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Photocatalysts for Energy and Environmental Sustainability

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Chapter 1

An introduction to photocatalysts and their applications

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This chapter introduces the fundamentals of photocatalysts and their role in the development of sustainable technologies. It explains the basic principles, mechanisms, and workings of photocatalysts for wastewater treatment and hydrogen generation. It also explores the different types of photocatalysts, including their characteristics and features at both the nanoscale and the microscale. The methods of synthesis and the importance of green synthesis compared to other conventional routes are discussed in detail. In addition, this chapter discusses some other important parameters reported in the research literature, such as the reusability and stability of photocatalysts, factors affecting the photocatalytic performance of photocatalysts, and the need for new and advanced strategies to improve the photocatalytic efficiency of photocatalysts for the production of energy and the development of environmentally friendly technology.

1.1 Introduction

In the last few decades, a major worldwide focus has been placed on the development of sustainable technology to protect the environment and maintain the harmony of nature on our mother planet. It is our social responsibility to protect and balance the environment through the development of new and advanced sustainable technologies. Nowadays, there is tremendous growth and strong competition everywhere due to the supply of, and demand for products in the global market due to the vast increase in populations in underdeveloped countries. Thus, to meet the need for low-cost products and the need to recycle cheaper raw materials, many new small- and large-scale industries have been set up to fulfill the global demands for materials and related products. During the recycling of technologically outdated products and devices, many kinds of toxic gases and heavy elements are

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produced and dispersed into the air, water, and soil; these not only affect the quality of the air, water, and soil but also increase their toxicity levels. Thus, among these three sources of pollution, the prevention of air and water pollution are the top priorities, as they impact all living things on our planet. They also have a major impact. In terms of the social and economic development of nations, further increases in pollutant levels in fresh air and water increase the potential risks to people's health and cause many health issues related to respiratory disorders, dermatitis, asthma, mutagenicity, cancer, etc [1]. Photocatalysis is a more promising and sustainable way to resolve to resolve such global environmental issues related to air and water pollution than other techniques. Because it can effectively convert and utilize solar energy, it has received more attention in recent years for its prospective use in photocatalytic wastewater treatment and advanced water splitting processes for the production of H_2, which is considered to be a clean and environmentally friendly source of energy [2, 3]. Basically, a photocatalyst is a material involved in specific chemical reactions that take place under exposure to light radiation, in which it converts the solar energy into other useful forms. For the photocatalytic process, sunlight is the most prominent inexhaustible and clean source of driving energy that leads to slow reaction conditions, high energy of the active species, and a deep oxidation effect during the photocatalytic reaction. This reaction can be caused by the absorption of sunlight in different regions of the spectrum, such as UV, visible light, and infrared radiation; the specific region involved usually depends on the photocatalyst material [4–7]. Thus, the photocatalytic process has the ability to resolve the problems related to the environment and energy without the utilization of excessive fossil fuels. Photocatalysts are capable and operate well under natural sunlight, but more effort is needed for the development of highly efficient visible-light-driven photocatalyst materials [8]. Khan *et al* [9] reported that research and development into the photocatalytic process exhibits a broad scope for widespread application in the near future. However, a few parameters of photocatalytic materials, such as their efficiency, thermal stability, purity, environmental compatibility, and low efficiency in photocatalytic reactors, are major hurdles that restrict their application at scale. In recent years, inorganic bandgap semiconductors such as ZnO, CdS, ZnS, ZnSe, CdSe, ZnTe, etc. have been widely studied for the photocatalytic process due to their unique chemical properties and high stability [10–13]. Among these, zinc oxide (ZnO) is the most favorable, environmentally friendly, and economically viable for large-scale wastewater treatment. In the following section, we discuss the details, principles, and working mechanisms of the photocatalytic materials and their types that are proposed for the advanced water treatment and hydrogen generation processes.

1.2 The principles and mechanism of photocatalysis

The photocatalytic process is based on the absorption of light by the photocatalyst, for which metal-oxide semiconductors are preferable because of their suitability for the formation of electron–hole pair creation in the conduction band (CB) and the valence band (VB) [14]. Thus, during the absorption of light, electrons in the VB are

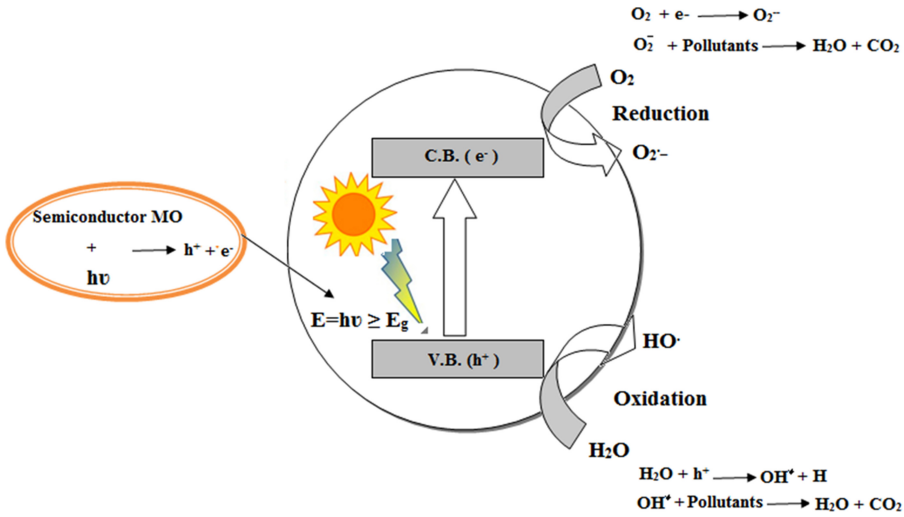

Figure 1.1. The photocatalytic mechanism under solar illumination.

excited into the CB where they form electron (e^-) and hole (h^+) pairs. There are two photochemical reactions that involve the photoinduced electrons and holes, which are continuously generated. A schematic of the photocatalytic process and its mechanism of pollutant degradation under solar illumination are shown in figure 1.1. In general, photocatalytic materials play a major role in initiating the oxidation and reduction reactions in the presence of solar energy. The following steps are followed during the photocatalytic process:

Step **I. The g**eneration of hole/electron pairs
Step **II.** The separation of charge carriers and their diffusion towards the electrode surface
Step **III.** Photooxidation and -reduction reactions take place at the surface of the photocatalyst.

