Review

A CeO\(_2\) Semiconductor as a Photocatalytic and Photoelectrocatalytic Material for the Remediation of Pollutants in Industrial Wastewater: A Review

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Abstract: The direct discharge of industrial wastewater into the environment results in serious contamination. Photocatalytic treatment with the application of sunlight and its enhancement by coupling with electrocatalytic degradation offers an inexpensive and green technology enabling the total removal of refractory pollutants such as surfactants, pharmaceuticals, pesticides, textile dyes, and heavy metals, from industrial wastewater. Among metal oxide—semiconductors, cerium dioxide (CeO\(_2\)) is one of the photocatalysts most commonly applied in pollutant degradation. CeO\(_2\) exhibits promising photocatalytic activity. Nonetheless, the position of conduction bands (CB) and valence bands (VB) in CeO\(_2\) limits its application as an efficient photocatalyst utilizing solar energy. Its photocatalytic activity in wastewater treatment can be improved by various modification techniques, including changes in morphology, doping with metal cation dopants and non-metal dopants, coupling with other semiconductors, and combining it with carbon supporting materials. This paper presents a general overview of CeO\(_2\) application as a single or composite photocatalyst in the treatment of various pollutants. The photocatalytic characteristics of CeO\(_2\) and its composites are described. The main photocatalytic reactions with the participation of CeO\(_2\) under UV and VIS irradiation are presented. This review summarizes the existing knowledge, with a particular focus on the main experimental conditions employed in the photocatalytic and photoelectrocatalytic degradation of various pollutants with the application of CeO\(_2\) as a single and composite photocatalyst.

Keywords: ceria; semiconductor; photocatalysis; photoelectrocatalysis; wastewater remediation

1. Introduction

Water resource contamination and energy crises constitute the most important issues in the modern world. Both problems affect not only the quality of human life, but also human health, considering the availability of drinking water and energy resources, as well as increasing contamination of the environment, which is especially noticeable with regards to climate change.

One of the main sources of environmental pollution is untreated industrial wastewater. Its direct release to surface water results in a serious contamination of fresh water. Photocatalytic and photoelectrocatalytic treatment with the application of sunlight offers an inexpensive and green technology for possible complete removal of refractory pollutants, such as surfactants, pharmaceuticals, pesticides, textile dyes, and heavy metals, from industrial wastewater. Furthermore, photoelectrochemical treatment of wastewater can be coupled with a simultaneous recovery of energy stored in the wastewater. This chemical energy is often wasted [1].

The demand for efficient and stable materials which can be applied as a photocatalyst or photoelectrocatalyst in wastewater treatment under visible light irradiation has increased during the last two decades. In particular, metal oxide—semiconductors have attracted great interest. Among these
materials, cerium dioxide (CeO2) is one of the semiconductors most often applied, with the exception of titanium dioxide (TiO2). Metal oxides have been successfully applied as photocatalysts and photoelectrocatalysts in treatment processes of various pollutants [2–16]. They offer a number of ways to enhance the treatment process efficiency and energy efficiency with a simultaneous reduction of environmental pollution. TiO2 is the most commonly applied semiconductor photocatalyst due to its properties, such as its non-toxicity to living organisms, chemical stability and inertness, low-cost preparation, and photocatalytic properties resulting from its band gap energy and positions of conduction band (CB) and valence band (VB) [17–19]. This photocatalyst can be applied under UV irradiation, which is hazardous and constitutes only 2–5% of total solar light. TiO2 exhibits another limitation—a relatively high rate of recombination of photogenerated electron/hole (e−/h+) pairs, which results in a decrease of its photocatalytic activity [20,21].

CeO2 is another semiconductor photocatalyst with various applications and similar properties to TiO2. However, its band gap is in the wide range of 2.6 to 3.4 eV, depending on the preparation method [22,23]. Furthermore, CeO2 exhibits promising photocatalytic activity. Nonetheless, the position of CB and VB limits its application as an efficient photocatalyst utilizing solar energy, even though CeO2 can absorb a larger fraction of the solar spectrum than TiO2 [24]. The photocatalytic and photoelectrocatalytic activity of CeO2 in wastewater treatment can be improved by various modification techniques, including changes in morphology, doping with metal cation dopants and non-metal dopants, coupling with other semiconductors, combining it with carbon supporting materials, etc. [24–33].

The main properties that make CeO2 significant as a photocatalyst and photoelectrode material applied in the degradation of various pollutants result from its high band gap energy, high refractive index, high optical transparency in the visible region, high oxygen storage capacity, and chemical reactivity [34–41]. The other properties of CeO2 which should be mentioned include its high thermal stability, high hardness, oxygen ion conductivity, special redox features, and easy conversion between Ce3+ and Ce4+ oxidation states [30,42,43].

The above-mentioned properties indicate the possible practical application of CeO2 as a photocatalyst or photoelectrocatalyst in wastewater treatment. CeO2 also has other versatile practical applications as a coating for corrosion protection for metals and alloys [44,45], as an oxygen ion conductor in solid oxide fuel cells [46,47], as glass-polishing material [48], as an electro-chromic thin film [39,49], as sunscreen in cosmetics [50,51], as a gas sensor [52,53], as an additive in ceramics [54,55], as anode material for the lithium ion battery system [56], in three-way catalysis (TWC) [57,58], in fluid catalytic cracking [59], in oxygen pumps and amperometric oxygen monitors [60], in water splitting for the generation of hydrogen [61], in solar cells [62], etc.

The aim of this paper is to present a general overview of CeO2 semiconductor materials applied as photocatalysts and photoelectrocatalytic materials in the treatment of various pollutants present in industrial wastewater. The characteristics of CeO2 semiconductors, as well as parameters characterizing the treatment process, are presented. They are followed by examples of CeO2 applied in the photocatalytic and photoelectrocatalytic treatment of different kinds of pollutants, in order to prove the extraordinary properties of CeO2. This review summarizes the existing knowledge, with a particular focus on the experimental conditions of pollutant degradation in photocatalytic and photoelectrocatalytic processes.

2. Ceria Characterization

Cerium dioxide (CeO2) is an n-type semiconductor material characterized by a relatively high dielectric constant value (ε = 23–52) [63] and a wide band gap of about 3.0 eV [22]. Although rare earth elements usually exist in a trivalent state, cerium exists not only in a trivalent (+3) state, but also in a tetravalent (+4) state. The Ce4+ oxidation state is regarded as more stable than Ce3+ due to Ce4+’s electronic structure ([Xe]4f15), which is more stable than that of Ce3+ ([Xe]4f10). Cerium oxide also exists in two forms, with ongoing transformation between the oxygen-rich CeO2 and the oxygen-poor Ce2O3 [64].
Generally, CeO$_2$ exhibits a simple and stable cubic fluorite structure with the space group $Fm3m$. Cerium ions form a face-centered-cubic (fcc) structure, while oxygen ions form a cubic sublattice [65]. Each cerium cation is coordinated by the eight nearest oxygen ions and each oxygen anion is coordinated by the four nearest cerium cations [46,66,67]. The coordination of 8 to 4 enables oxide defects in CeO$_2$(2–3). Oxide defects play an important role in the catalytic and photocatalytic properties of CeO$_2$ [68].

In bulk materials, both forms of cerium oxide are present, i.e., CeO$_2$ and Ce$_2$O$_3$. In the case of Ce$_2$O$_3$, charge deficiency is compensated for by oxygen vacancies in the lattice, resulting in the formation of oxygen defects [69,70]. The transition between the two oxidation states of cerium ions, i.e., from Ce$^{3+}$ to Ce$^{4+}$, may generate neutral oxygen vacancies in ceria according to the following reaction [46]:

$$O^{2−} + 2Ce^{4+} \rightarrow 2Ce^{3+} + 1/2O_2(g). \tag{1}$$

The transition between Ce$^{3+}$ and Ce$^{4+}$ accompanies the process of oxygen vacancy formation. In the case of a cubic fluorite structure, atoms of oxygen can quickly diffuse since they are all in one plane. The oxygen vacancies can be formed in the following reaction [46,71]:

$$O_X^O \leftrightarrow V_{O^{••}} + 2e^{−} + 1/2O_2(g), \tag{2}$$

where $O_X^O$ denotes oxide ions in the lattice, $V_{O^{••}}$ represents a doubly charged oxygen vacancy, and $e^{−}$ stands for electrons in CB. The conduction band is formed of Ce 4f energy states [67]. The number of oxygen vacancies is directly proportional to the concentration of Ce$^{3+}$ ions. Furthermore, a reduction of the ceria particle size results in the formation of oxygen vacancies related to an increase in the levels of Ce$^{3+}$ [72]. The catalytic activity of ceria strongly depends not only on the particle size, but also on the morphology, as proven in different oxidation and reduction processes, e.g., the oxidation of CO [73,74] and NO reduction [75,76]. Various shapes of CeO$_2$ exhibit different exposures of lattice planes. Nanoparticles are often present in the form of octahedra or a truncated octahedral shape, and their most stable facet is [111] due to the minimization of surface energy. Nanorods expose [110] facets, while nanocubes expose [100] facets [66,76]. The stability of different facets is in the following order: {111} > {110} > {100}. Furthermore, the formation energy of oxygen vacancies on the {111} facet is higher than on {110} and {100} facets, which means that the number of oxygen vacancies depends on the facet. Therefore, different catalytic activity was determined in the case of ceria applied in the form of nanorods, nanocubes, and octahedra in CO oxidation [73,74,76]. The highest catalytic activity was determined for nanorods and the lowest for octahedra. This means that more oxygen vacancies are formed on the surface of nanorods and nanocubes.

If an organic pollutant is oxidized at ceria, surface lattice oxygen atoms act as an oxidant and an oxygen vacancy is formed, according to the Mars and van Krevelen (MvK) mechanism [71]. This mechanism explains oxidation reactions on catalysts consisting of metal oxides and based on redox reactions of active sites [77,78]. The oxygen vacancies in CeO$_2$ are important not only because they enhance the activity and stability of supported catalysts, but also because they stimulate oxygen-containing bonds for hydrogen production with the application of a water-splitting reaction [79]. They act as electron scavengers and specific reaction sites in heterogeneous catalysis, and generate superoxide radicals [80–83]. Furthermore, oxygen vacancies bind adsorbates (e.g., molecules of pollutants) more strongly than normal oxide sites and also assist in their dissociation [84–86].

Although a higher concentration of Ce$^{3+}$ in ceria means the formation of more defects, a higher concentration of Ce$^{4+}$ ions results in a narrower bandgap of CeO$_2$. CeO$_2$ exhibits strong absorption in the UV region, and high transparency in the VIS region and near IR region. In comparison with TiO$_2$, the CeO$_2$ absorption spectrum is shifted by 80 nm towards the VIS region [88,89]. Additionally, the photogenerated pairs e$^-$/h$^+$ have much longer lifetimes than those generated in TiO$_2$.

CeO$_2$ is an n-type semiconductor with a relatively wide band gap. Its experimentally determined band gap energy is about 6 eV, and was measured from VB with a predominantly O 2p character to CB.
with a predominantly Ce 5d character [90–93]. However, localized and empty Ce 4f states lie within the gap, and the band gap in ceria can be described by the value of about 3 eV as the distance from VB to the bottom of the empty 4f states [90,94]. The unoccupied Ce 4f electronic states were proved to lie above the Fermi level [95]. The position of the CB edge and VB edge can be calculated at the point of zero charge, according to the following equations [96–99]:

\[
E_{CB}^0(\text{CeO}_2) = \chi(\text{CeO}_2) - E_c - \frac{1}{2}E_g(\text{CeO}_2),
\]

\[
E_{VB}^0(\text{CeO}_2) = E_g(\text{CeO}_2) - E_{CB}(\text{CeO}_2),
\]

where \(E_{CB}\) and \(E_{VB}\) denote conduction and valence band potentials, respectively; \(\chi\) is the absolute electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms (5.56 eV for CeO\(_2\)) [97,100]; \(E_g\) is the band gap energy; and \(E_c\) is the energy of free electrons on the hydrogen scale (~4.5 eV). Therefore, the calculated values of \(E_{CB}\) and \(E_{VB}\) for CeO\(_2\) with the band gap energy of ~3 eV are equal to ~0.44 and 2.56 eV, respectively. The positions of VB and CB in ceria compared with several selected redox potentials occurring at the semiconductor surface are presented in Figure 1.

