Abstract

Long-term environmental health is a top priority in today's world as scientific community is striving hard to cater to the needs of the hour and nano catalysts have shown promising advances in addressing a number of environmental problems. In particular, nano catalysts have shown key applications in reduction of CO₂ to valuable energy-rich products. production of sustainable energy through H₂ evolution, removal of heavy metals and degradation of compounds such as antibiotics, toxic pesticides and dyes that have toxicological effects on ecosystems and human health. Nano catalysts are crucial for enabling these ecologically friendly reactions through light mediated processes. They possess outstanding catalytic properties, such as enhanced reactivity, selectivity and stability, making them highly effective at triggering desired reactions while avoiding negative environmental impacts. Since photocatalysis harnesses abundant light energy enabling simultaneous reaction initiation and catalyst activation, facilitating extensive reactions under mild conditions, this chapter intends to provide specifics of the leading studies, challenges and future perspectives of the long-term environmental welfare of lightmediated catalytic processes of nano catalysts.

Keywords: Photocatalysis, Nano catalysts, CO₂ reduction, Energy materials, Heavy metal removal, Dye degradation, Waste water treatment.

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I. INTRODUCTION

Climate change, biodiversity, soil, water, air, and chemical exposure are major contributors of environment's health. Ecosystem sustainability is altered based on the change in these factors. The goal of research is to transform dangerous materials into useful, less dangerous chemicals and energy products. Utilising small amounts, nanomaterials provide efficient interactions with the environment & biological systems. With many possibilities in environmental remediation and energy production, photocatalysis uses light to activate catalysts, accelerating chemical reactions. This method enables efficient and sustainable solutions for many industries, addressing critical challenges in a cost-effective way[1]. Pesticides help crops grow and prevent illness, but they adversely affect wildlife and human health. In this regard Nano-TiO₂, phosphorus nanocomposites, and graphene oxide nanoparticles are gaining popularity due to their stability, affordability, environmental friendliness and also due to their photocatalytic activities toward pesticide degradation[2]. During the COVID-19 epidemic, there has been an increase in the overuse of pharmaceutical medications, notably antibiotics[3]. India uses a lot of antibiotics, which raises questions about resistance. Potential water filtration through photocatalytic remedies includes metal oxides, rGO-based nanocomposites, and MOFs[4,5]. Heavy metals often found in wastewater, particularly Mercury, Cadmium, Chromium and Arsenic. Industries, mining, and agricultural practices can all contribute to their increased concentrations and their continued presence in the eco system. This bioaccumulation in plants and animals disturbs the ecological balance. TiO₂, ZnO, and Fe₂O₃ and their derivatives have been utilised recently which have shown great efficiency and several green nanoparticles derived from plants also work well as photocatalysts in this process[6,7]. Photocatalysis provides options for effective hydrogen production, which is a preferred clean fuel[8,9]. The limitations of Pt catalysts can be overcome by nanomaterials like M/TiO₂, CdS, Fe₃O₄@Fe₂O₃-TiO₂, and composites based on rGO[10–12]. Aquatic life is seriously threatened by water contamination. The largest chemical oxygen demand is caused by carcinogenic and very poisonous synthetic dyes[13]. For effective dye breakdown by photocatalysis, metal oxide nanoparticles such as CdS/TiO₂, Bi_2O_3 nano-sphere photocatalyst doped with Ce^{3+} and Ce^{4+} , nanostructured $CaFe_2O_4$ and other previously reported nanomaterials offer economical and environmentally benign options[14-17]. Global warming is brought on by greenhouse gas accumulation which is majorly due to vehicle emissions. By converting CO_2 with solar energy into useful molecules, the carbon cycle is improved and fuel and environmental concerns are lessened. To serve for the reduction of CO₂, Ru nanoparticles, Ni, Bi-doped TiO₂, 2D Fe-MOF, and nickel on barium titanate were good photocatalysts [18]. The book chapter highlights gaps in current knowledge and explores the utilization of nanomaterials for environmentally friendly applications involving light.

II. APPLICATIONS OF NANO CATALYSTS: AN OVERVIEW ON PHOTOCATALYSIS

1. Photocatalysts For H₂ Evolution: In a study, L. Dáz et al. developed inexpensive M/TiO_2 semiconductor catalytic materials with five distinct first row transition-metal elements (M = Fe, Co, Ni, Cu or Zn) by an impregnation approach. On examining the photocatalytic activity of M/TiO_2 to UV and visible light for hydrogen photoproduction, Cu/TiO₂ photocatalyst showed maximal hydrogen generation efficiency with rates of 5000 and 220 µmol h⁻¹ g⁻¹ for UV and visible radiation, respectively. The produced Schottky barrier from the different Fermi level among the metal particles and a

