

Preparation and characterization of nanocomposite thin films for electronic and catalytic applications

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Doctoral Thesis Summary



Tomas Bata University in Zlín

Centre of Polymer Systems

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Preparation and characterization of nanocomposite thin films for electronic and catalytic applications

Příprava a charakterizace nanokompozitních tenkých vrstev pro elektronické a katalytické aplikace

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DEDICATION

This PhD thesis is dedicated to my parents (Farzana Begum and Sher Md.) and cooperative colleagues working in CPS.

ABSTRACT

Remediation of persistent environmental pollutants is one of the critical issues that need to be addressed in the 21st century. In this regard, photocatalysis has garnered huge interest due to due to the utilization of inexhaustible solar energy and simple operational requirements to accomplish various versatile applications including the degradation of various toxicants as well bactericidal activity. However, current developed materials are inefficient for large scale implementation, therefore, research efforts are currently devoted to improvement in visible light harvesting of photocatalysts combined with high redox efficiency.

In this thesis, the preparation and characterization of the as-prepared photocatalytic composite materials for the degradation of harmful pollutants are reported. The materials chosen are free of toxic and noble earth metals. By using ingenious design strategies, visible light active photocatalysts possessing superior redox efficiency in comparison to individual components have been designed. Common synthetic dyes and advanced emerging endocrine-disrupting chemicals are used as model pollutants to evaluate the efficiency of the as-prepared nanocomposite. This work has been also focused on the kinetics, recyclability and immobilization of the nanocomposite considering environmental sustainability goals.

Keywords: *photocatalysis; heterojunction; nanocomposites; bandgap; mechanism; environmental remediation*

ABSTRAKT

Sanace perzistentních látek znečišťujících životní prostředí je jedním z kritických problémů, které je třeba v 21. století řešit. V tomto ohledu si fotokatalýza získala obrovský zájem díky využití nevyčerpatelné sluneční energie a jednoduchým provozním požadavkům pro dosažení různých všestranných aplikací včetně degradace různých toxických látek a také baktericidní aktivity. Současné vyvinuté materiály jsou však pro implementaci ve velkém měřítku neefektivní, a proto je výzkumné úsilí v současné době věnováno zlepšení sklizně viditelného světla fotokatalyzátorů v kombinaci s vysokou redoxní účinností.

V této práci je popsána příprava a charakterizace takto připravených fotokatalytických kompozitních materiálů pro degradaci škodlivých polutantů. Zvolené materiály neobsahují toxické a ušlechtilé kovy zeminy. Použitím důmyslných konstrukčních strategií byly navrženy fotokatalyzátory aktivní ve viditelném světle, které mají v porovnání s jednotlivými součástmi vyšší redoxní účinnost. Běžná syntetická barviva a pokročilé chemické látky narušující endokrinní systém se používají jako modelové znečišťující látky k vyhodnocení účinnosti takto připraveného nanokompozitu. Tato práce byla také zaměřena na kinetiku, recyklovatelnost a imobilizaci nanokompozitu s ohledem na cíle environmentální udržitelnosti.

Klíčová slova: fotokatalýza; heteropřechod; nanokompozity; bandgap; mechanismus; sanace prostředí

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1. INTRODUCTION

Rapid industrialization and human population growth over the past century have resulted in various environmental and energy issues globally. Currently, the energy demand is still being met mostly by fossil fuels which is predicted to rise about drastically. However, over-reliance on fossil fuels has resulted in a gradual increase in atmospheric carbon dioxide and various other toxic gases CO, NO_x, O₃, and SO_x. The burning of fossil fuels on an unprecedented scale is to blame for the rise of environmental issues like pollution, global warming, and ocean acidification which pose grave risks to humans and animals alike [1]. Apart from these anthropogenic activities, industrialization has also resulted in the production and release of numerous micropollutants, which are being released via wastewater effluents into the environment without proper treatment. The established source of these micropollutants is primarily human consumption, and they can be broadly categorized as antibiotics, pharmaceuticals, personal care products, endocrine-disrupting chemicals (EDCs), and pesticides [2–4]. Although most of the known micropollutants have been in use for decades, their relative environmental and biotoxicity have been established only recently due to the advancements in the chemical analytical techniques and pathophysiological pathways of micropollutants [5,6].

Environmental toxicants are bioactive even in minuscule concentration and capable of interfering with the endocrine system, which controls key bodily functions, such as sleep, memory, and coordination. Concernedly, the occurrence and accumulation of these potentially harmful and potent chemicals in the environment have been increasing gradually [7,8]. Considering the urgency of this matter, several environmental protection agencies globally have started regulating by establishing the minimum threshold of currently known and emerging pollutants that potentially carry biohazardous risk. In this matter, the European Commission recently published its chemical strategy as a part of a broader new green deal, under which a robust framework was provided to get rid of various persistent and commonly used chemicals associated with cancer and other neurodegenerative disorders by the year 2030 [9].

Several techniques have been employed so far for environmental remediation of persistent environmental pollutants, such as ozonation, Fenton process, membrane filtration, adsorption process, reverse osmosis, and photocatalysis. Among these, photocatalysis has emerged highly effective option to address various environmental issues owing to, in principle, via the development of highly efficient photocatalytic materials capable of harvesting visible light spectrum

resulting in low energy-cost requirements in comparison to other available alternatives [10–15].

This thesis is a compilation of the experimental results for designing and fabricating highly efficient photocatalytic materials for the elimination of highly persistent environmental pollutants. By employing various modification techniques, pristine semiconducting materials are modified to enhance their photoactivity by imparting synergistic effects to induce feasible charge transfer routes and to reduce backward charge recombination reactions. The photoactivity of the developed material and the associated photocatalytic mechanism is thoroughly discussed.

2. THEORETICAL BACKGROUND

2.1. The urgency of environmental remediation

Rapid population growth and human activity over the last few decades have resulted in serious environmental concerns for humans and animals alike. Different types of pollution such as air, water, and land pollution are a source. During the rapid developments in the 19th and 20th centuries, sources of pollution were not regulated until the role of several pollutants was elucidated in various illnesses resulting in establishing a threshold of release in environmental toxicants, and subsequently stricter environmental regulations were enforced. Pollution has a far-reaching impact on humans and animals alike. Among various sources of pollution, wastewater pollution is considered urgent due to the presence of potentially life-threatening pollutants present in the environment. About 1 to 2 billion people lack access to clean drinking while up to 80 percent of the illness in developing countries are associated with polluted water sources [16].

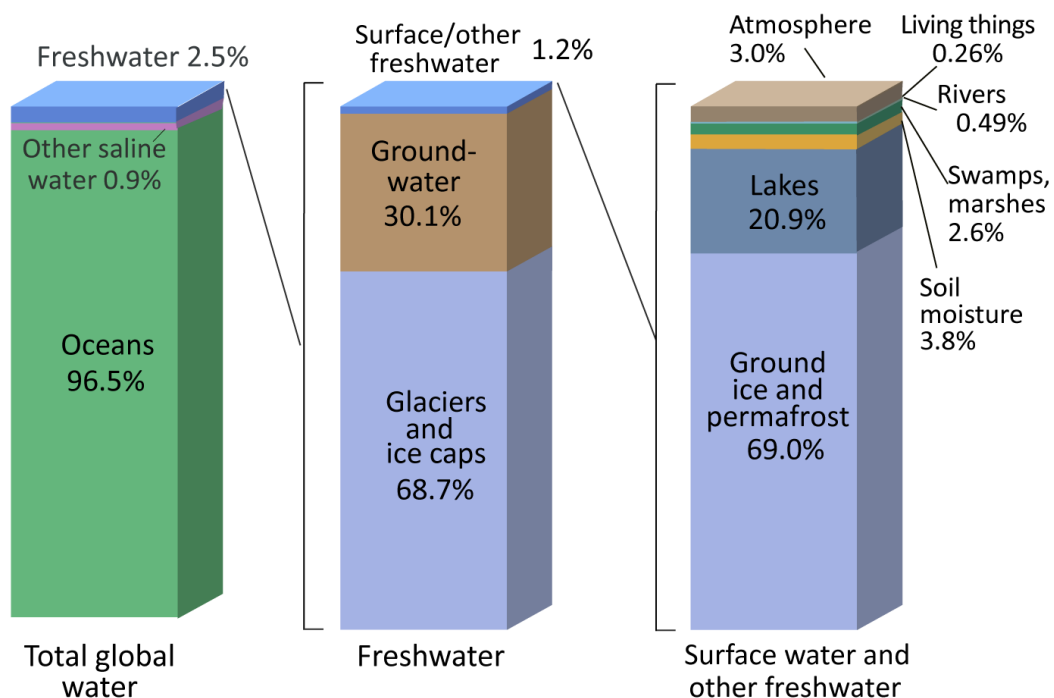


Figure 2.1 Distribution of Earth's water sources [19].

Contaminated water results in more than half a million deaths each year [17]. This high death greatly impacts the social and economic balance of a country. Considering the huge impact and increased environmental regulations, access to clean water is considered one of the fourteen grand challenges of the 21st century by the US Academy of Engineering [18]. Fresh water comprises almost 2.5% of the earth's water distribution which is not sufficient enough to meet every growing

need due to the increased population as shown in Figure 2.1 [19]. Therefore, current efforts are devoted to the elimination of numerous pollutants present in wastewater. These pollutants include heavy metals, synthetic dyes, microplastics, endocrine-disrupting chemicals, microbial pathogens, and pollutants of emerging concern [4,20,21].

