Solid State Nanostructured Metal Oxides as Photocatalysts and Their Application in Pollutant Degradation: A Review

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Abstract: Most dyes used in various industries are toxic and carcinogenic, thus posing a serious hazard to humans as well as to the marine ecosystem. Therefore, the impact of dyes released into the environment has been studied extensively in the last few years. Heterogeneous photocatalysis has proved to be an efficient tool for degrading both atmospheric and aquatic organic contaminants. It uses the sunlight in the presence of a semiconductor photocatalyst to accelerate the remediation of environmental contaminants and the destruction of highly toxic molecules. To date, photocatalysis has been considered one of the most appealing options for wastewater treatment due to its great potential and high efficiency by using sunlight to remove organic pollutants and harmful bacteria with the aid of a solid photocatalyst. Among the photocatalysts currently used, nanostructured metal oxide semiconductors have been among the most effective. This review paper presents an overview of the recent research improvements on the degradation of dyes by using nanostructured metal oxide semiconductors obtained by a solid-state method. Metal oxides obtained by this method exhibited better photocatalytic efficiency than nanostructured metal oxides obtained using other solution methods in several cases. The present review discusses examples of various nanostructured transition metal oxides such as TiO2, Fe2O3, NiO, ReO3, IrO2, Rh2O3, Rh/RhO2, and the actinide ThO2—used as photocatalysts on methylene blue. It was found that photocatalytic efficiency depends not only on the bandgap of the metal oxide but also on its morphology. Porous nanostructured metal oxides tend to present higher photocatalytic efficiency than metal oxides with a similar band gap.

Keywords: photocatalyst; metal oxides; environmental remediation; solid state

1. Introduction

Currently, researchers and scientists are becoming increasingly interested in metal oxide nanostructures due to their important technological applications in electronic and optoelectronic devices, sensors, medicines, and renewable energy sources. Reducing the size of materials (metal oxides) to nano-level imparts properties different from the bulk or crystalline forms; these nanoparticles demonstrate behaviors characteristic of isolated atoms and molecules [1–5].

Industrial plants generate increasing amounts of wastewater, which often causes severe environmental problems [6,7]. Wastewater produced in many industrial processes typically contains organic compounds that are toxic and not amenable to biological treatments [7]. There are several different types of organic pollutants, including dyes, phenols, biphenyls, pesticides, fertilizers, hydrocarbons, plasticizers, detergents, oils, greases, pharmaceuticals, proteins, carbohydrates, and so on [8].
Among the various physical, chemical, and biological technologies used in pollution control, advanced oxidation processes such as photocatalysis are being increasingly adopted in the destruction of organic contaminants due to their high efficiency, simplicity, good reproducibility, and ease of handling [8]. Heterogeneous photocatalysis possesses some critical advantages that have feasible applications in wastewater treatments, including: ambient operating temperatures and pressures, and the complete mineralization of contaminants and their intermediate compounds without leaving secondary pollutants. However, for large scale municipal applications, current photocatalytic water treatment systems are less attractive because they are more time consuming and have higher costs than other existing advanced oxidation techniques such as UV/H₂O₂, O₃/H₂O₂, and UV/O₃ technologies [9].

Therefore, semiconducting metal oxides have high potential due to their capability to generate charge carriers when stimulated with the required amount of energy, and to their applications in environmental remediation and electronics. Some semiconducting metal oxide synthesis methods are the chemical vapor deposition technique, the hydrothermal method, the laser ablation technique, and the electro-deposition method [10,11]. Out of these techniques, the hydrothermal method is the most user-friendly because of its reduced cost and ease of handling as well as being chemically reactive at low temperatures. However, other methods including the thermal decomposition of solids such as molecular complexes and macromolecular complexes [12] are gaining relevance due to their ease of preparation and final product purity.

An example of environmental remediation processes is the degradation of organic dyes [13] and the generation of clean energies such as “green hydrogen” [14].

In this context, one of the main applications of nanostructured metal oxides is the photocatalytic degradation of organic pollutants, which is in the field of environmental remediation.

The main characteristics that a suitable metal oxide photocatalytic system must have are [15]:

1. An adequate bandgap;
2. Suitable morphology;
3. High surface area;
4. Stability and reusability.

Semiconductor metal oxides with a bandgap near 3.2 eV are UV-light active, while semiconductor metal oxides with a bandgap near 2.7 eV are Visible-light active [16,17]. Metal oxides exhibiting these features—such as oxides of vanadium, chromium, titanium, zinc, tin, and cerium—follow similar primary photocatalytic processes such as light absorption, which induces a charge separation process with the formation of positive holes that can oxidize organic substrates. In this process, a metal oxide is activated with either UV light, visible light, or a combination of both, and photoexcited electrons are promoted from the valence band to the conduction band, forming an electron/hole pair (e⁻/h⁺).

The photogenerated pair (e⁻/h⁺) can reduce and/or oxidize a compound adsorbed on the photocatalyst surface. A schematic representation of this process is shown in Figure 1.

As Figure 1 shows, the bandgap of the metal oxides dictates their photocatalytic activity; crucially, it establishes whether their energy matches or exceeds the band gap energy of the semiconductor. In Table 1, a summary of the bandgap values for the most common metal oxides along the periodic table is displayed. It is important to note that the bandgap values vary with the size of the nanoparticle, preparation method, doping, etc.

The photocatalytic activity of metal oxides comes from two sources [13]:

(i) Generation of *OH radicals by oxidation of OH⁻ anions;
(ii) Generation of O₂⁻ radicals by reduction of O₂.

Nanostructured metal oxide semiconductors have been widely used in photocatalytic redox processes because of their filled valence band (VB) and empty conduction band (CB) electronic configurations. When exposed to a photon with energy exceeding the bandgap (hv > E₉), it generates an electron-hole pair with one electron in VB pumped
into CB, leaving a hole behind in VB. The holes generated in VB have great oxidation capability, while the electrons in the CB have high reduction potential.

Figure 1. Photocatalytic activity of nanostructured metal oxides.