Here, photoinduced holes and electrons react with O_2 and H_2O on the photocatalyst's surface, which leads to the formation of O^{-2} and $OH^{\bullet}$ radicals. These radicals have strong redox potentials, and hence, when they react with pollutants, photodegradation takes place. A possible photocatalysis reaction is shown in figure 1.1.

When active species are adsorbed by the photocatalyst's surface, the electron transfer process becomes more prominent [15]. Further, during the water cleaning process, oxygen acts as a common electron acceptor. When photogenerated electrons react with oxygen, they reduce to $O^-{}_2$ and can be transformed into various oxygen-activated species, such as $HO^{\bullet}$, H_2O_2, $HO_2^{\bullet}$ and HO_2 anions [16, 17], which involve the oxidation of the electron donor [18], while the generated holes can oxidize the electron donor. At the same time, reactive oxidizing species and free

carriers react with absorbed surface impurities, and the degradation of pollutants takes place. The efficiency of the photocatalysis process depends on the ability of the photocatalyst to produce a large number of holes and electrons, which results in the production of reactive free radicals. A shift in the light absorption range of the photocatalyst into the visible spectral range helps to generate a large number of electron–hole pairs, thereby improving the degradation response of the photocatalyst [19]. Hence, the absorption range plays a key role for highly active photocatalysts.

1.2.1 Types of photocatalyst

As compared to conventional water treatment processes, advanced oxidation processes are assigned great importance due to their stronger oxidation capabilities, faster reaction times, and production of smaller amounts of secondary pollutants. These processes are generally categorized into homogeneous and heterogeneous processes, depending on the type of reaction medium. Further, they can be classified into energy- and non-energy-related categories [20]. The abovementioned heterogeneous photocatalytic oxidation technique is widely accepted for the degradation of pollutants in wastewater [21]. This technique has some advantages, such as flexibility, simplicity, low cost, the use of an environmentally friendly catalyst, and high photocatalytic efficiency. In the recent years, many new types of photocatalysts have been proposed and used for the removal of organic pollutants from wastewater [22, 23], Some of these are discussed below.

1.2.1.1 Homojunction semiconductor photocatalysts

Homojunction semiconductor photocatalysts are synthesized by incorporating semiconductor interfaces that have compatible bandgap energies and chemical compositions and specific dimensions [24]. They also possess particular physical, electrical, and optical properties and exhibit superior photocatalytic activities for the photodegradation of waterborne organic pollutants [25]. Nanoscale photocatalytic devices have been fabricated by using homojunction photocatalysts and are applicable in various disciplines [26, 27]. Further, homojunction photocatalysts help to improve photocatalytic efficiency in the production of hydrogen via the water splitting process [28]. But the use of semiconductors for photocatalytic applications has some limitations.

1.2.1.2 Hetrojunction semiconductor photocatalysts

Heterogeneous semiconductor photocatalysis is another type of advanced oxidation process that has received great attention due to its prospective use in resolving energy and environmental issues by, for example, generating hydrogen through the water splitting process and degrading organic pollutants through redox reactions [29]. Semiconductor heterojunctions are constructed by combining two semiconductors, and they have been demonstrated to be one of the most efficient ways to spatially separate photoexcited electron–hole (e^-/h^+) pairs [30, 31]. When a heterojunction photocatalyst is illuminated by a light source, photoexcited charge carriers

are forced to move between the two semiconductors, building up an electric field and hence inhibiting the recombination of the charge carriers. The formation of a built-in electric field at the semiconductor heterojunction interface and the transfer rate of a photoexcited charge carrier depend on the semiconductivity of the materials, the work function, and the ratio of the CB to VB potentials of the semiconductors.

1.2.2 Single-atom photocatalysts

Single-atom photocatalysts (SACs) are considered to be low-cost, high-efficiency photocatalysts and have been assigned more importance in the field of catalysis [32]. Qiao *et al* [33] were the first to report the concept of 'single-atom catalysis' [34]. SACs have been synthesized by loading a single metal atom onto a suitable support; further electrons are exchanged with the support to form single-atom active sites, enhancing the photocatalytic performance of the material [35]. Due to continuous research into, and development of the preparation of SACs, many preparation techniques have come into existence. Thus, the flexible pairing of metal centers and charge carriers facilitates the preparation of environmentally friendly and sustainable single-atom photocatalysts with high catalytic efficiency [36, 37]. SACs are also used to produce both homogeneous and heterogeneous catalysts [38, 39]. The absorption range and charge separation efficiency of SACs are high [40]. As a result of these characteristics, SACs are emerging materials in the photocatalytic field for the evolution of photocatalytic H_2 and the removal of toxic contaminants from wastewater [41, 42].