2.2. Strategies for treatment of wastewater

Due to increased human activity, the generation of wastewater has also grown at a rapid pace. Several techniques are being used in conventional wastewater treatment plants to ensure the viability of freshwater sources without causing any concern for increased concentration of toxic effluents. Conventional and advanced technologies for treating wastewater are briefly described in the following sections.

i) Conventional methods for water treatment

In conventional wastewater treatment plants (WWTP), physical, chemical, and/or biological technologies are combined to achieve a high rate of water treatment. These processes include screening, flocculation process, chlorination, coagulation, sedimentation, and centrifugation.

ii) Advanced methods for water treatment

Besides commonly used conventional methods for wastewater treatment, a lot of research efforts have been devoted to developing newer techniques for the remediation of environmental toxicants. So far, advanced oxidation processes, membrane technologies, and biological treatment methods have emerged as effective solutions in comparison to conventional methods.

Membrane technologies

Wastewater treatment can be treated to remove various chemical pollutants and other nanosized microbes with relative ease and high efficiency by utilizing suitable membranes which allow only selective movement of components across the suitable membranes. Membranes can be highly functionalized and easy to fabricate maintaining uniform chemical and physical features. They can be either nano-porous or microporous. Membranes are usually fabricated from polymeric materials such as polyethylene (PE), polytetrafluoroethylene (PTFE), polyurethane (PU), and cellulose acetate (AC) as well as inorganic materials such as zeolites, silica, and ceramics [22–27]. The membranes are utilized in four main treatment processes, i.e., low-pressure filtration (micro and ultra-filtration) and high-pressure filtration (nanofiltration and reverse osmosis).

Advanced oxidation processes

Advanced oxidation processes (AOP) is one of the most investigated chemical methods for the treatment of wastewater effluents which has proved highly effective for the degradation of organic pollutants and microbial pathogens [28]. The method involves the generation of a sufficient amount of reactive oxygen species in aqueous water especially hydroxyl radicals $\text{OH}\cdot$ which are reactive enough to degrade organic pollutants and eliminate viruses, bacteria, fungi, and algae. Among the AOPs, the most common techniques are ozone, UV, electrochemical based as well as photocatalysis [29].

2.3. Persistent environmental toxicants

Advances in medicine and biochemistry over the recent decades have elucidated the harmful role of various pollutants which were previously not deemed to be a cause of environmental concern. These compounds are broadly classified into various categories, such as Polychlorinated biphenyls, estrogenic hormones, synthetic steroids, polyelectrolytes, endocrine disrupting chemicals (EDCs), and pollutants of emerging concern [30–33] illustrated in Figure 2.2.

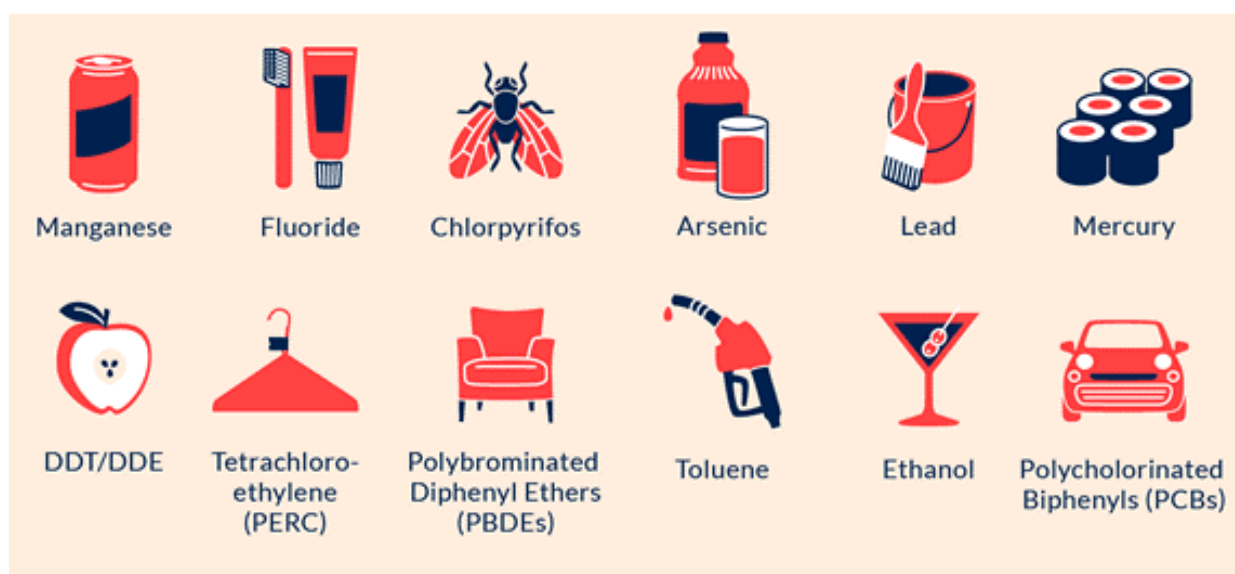


Figure 2.2: Different types of commonly encountered pollutants [34]

EDCs represent a new class of toxicants that have been present in the environment for decades, however; their toxicity has only recently been determined. EDCs are ubiquitous as they are found in nearly all common household items, mostly in personal care and hygiene products, plastics, food storage, sunscreen, Teflon, nonstick wrappers, electronics, and building materials [34].

2.4. Photocatalysis principles and current trends

A typical photocatalysis process only involves a suitable semiconductor and solar energy as an input to promote chemical reactions and proceeds via four main steps: (i) absorption of photons having energy equal to or greater than the bandgap of the semiconductor, (ii) excitation of the electrons from the valence band (VB) of the semiconductor to the conduction band (CB), (iii) migration of photoexcited charge carriers to the surface without futile recombination, and (iv) participation of the photoexcited electrons and holes to participate in the redox reactions [35].

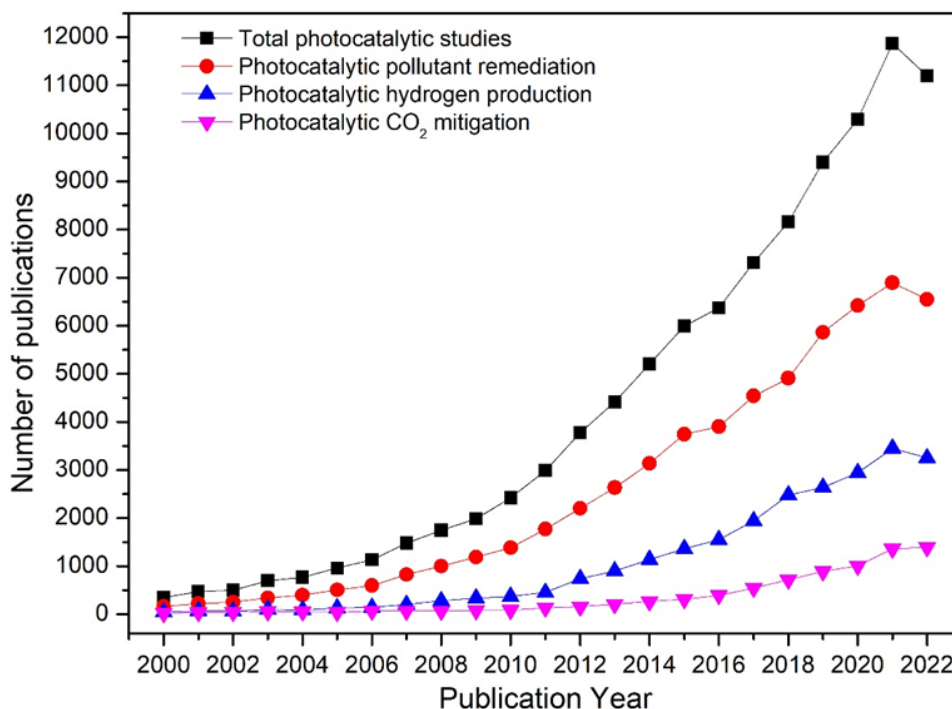


Figure 2.3: Yearly number of reports on photocatalytic applications (self-presentation)

Current efforts focus on maximizing the light absorption spectrum and charge transfer to the surface and preventing charge recombination. Some common strategies to overcome those limitations broadly include structural modifications (for optimizing active sites and minimizing charge recombination), doping (for optimizing bandgap and light absorption), surface sensitization (for increasing light absorption and charge migration dynamics), and the formation of heterojunction [36]. Over the years, the number of scientific publications has gradually risen in the field of photocatalysis and sustainability due to transitioning towards a greener economy as shown in Figure 2.3. In broader terms, photocatalytic materials can be classified into single-component materials and dual-component materials described in detail in the following sections.

2.5. Single-component photocatalytic materials

Single-component semiconductor photocatalysts (n or p-type) have been extensively investigated over the last few decades. A schematic in Figure 2.4, illustrates a photocatalytic process accompanying single-component materials. Their popularity decreases over the years mainly due to inhibitive low performance, large bandgap, poor availability of active sites, and the suppression of charge carrier carriers. Significant efforts have been put forward for improving and optimizing the photoactivity of single-component photocatalysts as well as extending visible light harvesting. These common strategies include doping to modulate the electronic and optical properties, optimizing the surface morphology to enrich the surface area with active sites, manipulation of native defects (vacancies and interstitials), and using sensitizers to extend the light absorption to the visible spectrum [37,38].

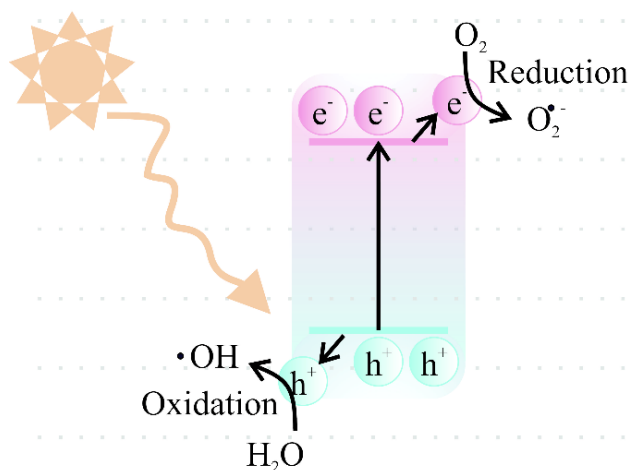


Figure 2.4: Single component photocatalytic mechanism [39]. Schematic illustration provided by the courtesy of Milan Masar.

