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PHOTOCATALYTIC ASPECT OF NANOMATERIALS: A COMPREHENSIVE REVIEW

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Abstract

Severe environmental threats have surged lately, fuelled by the excessive release of toxic organic pollutants from industries like pesticides, printing, and paint manufacturing. These pollutants pose hazards due to their toxicity, non-biodegradability, and carcinogenic effects, presenting a pressing challenge for their removal before discharge. Scientists are fervently exploring visible photocatalysts that harness solar energy efficiently to address this issue. Research has homed in on synthesizing nanostructures, investigating parameters such as annealing temperature, solution pH, and precursor solvent to understand their structural, morphological, optical, and photocatalytic properties. Evaluations on the nanostructures performance in degrading organic dyes under visible light have been conducted. Semiconductor and transition metal oxides-based nanomaterials, along with rare-earth ion doping, show promise in enhancing photocatalytic efficacy by mitigating charge carrier recombination. Advanced oxidation processes, particularly photocatalysis, offer effective organic compound degradation through reactive oxygen species. Heterojunction semiconductor modification with elements through ion implantation, demonstrates substantial progress in visible region photocatalysis, augmenting charge carrier separation and retarding recombination rates.

Keywords: Photocatalyst, Nanostructure, Organic Dyes, Heterojunction Semiconductor, Doping, Nanotechnology, Degradation.

1. INTRODUCTION

Nanotechnology, being the novel and futuristic technological revolution has a major impact over all the diverse array of fields namely medicine, computer technology, biotechnology, engineering, energy production and storage, material technology, engineering, instrumentation, environmental applications, and protection[1-3]. It is recognized as an enabling technology clubbed with other innovations. It has the ability to affect most other industries in multitude of ways. R.P. Feynman introduced the idea of nanotechnology through his lecture at Caltech on APS meet in 1959[4-5].

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Nanotechnology is a universal fabrication technology considered to be a boon, as it paves the possibility of developing materials with alluring and exceptional properties. Nanofabrication approach namely, bottom-up approach (includes synthesis methods like, precipitation, sol-gel, hydrothermal, chemical vapour deposition, pyrolysis, electro deposition, etc.) and top-down approach (includes laser ablation, high-energy wet ball milling, sputtering, thermal decomposition, etc.)[6-9].

On miniaturization, surface effects and quantum-size effects dominate and nanomaterials exhibit the novel, alluring and unexpected characteristics such as chemical reactivity, strength, electrical conductivity, photocatalytic properties, super magnetic behaviour. Researchers around the world have been able to comprehend the behaviour of nanomaterials with bulk materials since last few decades and now they can regulate the size and type of particles.

Over the past few decades, the dyes pollution (due to discharge from diverse sectors namely, paper, rubber, garment, cosmetics, paint, food, etc.) are alarming for the human health and wildlife[10-11].Toxins dyes have been proven to be poisonous, carcinogenic and xenobiotics in water[12].Photocatalyst are activated through the mechanism of photocatalysis in the presence of light, results in alteration of reaction rate without the involvement of any chemical transformation.

Advanced, successful, technical, and novel water purification processes, for instance, flocculation, ozonation, coagulation, reverse osmosis, and adsorption, advanced oxidation processes (AOPs) are employed to degrade organic compounds[13].

Among several AOPs, photocatalysis is preferred over other technologies due to the complete mineralization of organic pollutants by reactive oxygen species (ROS)[14-16]. These radicals are extremely reactive, short-spanned, easily generated and aids in depletion of hazardous pollutants from water. Basically, the photocatalytic systems rely on the high redox potential of ROS[17].

2. LIGHT IRRADIATION ON SOLIDS

Life on Earth relies heavily on the presence of water, which blankets about three-fourths of the planet's surface. However, only a small fraction, approximately 2.7%, of all water is freshwater suitable for consumption. The bulk of water exists as ice or groundwater, while the rest congregates in lakes and rivers[18].

The quest for clean, sustainable, and renewable energy, as well as environmental remediation, has sparked a surge of research interest in the field of photo catalysis, a strong technique for harnessing sunlight as the major energy source[19-20].

Thorough investigation of photo catalytic technology broadens the potential range of applicability of photocatalysts. Water splitting for H_2 generation, CO_2 reduction into organic fuels, and photocatalytic water treatment, and air purification are all emerging and promising sectors of photo catalysis[21-24]. The advancement in photocatalysis on semiconducting metal oxides and organic polymer materials that operate from UV to