![Figure 1. Band position (valence band top and conduction band bottom) of cerium dioxide (CeO\(_2\)) compared with several selected redox potentials of processes occurring at the semiconductor surface.](image)

The position of edges in CB and VB is one of the most important controlling factors in the production of reactive oxide species (ROS). Considering that the positions of CB and VB in CeO\(_2\) include the potentials of hydroxyl radical and superoxide anion radical formation (Figure 1), these reactive oxide species can be formed at the semiconductor surface and can participate in the degradation of pollutants present in industrial wastewater. Finally, water and carbon dioxide—the non-toxic products of pollutants degradation—are formed. Furthermore, the potential of CB in CeO\(_2\) is more negative than the potential of hydrogen evolution and the VB potential is more positive than the potential of oxygen evolution. This means that the requirements of hydrogen generation in a photocatalytic system are fulfilled. However, H\(_2\) and O\(_2\) formed during the water splitting process can undergo the reverse reaction, resulting in the generation of H\(_2\)O.

Ceria can be applied not only as a photocatalyst, but also as an electrode material, in the photoelectrocatalytic degradation of pollutants. Then, two other parameters characterizing
semiconductors—the Fermi level potential and flat band potential—should be considered. If a semiconductor is used as an electrode material, then the electrochemical potential or, equivalently, the Fermi level of electrons in the electrode \( E_F \), can be adjusted by changing the applied potential \( E \) vs. the reference electrode [101]:

\[
E_F = -eE + \text{const.},
\]

where \( e \) denotes the elementary charge.

Considering an n-type semiconductor, if the Fermi level in the redox electrolyte lies below the Fermi level in a semiconductor, then electrons can be transferred from the semiconductor to the oxidized species until equilibrium is achieved. This results in the formation of a depletion layer in the semiconductor due to the removal of electrons and in a bending of bands upward, toward the surface (Figure 2) [102,103]. The difference between the Fermi levels in the semiconductor and the redox electrolyte determines the band bending. Under irradiation, the Fermi level rises up and undergoes splitting into two quasi-Fermi levels: \( E_{F,e^-} \), representing the quasi-Fermi level of electrons for the CB, and \( E_{F,h^+} \), representing the quasi-Fermi level of holes for the VB [104]. The quasi-Fermi level of the majority of charge carriers is close to the original Fermi level. The quasi-Fermi level of the minority of charge carriers clearly shifts away from the original Fermi level (Figure 2).

![Figure 2](image.png)

**Figure 2.** Energy of a CeO\(_2\) semiconductor (n-type) and band positions in the semiconductor under equilibrium conditions after semiconductor–electrolyte contact and after irradiation.

The Fermi level in the semiconductor can be controlled by the application of a bias potential, which changes the band bending [105–107]. If the applied potential causes flattening of the band edges, then it is called flat band potential \( E_{fb} \). This results in a lack of differences between the potential at the surface and in the bulk of the semiconductor. If the applied potential is higher than \( E_{fb} \), the potential causes higher band bending [105,108]. \( E_{fb} \) can be determined from a Mott–Schottky plot \( (1/C^2 \text{ vs. } E) \) by its extrapolation to \( 1/C^2 = 0 \) resulting from the Mott–Schottky equation [22,23,101,109]:

\[
\frac{1}{C^2} = \left( \frac{2}{e\varepsilon_0\varepsilon_S A^2 N_D} \right) \left( E - E_{fb} - \frac{k_B T}{e} \right),
\]

where \( C \) denotes the space-charge capacitance, \( N_D \) \((\text{cm}^{-3})\) is the donor density, \( e \) represents the electronic charge \((1.602 \times 10^{-19} \text{ C})\), \( \varepsilon \) denotes the relative permittivity of the semiconductor, \( A \) \((\text{cm}^2)\) is the active geometric surface area, \( \varepsilon_0 \) represents the vacuum permittivity \((8.854 \times 10^{-12} \text{ F m}^{-1})\), \( E \) \((\text{V vs.})\)
the reference electrode) is the applied potential, \( k_B \) indicates the Boltzmann constant \((1.381 \times 10^{-23} \text{ J K}^{-1})\), and \( T \) is the temperature \((298 \text{ K})\).

Furthermore, a positive slope of the Mott–Schottky equation indicates the n-type nature of a semiconductor, while a negative slope is characteristic of a p-type semiconductor [110].

3. Ceria as a Photocatalyst and Photoelectrocatalyst Applied in Pollutant Degradation

Photocatalytic materials, including metals, metal oxides, semiconductors, carbon-based structures, quantum-dots, metal–organic frameworks, magnetic cored dendrimers, etc., can be applied in the degradation of various pollutants present in industrial wastewater. \( \text{CeO}_2 \) is a metal oxide and a semiconductor material. Generally, metal oxide photocatalysts can be divided into three generations [111]. The first generation includes single component oxides, sulfides, nitrides, and phosphates. The second generation was developed in order to improve the photocatalytic activity of catalysts belonging to the first generation and includes heterojunction materials. The photocatalytic materials deposited on different substrates constitute the third generation of photocatalysts. The last group of photocatalysts was created in order to immobilize the photocatalysts belonging to the first and second generation, and in order to avoid separation of the photocatalysts from wastewater after its treatment. \( \text{CeO}_2 \) is a metal oxide and a semiconductor material and belongs to the first generation of photocatalysts. However, ceria can also be applied in the form of heterojunction photocatalysts, and independent of its form, should be immobilized on proper substrates or supports.

The degradation of pollutants in the photocatalytic process performed under UV or VIS irradiation depends on many parameters, including the pH of wastewater, effect of catalyst loading expressed by the ratio of catalyst to pollutant or catalyst to volume of wastewater, adsorption of a pollutant on a photocatalyst surface, source and light intensity, pollutant loading, and presence of interfering compounds [111,112].

A comparison of the performance of various photocatalysts is very difficult, because it depends on many conditions and, primarily, on the type of photocatalyst and type of pollutant. Nevertheless, two parameters can be included in such a comparison. The first one is the quantum yield (QY) of a photochemical reaction. The quantum yield is usually defined as the ratio of the number of molecules changed, formed, or destroyed to the number of photons of the specified wavelength adsorbed in the same period of time [113]. In the case of the photocatalytic degradation of a pollutant, QY can be calculated according to the following equation [111,114,115]:

\[
\text{QY} = \frac{\text{Rate of pollutant degradation (molecules per second)}}{\text{Flux of absorbed photons (photons per second)}}.
\]

Anwer et al. introduced the second parameter, which enables a comparison of different photocatalysts and constitutes the supplementation of QY [111,116]. This parameter is called “a figure of merit” (FOM) and is based on important operation parameters:

\[
\text{FOM} = \frac{\text{Product obtained (L)}}{\text{Catalyst dosage (g/L) \cdot Time (h) \cdot Energy consumption (Wh/\mu\text{mole}) (Wh/\mu\text{mole})}}.
\]

However, the application of the above-described FOM requires a benchmark for the normalization of QY values determined for considered photocatalysts, for which the FOM value is established as 100. The relationship between QY and FOM values can be direct or reverse. A reverse relationship indicates a deficiency in at least one of the four parameters which are included in the formula describing FOM [111].

3.1. Pristine \( \text{CeO}_2 \)

The energy of the band gap in a semiconductor determines its possible application as a photocatalyst in wastewater treatment under UV or VIS/sunlight irradiation. Its value can be decreased by an
application of CeO₂ in the form of nanomaterials, e.g., nanoparticles, nanotubes, nanowires, or nanorods. A decrease in the band gap enables the performance of a photocatalytic degradation process under visible light irradiation or even sunlight, which is harmless and more economic than UV irradiation. Ceria nanomaterials can be fabricated in various ways, including by the sol-gel process, co-precipitation, hydrothermal synthesis, forced hydrolysis, electrochemical, solvothermal synthesis, reverse micelles route, sonochemical, or microwave methods [117]. The method of ceria preparation strongly affects the photocatalytic activity of CeO₂. It was proved that an increase in the specific surface area, a decrease in the pore size, and an increase in the amount of oxygen vacancies resulted in a high rate of hydrogen production in the photocatalytic process carried out under visible and solar light [118].

During the photocatalytic degradation of pollutants, the photoexcitation of CeO₂ in aqueous solution results in the generation of various radicals and charged species, according to the common route [102,119,120]:

\[
\text{CeO}_2 + h\nu \rightarrow \text{CeO}_2(e^-_{\text{CB}} + h^+_{\text{VB}}),
\]

\[
\text{CeO}_2(h^+_{\text{VB}}) + \text{H}_2\text{O} \rightarrow \text{CeO}_2 + \text{H}^+ + \text{OH}^*,
\]

\[
\text{CeO}_2(h^+_{\text{VB}}) + \text{OH}^- \rightarrow \text{CeO}_2 + \text{OH}^*,
\]

\[
\text{CeO}_2(e^-_{\text{CB}}) + \text{O}_2 \rightarrow \text{CeO}_2 + \text{O}_2^*^-.
\]

\[
\text{O}_2^*^- + \text{H}^+ \rightarrow \text{HO}_2^*.
\]

\[
2\text{HO}_2^* \rightarrow \text{H}_2\text{O}_2 + \text{O}_2.
\]

\[
\text{H}_2\text{O}_2 + \text{CeO}_2(e^-_{\text{CB}}) \rightarrow \text{CeO}_2 + \text{OH}^* + \text{OH}^-,
\]

where \(h\nu\) denotes the photon energy, VB is the valence band in CeO₂, CB represents the conduction band in CeO₂, \(h^+\) is a hole, and \(e^-\) denotes an electron.

Hydroxyl radicals (OH\(^*\)), as well as superoxide anion radicals (O\(_2^*\)), are the main reactive oxygen species (ROS) generated in the photocatalytic system in water oxidation by photogenerated holes (\(h^+\)) and oxygen reduction by photoexcited electrons (\(e^-\)) in CB. These species, along with hydroperoxide radicals (HO\(_2^*\)), are highly reactive and can take part in photocatalytic degradation of the pollutants present in industrial wastewater. The reactivity of ROS can be compared considering their oxidation potentials, which are as follows: 2.80 V for OH\(^*\); 1.78 V for H\(_2\)O\(_2\); 1.68 V for HO\(_2^*\); and 1.23 V for O\(_2\) vs. the normal hydrogen electrode (NHE) [121,122].

The properties of CeO₂ can be changed significantly when its particle size is reduced to a nanoscale and is applied in the form of nanostructures. This process affects CeO₂ properties such as the lattice symmetry, cell parameters, and structural characteristics [123]. Phases in a bulk form are characterized by a high surface energy and are unstable. When the particle size is reduced to a nanoscale, the surface energy decreases significantly, and nanostructured materials exhibit a high stability [124]. Furthermore, ceria in the form of nanoparticles shows high catalytic activity, which results from the high mobility of surface oxygen vacancies [73,75,125].

CeO₂ in the pristine form can be applied in the photocatalytic treatment of various pollutants (Table 1). It is mainly applied in the form of doped or composite materials. Since CeO₂, similarly to TiO₂, is characterized by a relatively high band gap energy and high rate of e\(^-\)/h\(^+\) pair recombination, its photoexcitation requires the application of UV irradiation. Although different methods of CeO₂ preparation, especially in the form of nanomaterials, enable these issues to be avoided, pristine CeO₂ is not commonly applied in the photocatalytic degradation of organic and inorganic pollutants. Examples of CeO₂ application as a single photocatalyst in pollutant degradation are presented in Table 1.
Table 1. Photocatalytic degradation of various pollutants with the application of CeO$_2$ as a semiconductor photocatalytic material.

| CeO$_2$ Form | Preparation Method | Band Gap | Catalyst Dose | Pollutant, Concentration | Light Source | Degradation Efficiency (Process Time) | Ref. |
|--------------|--------------------|----------|---------------|--------------------------|--------------|---------------------------------------|------|
| Nanowires    | Microwave-assisted hydrothermal method | 2.65 eV  | 0.2 g/L       | MO, 0.01 mM              | 250 W Hg lamp | Nanowires—8%, Nanorods—78% (100 min) | [126]|
| Crystal phase | Precipitation method | 1.0 g/L  | AO$_7$, 70 mg/L | 1000 W halogen lamp (>420 nm) | AO$_7$—97% (11 h), TOC—60% (12 h) | [127]|
| Crystal phase | Precipitation followed by calcination | 1.0 g/L  | AO$_7$, 70 mg/L, pH = 6.8 | 1000 W halogen lamp (>420 nm) | AO$_7$—92%, TOC—40% (10 h) | [128]|
| Nanostructure | Sol-gel method | 2.52 eV  | 1.0 g/L       | Xylene Milling Yellow 6G, 10 ppm | 125 Hg lamp (365 nm) | 100% (30 min) | [129]|
| NPs—nanoparticles, HNRs—hierarchical nanorods, HNWs—hierarchical nanowires | Electrodeposition method | 3.2 eV (HNRs and HNWs) | 0.2 g/L       | MO, 20 mg/L, pH = 3 | 500 W Xe lamp (200–800 nm) | NPs—68.8%, HNRs—98.2%, HNWs—99.3% (180 min) | [25]|
| NPs         | Dissolution and hydrolysis method | 2.94 eV  | 1.3 g/L       | Phenol (Ph), 2-chlorophenol (2-CP), 2-bromophenol (2-BP), 2-nitrophenol (2-NP), 50 mg/L | Sunlight, 900 $\times 10^2$ lx | Ph—<35%, 2-CP—98%, 2-BP—96%, 2-NP—99% (180 min), TOC Ph—20%, 2-CP—94%, 2-BP—91%, 2-NP—96% (180 min) | [130]|