2.6. Dual-component heterostructured photocatalysts

In a heterostructured photocatalyst, two suitable bandgap semiconductors are joined together in a tandem assembly, in which the charge transfer route depends on the band edge alignment and the electronic structures of both components. Depending on the alignment of the band edge position of the individual components and charge transfer route, different types of staggered configurations have been investigated as shown in Figure 2.5 and Figure 2.6. The overall charge dynamics is primarily reliant on the characteristic band bending at the interface when two semiconducting materials come into contact. While the band bending effect is more prominent in two structurally different components, the effect has been also observed in similar materials having different crystalline phases and or particle sizes. To date, type-II is the most commonly used heterostructure for

photocatalytic applications, in which one oxidizing component and a reducing component designated are joined to achieve interfacial charge transfer, as shown in Figure 2.5.

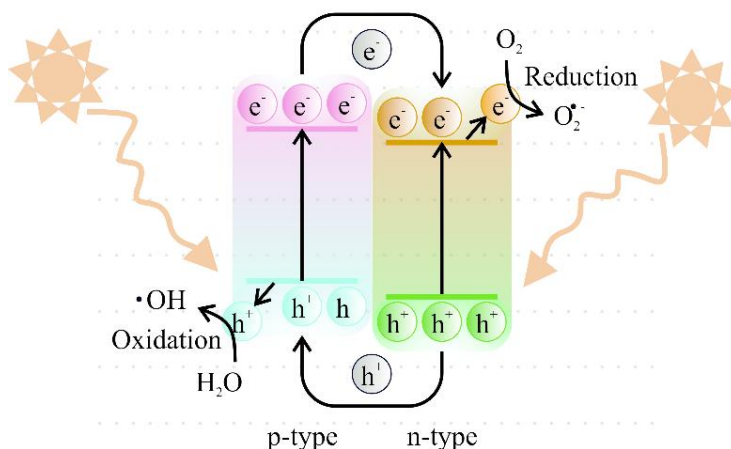


Figure 2.5: Type-II photocatalytic charge route [39]. Schematic illustration provided by the courtesy of Milan Masar.

In a type-II heterojunction, the reducing component must have a higher CB potential (more negative) relative to the oxidizing component while oxidizing component has a high VB potential (more positive) to derive the necessary redox reactions [40]. As evident from the schematic, the type-II photocatalyst can suppress the charge recombination, as electrons and holes migrate, leaving electrons and holes at CB and VB of respective components. The type-II scheme offers two primary advantages, mainly the provision of capturing light in the visible light spectrum, as a narrow and wide bandgap semiconductor can be assembled to obtain makes a functional photocatalytic system. Secondly, a greatly enhanced suppression of charge recombination can be attained resulting in improved photoactivity as compared to the single-component charge transfer route. In spite of the ingenious charge transfer route, it can be seen that type-II annihilates the highly reducing and oxidizing electrons and holes of the respective components. This results in suppressed photoactivity, which otherwise can be optimized by preserving electrons and holes with stronger redox ability. In order to tackle this intrinsic drawback, Z-scheme based photocatalysts offer not only provision extension in light absorption but also ensure a large energy difference between reduction and oxidation potential [41]. A typical Z-scheme is characterized by having a type-II band edge alignment but a radically different charge transfer route, i.e., charge recombination of low reducing electrons and oxidizing holes while maintaining electrons and holes with strong redox potentials, as shown in Figure 2.6. This results not only in the provision of visible

light harvesting but also in stronger spatial charge separation as well as the generation of powerful redox species. The Z-scheme charge transfer route mimics the natural photosynthesis route in which plants convert solar energy to CO₂, O₂, and other carbohydrates. The alphabet “Z” represents the characteristic charge transport pathway of natural photosynthesis as shown in Figure 2.6 [42]. The Z-scheme is further categorized into two distinct types, i.e., direct and indirect Z-scheme depending on if an external electron mediator is employed or not.

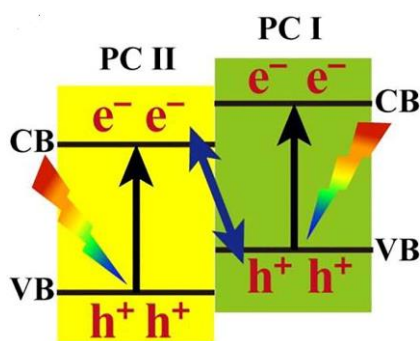


Figure 2.6: Z-scheme charge transfer mechanism [35]

2.7. Strategies for enhancing photocatalytic activity

Surface engineering

Surface engineering modifies parameters of crystalline phases, vacancies, crystalline facets, and surface states which greatly affect the reaction kinetics and selectivity of a particular reaction [43]. These factors increase the number of active adsorptive sites providing favorability for chemical reactions to proceed. E.g. when Pd/TiO₂ was utilized for the CO₂ reduction reaction, the reaction yield was almost negligible due to competing O₂ reduction reactions. To increase the selectivity for CO₂ reduction, Wang et al provided a proof-of-concept study in which porphyrin-based (HPP) polymers loaded onto the Pd-TiO₂ surface was prepared. The addition of HPP resulted in preferential adsorption of CO₂ over O₂ and as a result, a high degree of CO₂ conversion to CH₄ and CO was achieved during 2 h of visible light irradiation, 4.5 times higher than the bare Pd/TiO₂ [44].

Crystal facet engineering

Crystalline facets oriented perpendicular to the internal electric fields were shown photocatalytically more efficient than those oriented parallel to the field direction. For instance, Ma et al synthesized a narrow bandgap Cu₂O photocatalyst with (100) and (111) exposed crystalline facets by varying the amount of PVP. While the bandgap properties of the prepared Cu₂O samples were similar, a higher photoactivity for methyl orange degradation was recorded for the (100) facet in comparison to the (111) exposed facet Cu₂O [45].

Defects engineering

Initially, the role of defects was poorly understood, as they were considered to act as scattering centers for the diffusion of holes and electrons as well as charge recombination centers impeding the photoactivity of materials [38,46]. However, recent efforts have established the positive role of defects in enhancing photocatalytic performance. Defects are classified into four categories: (i) 0D defects (vacancies and dopants), (ii) 1D defects (dislocations), and (iii) 2D defects (grain boundaries) [47]. Since defects can be introduced and precisely controlled during the synthesis process, each material can be purposefully tailored to impart desired characteristics by introducing specific defect(s) or a combination thereof.

Plasmonic materials

Nano-scaled materials exhibit pronounced optoelectronic, thermal, chemical, and physical properties in comparison to their bulk or macro-sized counterparts [48]. These distinct features have been exploited in photocatalysis where particle size in the range of 1-10 nm is utilized at which quantum mechanical effects appear leading to the broadening of bandgap and extended light absorption particularly due to local surface plasmon resonance (LSPR). A necessary condition for localized surface plasmons to exist is that the wavelength of the incident light must be larger than the size of the nanoparticle.

Immobilization of photocatalysts

Considering from environmental and cost-energy perspective, recyclability and recovery are of paramount importance in heterogeneous photocatalysis. The characteristic features which are used to enhance efficiency are achieved by tailoring photocatalysis at the nanoscale in order to provide high surface area and active sites. However, most of the photocatalytic materials have been investigated in the aqueous phase with little attention paid to their recoverability in a conceptualized practical operation. Hence, efforts are being devoted to immobilizing photocatalysts onto a suitable support material to enhance their lifecycle, recyclability, and recoverability. In this context, a wide variety of materials have been investigated such as silica, thin films, nanofibers, indium tin oxide, membranes, zeolites, clays, and polymeric materials [49]. Among available support materials, mesoporous silica is the most commonly used support material, due to its high surface area, chemical inertness, adsorption capacity, thermal stability, and propensity for photodegradation. Commonly used photocatalysts, TiO_2 and ZnO as well as newly developed materials such as WO_3 have been used to achieve size-dependent quantum effects. Immobilization of nanoparticles onto thin glass films has recently gained much attention due to high light absorption

and reduced light scattering in comparison to particulate form. Moreover, an increasing amount of reaction solution layer thickness drastically reduces comparable light absorption and activation by all particles. In this regard, nanoparticles coated thin film offers an effective approach by delivering maximum light penetration with low utilization of photocatalyst as cost-energy benefits outweigh photoelectrochemical cell's efficiency.

2.8. Photocatalytic materials for pollutants degradation

Several classes of photocatalytic materials have been prepared. TiO_2 is the most investigated to date as a single component material or in a tandem heterostructured assembly. Some other classes of materials include ZnO , graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), metal sulfides, metal-organic frameworks (MOFs), metal ferrites, graphene-based materials, etc. [50–52]. Each class offers unique features such as chemical stability and favorable band edge position. For example, $\text{g-C}_3\text{N}_4$ offers a low bandgap of ~ 2.8 eV and suitable VB and CB edge positions, resulting in the provision of both reduction and oxidation reactions, however; pristine $\text{g-C}_3\text{N}_4$ is prone to chemical degradation in the presence of hydroxyl radiation and suffers from poor charge inhibition of charge recombination [53,54]. The choice of materials selected for any potential photocatalytic application can be made by consulting the energy band diagram as shown in Figure 2.7. The development of novel photocatalyst materials entails not only superior photoactivity in a limited cyclic run but sustained photoactivity throughout several cyclic runs without any or negligible degradation in the structural integrity. It should be also noted that any photocatalyst which employs toxic elements is undesirable due to higher associated costs and environmental sustainability.