semiconductor (TiO₂) caused this. Based on this study, the researchers were thrilled to see that Cu/TiO₂ photocatalyst might serve as a promising low-cost substitute[19]. Due to its characteristics of a low bandgap and a suitable conduction band location, cadmium sulphide (CdS) nanocatalyst has been widely used in another study by Wei Li and others to obtain very efficient H₂ generation under visible-light irradiation. It also showed that decrease in photo corrosion by adding N heteroatoms onto the hexagonal CdS NPs. The recombination behaviour of CdS body carriers was effectively inhibited in light of the synergistic advancement of heteroatom-semiconductor coordination (HSC) interaction, leading to an obviously increased photocurrent density (2 times) and noticeably improved photoexcited carrier's utilisation. This led to the achievement of a significant apparent quantum yield (AOY = 32.41%, at 500 nm). Approximately 3983.4 μ mol·h⁻¹·g⁻¹ of HER rate with exceptional photostability was attained using simulated sunlight (SSL) irradiation. Another study used a one-pot supercritical carbon dioxide (CO₂) gelling and drying process utilising reduced graphene oxide to make composites or rGO, aerogels that supported Pt/TiO₂ nanoparticles reduction in a N₂ atmosphere. Approximately 3983.4 μ mol·h⁻¹·g⁻¹ of HER rate with exceptional photostability was attained using SSL irradiation[20]. Another study used a one-pot supercritical carbon dioxide (CO₂) gelling and drying process utilising reduced graphene oxide to make composites orrGO, aerogels that supported Pt/TiO₂ nanoparticles reduction in a N₂ atmosphere. 3D monolith then formed had a meso/microporous nature. The experimentally determined H₂ production rate of the optimised system (18,800 μ molH₂h⁻¹gNPs⁻¹), utilising alcohol as a sacrificial agent, was noticeably greater than the reported values of the scientific literature for comparable Pt/TiO₂/rGO catalysts & reaction media (2000-10,000 µmolH₂h⁻¹gNPs⁻¹). This effect was due to the creation of new electronic pathways following the partial restoration of the graphene network and the favoured adsorption of methanol in the reduced structure[21]. In a study that used a MOF template technique, the development of a Fe₃O₄@Fe₂O₃-TiO₂complex oxide has tuned the bandgap of Fe₂O₃-TiO₂. Changing the pH, using various sacrificial reagents majorly methanol and using proton donors have all increased the rate hydrogen synthesis. The quantum efficiency was quite high by inclusion of 0.1 g aniline hydrochloride to be proton source, which increased the hydrogen evolution rate to 2. 366 mmol/0.5 g/h. In the same study, iron-based MIL101@FT with a covering of Fe₂O₃-TiO₂ oxide was synthesised, and Fe₃O₄@FT was created by annealing the MOF templated MIL101@FT. Fe₃O₄@FT's shape was adjusted to produce a structure resembling a rod with particles that ranged in size from 30-166 nm. The modified Fe₃O₄@FT nanomaterials' bandgap was successfully tuned to 2.8 eV, allowing for easier electron excitation[22].

2. Photo Catalysts for CO₂ Reduction: Ke Guo et al. we're excited to create the first Ru/TpPa-1 catalysts for the photo degradation of Carbon Dioxide in response to visible-light irradiation. These catalysts were of ketoamine-based covalent organic frameworks (COFs) and were loaded with Ru nanoparticles (NPs). Ru/TpPa-1 catalysts showed significantly improved photo reduction activity for CO₂ in comparison with TpPa-1, with a maximal HCOOH generation rate of 108.8 μ mol g_{cat}⁻¹ h⁻¹ at 3.0 wt% Ru/TpPa-1. Because of the suppression of electron-hole recombination caused by the noble metal nanomaterial loading, the strength of photocatalysis was high as active and targeted CO₂ reduction was backed by ruthenium (Ru). When exposed to visible light, Ru/TpPa-1, which was made through the amine-aldehyde condensation, was employed as photo catalyst in order to reduce CO₂. The SEM pictures demonstrated that TpPa-1 crystallises with a flower-like morphology and that the amount of loaded Ru NPs causes the surface

to become rougher[23]. A set of Ni & Bi doped TiO₂ catalysts ranging in Ni & Bi contents were synthesised by the sol-gel process in a study reported Reza Nematollahia et al. Doping these elements into the TiO_2 framework led to an increase in surface area, a decreased band gap energy, which led to the significantly greater light absorption efficiency, a reduction in the degree of electron-hole recombination, and a boost in CO₂ adsorption capacity in comparison to pure TiO₂. The co-doped TiO₂ with 1 weight percent Ni and 3 weight percent Bi had the maximum methane production (21.13 mol/ g_{cat}), which was over 6.5 times greater than the pure TiO₂. These particles resembled spheres in shape and ranged in size from 10 to 20 nm[24]. With an outstanding photocatalytic efficiency of 1637 µmol g⁻¹ h⁻¹, 2D Fe-MOF nanosheets (Fe-MNS) were developed by Ahmed Mahmoud Idris and others. These Fe-MNS had LUMO potentials of 0.11 V (vs. RHE). The particles in these materials resembled 2D sheets. Consequently, the Dye/Fe-MNS system's mechanism, electrons from $[Ru(bpy)]_3^{2+}$ dye were potentially efficiently were injected into 2D Fe-MNS during the photosensitizing processes, which caused LUMO potential of 2D Fe-MNS catalysts to shift negatively in order to conform to the presumed thermodynamic reduction potential of CO₂/CO. Therefore, the Dye/Fe-MNS system demonstrated a noteworthy photocatalytic CO generation rate of 1120 μ mol g⁻¹ h⁻¹ with 420 nm and with co-doping they attained an outstanding photocatalytic CO output rate of 1637 µmol g⁻¹ h⁻¹[25]. In order to hydrogenate CO₂ to CH₄ with nearly 100% selectivity and at rates that are as high as 103.7 µmol g⁻¹ h⁻¹ under UV-visible and visible light conditions (the generation rate: 40.3 µmol g⁻¹ h⁻¹ without any external heating), Diego Mateo et al developed a composite catalyst made of nanoparticles of nickel supported on barium titanate. The tiny NPs $(9.5\pm3.8 \text{ nm})$ are metallic Ni, according to X-ray examination, whereas the bigger particles (30-70 nm) are primarily made of Ba and Ti, similar to Barium titanate[26].