NPs—nanoparticles, HNRs—hierarchical nanorods, HNWs—hierarchical nanowires
| CeO$_2$ Form | Preparation Method | Band Gap | Catalyst Dose | Pollutant, Concentration | Light Source | Degradation Efficiency (Process Time) | Ref. |
|-------------|--------------------|----------|---------------|--------------------------|-------------|--------------------------------------|------|
| Nanostructure | Electron beam method | 3.36 eV—NPs, 3.15 eV—30 kGy, 3.12 eV—90 kGy | 0.1 g/L | p-nitrophenol (4-NP), 5 mg/L, MB, 10 mg/L | 400 W lamp (>420 nm) | 4-NP NPs—45%, 30 kGy—60%, 90 kGy—66% (6 h) | [131] |
| CeO$_2$ X-architecture particles | Hydrothermal route assisted by polyvinyl pyrrolidone | 2.54 eV—rods, 2.75 eV—beans, 2.76 eV—rods/cubes, 2.95 eV—hexagons | 1 g/L | MB, 40 mg/L | 500 W Hg lamp | 98% (120 h) | [132] |
| CeO$_2$ NPs | Microwave-assisted hydrothermal method | 2.80 eV—CeO$_2$, 2.20 eV—CeO$_2$/SCB | 10.0 g/L | MB, 20 ppm | 36 W lamp (365 nm), 145 µW/cm$^2$ | CeO$_2$—30%, CeO$_2$/SCB—90% (120 min) | [133] |

Abbreviations: MO—methyl orange; MB—methylene blue; AO7—acid orange 7; RhB—rhodamine B; TOC—total organic carbon; and NPs—nanoparticles.
Pristine CeO$_2$ can be fabricated with the application of different methods (Table 1) affecting its properties. This photocatalyst is usually applied in the form of nanomaterials, which increases its photocatalytic activity, but simultaneously generates problems in its separation from the solution after treatment. The examples presented in Table 1 clearly show that nanoparticles, nanowires, and nanorods exhibit a band gap energy lower than 3.2 eV, except for hierarchical nanostructures [25]. However, the application of hierarchical nanorods and nanowires in methyl orange (MO) photodegradation resulted in a higher degradation rate due to a higher surface area and improved light harvesting ability.

It is worth noting that CeO$_2$ can be applied in the photodegradation of organic pollutants, such as synthetic dyes or phenols, at low concentrations, but the duration of the process required for the complete removal of pollutants is relatively long—about 2–3 h or sometimes 10 h or more. Furthermore, the removal of organic pollutants does not mean their total degradation and total mineralization of the solutions. A decrease in total organic carbon (TOC) is rarely investigated along with pollutant removal. A significant decrease in TOC usually requires longer durations of photocatalytic degradation. However, CeO$_2$ nanoparticles obtained in the dissolution and hydrolysis method [130], and applied in phenol derivative photodegradation, resulted in comparable and high degradation efficiencies (>96%) and TOC removal (>91%) during the same time of 180 min under solar irradiation, except for phenol.

CeO$_2$ in the form of nanorods is also a promising material for obtaining an enhanced solar photocatalyst with a possible application in the photocatalytic production of H$_2$ [118]. Therefore, the application of CeO$_2$ as an electrode material in the photoelectrocatalytic degradation of pollutants under solar irradiation, combined with the simultaneous photoelectrocatalytic generation of H$_2$, seems to be an interesting alternative to the commonly applied photocatalytic treatment of industrial wastewater.

The last example presented in Table 1 is related to CeO$_2$ supported with sugarcane bagasse (SCB) adsorbent, in order to achieve higher photocatalytic activity in methylene blue (MB) photodegradation [134]. In fact, this photocatalyst constitutes a composite material showing the effect of a support on CeO$_2$ characteristics, but it is not a composite with another photocatalyst. CeO$_2$/SCB exhibits a higher BET (Brunauer-Emmett-Teller) surface area and more active sites, resulting in a three-times higher efficiency of MB photodegradation. Furthermore, the adsorption edge shifts towards longer wavelengths with a simultaneous decrease in the CeO$_2$/SB band gap.

3.2. CeO$_2$ Doped with Metals and Non-Metals

An enhancement of the photocatalytic activity and extension of light absorption into the visible region is possible by doping CeO$_2$. The doping can be performed with metal dopants or non-metal dopants. In both cases, the superior photocatalytic performance of doped CeO$_2$ is ascribed to a decrease in the band gap energy and bringing the absorption band from UV into the visible region, an increase in the specific surface area, and an increase in the number of oxygen vacancies.

The doping of CeO$_2$ with metals or non-metals results in a change in the position of the top valence band level and bottom of the conduction band level. The effect of CeO$_2$ doping with B, C, and N on the energy of CB and VB has been investigated [135]. In the case of B doping, the narrower band gap of 3.10 eV in comparison with pure CeO$_2$ (3.20 eV) resulted from a simultaneous shift of the CB and VB to more negative energies in relation to the Fermi level. A similar effect was observed in the case of C doping, although the movement was a little bit smaller than that observed for B doping and resulted in the energy band gap of 3.02 eV. In contrast to B and C doping, N doping caused a shift of the CB and VB towards more positive values while the band gap energy of N-CeO$_2$ was 3.01 eV [135].

CeO$_2$ doping with metals resulted in higher photocatalytic activity due to a better separation of $h^+/e^-$ pairs [26,29]. Metal dopants can act as electron acceptors and/or hole donors and facilitate charge carrier localization (Figure 3).
Figure 3. A schematic diagram of the effects of CeO$_2$ doping with metals (Me) on enhanced photogenerated hole (h$^+$)/photoexcited electron (e$^-$) pair separation.

CeO$_2$ doped with metals and non-metals was successfully applied as a photocatalyst in the degradation of different pollutants which are present in wastewater (Table 2).
Table 2. Photocatalytic degradation of various pollutants with the application of CeO$_2$ doped with metals and non-metals as a photocatalytic material.

| Photocatalyst         | Preparation Method               | Band Gap, eV          | Catalyst Dose | Pollutant, Concentration | Light Source           | Degradation Efficiency (Process Time) | Ref. |
|-----------------------|----------------------------------|-----------------------|----------------|--------------------------|------------------------|----------------------------------------|------|
| F-doped CeO$_2$       | Low temp. solution combustion    | CeO$_2$—3.16 eV,    | 0.375 g/L     | MB, 10 mg/L              | 300 W UV lamp          | CeO$_2$—46% (15 min), F-CeO$_2$—92.1% (6 min) | [136]|
| N-CeO$_2$ Microspheres| Solvothermal synthesis           | CeO$_2$—2.98 eV,    | 0.1 g/L       | Rhodamine 6G, 0.5 g/L    | 1000 W Xe lamp (>420 nm) | CeO$_2$—8.7%, N-CeO$_2$—68.8% (160 min) | [137]|
| N-CeO$_2$             | Wet-chemical route               |                       | MB            |                         | 150 W Xe lamp (>500 nm) | CeO$_2$—9%, N-CeO$_2$—18% (320 min) | [138]|
| C-N-CeO$_2$           | Solvothermal method with hexamethylenetramine | AO7, 0.2 mM, pH = 3 |                |                         | 100 W Hg lamp (HML), 10 W fluorescent lamp (CFL) | HML, CeO$_2$—68.4%, CeO$_2$—TiO$_2$—84%, C-N-CeO$_2$—94.4%, CFL TiO$_2$—43%, CeO$_2$—TiO$_2$—93.3%, C-N-CeO$_2$—98.8% (1 h) | [28]|
| Y-CeO$_2$ Nanorods    | Hydrothermal synthesis           | CeO$_2$—2.68 eV,    | 0.2 g/L       | Carmine indigo (CI)—15.55 mg/L, RhB, 5 mg/L | 450 W Hg lamp          | Cl CeO$_2$—39%, Y-CeO$_2$—58% RhB CeO$_2$—15%, Y-CeO$_2$—35% (100 min) | [82]|
| Y-CeO$_2$             | Nitrate-fuel self-sustaining combustion | CeO$_2$—3.31 eV,    | 1 g/L         | RhB, 1 g/L              | 250 W halogen lamp (532 nm) | 99% (3 h) | [139]|


| Photocatalyst                  | Preparation Method                      | Band Gap, eV | Catalyst Dose | Pollutant, Concentration | Light Source          | Degradation Efficiency (Process Time) | Ref.  |
|-------------------------------|-----------------------------------------|--------------|---------------|--------------------------|-----------------------|---------------------------------------|-------|
| Y-CeO₂                        | Hydrothermal process                    | CeO₂—3.20 eV, Y-CeO₂—3.35 eV | 20 mg spread on glass dish | Acetaldehyde, 500 ppm | LED diode (365 nm) | CO₂ evolution CeO₂—35 ppb, Y-CeO₂—350 ppb (24 h) | [140] |
| CeO₂ (CP) Mg-CeO₂ (CM) Ca-CeO₂ (CC) Sr-CeO₂ (CS) Ba-CeO₂ (CB) | Hydrothermal method                     | 0.05 g/L     | MB, 10 mg/L   | 12 W UV lamp             | CP—33%, CM—60%, CC—68%, CS—75%, CM—84% (120 min) | [141] |
| CeO₂ Ag-CeO₂ Bi-CeO₂ Cd-CeO₂ Pb-CeO₂ | Facile one-step precipitation method   | CeO₂—2.84 eV, Ag-CeO₂—1.86 eV, Bi-CeO₂—2.60 eV, Cd-CeO₂—2.70 eV, Pb-CeO₂—2.25 eV | 0.05 g/L | MB, 30 mg/L | Direct sunlight irradiation | CeO₂—10%, Ag-CeO₂—99.6%, Bi-CeO₂—90%, Cd-CeO₂—90%, Pb-CeO₂—80% (90 min) | [142] |
| Fe-CeO₂                        | Flame spray pyrolysis                   | CeO₂—3.18 eV, Fe(5%)-CeO₂—2.90 eV | 50 mL suspension in ethanol | HCOOH, 500 µg C, (COOH)₂, 500 µg C | 18 W fluorescent lamp (>400 nm) | HCOOH—100%, (COOH)₂—100% | [143] |
| Fe-CeO₂                        | Solvothermal method followed by thermal annealing | CeO₂—2.92 eV, Fe-CeO₂—2.63 eV | 1 cm × 1 cm thin film | MB, 0.5 mM | UV light source (365 nm), 2 mW/cm² | CeO₂—57%, Fe-CeO₂—80% (180 min) | [144] |
| Fe-CeO₂ Hollow microspheres (HMs) | Co-precipitation route                  | CeO₂(HMs)—3.21 eV, Fe-CeO₂(NPs)—3.37 eV, Fe-CeO₂(HMs)—3.10 eV | 0.2 g/L with H₂O₂ (1 mM) | AO7, 20 mg/L | Xe lamp (320–1100 nm) | CeO₂(HMs)—81%, Fe-CeO₂(NPs)—63%, Fe-CeO₂(HMs)—93% (80 min) | [145] |
| Fe-CeO₂                        | Homogeneous precipitation with homogeneous/impregnation method | CeO₂—2.98 eV, Fe(1.5%)-CeO₂—2.64 eV | thin film | MO, 0.025 mM | 50 W halogen lamp, 185 mW/cm² | CeO₂—55%, Fe-CeO₂—14% (120 min) | [26] |
| Photocatalyst      | Preparation Method         | Band Gap, eV | Catalyst Dose | Pollutant, Concentration | Light Source                        | Degradation Efficiency (Process Time) | Ref. |
|--------------------|-----------------------------|--------------|---------------|--------------------------|-------------------------------------|----------------------------------------|------|
| Co-CeO₂            | Co-precipitation method     | CeO₂—3.13 eV, Co(6%)-CeO₂—2.84 eV | 1 g/L         | MB, 15 ppm               | 30 W lamp (365 nm), sunlight (~900 lm/cm²) | UV CeO₂—34.5%, Co(6%)-CeO₂—98.7%, Sunlight CeO₂—34.5% Co(6%)-CeO₂—88.9% (7 h) | [27] |
| Co-CeO₂            | Hydrothermal technique      | 3.3 g/L      | AO7, 0.02 M   | UV light (2 mW) source (365 nm) | 96% (8 h)                           |                                        | [146]|
| La-CeO₂            | Co-precipitation route      | 0.25 g/L, In the presence of NaBH₄ | MB, 0.25 mM   | 500 W halogen lamp (400–600 nm) | La(10%)-CeO₂—99.99% (180 min)       |                                        | [147]|
| In-CeO₂ Nanocrystals | Facile, green hydrothermal method | CeO₂—2.9 eV, In(10%)-CeO₂—2.7 eV | 0.15 g/L      | MO, 15.5 mg/L, MB, 15.5 mg/L | 110 W UV light source               | MO CeO₂—53%, In-CeO₂—92%, MB CeO₂—38%, In-CeO₂—65% (100 min) | [96] |
| Ag-CeO₂            | Co-impregnation and co-precipitation method | CeO₂—3.12 eV, Ag(2%)-CeO₂—2.90 eV, Au(0.4%)-CeO₂—3.04 eV | 0.5 g/L       | Tributyltin, 12 mg/L     | 10 W LED lamp (390 nm)              | CeO₂—20%, Ag-CeO₂—60% (30 h)           | [97] |
| Ag-CeO₂ Au-CeO₃    | Co-precipitation route      | CeO₂—3.12 eV, Ag(2%)-CeO₂—2.90 eV, Au(0.4%)-CeO₂—3.04 eV | 0.25 g/L      | RhB, 1 mg/L              | Uv-Vis light                        | CeO₂—80%, Ag-CeO₂—97.7% (5 h) CeO₂—36%, Au-CeO₂—94.1% (2.5 h) | [29] |

