like catalyst with potential impact on sustainable design and environmental protection. A series of $CuCr_2O_4/TiO_2$ nanocomposites was synthesized by sonochemical mixing method followed by heat treatment. All the materials are thoroughly characterized by numerous physical and chemical techniques. The 100% CCO-loaded nanocomposite material (100%CCO/ $TiO_2$) obtained by heat-treatment at 400 °C is found as high performance catalyst towards the degradation of azo dyes like RhB (97% in 15 min), MB (99% in 15 min) and MO (90% in 15 min), antibiotics like TC-HCl (99% in 15 min) and NORF (97% in 75 min), and a promising Pt-free candidate for photoelectrocatalytic oxygen evolution reaction under domestic LED light irradiation. The details of recycling behavior, chemical stability, and photocatalytic mechanism are also discussed.

In **Chapter 6,** we have included our studies on Z-scheme type $LaNiO_3$/g-$C_3N_4$ (LNO/g-CN) photocatalyst for pollutants degradation under natural sunlight irradiation. The major issues in this chapter are (i) development of nanocomposite photocatalyst working through Z-scheme charge transfer pathway across the heterojunction, (ii) utilization of direct sunlight as the photo-source, (iii) prospect of ligand-hole in photocatalysis through enhanced sub-band gap absorption. The $LaNiO_3$/g-$C_3N_4$ nanocomposite photocatalysts are synthesized via a facile solid state mixing route followed by thermal treatment and are characterized by using several physicochemical techniques. The photocatalytic performance of Z-scheme photocatalyst (100%LNO/g-CN being the best photocatalyst) for the degradation of hazardous pollutants such as RB5 (94% in 60 min), MB (98% in 180 min) and colorless antibiotic-pollutant TC-HCl (96% in 300 min) in presence of natural sunlight is discussed here. The details of active species trapping, recycling activity and charge separation mechanism are also elucidated.

In **Chapter 7,** we have dealt with the synthesis, characterization and photoelectrochemical behavior of $CuCr_2O_4/BiVO_4$ (CCO/BVO) nanocomposite system. The synthesized materials have been characterized by various physical and chemical techniques. The hydrothermally synthesized electrocatalyst has been used as an active material for electrochemical oxygen evolution reaction under visible light and dark condition. 10 mole % CCO loaded sample (10%CCO/BVO) shows the best electrocatalytic (OER current density = 22.5 mA $cm^{-2}$) and photoelectrocatalytic (OER current density = 36.9 mA $cm^{-2}$) OER activity among whole nanocomposite series. The OER activity is effectively improved under visible LED irradiation.

In the end we have made concluding remarks with critical insights of this research work in **Chapter 8** and advocated for the necessity to continue further research in this very important and emerging area of heterogeneous photocatalysis and photoelectrocatalysis.

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