1.2.3 Quantum-dot-based photocatalysts

Quantum dot (QD)-based composite catalysts are considered to be promising candidates for resolving issues related to energy and environmental sustainability. QDs are zero-dimensional spherical nanoparticles, and their physical dimension is smaller than the exciton's Bohr radius [43, 44]. Colloidal semiconductor nanocrystal QDs 2–10 nm in size may contain 10–50 atoms within their volume [45]. Recently, Kandi *et al* [46] discussed the scope and advantages of quantum dots in the photocatalytic hydrogen production process. There are some characteristics of QDs that make them suitable for enhanced H_2 production compared to other types of nanostructured materials with superior properties; these characteristics play a significant role in enhancing photocatalytic activity. Some of the important properties of QDs are given below:

(i) The capability to absorb light in the visible spectral range
(ii) A better multiple-exciton generation rate under solar illumination due to the quantum confinement effect.
(iii) Better charge transport and separation characteristics.
(iv) Size-dependent tuneable optical properties.
(v) Their visible-light absorption edge can be enhanced by doping them with wide-bandgap semiconductors.

At present, many research groups are working on the development of highly efficient QDs based on hybrid systems that have the above characteristics and properties and are applicable for effective photocatalysis.

1.2.4 Perovskite-based photocatalysts

Perovskite-structured materials represented by the chemical formula ABX_3 belong to a ternary family of crystalline structures in which the A-site contains metal cations, rare earth ions, or alkaline earth metal ions with larger ionic radii and the B-site contains transition-metal ions with smaller ionic radii, while X indicates the oxygen atoms available in the host structure. Perovskite-structured materials exhibit many interesting properties; further, perovskite nanomaterials show excellent photocatalytic efficiency due to their characteristics such as superior chemical and thermal stability, nontoxicity, cost-effectiveness, tuneable properties, adjustable bandgap, large charge carrier lifetime, etc [47]. The shape- and size-dependent properties of a perovskite nanostructure depend on the method of synthesis and its structural characteristics. Today, perovskite nanoparticles have the potential to be used in a variety of applications, such as chemical sensing, catalysis, water splitting, and the photodegradation of organic pollutants. But single-component perovskite materials have a broader bandgap, and hence recombination of the charge carrier takes place much faster, which restricts their performance in visible-light-driven photocatalysis. For effective photocatalysis under solar illumination, strong absorption near 520 nm is needed. Further challenges still remain, such as resolving the problems of the separation and recycling of perovskite materials in treated water. To overcome these challenges, further research activity and strategies, such as modification of their surface, doping with metal ions, coupling with metal nanoparticles, the synthesis of nanocomposites, etc. [48], are required to improve the photocatalytic performance of these materials.

1.2.5 S-scheme photocatalysts

S-scheme heterojunction photocatalysts exhibit characteristics such as a superior light absorption ability, a high charge carrier separation efficiency, a strong redox potential, and a diverse range of both inorganic and organic semiconductors. Considering the related advantages and disadvantages of conventional heterojunction photocatalysts, the step-scheme (S-scheme) is a novel semiconductor catalyst that fulfills the current need for efficient photocatalysts [49]. Here, the heterojunction is formed by contact between two different semiconductors, which helps to increase the absorption band edge of the semiconductors, further improving the separation and migration rate of the photogenerated carriers [50]. As a result of the close contact between the different semiconductors, the electrons from the reduced semiconductor spontaneously migrate toward the oxidized semiconductor and build an electric field that is directed toward the oxidized semiconductor. At the same time, the holes in the VB of the reduced semiconductor and the electrons in the CB of the oxidized semiconductor combine, which results in the accumulation of a

greater number of negatively charged carriers (i.e. electrons) in the CB of the reduced semiconductor and a greater number of positively charged carriers (i.e. holes) in the VB of the oxidized semiconductor. Thus, the S-scheme heterojunction photocatalyst shows strong redox capacity [51] and has a wide range of potential applications. S-scheme heterojunction photocatalysts can be categorized as inorganic–inorganic [52], inorganic–organic [53], or organic-organic composites [54]. The inorganic–inorganic types of S-scheme heterojunction photocatalysts are of great interest for the photocatalysis process.

1.2.6 rGO-based composite photocatalysts

Graphene is a zero-bandgap material, which restricts its applications, particularly in the electronics field. Therefore, doping graphene with heteroatoms can form a number of localized energy levels in its bandgap, and hence it can exhibit tuneable properties that make it responsive in visible light. However, there are some restrictions on the use of GO, such as its toxicity and corrosiveness, the explosive nature of the reducing agents, etc [55]. However, reduced graphene oxide (rGO) also exhibits excellent properties such as tunable electrical properties, transparency, and the ability to integrate with various photoactive surfaces to enhance their efficiencies. Further, it has good electrical conductivity and a large surface area and is a better substitute for pure graphene which can be synthesized at low production costs using a simple reduction process [56]. Thus, it makes rGO a desirable candidate for solar-driven photocatalytic applications. Coupling rGO with oxide materials promotes electron separation, boosting their photodriven activity in the visible spectral region and promoting the degradation of some harmful dyes. Thus, 0D, 1D, and 2D nanostructured semiconductors coupled with rGO nanocomposites play an important role in improving photocatalytic activity, hydrogen generation, nitroaromatic reduction, etc. In the case of semiconductor composites, coupling the semiconductor with rGO helps to separate the photogenerated charge carriers at the catalyst/RGO interface. Here, the nature of the semiconductor/rGO interface and defects in the rGO play an important role in enhancing the photocatalytic activity. Recently, Witjaksono *et al* synthesized and reported visible-light-driven N-doped rGO with reduced bandgap energy, i.e. from 3.4 to 2.2 eV [57]. This material reduced the electron–hole pair recombination rate by exhibiting the characteristics and features of a visible-light-driven photocatalyst [58]. Similarly, ferrite-based rGO nanostructures are magnetic materials and have good absorption in the visible spectral range. Further, they are strongly responsive to applied magnetic fields and can be readily recovered using conventional magnetic bars [59]. Today, rGO is one of the benchmark materials for improving the performance of some advanced materials used in the development of sustainable technology [59]. Recyclability and recovery are also important aspects of the development of new photocatalyst materials. Researchers have made many efforts to resolve current issues and future challenges in these fields.

