Advanced Nano Catalysts for Light-Mediated Environment-Friendly Applications

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**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 toxic compounds such as antibiotics, 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 light-mediated catalytic processes of nano catalysts.

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

**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, Bi2O3 nano-sphere photocatalyst doped with Ce3+ and Ce4+,nanostructured CaFe2O4 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 CO2 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**

A. **Photocatalysts for H2 evolution**

In a study, L. Dáz et al. developed inexpensive M/TiO2 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/TiO2 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 (AQY = 32.41%, at 500 nm). Approximately 3983.4 μmol·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 μmol·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 or rGO, 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 µmolH2h −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-TiO2 complex 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].

B. **Photocatalysts for CO2 reduction**

Ke Guo et al. were excited to create the first Ru/TpPa-1 catalysts for the photodegradation 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 photoreduction activity for CO2 in comparison with TpPa-1, with a maximal HCOOH generation rate of 108.8 108.8 μmol gcat−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 TiO2 framework led to an increase in surface area, a decreased band gap energy, which leads to 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/gcat), 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)]32+ 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 μmol 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±3.8 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 BTO [26].

C. **Photocatalysts 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 TiO2 calcined at 300, 350, 400, and 450°C, respectively, at 295 nm were 91%, 87%, 76%, and 64%. The anatase shape of the TiO2 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 Bi4O5Br2 compared to pure Bi4O5Br2, 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 m2 /g and big pore volume of 0.057 cm3 /g. The study's crucial discovery was that the CIP degradation (100%) could be accomplished in 30 minutes and was 20 times 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].

D. **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 O2. 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 O22- [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].

E. **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 Sb3+ 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/cm2), 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+2 was 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 cm2 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].

F. **Photocatalysts for dye degradation**

Fabrication of Copper-Zinc Oxide nanocomposite via chemical co-precipitation technique, followed by calcination 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 electron-hole recombination, ZnO/CuO exposed a greater degradation rate towards CR dye [40]. Muhammad Tariq Saeed Chani worked on the synthetic pathways of preparation of metal-oxides 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 × 10-4mol 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 × 10-4mol 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 H2, CO2 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.

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