



V.H.N. Senthikumara Nadar College (Autonomous)

VIRUDHUNAGAR-626 001

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PG & RESEARCH DEPARTMENT OF CHEMISTRY

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Ph.D. PUBLIC VIVA-VOCE EXAMINATION

As per the regulations of Madurai Kamaraj University, Madurai, **Ms. S. LAKSHMI PRABAVATHI, M.Sc., (Reg. No. F9742)**, Full Time Research Scholar, Department of Chemistry, V.H.N. Senthikumara Nadar College (Autonomous), Virudhunagar, will defend her thesis at a Public Viva-Voce examination through Video Conference mode using Google Meet Platform.

Title of the Ph.D. Thesis

**CARBON BASED METAL NANOPARTICLES: FABRICATION,
CHARACTERIZATION AND ITS APPLICATIONS**

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Google Meet

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VIRUDHUNAGAR-626 001

(With a request to display on the Notice Board)

**CARBON BASED METAL NANOPARTICLES : FABRICATION,
CHARACTERIZATION AND ITS APPLICATIONS**

**Synopsis submitted to Madurai Kamaraj University, Madurai, in partial fulfillment
for the award of the Degree of**

DOCTOR OF PHILOSOPHY IN CHEMISTRY

By

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1. Introduction

Antibiotics have been extensively application in medical an animal husbandry and human beings, which inhibit the growth of pathogenic micro-organism and promote the growth of aquaculture, livestock, agriculture and beekeeping. Therefore, they can reach surface and ground water bodies through different way, such as surface runoff, wastewater treatment plant effluents and infiltration of water used for agricultural purposes. Antibiotics are not entirely mineralized within humans and animals, approximately 30-90% of the antibiotics used for the animals and excreted through urine and faeces. The misuse and over use has led to serious risks to the human, aquatic life and wildlife. It has produced negative effects they are ecotoxicological effects (acute and chronic toxicity, genotoxicity and carcinogenicity), resistance development of micro-organism and pharmacological effects (interference of the hormones and immune system) [1-5]. The most conventional water purification and wastewater effluent treatment were used to control and degrade the antibiotics pollutants. Among various strategies, semiconductor photocatalysts technology can achieve high efficient degradation low concentration of antibiotics under visible light. The advantage of semiconductor photocatalyst was lots pollutants degraded by light radiation under ambient condition [6, 7].

Numerous efficient semiconductor photocatalyst for antibiotic pollutants degradation, graphitic carbon nitride ($g-C_3N_4$) is a metal free polymeric semiconductor photocatalyst with exceptional chemical and thermal stability, low cost, nontoxicity and excellent photoelectric properties [8, 9]. Unfortunately, $g-C_3N_4$ practical application was sternly restricted by large size, which result from low mass transfer and low quantum efficiency owing to severe agglomeration. Additionally, low degree of polymerization, small surface area, fast recombination of charge carriers and numerous structural defects were also hampering the photocatalytic activity of

g-C₃N₄ [10, 11]. To optimize the photocatalytic performance of g-C₃N₄, preparation of g-C₃N₄ based heterojunction *via* coupling with other semiconductor, structural modification and metal or non-metal doping has therefore attracted immense attention [12-14].

Among them, design and construction of g-C₃N₄ based heterojunction (such as g-C₃N₄ /BiVO₄, CNT/g-C₃N₄, g-C₃N₄/ZnWO₄ and Bi₂O₃/g-C₃N₄) offers a promising approach for to enhance the photocatalytic activity in water splitting, organic pollutant degradation and CO₂ reduction [15-18]. However, in the case of metal tungstate coupled/doped g-C₃N₄ has higher photocatalytic activity due to their suitable band gap, synergetic effect between the two semiconductors, highly separate the recombination charge carriers and long life time of the charge carriers. Moreover, metal tungstate contains a small cationic radius so the band gap of the metal tungstate is smaller or narrow, which will increase the visible light absorption [19, 20]. Therefore, till date many researchers are engaged to enlarge metal tungstate doped/coupled with g-C₃N₄ photocatalyst and used for the photocatalytic degradation toxic organic pollutants from the waste water.