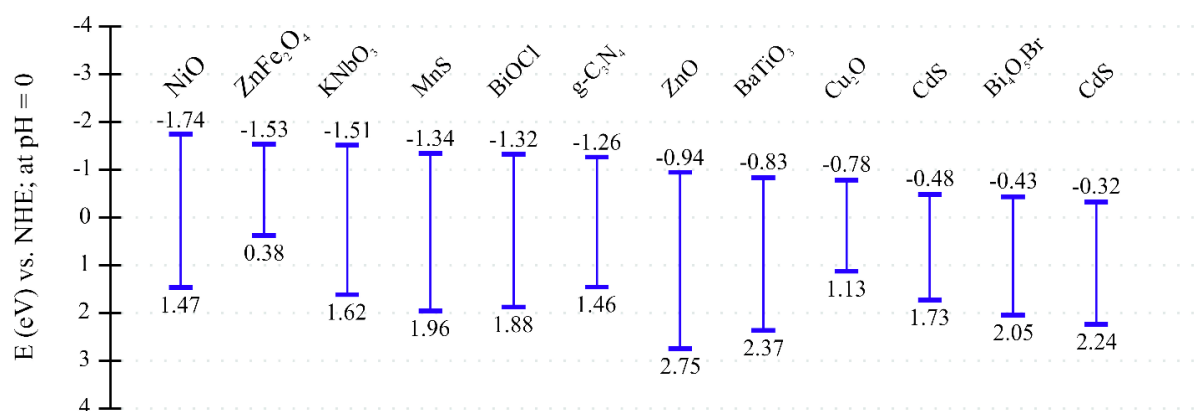


Figure 2.7: Bandgaps and band edge positions of highly oxidizing and reducing photocatalysts [39]. Schematic illustration provided by the courtesy of Milan Masar.

3. SUMMARY OF LITERATURE SURVEY AND MOTIVATION

Increased industrialization and anthropogenic activities have resulted in releasing a wide variety of toxic chemical effluents into natural water resources. These toxic pollutants are found in every major household item and industry, such as pharmaceuticals, pesticides, personal care products, kitchen products, plastics, and industrial solvents. Although the role of toxic pollutants such as heavy metals has been well known for a long time, it has only been recently that role of various highly bioactive and toxic organic pollutants has been established due to advances in pathophysiology and their respective interference in crucial bodily functions. Therefore, mitigating the environment from persistent environmental pollutants is one of the serious challenges of the 21st century.

Photocatalysis has recently as emerged as an alternative to conventional techniques for the remediation of environmental pollutants, mainly due to the utilization of inexhaustible solar energy and utilizing only a suitable semiconductor. However, current research and literature survey suggest that the current efficiencies of the developed photocatalytic systems still lack in comparison to other available alternatives. This necessitates the development of highly efficient photocatalytic materials that are environmentally sustainable and capable of achieving high quantum efficiency. Therefore, this creates a research gap for comprehensive work to develop semiconductor nanocomposites to address the ever-growing environmental pollution.

To bridge this gap, doctoral research work was carried out to further advance the knowledge and understanding of the photocatalytic processes and the development of highly efficient materials by ingenious material design and band engineering. In particular, highly reducing and oxidizing semiconductors were used to achieve visible light absorption while maintaining high redox capabilities. The as-prepared materials were tested against synthetic dyes and estrogenic hormones as model pollutants. Considering aspects of environmental sustainability, recyclability and stability of samples were also determined. Methods of immobilization by thin-film glass have also been explored. The developed materials and techniques offered can be implemented in a pilot-scale experiment for photocatalytic elimination of persistent environmental pollutants.

4. AIMS OF DOCTORAL THESIS

The aims of this doctoral work are set according to the state-of-the-art study and to further advance understanding in the field of photocatalysis for environmental applications, especially water remediation.

Thus, the aim of the dissertation is to study and develop novel photocatalytic materials for the efficient treatment of emerging pollutants in water. In order to achieve the aim, the following goals are specified.

- Material design and preparation of photocatalysts in powder form and characterization of their basic properties. Zinc oxide, cuprous oxide, tungsten trioxide, and graphitic carbon nitride are the systems to be examined. Metal nanoparticle decoration will be investigated as well.
- Immobilization of the photocatalysts in suitable forms of thin films, including the development of the preparation method.
- Development or adaptation of suitable testing methods for experimental evaluation of the photocatalytic effectivity and efficiency of prepared systems.

Based on that, the main doctoral work is classified into four main categories as illustrated in the schematic diagram below (Figure 4.1):

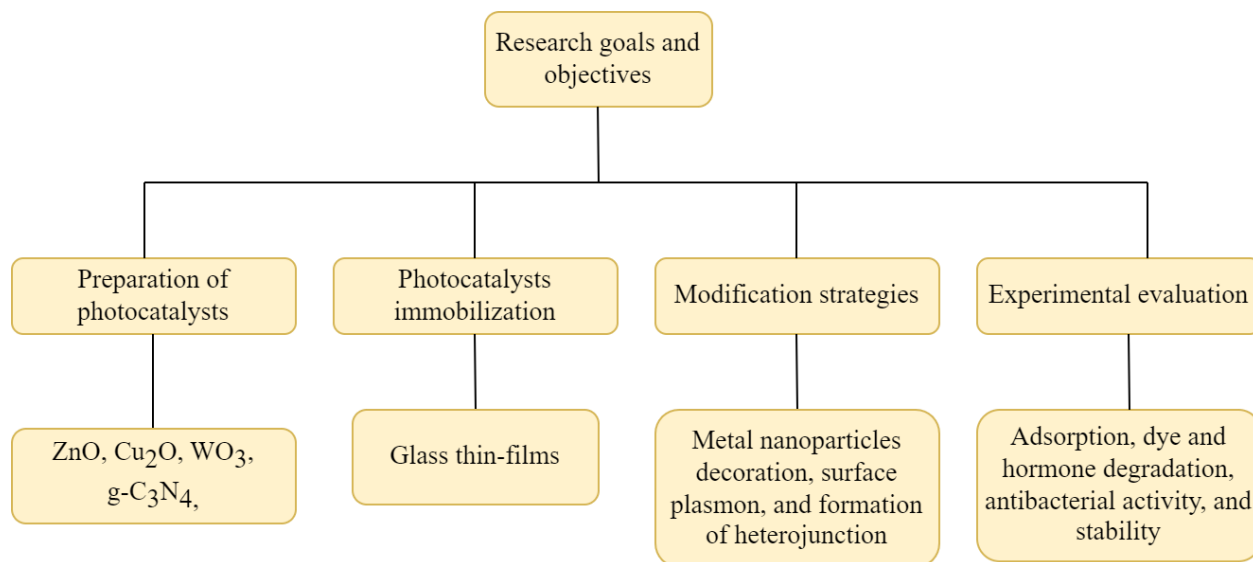


Figure 4.1: Summarized research plan for the doctoral thesis (self-presentation).

5. EXPERIMENTAL PART

5.1. Materials used and synthesis techniques

The following photocatalytic materials were synthesized by solid-state synthesis method, hydrothermal and heat treatment routes, according to the procedure described briefly below:

5.2. Heterostructured WO₃/Cu₂O

Two-dimensional WO₃ nanoplates were synthesized via a two-step method. In the first step, peroxotungstic acid ([WO₂(O₂)H₂O]·nH₂O, PTA) to be used as a precursor was prepared by recrystallization from the solution obtained by dissolving 2 g of tungsten powder in 20 mL of H₂O₂ (about 32–35 wt. %). Tungsten powder dissolved quickly under vigorous stirring and at elevated temperature (50–60 °C), resulting in a transparent solution. Evaporation of the preceding prepared solution in a hot air oven at a temperature of 90 °C resulted in a white crystalline PTA precursor material. Pure two-dimensional WO₃ nanoplates were obtained by thermal decomposition of the precursor at 550 °C for 1 h in an open-air atmosphere in the second step. The preparation of Cu₂O/WO₃ photocatalyst nanocomposites was carried out by solid-state method. The process used was as follows. Initially, an appropriate amount of copper acetate as a precursor and 0.5 g of WO₃ were mixed and ground together in an agate mortar for about 10 min until a uniform mixture was obtained. The powdered mixture was then transferred to an alumina crucible with a cover and calcined by heating the samples, starting from room temperature to 400 °C. The samples were kept at 400 °C for 5 min to achieve sufficient crystallinity. The heating rate of the muffle furnace was set at 50 °C/min. Finally, different Cu₂O(x wt. %)/WO₃ nanocomposites (x = 1.0, 5.0, 10.0) were obtained [HA 1].

5.3. Heterostructured g-C₃N₄/WO₃

Silica-supported g-C₃N₄/WO₃ was synthesized via a two-step heat treatment route. Initially, 20 g of urea was dissolved in 40 mL of deionized water (≥ 0.06 μ S/cm). Afterward, 5 g of silica was added into the aqueous solution of urea to obtain a paste which was spread over a petri dish and left for drying overnight in an oven at 60 °C. The dried paste was further crushed in a mortar to a fine powder and annealed at 550 °C for 2 h in a muffle furnace in a self-supporting atmosphere to obtain silica-supported g-C₃N₄. After that, silica-supported g-C₃N₄ was sonicated in the solution prepared by dissolving tungstic acid in ammonia for 30 min and subsequently filtered. Finally, silica-supported g-C₃N₄ impregnated with ammonium paratungstate was annealed to 500 °C for 2 h to obtain silica-supported g-C₃N₄/WO₃ [HA 2].

