# $CuWO_4$-based composite photocatalysts for the degradation of organic pollutants

Thesis submitted in partial fulfillment for the
Award of Degree

**Doctor of Philosophy**

By

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*Dedicated to my loving parents*

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I, **"*Neha Jatav*"**, certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of ***"Dr. Indrajit Sinha"*** from December 2017 to May 2023, at the ***Department of Chemistry***, Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not wilfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, theses, etc., or available on websites and have not included them in this thesis and have not cited as my own work.

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# Table of Contents

# List of Figures

# List of Tables

# List of Schemes

# Abbreviations

| | |
|---|---|
| **Eg** | Bandgap |
| **VB** | Valence band |
| **CB** | Conduction band |
| **eV** | Electron volt |
| **JCPDS** | Joint Committee on Powder Diffraction Standards |
| **Kg** | Kilogram |
| **W** | Watts |
| **KJ/mol** | Kilojoule per mole |
| **kV** | Kilovolt |
| **nm** | Nanometre |
| **T** | Temperature |
| **t** | Time |
| **°C** | Degree Celsius |
| **K** | Kelvin |
| **k** | Rate constant |
| **λ** | Lambda |
| **θ** | Theta |
| **χ** | Electronegativity of semiconductor |
| **Ee** | Energy of free electron on hydrogen scale |
| **Å** | Angstrom |
| **mM** | Micrometre |
| **UV-Vis** | Ultraviolet-visible |
| **XRD** | X-ray diffraction |
| **EDX** | Energy dispersive X-ray |
| **TEM** | Transmission electron microscopy |

| | |
|---|---|
| **XPS** | X-ray photo electron spectroscopy |
| **UV-DRS** | Ultraviolet Visible Diffuse Reflectance Spectroscopy |
| **MO** | Methyl Orange |
| **RhB** | Rhodamine B |
| **CIP** | Ciprofloxacin |
| **TET** | Tetracycline |
| **DDDW** | Deionized double distilled water |
| **IPA** | Isopropyl alcohol |
| **PBQ** | p-benzoquinone |
| **KI** | Potassium iodide |
| **$e^-$** | Electron |
| **$^{\bullet}OH$** | Hydroxyl Radical |
| **NaOH** | Sodium Hydroxide |
| **$O_2^{\bullet -}$** | Superoxide radical |
| **OVs** | Oxygen vacancies |

It is extremely concerning that freshwater supplies are being contaminated by organic contaminants from industrial effluent discharges, posing a severe threat to the environment and biodiversity. This thesis focuses on using photocatalytic nanostructures to remove organic effluents from water resources. Due to their potential for being cost-effective, efficient, and environmentally friendly procedures for degrading water contaminants (dyes, antibiotics, etc.), photocatalytic processes over semiconductors have garnered attention on a global scale. When exposed to light, a semiconductor photocatalyst absorbs photon energy. The material's electrons are excited to move from the valence band (VB) to the conduction band (CB) through the energy absorbed. Therefore, the material can carry out oxidation and reduction reactions since it produces a significant number of holes ($h^+$) and electrons ($e^-$).

Various tungsten-based materials such as $WO_3$, $WS_2$, $Bi_2WO_6$, $MnWO_4$, $FeWO_4$, $CoWO_4$, $NiWO_4$, $ZnWO_4$, $Ag_2WO_4$, etc. have been reported as potential photocatalysts for water splitting as well as environmental remediation. These semiconductor materials garnered more attention than others because they are active in visible light. Due to their limited photostability and high rate of photogenerated exciton recombination, these semiconductor materials' photocatalytic efficiency is comparatively low. Therefore, it is an exciting research topic to increase the stability in light and photocatalytic efficiency of these semiconductor-based materials. An especially effective technique for achieving this is combining two semiconductors with an appropriate band edge position to form heterostructures, especially Z-scheme photocatalysts.

An extensive literature survey revealed comparatively less research on $CuWO_4$-based composite photocatalysts. But the visible range bandgap of $CuWO_4$ and its band positions are attractive for potential composite photocatalysts. For instance, $CuWO_4$

has been reported as a photoanode in photoelectrochemical water splitting. Heterostructures (p-n junction or Z-scheme) containing $CuWO_4$ as one of the components include $BiFeO_3/CuWO_4$, $VO_2/CuWO_4$, $CuWO_4$/ZnO, $CuWO_4$/MWCNT, g-$C_3N_4/Fe_3O_4/CuWO_4$, $CuWO_4$/GO, g-$C_3N_4/CuWO_4$, $CuWO_4/Bi_2S_3$, etc. These composites have generally demonstrated effective photocatalytic activity toward certain organic compounds.

The present thesis studies the photocatalytic properties of Ag-based semiconductor/$CuWO_4$ composites. Note that single-component Ag-based semiconductors generally have a bandgap in the visible range but suffer from photostability issues. Ag-based semiconductors include $Ag_2O$, $Ag_2S$, AgX (Cl, Br, I), $Ag_3PO_4$, $Ag_3VO_4$, $Ag_2CO_3$, and others. The photostability problems of such Ag-based semiconductors are also improved when combined with a different photocatalytic phase. Furthermore, before this thesis, there was no report on Ag-based semiconductor/$CuWO_4$ heterostructure (Z-scheme photocatalyst). This thesis investigates the photocatalytic properties of composites of AgI, $Ag_3PO_4$, $Ag_3VO_4$, and $Ag_2MoO_4$ with $CuWO_4$ for the degradation of organic contaminants. These Z-scheme photocatalysts were made using simple coprecipitation and hydrothermal procedures. The synthesized photocatalysts were characterized using a variety of techniques, including XRD, UV-DRS, TEM, SEM, PL, and XPS. Further, the photocatalytic capabilities of these photocatalysts for specific organic pollutant degradation were assessed.