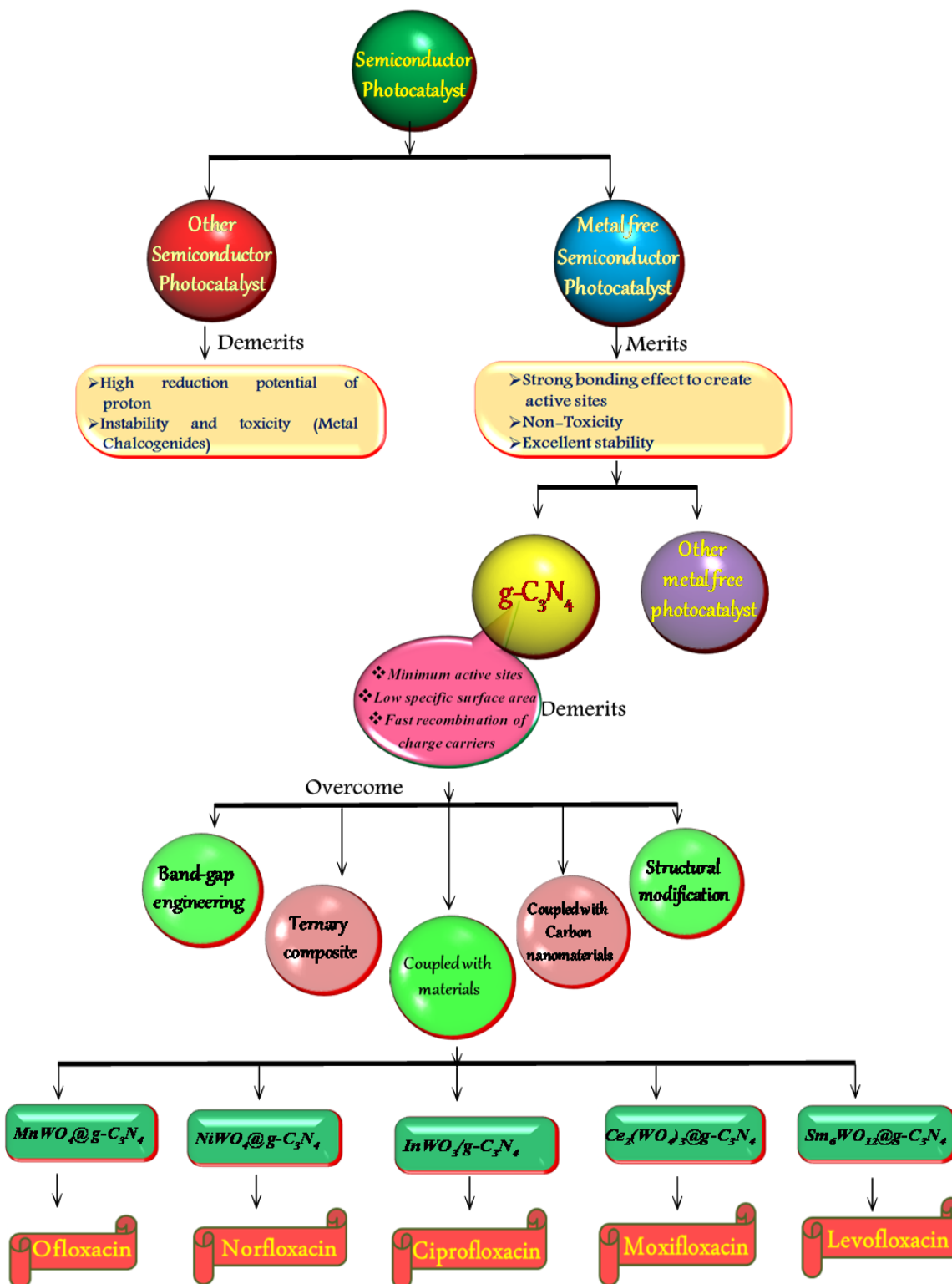
Objective and scope of the work

From the aforesaid literature survey, the metal tungstate doped/coupled g-C₃N₄ photocatalyst have been subject of increased attention in recent years. Therefore the author has developed metal tungstate doped/coupled g-C₃N₄ nanocomposite and photocatalyst towards the applications of degradation of pharmaceutical pollutants. The metal tungstate doped g-C₃N₄ synthesized method has simple and cost effective technique and this photocatalyst enriched photocatalytic activity. These present thesis describes encouraged us to synthesize modified g-C₃N₄ nanosheets with various metal tungstates such as MnWO₄, NiWO₄, InWO₃, Ce₂(WO₄)₃ and Sm₆WO₁₂.