Table 1. Bandgap values for the main metal oxides along the periodic table.

| Metal Oxides | Compounds | Bandgap (eV) $^{a,b}$ | Ref. |
|--------------|-----------|-----------------------|------|
|              | Cr$_2$O$_3$ | 3.2 | [18] |
|              | V$_2$O$_5$ | 2.3 | [18] |
|              | Co$_3$O$_4$ | 1.5 | [18] |
|              | TiO$_2$ | 3.3 (anatase) | [18] |
|              | TiO$_2$ | 3.0 (rutile) | [18] |
|              | Mn$_2$O$_3$ | 3.27 | [19] |
|              | WO$_3$ | 2.8 | [19] |
|              | MoO$_3$ | 3.14 | [18] |
| Metal transition | NiO | 3.5 | [19] |
|              | Fe$_2$O$_3$ | 2.1 | [18] |
|              | Fe$_3$O$_4$ | 2.61 | [19] |
|              | Cu$_2$O | 2.2 | [18] |
|              | CuO | 1.6 | [18] |
| Metal representative | ZnO | 3.2,34 | [19,20] |
|              | SnO$_2$ | 4.2 | [19] |
|              | Ga$_2$O$_3$ | 4.85 | [19] |
|              | Sb$_2$O$_3$ | 4.49 | [19] |
| Lanthanides | CeO$_2$ | 3.0–3.6 | [19] |
|              | La$_2$O$_3$ | 4.3 | [19] |
| Actinides | ThO$_2$ | 3.1 | [21] |

$^{a}$ Values from references: [17–22]. $^{b}$ Other similar values are reported for some of the metal oxides.

These highly-reactive electrons and holes participate in the photocatalytic organic degradation.

As mentioned above, the factors relevant for a photocatalyst to be efficient include adequate bandgap, suitable morphology, high surface area, stability, and reusability.

Whether a given nanostructured metal oxide meets these characteristics depends on its preparation method. For instance, TiO$_2$ is one of the most used and efficient metal
oxides for the photocatalytic degradation of several organic dye pollutants [23]. However, its relative efficiency depends on the preparation method, which in turn determines its bandgap, morphology, surface area, stability and reusability.

For instance, the dependence of the catalytic effectiveness of TiO\textsubscript{2} on the preparation method is illustrated in Table 2.

Table 2. Photocatalytic Performances and Key Factors (Crystal Phase, Size and Morphology) of Different TiO\textsubscript{2} Materials in the Degradation of Organic Water Pollutants [24].

| Organic Water Pollutant | Photocatalyst (Concentration) | Irradiation Light | Reaction Kinetic | Removal % | Irradiation Time |
|-------------------------|-------------------------------|-------------------|------------------|-----------|-----------------|
| MB (1 × 10\textsuperscript{-5} M) | TiO\textsubscript{2} anatase. 1 g \times \text{Lt}\textsuperscript{-1} with 340 nm cut-off filter, 330 nm > λ > 680 nm | Xe lamp (150 W) | Pseudo first-order kinetic | 86.5% | 25 min |
| MB (10 ppm) | TiO\textsubscript{2} nanoparticles (2.5 g L\textsuperscript{-1}) | UV lamp (40 W) | Langmuir–Hinshelwood | 71% | 60 min |
| MB (50 ppm) | TiO\textsubscript{2} nanofibers | Xenon lamp UV-vis (150 W) with AM 1.5 G filter λ > 400 nm | NM | 100% | 180 min |
| MB (10 mgL\textsuperscript{-1}) | TiO\textsubscript{2} nanotubes (0.16 g L\textsuperscript{-1}) | xenon visible light (500 W) UV light irradiation using eight tubes with a power source of 6 W, λ = 365 nm | NM | 99.1% | 40 min |
| MB (0.01 mM) | mesoporous TiO\textsubscript{2} 0.17 g L\textsuperscript{-1} | | NM | 85% | 60 min |
| MB (0.75 × 10\textsuperscript{-5} M) | Hollow titania micro-spheres (HTS) | UV lamp 15 W | Pseudo first-order kinetic | 53% | 90 min |
| MB (1 mM) | TiO\textsubscript{2} nanoparticles | Blacklight lamp (1 mW) | NM | 45% | 20 min |
| MB (10 mg L\textsuperscript{-1}) | TiO\textsubscript{2} nanoparticles (2.5 g L\textsuperscript{-1}) | UV lamp (40 W) | Langmuir–Hinshelwood | 78% | 60 min |
| Other similar organic water pollutants | | | | | |
| malachite green, MG (10 ppm) | | | | | |
| Rhodamine B, RhB, and methyl orange | TiO\textsubscript{2} hollow tetragonal nanocone (0.1 g L\textsuperscript{-1}) | full-arc Xe lamp (300 W) with a cutoff filter, λ > 420 nm | NM | 95.0% for RhB, 90.7% for MO | 30 min |
| MO (0.01 mM) | TiO\textsubscript{2} powder, Degussa P25 (0.5 g L\textsuperscript{-1}) | Xe arc lamp (300 W), IR water filter and cutoff filter, λ > 420 nm | Pseudo first-order kinetic | 75% for BPA | 4 h |
| Bisphenol A BPA, (200 µM) | TiO\textsubscript{2} powder, Degussa P25 (NM) TiO\textsubscript{2} nanopowder (0.3 g L\textsuperscript{-1}) | UVA/LED \(\lambda_{\text{max}} = 366\) nm visible light \(\lambda > 420\) nm | NM | 100% | 8 min |
| acetaminophen, Ace (1.3 µM) | TiO\textsubscript{2} powder, Degussa P25 (NM) TiO\textsubscript{2} nanopowder (0.3 g L\textsuperscript{-1}) | Xe lamp 300 W | NM | 90% | 5 h |
| RhB (NM) | TiO\textsubscript{2} powder (10 mg) | | | 90% | 3 h |
| Methyl orange 4 × 10\textsuperscript{-5} M | | | | | |
The $E_g$ bandgap also exhibits an inverse dependence on particle size. For instance, theoretical studies have explained this relationship with the following expression [25]:

$$
E_g^* \cong E_{g \text{bulk}} + \frac{\hbar^2 \pi^2}{2r^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon r}
$$

where $E_{g \text{bulk}}$ is the bulk energy gap, $r$ is the particle radius, $m_e$ is the effective mass of the electrons, $m_h$ is the effective mass of the holes, $\varepsilon$ is the relative permittivity, $\varepsilon_0$ is the permittivity of free space, $\hbar$ is Planck’s constant divided by $2\pi$, and $e$ is the charge of the electron.

The experimental inverse, $E_g$ vs. particle size, has been observed for several nanostructured metal oxide nanoparticles [25–27], including ZnO, Fe$_2$O$_3$, Co$_3$O$_4$, NiO and SnO$_2$.

On the other hand, the bandgap can also be modified by doping. In general, doping decreases the bandgap, as is reported in the case of ZnO/Mn$^{2+}$, ZnO/Cu and TiO$_2$/doping, among others [24]. Some of the most studied are the TiO$_2$/dopant and ZnO/dopant. Tables 3 and 4 summarize some of the results of Mn$_x$O$_y$/dopant systems. One of the explanations for this decrease in bandgap after doping is the increase in surface area. The increased surface area of the photocatalyst also increases the photodegradation of dye pollutants. This is because materials with a large surface area have more active sites than materials with a low surface area. This is illustrated in Table 3.