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visible light has been discussed in this chapter. Many physicists observed the impact of UV irradiation on inorganic semiconducting materials such as TiO_2 and ZnO in the early 1960s and discovered the adsorption and/or desorption of various molecules such as O_2 and H_2O. In 1972, Honda and Fujishima published their remarkable work in Nature on the sensitization effect of a TiO_2 and dark Pt electrode for the electrolysis of water to give stoichiometric amounts of H_2 and O_2 [25]. Soon after, a frenetic series of studies took place to explore the field of photocatalysis to produce H_2 fuel due to the 1973 oil crisis. Their publication was in fact responsible for launching what has come to be known as modern heterogeneous photocatalysis, with TiO_2 serving as the factotum among other possible photocatalytic materials. In 1955, Markham described the photocatalytic properties of some metal oxides such as ZnO, Sb_2O_3, and TiO_2, and the different kinds of photochemical changes that these oxides could undergo, under UV irradiation. By the end of 1970s, Bard, and his co-workers at the University of Texas at Austin, among others, worked relentlessly in that direction and in photo-electrochemistry[26-27]. The 1980s saw the start of an exponential growth in photocatalytic studies, with a particular emphasis on the use of nanosized TiO_2 nanoparticles, which resulted in thousands of related publications till now. Redox reactions take place simultaneously in photocatalytic reactions. We require such photocatalysts that can support both oxidation and reduction reactions. Materials are classified into three types based on their electronic properties: conductors, insulators, and semiconductors. In conductors, the valence band and conduction band overlap with each other. The photocatalytic reaction requires simultaneous oxidation and reduction, but in conduction only free electrons are available.

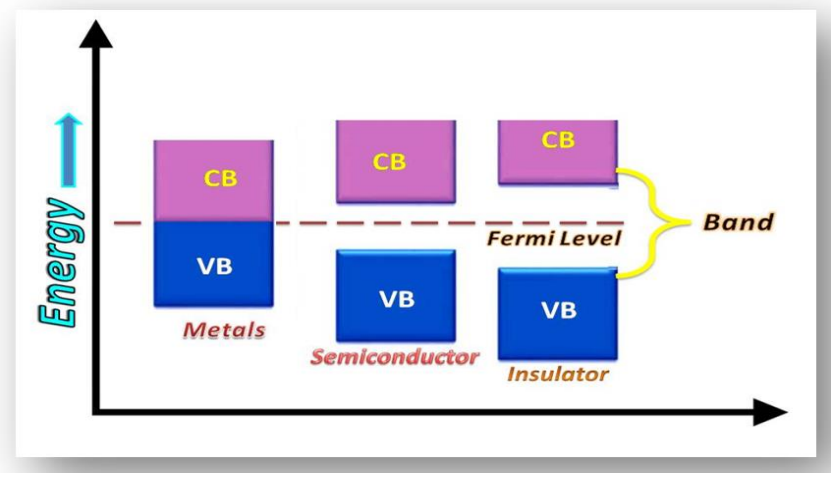

Fig 1: Schematic diagram representing the difference in energy band gap for metal, semiconductors, and insulators

In the case of a conductor, we only perform one oxidation reaction at a time, rather than both reactions at the same time. Alkali, alkaline earth metals, and transition metals are the best examples of conductors. They have no suitable band gap or, often, they overlap in the conduction and valence bands as shown in Fig. 1. They were unsuited for catalytic

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activity in a reaction. The insulators have a large band gap, they require a lot of energy to perform redox reactions. We can't split water molecules with an insulator as a catalyst because it requires too much energy. We require a catalyst that can activate in the visible or ultraviolet ranges. Furthermore, insulators lack free electrons, hence, no oxidation occurs, making them unsuitable for photolytic reactions. All gases in the periodic table, such as halogens and noble gases, and materials such as foam, diamond, and polystyrene are insulators that were incompatible with the photocatalytic reaction.

In semiconductors, a moderate band gap exists, and they have the ability to perform redox reactions simultaneously. When light of sufficient energy strikes a semiconductor material, photogenerated electron hole pairs are created (see Fig. 2). A low recombination rate is required for a semi-conductor material to function as a photocatalyst. Furthermore, semiconductors with absorption in visible range (350–700 nm) of electromagnetic spectrum are preferred for photocatalytic activity. Since, semiconductors have a wide band gap range, hence, a semiconductor to act as a photocatalyst in the UV visible region; we require the energy band gap in the range of 1.5–3.5 eV. Metal oxide is a type of oxide which satisfies both of the former conditions[28-29]. To achieve the desired photo-chemical reaction, an adequate semiconductor, whether organic or inorganic, is simply required. Aside from being cost-effective and environmentally friendly, the viability of a semiconductor for specific applications is primarily dependent on the solar energy conversion efficiency of the nanomaterial.