3. Photo Catalysts For Antibiotic Degradation: For the efficient photocatalytic breakdown of the antibiotic Ofloxacin, titanium-based nanoparticles were made using the sol-gel process in a work by Kanza Mushtaq and others to research the way various three hours of exposure, the rates of degradation for TiO_2 calcined at 300, 350, 400, and 450°C, respectively, at 295 nm were 91%, 87%, 76%, and 64%. The anatase shape of the TiO_2 calcined at 300 °C was seen. Because of their distinctive dimensionality and tunable band gap, which dynamically improve their photocatalytic efficiency, TiO₂ nanoscale materials exhibit outstanding performance. Given the rise in the radiation exposure time between thirty minutes to one eighty minutes, the rate of degradation of ofloxacin improved from 15% to 90% [27]. In a study by K. Divyarani et al. new two-dimensional bimetallic MOFs, specifically CoZn@MOF and CoZn@MOF/GO nanosheets, were synthesised. Isonicotinic acid was utilised as an organic linker and it was utilized to degrade tetracycline hydrochloride. In contrast, adding GO has enhanced the assimilation of visible light, band gap remodelling, and therefore photocatalysis. In light, persulfate, and oxygen were crucial for the increased photocatalysis of TCn at CoZn@MOF/GO, according to investigations on radical scavengers and electron resonance[28]. In an investigation by Mengwen Xu et al. rGO/ Bi₄O₅Br₂ nanocomposites created via a solvothermal methods with 1.0wt%-rGO/ Bi₄O₅Br₂ nanocomposite provided effective photodegradation of antibiotics like 80.7% of norfloxacin (NOR), 92.5% of ciprofloxacin (CIP) and 95.2% of tetracycline (TC) within 60 minutes. rGO increased the transport of electrons photogenerated by $Bi_4O_5Br_2$ compared to pure $Bi_4O_5Br_2$, which suppressed the recombination of pairs of electrons and holes. Since these medicines showed degradation with rGO based nanocomposite, the adsorption was likely caused by the interaction

between the aromatic antibiotic domains and the conjugated structure of rGO and substantial specific surface area[29]. During their investigation, Solmaz Aghdasi et al. used immobilised nanoparticles of ZnO on glass plates to study the photocatalytic breakdown of the antibiotic ciprofloxacin (CIP) in aqueous solution. The method of chemical precipitation was used for synthesis. CIP was deteriorating when exposed to UV-C light. The photodegradation efficiency was determined to be 69.5% with a starting concentration of 10 mg L⁻¹ of CIP, pH = 6.8, and light intensity = 42 W m⁻²[30]. A fantastic study was conducted on the photodegradation of the drug ciprofloxacin (CIP) using porous Cr₂O₃@ZnO photocatalysts designed by Reda M. Mohamed et al. for the very first time. They have a large surface area of 1690 m^2 /g and big pore volume of 0.057 cm^3 /g. The study's crucial discovery was that the CIP degradation (100%) could be accomplished in 30 minutes and was 20times much more efficient than pure ZnO. The hexagonal structure of these nanocrystals, which had side lengths of between 100 and 200 nm, was indicated by their dodecahedral sheet-with-shaped structures morphology and regular shape. The integrated heterojunctions of Cr₂O₃ and ZnO semiconductors, the porous Cr₂O₃@ZnO nanocomposites' intense and broad UV/Vis absorption, the nanoscale synthesis of the nanocomposites, the reduction light scattering effect, and the swift transfer of CIP to the sites of action via the porous Cr₂O₃@ZnO network all contributed to the highly improved photocatalytic efficiency of these materials[31].