Table 3. Photocatalytic improvement parameter of various ZnO nano-photocatalysts (Adapted from reference [24]).

| Photocatalyst | Bandgap | Surface Area |
|--------------|---------|--------------|
| Bi$^{3+}$-ZnO | 3.15–2.6 | Increase |
| Co-ZnO       | 3.34–3.06 | Increase |
| N-ZnO        | 3.15–2.86 | Increase |
| F-ZnO        | 3.35–2.51 | Increase |
| Fe-ZnO       | 3.24–3.16 | Increase |
| Ag/ZnO       | 3.30–3.21 | Increase |
| B/ZnO        | 3.2–3.1  | Increase |
| Bi-TiO$_2$   | 2.99–3.08 | Increase |
| Ni-TiO$_2$   | 3.02, 2.99–3.03 Decrease |
| Ag-TiO$_2$   | 3.0–2.6  | Increase |
| Fe-TiO$_2$   | 3.2–2.98 | Increase |
| N-TiO$_2$    | 3.1–2.7  | Increase |
| Ti/WO$_3$    | 3.4–3.31 | Decrease |
| Zn-WO$_3$    | 3.2–3.12 | Slight decrease |
| Fe-SnO$_2$   | 3.8–1.65 | Increase |
| Zn-SnO$_2$   | 3.50–3.17 | Increase |
| Cu-SnO$_2$   | 3.02–2.2 | Increase |

As mentioned before, ZnO is one of the most common and effective photocatalysts for the photodegradation of organic dye pollutants. ZnO is insoluble in water, existing in the form of a white powder, and is extracted from the mineral Zincite through synthetic methods. Plastic, rubber, glass, ceramic, and cement industries use ZnO in various processes. ZnO is an n-type semiconductor with high bandgap energy that belongs to group II–IV of the periodic table [26,27]. ZnO is chemically stable, nontoxic, and inexpensive. It possesses high radiation hardness, effective transparency, remarkable optical absorption in the UV range, and outstanding thermal properties. Due to these characteristics, ZnO is used in a number of applications, such as optoelectronics, solar cells, medicine, catalysis, photocatalysis, and as an antibacterial agent. Doping in ZnO produces a decrease in the bandgap, which enhances photocatalytic efficiency. In Table 4, some doped ZnO are shown.
Table 4. Photocatalytic improvement performance of various ZnO nano-photocatalysts (Adapted from reference [24]).

| No | Composite | Synthesis Method | Pollutant for Degradation | PC Performance | Irradiation |
|----|-----------|------------------|---------------------------|---------------|-------------|
| 1  | Co-ZnO   | Sol-gel          | MB                        | 3 at.% Co-ZnO exhibited 92% degradation in 60 min. | Visible light |
| 2  | La-doped ZnO | Hydrothermal oxidation Microwave hydrothermal, borohydride and photoreduction | MO and MB | Best PCA observed by S0.005 due to defects. | UV light |
| 3  | Pd/ZnO   |               | CR                        | Pd/ZnO synthesized by borohydride method has the highest PCA compared to other routes. | UV light |
| 4  | C, N co-doped ZnO | Two-step pyrolysis | MB                        | 6C25 showed the best degradation due to its larger number of active sites. | Solar stimulated light |
| 5  | X-ZnO (X = Li, Al, N, P) | Mass production technology | RhB | PCA decreased as follows: N > Li > P > Al | Sunlight |
| 6  | Fe-doped ZnO | Combustion | BPA | FexZn1−xO (where x = 0.03) showed noticeable efficacy in the series. | Sunlight |
| 7  | Gd-ZnO films | RF magnetron sputtering | MB | 0.7 at.% Gd-ZnO exhibited higher PCA than ZnO. | UV light |
| 8  | Ag-ZnO   | Combustion | MB | Ag-ZnO demonstrated better activity than Au-ZnO. | UV light |
| 9  | Eu3+-doped ZnO | Coprecipitation | RhB | Doped ZnO (100%) degraded dye faster than ZnO. | UV light |
| 10 | Ce-ZnO   | Hydrothermal | Pharmaceutica | No degradation information, but increase in PC efficiency was around 95% within 4 h. | UV light |
| 11 | Cu-ZnO   | Chemical growth | MO and MB | Increase in PC efficiency was 57.5% for MO and 60% for MB in 180 min. | UV light |
| 12 | B-ZnO    | Sol-gel         | CN−                      | 4 at.% In-ZnO showed improved PCA compared to ZnO and 8 at.% In-ZnO. | Solar stimulated light |
| 13 | In-ZnO   | Plasma assisted chemical vapors | MB | Zn1−xSmxO x = 0.04 expressed maximum PC degradation (94.94%). | Solar stimulated light |
| 14 | Sm-ZnO   | Chemical precipitation | MB | 10 mg/L diazinon, 10 g/cm²−2% O2-ZnO exhibited 99% degradation in 180 min. | Visible light |
| 15 | WO3-doped ZnO | Hydrothermal | Diazinon | | UV light |

Titanium dioxide, TiO2, is also known as Titania or titanium (IV) oxide. TiO2 is the most promising photocatalyst since it possesses long-term chemical and physical stability along with low production costs [28]. It has a wide bandgap (3.0–3.2 eV) in the UV light range and exhibits three polymorphs, namely rutile, anatase, and brookite. Among these three phases, rutile is the most stable phase; the others are metastable, but they can transform into rutile phase irreversibly at elevated temperatures. Furthermore, the TiO2 photocatalyst has important uses in water treatment, lithium-ion batteries, sensors, catalysis, antibacterial, and anticancer applications [29–31]. Table 5 shows some examples of TiO2/dopants and their photocatalytic activity toward different organic dye pollutants.
Table 5. Summary of various TiO$_2$ nano-photocatalysts, pollutants, and irradiation sources along with their measured Photocatalysis (Adapted from reference [24]).