Keeping all these facts, the present task/research have been undertaken with the following objectives:

- To synthesize MnWO_4 nanorods decorated on $\text{g-C}_3\text{N}_4$ nanosheets by simple hydrothermal method and treatment followed by ultrasonication method.
- To characterize the synthesized catalyst by UV, FTIR, XRD, SEM, TEM, PL and XPS and discussed.
- To investigate the photocatalytic activity of $\text{MnWO}_4@\text{g-C}_3\text{N}_4$ heterojunction for the degradation of ofloxacin under visible light.
- To study the effect of various parameters such as catalyst dosage and initial concentration of the drug concentration.
- To evaluate the possible photocatalytic degradation mechanisms based on the radical trapping experiments.
- ❖ To prepare NiWO_4 nanorods anchored on $\text{g-C}_3\text{N}_4$ nanosheets and characterized by various microscopic and spectroscopic techniques.
- ❖ To assess photocatalytic performance of the as-designed samples for the photodegradation of norfloxacin (NRF).
- ❖ To study the rate of degradation and discuss the mechanism of the photocatalyst.
- ❖ To discover the stability and reusability efficiency of the $\text{NiWO}_4@\text{g-C}_3\text{N}_4$ nanocomposite.
- ◆ To design and fabricate the $\text{InWO}_3@\text{g-C}_3\text{N}_4$ heterojunction and characterize the catalyst by using various instrumentation techniques.
- ◆ To study the photocatalytic degradation of ciprofloxacin employing $\text{InWO}_3@\text{g-C}_3\text{N}_4$ catalyst.

- ◆ To analyze the performance of different synthesized catalysts like InWO_3 , $\text{g-C}_3\text{N}_4$ and $\text{InWO}_3@\text{g-C}_3\text{N}_4$.
- ◆ To survey catalyst loading and concentration of ciprofloxacin were optimized conditions for effective degradation.
- ◆ To fabricate the $\text{Ce}_2(\text{WO}_4)_3@\text{g-C}_3\text{N}_4$ heterojunction and characterize the catalyst by various spectroscopic and microscopic techniques in order to assess the crystallinity, band energy and particle size.
- ◆ To examine the photodegradation of moxifloxacin aqueous solution by using $\text{Ce}_2(\text{WO}_4)_3@\text{g-C}_3\text{N}_4$ heterojunction.
- ◆ To investigate the photostability and reusability efficiency of the $\text{Ce}_2(\text{WO}_4)_3@\text{g-C}_3\text{N}_4$ heterojunction.
- ◆ To utilize the $\text{Sm}_6\text{WO}_{12}@\text{g-C}_3\text{N}_4$ nanocomposite and applied for the degradation of fluoroquinolone drug levofloxacin under visible light.
- ◆ To analyze crystallinity, chemical composition, optical and morphological characteristic of the photocatalyst by XRD, XPS, UV-DRS, SEM-EDX and TEM studies.
- ◆ To scrutinize the effect of initial drug concentration and catalyst weight on the photocatalytic degradation of these drug.
- ◆ To explore the possible photocatalytic mechanism of drug degradation by using $\text{Sm}_6\text{WO}_{12}@\text{g-C}_3\text{N}_4$ nanocomposite photocatalyst.



Scheme 1: Schematic representation of scope of the present work.

2. Experimental sections

2. 1. Synthesis of g-C₃N₄

A simple thermal treatment of melamine was used to fabricate the polymeric g-C₃N₄. Briefly, melamine (5 g) was placed in ceramic crucible with a lid and heated at 550 °C for 4 h in muffle furnace. After the completion of the reaction, the crucible was cooled to room temperature and the yellow crumbs of g-C₃N₄ were collected. The g-C₃N₄ fragments were ground into a fine powder and kept for further use.

2.2. Synthesis of metal tungstate

2.2.1. Synthesis of MnWO₄ nanorods

MnWO₄ nanorods were synthesized by a one-pot hydrothermal method using sodium tungstate dihydrate (Na₂WO₄·2H₂O) and MnCl₂ as precursors. Typically, MnCl₂ (1.0 g, 0.2 mol) and Na₂WO₄·2H₂O (2.5 g, 0.2 mol) were dissolved separately in deionized water (15 mL) in a 100 mL beaker to form the precursor solutions. Thereafter, the Na₂WO₄·2H₂O solution was added drop-wise to the MnCl₂ solution under magnetic stirring for 3 h at room temperature. Subsequently, the solution was transferred into an 80 mL teflon-lined stainless steel autoclave and heated at 180 °C for 12 h. After heating, the autoclave was allowed to cool to room temperature and the precipitate was collected, washed with DI water and ethanol 3 times and dried at 60 °C for 16 h. Finally, the powdered product was calcined at 550 °C for 4 h in a furnace to yield MnWO₄ nanorods.