4. **Photocatalysts for Pesticide Degradation:** The material modified oyster shell powder raised the specific surface area, whereas Ce-N-TiO₂ formed anatase crystal composed of Ce and N doping, providing it the property sensitivity to light. Wei Zhang et al. studied glyphosate degradation via hydrothermally synthesized Ce/N co-doped TiO₂ composite nano-photocatalysts packed on modified oyster shell powder (CeNT@Oys) which increased the available specific surface area from 61.649 m² per g to 75.301 m² per g. The modified oyster shell powder exhibits a consistent particle size and layered, plate-like microstructure. Particles are 9.02 nm 25.04 nm in size on average. The maximum catalyst degradation efficiency at 426 nm was attained at a doping rate of 0.5% Ce by breakdown of the C-P and C-N bonds. h⁺ was the main reactive species for the breakdown of glyphosate, with OH and O_2 being the secondary reactive species [32]. Philani V. Hlophe and colleagues used two-step hydrothermal and sonication process to create a nanocomposite containing black phosphorus & MIL-125(Ti), known as BpMIL, in their quest to degrade diazinon. These methods demonstrated that the nanocomposites' circular and sheet-like shape exhibited minimal charge recombination, making them efficient photocatalysts. It was found that 4% BpMIL was the ideal composite. The ideal conditions for diazinon removal and degradation were a neutral pH, 20 mg/L of diazinon, and 0.5 g/L of photocatalyst, which resulted in 96% elimination of the pesticide within 30 minutes with 4%BpMIL and 40% removal with MIL-125(Ti). Due to the synergistic interaction of MIL-125(Ti) and Bp, as well as the Ti³⁺ ions - Ti⁴⁺ ions intervalence electron transfer, the 4%BpMIL composite's increased photodegradation efficiency was explained[33]. Cd₃OSO₄ nanomaterial was researched by Roya Mohammadzadeh Kakhki and associates. It was made using a co precipitation method. This Cd₃OSO₄ photocatalyst's 1.85ev band gap indicated that the material was a sunlight driven photocatalyst. Its photodegradation efficiency was 90% under the ideal experimental conditions for diazinon degradation, which included a concentration of 10 ppm and a photocatalyst dose of 15 mg/l. The synthesised nanoparticles were virtually spherical and measured in three dimensions at the nanoscale scale, according to FESEM pictures. The photodegradation process was significantly influenced by holes, OH radicals, and O_2^{2-1}

[34]. The pesticide chlorpyrifos (CP) was successfully removed and then photodegraded using the newly created magnetically separable composite composed of graphene oxide, nickel ferrite, and titanium dioxide (GO-Cys@NiFe₂O₄@TiO₂ The pesticide chlorpyrifos (CP) was successfully removed and then photodegraded using the newly created magnetically separable composite composed of graphene oxide, nickel ferrite, and titanium dioxide (GO-Cys@NiFe₂O₄@TiO₂). The photocatalyst's band gap was discovered to be 2.8 eV. The material's adsorption efficiency was raised by the presence of active sites in GO-Cys@NiFe₂O₄@TiO₂ like -OH, -SH, -NH₂, and -COO that significantly interacted with the pesticide CP's binding sites by hydrogen bonding. Within 60 minutes, CP in GO-Cys@NiFe₂O₄@TiO₂ showed a 100.0% decline in chlorpyrifos concentration. And for these materials, the SEM pictures revealed thick, layered sheets-like shape[35].

5. Photocatalysts For Heavy Metal Removal: In a scientific work by M. Kamaraj et al., ZnO-NPs were successfully loaded onto the surface of activated carbon made from a common weed called parthenium to create the composite material (ZnONPs-PWAC). For PWAC and ZnONPs-PWAC (parthenium weed activated carbon), the highest equilibrium percentage removal of Cr (VI) is determined to be 99% at around 160 and 90 minutes, respectively. PWAC demonstrates that the morphology has numerous holes and cave structures of varied sizes. These particles are observed to be irregularly grouped shapes and have an average size between 25 and 95 nm. ZnO-NPs may be able to load into activated carbon more easily due to its porous structure. The ZnO-NPs addition to PWAC increased the surface area and active sites of the material that enhanced the effectiveness of the pollutants' adsorption. It demonstrates that the ZnONPs-PWAC removes MB and Cr (VI) more effectively than PWAC[36]. In another study by Qingyao Wang et al., solvothermal synthesis was used to deposit rose-shaped Bi₂WO₆ particles on TiO₂ NTAs (nanotube arrays), and Sb^{3+} doping was applied to increase the photoelectrochemical activity. Due to their rose-like morphology and impurity energy level, which could increase solar absorption and reduce charge carrier recombination, exceptional photocatalytic performance was seen. Under visible light irradiation, the rose-shaped BWO-10 photoelectrode displayed superior photocurrent (0.24 mA/cm^2) , remarkable photovoltage (0.24 V), and interface resistance compared to those of other samples. For Cr (VI) ions, the BWO-10 photoelectrode showed very good photocatalytic activity of 93.84% efficiency. Pure TiO₂ NTAs showed homogenous and clean tubular structures in their morphology. The major species involved in the breakdown of organic dyes were oxygen radicals[37]. Employing Moringa oleifera seeds (MOS) as a reducing or capping agent, Hafiza Mahreen Mehwish et al., conducted research and discovered a low-cost method of producing green silver nanoparticles (AgNPs), which are used in photocatalytic oxidation for the purification of water. The outcomes showed the particles of MOS-AgNPs were aggregates with average size of 4.0 nm that were crystalline and spherical. More than 80% of the harmful Pb⁺²was eliminated with the treated water by the MOS-AgNPs. Pb⁺² concentrations in the supernatant significantly decreased after combining MOS-AgNPs with Pb⁺² solutions for 30 minutes[38]. For the remediation of arsenic water, Mara Y. Paredes et al. created colloidal core-satellite nanoparticles, which have a magnetic iron oxide core made of magnetite (Fe₃O₄) and maghemite (γ -Fe₂O₃) and are enclosed by gold nanoparticle (AuNP) satellites. The process of oxidation of As (III) to As(V) was aided by the catalytic and photocatalytic characteristics of AuNPs, and the magnetic cores served as carriers for adsorption and removal of arsenic by external magnets. The oxidation rate increased by 190 times when added with 15 nm AuNPs.