| N$^\circ$ | Doped Pollutants | PCA | Irradiation Source |
|------------|------------------|-----|---------------------|
| 1          | Ce-TiO$_2$       | RhB | 1.0%-Ce-TiO$_2$ > 1.0%-V-TiO$_2$ > undoped TiO$_2$ showed degradation (%) 83.43 > 53.74 > 21.56 > 11.09, respectively. | Solar light |
| 2          | PF co-doped anatase TiO$_2$ | MO | It demonstrated excellent PCA compared to undoped TiO$_2$, F-TiO$_2$, P-TiO$_2$ and Degussa P25. | Full-spectrum light |
| 3          | Ga-doped TiO$_2$ nanopowder | MO | 0.6 mol% Ga-TiO$_2$ demonstrated up to 82% degradation. | Visible light |
| 4          | F, N co-doped TiO$_2$ | MB | 97.31% degradation was achieved within 5 h. | Visible light |
| 5          | Nd-TiO$_2$ film | MB | 0.1% Nd-doped TiO$_2$ showed maximum degradation (92%). Its degradation increased at high values of pH, initial concentration and amount of catalyst. | UV light |
| 6          | Moroccan natural P-TiO$_2$ | IC | 5 mol% expressed the highest PCA under visible light and equal efficiency as TiO$_2$ under UV. | UV light |
| 7          | Nb$_2$O$_5$-TiO$_2$ | MB | TiO$_2$ with the lowest content of Ag exhibited higher PCA. | UV and Visible light |
| 8          | Mesoporous Ag-TiO$_2$ | MO | Degradation kinetics rate increased with an increase in iron content. 0.4 wt% Ru/TiO$_2$ showed high PCA using UV light and 0.2% Ru/TiO$_2$ using visible light. | UV and solar light |
| 9          | Fe$^{3+}$-TiO$_2$ | CV | TiO$_2$ | UV |
| 10         | Ru/TiO$_2$       | 2-CP | UV light and 0.2% Ru/TiO$_2$ using visible light. | UV and visible light |
| 11         | Gd-TiO$_2$       | RhB | 0.3% Gd-TiO$_2$ demonstrated the best PCA. More decolorization compared to fluorescence spectroscopy. Maximum degradation shown by 0.75 wt% Pd-TiO$_2$ for mixture of dyes and 0.5 wt% Pd-TiO$_2$ for single dye. | Visible light |
| 12         | C-TiO$_2$        | RhB | It showed remarkable PCA compared to pure TiO$_2$. | Visible or solar light |
| 13         | Pd-TiO$_2$       | MB and MO | 94% degradation achieved. | Solar light |
| 14         | Graphene/TiO$_2$ | BPA | 94% degradation achieved. | UV light |

2. Materials and Methods

*Nanostructured Metal Oxides Preparation Methods*

Several solution methods have been developed for synthesizing metal or metal oxide nanoparticles, such as the solvothermal, hydrothermal, and sol-gel methods [10,11]. Several of these nanostructured metal oxides have been suitable for photocatalytic degradation of organic dye pollutants. Usually, the preparation of nanostructured metal oxides for photocatalysis involves some solution method. However, for some of these methods, drawbacks like the aggregation of the NPs during the adsorption stage cause a reduction in the efficiency of the desired application [32–34]. When the metal or metal oxide is obtained as a colloid, as is commonly observed, their separation by centrifugation often produces agglomeration of the NPS [34]. To solve this type of problem, a solid-state method is used in which the metal nanoparticles are generally obtained as solid pure phase material. Therefore, the solventless synthesis of nanostructures is highly significant due to its economical, eco-friendly, and industrially viable nature. However, the development of new solid-state methods to prepare metallic nanostructured materials is a constant challenge. We have previously described a new solid-state method to synthesize metallic nanostructured nanomaterials from the pyrolysis of metallic and organometallic derivatives of poly- and oligo-phosphazene under air and at 800 °C [35–38]. Metallic nanostructured
materials of the type M, M_xO_y, and M_xP_yO_z are obtained depending on the nature of the metal. Another method—used when the respective metallic or organometallic derivative is not possible to prepare—uses MLn/[NP(O2C12H8)]_x mixtures [39–41]. However, in several of these systems, the M or M_xO_y phase is accompanied by a phosphate phase. These methods have been discussed in detail in several papers [35–41] and books [32,33,42–44]. When we used a polymer that does not contain phosphorus in its polymeric chain—such as the chitosan MXn and PS-co-4-PVP MXn macromolecular precursors (MXn = metallic salt)—and then subjected it to solid-state pyrolysis under air and at 800 °C (see Figure 2), pure phase nanostructured M_xO_y were obtained [45–57]. Now we will discuss the use of these nanostructured metal oxides M_xO_y obtained by this method in the degradation of organic dye pollutants.

![Figure 2](image_url). Schematic representation of the solid-state method and its application in environmental remediation.

3. Results

3.1. TiO_2

The titania to be used as photocatalyst was obtained by pyrolysis of the (Cp2TiCl2) (Quitosano) (I), (Cp2TiCl2)(PS-co-4-PVP) (II), (TiOSO4)(Chitosan) (III), (TiOSO4)(PS-co-4-PVP) (IV), (TiO(acac)2)(Chitosan) (V), and (TiO(acac)2)(PS-co-4-PVP) (VI) macromolecular precursors under air and at several temperatures (500 °C, 600 °C, 700 °C, and 800 °C [23]. The bandgaps of the TiO_2 obtained using these precursors are displayed in Table 6. The values range from 3.21 to 3.72 eV, which are adequate for photocatalytic degradation of organic dyes using UV-visible irradiation.

The results of the photocatalytic degradation of methylene blue are shown in Table 7. As can be seen in Table 7, the most efficient catalytic degradation arises from the TiO_2 produced from the TiO_2-A-(III)p(800) system precursors, with 87% degradation after 25 min. Based on this table, the photocatalytic efficiency could be expressed by the following multifactorial relationship:

\[ PE = a \text{ bandgap} + b \text{ particle morphology} + c \text{ particle size} + d \text{ Titania phase} + e \text{ pyrolysis temperature} \]  

where PE is photocatalytic efficacy and the Titania phase can be anatase, rutile, or brookita. In the case of TiO_2 obtained by our solid-state method using TiO_2-A-(III)p(800) as the precursor, factor b is highly porous (see Figure 3) since, as it is known, the anatase form is the most efficient phase as a photocatalyst and, in solid-state, the temperature of the thermal treatment is crucial to determine morphology and particle size. In this case, factor a does not appear to be very important since, as shown in Table 7, the values are similar.
Table 6. Bandgap for TiO$_2$ obtained using different precursors and temperatures (Adapted from reference [23]).

| Temperature ($°$C) | Phase  | Bandgap (eV) | Temperature ($°$C) | Phase  | Bandgap (eV) |
|-------------------|--------|--------------|-------------------|--------|--------------|
| 500               | Anatase| 3.66         | 500               | Anatase| 3.43         |
| 600               | Mixture| 3.43         | 600               | Anatase| 3.30         |
| 700               | Mixture| 3.63         | 700               | Anatase| 3.22         |
| 800               | Rutile | 3.40         | 800               | Mixture| 3.27         |

| Temperature ($°$C) | Phase  | Bandgap (eV) | Temperature ($°$C) | Phase  | Bandgap (eV) |
|-------------------|--------|--------------|-------------------|--------|--------------|
| 500               | Anatase| 3.32         | 500               | Anatase| 3.53         |
| 600               | Anatase| 3.43         | 600               | Anatase| 3.45         |
| 700               | Anatase| 3.28         | 700               | Mixture| 3.37         |
| 800               | Anatase| 3.65         | 800               | Mixture| 3.38         |

Table 7. Kinetic data for degradation of methylene blue with nanostructured TiO$_2$ (Adapted from reference [23]).