1.2.7 Semiconductor photocatalysts

Semiconductor photocatalysts contain different materials such as metal oxides, nitrides, or sulfides (e.g. TiO_2 and MoS_2) [60, 61] as well as metal-free semiconductors such as C_3N_4. Other materials, such as copper, gold, and silver metal nanoparticles, exhibit strong localized surface plasmon resonance (LSPR) properties under visible-light irradiation. These nanoparticles were assigned great importance at the beginning of 21st century, but they have higher costs, which restricts their wider industrial scope. However, semiconductor photocatalysts are comparatively lower in cost and have been a topic of research for more than 50 years, but they suffer from the issue of a low absorption band in visible light and hence lower degradation efficiency. Based on some characteristics, features, and innovative approaches, they are considered promising materials for use in industrial applications at enhanced photocatalytic efficiencies. Semiconducting nanomaterial-based photocatalysts such as ZnO, CdS, ZnS, ZnSe, CdSe, ZnTe, etc. have been studied many times in the last few decades, and they are widely accepted due to their unique properties and good stability, which also promote strong redox reactions [10, 11]. ZnO is the most favorable, environmentally friendly, and economical catalyst for the large-scale treatment of wastewater due to its direct bandgap energy, which is of the order of 3.37 eV. It also seems to have an excellent degradation response under UV light illumination. The available wavelength spectrum of solar radiation contains only 4% of UV light but 43% of the visible-light component. To shift the response of ZnO under visible light, there is a need to alter the optical properties of ZnO by adding a narrow energy gap semiconductor, which improves its absorption capacity in visible light and also reduces the e^-/h^+ recombination rate [62]. ZnSe/ZnO is a well-known example of a composite catalyst, in which ZnO is combined with ZnSe, which acts as a narrower-bandgap semiconductor (2.67 eV). The bandgap of ZnSe is well aligned with that of ZnO, hence, it improves the photocatalytic degradation efficiency of ZnO [63]. However, much more investigation is still needed to explore the future prospects of advanced semiconductor materials to fully meet the needs of energy and environmental sustainability.

1.3 Synthesis methods

1.3.1 Chemical methods

In recent years, many conventional methods have been used to prepare nanostructures of different dimensions [64]. Thus, the top-down and bottom-up approaches are popular methods for the preparation of oxides and other forms of materials. The bottom-up approach is well suited for the fabrication of defect-free nanostructured materials of specific shapes and sizes. Some of the techniques, such as combustion, the hydrothermal method, the solvothermal method, the sonochemical method, the sol–gel method, etc. fall into the category of bottom-up approaches, as shown in figure 1.2. These are well-known methods used in materials synthesis. Among these techniques, great importance it attached to the green synthesis route, which involves the use of nonacid mediums as well as nontoxic materials for the

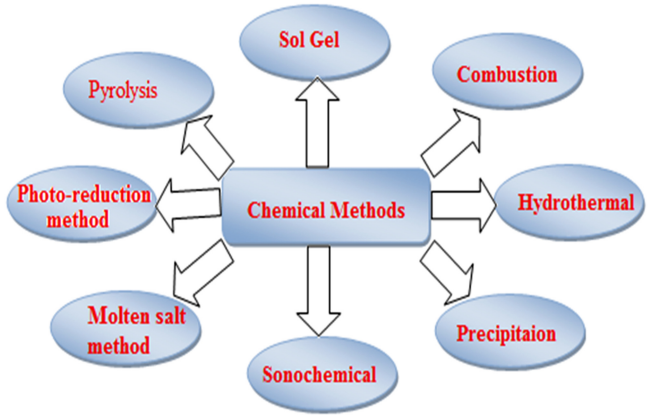

Figure 1.2. Chemical methods used for the synthesis of materials.

preparation of materials [64, 65]. Thus, the chemical approach is well suited for the preparation of inorganic nanostructured photocatalytic materials because of its ability to produce materials in the desired shape and size, and the methods used in the bottom-up approach are also cheaper than those of the top-down approach. But there is always a need to take care in the selection of nontoxic raw materials and the formation of the final pure-phase product while avoiding the presence of the acid medium, impurities, etc. High-temperature solid-state diffusion is also a well-known technique that corresponds to the top-down approach used to prepare perovskite oxide nanostructures, but this technique leads to the formation of an impure phase that contains inhomogeneous perovskite oxide nanomaterials due to repeatedly grinding, crushing, and preheating them before calcination. This leaves some defects on the surface of the nanostructured materials, and the presence of such defects may affect the properties of the nanostructured materials. In contrast, using the sol–gel method, the coprecipitation method, or the combustion method, it is possible to obtain pure perovskite oxide nanomaterials with a high surface area and an ideal nanostructure size. These are the simplest and most efficient techniques with which perovskite oxide materials are synthesized. Hydrothermal methods are also well-known synthesis techniques that allow the nanostructure's shape and size to be controlled. However, these techniques require precursors that readily mix well in aqueous solution at high temperature and constant pressure [66]. Therefore, the hydrothermal method is an important branch of inorganic synthesis that depends on the solubility of material in hot water under high pressure [67]. During the hydrothermal reaction, parameters such as the type of solvent, temperature, and time of reaction play an important role; in such reactions, nucleation and grain mechanisms form nanosized crystallites.