However, the redox process moved 2.2 times more quickly when 1.9 W cm^2 of irradiance was applied resonantly. In the core-satellite nano system, the same AuNPs mounted on iron oxides achieved a reaction rate that was 120 times more than in the homogeneous condition 2.2 times greater when lighted[39].

6. Photocatalysts For Dye Degradation: Fabrication of Copper-Zinc Oxide nanocomposite via chemical co-precipitation technique, followed by calcinations above 400 °C for 4 hours, was a fresh method by Gaurav Hitkari et al for the photocatalytic decomposition of Congo red (CR) dye. 95% of the CR dye was destroyed by the ZnO/CuO combination. ZnO/CuO has a spherical structure and a consistent size range of 50.79 to 48.59 nm. Due to the increase in surface area, decrease in band gap, and efficient prevention of electronhole recombination, ZnO/CuO exposed a greater degradation rate towards CR dye[40]. Muhammad Tariq Saeed Chani worked on the synthetic pathways of preparation of metaloxides nanopowders of zinc-iron-calcium (Zn-Fe-Ca), zinc-iron-antimony (Zn-Fe-Sb), zinc-iron-titanium (Zn-Fe-Ti) and zinc-iron-cobalt (Zn-Fe-Co). All the mixed-oxides used for acridine orange (AO) degradation in the presence of light where Zn-Fe-Sb degraded the 98 % of acridine orange (AO), within 20 mins under conditions of pH 7, sunlight and 1.0 mg/ml catalyst concentration while the same level of degradation was attained by Zn-Fe-Ti and Zn-Fe-Ca mixed-oxides in 80 min and 90 min, respectively. Zn-Fe-Ca and Zn-Fe-Ti nanoparticles were spherical in shape with 10 ± 5 nm diameter. Zn-Fe-Sb consists of rectangular particles of average size 20 ± 10 nm. The mixed oxides of Zn-Fe-Co consist of 10 ± 3 nm thick and one hundred to two hundred nanometer long flakes type particles. The conversion of organic pigments (pollutants) as CO₂ gas, ammonium, nitrate, and sulphate ions is the basis of the photo-degradation mechanism[41]. Nida Qutub and colleagues investigated modified chemical precipitation-produced cadmium sulphide (CdS) nanoparticles doped using titanium oxide (CdS/TiO₂) nanocomposites for the visible light mediated breakdown of acid blue dye. Although the CdS/TiO₂ degradation rate is 84%, CdS and TiO2 only displayed 68% and 9%, respectively, at 1 hour and 30 minutes under visible light. In comparison to the stated decolorization rates of CdS (4.5×10^{-4} mol L⁻¹ min⁻¹) and TiO₂ (0.6×10^{-4} mol L⁻¹ min⁻¹), it was greater in the context of CdSTiO₂ photocatalyst (5.8×10^{-4} mol L⁻¹ min⁻¹). As a result, in CdS-TiO₂, TiO₂'s optical sensitivity was shifted towards the visible range, making it photo catalytically functional in visible light as well[42]. J.R. Adarsha and colleagues created nanostructured matter calcium ferrite (CaFe2O4) materials by solution combustion technique to facilitate the photocatalytic breakdown of Evans blue dye in the current experimental study. The ferrite composition, that utilised citrous juice extract for its fuel, combined calcium to make the nanoparticles more biocompatible. The greatest absorption was at 220 nm and the bandgap value was 1.92 eV as per the NPs Dispersive reflectance spectra. Large holes and voids were visible on the outermost layer of NPs in the SEM micrograph, which improved adsorption along with photodegradation. The synthesised nanoparticle shape was practically spherical, an average size of 45 nm. The Sips isotherm was the suitable best-fitting model to explain, and the catalyst had an optimal Langmuir removal capacity of 42.4 mgg⁻¹[43].

III. CONCLUSION

Nano catalysts have demonstrated to be very adaptable in a variety of photocatalysis applications. They demonstrate promise in the evolution of H_2 , CO_2 reduction, degradation of antibiotics and pesticides, elimination of heavy metals & for degradation of dyes. For a more

sustainable and environmentally friendly future, additional research and development are required to improve their efficiency, stability, and scalability.