2.2.2. Preparation of NiWO₄ nanocomposite

In typical experiment, first 0.5 mol of nickel nitrate was dissolved in 15 mL distilled water to form a solution. Secondly 15 mL of sodium tungstate dihydrate (0.5 mol) solution was added to the above solution and vigorously stirred for 1 h. Then the suspension was transferred

into Teflon-lined stainless steel autoclave and heated at 180 °C for 16 h. The precipitate was washed with water and ethanol for several times, dried at 60 °C for 12 h and calcined at 700 °C for 4 h to obtain the NiWO₄ nanocomposite.

2.2.3. Synthesis of InWO₃ nanospheres

The InWO₃ nanosphere was synthesized by simple hydrothermal method. Typically, 2.4 g of sodium tungstate dihydrate (Na₂WO₄·2H₂O) was dissolved in 15 ml of distilled water. Then 15 ml of indium nitrate (InN₃O₉, 1 g) solution was added drop wise and 10 mL of nitric acid was added to the above mixture under stirring at room temperature for 3 h. After 3 h, the solution was transfer to 100 ml Teflon-lined stainless steel autoclave and sealed and heated at 160 °C for 12 h. After the hydrothermal treatment the autoclave was cooled to room temperature and the precipitate was collected and washed with water and ethanol. Then the precipitate was dried at 60 °C for 16 h. Finally they obtained precipitate was annealed at 800 °C for 2 hour in an air.

2.2.4. Synthesis of Ce₂(WO₄)₃

Synthesis of Ce₂(WO₄)₃ was achieved *via* a hydrothermal treatment route. In typical procedure, ammonium ceric nitrate (1.6 g, 0.2 mol) was dissolved in double deionized water (15 mL) in a 50 mL beaker and kept stirring for 10 min. In a second beaker, sodium tungstate (1 g, 0.2 mol) was dissolved in double deionized water (15 mL) and added to the above solution with vigorous stirring for 3 h at room temperature. After 3 h, the mixed solution was transferred into 100 mL Teflon lined stainless steel autoclave and heated at 180 °C for 12 h. Thereafter, the autoclave was cooled to room temperature and the precipitate was filtered, washed 3 times with deionized water and alcohol. Finally, the precipitate was dried overnight at 60 °C and annealed at 800 °C for 3 h to obtain Ce₂(WO₄)₃.

2.2.5. Synthesis of Sm₆WO₁₂ nanocomposite

Sm₆WO₁₂ nanocomposite was synthesized by one spot hydrothermal method using sodium tungstate dihydrate (Na₂WO₄·2H₂O) and Sm(NO₃)₃ as the precursor. Sm(NO₃)₃ (1.33 g) and Na₂WO₄·2H₂O (1 g) each were dissolved separately in 15 ml of deionized water in 100 mL beaker. Then Na₂WO₄·2H₂O was added drop-wise to the Sm(NO₃)₃ solution under magnetic stirring for 3 h at room temperature. After 3 h, the solution was transfer to 80 ml stainless steel autoclave and heated at 180 °C for 12 h. After heating the autoclave was cooled at room temperature and the precipitate was collected. The precipitate washed with water and ethanol for 3 times and allowed dry at 60 °C for 16 h. The above obtained product was calcined at 800 °C for 4 h.

2.3. Synthesis of metal tungstate doped g-C₃N₄ nanocomposite

Synthesis of metal tungstate doped g-C₃N₄ proceeded as follows: equal amounts of metal tungstate (MnWO₄, NiWO₄, InWO₃, Ce₂(WO₄)₃ and Sm₆WO₁₂) and g-C₃N₄ (1:1 mass ratio) were added to the mortar and ground for 15 min. The ground powder was mixed with ethanol (30 mL) and ultrasonicated for 1 h at room temperature. Finally, the obtained precipitate was washed with ethanol and dried at 60 °C for 16 h in a hot-air oven.

2.4 Characterization techniques

- ◆ X-ray Diffraction
- ◆ Fourier Transform Infrared Spectroscopy
- ◆ X-ray Photoelectron Spectroscopy
- ◆ Scanning Electron microscopy
- ◆ Transmission Electron Microscopy
- ◆ Elemental Mapping Analysis

- ◆ Energy Dispersive X-ray Spectroscopy
- ◆ UV visible Spectroscopy
- ◆ Photoluminescence
- ◆ Brunauer-Emmet-Teller Surface Area Analysis

2.5. Test for photocatalytic activity

For studying the photocatalytic performance of synthesized photocatalyst was evaluated by the degradation of pharmaceutical pollutant under visible light irradiation of. In a typical experiment, the photocatalyst (50 mg) was added to the sample solution (10 mg/L, 100 mL) in a 150 mL beaker. Prior to irradiation, the mixture was magnetically stirred in the dark for 30 min to achieve absorption-desorption equilibrium between the photocatalyst and drug solution. Thereafter, the reactor was irradiated with a 150 W tungsten lamp as a source of visible light. Aliquots (3 mL) were drawn at fixed intervals and centrifuged to separate the photocatalyst from the solution. Finally, the solution was analyzed using a UV-vis spectrophotometer (Shimadzu, UV-1601). The degradation efficiency of drug was calculated using **equation 2.1**.

$$\text{Degradation efficiency} = [1-(C/C_0)] \times 100 \quad (2.1)$$

Where C is the concentration of the solution suspension at reaction time interval t and C₀ is the concentration of solution suspension at time 0.