5.4. Immobilized heterostructured ZnO/WO₃/Pt

Elongated ZnO structures were prepared by hydrothermal method. First, a seed layer was prepared by using zinc acetate solution coated etched microscope glass followed by annealing at 500 °C. After that, the seeded substrate was immersed into equimolar (0.05 M) zinc nitrate hexahydrate and hexamethylenetetramine and (0.016 M) polyethyleneimine (PEI) aqueous solution with the seeded substrates up-side down at 93 °C for 16 h to grow (ZnOnr) arrays. By doubling the amount of PEI, nanowires (ZnOnw) were obtained, keeping the same procedure otherwise. The obtained samples were rinsed with de-ionized water, dried, and annealed at 500 °C in a Muffle furnace to remove PEI and improve ZnO crystallinity prior to heterojunction fabrication. For fabrication of ZnO/WO₃/Pt heterojunction, platinized WO₃ nanoparticles (RENECAT, Toshiba, Japan) were sprayed over prepared ZnOnr/nw and left for room drying [HA 3].

5.5. Source of materials used

All chemicals used throughout the doctoral work were obtained from Sigma-Aldrich with high purity grade. Ammonium hydroxide solution 25%, was provided by (p.a., Lach-Ner) while tungsten powder ISS Nippon Kayaku group. Filters with pores size of 0.45 µm and 25 mm in width were provided by Whatman, Czech Republic for the collection of aliquots for HPLC analysis. Deionized water was used throughout the experiments obtained from the Milli-Q water purifier. (Biopak, Merck, USA).

5.6. Experimental design

The photocatalytic experiments for the evaluation of developed materials were carried out in LEDs based photoreactor (due to cost-energy advantage) and UV tube light irradiation for a continuous flow reactor [55]. For each experiment, a light intensity of 2 mW/cm⁻² was maintained by keeping the reactor at a specific distance from the light source. Evaluation of synthetic dye was carried out using UV-vis spectrophotometer while for the organic estrogenic hormones, HPLC was utilized for which the optimized method of detection was used according to the previous report [56]. The detailed kinetics study was carried out by using Design-Expert 11.0v software. Response surface methodology is an excellent tool for establishing a relationship between several parameters and the response output of a system in the form of a second-order polynomial equation. A total of 17 experimental runs were randomly generated for analysis via the Box-Behnken method thereby allowing the study of linear, quadratic effects, pseudo-first-order, pseudo-second-order, and intra-particle diffusion kinetic models. The Box-Behnken design (BBD) polynomial quadratic model equation is presented below:

$$R = Y_0 + Y_1A + Y_2B + Y_3C + Y_12AB + Y_13AC + \dots \quad 4.1$$

where R is the response (photodegradation), Y is the coefficient related to the factors, while A , B , and C represent the investigated factors in the model. This polynomial equation was further used for predicting the optimal removal parametric values using RSM experimental design based on the BBD model within low and high factor levels, as shown in Table 1 [HA 2].

Table 5.1 Investigated factors with their high and low levels within the experimental design space.

Factor	Name	Low level	High levels	Mean
A	Hormone conc. ($\mu\text{g/L}$)	100	500	300
B	Dosage (μg)	1000	5000	3000
C	pH of solution	3	9	7

OriginLab 9.0v and Design expert software 11.0v were used for the statistical analysis and plotting of relevant graphs used throughout the study. For the determination of the significance of each experimental factor, single-factor ANOVA analysis was employed in which $p < 0.05$ was taken to be statistically significant. Determination of coefficient (R^2) was used to predict the suitability of the predicted model in comparison to the actual experimental data. Additionally, the sum of squared errors (SSE) and Chi-squared (χ^2) values were calculated to minimize deviations from the response values. The bactericidal activities of the prepared nanocomposites were evaluated against *Escherichia coli* and *Staphylococcus aureus* bacteria using the common agar plate method [57].

5.7. Characterization techniques

Photocatalytic materials can be characterized, and their performance evaluated regardless of the intended application via the following classified methods:

1. Chemical composition of photocatalytic materials is characterized by:

- X-ray diffraction (XRD)
- Fourier transform infrared spectroscopy (FTIR)
- Raman spectroscopy

2. Morphology and physical features of as-developed materials are characterized by:

- Scanning electron microscope (SEM)
- Transmission electron microscope (TEM)
- BET adsorption isotherm (Brunauer, Emmett, Teller)
- Energy dispersive x-ray spectroscopy (EDX)

3. Optoelectronic properties are characterized by:

- Photoluminescence Spectroscopy (PL)
- UV-vis spectroscopy (UV-vis)
- Diffuse reflectance spectroscopy (DRS)

4. Thermal stability of materials is characterized by:

- Thermogravimetric analysis (TGA)
- Differential scanning calorimetry (DSC)

5. Analytical analysis was carried out via:

- High-performance liquid chromatography (HPLC)
- Liquid chromatography–mass spectrometry (LC-MS)

6. CONCLUDING REMARKS

6.1. Summary of achievements according to specified research goals

The research work in this thesis is on the preparation and optimization of new highly efficient photocatalytic materials for prospective water remediation applications. A succinct description of the steps to achieve the preceding goal is given in chronological order as follows:

- Selection of highly efficient photocatalytic materials based on their relative bandgap and band-edge positions. Materials selected which are active in visible light and UV spectrum, particularly visible light active g-C₃N₃, Cu₂O and WO₃, as well as UV-active ZnO, which was decorated with WO₃ and Pt metal to improve photoactivity, were utilized.
- Based on their suitable optoelectronic properties, the selected materials are synthesized using facile chemical synthesis routes, particularly the hydrothermal method for ZnO/WO₃/Pt system and the solid-state synthesis method for synthesis of Cu₂O/WO₃ and C₃N₄/WO₃ systems, which were considered after a careful survey of literature and established methods. The choice of solid-state synthesis avoided the otherwise inevitable formation of CuWO₄ phase in wet syntheses, whereas the C₃N₄/WO₃ system required a primary urea pyrolysis step for C₃N₄ preparation.
- From a sustainability and application perspective, immobilization techniques for developed photocatalysts are explored in detail using thin films. The thin films provided a way to avoid the waste of photocatalytic particles and their spoilage into the environment during the wastewater treatment process; thus, secondary pollution is further avoided. Hence, besides evaluating the as-prepared photocatalysts in powdered suspension, a modified continuous drip flow photoreactor operating with the liquid film thickness of 1 mm over the photocatalytic surface was utilized and reported for photocatalytic activity evaluation and testing.
- The synthesized materials are further modified using novel strategies to increase photocatalytic efficiency and extend light absorption capability in the visible light spectrum. Metal decoration (Pt) was primarily used to achieve a synergistic effect from the surface plasmon effect. Moreover, to

achieve visible light response while maintaining the high redox potentials of the photocatalytic system, heterostructure was designed by combining highly oxidizing and reducing components, particularly WO_3 , g- C_3N_4 , and Cu_2O . The formation of direct Z-scheme heterojunction was successful and studied in detail for the $\text{Cu}_2\text{O}/\text{WO}_3$ nanocomposite photocatalyst.

- Determination of optimized experimental conditions using the response surface methodology coupled with Box-Behnken design by variation in common independent parameters, such as photocatalyst dose, the concentration of pollutants, and pH. The obtained optimized parameters were further experimentally tested for validation. The obtained response equation was observed to show a high correlation with the predicted vs actual data.
- The developed materials were evaluated rigorously using commonly used synthetic organic dyes and emerging pollutants, particularly estrogenic hormones, which are model endocrine disruptors in the environment. Photodegradation rate constants were determined, and kinetics studies were carried out in detail. Moreover, the antibacterial activity of g- $\text{C}_3\text{N}_4/\text{WO}_3$ nanocomposite was studied in dark conditions and under UV irradiation. A significant antibacterial activity of the nanocomposite towards the gram-positive *Staphylococcus aureus* was observed under both UV and visible light irradiation, whereas the antibacterial activity was greatly reduced towards gram-negative *Escherichia coli*.
- All the obtained experimental data and results presented in this dissertation have been published in Q1/Q2 impact factor journal in accordance with the University Policy and the rector's directive.

6.2. Summary of research work reports

A summary of the already accomplished research work and concerned published work for this doctoral thesis is given:

➤ *Article I* titled “Solid-State Synthesis of Direct Z-Scheme $\text{Cu}_2\text{O}/\text{WO}_3$ Nanocomposites with Enhanced Visible-Light Photocatalytic Performance”.

Main theme: Designing and fabrication of highly effective photocatalyst mimicking natural photosynthesis reaction pathway

This research work was carried out to develop direct Z-scheme based nanocomposite mimicking natural photosynthesis reaction to generate a highly efficient photocatalytic reaction pathway. The photocatalytic performance of the prepared samples under UV and visible light was studied by monitoring the discoloration of methylene blue under illumination by selected wavelengths, allowing for the distinguishing between the contributions of the two semiconductive components. Experimental results showed that the decoration of WO_3 nanoplates by Cu_2O nanoparticles led to an improvement in photocatalytic performance, regardless of the used LEDs wavelength, even at low concentrations. By using scavengers selectively blocking reactive species involved in the discoloration reaction, it was conclusively determined that the $\text{Cu}_2\text{O}/\text{WO}_3$ nanocomposite exhibited the characteristics of a direct Z-scheme-type photocatalyst. The obtained results concludes that development of modified photocatalytic with ingenious design principles can effectively eliminate toxic environmental pollutants.

Contribution: Investigation, writing, reviewing, and editing.