| Sample                      | Apparent Photodegradation Rate Constant k ($10^{-2}$ min$^{-1}$) | Degradation η (%) | R$^2$ (%) |
|-----------------------------|---------------------------------------------------------------|-------------------|-----------|
| TiO$_2$-Anatase-(I)p 500 °C | 0.40 ± 0.04                                                   | 11                | 93.9      |
| TiO$_2$-Mixture-(I)p 600 °C | 0.80 ± 0.04                                                   | 20                | 98.4      |
| TiO$_2$-Mixture-(I)p 700 °C | 0.06 ± 0.03                                                   | 14                | 98.0      |
| TiO$_2$-Rutile-(I)p 800 °C | 1.30 ± 0.10                                                   | 30                | 93.8      |
| TiO$_2$-Anatase-(II)p 500 °C| 0.40 ± 0.04                                                   | 11                | 91.9      |
| TiO$_2$-Anatase-(II)p 600 °C| 0.33 ± 0.03                                                   | 7                 | 88.8      |
| TiO$_2$-Anatase-(II)p 700 °C| 0.40 ± 0.02                                                   | 10                | 97.6      |
| TiO$_2$-Mixture-(II)p 800 °C| 1.00 ± 0.06                                                   | 23                | 97.2      |
| TiO$_2$-Anatase-(III)p 500 °C| 3.90 ± 0.20                                                  | 65                | 96.9      |
| TiO$_2$-Anatase-(III)p 600 °C| 4.10 ± 0.20                                                  | 65                | 97.4      |
| TiO$_2$-Anatase-(III)p 700 °C| 2.00 ± 0.06                                                  | 39                | 99.2      |
| TiO$_2$-Anatase-(III)p 800 °C| 7.13 ± 0.01                                                  | 87                | 99.8      |
| TiO$_2$-Anatase-(IV)p 500 °C| 2.40 ± 0.01                                                  | 45                | 97.8      |
| TiO$_2$-Anatase-(IV)p 600 °C| 3.10 ± 0.01                                                  | 55                | 98.0      |
| TiO$_2$-Anatase-(IV)p 700 °C| 0.20 ± 0.02                                                  | 5                 | 91.1      |
| TiO$_2$-Mixture-(IV)p 800 °C| 4.00 ± 0.20                                                  | 63                | 97.1      |
| TiO$_2$-Anatase-(V)p 500 °C| 3.40 ± 0.10                                                  | 59                | 99.1      |
| TiO$_2$-Anatase-(V)p 600 °C| 1.30 ± 0.04                                                  | 27                | 99.2      |
| TiO$_2$-Mixture-(V)p 700 °C| 1.30 ± 0.09                                                  | 27                | 96.4      |
| TiO$_2$-Mixture-(V)p 800 °C| 0.60 ± 0.03                                                  | 14                | 98.0      |
| TiO$_2$-Anatase-(VI)p 500 °C| 1.70 ± 0.03                                                  | 34                | 99.7      |
| TiO$_2$-Mixture-(VI)p 600 °C| 2.40 ± 0.02                                                  | 48                | 95.9      |
| TiO$_2$-Mixture-(VI)p 700 °C| 2.60 ± 0.02                                                  | 51                | 94.6      |
| TiO$_2$-Rutile-(VI)p 800 °C| 0.50 ± 0.02                                                  | 14                | 98.5      |
Figure 3. FE-SEM images of TiO$_2$-Anatase-(III)p (800) (a) and an amplification of a portion of the structure (b) (Adapted from reference [23]).

The results shown in Table 7 were obtained at pH 6.5; however, a pH effect study showed that, at alkaline pH 9.5, the degradation was 98% [23].

3.2. Fe$_2$O$_3$

Fe$_2$O$_3$ was prepared by pyrolysis of the Chitosan(FeCl$_3$)$_y$, Chitosan(FeCl$_2$)$_y$, PS-b-4-PVP(FeCl$_2$)$_y$, and PS-b-4-PVP(FeCl$_3$)$_y$ macromolecular complexes under air and at 800 °C [47]. The product was Fe$_2$O$_3$ in the hematite phase in all the cases. The bandgap of the as-prepared Fe$_2$O$_3$ ranged from 1.83 eV to 2.12 eV, which indicated an effective photocatalyst behavior under UV-visible irradiation (see Table 8).

Table 8. Kinetic data for the degradation of MB with α-Fe$_2$O$_3$ obtained from PS-co-4-PVP and chitosan macromolecular precursors (Adapted from reference [47]).

| Precursor                          | $E_g$ (eV) |
|-----------------------------------|------------|
| Chitosan(FeCl$_3$) 1:1           | 1.83       |
| Chitosan(FeCl$_3$) 1:5           | 2.15       |
| PS-co-4-PVP(FeCl$_3$) 1:1        | 2.12       |
| Fe$^{3+}$-PS-co-4-PVP(FeCl$_3$) 1:5| 2.12       |
| Chitosan(FeCl$_2$) 1:1           | 2.15       |
| Chitosan(FeCl$_2$) 1:5           | 2.15       |
| PS-co-4-PVP(FeCl$_2$) 1:1        | 1.90       |
| PS-co-4-PVP(FeCl$_2$) 1:5        | 2.09       |

Some parameters for the degradation experiments of MB with α-Fe$_2$O$_3$ obtained from PS-co-4-PVP and chitosan macromolecular precursors are summarized in Table 9. The highest extent of degradation of MB (98.6%) at 150 min of irradiation time was achieved for α-Fe$_2$O$_3$ obtained from the PS-co-4-PVP(FeCl$_3$)$_y$ precursor in a 1:1 ratio.

Table 9. Kinetic data for the degradation of MB with α-Fe$_2$O$_3$ obtained from PS-co-4-PVP (1:1) and chitosan (1:1) macromolecular precursors (Adapted from reference [47]).

| Photocatalyst              | Apparent Photodegradation Rate Constant k ($10^{-2}$ min$^{-1}$) | Discoloration Rate η(%) at 60 min | Discoloration Rate η(%) at 150 min |
|---------------------------|---------------------------------------------------------------|---------------------------------|----------------------------------|
| α-Fe$_2$O$_3$ (PS-co-4-PVP)| 1.2 ± 0.04                                                    | 62.6                            | 86.9                             |
| α-Fe$_2$O$_3$ (Chitosan)   | 2.1 ± 0.1                                                     | 73.4                            | 94.6                             |

The size and morphology of the two systems were determined by electron microscopy studies, showing fused nanoparticles and 3D networks with average sizes of 150–200 nm.
for α-Fe₂O₃ from the precursor Chitosan(FeCl₂) 1:1 and 55–100 nm for α-Fe₂O₃ from the precursor PS-co-4-PVP(FeCl₂) 1:1. These morphologies show a random network of the surface area, quasi-linear nanoparticle chains that fold into larger porous powder particles [47]. It appears to be that for these Fe systems, the multifactorial relationship that holds this behavior could be the following:

\[ PE = a \text{ bandgap} + b \text{ particle morphology} + c \text{ particle size} + d \text{ (Fe precursor)} \]  

(3)

where the (Fe precursor) factor refers to the FeCl₂ or FeCl₃ metal salt source linked to the polymer. Once again, the most important factor dictating the photocatalyst efficiency of α-Fe₂O₃ toward the degradation of methylene blue is the \( b \) factor, more specifically, the material porosity. Table 9 shows that the bandgaps of α-Fe₂O₃ are similar; however, factor \( a \) could be less important. On the other hand, factors \( c \) and \( d \) could be somewhat significant.