REFERENCES

- [1] Nabgan W, Nabgan B, Ikram M, Jadhav AH, Ali MW, Ul-Hamid A, et al. Synthesis and catalytic properties of calcium oxide obtained from organic ash over a titanium nanocatalyst for biodiesel production from dairy scum. Chemosphere 2022;290:133296. https://doi.org/10.1016/J.CHEMOSPHERE.2021.133296.
- [2] Yogesh Kumar K, Prashanth MK, Parashuram L, Palanivel B, Alharti FA, Jeon BH, et al. Gadolinium sesquisulfide anchored N-doped reduced graphene oxide for sensitive detection and degradation of carbendazim. Chemosphere 2022;296:134030. https://doi.org/10.1016/J.CHEMOSPHERE.2022.134030.
- [3] Nandi A, Pecetta S, Bloom DE. Global antibiotic use during the COVID-19 pandemic: analysis of pharmaceutical sales data from 71 countries, 2020–2022. EClinicalMedicine 2023;57. https://doi.org/10.1016/j.eclinm.2023.101848.
- [4] Hamzad S, Kumar KY, Prashanth MK, Radhika D, Parashuram L, Alharti FA, et al. Boron doped RGO from discharged dry cells decorated Niobium pentoxide for enhanced visible light-induced hydrogen evolution and water decontamination. Surfaces and Interfaces 2023;36. https://doi.org/10.1016/j.surfin.2022.102544.
- [5] Nabgan W, Jalil AA, Nabgan B, Ikram M, Ali MW, Ankit kumar, et al. A state of the art overview of carbon-based composites applications for detecting and eliminating pharmaceuticals containing wastewater. Chemosphere 2022;288:132535. https://doi.org/10.1016/J.CHEMOSPHERE.2021.132535.
- [6] Raghu MS, Parashuram L, Prashanth MK, Kumar KY, Kumar CBP, Alrobei H. Simple in-situ functionalization of polyaniline with boroncarbonitride as potential multipurpose photocatalyst: Generation of hydrogen, organic and inorganic pollutant detoxification. Nano-Structures & Nano-Objects 2021;25:100667. https://doi.org/10.1016/J.NANOSO.2021.100667.
- [7] Kumar KY, Prashanth MK, Shanavaz H, Parashuram L, Alharti FA, Jeon BH, et al. Green and facile synthesis of strontium doped Nb2O5/RGO photocatalyst: Efficacy towards H2 evolution, benzophenone-3 degradation and Cr(VI) reduction. Catal Commun 2023;173. https://doi.org/10.1016/j.catcom.2022.106560.
- [8] Kumar KY, Saini H, Pandiarajan D, Prashanth MK, Parashuram L, Raghu MS. Controllable synthesis of TiO2 chemically bonded graphene for photocatalytic hydrogen evolution and dye degradation. Catal Today 2020;340:170–7. https://doi.org/10.1016/j.cattod.2018.10.042.
- [9] Kumar KY, Saini H, Pandiarajan D, Prashanth MK, Parashuram L, Raghu MS. Controllable synthesis of TiO2 chemically bonded graphene for photocatalytic hydrogen evolution and dye degradation. Catal Today 2020;340:170–7. https://doi.org/10.1016/J.CATTOD.2018.10.042.
- [10] Parashuram L, Prashanth MK, Krishnaiah P, Kumar CBP, Alharti FA, Kumar KY, et al. Nitrogen doped carbon spheres from Tamarindus indica shell decorated with vanadium pentoxide; photoelectrochemical water splitting, photochemical hydrogen evolution & degradation of Bisphenol A. Chemosphere 2022;287:132348. https://doi.org/10.1016/J.CHEMOSPHERE.2021.132348.
- [11] Prashanth KS, Raghu MS, Alharthi FA, Sreenivasa S, Anusuya Devi VS, Krishnaiah P, et al. Solar light sensitive hybrid Ce4+/3+doped perovskite magnesium zirconate nano cubes for photocatalytic hydrogen evolution and organic pollutant degradation in water. J Environ Chem Eng 2021;9:105364. https://doi.org/10.1016/j.jece.2021.105364.
- [12] Yallur BC, Adimule V, nabgan W, Raghu MS, Alharthi FA, Jeon BH, et al. Solar-light-sensitive Zr/Cu-(H2BDC-BPD) metal organic framework for photocatalytic dye degradation and hydrogen evolution. Surfaces and Interfaces 2023;36:102587. https://doi.org/10.1016/J.SURFIN.2022.102587.
- [13] Akshatha S, Sreenivasa S, Parashuram L, Udaya Kumar V, Chakrapani Rao TM, Kumar S, et al. Solvothermal synthesis of nanoscale disc-like gadolinium doped magnesium zirconate for highly efficient photocatalytic degradation of rhodamine B in water. SN Appl Sci 2020;2:1–10. https://doi.org/10.1007/s42452-020-2686-3.
- [14] Akshatha S, Sreenivasa S, Parashuram L, Udaya Kumar V, Sharma SC, Nagabhushana H, et al. Synergistic effect of hybrid Ce3+/Ce4+ doped Bi2O3 nano-sphere photocatalyst for enhanced photocatalytic degradation of alizarin red S dye and its NUV excited photoluminescence studies. J Environ Chem Eng 2019;7:103053. https://doi.org/10.1016/j.jece.2019.103053.
- [15] Alkorbi AS, Kumar KY, Prashanth MK, Parashuram L, Abate A, Alharti FA, et al. Samarium vanadate affixed sulfur self doped g-C3N4 heterojunction; photocatalytic, photoelectrocatalytic hydrogen evolution

and dye degradation. Int J Hydrogen Energy 2022;47:12988–3003. https://doi.org/10.1016/J.IJHYDENE.2022.02.071.