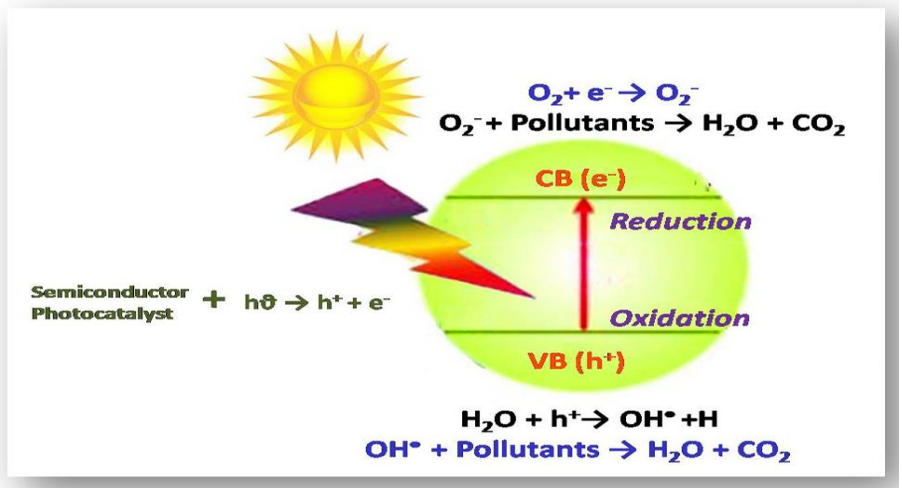

Fig 2: Pictorial representation of photocatalysis mechanism in semiconducting metal oxides

Photocatalysis engages a chemical mechanism in which photons and a catalyst interact, harnessing light and a photoactive substance to initiate or expedite a chemical reaction[30]. When a semiconductor absorbs a photon with energy equal to or greater than its band gap, electrons in the filled valence band (VB) move to the empty conduction band (CB), leaving behind a hole in the VB.

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This process creates electron-hole pairs within the semiconductor. Some of these pairs recombine through heat or radiative processes, while others move towards reaction sites, as depicted in Fig. 3. The electrons and holes in the conduction band (CB) and valence band (VB) diffuse to the catalyst surface and photocatalyst surface, respectively and participate in a redox reaction. During the reaction, the electrons can form H_2O_2 or a superoxide radical O_2 with H^+ and dissolved O_2 in the aqueous solution, and the holes can oxidise OH^- to produce hydroxyl radicals $OH^\bullet$ and thus degrade pollutants into mineralized products[31-32].

Semiconductor + light $\longrightarrow$ **Semiconductor** $(e_{cb}^- + h_{vb}^+)$

Dye + Semiconductor $(h_{vb}^+) \longrightarrow$ **Oxidation Process**

Semiconductor $(h_{vb}^+) + H_2O \longrightarrow$ **Semiconductor** $+ H^+ + OH^-$

Semiconductor $(h_{vb}^+) + OH^- \longrightarrow$ **Semiconductor** $+ \bullet OH$

Dye + Semiconductor $(e_{cb}^-) \longrightarrow$ **Reduction Process**

Semiconductor $(e_{cb}^-) + O_2 \longrightarrow$ **Semiconductor** $+ O_2^{\bullet -}$

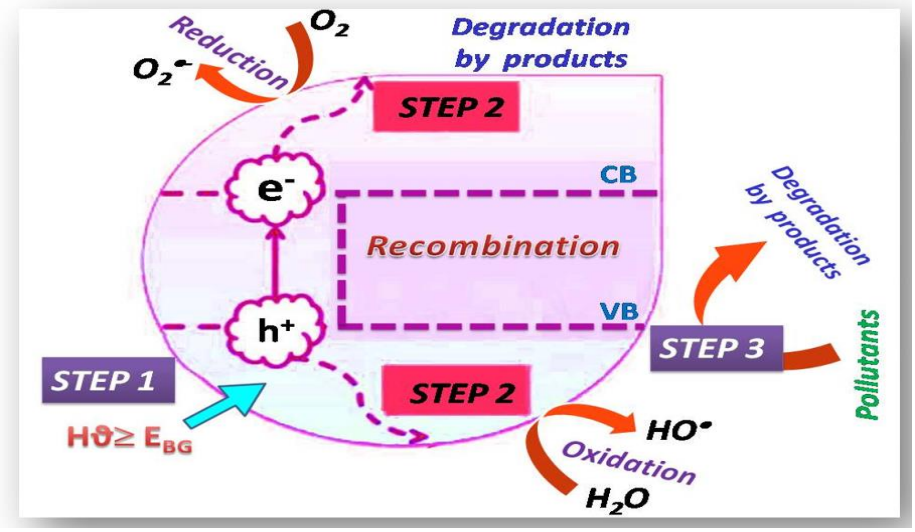

Fig 3: Schematic diagram representing the mechanism of photocatalysis

3. VISION ON METAL OXIDE SEMICONDUCTORS

A large number of nanoscales photocatalysts have already been reported in the literature, and they can be categorised as metal oxides, metal sulphides, metal nitrides, or metal free compounds such as polymers or graphene. In this section, we are primarily interested in metal-oxide materials, which are unquestionably the most researched when it comes to photocatalytic applications. Metal oxides such as TiO_2, ZnO, Fe_2O_3, SnO_2, MgO, SnO_2, Sb_2O_3, V_2O_5, WO_3, CuO, In_2O_3, Nb_2O_5, and perovskites are among the most

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researched materials for photocatalysis today[33-35]. TiO_2 or ZnO had photocatalytic activity as early as the 1970s. This is due to their biocompatibility, remarkable stability under a wide range of conditions, and potential to create charge carriers when incident with the appropriate amount of light energy. Metal oxides serve as photocatalysts because of their favorable blend of electronic structure, light absorption capabilities, charge transport properties, extended the excited lifetimes[36-37].