3.3. NiO

NiO is a p-type semiconductor with \( E_g = 3.5 \text{ eV} \) with multiple practical applications [57–60]. However, its bandgap can be modified by doping with other metal oxide semiconductors or by formation of nanocomposites in which one of the components would be in less quantity (mainly its photocatalyst properties) [59,60]. NiO has been used in catalysis, battery cathodes, fuel-cell electrodes, electrochromic films, electrochemical supercapacitors, and magnetic materials [59,60]. As these applications depend on its bandgap value and, in turn, the bandgap properties of superconductors depend on the environment of the metal oxide materials [61,62], there are no systematic, detailed studies on the effect of the medium on the bandgap. Although some \( M_xO_y/M'_xO'_y \) have been prepared—where \( M_xO_y \) is a nanostructured metal oxide and \( M'_xO'_y \) is a metal oxide matrix—no systematic effect of the matrix on the photocatalytic efficiency toward the degradation of organic dyes has been reported. By preparing the NiO/SiO₂, NiO/TiO₂, NiO/Al₂O₃, and NiO/glasses nanocomposites through a solid-state method, we have investigated the effect of the SiO₂, TiO₂, Al₂O₃, and Na₄.2Ca₂.8(Si₆O₁₈)(glass) matrices on the photocatalytic properties of NiO toward the degradation of methylene blue [57]. The composites were prepared by solid-state thermal treatment of the Chitosan(NiCl₂)_x/M'_xO'_y and PS-co-4-PVP(NiCl₂)_x/M'_xO'_y precursors, where \( M'_xO'_y \) could be SiO₂, TiO₂, and Al₂O₃ glasses. Kinetic data for the photodegradation process of MB with NiO and with the NiO/SiO₂, NiO/TiO₂, NiO/Al₂O₃, and NiO/glasses composites are displayed in Table 10.

| Photocatalyst | Apparent Photodegradation Rate Constant k (10⁻² M min⁻¹) | Discoloration Rate (%) | R² Linear Fit (%) |
|--------------|--------------------------------------------------------|------------------------|------------------|
| NiO-chitosan * | 2.4                                                     | 71%                    | 0.998            |
| NiO-PS-4-PVP | 2.2                                                     | 68%                    | 0.991            |
| NiO/SiO₂-chitosan | 2.3                                                     | 69%                    | 0.999            |
| NiO/SiO₂-PS-4-PVP | 1.6                                                     | 48%                    | 0.996            |
| NiO/TiO₂-chitosan | 2.9                                                     | 91%                    | 0.992            |
| NiO/TiO₂-PS-4-PVP | 2.6                                                     | 81%                    | 0.980            |
| NiO/Al₂O₃-chitosan | 1.5                                                     | 45%                    | 0.990            |
| NiO/Na₄.2Ca₂.8(Si₆O₁₈) | 2.6                                                     | 75%                    | 0.990            |

* Nomenclature: Composite, hyphen (-), name of the precursor polymer.

As can be observed in Table 6, the NiO from the precursor containing the chitosan as a solid-state template produces much higher activity than the NiO sample arising from the PSP-4-PVP(NiO)_x precursor. The polymer precursor clearly influences the photocatalytic activity. In this sense, using chitosan as a solid-state template produces much higher activity than the NiO sample arising from the PSP-4-PVP(NiO)_x precursor. On the other hand, the
most efficient photocatalytic activity was observed for the NiO/TiO₂ composite, with 90% degradation of methylene blue in 5 h.

In general, the photocatalytic activity shown in Table 10 is probably related to a matrix effect of NiO inside the different SiO₂, TiO₂, and Al₂O₃ matrices. Different matrices can influence NiO in different ways. For example, when the matrix is TiO₂, a p-n junction p-NiO/TiO₂ can be formed; this reduces the recombination rate of the photogenerated electron-hole pairs, which is known to enhance the photocatalytic activity of TiO₂ (see Figure 4) [60]. In the case of the NiO/TiO₂ composite, which has the highest catalytic behavior, the matrix effect may arise from the enhanced activity of TiO₂ by NiO. Therefore, in this case, NiO acts as a matrix in the active semiconductor for the degradation of methylene blue. On the other hand, the NiO/Al₂O₃ compound is one of the least efficient photocatalysts for the degradation of methylene blue, which is probably due to an insulating effect caused by Al₂O₃ that cuts off the communication between p-NiO and methylene blue to start the degradation of the dye. This is also in agreement with the low photocatalyst efficiency of the insulating SiO₂ matrix. An explanation for the results of the photocatalytic activity of the NiO/Na₄.₂Ca₂.₈(Si₆O₁₈) composite obtained from the Chitosan(NiCl₂·6H₂O)x//Na₂O·CaO-SiO₂ precursor is that Na₄.₂Ca₂.₈(Si₆O₁₈) has similar characteristics to those of SiO₂ as a matrix.

![Figure 4](image)

**Figure 4.** Schematic diagrams for (a) energy bands of p-NiO and (b) TiO₂ before contact, (c) formation of p-n junction and its energy diagram at equilibrium, and (d) transfer of holes from n-TiO₂ to p-NiO under UV irradiation (Adapted from reference [57]).

3.4. Precious Metal Oxides Ir, Rh, Re: IrO₂, Rh/RhO₂, Rh₂O₃, ReO₃

Among the metals in the periodic table, the so called precious—such as Ir, Rh, and Re, among others—are some of the most catalytically active [63]. Their activity is hugely enhanced at the nano-level [64,65]. These metals, as well as their metal oxides, exhibit high catalytic activity [63,65].