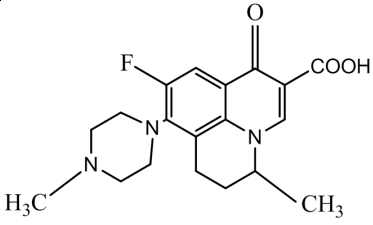
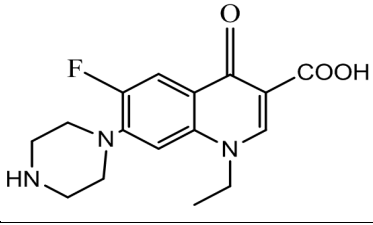
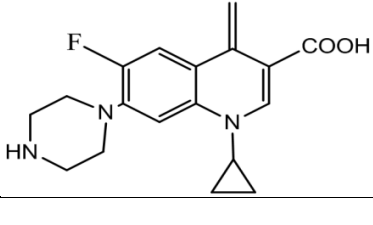
2.5.1. Identification of reactive species

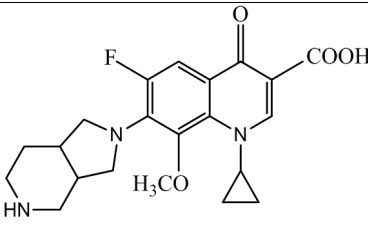
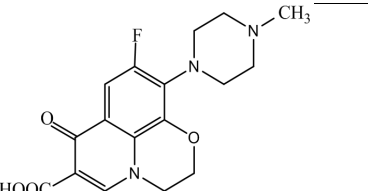
To understand the charge transfer mechanism, radical trapping experiments were carried out to identify the major reactive species responsible for the photodegradation process. Here, different kinds of scavengers were used like isopropyl alcohol, ammonium oxalate and benzoquinone. 0.01 M of scavengers was utilized for the trapping experiments in the present investigation. The photodegradation process was monitored for the detection of active species.

2.5.2. Test for stability and reusability

The stability and reusability of a photocatalyst was investigated by carried out consecutive runs using an aqueous drug solution. After each cycle, the photocatalyst was centrifuged, washed with water and ethanol and dried at 60 °C for overnight, then used in the next cycle. All photocatalytic degradation process was carried out under the similar experimental condition as illustrated in the above method. To compensate the loss of the catalyst during the washing process, a constant quantity of the catalyst concentration was retained each cycle test, and numerous degradation process were carried out simultaneously at each cycle test.

Table 2.1: The physical properties and side effects of some FQs drugs.

| Drug Name | Structure | Water solubility (mg/L) | λ_{\max} (nm) | Side Effects |
|---------------|---|---------------------------------|-----------------------|---|
| Ofloxacin |  | 6.05, 8.11 | 291 | Peripheral neuropathy, Tendon effect, Gastrointestinal effect |
| Norfloxacin |  | 6.22, 8.38 | 276 | Permanent nerve damage, Tendon rupture |
| Ciprofloxacin |  | 3.32, 5.59, 6.14, 8.85 | 280 | Tendon rupture, Peripheral neuropathy, Seizure, Depression or Suicidal thoughts |

| | | | | |
|---------------|---|---------------|-----|--|
| Moxifloxaacin |  | 6.13, 9.61 | 295 | Liver damage, Tendon rupture, Heart rhythm problems stevens- johnson syndrome, Kidney failure |
| Levofloxacin |  | 5.19, 7.07 | 287 | Hypersensitivity, Dermatological, Psychoneurological, Renal, Hepatic, Hematologic |

CHAPTERS

CHAPTER – 3: 1D/2D MnWO₄ nanorods anchored on g-C₃N₄ nanosheets for enhanced photocatalytic degradation of ofloxacin under visible light irradiation