Abbreviations: RhB—rhodamine B; MO—methyl orange; MB—methylene blue; AO7—acid orange 7; and NPs—nanoparticles.
One of the non-metal dopants of CeO$_2$ is nitrogen, which has drawn great attention due to its size similar to oxygen and its relatively low ionization energy [138]. Nitrogen can be doped to other metal oxides, especially those applied in the form of nanomaterials, with the application of a wet-chemical route, high-temperature treatment sintering, and ion implementation [148]. These methods were successfully applied in the case of TiO$_2$. Ceria powder was doped with N by sintering in the presence of NH$_3$ at the temperature of 700 °C and XPS analysis confirmed the introduction of N to a cubic fluorite-type structure of CeO$_2$ [149]. The wet-chemical method was applied in the incorporation of N into CeO$_2$ nanoparticles, resulting in the enhancement of visible light absorption [138]. The degradation of MB proceeded with a clearly higher efficiency under visible light in comparison with the undoped ceria.

Fluorine is another non-metal element applied in ceria doping, performed in order to enhance its photocatalytic activity. F-doped CeO$_2$ nanoparticles were synthesized using low-temperature solution combustion followed by heat treatment in air [136], resulting in the formation of a smaller particle size in the form of nanocubes with a higher percentage of reactive facets. At the same time, the band gap energy was decreased in comparison with the undoped ceria.

The solvothermal method with hexamethylenetetramine as a precipitator was applied in the preparation of CeO$_2$ nanomaterials co-doped with C and N [28]. These nanomaterials exhibited significantly higher photocatalytic activity when tested in acid orange 7 (AO7) photodegradation.

An enhancement of ceria’s photocatalytic activity can also be achieved by doping it with different transition metals characterized by valences lower than 4+ [142]. Such doping usually results in an increase in oxygen vacancies. Ceria nanomaterials doped with Ti, Co, Mn, or Fe were synthesized using a reverse co-precipitation method [150] and their photocatalytic activity was determined in MB photocatalytic degradation. The rate constant of MB degradation calculated for doped ceria nanoparticles (Ce-NP) decreased in the following order: Ce(Co)-NP > Ce(Mn)-NP > Ce(Ti)-NP > Ce(Fe)-NP > Ce-NP. This order is according to a decrease in band gap energy values determined for co-doped ceria materials in comparison to undoped ceria, i.e., 2.69 eV (Ce(Co)-NP), 2.77 eV (Ce(Ti)-NP), 2.78 eV (Ce(Mn)-NP), and 2.81 eV (Ce(Fe)-NP) in comparison to 3.07 eV determined for pristine Ce-NP.

Cobalt-doped ceria obtained in the co-precipitation method was tested in MB photodegradation under UV irradiation and sunlight [27]. In the case of ceria nanoparticles doped with 6% Co, only a slightly lower photodegradation efficiency of MB under sunlight (88.9%) was observed in comparison with the UV-assisted process (98.7%). The hydrothermal method was employed in the synthesis of alkaline metal ion-doped cerium oxide in the form of nanostructures [141]. Mg, Ca, Sr, and Ba were applied as dopants and significantly increased the photocatalytic activity of CeO$_2$, which was proved by the at least two-times higher degradation degree of MB. Similar investigations were carried out with the application of CeO$_2$ doped with Ag, Bi, Cd, and Pb in the form of nanoparticles obtained in a facile one-step precipitation method [142]. Doping resulted in a significantly (at least several times) higher photocatalytic degradation of MB. Among the tested doped ceria, CeO$_2$/Ag exhibited the highest photocatalytic activity, resulting from the highest decrease in the band gap to 1.86 eV, a high stability, a large surface area, and high electrical conductivity.

Fe dopants were introduced to CeO$_2$ in flame spray electrolysis. Fe$^{3+}$ ions could easily substitute Ce ions or could be introduced to interstices of the crystal lattice of CeO$_2$, leading to the formation of donor or acceptor levels between VB and CB [143]. This resulted in a decrease in the band gap from 3.19 eV (pristine CeO$_2$) to 2.90 eV for Fe-doped CeO$_2$ (5% Fe) and an increase in photocatalytic activity. The hierarchically nanoporous structure of CeO$_2$ was also doped with Fe using facile solvothermal synthesis. Doped CeO$_2$ revealed the band gap energy of 2.63 eV, which was lower than that for the undoped CeO$_2$ (2.92 eV) [144]. Application of the doped CeO$_2$ resulted in a higher photocatalytic degradation of methylene blue under VIS irradiation and proved the higher photocatalytic activity of Fe-doped CeO$_2$. Fe-doped CeO$_2$ synthesized with the yeast-templating method exhibited higher photocatalytic activity in acid orange 7 dye photodegradation in the presence of H$_2$O$_2$, which was attributed to more oxygen vacancies, a larger specific surface area, and a smaller band gap [145].
Yttrium-doped CeO₂ in the form of nanorods is also worth mentioning. The photocatalysts were prepared with the application of a hydrothermal method [82]. The doped nanorods exhibited higher photocatalytic activity in dye photodegradation, which was attributed to a lower band gap energy and an increase in oxygen vacancies. In order to enhance the photocatalytic properties of CeO₂, yttrium was also doped to a hedgehog-like hierarchical structure using a common hydrothermal process [144]. During the photocatalytic decomposition of acetaldehyde, the highest amount of CO₂ was detected while the Y dopant amount was the highest (0.747 mmol). Although Y-doped CeO₂ with a hedgehog-like structure exhibited a higher band gap energy (3.35 eV) than pure CeO₂ (3.20 eV), it was characterized by a larger specific surface area and higher concentration of oxygen vacancies.

Lanthanum-doped CeO₂ was found to have superior catalytic properties due to the replacement of Ce⁴⁺ ions with La³⁺ ions. The reactivity of aliovalent-doped ceria (e.g., La³⁺, Eu³⁺, and Sm³⁺) was reported to be significantly higher in CO oxidation reactions in comparison with isovalent (Zr⁴⁺)-doped CeO₂, resulting from the enhancement in oxygen vacancies [151]. Therefore, CeO₂ nanocrystals heavily doped with La³⁺ (10, 20, and 50%) were tested in the photocatalytic degradation of methylene blue under visible light irradiation [147]. La-doped CeO₂ (10% La³⁺) presented the highest photocatalytic activity. In this case, the enhancement of CeO₂ activity was attributed to an increase in the Ce³⁺ concentration. However, there is a final limit of Ce⁴⁺ to Ce³⁺ conversion which cannot be enhanced, even after increasing the dopant amount.

The results of the photocatalytic degradation of various pollutants which can be present in industrial wastewater prove the purposefulness of CeO₂ doping with metal and non-metal dopants. The doping resulted in the following: (1) The formation of surface defects, which prevented electron-hole recombination or decreased recombination rates; (2) an increase in the surface area and a higher number of sites accessible for the adsorption of pollutants on CeO₂ particles; (3) a decrease in the band gap energy, leading to visible light absorption; and (4) higher photocatalytic activity of pollutant degradation.

The amount of doped CeO₂ catalyst applied in the photodegradation process usually does not exceed the value of 0.4 g/L, with a few exceptions, such as when this amount was 1 and 3.3 g/L in the case of Co-doped CeO₂ applied in acid orange 7 degradation (Table 2). Almost all doped CeO₂ photocatalysts were applied in the form of suspension. Only in a few cases were doped photocatalysts immobilized [26, 140, 144], eliminating a subsequent process of photocatalyst removal.

The duration of the photodegradation process is another parameter which attracts attention. Usually, the duration of the process required to achieve a significant decrease in the pollutant concentration is relatively long—about a couple of hours, with the exception of F-doped CeO₂ [136], for which only a 6 min process was enough to remove 91.2% of the methylene blue. However, this was attributed to decolorization of the dye solution, not its mineralization. Total removal of the dye could be confirmed by a significant decrease in total organic carbon (TOC).

Therefore, further development of doped ceria photocatalysts should target not only visible light application in the process, but also a significant decrease in its duration and the elimination of photocatalyst application in the form of a suspension.

3.3. CeO₂ Composite Photocatalysts

During the last two decades, various strategies have been employed to improve the photocatalytic activities of photocatalysts applied in the degradation of different pollutants present in industrial wastewater. These strategies include the formation of a semiconductor heterojunction via the combination of a semiconductor with metal or/and other semiconductors [152]. CeO₂ is often combined with other semiconductor materials in order to decrease e⁻/h⁺ pair recombination and enhance the utilization of sunlight in catalyst photoexcitation.

Generally, four types of heterojunction photocatalysts can be distinguished: (1) The semiconductor–semiconductor heterojunction; (2) the semiconductor–metal heterojunction; (3) the semiconductor–carbon group heterojunction; and (4) the multicomponent heterojunction [152].
The heterojunction between two or more semiconductors is the most common. The coupling of appropriate semiconductors results in an alignment of the band energy levels, which leads to the migration of charges and the creation of an electric field, resulting in an extended lifetime of photogenerated holes and electrons. Three combinations of n-type and p-type semiconductors are possible: (1) n–n heterojunctions; (2) p–p heterojunctions; and (3) p–n heterojunctions [153]. A comparison of CB and VB positions in two coupled semiconductors enables the division of conventional heterojunctions into three types with different gaps: A straddling gap (type I); staggered gap (type II); and broken gap (type III) [154,155].

CeO$_2$ heterojunctions with other semiconductors usually belong to n–n and p–n heterojunctions, e.g., CeO$_2$/TiO$_2$ [156] and CeO$_2$/CuO [157], respectively. Furthermore, CeO$_2$ can form Z-scheme heterojunctions, e.g., Mn$_3$O$_4$/CeO$_2$ [158] and g-C$_3$N$_4$/CeO$_2$ [159]. A Z-scheme heterojunction is formed by two semiconductors with a staggered band structure (type II) and an electron acceptor/donor pair [154]. The photoinduced electrons are transferred to less negative CB and the holes to less positive VB in typical type II heterojunctions, resulting in a lower redox ability of electrons and holes that leads to a lower photocatalytic efficiency [160]. In the case of a Z-scheme heterojunction, the photoinduced electrons in less negative CB and holes in less positive VB can recombine at the heterojunction interface, while electrons and holes with a higher redox ability remain on two respective semiconductors [159]. This results in efficient charge separation and a high redox ability, leading to a higher photocatalytic efficiency.

The above-mentioned types of heterojunctions present in the case of CeO$_2$ composites applied in the photodegradation of different pollutants are presented in the next three subsections.

3.3.1. CeO$_2$ Coupled with TiO$_2$

CeO$_2$ is often coupled with TiO$_2$ due to its oxygen storage ability and photocatalytic activity. The presence of Ce$^{4+}$ and Ce$^{3+}$ oxidation states results in excellent CeO$_2$ characteristics manifesting themselves in transferring electrons and enhancement of the light absorption capability in near ultraviolet and ultraviolet ranges [161]. CeO$_2$ composites with TiO$_2$ also show a higher thermal stability and higher electrical conductivity [162]. In addition to these advantages, CeO$_2$/TiO$_2$ composites can be further improved considering their photocatalytic activity related to their agglomeration, specific surface area, and mass-transfer limitation of target pollutants [161]. Furthermore, the separation of CeO$_2$/TiO$_2$ composite photocatalysts from the solution after the treatment of pollutants requires the application of an additional post-treatment process, which is not easy and is energy consuming [163,164]. These disadvantages can be overcome by an application of CeO$_2$/TiO$_2$ composites in the form of nanofilms or nanotube arrays, which are characterized by a large surface area and more convenient separation of the suspensions.