**Chapter 1** of this thesis describes the types and threats associated with organic pollutants and gives an overview of various techniques for water remediation. It highlights the basic concepts and mechanisms associated with photocatalysis. Various parameters and challenges associated with the design of photocatalysts have been

described. Several factors like light absorption, charge separation, charge migration (with potential recombination), and finally, charge utilization for redox reactions play a role in the photocatalytic efficiency of photocatalysts. Thus, designing an efficient photocatalyst has become very important. It has been found that fabricating Z-scheme photocatalysts is an efficient strategy for encountering those issues. An extensive literature survey has been performed to find out the lacuna of the research and found that the photocatalytic properties of Ag-based semiconductor/$CuWO_4$ heterostructures have not been explored. The primary goals of the thesis have been outlined at the end of the chapter.

**Chapter 2** describes the experimental details, including the materials employed, photocatalytic techniques, and the equipment required to characterize the created photocatalysts and examine reaction kinetics, which have been defined in this chapter.

**Chapter 3** of this thesis investigates the synthesis and efficacy of AgI/$CuWO_4$, a nanocomposite, for the aerobic breakdown of ciprofloxacin and rhodamine under visible light irradiation. The AgI/$CuWO_4$ photocatalyst systems were synthesized by a coprecipitation protocol with different weight % (10, 20, and 30) of AgI viz. 1 A/C, 2 A/C, and 3 A/C. The as-prepared samples were characterized by various physiochemical techniques, including XRD, TEM, HR-TEM, XPS, and photoluminescence studies. These generated heterostructures gave better efficiency and appropriate recyclability for photocatalytic CIP and RhB degradation. Among the 1 A/C, 2 A/C, and 3 A/C, 2 A/C was found to be best for CIP and RhB degradation; this is due to better charge separation in 2 A/C as investigated by photoluminescence studies. The 2 A/C nanocomposite's XPS analysis revealed charge transfer from the $CuWO_4$ to the AgI side, indicating a Z-scheme mechanism. Further, scavenger

experiment results reveal that superoxide species were predominantly responsible for the degradation of CIP and RhB.

**Chapter 4** discusses the fabrication of Z-scheme $Ag_3PO_4/CuWO_4$ photocatalysts for the degradation of popular antibiotics CIP and TET under visible light irradiation. A step-by-step precipitation technique was used to prepare the nanocomposites with different weight percentages of $Ag_3PO_4$ on $CuWO_4$, namely 10% AW, 20% AW, and 30% AW. XRD and TEM were used to characterize the photocatalysts that were synthesized. The 20% AW photocatalyst had been found most effective for photocatalytic degradation of CIP and TET owing to better charge separation as revealed by photoluminescence studies. Furthermore, these photocatalysts show good recyclability. In addition, XPS analyses revealed that photocatalysis was carried out via a Z-scheme mechanism. Appropriate reactive species trapping tests indicated that photoexcited holes were the primary species responsible for the degrading reaction.

**Chapter 5** focuses on the fabrication, characterization, and photocatalytic characteristics of $Ag_3VO_4/CuWO_4$. The nanostructures were also prepared by using a step-by-step coprecipitation process. XRD, TEM, and XPS techniques were used to characterize the nanostructures that were synthesized. UV-DRS and valence band XPS plots were used to determine the band gaps and band positions of the various components of the composite nanoparticles. XPS analysis showed the electron migration from the $CuWO_4$ side to the $Ag_3VO_4$ side confirms the Z-scheme mechanism. These nanostructures are effective visible-light catalysts for aerobic MO degradation, and the best one has been 20 wt% $Ag_3VO_4/CuWO_4$. Furthermore, these nanostructures demonstrated excellent recyclability. The oxidation of MO on photoexcited holes has been found by active species analysis using a suitable scavenger.

Further, **Chapter 6** explores the fabrication of $Ag_2MoO_4/CuWO_4$ heterojunction via a simple precipitation process, with different weight% (5, 10, and 15) of $Ag_2MoO_4$ particles deposited on the surface of $CuWO_4$ nanoparticles (5% MW, 10% MW, and 15% MW). These synthesized nanostructures were characterized through XRD, TEM, PL, and XPS techniques. When compared to pure $Ag_2MoO_4$ and $CuWO_4$, synthesized heterojunctions 5% MW, 10% MW, and 15% MW demonstrated improved photocatalytic activities for the degradation of RhB, under UV-light irradiation. Furthermore, the heterojunction with 10% MW has the best photocatalytic performance, which is good as pure $CuWO_4$ or $Ag_2MoO_4$. This substantial improvement in photocatalytic activity is due to the staggered bandgap between $Ag_2MoO_4$ and $CuWO_4$, which effectively suppresses electron-hole pair recombination. Furthermore, the superoxide radical anions and photogenerated holes are the main active oxidizing species, according to the radical trapping experiment.

**Chapter 7** summarizes the photocatalytic activity of the various Ag-based semiconductor/$CuWO_4$ photocatalysts fabricated as part of this thesis and compares (TOF) for the MO, RhB, TET, and CIP degradation among those taken into consideration in this work as well as with those in the literature. Finally, a summary of the work's future scope is offered.