MnWO₄ nanorods coupled with g-C₃N₄ nanosheets were fabricated by a simple hydrothermal method, followed by an ultrasonication method. Morphological features, chemical composition, optical properties and crystallographic information of the prepared materials were obtained using SEM-EDX, TEM, XRD, XPS, FT-IR, UV-vis DRS, and PL techniques. The synthesized MnWO₄@g-C₃N₄ nanocomposite displayed excellent photocatalytic activity towards ofloxacin (OFX) under visible light irradiation. Moreover, the influence of reaction parameters such as the catalyst dosage, pollutant concentration and presence of inorganic anions (Cl⁻, CO₃²⁻ and SO₄²⁻), was investigated during the photocatalytic process. Notably, among the inorganic anions, SO₄²⁻ and CO₃²⁻ significantly hampered OFX degradation, while Cl⁻ ions showed minimal effect on the degradation process. The apparent rate constant for MnWO₄@g-C₃N₄ from first order kinetics was 3.5 and 4.8 times higher than that of pure g-C₃N₄ and MnWO₄, respectively. Based on the obtained results, the possible charge transfer mechanism was proposed. The enhanced photocatalytic performance of the binary nanocomposite could be

ascribed to the synergistic effect between MnWO_4 nanorods and $\text{g-C}_3\text{N}_4$ nanosheets resulting in efficient visible light utilization and inhibition of the charge carrier recombination.

CHAPTER – 4: Superior visible light driven photocatalytic degradation of fluoroquinolone drug norfloxacin over novel NiWO_4 nanorods anchored on $\text{g-C}_3\text{N}_4$ nanosheets

A heterojunction nanocomposite $\text{NiWO}_4@ \text{g-C}_3\text{N}_4$ photocatalyst was designed by simple hydrothermal method and followed by sonication method. The structure, optical, surface area and morphological properties of the as synthesized photocatalyst were broadly investigated by UV-vis diffuse reflectance spectroscopy (UV-vis DRS), Brunauer Emmet Teller (BET), X-ray photoelectron spectroscopy (XPS), X-ray diffractometer (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), photoluminescence spectroscopy (PL) and fourier transform infrared (FT-IR) spectroscopy. The photocatalytic performance of the as-designed samples was studied based on the photodegradation of norfloxacin (NRF) under visible light irradiation. As compared, the photocatalytic activity of $\text{NiWO}_4@ \text{g-C}_3\text{N}_4$ nanocomposite higher than that of single phase of $\text{g-C}_3\text{N}_4$ and NiWO_4 . The optimal NRF degradation rate of the synthesized nanocomposite was reached at 0.0547, which is 3.59 times higher than that of $\text{g-C}_3\text{N}_4$. Based on the result, enhancement of photocatalytic activity was attributed to the efficient visible light absorption, large surface area and retard charge carriers separation. Hydroxyl radical ($\bullet\text{OH}$) and hole (h^+) were played crucial role in the photocatalytic degradation process, it systematically explained by trapping experiments.

CHAPTER – 5: Facile synthesis of high performance $\text{InWO}_3/\text{g-C}_3\text{N}_4$ heterostructure for photocatalytic degradation of ciprofloxacin

Novel visible-light-driven $\text{InWO}_3/\text{g-C}_3\text{N}_4$ heterostructure catalyst were fabricated and designed with simplistic hydrothermal and followed by ultrasonicated process. Synthesized

materials were characterized various spectroscopic and microscopic method such as XRD, UV-vis DRS, FT-IR, PL, SEM and TEM. The photodegradation efficiency of ciprofloxacin (CIP) was examined by utilizing InWO₃ modified g-C₃N₄ heterostructure. In contrast with InWO₃ and g-C₃N₄, the InWO₃/g-C₃N₄ heterostructure exhibit more outstanding photocatalytic activity for the degradation of CIP under visible light. However, the InWO₃/g-C₃N₄ heterostructure posses admirable stability and reusability without loss of photocatalytic performance with five successive runs. The improved photocatalytic motion *via* accelerating the migration and restrain the fast recombination of charge carriers, causing to generate strong active species like h⁺ and O₂^{•-} for degradation of CIP to mineralized product.