- [16] Rao Akshatha S, Sreenivasa S, Parashuram L, Raghu MS, Yogesh Kumar K, Madhu Chakrapani Rao T. Visible-Light-Induced Photochemical Hydrogen Evolution and Degradation of Crystal Violet Dye by Interwoven Layered MoS2/Wurtzite ZnS Heterostructure Photocatalyst. ChemistrySelect 2020;5:6918–26. https://doi.org/10.1002/slct.202001914.
- [17] Yogesh Kumar K, Parashuram L, Prashanth MK, Pradeep Kumar CB, Alharti FA, Krishnaiah P, et al. N-doped reduced graphene oxide anchored with δTa2O5 for energy and environmental remediation: Efficient light-driven hydrogen evolution and simultaneous degradation of textile dyes. Adv Powder Technol 2021;32:2202–12. https://doi.org/10.1016/J.APT.2021.04.031.
- [18] Alhamzani AG, Yousef TA, Abou-Krisha MM, Kumar KY, Prashanth MK, Parashuram L, et al. Fabrication of layered In2S3/WS2 heterostructure for enhanced and efficient photocatalytic CO2 reduction and various paraben degradation in water. Chemosphere 2023;322:138235. https://doi.org/10.1016/J.CHEMOSPHERE.2023.138235.
- [19] Díaz L, Rodríguez VD, González-Rodríguez M, Rodríguez-Castellón E, Algarra M, Núñez P, et al. M/tio2(m = fe, co, ni, cu, zn) catalysts for photocatalytic hydrogen production under uv and visible light irradiation. Inorg Chem Front 2021;8:3491–500. https://doi.org/10.1039/d0qi01311k.
- [20] Li W, Wang F, Liu X yun, Dang Y yan, Li J yuan, Ma T hao, et al. Promoting body carriers migration of CdS nanocatalyst by N-doping for improved hydrogen production under simulated sunlight irradiation. Appl Catal B Environ 2022;313:121470. https://doi.org/10.1016/j.apcatb.2022.121470.
- [21] Kubovics M, Silva CG, López-Periago AM, Faria JL, Domingo C. Photocatalytic Hydrogen Production Using Porous 3D Graphene-Based Aerogels Supporting Pt/TiO2 Nanoparticles. Gels 2022;8:1–19. https://doi.org/10.3390/gels8110719.
- [22] Jineesh P, Hossain A, Remya R, Sebeelamol JN, Manavalan RK, Ahmed J, et al. Iron-based composite nanomaterials for eco-friendly photocatalytic hydrogen generation. Ceram Int 2022;48:15026–33. https://doi.org/10.1016/j.ceramint.2022.02.031.
- [23] Guo K, Zhu X, Peng L, Fu Y, Ma R, Lu X, et al. Boosting photocatalytic CO2 reduction over a covalent organic framework decorated with ruthenium nanoparticles. Chem Eng J 2021;405:127011. https://doi.org/10.1016/j.cej.2020.127011.
- [24] Nematollahi R, Ghotbi C, Khorasheh F, Larimi A. Ni-Bi co-doped TiO2 as highly visible light response nano-photocatalyst for CO2 photo-reduction in a batch photo-reactor. J CO2 Util 2020;41:101289. https://doi.org/10.1016/j.jcou.2020.101289.
- [25] Mahmoud Idris A, Jiang X, Tan J, Cai Z, Lou X, Wang J, et al. Dye-Sensitized Fe-MOF nanosheets as Visible-Light driven photocatalyst for high efficient photocatalytic CO2 reduction. J Colloid Interface Sci 2022;607:1180–8. https://doi.org/10.1016/j.jcis.2021.09.014.
- [26] Mateo D, Morlanes N, Maity P, Shterk G, Mohammed OF, Gascon J. Efficient Visible-Light Driven Photothermal Conversion of CO2 to Methane by Nickel Nanoparticles Supported on Barium Titanate. Adv Funct Mater 2021;31:1–6. https://doi.org/10.1002/adfm.202008244.
- [27] Mushtaq K, Saeed M, Gul W, Munir M, Firdous A, Yousaf T, et al. Synthesis and characterization of TiO2 via sol-gel method for efficient photocatalytic degradation of antibiotic ofloxacin. Inorg Nano-Metal Chem 2020;50:580–6. https://doi.org/10.1080/24701556.2020.1722695.
- [28] Divyarani K, Sreenivasa S, Rao TMC, Nabgan W, Alharthi FA, Jeon BH, et al. Boosting sulfate radical assisted photocatalytic advanced oxidative degradation of tetracycline via few-layered CoZn@MOF/GO nanosheets. Colloids Surfaces A Physicochem Eng Asp 2023;671:131606. https://doi.org/10.1016/j.colsurfa.2023.131606.
- [29] Xu M, Wang Y, Ha E, Zhang H, Li C. Reduced graphene oxide/Bi4O5Br2 nanocomposite with synergetic effects on improving adsorption and photocatalytic activity for the degradation of antibiotics. Chemosphere 2021;265:129013. https://doi.org/10.1016/j.chemosphere.2020.129013.
- [30] Aghdasi S, Shokri M. Photocatalytic degradation of ciprofloxacin in the presence of synthesized ZnO nanocatalyst: The effect of operational parameters. Iran J Catal 2016;6:481–7.
- [31] Mohamed RM, Ismail AA, Alhaddad M. A novel design of porous Cr2O3@ZnO nanocomposites as highly efficient photocatalyst toward degradation of antibiotics: A case study of ciprofloxacin. Sep Purif Technol 2021;266:118588. https://doi.org/10.1016/j.seppur.2021.118588.
- [32] Zhang W, You Q, Shu J, Wang A, Lin H, Yan X. Photocatalytic degradation of glyphosate using Ce/N codoped TiO2 with oyster shell powder as carrier under the simulated fluorescent lamp. Front Environ Sci 2023;11:1–14. https://doi.org/10.3389/fenvs.2023.1131284.
- [33] Hlophe P V., Dlamini LN. Photocatalytic degradation of diazinon with a 2d/3d nanocomposite of black phosphorous/metal organic framework. Catalysts 2021;11. https://doi.org/10.3390/catal11060679.