TiO$_2$/CeO$_2$ composites can be prepared with the application of various methods, such as sol-gel techniques, magnetron sputtering, flame spray pyrolysis, electrodeposition, the hydrothermal method, etc. [31], which significantly affect their properties. In particular, the position of the bottom CB level and top VB level depends on the preparation method and determines the photocatalytic activity of the composite material. The possible photoexcitation of CeO$_2$/TiO$_2$ composites under UV and VIS irradiation is presented in Figure 4.
Table 3.

This leads to the formation of photogenerated holes and electrons in the VB and CB of both pollutant molecules. Simultaneously, photogenerated holes in the VB of TiO$_2$ pairs, leading to a higher photocatalytic activity of the composite materials. The possible photoexcitation of CeO$_2$/TiO$_2$ composites under UV and VIS irradiation is presented in Figure 4.

When a CeO$_2$/TiO$_2$ composite is irradiated by UV light, then both CeO$_2$ and TiO$_2$ are excited. This leads to the formation of photogenerated holes and electrons in the VB and CB of both semiconductors. Due to less negative CB energy in TiO$_2$, photogenerated electrons in CB of CeO$_2$ are easily transferred to the CB of TiO$_2$ and form superoxide anion radicals (O$_2$•−) which react with pollutant molecules. Simultaneously, photogenerated holes in the VB of TiO$_2$ are moved to the VB of CeO$_2$ and produce OH$^+$ radicals which also react with the pollutant molecules. The formation of reactive radicals can be described by the following reactions [165,166]:

\[
\text{TiO}_2 + \text{hv} \rightarrow e_{CB}^{-} + h_{VB}^{+} \quad (16)
\]

\[
\text{Ce}^{4+} + e_{CB}^{-} \rightarrow \text{Ce}^{3+} \quad (17)
\]

\[
\text{Ce}^{3+} + \text{O}_2 \rightarrow \text{Ce}^{4+} + \text{O}_2^{•−} \quad (18)
\]

\[
\text{H}_2\text{O} + h_{VB}^{+} \rightarrow \text{OH}^{•} + H^{+} \quad (19)
\]

\[
\text{O}_2^{•−} + 4\text{H}^{+} \rightarrow 2\text{OH}^{•} \quad (20)
\]

Ce$^{4+}$ species scavenge the excited photoelectrons in TiO$_2$ and limit the recombination of h$^+/e^-$ pairs, leading to a higher photocatalytic activity of the composite materials. When both semiconductors are irradiated with visible light, then CeO$_2$ is predicted to absorb light and generate photoexcited h$^+/e^-$ pairs. The photogenerated electrons are transferred to the CB of TiO$_2$ (Figure 4) [156,167]. This limits the recombination of h$^+/e^-$ pairs and improves the photocatalytic properties of the composite material.

Exemplary applications of CeO$_2$/TiO$_2$ composite materials in the photocatalytic degradation of various pollutants present in industrial wastewater with the main process parameters are presented in Table 3.
Table 3. Photocatalytic degradation of various pollutants with the application of CeO$_2$ composites with TiO$_2$ as photocatalytic material.

| Composite          | Preparation Method                              | Band Gap, eV | Catalyst Dose | Pollutant, Concentration | Light Source                      | Degradation Efficiency (Process Time) | Ref.  |
|--------------------|-------------------------------------------------|--------------|---------------|--------------------------|-----------------------------------|--------------------------------------|-------|
| CeO$_2$/TiO$_2$ NPs | Hydrothermal method                             | TiO$_2$—3.38 eV, CeO$_2$—2.88 eV, CeO$_2$ (10%)/TiO$_2$—2.30 eV | 1 g/L | p-chlorophenol (p-CP), 0.47 mM | 1000 W tungsten lamp (>420 nm), 250 W Hg lamp (365 nm) | UV (CeO$_2$/TiO$_2$) p-CP—95.3%, TOC—85.3% (2.5 h) | [168] |
| CeO$_2$/TiO$_2$     | Hydrothermal method                             | TiO$_2$—3.18 eV, CeO$_2$/TiO$_2$—2.67 eV | 1 g/L | Bromophenol dye | 300 W Xe lamp (>400 nm) | TiO$_2$—6%, CeO$_2$/TiO$_2$—72% (180 min) | [156] |
| CeO$_2$/TiO$_2$ NTA's | Anodization and microwave homogeneous synthesis | TiO$_2$—3.2 eV, CeO$_2$/TiO$_2$—2.72 eV | 1.1 g/L, in the presence of H$_2$O$_2$ | Benzothiophene in n-octane, 200 ppm (sulfur content) | 300 W Xe lamp with UV cut filter | TiO$_2$—35%, CeO$_2$/TiO$_2$—42%, CeO$_2$/TiO$_2$—90% (5 h—desulfurization) | [169] |
| CeO$_2$@TiO$_2$ Core-shell | Hydrothermal route with the Stober method        | CeO$_2$—2.84 eV, TiO$_2$—2.91 eV, CeO$_2$@TiO$_2$—2.73 eV | 1 g/L | RhB, 0.01 mM | 300 W Xe lamp (>400 nm) | CeO$_2$—19%, TiO$_2$—17%, CeO$_2$@TiO$_2$—57% (60 min) | [170] |
| CeO$_2$/TiO$_2$     | Hydrothermal synthesis                          | CeO$_2$—3.18 eV, CeO$_2$/TiO$_2$—2.17 eV | 0.5 g/L | RhB, 1 mM | 15W/G15 T8 (<400 nm, Phillips), 0.15 W/m$^2$, 18W/541M7 (>400 nm, Phillips, 14.5 W/m$^2$) | Solar light—99.89% (8 h), UV—93% (2 h) Antibacterial activity | [17]  |
| CeO$_2$/TiO$_2$ (0.05:1) | Peroxo sol-gel method                          | 0.1 g/L | MB, 10 mg/L | 10 W UVC lamp (254 nm), 18 W Germicidal lamp (>420 nm) | UVC TiO$_2$—77%, CeO$_2$/TiO$_2$—98%, VIS TiO$_2$—85%, CeO$_2$/TiO$_2$—92% (6 h) | [165] |
| CeO$_2$-TiO$_2$/SiO$_2$ | Co-precipitation method                        | TiO$_2$—2.92 eV, CeO$_2$-TiO$_2$/SiO$_2$—2.51 eV | 0.1 g/L | Phenol, 30 mg/L | 330 W solar simulator (300–2500 nm) | TiO$_2$—38%, CeO$_2$/TiO$_2$/SiO$_2$—96.5% (180 min) | [161] |
| Composite | Preparation Method | Band Gap, eV | Catalyst Dose | Pollutant, Concentration | Light Source | Degradation Efficiency (Process Time) | Ref. |
|-----------|--------------------|-------------|---------------|--------------------------|-------------|-----------------------------------|------|
| TiO$_2$/CeO$_2$ Core-shell NTs | Sol-gel technique | 15 L/m$^2$ | MO, 5 mg/L, pH = 3 | 300 W Hg lamp (254 nm) | CeO$_2$—30%, TiO$_2$—70%, TiO$_2$/CeO$_2$—80% (180 min) | [31] |
| Ti$^{3+}$-TiO$_2$/Ce$^{3+}$-CeO$_2$ | Hydrothermal route combined with wet-chemical deposition precipitation and in-situ solid-state chemical reduction | CeO$_2$—3.00 eV, TiO$_2$—3.20 eV, Ti$^{3+}$-TiO$_2$/Ce$^{3+}$-CeO$_2$—2.70 eV | MO, 10 mg/L, MB, 10 mg/L | 300 W Hg lamp (>420 nm) | MO—93.3%, MB—97.1% (180 min) | [30] |
| TiO$_2$@h-CeO$_2$ Yolk-shell microspheres | Calcination method | TiO$_2$—3.22 eV, h-CeO$_2$—2.95 eV, h-CeO$_2$—hollow CeO$_2$ | 0.1 g/L | MB, 0.01 mM | 125 W Hg lamp | MB—50% h-CeO$_2$—14 min, TiO$_2$—13 min, TiO$_2$@h-CeO$_2$—7 min | [171] |
| CeO$_2$@TiO$_2$ | Precipitation-co-hydrothermal method | TiO$_2$—3.15 eV, CeO$_2$—2.73 eV, CeO$_2$@TiO$_2$—2.42 eV | 1 g/L | RhB, 10 mg/L | 500 W Xe lamp, 100 W Hg lamp | UV CeO$_2$—60%, TiO$_2$—82%, CeO$_2$@TiO$_2$—95% (60 min) UV CeO$_2$—58%, TiO$_2$—50%, CeO$_2$@TiO$_2$—75% (180 min) | [172] |
| TiO$_2$@CeO$_2$ | — | 0.4 g/L | CN$^-$, 4.7 mM, pH = 12.5 | 300 W Hg lamp (>420 nm) | CeO$_2$—6.4%, TiO$_2$—25.5%, TiO$_2$@CeO$_2$—96.2% (90 min) | [173] |
| CeO$_2$/TiO$_2$ | Evaporation-induced self-assembly method | TiO$_2$—3.10 eV, CeO$_2$/TiO$_2$—1.85 eV | 1.33 g/L | MB, 10 ppm, 4-chlorophenol (4-CP), 0.1 mM | 300 W tungsten lamp (400–660 nm) | MB TiO$_2$—9%, CeO$_2$/TiO$_2$—75% (3 h) 4-CP TiO$_2$—0%, CeO$_2$/TiO$_2$—66% (3 h) | [162] |
Table 3. Cont.

| Composite               | Preparation Method | Band Gap, eV                  | Catalyst Dose | Pollutant, Concentration                  | Light Source                  | Degradation Efficiency (Process Time) | Ref.   |
|-------------------------|--------------------|-------------------------------|----------------|------------------------------------------|------------------------------|--------------------------------------|--------|
| CeO$_2$–TiO$_2$         | Co-precipitation method | TiO$_2$—2.82 eV, CeO$_2$–TiO$_2$—2.30 eV | 0.1 g/L        | Disopropanolamine (DIPA), 1000 ppm With the addition of H$_2$O$_2$ | 500 W halogen lamp           | DIPA TiO$_2$—66%, CeO$_2$–TiO$_2$—82% COD TiO$_2$—43.2%, CeO$_2$–TiO$_2$—54.8% (5 h) | [174] |
| CeO$_2$–TiO$_2$–NTs     | Hydrothermal method | TiO$_2$–NTs—3.08 eV, CeO$_2$—2.93 eV CeO$_2$–TiO$_2$–NTs—2.64 eV | 0.8 g/L        | MB, 15 mg/L                             | 250 W Hg lamp                 | MB CeO$_2$—10%, TiO$_2$–NTs—92% CeO$_2$–TiO$_2$–NTs—100% COD CeO$_2$–TiO$_2$–NTs—62% (2 h) | [167] |
| CeO$_2$–TiO$_2$         | Hydrothermal route  | TiO$_2$—3.20 eV, CeO$_2$–TiO$_2$—3.23 eV | 0.5 g/L        | Polyvinylpyrrolidone (PVP), 300 mg/L, MB, 20 mg/L | Visible light (400–800 nm), Hg lamp, 41 W/m$^2$ | PVP—VIS—4 h TiO$_2$—4%, CeO$_2$–TiO$_2$—2%, PVP—UV—4 h TiO$_2$—23%, CeO$_2$–TiO$_2$—7% MB—VIS—1.5 h TiO$_2$—6%, CeO$_2$–TiO$_2$—92% MB—UV—1.5 h TiO$_2$—99%, CeO$_2$–TiO$_2$—90% | [175] |
| TiO$_2$–CeO$_2$         | Calcination method | CeO$_2$—2.01 eV, TiO$_2$–3.26 eV TiO$_2$/CeO$_2$—3.28 eV | 0.4 g/L        | Phenazopyridine (PhP), 12 mg/L           | 15 W Hg lamp (254 nm)        | CeO$_2$—17%, TiO$_2$—55%, TiO$_2$/CeO$_2$—66% (20 min) | [166] |

Abbreviations: RhB—rhodamine B; MO—methyl orange; MB—methylene blue; TOC—total organic carbon; COD—chemical oxygen demand; NPs—nanoparticles; NTs—nanotubes; and NTAs—nanotube arrays.
CeO$_2$/TiO$_2$ composites belong to n–n heterojunctions and can also be classified as staggered gap (type II) heterojunctions. Usually, the bang gap of the composite material displays a lower energy than TiO$_2$ or CeO$_2$ (Table 3). Nonetheless, in a few cases, composite materials exhibited a larger band gap than pristine semiconductors, even though their photocatalytic activity in the degradation of pollutants was higher [166,175]. The lower band gap energy enables photoexcitation of the composite materials by visible light irradiation.