Metal oxide-based photocatalysts rely on two crucial parameters throughout their operation: the bandgap and the band position of the photocatalyst[38]. The bandgap specifies the energy absorbed by photons and the energy of the photogenerated exciton. For photocatalytic water splitting, metal oxide-based photocatalysts must possess a minimum bandgap of 1.23 eV to align with the redox potentials of the H+/H2 and O2/H2O pairs [refer to Fig. 4]. Additionally, to facilitate smooth electron transfer and subsequent hydrogen production, a larger bandgap (Eg > 2.0 eV) is often necessary[39]. Furthermore, the photocatalyst should have a sufficiently small bandgap to enable efficient utilization of solar energy (Eg < 3.0 eV). Conversely, the band position determines the oxidation and reduction potentials of the photocatalyst. An appropriate conduction-band minimum should be situated at a more negative potential than the NHE to ensure effective photocatalysis[40-41], as illustrated in Fig. 4.

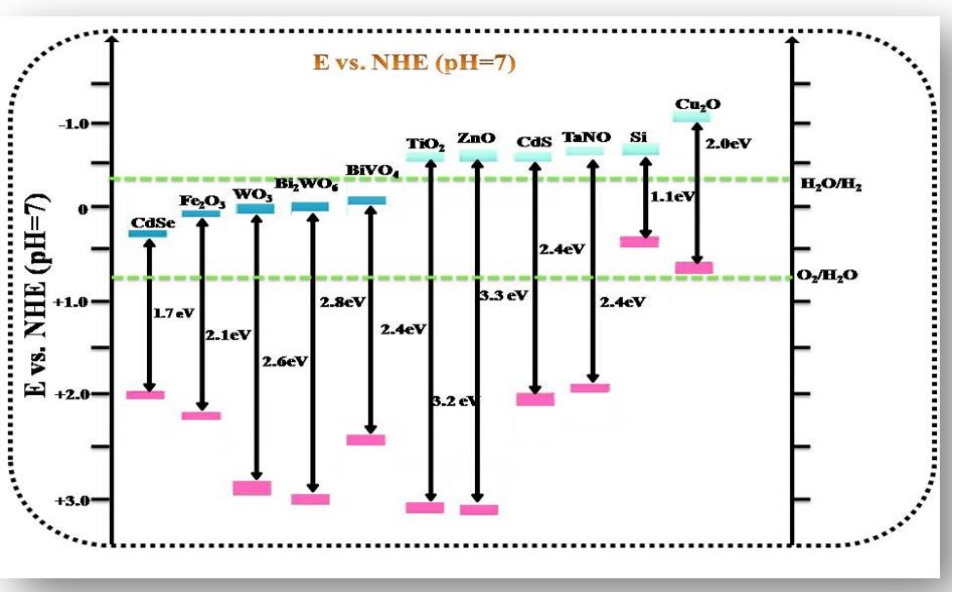

Fig 4: Schematic representation of band gaps and band edge potentials for semiconductor photocatalysts relative to redox potentials of water

Metal oxide-based photocatalysts exhibit varying abilities to undergo photocatalysis under UV light, visible light, or a combination of both, depending on their bandgaps [refer to Fig. 5]. Nevertheless, the photocatalytic efficacy of all nanosized metal oxides is chiefly governed by their physicochemical characteristics, including shape, morphology, surface

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area, composition, and size[42-43]. Consequently, controlled synthetic approaches tailored to their structure and morphology yield specific sets of photocatalytic activity features.

This type of synthesis includes thin film and powder-like forms. The source and type of light employed are important factors in photocatalytic activity[44-45].