➤ *Article II* titled “ZnO nanowires and nanorods based $\text{ZnO}/\text{WO}_3/\text{Pt}$ heterojunction for efficient photocatalytic degradation of Estriol (E3) hormone”.

Main theme: Immobilization of heterostructured photocatalyst in a continuous flow reactor to achieve high efficiency, recyclability, and recoverability of the photocatalyst

This research work was carried out to use immobilization on thin films. In this report, ZnO nanowires and nanorods-based $\text{ZnO}/\text{WO}_3/\text{Pt}$ heterojunction were successfully prepared on glass substrates via a facile hydrothermal growth method followed by spraying. The photocatalytic performance was evaluated by the degradation of estriol (E3) hormone under UV light irradiation (~ 365 nm) in a closed continuous flow reactor. The as-prepared samples achieved an excellent photodegradation rate in the range of 23–37% and 63–86% for the nanorods and

nanowires morphology, respectively. This article provides new insight into the construction of suitable geometrically optimized heterojunction for the remediation of persistent bio toxicants

Authorship contribution: Hassan Ali: Investigation

➤ *Article III titled “Boosting photocatalytic degradation of estrone hormone by silica-supported g-C₃N₄/WO₃ using response surface methodology coupled with Box-Behnken design”.*

Main theme: Optimization of kinetics of a photocatalytic system to reduce energy-cost for effective elimination of toxic pollutants.

This research work was carried out to develop and employ metal-free graphitic carbon nitride. This article reports on the preparation and characterization of silica-supported g-C₃N₄/WO₃ nanocomposite with boosted photocatalytic performance towards the degradation of estrone hormone by using response surface methodology (RSM) coupled with the Box-Behnken model to determine the synergistic effects of three independent experimental parameters (hormone concentration, solution pH, and photocatalyst dosage). The RSM results were consistent with the prediction model ($R^2 > 0.958$ and 0.934 for UV and visible light irradiation, respectively). The optimized experimental test conditions were evaluated as follows: 3000 μg of photocatalyst dosage, 300 $\mu\text{g/L}$ of hormone concentration, and pH 7. The hormone photodegradation efficiencies under these experimental parameters were 100% and 96% after 3 h of UV and visible light irradiation, respectively. Additionally, degradation kinetics (first-order, second-order, and intraparticle diffusion model), adsorption isotherms (Freundlich and Langmuir), and antibacterial activity of the prepared sample were also examined. Radical scavenging tests were performed to elucidate the photodegradation mechanism and the existence of reactive oxygen species. The recyclability test showed that the efficiency remained above 75% after seven consecutive cycles. The results indicate that the RSM based on the Box-Behnken model is an excellent approach for determining optimized experimental parameters for specific degradation of estrogenic hormones.

Authorship contribution: Hassan Ali: Conceptualization, Methodology, Investigation, Writing – original Draft.

6.3. Contribution to science and praxis, and future prospects

The primary aim of this doctoral research was on the development of highly efficient photocatalytic materials for environmental pollution remediation. The aim was successfully achieved by the preparation of novel and highly stable photocatalytic materials with an ingenious charge transfer mechanism. The developed materials were able to effectively eliminate toxic environmental pollutants, especially highly bioactive and bioaccumulating endocrine-disrupting pollutant hormones, which were used as model compounds. Additionally, the developed materials possessed high stability, and they were able to maintain their photocatalytic even after several cyclic runs.

However, the current work mainly pertains to small-scale studies without long-term practical applications. Moreover, the current sources of pollutants posing great environmental risk also include excessive CO₂ and nitrogen emissions as well as emerging pollutants of greater concern. So, considering the current research trends and future research direction, the following goals can generally be set for future work in photocatalytic environmental remediation as follows:

- Development of highly reducing photocatalytic materials sufficient to derive hydrogen evolution reaction, CO₂ and N₂ reduction while controlling the specificity of each competing reaction.
- Elucidation of factors affecting the charge transfer mechanism and modulation of optoelectronic properties to achieve optimized electron transfer pathway with minimized charge recombination.
- Development of materials with optimized structural features to induce high-performance efficiency while reducing backward reactions and maintaining long-term chemical stability.
- Implementation of photocatalytic in small-scale experiments to evaluate the viability of each application such as hydrogen generation, wastewater treatment, ammonia, and fuel production in comparison to available alternatives.
- Evaluation of life-cycle assessment of the developed materials and synthesis by keeping in view environmental sustainability goals and recoverability of materials without causing any secondary pollution.

REFERENCES

Author's works

- [HA 1] Ali, H., Guler, A., Masar, M., Urbanek, P., Urbanek, M., Skoda, D., Suly, P., Machovsky, M., Galusek, D., & Kuritka, I. (2021). Solid-State Synthesis of Direct Z-Scheme Cu₂O/WO₃ Nanocomposites with Enhanced Visible-Light Photocatalytic Performance. *Catalysts*, 11(2), 293. <https://doi.org/10.3390/catal11020293>
- [HA 2] Ali, H., Yasir, M., Ngwabebhoh, F. A., Sopik, T., Zandraa, O., Sevcik, J., Masar, M., Machovsky, M., & Kuritka, I. (2023). Boosting photocatalytic degradation of estrone hormone by silica-supported g-C₃N₄/WO₃ using response surface methodology coupled with Box-Behnken design. *Journal of Photochemistry and Photobiology A: Chemistry*, 441, 114733. <https://doi.org/10.1016/J.JPHOTOCHEM.2023.114733>
- [HA 3] Yasir, M., Masar, M., Sopik, T., Ali, H., Urbanek, M., Antos, J., Machovsky, M., & Kuritka, I. (2022). ZnO nanowires and nanorods based ZnO/WO₃/Pt heterojunction for efficient photocatalytic degradation of estriol (E3) hormone. *Materials Letters*, 319, 132291. <https://doi.org/10.1016/J.MATLET.2022.132291>

Other references

- [1] F. Perera, Pollution from Fossil-Fuel Combustion is the Leading Environmental Threat to Global Pediatric Health and Equity: Solutions Exist, *International Journal of Environmental Research and Public Health* 2018, Vol. 15, Page 16. 15 (2017) 16. <https://doi.org/10.3390/IJERPH15010016>.
- [2] L.G. Kahn, C. Philippat, S.F. Nakayama, R. Slama, L. Trasande, Endocrine-disrupting chemicals: implications for human health, *Lancet Diabetes Endocrinol.* 8 (2020) 703–718. [https://doi.org/10.1016/S2213-8587\(20\)30129-7](https://doi.org/10.1016/S2213-8587(20)30129-7).
- [3] N. Aryal, J. Wood, I. Rijal, D. Deng, M.K. Jha, A. Ofori-Boadu, Fate of environmental pollutants: A review, *Water Environment Research.* 92 (2020) 1587–1594. <https://doi.org/10.1002/wer.1404>.
- [4] I. Haddaoui, J. Mateo-Sagasta, A review on occurrence of emerging pollutants in waters of the MENA region, *Environmental Science and*

- Pollution Research. 28 (2021) 68090–68110.
<https://doi.org/10.1007/s11356-021-16558-8>.
- [5] R. Lauretta, A. Sansone, M. Sansone, F. Romanelli, M. Appetecchia, Endocrine Disrupting Chemicals: Effects on Endocrine Glands , *Frontiers in Endocrinology* . 10 (2019).
<https://www.frontiersin.org/article/10.3389/fendo.2019.00178>.
- [6] T.T. Schug, A.F. Johnson, L.S. Birnbaum, T. Colborn, L.J. Guillette, D.P. Crews, T. Collins, A.M. Soto, F.S. vom Saal, J.A. McLachlan, C. Sonnenschein, J.J. Heindel, Minireview: Endocrine Disruptors: Past Lessons and Future Directions, *Molecular Endocrinology*. 30 (2016) 833–847. <https://doi.org/10.1210/me.2016-1096>.
- [7] Y. Tang, Y. Zhong, H. Li, Y. Huang, X. Guo, F. Yang, Y. Wu, Contaminants of emerging concern in aquatic environment: Occurrence, monitoring, fate, and risk assessment, *Water Environment Research*. 92 (2020) 1811–1817. <https://doi.org/10.1002/WER.1438>.
- [8] M. Muller, S. Combalbert, N. Delgenès, V. Bergheaud, V. Rocher, P. Benoît, J.P. Delgenès, D. Patureau, G. Hernandez-Raquet, Occurrence of estrogens in sewage sludge and their fate during plant-scale anaerobic digestion, *Chemosphere*. (2010).
<https://doi.org/10.1016/j.chemosphere.2010.06.062>.
- [9] Zero pollution action plan, (n.d.).
https://environment.ec.europa.eu/strategy/zero-pollution-action-plan_en (accessed April 17, 2023).
- [10] E. Matei, C.I. Covaliu-Mierla, A.A. Țurcanu, M. Râpă, A.M. Predescu, C. Predescu, Multifunctional Membranes—A Versatile Approach for Emerging Pollutants Removal, *Membranes* . 12 (2022).
<https://doi.org/10.3390/membranes12010067>.
- [11] S. Iravani, R.S. Varma, MXene-Based Photocatalysts in Degradation of Organic and Pharmaceutical Pollutants, *Molecules* 2022, Vol. 27, Page 6939. 27 (2022) 6939. <https://doi.org/10.3390/MOLECULES27206939>.
- [12] C. Gil-Lozano, E. Losa-Adams, A.F. Dávila, L. Gago-Duport, Pyrite nanoparticles as a Fenton-like reagent for in situ remediation of organic pollutants, *Beilstein Journal of Nanotechnology* 5:97. 5 (2014) 855–864.
<https://doi.org/10.3762/BJNANO.5.97>.
- [13] K. Prakruthi, M.P. Ujwal, S.R. Yashas, B. Mahesh, N. Kumara Swamy, H.P. Shivaraju, Recent advances in photocatalytic remediation of

emerging organic pollutants using semiconducting metal oxides: an overview, *Environmental Science and Pollution Research*. (2021).
<https://doi.org/10.1007/s11356-021-17361-1>.