The dose of CeO$_2$/TiO$_2$ composites applied in the photodegradation of various pollutants did not exceed the value of 1.3 g/L. The composite materials were applied in a form of suspension and their further removal from the solution was necessary. The duration of the photocatalytic processes was still relatively long—a few hours. Furthermore, the photocatalytic efficiency of the processes performed with the application of visible light was clearly lower than in the presence of more energetic UV light. Determination of TOC or the chemical oxygen demand (COD) proved that mineralization of the solution requires a significantly higher duration of the process than a decrease in the pollutant concentration, leading to the formation of intermediate degradation products [167,168]. This fact is especially important in the case of synthetic dye photodegradation, which is often related to the decolorization of dye solution and does not mean its total degradation.

3.3.2. CeO$_2$-Based Carbon Materials

Although CeO$_2$ displays unique photocatalytic activity and UV absorption, its optical properties can still be enhanced. One of the enhancement methods involves a combination of a semiconductor with carbon supporting materials, such as carbon black, carbon nanotubes, graphene, or graphitic carbon nitride (g-C$_3$N$_4$) [176–178]. In the case of CeO$_2$, graphene oxide or reduced graphene oxide is often applied as a supporting material.

Graphene containing single layers of sp$^2$-bonded carbon atoms packed into a 2D structure exhibits unique properties, such as a large specific surface area (~2600 m$^2$/g), high adsorption ability, significant mobility of charge carriers (200,000 cm$^2$/V·s at room temperature), high electrical conductivity (10$^6$ s/cm), strong mechanical properties, ability of chemical modification, and electrochemical stability [179,180]. Pure graphene exhibits weak absorption for light (~2.3% light over a broad wavelength range), which makes graphene suitable for some optoelectronic applications, but not suitable for efficiently collecting solar light [181]. It was reported that several graphene-based materials presented some photocatalytic activity due to the presence of defects. The common defects in graphene have been identified as heteroatoms (O, N, B, P, etc.) [182]. Small amounts of metal oxide nanoparticles can form a heterojunction that improves the photocatalytic activity of graphene.

Graphene-based materials are characterized by different contents of oxygen, and are formed in consecutive steps starting from graphite, involving deep chemical oxidation to graphite oxide, exfoliation to graphene oxide (GO), and a final partial reduction to reduced graphene oxide (r-GO) [182,183]. The content of O in GO can vary between 40 and 60%, depending on the conditions of chemical oxidation. Graphene oxide reduced to r-GO with the application of physical and chemical methods is characterized by a high density of defects in comparison with graphene. Graphene is regarded as a 0 band gap semiconductor due to the electronic band overlap, while GO and r-GO exhibit behavior of semiconductor materials [182]. GO is a p-type semiconductor with a lower electron mobility and a band gap with an energy in the range of 2.4 to 4.3 eV [180].

Graphitic carbon nitride (g-C$_3$N$_4$) is another carbon compound which can be combined with CeO$_2$. Its structure is similar to graphite and composed of hexagonal rings of carbon atoms with sp$^2$ hybrid bonds [184]. The g-C$_3$N$_4$ is a metal-free photocatalyst with a good chemical and thermal stability under ambient conditions, characterized by non-toxicity, low costs, and facile preparation [185]. Although its photocatalytic efficiency is comparable to TiO$_2$, g-C$_3$N$_4$ suffers from a high recombination rate of h$^+$/e$^-$ pairs and low visible light utilization. Its band gap is characterized by the energy of 2.7 eV and the position of CB and VB at −1.4 and +1.3 eV, respectively [185,186]. The position of CB and VB in CeO$_2$
and g-C$_3$N$_4$ indicates that type II (staggered gap) heterojunctions can be formed between these two semiconductors (Figure 5).

![Figure 5. A schematic diagram of h$^+$/e$^-$ pair separation in CeO$_2$ composites with graphitic carbon nitride (g-C$_3$N$_4$) in a type II heterojunction.](image)

The application of CeO$_2$ composites with GO, rGO, and g-C$_3$N$_4$ in the photodegradation of different pollutants is presented in Table 4.
Table 4. Photocatalytic degradation of various pollutants with the application of CeO₂ composites with carbon materials.

| Composite                  | Preparation Method              | Band Gap, eV         | Catalyst Dose | Pollutant, Concentration | Light Source          | Degradation Efficiency (Process Time)                  | Ref. |
|----------------------------|--------------------------------|----------------------|----------------|--------------------------|-----------------------|--------------------------------------------------------|------|
| rGO-CeO₂                   | Hydrothermal method             | CeO₂ NPs—2.94 eV, rGO-CeO₂—2.91 eV | 1 g/L          | MB, 0.01 mM              | Direct sunlight       | rGO—3.5%, CeO₂ NPs—35%, rGO-CeO₂—72% (50 min)         | [87] |
| rGO/CeO₂                   | In-situ growth and self-assembly approach |                       | 0.3 g/L         | MB, 20 mg/L, with addition of 1 mL 30% H₂O₂ | 500 W tungsten lamp | RGO—7.8%, CeO₂—10%, RGO/CEo₂—74.8% (140 min) | [187] |
| CeO₂ HS/rGO HS—hollow nanospheres | Hydrothermal method            |                      | 0.5 g/L         | MO, 30 mg/L, pH = 6.5 | 800 W Hg lamp     | CeO₂ HS—16%, rGO—22%, CeO₂ HS/rGO—97% (50 min)       | [177] |
| ZnO-CeO₂-rGO Possible H₂ generation in PEC | Hydrothermal process | ZnO-rGO—3.04 eV, ZnO-CeO₂-rGO—2.20 eV | 1 g/L          | MB, 100 mM, pH = 3 | Xe lamp (AM 1.5G filter), 100 mW/cm² | ZnO—20%, ZnO-CeO₂-rGO—90%, TOC—11%, ZnO-CeO₂-rGO—72% (90 min) | [188] |
| rGO-CeO₂ NCs               | Hydrothermal process            | CeO₂ NWs—2.88 eV, CeO₂ NCs—2.76 eV | 0.375 g/L       | MB, 0.01 mM              | 500 W Hg lamp, 40 mW/cm² | CeO₂ NWs—58%, CeO₂ NCs—65%, RGO-CeO₂ NCs—87% (90 min) | [33] |
| CeO₂/Graphene NPs         | Hydrothermal method             | CeO₂ NPs—3.16 eV, CeO₂·Graphene—2.69 eV    | 0.08 g/L        | CR, 5 mg/L, MB, 5 mg/L  | 400 W lamp, (>500 nm) | CR—16%, CeO₂·Graphene—94.5%, MB—Graphene—20%, CeO₂·Graphene—98% (180 min) | [119] |
| UCNCs@SiO₂@CeO₂:Tm/GN GN-graphene Core/shell structure upconversion nanocrystals—UCNCs | Two-step wet-chemical route |                        | 0.4 g/L         | RbB, 20 mg/L             | 500 W Xe lamp (500–2500 nm) | CeO₂—46%, CeO₂·Tm—55%, UCNCs@SiO₂@CeO₂·Tm—82%, UCNCs@SiO₂@CeO₂·Tm/GN—95% (210 min) | [24] |
| Composite | Preparation Method | Band Gap, eV | Catalyst Dose | Pollutant, Concentration | Light Source | Degradation Efficiency (Process Time) | Ref. |
|-----------|--------------------|-------------|---------------|--------------------------|--------------|---------------------------------------|------|
| CuO-CeO$_2$/GO | Dip-molding and ultrasound-assisted process | CeO$_2$—3.28 eV, CuO—2.61 eV | 0.5 g/L | MO, 10 mg/L, with addition of 0.2 mL 3% H$_2$O$_2$ | 300 W Xe lamp (>400 nm) | CuO—65.7%, CuO/CeO$_2$—79.8%, CuO-CeO$_2$/GO—97.8% (150 min) | [189] |
| CeO$_2$/g-C$_3$N$_4$ | Mixing-calcination technique | CeO$_2$—2.89 eV, g-C$_3$N$_4$—2.70 eV | 1 g/L | MB, 10 mg/L 4-CP, 5 mg/L | 300 W Xe lamp (>400 nm) | MB CeO$_2$—2.8% (TOC—16%), g-C$_3$N$_4$—75% (TOC—49%), CeO$_2$/g-C$_3$N$_4$—95% (TOC—81%) (3 h) 4-CP CeO$_2$—15.1%, g-C$_3$N$_4$—2.3%, CeO$_2$/g-C$_3$N$_4$—45% (5 h) | [190] |
| CeO$_2$/g-C$_3$N$_4$ | In-situ co-pyrolysis method | CeO$_2$—2.82 eV, g-C$_3$N$_4$—2.70 eV | 1 g/L | Phenol, 10 mg/L | 500 W Xe lamp (>420 nm) | CeO$_2$—1%, g-C$_3$N$_4$—3%, CeO$_2$/g-C$_3$N$_4$—55%, (5 h) | [191] |
| g-C$_3$N$_4$/CeO$_2$ | Calcination method | CeO$_2$—2.98 eV, g-C$_3$N$_4$—2.78 eV, g-C$_3$N$_4$/CeO$_2$—2.6 eV | 0.06 g/L | MB, 20 mg/L | 50 W fluorescent lamp (>400 nm) | CeO$_2$—8%, g-C$_3$N$_4$—20%, g-C$_3$N$_4$/CeO$_2$—70% (4 h) | [159] |
| g-C$_3$N$_4$/CeO$_2$ | Hydrothermal method | g-C$_3$N$_4$—2.82 eV, CeO$_2$—2.76 eV | 1 g/L | Doxycycline hydrochloride, 0.01 g/L, with addition of 100 µL H$_2$O$_2$ | 150 W Xe lamp (>400 nm) | g-C$_3$N$_4$—66.7%, CeO$_2$—71.7%, g-C$_3$N$_4$/CeO$_2$—84% (1 h) | [192] |
| CeO$_2$/S-doped g-C$_3$N$_4$ (CeO$_2$/CNS) | One-pot thermal condensation method | CNS—2.55 eV, CeO$_2$—2.80 eV | 1 g/L | MB, 10 mg/L | 300 W halogen lamp (>400 nm), 21.9 mW/cm$^2$ | CeO$_2$—39%, CNS—54%, CeO$_2$/CNS—91.4% (150 min) | [193] |
| CeO$_2$/ATP/g-C$_3$N$_4$ | Electrostatic-induced self-assembly method | CeO$_2$/ATP—3.2 eV, g-C$_3$N$_4$—2.7 eV, CeO$_2$/ATP/g-C$_3$N$_4$—2.55 eV | m(catal.)/m(DBT) = 1:10 | Dibenzothiophene (DBT), 200 ppm (sulfur conc.), with addition of 30% H$_2$O$_2$ | 300 W Xe lamp (>420 nm) | Desulfurization g-C$_3$N$_4$—42%, CeO$_2$/ATP/g-C$_3$N$_4$—83%, CeO$_2$/ATP/g-C$_3$N$_4$—98% (3 h) | [194] |
| Composite                     | Preparation Method                          | Band Gap, eV | Catalyst Dose | Pollutant, Concentration | Light Source | Degradation Efficiency (Process Time) | Ref.  |
|-------------------------------|---------------------------------------------|--------------|---------------|--------------------------|--------------|---------------------------------------|-------|
| g-C$_3$N$_4$/CeO$_2$/ZnO      | Pyrolysis and subsequent exfoliation method | 0.375 mg/L   | MB, 10 mg/L   | 5 W fluorescent lamp (>400 nm), 300 W UV lamp | UV ZnO—50%, g-C$_3$N$_4$—40.1%, g-C$_3$N$_4$/CeO$_2$—62%, g-C$_3$N$_4$/CeO$_2$/ZnO—98.9% (25 min), VIS ZnO—22%, g-C$_3$N$_4$—20%, g-C$_3$N$_4$/CeO$_2$—32%, g-C$_3$N$_4$/CeO$_2$/ZnO—52% (4 h) | [195] |
| g-C$_3$N$_4$/α-Fe$_2$O$_3$/CeO$_2$ | Hydrothermal technique                      |              | 50 mg         | MB, 30 ppm               | 500 W Xe lamp (>420 nm) | g-C$_3$N$_4$—36%, g-C$_3$N$_4$/α-Fe$_2$O$_3$—59%, g-C$_3$N$_4$/α-Fe$_2$O$_3$/CeO$_2$—97.5% (120 min) | [196] |

Abbreviations: RhB—rhodamine B; MO—methyl orange; MB—methylene blue; CR—Congo red; TOC—total organic carbon; NPs—nanoparticles; NCs—nanocubes; rGO—reduced graphene oxide; and g-C$_3$N$_4$—graphitic carbon nitride.
CeO₂ composites with graphene (G), GO, or r-GO are mainly prepared with the application of a hydrothermal method, in-situ growth strategy, or two-step wet-chemical route (Table 4). The composites show a lower energy of the band gap than pristine CeO₂, facilitating better utilization of visible light. During irradiation, the photogenerated electrons are quickly transferred from CB in CeO₂ to VB in graphene materials and react with oxygen dissolved in a solution, resulting in the formation of superoxide radicals (O₂⁻) according to the following reactions [119]:

\[
\text{CeO}_2 + \hbar \nu \rightarrow \text{CeO}_2(h^+ + e^-),
\]

\[
\text{CeO}_2(h^+) + \text{H}_2\text{O} \rightarrow \text{CeO}_2 + \text{OH}^* + \text{H}^+,
\]

\[
\text{CeO}_2(h^+) + \text{OH}^- \rightarrow \text{CeO}_2 + \text{OH}^*;
\]

\[
\text{CeO}_2(e^-) + \text{G} \rightarrow \text{CeO}_2 + \text{G}(e^-),
\]

\[
\text{G}(e^-) + \text{O}_2 \rightarrow \text{G} + \text{O}_2^*.
\]

The superoxide and hydroxyl radicals can react with pollutant molecules and mineralize solutions with the formation of simple inorganic products, such as CO₂, H₂O, SO₄²⁻, NO₃⁻, etc. In this way, the recombination rate of photogenerated h⁺/e⁻ pairs in CeO₂ is reduced. CeO₂ composites with G, GO, and r-GO are characterized by a significantly higher photodegradation efficiency of different pollutants [119,177,187], but the duration of degradation processes is still long. These composite materials were mainly tested in the photocatalytic degradation of synthetic dyes at low concentrations. In industrial wastewater, the concentration of dyes can be significantly higher. Taking into consideration the fact that the photodegradation efficiency usually decreases with an increase in the pollutant concentration, the degradation still requires improvement.