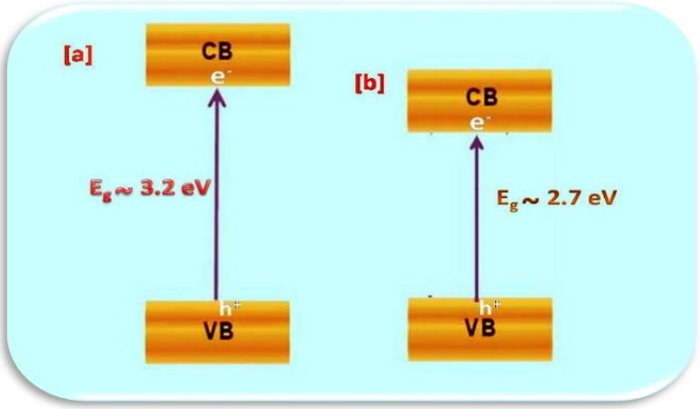

Fig 5: Schematic diagram representing the response of metal oxide to [a] UV light, [b] Visible light

Metal oxides are utilized in a variety of industries and have a wide range of applications due to their unique properties. TiO_2 exhibits a variety of micro as well as nanostructures with excellent properties and fascinating morphologies. TiO_2 has a variety of morphologies, including nanosheets, fibres, nanosheets, nanorods, and spheres[46-49]. TiO_2 catalysts are used in photocatalytic detoxification of the environment, as well as additives in foods and medicines[50-51]. Yet, the photocatalytic potential of pure ZnO and TiO_2 photocatalysts is limited as they solely exhibit activity under UV light owing to their significant band gaps. Various methods have been employed to render these photocatalysts effective within the visible spectrum since visible light constitutes the bulk of the solar spectrum. Energy bandgap of ZnO (~3.3 eV) is approximately near to that of TiO_2 (~3.2 eV). Since ZnO is photo corrosive, it is difficult to use in an aqueous solution under UV irradiation[52-53]. Due to their large surface-to-volume ratio, nanoscale availability, and superparamagnetic properties, iron oxide-based photocatalysts have also been used for the degradation of wastewater[54]. In comparison to TiO_2, WO_3 has a smaller band gap, resulting in better absorption of visible light. WO_3 has several advantages, including large specific surface area, excellent absorbency, and the ability to be used as an invisible material [55-56]. WO_3 has a band gap of 2.8 eV and is stable. It can be used as a primary catalyst as well as a co-catalyst. Copper oxide-based nanostructures exhibit promising behaviour in photocatalytic water splitting, thus, allowing the production of clean H_2 fuel. CuO and Cu_2O, when used separately, increase the rate of electron and hole recombination, making them incapable of splitting H_2O[57-58]. Ghamdi et al used RF magnetron sputtering technique for the fabrication of the nanocrystalline CuO films. Further, the CuO thin film demonstrated remarkable decolourization efficiency for MB

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degradation dye due to the presence of surface defects and oxygen vacancy[59]. CuO NPs can be used to decolorize various dyes depending upon the molecular weights of the dye molecule. The kinetic rate constant shows an increase with increase in molecular weight of the dye molecule[60].

4. TYPES OF PHOTOCATALYSIS

There are several categories into which photocatalysts can be divided according to characteristics like composition, size, diameter, and electrical properties. Xiaogang et al. identified six categories of photocatalysts according to their constituent materials: molecular, plasmonic, quantum dots, traditional semiconductor, 2D, and traditional semiconductor-based photovoltaic-assisted photocatalysts[61]. Serpone et al. and Emeline et al. categorized photocatalysts based on the materials used and time of development, dividing them into first, second, and third generations. They additionally suggested ideas for photoactive materials capable of multi-photon excitation, selective photoexcitation, and heterojunctions [62-63]. Ren et al. and Boyjoo et al. categorized photocatalyst materials into binary and complex metal oxides, metal sulfides, and metal-free materials, organized according to their composition[64-65]. With the proliferation of numerous photocatalytic materials, distinguishing between many materials within a certain group has become increasingly challenging. Depending upon their type and composition, the photocatalysts can be classified in eleven categories as follow: Oxides, Nitrides, Carbon-based material, Halides, II-VI, III-V, Doped metal/non-metal oxides, elemental/metal nanoparticles, molecular organic frameworks, and various complex structures like hybrids/composites, including core-shells and bilayers, have been identified to exhibit improved photocatalytic performance [66-80].

However, this chapter aimed to classify photocatalyst materials into two groups based on the mechanism of their operation: homogeneous or heterogeneous.

4.1 Heterogeneous Photocatalysis

When both the reactants and photocatalysts exist in different phases, then the photocatalysis process involved is known as heterogeneous photocatalysis. Heterogeneous photocatalysis encompasses a wide range of reactions, including dehydrogenation reactions, metal deposition, water detoxification, hydrogen transfer reactions, metal deposition, and water detoxification, gaseous pollutant removal processes, and so on. Wastewater treatment with a heterogeneous photocatalyst is a viable approach due to the abundance of solar light, the method's convenience, and expenditure. It is not possible for a photocatalyst to generate ROS., such as superoxide radicals, hydroxyl ions, hydroxyl radicals, required to degrade contaminants if the band structure is not suitable. Hence, the valence band edge and conduction band edges must be sufficiently positive and negative with respect to the normalised hydrogen electrode (NHE) for a semiconductor to be photo catalytically active (Table 1). ROS have a very brief lifetime, ranging from microseconds-nanoseconds[81-82].