3.5. Ir

IrO₂ is a promising conducting oxide used, for example, as an electrode material in ferroelectric capacitors for nonvolatile memory applications [66]. However, to the best of our knowledge, there are no reports on its photocatalytic activity. The only related studies are those about the catalytic reduction of 4-Nitrophenol [67] and its electrochemical catalytic activity toward oxygen evolution [68]. As with the previous metal oxides, the iridium oxide for the catalytic experiments was prepared by thermal treatment of the Chitosan(IrCl₃)ₓ and PSP-4-PVP(IrCl₃)ₓ macromolecular precursors [55]. The as-prepared IrO₂ has an adequate bandgap for the degradation of methylene blue under UV-visible irradiation (see Table 11). As previously mentioned, we have used this dye as a model dye to assay the photocatalytic properties of IrO₂. Kinetic data for the photodegradation process of MB with IrO₂ are displayed in Table 11. IrO₂ from the PVP precursor exhibits better photocatalytic activity (57% photodegradation in 300 min) than the IrO₂ from the
chitosan precursor (38% photodegradation in 30 min). This effect was associated with the more porous morphology of IrO₂ from the PVP precursor [55].

Table 11. Kinetic data for the photodegradation process of MB with IrO₂, Rh/RhO₂, Rh/Rh₂O₃, and ReO₃.

| Photocatalyst       | Photodegradation Rate Constant k (10⁻³ M min⁻¹) | Discoloration Rate (%) | R² Linear Fit (%) | Ref. |
|---------------------|------------------------------------------------|------------------------|-------------------|------|
| IrO₂-PS-4-PVP       | 1.7                                            | 53%                    | 0.995             | [55] |
| IrO₂-chitosan       | 2.4                                            | 38%                    | 0.991             | [55] |
| Rh/RhO₂             | a                                              | 78%                    | b                 | [56] |
| Rh₂O₃               | a                                              | 70%                    | b                 | [56] |
| ReO₃-PS-4-PVP       | 2.8                                            | 64%                    | 0.977             | [54] |
| ReO₃-chitosan       | 2.8                                            | 53%                    | 0.997             | [54] |

a Photodegradation rate constant k not informed. b Linear fit not informed.

3.6. Rh

In this case, the Rhodium oxides Rh/RhO₂ and Rh/Rh₂O₃ were obtained by pyrolysis of the PSP-4-PVP(RhCl₃)ₓ and Chitosan(RhCl₃)ₓ macromolecular precursors, respectively [56]. The bandgap values (see Table 12) are adequate for photocatalytic activity under UV-visible irradiation. The results (see Table 11) indicate that the Rh/RhO₂ sample exhibits better photocatalytic activity (78% photodegradation in 300 min) than the Rh/Rh₂O₃ one (70% photodegradation in 300 min). As the porosity of both materials is similar, the higher photocatalytic activity of Rh/RhO₂ could be due to its small particle size in the range 10–20 nm [56].

Table 12. Bandgap for the Ir, Rh, and Re oxides.

| Photocatalyst | Bandgap (eV) | Ref. |
|---------------|--------------|------|
| ReO₃          | 4.36         | [54] |
| IrO₂          | 2.4–2.6      | [55] |
| Rh/RhO₂       | 3.7          | [56] |
| Rh₂O₃         | 3.0          | [56] |

3.7. Re

ReO₃ for the photocatalytic essays was obtained by solid-state thermal treatment of the Chitosan(ReCl₃)ₓ and PSP-4-PVP(ReCl₃)ₓ macromolecular precursors [54]. The bandgap for ReO₃ indicates an adequate value for UV-visible photoactivation (see Table 12). ReO₃ was also found to catalyze the photodegradation of MB with an efficiency of 53% and 64% in 300 min for the chitosan and PVP precursors, respectively (see Table 11). ReO₃ is an unusual transition metal oxide as it presents a metallic behavior with conductivity close to that of copper [69]. Therefore, nanoparticles of rhenium trioxide produce a SERS (surface-enhanced Raman spectra) effect on some organic compounds, such as pyridine [70]. Despite this, their catalytic activity has only been proved in the catalytic degradation of methyl orange [71].

3.8. Th

Among the actinides oxides, thoria is an important and promising material used in ceramic catalyst sensor solid electrolytes, catalysis, optical materials, and the traditional nuclear industry [72–75]. The thorium oxide was prepared by thermal treatment of the Chitosan Th(NO₃)₄ and PS-co-4-PVPTh(NO₃)₄ macromolecular precursors at 800 °C. The ThO₂/SiO₂ and ThO₂/TiO₂ composites were also synthesized by pyrolysis of the Chitosan Th(NO₃)₄//MO₂ and PS-co-4-PVP Th(NO₃)₄//MO₂ macromolecular composites, where MO₂ is SiO₂ or TiO₂.
To the best of our knowledge, no photocatalytic studies on ThO$_2$, ThO$_2$/SiO$_2$, or ThO$_2$/TiO$_2$ have been reported. Regarding thoria, scarce literature data have been reported. As for ThO$_2$ nanoparticles, Aller et al. [76] report values ranging from 5.13 eV to 4.5 eV, while for ThO$_2$ thin films, Buono-Core et al. [77] report values from 4.5 eV to 4.61 eV. However, some of these values are theoretical calculations. Using the solid-state UV-visible absorption and the Tauc plot for ThO$_2$, a value of 5.66 eV is estimated for the chitosan polymer precursor and 5.76 eV for the PS-4-co-PVP polymer precursor.

With this in mind, using UV-visible radiation, some catalytic activity for ThO$_2$ could be expected. In fact, the values for the catalytic results are shown in Table 13. The values for the ThO$_2$/SiO$_2$ and ThO$_2$/TiO$_2$ nanocomposites are also shown for comparison. On the other hand, the bandgap values for thoria included in TiO$_2$ as matrix exhibited values of 3.14 eV and 3.15 eV for the ThO$_2$/TiO$_2$ composites from chitosan and PS-4-co-PVP polymer precursors, respectively. These values are lower than those of ThO$_2$ and ThO$_2$/SiO$_2$; however, as Buono-Core et al. point out [77], the optical bandgap energy is very sensitive to the preparation method and the experimental parameters applied in the synthesis [77]. In fact, Mahmoud reported a value of 3.82 eV for ThO$_2$ prepared by a spray pyrolysis technique [78]. The estimated rate constant for the degradation of methylene blue in the presence of thorium prepared without the SiO$_2$ and TiO$_2$ matrices is greater than that of the pristine compounds, suggesting that the structural modification and synergy of the inorganic components play a fundamental role. This is related to the increase in the photocatalytic efficiency of the semiconductor as a result of the greater number of active sites provided by the (ThO$_2$) PS-4-co-PVP and (ThO$_2$) chitosan precursors.