1.3.2 Green synthesis

Today, green synthesis is an environment-friendly technique for the preparation of nontoxic metal-oxide nanoparticles and has received great interest in the field of

nanotechnology. During the synthesis of nanomaterials by chemical methods, some toxic gases are liberated during chemical reactions, and the harmful chemical species present are also adsorbed on the surfaces of nanoparticles. Thus, considering this drawback, green synthesis is an emerging technique for the production of NPs. Further, this method is clean, safe, and a cost-effective way to deploy environmentally friendly processes [68]. It is possible to synthesize nanoparticles of different shapes and sizes using this technique. The use of different fuels or reducing agents also plays an important role in obtaining the pure phase and the desired nanostructure morphology [69].

1.4 The reusability and stability of photocatalysts

Efficiency and reusability are two basic parameters that play an important role in the practical use of photocatalysts. They can be recycled at least five times, and the photocatalytic materials must remain stable during this process. The recovery of the materials can be carried out through the centrifugation technique after each cycle. The separated materials are then rinsed more than two times with deionized water. Later, the recovered materials are reused in the photocatalytic dye degradation process. Metal-oxide nanostructures such as acid protease functionalized silver nanoparticles (APTs–AgNPs) exhibit excellent catalytic performance that removes up to 95% of methylene blue (MB) dye from wastewater, and the reuse of the materials does not significantly alter their efficiency after each run. Hence, they can be reused more often with a minimal reduction in their efficiencies. But there is a need for more research to resolve the issues of the maintenance of effective photocatalysis and NP reusability associated with structural effects such as the porosity and surface area of metal oxides [70]. $NaYF_4$:(Gd, 1% Si)/TiO_2 is another well-known metal-oxide-coupled phosphor composite photocatalyst; it can be reused and is stable for up to three cycles, but the degradation efficiency of this material decreases from 95% to 60% and 40% in the 2nd and 3rd cycles, respectively. However, $NaYF_4$: (Gd, Si)/TiO_2 composites can be considered to be low-cost and efficient photocatalysts for the removal of pollutants from wastewater [71].

1.5 Factors affecting photocatalytic activity

1.5.1 The bandgap

In recent decades, wide-bandgap semiconductor photocatalysts have been assigned more importance due to their use in environmentally friendly wastewater treatment processes. Among the different types of oxides, ZnO and TiO_2 are the most promising materials; they have been studied many times because of their characteristics, such as high chemical stability, low cost, and nontoxic nature [72–74]. However, due to their large bandgap, these types of large-bandgap semiconductors can absorb only light in the UV region and are unable to absorb visible light. They also have a fast recombination rate of photogenerated electron–hole pairs that restricts the effective degradation of pollutants [75]. These issues related to semiconductor photocatalysts could be resolved if their light absorption range in the UV region could be easily extended to the visible region by tuning their bandgap; this

might be made possible by adding some impurities to their structure or by adopting some new methods of synthesis [76]. In general, semiconductor photocatalysts bandgaps that fall between 1.23 and 3 eV include the oxidation and reduction potential ranges of H_2O. The redox potentials of the photocatalytic water splitting process correspond to $EH^+/H_2 = -4.44$ eV and $EO_2/H_2O = -5.67$ eV, respectively [77]; the difference between these is 1.23 eV, which is therefore the minimum bandgap that must be present for a material to be considered an effective photocatalyst. Fujishima and Honda reported water splitting by the photocatalytic approach; they studied both large- and narrow-bandgap semiconductor materials theoretically and experimentally [78, 79]. Semiconductor materials with a large bandgap (greater than 3 eV) have band edge positions suitable for the overall water splitting and hydrogen evolution processes, but their light absorption range is not compatible with the visible spectrum. Thus, there is a need for more efforts to search out new materials or design innovative materials with a broad absorption range that covers the full spectral component of visible light.

1.5.2 Particle size

The shape, size, and morphology of a material can affect its photocatalytic properties. Consider the bandgaps of bulk materials: the atomic orbitals overlap, producing bands with a small energy gap as compared to those of nanomaterials. However, in nanoscale metals, the orbitals are discontinuous; they rather form discrete energy levels in the band structure, which can be tuned by changing the nanoparticle diameter, as shown in figure 1.3. Hence, as the particle size decreases, the electrons become more confined in the particle, and confined electrons have more energy. Thus, the atomic orbitals of nanoparticles become discrete or quantized. The presence of the quantum confinement effect in nanomaterials leads to tunable electrical and optical properties.

Therefore, the bandgaps of bulk and nanostructured materials are different, and changes in particle size affect the bandgap energy, the light absorption capacity, and

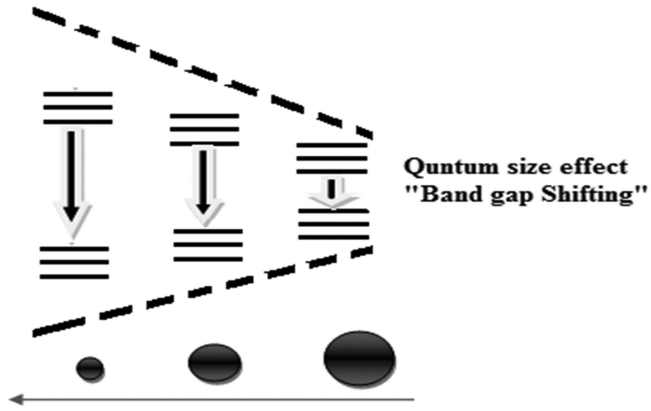

Figure 1.3. The effect of particle size on the bandgap.

the average free range of photogenerated charge carriers in the material. When the particle size of the material is smaller than the thickness of its space charge layer, which is negligible, then photogenerated charge carriers migrate from the bulk phase to the material's surface via the diffusion process and take part in surface redox reactions. The charge transfer rate of carriers and their separation efficiency can be improved by reducing the charge migration distance [80]. Therefore, small particles usually have a high specific area and show better adsorption properties that help to initiate the interaction between the catalyst and the reactants. Small particles thereby provide abundant active sites and a large light absorption area that hosts redox reactions and hence improves the photocatalytic performance [81].