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$$O_2 \longrightarrow {}^1O_2$$

$$O_2 \longrightarrow O_2^{\bullet -}$$

$$O_2^{\bullet -} \xrightarrow{H^+} HO_2^{\bullet}$$

$$O_2^{\bullet -} \xrightarrow{e^- + 2H^+ (+0.94\ V)} H_2O_2$$

$$H_2O_2 \xrightarrow{e^- + H^+ (+0.38\ V)} {}^{\bullet}OH$$

$${}^{\bullet}OH \xrightarrow{e^- + H^+ (+2.33\ V)} H_2O$$

Table 1: Lifetime of ROS generated in the photocatalysis

Name	Formula	Oxidation Potential (V)	Lifetime (s)	Number of e^-
Superoxide anion radical	$O_2^{\bullet -}$	-0.16	10^{-6}	17
Hydroxyl Radical	$^{\bullet}OH$	2.8	10^{-9}	9
Singlet Oxygen	$^1O_2$	2.42	$2 * 10^{-6}$	16
Hydroperoxy Radical	$HO_2^{\bullet}$	1.7	10^{-9}	17
Hydroxyl ions	OH^-	1.30	$70 * 10^{-6}$	10
Ozone	O_3	2.07		24

TiO_2 is the most widely used semiconductor metal oxide nanoscale photocatalyst in heterogeneous photocatalysis. TiO_2 has exceptional photocatalytic efficiency, appropriate band edge values, and stability in extreme conditions as a heterogeneous photocatalyst[83-84]. The advantages of heterogeneous photocatalysis are as follow [85]:

- The primary requirement is the presence of a wide bandgap and oxygen; thus, semiconductor nanoparticles are very popular for photocatalysis, and air can easily fulfil the requirement of oxygen.
- The photocatalysts are renewable, eco-friendly, and economical.
- The reaction occurs at ambient temperature.
- The by-products of photocatalysis are simpler mineralized molecules such as H_2O and CO_2.

4.2 Homogeneous Photocatalysis

When both the reactants and photocatalysts exist in the same phase and uniformly distributed, for example if both can be in the form of gases, then the photocatalysis process involved is known as homogeneous photocatalysis[86]. It is an assembly of soluble catalysts that includes a light-absorption system (photosensitizer), and catalytic sites for redox reactions (solution). Transition-metal complexes are commonly used as homogeneous photocatalysts because they have the required stability and energy band gap[87].

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Ozone and photo-Fenton systems (Fe^{+} and Fe^{+}/H_2O_2) are the most common processes used by homogeneous photocatalysts. These reactions incorporate the formation of $OH^{\bullet}$ by the ozonation process[88].

$$\mathbf{O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet}}$$

$$\mathbf{HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2}$$

$$\mathbf{H_2O_2 + O_2^{\bullet -} \longrightarrow {\bullet}OH + OH^- + O_2}$$

$$\mathbf{Dye + {\bullet}OH \longrightarrow Degradation\ Product}$$

$$\mathbf{Fe^{2+} + H_2O_2 \longrightarrow HO^{\bullet} + Fe^{3+} + H^+}$$

$$\mathbf{Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2^{\bullet} + H^+}$$

$$\mathbf{Fe^{2+} + HO^{\bullet} \longrightarrow Fe^{3+} + OH^-}$$

Homogenous photocatalysts are extremely selective for contaminant degradation and have an excellent photocatalytic activity due to their uniform distribution. Moreover, they are difficult to separate after the reaction is complete, and they have temperature restrictions. To address the shortcomings of homogeneous catalysts, hybrid processes combining both, heterogeneous and homogeneous photocatalysts have been established.

5. METHODS TO ENHANCE PHOTOCATALYTIC ACTIVITY

Semiconductor metal oxides have stimulated the interest of the research and industrial communities for the last five decades as they exhibit high photocatalytic activity and chemical stability, less toxicity, cost-effective and long-term photostability. However, one of their major disadvantages is their inability to perform in the visible range of the solar spectrum.

Photonic efficiency, instead of quantum yield, serves as the prevalent approach for assessing photocatalytic activity. It quantifies the photocatalytic activity of a catalyst in relation to the intensity of radiation flux.

Photonic efficiency (ξ) is calculated as the ratio of the reaction rate to the radiation flux intensity[89-90]. This method is contingent upon diverse reactor setup parameters, enabling solely relative comparisons of photocatalyst efficiencies. The equation utilized for computing photonic efficiency is as follows:

$$\xi = \frac{V\Delta C N_A hc}{\lambda I A \Delta t}$$

In the equation, ΔC represents the change in concentration, NA denotes Avogadro's number, h stands for Planck's constant, c signifies the speed of light, V indicates volume, λ denotes the effective incident wavelength, Δt signifies the change in time measured in seconds, I represents the intensity of light, and A denotes the area of illumination.