CHAPTER – 6: Design and synthesis of highly efficient and stable Ce₂(WO₄)₃/g-C₃N₄ heterojunction photocatalyst with enriched visible light photocatalytic activity

Wolframite cerium tungstate (Ce₂(WO₄)₃) hybridized with g-C₃N₄ nanosheets was synthesized *via* a simple ultrasound-assisted method. The prepared Ce₂(WO₄)₃/g-C₃N₄ heterojunction was investigated for photocatalytic degradation of the fluoroquinolone drug moxifloxacin under visible light irradiation. The structure, morphology and optical properties of the as-synthesized heterojunction were investigated by transmission electron microscopy (TEM), X-ray diffraction (XRD), diffuse reflectance UV-vis spectroscopy (UV-vis DRS) and photoluminescence (PL). Significantly higher MRF photocatalytic degradation was observed over the binary nanostructure (Ce₂(WO₄)₃/g-C₃N₄) (94.1 %) compared to g-C₃N₄ (53.6 %) and Ce₂(WO₄)₃ (46.4 %). Such enhanced activity could be ascribed to efficient suppression of the charge carriers' recombination, leading to formation of the reactive species responsible for moxifloxacin degradation. Furthermore, the Ce₂(WO₄)₃/g-C₃N₄ heterojunction showed remarkable stability over five consecutive cycles, with only 11.5 % reduction after the 5th cycle.

CHAPTER – 7: A novel Sm₆WO₁₂/g-C₃N₄ heterojunction photocatalyst for superior photocatalytic degradation of levofloxacin under visible light irradiation

Novel Sm₆WO₁₂/g-C₃N₄ heterojunction photocatalyst was synthesized *via* simple facile method. The sequence of characterization results verified that the Sm₆WO₁₂/g-C₃N₄ synergistically integrate the excellent properties of the Sm₆WO₁₂ and g-C₃N₄. As exhibited by photoluminescence studies, the heterojunction can effectively reduce the undesirable recombination of charge carriers, resulting in the high photocatalytic activity. The degradation efficiency of levofloxacin by Sm₆WO₁₂/g-C₃N₄ heterojunction is 90.8%, much higher than those by the pure g-C₃N₄ and pristine Sm₆WO₁₂. The Sm₆WO₁₂/g-C₃N₄ heterojunction shows excellent photocatalytic activity towards degrading pharmaceutical pollutant levofloxacin under visible light compared to individual g-C₃N₄ and Sm₆WO₁₂ photocatalyst. Furthermore, the synthesized Sm₆WO₁₂/g-C₃N₄ heterojunction demonstrated excellent reusability and stability without loss of photocatalytic activity after five successive runs.

8. Summary

A simple approach method was used to synthesize MnWO₄@g-C₃N₄ nanocomposite using a hydrothermal and an ultrasonication process. The MnWO₄@g-C₃N₄ nanocomposite showed superb photocatalytic activity towards the degradation of OFX under visible light irradiation, which was superior to that of pure MnWO₄ and g-C₃N₄ nanosheets. This was mainly attributed to high separation efficiency of the photogenerated electron/hole pairs, availability of sufficient active sites and improved visible light utilization. The novel NiWO₄@g-C₃N₄ photocatalyst was successfully synthesized *via* simple one spot hydrothermal method followed by ultrasonication method. The activity of the as synthesized photocatalyst was examined toward the degradation of NRF solution under visible light. The as-synthesized NiWO₄@g-C₃N₄

photocatalyst has outstanding photocatalytic activity compared with single component of pristine g-C₃N₄ nanosheets and NiWO₄ nanorods. The more active sites and well-separated electron-hole pairs would enhance the photocatalytic activity of NiWO₄@g-C₃N₄ nanocomposite. •OH and h⁺ species played the critical role for the degradation of NRF, which have been identified by scavenger study.

In summary, g-C₃N₄ photocatalyst with InWO₃ composite doped on the surface are successfully constructed by hydrothermal and followed ultrasonic method. The composition and morphology of the visible light driven photocatalyst were examined systematically. The InWO₃/g-C₃N₄ heterostructure has exhibited a higher photocatalytic activity towards the degradation of CIP among individual photocatalysts g-C₃N₄ and InWO₃. In summary, a novel Ce₂(WO₄)₃/g-C₃N₄ heterojunction was successfully synthesized with a relatively simple facile method was initiated as visible light photocatalyst for the degradation of moxifloxacin drug. In depth characterization of synthesized heterojunction has tremendous photocatalytic activity owing to the enhancing the light harvesting and suitable band gap energy position. Novel Sm₆WO₁₂/g-C₃N₄ heterojunction photocatalyst by hydrothermal followed by ultrasonication method and investigated the photocatalytic activity towards degradation of levofloxacin. The photocatalytic activity of the Sm₆WO₁₂/g-C₃N₄ heterojunction was greatly boosted, which is about 3.69 and 2.93 times high as that of single Sm₆WO₁₂ and g-C₃N₄, respectively. The admirable photocatalytic performance may be ascribed to the efficient transfer and quenched the fast recombination charge carriers and the massive active sites.