1.5.3 Doping

Doping elements into a different host material is the most common strategy for improving the performance of metal-oxide semiconductors [82–85]. It can affect many parameters, such as the morphology, particle size, bandgap, binding energy, lattice defects, and other associated properties [86, 87]. For example, if the average particle size of pure SnO_2 particles is 52.3 nm, then the addition of Ag results in a reduction in the particle size of SnO_2; the new particle size may turn out to be 45.5 nm [88]. Further, Yakout *et al* [88] reported that the use of Co doping in an Ag/SnO_2 system was not effective in reducing the particle size. But the addition of higher amounts of dopants may affect the particle size, which may also result in a more uniform grain size distribution. Entradas *et al* also reported [89] that the particle size distribution was narrower when the amount of Co codoping was increased. This created agglomeration clusters of particles in pure SnO_2 due to the presence of the dopants [90].

1.6 Strategies for boosting photocatalytic efficiency

In the last few years, many researchers have made concerted efforts to design and develop new energy-efficient photocatalysts which are better at harvesting the maximum component of the solar spectrum, generating large numbers of charge carriers, and providing catalytic sites to support effective photocatalytic process [91]. To resolve the issues related to metal-oxide photocatalysts, various strategies have been proposed in the research literature to boost the photocatalytic efficiency of catalysts; some of these are discussed below.

1.6.1 Spatial separation of excitons

As discussed above, the photocatalytic efficiency of catalysts greatly depends on the separation rate of electron/hole pairs. In order to generate photoinduced charge carriers, a photocatalyst must be adequately excited by the incident photon flux energy. These positive and negative charge carriers can take femtoseconds (fs) to picoseconds (ps); they also subsequently take time to transit the surface of the photocatalyst (nanoseconds (ns) to microseconds (μs)) to reach the corresponding bands to initiate the redox reactions [92]. During the transit of charge carriers in the catalyst, there is a high probability of e−/h+ recombination that can release heat.

The recombination of e−/h+ pairs occurs within picoseconds to nanoseconds, which is much faster than their transfer rate to the surface of the catalyst (where they participate in oxidation and reduction reactions) [93]. Thus, to reduce the recombination rate, there is a need to develop new strategies to boost the separation of charge carriers and enhance the efficiency of photocatalysts.

1.6.1.1 The loading of cocatalysts

The loading of a cocatalyst improves the separation and transfer of excitons in the photocatalytic process, which helps to promote and stabilize the activity of the photocatalyst. Under light illumination, the photogenerated negative charge carriers in the CB of the catalyst are transferred toward the cocatalyst, which prevents the recombination of charge carriers in the VB [94]. Therefore, contact between the catalyst and the cocatalyst is essential for the transportation of charge carriers. When the charges reach the catalyst interface, the cocatalyst helps to improve the separation of charge carriers. When metallic cocatalysts are deposited on the surface of photocatalysts, they form a Schottky heterojunction that restricts the backward flow of electrons to the CB and thereby induces an electric field that enhances the separation of charge carriers, thereby promoting effective photocatalytic activity [95]. Semiconductor cocatalysts with narrow bandgaps also form heterostructures that improve charge separation. Similarly, cocatalysts consisting of transition-metal dichalcogenides have also exhibited better separation of electrons and holes because of their unique metallic and semiconductor structures. Among the different types of cocatalyst metals, cocatalysts such as Ag and Pt are excellent candidates for enhancing the photocatalytic efficiency of photocatalysts [96]. Recently, Sun *et al* [97] reported the photocatalytic response of CoP-loaded QDs as cocatalysts on CdS nanorods, confirming enhanced H_2 production under visible-light illumination.

1.6.1.2 Metal-oxide–coupled composites and their photocatalytic response

García *et al* [98] reported the photocatalytic performance of Bi codoped strontium aluminates blended with nanocrystalline TiO2. Here, small grains of TiO2 were made available on the surface of the strontium aluminate grains. With an increase in the surface area of the composite grains, an enhancement in photocatalytic activity was achieved. Figure 1.4 shows the photocatalytic degradation of MB achieved using the blended composite catalyst under UV light illumination. It can be seen that complete degradation of MB occurred after 210 min of UV exposure. Thus, the composite TiO_2–Bi codoped sample degraded 91.0% of the MB dye after 210 min of exposure time. Figure 1.4 shows that lower concentrations of Bi codoping in TiO_2–strontium aluminate composites exhibit a rapid photocatalytic degradation response as compared to pure TiO_2 powder.

1.6.1.3 Persistent phosphors and their photocatalytic response

Wang *et al* [99] reported the photocatalytic response of persistent phosphor used for the degradation of RhB. Figure 1.5 shows the persistent luminescence spectra of Zn^{2+} and Cr^{3+} codoped Ga_2O_3 phosphor. The photoluminescent excitation and emission spectra of the phosphor were observed in the UV–visible spectral range. When the

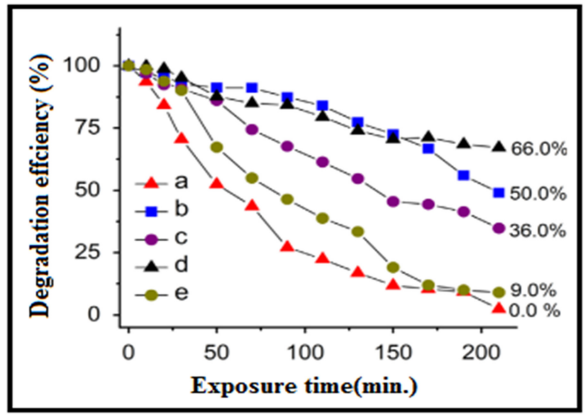

Figure 1.4. Photocatalytic degradation of MB as a function of exposure time under UV light illumination. The photodegradation responses of TiO_2–$Bi_{(2.0 \text{ and } 0.0 \text{ mol\%})}$ codoped strontium aluminate composites are shown in curves (a) and (b), and the response of pure TiO_2 is shown in curve (c); the responses of the TiO_2–$Bi_{(15.0 \text{ and } 1.0 \text{ mol\%})}$ codoped strontium aluminate composites are shown in curves (d) and (e), respectively. Reprinted from [98], Copyright (2015), with permission from Elsevier.