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To increase the current photocatalytic performances, the development of new photocatalysts appeared to be a necessity. A lot of research is being done right now to discover new materials and/or improve the properties of existing ones. Numerous approaches have been used over the last few decades to improve the photocatalytic efficiency of semiconductor photocatalysts. While TiO2 and ZnO are acknowledged as innovative photocatalysts, their photoactivity is constrained by their substantial band gaps, elevated charge carrier recombination rate, and limited effective surface area. Consequently, to enhance photocatalytic efficacy, alterations to the electronic band structure, enhancement of charge carrier separation and availability, and surface engineering are favoured[91-92]. Key strategic approaches for augmenting photoactivity include doping, combining with other metals or metal oxides, and sensitization with noble metals.

The most common method for reducing the band gap of photocatalysts is to incorporate or substitute foreign elements or ions into the host nano catalysts i.e. doping. Selective doping (metal/non-metal) of crystalline metal oxides improves light absorption into longer wavelength region of electromagnetic spectrum[93-94]. Ahmad et al. investigated Al-doped ZnO nanoparticles with varying Al concentrations (0.5-6 mol percent) using a simple combustion method. They revealed that the photocatalytic activity of the Al-doped ZnO photocatalyst increased significantly in the decolourization of methyl orange (MO) dye as the Al content dopant increased from 0.5 to 4 mol percent[95]. Meshram et al reported the photo degradation of MB and RhB dyes up to 99.98% and 99.78% using Cu-doped ZnO micro balls photocatalysts within 40 minutes[96].

A wave of anion doped photocatalysts like boron (B), carbon (C), fluorine (F), phosphorus, and sulphur (S) anion-doped visible light active titania-based photocatalysts have all been reported in last few decades[97-100]. In 1986, Sato et al. synthesised the anion-doped titania photocatalyst for the first time and found that NO_x-doped TiO_2 prepared by calcining commercial titanium hydroxide had higher photocatalytic efficiency in the visible region[101]. To overcome the key problems with ZnO, N-ZnO with significant light absorption ability in the visible region has been developed[102]. Wang and his colleagues used an innovative ion implantation method to create a gradient distributed N-ZnO (nanorod arrays) photo anode for photo - electrochemical (PEC) water splitting under visible light[103]. Carbon doping in metal oxide nano catalysts prevents agglomeration during the synthesis process and provides excellent pathways for transferring conduction band electrons to the surface of the photocatalyst[104].

Nanostructured Mg/MgO are used to kill gram-negative and gram-positive bacteria like E. coli and Bacillus megatherium. For advanced oxidation of organic pollutants and chemical oxygen demand (COD) reactions, the synthesis of Cu_2O and TiO_2nanoprobes for electrocatalytic oxidation is a good strategy. Ag and SiO_2 nanostructures were found to be highly destructive against E. coli and Staphylococcus aureus [105]. Defect engineering, such as reducing the amount of photocatalyst to improve the native defect properties, is another approach for enhancing photocatalytic activity and expanding the absorption

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in visible region for the photocatalysis. Earlier, it was reported that defect engineering (i.e., the production of surface oxygen vacancies) increased the charge carrier separation [106-107].

A more innovative approach to tackle the rapid recombination of photogenerated charge carriers in photocatalysts involves coupling two or more metal oxides with distinct energy levels, such as ZnO/SnO_2, TiO_2/WO_3, TiO_2/SnO_2, TiO_2/CdS, TiO_2/ZnO, CdS/TiO_2/WO_3, and TiO_2/WO_3/ZnO.

The combination of binary or ternary metal oxides offers several advantages, including (1) efficient separation of charges, (2) prolonged exciton lifetimes, and (3) accelerated migration of charge carriers to the catalyst's surface. There are four types of heterostructures distinguished by the separation of photoexcited charges and the alignment of conduction band minima and valence band maxima of the constituent semiconductor nanomaterials, where the discontinuity or band-offset occurs.

These are illustrated in Fig. 6 with semiconductors A and B: (i) Type I (straddling gap), (ii) Type II (staggered gap), (iii) Type II (direct Z-scheme), and (iv) Type III (broken gap). The presence of a band-offset leads to a potential barrier at the junction, controlling the movement of electrons and holes. Unlike Type I heterostructures, where photoexcited holes and electrons transfer from one semiconductor to another, Type II heterostructures facilitate the transfer of photoexcited holes and electrons in opposite directions.

The mechanism of charge transfer in Type II heterojunctions can take place via two different pathways, (as shown in the Fig. 6) conventional and direct Z-schemes. Because the redox reactions occur on different semiconductors in Type II heterostructures while the redox reactions occur on a single semiconductor in Type I heterostructures. n Type II heterostructures, the separation of charges and the involvement of charge carriers in a redox reaction are more pronounced compared to Type I heterostructures[108].