CeO₂ composites with g-C₃N₄ are also promising photocatalytic materials with a lower band gap energy [194,195] and significantly higher photocatalytic efficiency in degradation processes [190,191,196]. Considering the position of CB and VB in CeO₂ and g-C₃N₄ (Figure 5), the higher photocatalytic efficiency can be attributed to the transfer of photoexcited electrons and holes between CeO₂ and g-C₃N₄, which suppresses the recombination of photogenerated h⁺/e⁻ pairs. During irradiation, photogenerated electrons on CB in g-C₃N₄ are transferred to CB in CeO₂ and react with O₂, while photogenerated holes on VB in CeO₂ are transferred to VB in g-C₃N₄ and react with H₂O according to the following reactions [192]:

\[
g - \text{C}_3\text{N}_4/\text{CeO}_2 + \hbar \nu \rightarrow g - \text{C}_3\text{N}_4(h^+ + e^-)/\text{CeO}_2(h^+ + e^-),
\]

\[
g - \text{C}_3\text{N}_4(h^+ + e^-)/\text{CeO}_2(h^+ + e^-) \rightarrow g - \text{C}_3\text{N}_4(h^+ + h^+)/\text{CeO}_2(e^- + e^-),
\]

\[
e^- + \text{O}_2 \rightarrow \text{O}_2^*;
\]

\[
h^+ + \text{H}_2\text{O} \rightarrow \text{OH}^* + \text{h}^+.
\]

The superoxide and hydroxyl radicals formed in the above-presented reactions take part in the degradation of pollutants.

In the case of CeO₂ composites with graphene substrates (G, GO, and r-GO) and g-C₃N₄, two problems have still not been resolved. The first one is related to the lower rates of TOC or COD decrease in wastewater in comparison with the degradation rate of pollutants [188,190]. The second one is attributed to the immobilization of a composite photocatalyst, which could eliminate the post-treatment process of photocatalyst removal from the wastewater.

3.3.3. CeO₂ Composites with Other Materials

The photodegradation efficiency of CeO₂ can be enhanced not only by doping or coupling with carbon materials, but also by forming heterojunctions with photocatalysts other than TiO₂.
CeO$_2$ heterojunctions include n–n and p–n semiconductor heterojunctions belonging to the typical type II heterojunctions, and to more effective Z-scheme heterojunctions. Ag$_2$O/CeO$_2$ and CuO/CeO$_2$ composites are examples of a p–n heterojunction. In the p–n heterojunction, holes—the predominant charge carriers in the p-type semiconductor—are transferred to the n-type semiconductor, while electrons—the predominant charge carriers in the n-type semiconductor—are transferred in the opposite direction, i.e., to the p-type semiconductor [153]. When a p-type semiconductor is in contact with an n-type semiconductor, both sides around the interface become depletion layers. An electric field is formed from the n-side (positively charged) to the p-side (negatively charged) and increases the migration rate of photogenerated electrons and holes between semiconductors [197]. The coupling of a p-type semiconductor with an n-type semiconductor not only decreases the recombination of h$^+/e^-$ pairs, leading to a higher photocatalytic efficiency, but also enables the utilization of visible light. Furthermore, the p–n heterojunctions are more efficient than n–n heterojunctions due to a better separation of h$^+/e^-$ pairs.

Another way to improve CeO$_2$’s photocatalytic activity is to construct a Z-scheme heterojunction. A Z-scheme heterojunction can be classified as a type II heterojunction, according to the position of bands, but with different paths of charge carrier migration. When both semiconductors in a Z-scheme heterojunction are irradiated, the photogenerated electrons in the less negative CB in the second semiconductor may migrate to the less positive VB in the first semiconductor and recombine with photogenerated holes (Figure 6). This process results in charge separation within each semiconductor. Simultaneously, the photogenerated electrons in the more negative CB in the first semiconductor maintain their highest redox potential, while the photogenerated holes in the more positive VB in the second semiconductor also maintain their highest oxidation ability [198].

Figure 6. A schematic illustration of different types of Z-scheme heterojunctions: I—Z-scheme with a redox pair mediator; II—Z-scheme with a solid mediator; and III—direct Z-scheme. SC—semiconductor; D—donor; A—acceptor; and SM—solid mediator.

Three types of Z-scheme heterojunctions can be distinguished, depending on the “mediator” facilitating the transfer of electrons between semiconductors [197]:

1. direct Z-scheme—mediator-free;
2. Z-scheme with a solid mediator;
3. Z-scheme with a redox pair mediator.

CeO$_2$ composites with different photocatalysts were applied in the photodegradation of various pollutants and are presented along with the main process parameters in Table 5.
**Table 5.** Photocatalytic degradation of various pollutants with the application of CeO$_2$ composites with other materials.

| Composite | Preparation Method | Band Gap, eV | Catalyst Dose | Pollutant, Concentration | Light Source | Degradation Efficiency (Process Time) | Ref. |
|-----------|-------------------|--------------|---------------|--------------------------|--------------|----------------------------------------|------|
| CeO$_2$/Bi$_2$WO$_6$ | Homogeneous precipitation coupled with the hydrothermal method | CeO$_2$—2.58 eV, Bi$_2$WO$_6$—3.1 eV, 0.4CeO$_2$/0.6Bi$_2$WO$_6$—3.15 eV | 1 g/L | RhB, 0.02 mM | 50 W halogen lamp—simulated solar light | CeO$_2$—10.26%, Bi$_2$WO$_6$—61.46%, 0.4CeO$_2$/0.6Bi$_2$WO$_6$—75.94% (75 min) | [32] |
| CeO$_2$/Bi$_2$WO$_6$ | Precipitation coupled with the hydrothermal method | CeO$_2$—2.93 eV, Bi$_2$WO$_6$—2.86 eV, CeO$_2$/Bi$_2$WO—2.60 eV | 1 g/L | RhB, 0.02 mM, MB, 0.02 mM | 50 W halogen lamp (>400 nm) | CeO$_2$—7.7%, Bi$_2$WO$_6$—9.7%, CeO$_2$/Bi$_2$WO$_6$—54.1% | [100] |
| CeO$_2$/Bi$_2$WO$_6$ | A doctor blading method | CeO$_2$—2.70 eV, Bi$_2$WO$_6$—2.97 eV, 0.4CeO$_2$/0.6Bi$_2$WO$_6$—2.77 eV | 3-layer films controlled by scotch tape | RhB, 0.002 mM | 50 W halogen lamp | CeO$_2$—6.2%, Bi$_2$WO$_6$—37.9%, CeO$_2$/Bi$_2$WO$_6$—44.4% (120 min) | [199] |
| CeO$_2$/Bi$_2$WO$_6$ | Template-assisted synthesis followed by H$_2$ reduction | CeO$_2$—2.92 eV, Bi$_2$WO$_6$—2.68 eV, 0.4CeO$_2$/0.6Bi$_2$WO$_6$—2.75 eV | 0.5 g/L (Cr), 1 g/L (CN) | Cr(VI), 8 mg/L (pH = 5.7), CN$^-$, 4.78 mM (pH = 12.5) | 300 W Xe lamp (>420 nm) | Cr(VI) | CeO$_2$—85.2%, Bi$_2$WO$_6$—91.2%, CeO$_2$/Bi$_2$WO$_6$—99.6% (1 h), CN$^-$ | [200] |
| CeO$_2$/Bi$_2$MoO$_6$ | Molten salt method and ion-impregnation method | CeO$_2$—2.61 eV, BTO—2.91 eV | 1 g/L | Bisphenol A, 10 mg/L | 400 W halogen lamp, 580 mW/cm$^2$ | CeO$_2$—54.8%, BTO—70%, C-BTO—96.8% (60 min) | [201] |
| CeO$_2$/Bi$_2$MoO$_6$ | Solvothermal route | CeO$_2$—2.47 eV, Bi$_2$MoO$_6$—2.86 eV, CeO$_2$/Bi$_2$MoO$_6$—2.76 eV | 1 g/L | CO$_2$ bubbled in ultrapure water | 300 W Xe lamp (>420 nm) | Production | CH$_3$OH—32.5 µmol/g$_{catal}$, C$_2$H$_5$OH—25.9 µmol/g$_{catal}$ (4 h) | [202] |
| Composite                  | Preparation Method                       | Band Gap, eV                        | Catalyst Dose       | Pollutant, Concentration | Light Source                  | Degradation Efficiency (Process Time) | Ref. |
|---------------------------|------------------------------------------|-------------------------------------|---------------------|--------------------------|--------------------------------|---------------------------------------|------|
| Bi₂O₃/CeO₂                | Hydrothermal method                      | CeO₂—3.1 eV, Bi₂O₃—2.84 eV, Bi₂O₃/CeO₂—2.39 eV | Orange II dye, 0.1 mM | 150 W Xe lamp (>400 nm) | CeO₂—26%, Bi₂O₃—27%, Bi₂O₃/CeO₂—55% (5 h) | [203] |
| BiOI/CeO₂                 | In-situ chemical bath method             | CeO₂—2.81 eV, BiOI—1.70 eV         | 1 g/L               | MO, 10 mg/L, Bisphenol A (BPA)—10 mg/L | 300 W Xe lamp (>420 nm) | CeO₂—11.9%, BiOI—55.1%, BiOI/CeO₂—93.8%, (50 min) BPA CeO₂—28.1%, BiOI—55.8%, BiOI/CeO₂—92.0% (90 min) | [204] |
| CeOₓ/BiVO₄                | Hydrothermal and ion-impregnation method | BiVO₄—2.52 eV, CeOₓ(5.7%)/BiVO₄—2.48 eV | 1 g/L               | MB, 0.03 mM               | 100 W lamp (>420 nm)           | BiVO₄—24%, CeOₓ/BiVO₄—61% (150 min) | [205] |
| BiVO₄/CeO₂                | Homogeneous precipitation coupled with the hydrothermal method | CeO₂—2.76 eV, BiVO₄—2.51 eV, BiVO₄/CeO₂—2.46 eV | 1 g/L               | MB, 0.02 mM               | Halogen lamp (>400 nm), 185 mW/cm² | CeO₂—20%, BiVO₄—50%, BiVO₄/CeO₂—90% (30 min) | [206] |
| Ag₃PO₄/CeO₂               | Low-temperature solution combustion followed by annealing | CeO₂—3.2 eV, Ag₃PO₄—2.45 eV          | 0.375 g/L           | MB, 10 mg/L               | 300 W UV lamp, 55 W fluorescent lamp (>400 nm) | UV CeO₂—40.6%, Ag₃PO₄—92.4%, Ag₃PO₄/CeO₂—98.9% (6 min) VIS CeO₂—20.8%, Ag₃PO₄—82.1%, Ag₃PO₄/CeO₂—98% (60 min) | [207] |
| Ag₃PO₄/CeO₂               | Ultrasound-assisted method               | CeO₂—2.98 eV, Ag₃PO₄—2.45 eV, Ag₃PO₄/CeO₂—2.20 eV | 1 g/L               | MB, 10 mg/L               | 300 W Xe lamp | CeO₂—20%, Ag₃PO₄—88%, Ag₃PO₄/CeO₂—95% (40 min) | [208] |
| Composite                  | Preparation Method                                                                 | Band Gap, eV                                  | Catalyst Dose | Pollutant, Concentration                  | Light Source                          | Degradation Efficiency (Process Time)          | Ref. |
|----------------------------|-------------------------------------------------------------------------------------|----------------------------------------------|---------------|------------------------------------------|----------------------------------------|-----------------------------------------------|------|
| Ag/Ag₃PO₄/CeO₂             | Solvothermal method combined with co-precipitation and photoreduction                | CeO₂—2.54 eV, Ag₃PO₄—2.42 eV                | 1 g/L         | CO₂ bubbled in ultrapure water           | 300 W Xe lamp (>420 nm)                 | Production CH₃OH—40 μmol/g cath, C₂H₅OH—30 μmol/g cath (4 h) | [209]|
| AgI/CeO₂                   | Sol-gel auto-combustion method                                                       | CeO₂—2.81 eV, AgI—2.76 eV                   | 0.5 g/L       | RhB, 20 mg/L, Tetracycline (TC), 20 mg/L  | 300 W Xe lamp (>420 nm)                 | RhB CeO₂—20%, AgI 48%, AgI/CeO₂—98% (20 min) TC CeO₂—46%, AgI—74%, AgI/CeO₂—94% (1 h) | [210]|
| Ag₂O/CeO₂                  | Hydrolysis and calcination followed by thermal decomposition                         | CeO₂—2.72 eV, Ag₂O—1.30 eV                  | 1 g/L         | Enrofloxacin (EFA), 10 mg/L              | 300 W Xe lamp (>420 nm)                 | EFA CeO₂—11.7%, Ag₂O—43%, Ag₂O/CeO₂—87.1% (120 min) TOC Ag₂O/CeO₂—66.8% (120 min) | [211]|
| Ag₂CO₃/CeO₂/AgBr           | Hydrolysis and calcination followed by hydrobromic acid corrosion                    | CeO₂—2.72 eV, Ag₂CO₃—2.43 eV, AgBr—2.58 eV | 0.4 g/L       | Levofloxacin, 10 mg/L                    | 300 W Xe lamp (>420 nm)                 | CeO₂—11%, Ag₂CO₃—46%, Ag₂CO₃/CeO₂—69% (60 min) AgBr—45%, CeO₂/AgBr—53%, Ag₂CO₃/CeO₂/AgBr—88% (40 min) TOC—60.98% (80 min) | [212]|
| Fe₂O₃—CeO₂                 | Precipitation method                                                                | CeO₂—2.82 eV, Fe₂O₃—CeO₂—2.1 eV             | 2 g/L         | CR, 25 mg/L                             | 100 W tungsten lamp (>400 nm)           | Fe₂O₃—89%, Fe₂O₃—96% (adsorption—91%)            | [34] |
| Composite | Preparation Method | Band Gap, eV | Catalyst Dose | Pollutant, Concentration | Light Source | Degradation Efficiency (Process Time) | Ref. |
|-----------|-------------------|-------------|---------------|-------------------------|-------------|---------------------------------------|------|
| p-CuO/n-CeO₂ | Combination of ribbon-ignition and calcination methods | CeO₂—2.94 eV, CuO—1.54 eV, CuO/CeO₂—2.59 eV | 0.5 g/L | RhB, 10 mg/L, with addition of 2 mL 50% H₂O₂ | 350 W Xe lamp (>420 nm) | CeO₂—70%, CuO—77%, CuO/CeO₂—86.2% (12 min) | [157] |
| Cu₂S/CeO₂, Ag₂S/CeO₂ | Precipitation method | CeO₂—3.39 eV, Ag₂S—2.00 eV, Ag₂S/CeO₂—2.51 eV, Cu₂S—1.75 eV, Cu₂S/CeO₂—2.62 eV | 1 g/L | Rhodamine 6G—0.01 mM natural sunlight | | CeO₂—70%, CuO—77%, CuO/CeO₂—86.2% (12 min) | [213] |
| CeO₂/V₂O₅, CeO₂/CuO | Thermal decomposition method | CeO₂—3.28 eV, V₂O₅—2.66 eV, CuO—1.83 eV, CeO₂/V₂O₅—2.62 eV, CeO₂/CuO—2.59 eV | 1 g/L | MB, 0.03 mM, Textile effluent | 250 W Philips lamp (532 nm) | | [214] |
| CuBi₂O₄/CeO₂ | Solid state method | CeO₂—3.18 eV, CuBiO₄—1.38 eV, CuBiO₄(30%)/CeO₂(70%)—3.14 eV | 0.5 g/L | CR, 20 mg/L, pH = 7 | 6 W UV lamp (365 nm) | CeO₂—14.92%, CuBi₂O₄—3.13%, CuBi₂O₄/CeO₂—83.08% (100 min) | [215] |
| CeO₂/MgAl | Dispersion of insoluble metal oxides | CeO₂/MgAl—3.2 eV | 1 g/L | Phenol (Ph), 80 ppm, 4-chlorophenol (4-CP), 100 ppm, 2,4,6-trichlorophenol (2,4,6-TCP), 100 ppm | Pen Ray Power Supply lamp (254 nm), 4.4 mW/cm² | Ph—50% (7 h), 4-CP—96% (5 h), 2,4,6-TCP—90% (2 h) | [216] |
| CeO₂/Al₂O₃ | Wet-chemical method | CeO₂—3.0 eV, CeO₂/Al₂O₃—2.85 eV | 50 mg in 5 ppm dye solution | CR, 5 ppm, MO, 5 ppm, pH = 11 | 300 W tungsten lamp | | [217] |
Table 5. Cont.