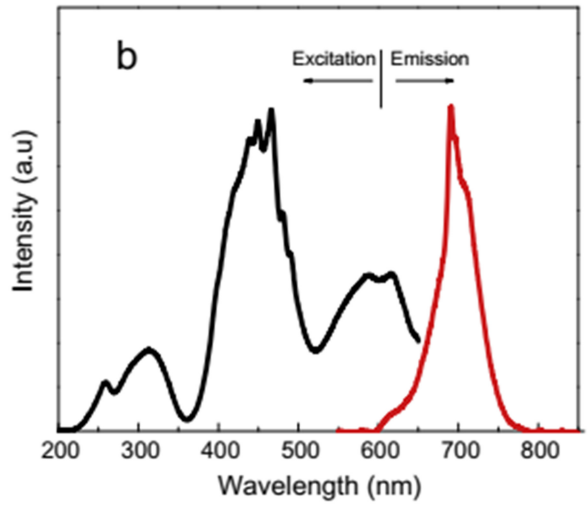

Figure 1.5. The persistent luminescence spectra of Ga_2O_3:$Cr^{3+}_{(0.01)}$ and $Zn^{2+}_{(0.005)}$ phosphors. Reprinted from [99], Copyright (2014), with permission from Elsevier.

phosphor is illuminated under ultraviolet light, a large number of charge carriers are created, and their energy is transferred to Cr^{3+} luminescence centers. These charge carriers are trapped by the oxygen vacancies, and after the irradiation source is cut off, the trapped electrons and holes are released and transferred to the luminescence centers by Cr^{3+} ions, which then emit characteristic persistent luminescence. Figure 1.6 shows the degradation of RhB as a function of the irradiation time.

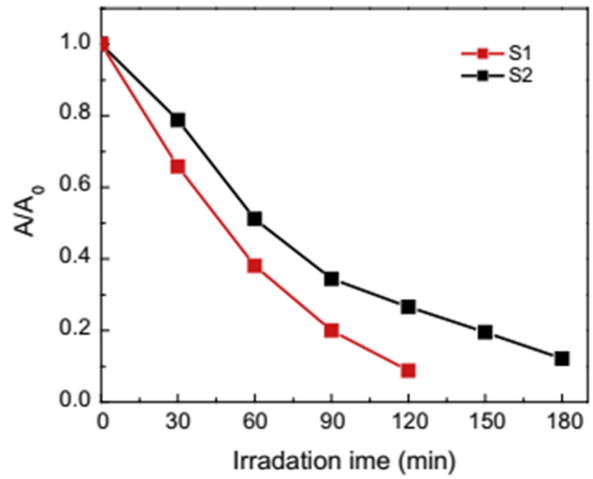

Figure 1.6. The absorption degradation of RhB as a function of irradiation time under ultraviolet light irradiation. Reprinted from [99], Copyright (2014), with permission from Elsevier.

It was found that the absorption of RhB photocatalyzed by $Ga_2O_3:Cr^{3+}_{(0.01)}$ reached 10% under UV light irradiation in 180 min, while the absorption of RhB photocatalyzed by the doping of $Zn^{2+}_{(0.005)}$ into $Ga_2O_3:Cr^{3+}_{(0.01)}$ took only 120 min. Thus, it can be seen that doping with Zn^{2+} can improve the photocatalytic properties of $Ga_2O_3:Cr^{3+}_{(0.01)}$ phosphor [100, 101].

1.6.1.4 The photocatalytic response of nanosized mixed metal oxides

It is well known that wide-bandgap nanosemiconductors such as TiO_2, ZnO, SnO_2, CeO_2, and NiO have excellent abilities to remove toxic dyes and organic pollutants from wastewater via photocatalytic degradation [102]. Nanosized titania (TiO_2) has a superior ability to remove textile dyes via degradation because of its effective generation of charge carriers under UV light illumination. However, due to its large bandgap, it does not work effectively under a visible-light source. Therefore, mixed metal-oxide systems have recently gained more importance due to their good photocatalytic degradation performance under visible or UV light sources. Various mixed metal-oxide systems that incorporate TiO_2, such as TiO_2–CeO_2, TiO_2–SnO_2, TiO_2–CuO, TiO_2–CdO, etc. have been shown to have excellent photocatalytic properties. These types of coupled metal-oxide systems exhibit better visible-light-driven photocatalytic activity and have higher dye degradation efficiency when used to remove toxic dyes and organic contaminants [103]. Recently, Rajendran *et al* [104] reported the photocatalytic response of a TiO_2/NiO composite catalyst used for the degradation of methyl orange. According to their experimental evidence, they observed 98% of methyl orange degradation within 60 min of irradiation. Here, the best performance (98%) of the composite catalyst was observed at pH = 7 (neutral), as shown in figure 1.7. In this composite system, the p–n junction takes a form in which Ni^{3+} states promote a large number of