In conclusion, compared to other synthesized metal tungstate doped/coupled g-C₃N₄ photocatalyst, NiWO₄@g-C₃N₄ heterojunction photocatalyst was achieved effective degradation rate for pharmaceutical pollutant degradation *viz* norfloxacin. The enhancement of photocatalytic

efficiency was mainly due to the suitable band gap, surface modification of g-C₃N₄ and synergistic effect between the NiWO₄ and g-C₃N₄ nanomaterials.

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List of Publications

1. **S. Lakshmi Prabavathi**, V. Muthuraj, Superior visible light driven photocatalytic degradation of fluoroquinolone drug norfloxacin over novel NiWO₄ nanorods anchored on g-C₃N₄ nanosheets, *Colloids and Surfaces A*, 567 (2019) 43–54.
2. **S. Lakshmi Prabavathi**, P. Senthil Kumar, K. Saravanakumar, V. Muthuraj, S. Karuthapandian, A novel sulphur decorated 1-D MoO₃ nanorods: Facile synthesis and high performance for photocatalytic reduction of hexavalent chromium, *Journal of Photochemistry and Photobiology A: Chemistry*, 356 (2018) 642–651.
3. P. Senthil Kumar, **S. Lakshmi Prabavathi**, P. Indurani, S. Karuthapandian, V. Muthuraj, Light assisted synthesis of hierarchically structured Cu/CdS nanorods with superior photocatalytic activity, stability and photocatalytic mechanism, *Separation and Purification Technology*, 172 (2017) 192–201.
4. M. Dhanalakshmi, K. Saravanakumar, **S. Lakshmi Prabavathi**, M. Abinaya, V. Muthuraj, Fabrication of novel surface plasmon resonance induced visible light driven iridium decorated SnO₂ nanorods for degradation of organic contaminants, *Journal of Alloys and Compounds*, 763 (2018) 512–524.

List of International/National Conferences

1. **S. Lakshmi Prabavathi** and V. Muthuraj, “Sulphur decorated MoO₃ nanorods for superior photocatalytic reduction of hexavalent chromium ions”, *Recent Advances in Chemical Research* (RACR – 2017), VHNSN College, Virudhunagar, 2017 January 24-25.
2. **S. Lakshmi Prabavathi** and V. Muthuraj, “Visible light photocatalytic detoxification of hexavalent chromium by hydrothermally synthesized CoWO₄ nanospheres”, *National*

- conference on Biomaterials in Medicinal Chemistry (BMC – 2017)*, Madurai Kamaraj University, Madurai, 2017 April 12–13.
3. **S. Lakshmi Prabavathi** and V. Muthuraj, “Efficient photocatalytic reduction of 4-nitrophenol to 4-aminophenol under visible light by MnWO_4 nanorods decorated on $\text{g-C}_3\text{N}_4$ nanosheets”, *International conference on Advanced Functional Materials for Energy, Environment and Biomedical Applications (AFMEEB – 2017)*, Madurai Kamaraj University, Madurai, 2017, December 11–12.
 4. **S. Lakshmi Prabavathi** and V. Muthuraj, “Superior photocatalytic reduction of hexavalent chromium over visible light responsive novel CoWO_4 decorated $\text{g-C}_3\text{N}_4$ nanosheets photocatalyst”, *Recent Trends in Synthetic Methods and Material Chemistry (RTSMC – 2018)*, Annamalai University, Chidambaram, 2018 February 2-3.
 5. **S. Lakshmi Prabavathi** and V. Muthuraj, “1D MnWO_4 nanorods anchored on 2D $\text{g-C}_3\text{N}_4$ nanosheets for enhanced photocatalytic degradation of Ofloxacin under visible light irradiation”, *International Conference on Recent Advances in Materials for Energy and Environmental Remediation (RAMEER – 2018)*, VHNSN College, Virudhunagar, 2018 January 28-29.
 6. **S. Lakshmi Prabavathi** and V. Muthuraj, “Enhanced visible light photocatalytic activity of $\text{NiWO}_4/\text{g-C}_3\text{N}_4$ heterojunction for the degradation of fluoroquinolone drug”, *International Conference on Nanomedicine (ICON – 2019)*, Madurai Kamaraj University, Madurai, 2019, February 25–26.
 7. **S. Lakshmi Prabavathi** and V. Muthuraj, “Construction of visible light driven photocatalyst $\text{Ce}_2(\text{WO}_4)_3/\text{g-C}_3\text{N}_4$ heterojunction for enhanced photocatalytic degradation of moxifloxacin”, *International Conference on Recent Trends in Chemistry and Biosciences (ICRTCB – 2019)*, Madurai Kamaraj University, Madurai, 2019, May 16–17.