- [34] Mohammadzadeh Kakhki R, Ahsani F. Development of a novel and high performance visible-lightinduced Cd3OSO4 nanophotocatalyst for degradation of diazinon. Appl Organomet Chem 2020;34:1–7. https://doi.org/10.1002/aoc.5770.
- [35] Anirudhan TS, Manjusha V, Shainy F. Magnetically retrievable cysteine modified graphene oxide@nickelferrite@titanium dioxide photocatalyst for the effective degradation of chlorpyrifos from aqueous solutions. Environ Technol Innov 2021;23:101633. https://doi.org/10.1016/j.eti.2021.101633.
- [36] Kamaraj M, Srinivasan NR, Assefa G, Adugna AT, Kebede M. Facile development of sunlit ZnO nanoparticles-activated carbon hybrid from pernicious weed as an operative nano-adsorbent for removal of methylene blue and chromium from aqueous solution: Extended application in tannery industrial wastewater. Environ Technol Innov 2020;17:100540. https://doi.org/10.1016/j.eti.2019.100540.
- [37] Wang Q, Li H, Yu X, Jia Y, Chang Y, Gao S. Morphology regulated Bi2WO6 nanoparticles on TiO2 nanotubes by solvothermal Sb3+ doping as effective photocatalysts for wastewater treatment. Electrochim Acta 2020;330:135167. https://doi.org/10.1016/j.electacta.2019.135167.
- [38] Mehwish HM, Rajoka MSR, Xiong Y, Cai H, Aadil RM, Mahmood Q, et al. Green synthesis of a silver nanoparticle using Moringa oleifera seed and its applications for antimicrobial and sun-light mediated photocatalytic water detoxification. J Environ Chem Eng 2021;9:105290. https://doi.org/10.1016/j.jece.2021.105290.
- [39] Paredes MY, Martinez LP, Barja BC, Marchi MC, Herran M, Grinblat G, et al. Efficient method of arsenic removal from water based on photocatalytic oxidation by a plasmonic-magnetic nanosystem. Environ Sci Nano 2022;10:166–77. https://doi.org/10.1039/d2en01082h.
- [40] Hitkari G, Chowdhary P, Kumar V, Singh S, Motghare A. Potential of Copper-Zinc Oxide nanocomposite for photocatalytic degradation of congo red dye. Clean Chem Eng 2022;1:100003. https://doi.org/10.1016/j.clce.2022.100003.
- [41] Chani MTS, Khan SB, Rahman MM, Kamal T, Asiri AM. Sunlight assisted photocatalytic dye degradation using zinc and iron based mixed metal-oxides nanopowders. J King Saud Univ - Sci 2022;34:101841. https://doi.org/10.1016/j.jksus.2022.101841.
- [42] Qutub N, Singh P, Sabir S, Sagadevan S, Oh WC. Enhanced photocatalytic degradation of Acid Blue dye using CdS/TiO2 nanocomposite. Sci Rep 2022;12:1–18. https://doi.org/10.1038/s41598-022-09479-0.
- [43] Adarsha JR, Ravishankar TN, Manjunatha CR, Ramakrishnappa T. Green synthesis of nanostructured calcium ferrite particles and its application to photocatalytic degradation of Evans blue dye. Mater Today Proc 2021;49:777–88. https://doi.org/10.1016/j.matpr.2021.05.293.