- [14] S. Bandehali, F. Parvizian, H. Ruan, A. Moghadassi, J. Shen, A. Figoli, A.S. Adeleye, N. Hilal, T. Matsuura, E. Drioli, S.M. Hosseini, A planned review on designing of high-performance nanocomposite nanofiltration membranes for pollutants removal from water, *Journal of Industrial and Engineering Chemistry*. 101 (2021) 78–125.
<https://doi.org/10.1016/j.jiec.2021.06.022>.
- [15] N. Fallah, E. Bloise, D. Santoro, G. Mele, State of Art and Perspectives in Catalytic Ozonation for Removal of Organic Pollutants in Water: Influence of Process and Operational Parameters, *Catalysts* 2023, Vol. 13, Page 324. 13 (2023) 324. <https://doi.org/10.3390/CATAL13020324>.
- [16] U.N. report finds 1 in 4 people don't have access to clean drinking water : NPR, (n.d.). <https://www.npr.org/2023/03/22/1165464857/billions-of-people-lack-access-to-clean-drinking-water-u-n-report-finds> (accessed April 17, 2023).
- [17] Water Crisis - Learn About The Global Water Crisis | Water.org, (n.d.). <https://water.org/our-impact/water-crisis/> (accessed April 17, 2023).
- [18] Grand Challenges - 14 Grand Challenges for Engineering, (n.d.). <http://www.engineeringchallenges.org/challenges.aspx> (accessed April 17, 2023).
- [19] P.H. Gleick, G.F. White, E. Pacific Institute for Studies in Development, Stockholm Environment Institute., *Water in crisis : a guide to the world's fresh water resources*, (1993) 473.
- [20] Y. Jeong, G. Gong, H.-J. Lee, J. Seong, S.W. Hong, C. Lee, Transformation of microplastics by oxidative water and wastewater treatment processes: A critical review, *J Hazard Mater*. 443 (2023) 130313. <https://doi.org/10.1016/J.JHAZMAT.2022.130313>.
- [21] V. Piazza, A. Uheida, C. Gambardella, F. Garaventa, M. Faimali, J. Dutta, Ecosafety Screening of Photo-Fenton Process for the Degradation of Microplastics in Water, *Front Mar Sci*. 8 (2022) 2126.
<https://doi.org/10.3389/FMARS.2021.791431>.
- [22] M.M. Foumani, A. Khorshidi, A.F. Shojaei, Polyethyleneimine Nanofibers Functionalized with Tetradentate Schiff Base Complexes of

- Dioxomolybdenum(VI) as Efficient Catalysts for Epoxidation of Alkenes, *ChemistrySelect*. (2019). <https://doi.org/10.1002/slct.201803047>.
- [23] M.H. Mohraz, F. Golbabaee, I.J. Yu, M.A. Mansournia, A.S. Zadeh, S.F. Dehghan, Preparation and optimization of multifunctional electrospun polyurethane/chitosan nanofibers for air pollution control applications, *International Journal of Environmental Science and Technology*. 16 (2019) 681–694. <https://doi.org/10.1007/s13762-018-1649-3>.
- [24] L.A. Goetz, N. Naseri, S.S. Nair, Z. Karim, A.P. Mathew, All cellulose electrospun water purification membranes nanotextured using cellulose nanocrystals, *Cellulose*. 25 (2018) 3011–3023. <https://doi.org/10.1007/s10570-018-1751-1>.
- [25] R. Araga, C.S. Sharma, Amine Functionalized Electrospun Cellulose Nanofibers for Fluoride Adsorption from Drinking Water, *J Polym Environ*. (2019). <https://doi.org/10.1007/s10924-019-01394-2>.
- [26] R.O.A. Rahman, A.M. El-Kamash, Y.-T. Hung, Applications of Nano-Zeolite in Wastewater Treatment: An Overview, *Water* . 14 (2022). <https://doi.org/10.3390/w14020137>.
- [27] J. Zhou, J. Zhao, R. Liu, Defect engineering of zeolite imidazole framework derived ZnS nanosheets towards enhanced visible light driven photocatalytic hydrogen production, *Appl Catal B*. (2020). <https://doi.org/10.1016/j.apcatb.2020.119265>.
- [28] D. Ghime, P. Ghosh, Advanced Oxidation Processes: A Powerful Treatment Option for the Removal of Recalcitrant Organic Compounds, *Advanced Oxidation Processes - Applications, Trends, and Prospects*. (2020). <https://doi.org/10.5772/INTECHOPEN.90192>.
- [29] L. Xiong, J. Tang, Strategies and Challenges on Selectivity of Photocatalytic Oxidation of Organic Substances, *Adv Energy Mater*. 11 (2021) 2003216. <https://doi.org/10.1002/aenm.202003216>.
- [30] S.M. Choi, S.D. Yoo, B.M. Lee, Toxicological Characteristics of Endocrine-Disrupting Chemicals: Developmental Toxicity, Carcinogenicity, and Mutagenicity, *Journal of Toxicology and Environmental Health, Part B*. (2004). <https://doi.org/10.1080/716100635>.
- [31] Z. Xie, P. Zhang, Z. Wu, S. Zhang, L. Wei, L. Mi, A. Kuester, J. Gandrass, R. Ebinghaus, R. Yang, Z. Wang, W. Mi, Legacy and emerging organic contaminants in the polar regions, *Science of The Total Environment*. 835 (2022) 155376. <https://doi.org/10.1016/J.SCITOTENV.2022.155376>.

- [32] K.J. Choi, S.G. Kim, C.W. Kim, S.H. Kim, Effects of activated carbon types and service life on removal of endocrine disrupting chemicals: Amitrol, nonylphenol, and bisphenol-A, *Chemosphere*. (2005). <https://doi.org/10.1016/j.chemosphere.2004.11.080>.
- [33] C. Peiris, S. Nawalage, J.J. Wewalwela, S.R. Gunatilake, M. Vithanage, Biochar based sorptive remediation of steroidal estrogen contaminated aqueous systems: A critical review, *Environ Res*. 191 (2020) 110183. <https://doi.org/https://doi.org/10.1016/j.envres.2020.110183>.
- [34] Chiropractor in Matthews | Environmental Toxicity in Matthews | The Balanced Body Center, (n.d.). <https://www.knowbalance.com/environmental-toxicity-testing> (accessed April 17, 2023).
- [35] Q. Xu, L. Zhang, J. Yu, S. Wageh, A.A. Al-Ghamdi, M. Jaroniec, Direct Z-scheme photocatalysts: Principles, synthesis, and applications, *Materials Today*. 21 (2018) 1042–1063. <https://doi.org/https://doi.org/10.1016/j.mattod.2018.04.008>.
- [36] A.B. Djurišić, Y. He, A.M.C. Ng, Visible-light photocatalysts: Prospects and challenges, *APL Mater*. 8 (2020) 030903. <https://doi.org/10.1063/1.5140497>.
- [37] F. Amano, K. Nogami, M. Tanaka, B. Ohtani, Correlation between Surface Area and Photocatalytic Activity for Acetaldehyde Decomposition over Bismuth Tungstate Particles with a Hierarchical Structure, *Langmuir*. 26 (2010) 7174–7180. <https://doi.org/10.1021/la904274c>.
- [38] D. Chen, Z. Wang, T. Ren, H. Ding, W. Yao, R. Zong, Y. Zhu, Influence of defects on the photocatalytic activity of ZnO, *Journal of Physical Chemistry C*. 118 (2014) 15300–15307. <https://doi.org/10.1021/JP5033349>.
- [39] H. Ali, M. Masar, A.C.C. Güler, M. Urbánek, M. Machovsky, I. Kuřitka, Heterojunction-based photocatalytic nitrogen fixation: Principles and current progress, *Nanoscale Adv*. (2021). <https://doi.org/10.1039/D1NA00565K>.
- [40] Y. Wang, Q. Wang, X. Zhan, F. Wang, M. Safdar, J. He, Visible light driven type II heterostructures and their enhanced photocatalysis properties: a review, *Nanoscale*. 5 (2013) 8326. <https://doi.org/10.1039/c3nr01577g>.