The interfacial energy between the linked metal oxides acts as a driving force for the separation and transfer of charge carriers from one metal oxide to another[109-112]. Khiva et al observed that CuO–Cu_2O heterojunction thin films can substantially increase charge collection, decrease recombination rate of photogenerated charge carriers, and improve photocatalytic efficiency[113].

Sajjad et al. observed that for a photocatalyst loading of 1.0g/L and 4.0%WO_x/TiO_2 nanocomposites can completely degrades Acid Orange 7 and Methyl Orange dyes in 240 and 300 minutes, respectively, under visible light irradiation. This composite catalyst outperformed pure TiO_2 by a considerable change in photocatal ytic activity[114].

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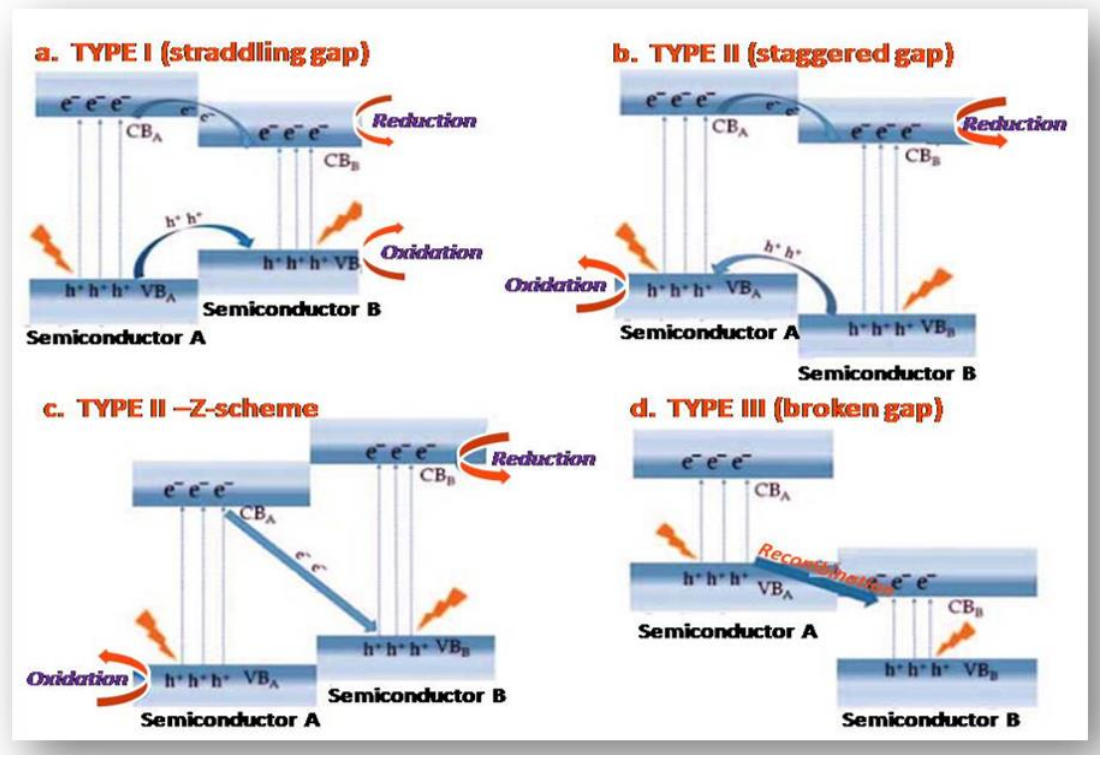

Fig 6: Charge transfer mechanism in different types of semiconductor heterojunction photocatalysts for semiconductor A and semiconductor B: (a) Type-I (straddling gap); (b) Type-II (staggered gap); (c) Type-II (Z-scheme); (d)Type-III (broken)

6. CONCLUSION

In this chapter, we explored the photocatalytic process along with its advantages and diverse applications. Semiconductors possess the capability to oxidize and reduce target pollutants using photogenerated charge carriers when exposed to UV and visible light, presenting a promising approach for mitigating environmental impact. Metal oxides are effective semiconductors in photocatalysis thanks to nano-synthesis. As previously stated, nanoparticles of these semiconductors grow in size, surface area, and stability. The photocatalytic performance of metal oxides is influenced by their morphology and energy bandgap. Among the frequently utilized metal oxides, there are differences in photocatalytic activity and responses to both visible and UV light. This chapter discusses the mechanisms involved in the semiconductor photocatalysts. Heterogeneous photocatalysis has been used to degrade natural volatile organic compounds as well as organic matter in water, air, and soil, in addition to destroying bacteria and viruses. This chapter investigated the effects of various factors that can influence the photocatalytic efficiency in nanomaterials. Increasing the efficiency of the photocatalytic process ensures a sustainable environment, which is necessary for healthy and clean surroundings.

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