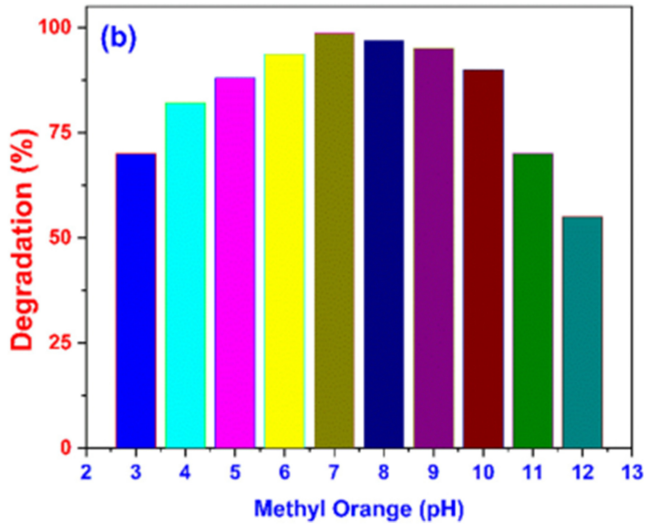

Figure 1.7. The degradation performance of the composite catalyst at different pH values. Reprinted from [104], Copyright (2020), with permission from Elsevier.

electrons, which reduces the recombination rate and helps to enhance the photocatalytic degradation process under visible light.

1.7 Applications

Due to globalization in the industrial sector, issues related to energy and the environment are becoming more serious. Nowadays, water and air pollution are hot topics due to their adverse effects on human health. To control and resolve these issues, there is a need to adopt sustainable technology for the betterment of mankind. Photocatalysis is an evergreen and economically viable way of solving the problems associated with wastewater treatment and air pollution. Hence, this research topic has become more attractive in the fields of science and engineering. Considering the global need for sustainable energy and environmental technology to replace traditional polluting technologies, photocatalysis is one of the better approaches with which to explore the innovative idea of using clean and natural solar light energy [105]. In the 1970s, Honda and Fujishima published their important discoveries related to water splitting and hydrogen generation using TiO_2 semiconductors for photocatalysis [60]. The scope of photocatalysts in energy and environmental sustainability is discussed below.

1.7.1 Energy sustainability

In the last few decades, many countries have used fossil fuels such as coal, oil, and agricultural waste products to generate electricity in power plants to fulfill the demand for energy in all sectors; such fossil fuel uses have made a major contribution to air, water, and soil pollution all over the world. The utilization of oil and petroleum products in automobiles and heavy transportation vehicles is

another major cause of air pollution. The use of this type of traditional power generation technology disperses many kinds of harmful pollutants into the atmosphere, so the level of toxic contaminants affecting the air quality index is increasing rapidly; these pollutants are also a major cause of global warming. To reduce environmental damage, there is an urgent need to develop and replace the traditional sources of energy and related polluting technologies with sustainable energy sources. Among the different renewable and sustainable energy sources, hydrogen is the most promising source for the current century, as it has the advantages of being an eco-friendly form of energy with lower production costs; however, it still has some challenges, such as increasing the production rate, storing the fuel, etc [106]. The photocatalytic production of hydrogen results in pure hydrogen that can be converted into energy and H_2O, which is also environmentally friendly [107]. In the past, hydrogen was produced using nonrenewable resources such as natural gas and petroleum-based technologies. However, these processes suffer from some disadvantages and liberate some other pollutants that are not much cheaper to deal with from a commercial perspective [108]. Hence, considering the previous drawbacks as well as the economic and environmental benefits of the new and advanced photocatalytic hydrogen generation process using solar light energy as the source of clean and low-cost sustainable energy technologies [109].

1.7.2 Environmental sustainability

In recent years, water pollution from industrial waste has been a very serious global issue. Contamination due to heavy metals and organic dye molecules in natural water resources accumulates for a long time, causing negative effects for organisms and human health.

To conserve natural water resources and control environmental pollution, there is an urgent need to develop environmentally friendly water purification technology and other sustainable energy technologies to avoid environmental issues in the air, water, and soil. From the literature database [100–110], it can be seen that approximately 10 000 types of dyes are used in industry for different purposes; therefore, the amounts of textile dyes and other dyes found in industrial wastewater are excessive. When these spread into fresh water resources, many types of toxic contamination can affect the quality of the water. The consumption and use of such contaminated water may cause health issues such as skin rashes, sinus infections, and cancer by entering the human ecosystem through water and animals [110]. Traditional methods including biological treatment, reverse osmosis, coagulation, adsorption, and ultrafiltration are ineffective water treatment processes [111]. Compared to these methods, the energy-efficient photocatalysis process has great potential to remove and degrade organic pollutants naturally using solar energy; it represents the lowest-cost and most favorable method that can utilize low-cost and nontoxic catalysts for the development of technology for water purification and environmental protection [112, 113]. Therefore, many research organizations are currently working in fundamental and applied research areas in the field of environmental sustainability to protect our planet and maintain the harmony of nature.

1.8 Conclusions and future prospects

Photocatalysis is a promising low-cost, energy-efficient, and environmentally friendly technique for resolving environmental and energy problems. There is a great demand for metal-oxide photocatalysts with a visible-light-driven photocatalytic response for the production of hydrogen and wastewater treatment. Further, research into large-scale production and treatment processes remains incomplete. So, in the future, more work is needed to develop this environmentally friendly technology that utilizes natural sunlight for the photocatalytic reaction. In this century, more research is focused on the development of sustainable technology, and photocatalysis has attracted great interest due to its attractive and broad scope for use in the near future due to the current global problems related to energy and the environment. There are still a few challenges in the development of photocatalytic materials, such as achieving high efficiency, thermal stability, purity, and environmental friendliness and overcoming low efficiency in photocatalytic reactors, which is also a major hurdle for their use on a large scale.

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