- [41] J. Low, C. Jiang, B. Cheng, S. Wageh, A.A. Al-Ghamdi, J. Yu, A Review of Direct Z-Scheme Photocatalysts, *Small Methods*. 1 (2017) 1700080. <https://doi.org/https://doi.org/10.1002/smtd.201700080>.
- [42] J. Barber, Photosynthetic energy conversion: natural and artificial, *Chem Soc Rev*. 38 (2009) 185–196. <https://doi.org/10.1039/B802262N>.
- [43] E. Kowalska, Z. Wei, M. Janczarek, Band-gap Engineering of Photocatalysts: Surface Modification versus Doping, *Visible Light-Active Photocatalysis*. (2018) 447–484. <https://doi.org/10.1002/9783527808175.CH16>.
- [44] Y. Ma, X. Yi, S. Wang, T. Li, B. Tan, C. Chen, T. Majima, E.R. Waclawik, H. Zhu, J. Wang, Selective photocatalytic CO₂ reduction in aerobic environment by microporous Pd-porphyrin-based polymers coated hollow TiO₂, *Nature Communications* 2022 13:1. 13 (2022) 1–10. <https://doi.org/10.1038/s41467-022-29102-0>.
- [45] J. Li, M. He, J. Yan, J. Liu, J. Zhang, J. Ma, Room Temperature Engineering Crystal Facet of Cu₂O for Photocatalytic Degradation of Methyl Orange, *Nanomaterials*. 12 (2022) 1697. <https://doi.org/10.3390/NANO12101697>.
- [46] W.H. Saputera, J. Rizkiana, W. Wulandari, D. Sasongko, Role of defects on TiO₂/SiO₂composites for boosting photocatalytic water splitting, *RSC Adv*. (2020). <https://doi.org/10.1039/d0ra05745b>.
- [47] S. Bai, N. Zhang, C. Gao, Y. Xiong, Defect engineering in photocatalytic materials, *Nano Energy*. 53 (2018) 296–336. <https://doi.org/https://doi.org/10.1016/j.nanoen.2018.08.058>.
- [48] T.J. Antosiewicz, S.P. Apell, Optical enhancement of plasmonic activity of catalytic metal nanoparticles, *RSC Adv*. 5 (2015) 6378–6384. <https://doi.org/10.1039/C4RA13399D>.
- [49] V. Porley, N. Robertson, Substrate and support materials for photocatalysis, *Nanostructured Photocatalysts: From Materials to Applications in Solar Fuels and Environmental Remediation*. (2020) 129–171. <https://doi.org/10.1016/B978-0-12-817836-2.00006-5>.
- [50] T. Di, Q. Xu, W. Ho, H. Tang, Q. Xiang, J. Yu, Review on Metal Sulphide-based Z-scheme Photocatalysts, *ChemCatChem*. 11 (2019) 1394–1411. <https://doi.org/https://doi.org/10.1002/cctc.201802024>.

- [51] B. Witkowski, Applications of ZnO Nanorods and Nanowires - A Review, *Acta Phys Pol A*. 134 (2018) 1226–1246.
<https://doi.org/10.12693/APhysPolA.134.1226>.
- [52] K. Qi, B. Cheng, J. Yu, W. Ho, A review on TiO₂-based Z-scheme photocatalysts, *Chinese Journal of Catalysis*. 38 (2017) 1936–1955.
[https://doi.org/https://doi.org/10.1016/S1872-2067\(17\)62962-0](https://doi.org/https://doi.org/10.1016/S1872-2067(17)62962-0).
- [53] M. Baudys, Š. Paušová, P. Praus, V. Brezová, D. Dvoranová, Z. Barbieriková, J. Krýsa, Graphitic Carbon Nitride for Photocatalytic Air Treatment, *Materials* 2020, Vol. 13, Page 3038. 13 (2020) 3038.
<https://doi.org/10.3390/MA13133038>.
- [54] P. Niu, J. Dai, X. Zhi, Z. Xia, S. Wang, L. Li, Photocatalytic overall water splitting by graphitic carbon nitride, *InfoMat*. 3 (2021) 931–961.
<https://doi.org/10.1002/INF2.12219>.
- [55] W.K. Jo, R.J. Tayade, New generation energy-efficient light source for photocatalysis: LEDs for environmental applications, *Ind Eng Chem Res*. 53 (2014) 2073–2084. <https://doi.org/10.1021/IE404176G>.
- [56] M. Yasir, T. Šopík, L. Lovecká, D. Kimmer, V. Sedlařík, The adsorption, kinetics, and interaction mechanisms of various types of estrogen on electrospun polymeric nanofiber membranes, *Nanotechnology*. 33 (2021) 075702. <https://doi.org/10.1088/1361-6528/AC357B>.
- [57] J. Guo, J. Zhou, Z. Sun, M. Wang, X. Zou, H. Mao, F. Yan, Enhanced photocatalytic and antibacterial activity of acridinium-grafted g-C₃N₄ with broad-spectrum light absorption for antimicrobial photocatalytic therapy, *Acta Biomater*. 146 (2022) 370–384.
<https://doi.org/10.1016/J.ACTBIO.2022.03.052>.

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LIST OF ABBREVIATIONS AND SYMBOLS

BBD	Box-Behnken Design
BET	Brunauer, Emmett, Teller
CB	Conduction band
E1	Estrone
E2	Estradiol
E3	Estriol
EDCs	Endocrine disrupting chemicals
EDX	Energy dispersive X-ray analysis
EE2	Ethinylestradiol
FTIR	Fourier transform infrared spectroscopy
g-C ₃ N ₄	Graphitic carbon nitride
HPLC	High performance liquid chromatography
RSM	Response surface methodology
SEM	Scanning electron microscope
TEM	Transmission electron microscope
TGA	Thermogravimetric analysis
TiO ₂	Titanium dioxide
UV-vis	Ultraviolet-visible
VB	Valence band
XRD	X-ray diffraction
ZnO	Zinc oxide
WO ₃	Tungsten trioxide
<i>S. aureus</i>	<i>Staphylococcus aureus</i>
<i>E. coli</i>	<i>Escherichia coli</i>

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- 2) Ali, H., Masar, M., Güler, A. C. C., Urbánek, M., Machovsky, M., & Kuřitka, I. (2021). Heterojunction-based photocatalytic nitrogen fixation: Principles and current progress. *Nanoscale Advances*. <https://doi.org/10.1039/D1NA00565K>
- 3) Ali, H., Yasir, M., Ngwabebhoh, F. A., Sopik, T., Zandraa, O., Sevcik, J., Masar, M., Machovsky, M., & Kuritka, I. (2023). Boosting photocatalytic degradation of estrone hormone by silica-supported g-C₃N₄/WO₃ using response surface methodology coupled with Box-Behnken design. *Journal of Photochemistry and Photobiology A: Chemistry*, 441, 114733. <https://doi.org/10.1016/J.JPHOTOCHEM.2023.114733>
- 4) Masar, M., Ali, H., Guler, A. C., Urbanek, M., Urbanek, P., Hanulikova, B., Pistekova, H., Annusova, A., Machovsky, M., & Kuritka, I. (2023). Multifunctional bandgap-reduced ZnO nanocrystals for photocatalysis, self-cleaning, and antibacterial glass surfaces. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 656, 130447. <https://doi.org/10.1016/J.COLSURFA.2022.130447>
- 5) Yasir, M., Asabuwa Ngwabebhoh, F., Šopík, T., Ali, H., & Sedlarík, V. (2022). Electrospun polyurethane nanofibers coated with polyaniline/polyvinyl alcohol as ultrafiltration membranes for the removal of ethinylestradiol hormone micropollutant from aqueous phase. *Journal of Environmental Chemical Engineering*, 10(3), 107811. <https://doi.org/10.1016/J.JECE.2022.107811>
- 6) Yasir, M., Masar, M., Sopik, T., Ali, H., Urbanek, M., Antos, J., Machovsky, M., & Kuritka, I. (2022). ZnO nanowires and nanorods based ZnO/WO₃/Pt heterojunction for efficient photocatalytic degradation of estriol (E3) hormone. *Materials Letters*, 319, 132291. <https://doi.org/10.1016/J.MATLET.2022.132291>

Conference publications

- 1) Ali, H., Masar, M., Urbánek, M., Guler, A. C., Urbánek, P., Machovsky, M., & Kuřitka, I. (2021). Effect of annealing on luminescence and photocatalytic activity of ZnS nanocrystals under UV light irradiation. NANOCON Conference Proceedings, 2020-October, 261–266. <https://doi.org/10.37904/NANOCON.2020.3707>
- 2) Yasir, M., Šopík, T., Ali, H., Kimmer, D., & Sedlařík, V. (2021). GREEN SYNTHESIS OF TITANIUM AND ZINC OXIDE NANOPARTICLES FOR SIMULTANEOUS PHOTOCATALYTIC REMOVAL OF ESTROGENS IN WASTEWATER. NANOCON Conference Proceedings - International Conference on Nanomaterials, 189–196. <https://doi.org/10.37904/NANOCON.2021.4333>
- 3) ALI, H., MASAR, M., YASIR, M., SOPIK, T., URBANEK, P., MACHOVSKY, M., & KURITKA, I. (2021). Silica supported WO₃/Cu₂O heterostructured nanoparticles for photocatalytic degradation of hormones. NANOCON 2021 Conference Proceedings, 2021, 104–109. <https://doi.org/10.37904/NANOCON.2021.4343>
- 4) MASAR, M., ALI, H., YASIR, M., Sevcik, J., Urbánek, M., SOPIK, T., MACHOVSKY, M., & KURITKA, I. (2022). ZnO/Cu₂O heterojunctions treated glass surface for photocatalytic and self-cleaning applications, NANOCON, Brno, Czech Republic. NANOCON 2022 Conference Proceedings, 2022, 107–112. <https://doi.org/10.37904/nanocon.2022.4598>
- 5) Silica supported visible light active graphitic carbon nitride (g-C₃N₄) photocatalyst for estrogenic hormones removal and antibacterial activity, Energy and Fuels Conference, 2022, Krakow, Poland. <http://ef-conference.agh.edu.pl/wp-content/uploads/2022/09/Book-of-Abstract-EFE2022.pdf>

Projects

- IGA/CPS/2020/003 - "Preparation and characterization of nanoparticles for advanced applications", member of the research team.
- IGA/CPS/2021/002 - "Preparation and characterization of nanocomposite systems", member of the research team.
- IGA/CPS/2022/002 - "Preparation and characterization of advanced nanocomposite systems", member of the research team.
- IGA/CPS/2023/006 - "Preparation and characterization of advanced functional nanocomposite systems", member of the research team.

- LTT20010 - Surface functionalized glass: “Concept of heterostructured nanoparticles inspired by artificial photosynthesis” (2020-2024), member of the research team.

**Preparation and characterization of nanocomposite thin films
for electronic and catalytic applications**

**Příprava a charakterizace nanokompozitních tenkých vrstev
pro elektronické a katalytické aplikace**

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