### Table 13. Kinetic data for the photodegradation process of MB with ThO$_2$ and with the ThO$_2$/SiO$_2$, ThO$_2$/TiO$_2$ composites (Adapted from reference [21]).

| Photocatalyst                  | $E_g$ (eV) | Apparent Photodegradation | Discoloration Rate (%) | $R^2$ Linear Fit (%) |
|-------------------------------|------------|---------------------------|------------------------|----------------------|
| ThO$_2$ (chitosan precursor)  | 5.66       | $3.7 \times 10^{-3}$      | 67                     | 0.992                |
| ThO$_2$ (PS-4-PVP precursor)  | 5.75       | $2.2 \times 10^{-3}$      | 66                     | 0.967                |
| ThO$_2$/SiO$_2$ (chitosan precursor) | 5.50   | $7.7 \times 10^{-4}$      | 24                     | 0.979                |
| ThO$_2$/SiO$_2$ (PS-4-PVP precursor) | 5.6    | $8.5 \times 10^{-4}$      | 25                     | 0.923                |
| ThO$_2$/TiO$_2$ (chitosan precursor) | 3.14   | $1.4 \times 10^{-3}$      | 39                     | 0.815                |
| ThO$_2$/TiO$_2$ (PS-4-PVP precursor) | 3.14   | $8.7 \times 10^{-4}$      | 27                     | 0.941                |

In general and according to the examples shown here, the efficiency in photocatalysis using photocatalyst semiconductor oxides obtained by a solid method is higher than that exhibited by the same photocatalysts obtained by solution methods. This may be due to the high porosity of the catalysts obtained by the solid state method.

#### 3.9. Heterojunction Structure

These structures are formed by coupling two semiconductors whose band structures are aligned in such a way that they allow for an enhanced charge separation compared to the single system. A maximum of two alignments are feasible with this binary combination, viz., type I and type II [79–82]. Figure 5 shows a schematic of the band alignment of the nanocomposites for both heterostructures. In the type I alignment, both the VB and CB edge potential of either semiconductor lies within the bandgap of the other semiconductor, as the latter possesses a wider bandgap. Since one has lower VB and CB potentials than the other, both bands act as hole and electron collecting sites, as is shown in Figure 5. In the type II heterostructure, the CB position of the first semiconductor lies above that of the second, whereas its VB lies within the bandgap of the second. Therefore, the photogenerated holes tend to migrate to the VB of the first one, whereas the excited electrons tend to migrate to the CB of the second. The mentioned band position and migration of the charge carriers are depicted in Figure 5b. In general, the type II heterostructure is widely preferred because it allows the migration of electrons and holes in the opposite direction (see Figure 5b) [79–82].
Some examples of both type I and type II band alignments are presented and discussed in reference [81].

3.10. Photocatalyst Mechanism of Dye Degradation by Nanostructures

In general, the system of heterogeneous photocatalysis using semiconductor materials consists of a light-harvesting antenna and several active species to facilitate pollutant degradation [83]. The series of chain oxidative-reductive reactions that occur at the photon-activated surface has been broadly proposed as:

\[
\text{Photocatalyst} + h\nu \rightarrow h^+ + e^- \\
h^+ + H_2O \rightarrow \cdot OH + H^+ \\
h^+ + OH^- \rightarrow \cdot OH \\
h^+ + \text{Pollutant} \rightarrow (\text{Pollutant})^+ \\
e^- + O_2 \rightarrow \cdot O_2^- \\
\cdot O_2^- + H^+ \rightarrow \cdot OO\cdot H^- \\
2 \cdot OO\cdot H \rightarrow O_2 + H_2O_2 \\
H_2O_2 + \cdot O_2^- \rightarrow \cdot OH + OH^- + O_2 \\
H_2O_2 + h\nu \rightarrow 2 \cdot OH
\]

Hence, the final reaction is:

\[
\text{Pollutant} + (\cdot OH, h^+, \cdot OO\cdot H \text{ or } O_2^-) \rightarrow \text{degradation products}
\]

which produces the degradation of the pollutant.

When the semiconductor is irradiated by an input light possessing ultra-band-gap energy \((h\nu > E_g)\), a valence band (VB) electron \((e^-)\) is excited to the conduction band (CB), leaving behind a photogenerated hole \((h^+)\) at the VB. Accordingly, the produced \(e^-/h^+\) pairs are able to migrate to the surface of the semiconductor and participate in redox reactions.

The photocatalytic reaction usually involves three main active species: a hydroxyl radical \((\cdot OH)\), \(h^+\), and a superoxide radical \((\cdot O_2^-)\), where \(\cdot OH\) is the primary oxidant in the photocatalytic degradation of the pollutant in the aqueous solution. \(\cdot OH\) radicals are normally generated via two routes: (i) \(H_2O\) and \(OH^-\) in a water environment are readily oxidized by photogenerated \(h^+\) to form \(\cdot OH\) radicals; (ii) \(O_2\) present in an aqueous solution is reduced by photogenerated \(e^-\) to form \(O_2\) radicals, which subsequently react with \(h^+\) forming \(\cdot OO\cdot H\) radicals, whose further decomposition produces \(\cdot OH\) radicals.

Complementary to what was discussed above, two interesting reviews [84,85] analyze the photocatalytic properties of the TiO\(_2\) system incorporated in a carbon gel matrix and covalent organic frameworks (COFs). In Dongge et al., although still in its incipient stage in comparison with other traditional inorganic metal oxides, titania is proposed as having some advantages such as having a high surface due to the high porosity of the carbon gel matrix. In the second case, Yuhang et al. point out that even when COFs are highly
porous and crystalline polymeric materials, they are photocatalytic systems different from nanostructured metal oxide semiconductors, and are a valid alternative in environmental remediation. Meanwhile, recent investigations [86,87] have proven that photocatalysis of nanostructured metal oxides is being increasingly adopted.

4. Conclusions

Nanostructured metal oxides play an important role in the environmental decontamination of organic dyes. An alternative route that often improves photocatalytic efficiency is the use of photocatalysts based on metal oxides obtained by a solid-state method. Specifically, the solid-state method based on the thermal treatment of Chitosan MXn and PS-co-4-PVP MXn precursors affords pure nanostructured metal oxides MxOy, which are often more efficient photocatalysts than the respective MxOy obtained by other solution methods. It was found that the photocatalytic efficiency depends on the nature of the MXn precursor salts and the calcination temperature, as in the case of TiO2, where the most efficient photocatalyst was the one obtained from the Chitosan TiSO4 precursor pyrolyzed at 800 °C. The efficiency of most of the studied photocatalysts can be described by the following relationship:

\[ PE = a \text{ band gap} + b \text{ particle morphology} + c \text{ particle size} + d \text{ crystalline phase} + e \text{ pyrolysis temperature} \]  

where PE is the photocatalyst efficiency. In particular, for a nanostructured metal oxide semiconductor photocatalyst obtained using our solid-state method, morphology is more important than the bandgap. In turn, when using the solid-state preparation method of the metal oxide photocatalyst, the temperature often modulates the morphology. This can, for example, generate a highly porous morphology, thus causing a very efficient photocatalytic activity.

However, research on this topic is a challenge since the parameters that induce a more efficient photocatalysis in solid-state synthesis are not fully known. An achievement in this matter could be a significant advance for environmental decontamination.

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