| Composite          | Preparation Method             | Band Gap, eV                  | Catalyst Dose | Pollutant, Concentration | Light Source                  | Degradation Efficiency (Process Time) | Ref. |
|--------------------|--------------------------------|-------------------------------|----------------|--------------------------|-------------------------------|---------------------------------------|------|
| NiO/CeO₂            | Electrospinning technique      | CeO₂—3.2 eV, NiO—3.5 eV      | 0.375 g/L      | MB, 10 mg/L              | 300 W UV lamp                 | NiO—47.3%, CeO₂—69.2%, NiO/CeO₂—96% (40 min) | [218]|
| CeO₂-ZrO₂ 3DOM—3 dimensionally ordered microporous structure | Sol-gel method combined with the decomposition filling method | CeO₂—2.73 eV, ZrO₂—3.25 eV, CeO₂-ZrO₂—2.44 eV | 1.7 g/L | CR, 50 mg/L | 400 W Xe lamp (>410 nm), 1000 W Xe lamp—simulated sunlight | CeO₂ VIS—55%, Sunlight—53%, UV—55%, ZrO₂ VIS—24%, Sunlight—52%, UV—40%, ZnO—5% (120 min) | [98]|
| CeO₂/SnO₂           | Wet-chemical method            | CeO₂-SnO₂—3.4 eV             | 0.1 g/L        | MB, 0.03 mM              | 250 W lamp (532 nm)           | 80% (150 min)                        | [219]|
| ZnO/CeO₂            | Thermal decomposition method   | ZnO—3.2 eV, CeO₂—3.25 eV     | 1 g/L          | MO, 0.03 mM, MB, 0.03 mM, Phenol (Ph), 0.03 mM, Industrial textile effluent (Ite) | 250 W lamp (532 nm) | ZnO—4.0%, MO—4.2%, MB—4.7%, Pb—1.9%, CeO₂—3.25 eV, ZnO/CeO₂—95.9%, MO—95.9%, MB—97.4%, Ph—96.2%, ZnO/CeO₂—95.9%, ZnO—38% (150 min) Ite—ZnO/CeO₂ TOC—90.2% (6 h) | [220]|
| ZnO/CeO₂            | Wet chemistry method with the calcination technique | ZnO—3.13 eV, CeO₂—2.86 eV | 0.5 g/L | RhB, 10 mg/L | 300 W Xe lamp (>400 nm), 0.95 mW/cm² | CeO₂—56%, ZnO—38%, ZnO/CeO₂—96% (80 min) | [158]|
### Table 5. Cont.

| Composite | Preparation Method | Band Gap, eV | Catalyst Dose | Pollutant, Concentration | Light Source | Degradation Efficiency (Process Time) | Ref. |
|-----------|--------------------|-------------|---------------|--------------------------|--------------|----------------------------------------|------|
| CeO$_2$-ZnO-TiO$_2$ | Sol-gel method | CeO$_2$—ZnO-TiO$_2$—3.13 eV | 0.2 g/L | RhB, 5 mg/L | 300 W tungsten lamp (8500 lumen) | 80% (180 min) | [221] |
| Mn$_3$O$_4$/CeO$_2$ | One-step hydrothermal method | CeO$_2$—2.94 eV, Mn$_3$O$_4$—2.02 eV, Mn$_3$O$_4$/CeO$_2$—2.25 eV | 0.67 g/L | RhB, 10 mg/L | 300 W Xe lamp | CeO$_2$—60%, Mn$_3$O$_4$—50%, Mn$_3$O$_4$/CeO$_2$—93% (180 min) | [222] |
| Tm$^{3+}$:CeO$_2$/palygorskite | Hydrothermal-deposition method | Tm$^{3+}$:CeO$_2$—2.92 eV, Pal—3.5 eV | 0.5 g/L | Bisphenol A | 300 W Xe lamp (>420 nm) | Pal—32%, CeO$_2$/Pal—33%, Tm$^{3+}$:CeO$_2$/Pal—86% (180 min) | [223] |
| CeO$_2$/CdS-DETA | Two-step hydrothermal method | CeO$_2$—3.07 eV, CdS-DETA—2.33 eV | 0.5 g/L, with 0.6% Pt as co-catalyst | 0.35 M Na$_2$S + 0.25 M Na$_2$SO$_3$ | 300 W Xe lamp (>420 nm) | H$_2$ production, 14.84 mmol/(g·h) | [79] |
| CeO$_2$/CdS | Electrochemical method | 0.5 g/L | 0.43 M Na$_2$S + 0.5 M Na$_2$SO$_4$ | 300 W Xe lamp, UV or VIS (>420 nm) | H$_2$ formation UV 0.782 mmol/(g·h), VIS 0.223 mmol/(g·h) | [224] |

**Abbreviations:** RhB—rhodamine B; MO—methyl orange; MB—methylene blue; CR—Congo red; and TOC—total organic carbon.
CeO$_2$ composites with Bi$_2$WO$_6$, Bi$_2$MoO$_6$, BiVO$_4$, Bi$_4$Ti$_3$O$_{12}$, ZnO, and Ag$_2$S belong to n–n heterojunctions which are prepared with the application of hydrothermal, solvothermal, or precipitation methods (Table 5). CeO$_2$/Bi$_2$WO$_6$ composites obtained in the precipitation method coupled with a hydrothermal route were applied in rhodamine B (RhB) dye degradation. Although the same amount of catalyst was applied and the concentration of dye was the same, the degradation efficiency was 76% [32] and 54% [100], and it was achieved in a process lasting 75 min. The higher efficiency was observed in the case of the composite with the band gap energy of 3.15 eV, while a lower efficiency was achieved with the composite photocatalyst with 2.60 eV. The differences in the degradation efficiency can be attributed to the different contents of the two semiconductors, i.e., CeO$_2$ and BiWO$_6$ in the composite photocatalysts. The method of preparation also plays an important role in the composite photocatalyst activity. CeO$_2$/Bi$_2$WO$_6$ prepared with a doctor blading method exhibited a band gap energy of 2.77 eV [199], but the degradation efficiency of RhB with a ten-fold lower concentration was only 44% in a process lasting 2 h. The lower degradation resulted not only from a different preparation method, but also from immobilization of the composite. The photocatalyst was applied in the form of a 3-layer film controlled by scotch tape, which eliminated the post-treatment process of photocatalyst removal. Nonetheless, the immobilization of a photocatalyst often results in its lower degradation efficiency.

CeO$_2$ composites with ZrO$_2$, Cu$_2$S, CuO, Cu$_2$Bi$_2$O$_6$, Bi$_2$O$_3$, BiOI, Ag$_2$O, and NiO are classified as p–n heterojunctions. CuO enables the utilization of solar energy due to its narrow band gap. It presented a relatively high photodegradation efficiency of 86.2% in RB dye treatment in only a 12 min process under visible light irradiation [157]. The degradation of Congo red dye with the application of Cu$_2$Bi$_2$O$_6$/CeO$_2$ required UV irradiation, in order to achieve a comparable photodegradation efficiency in the process lasting 100 min [215]. The photodegradation of Rh 6G dye was performed under natural sunlight with the application of a Cu$_2$S/CeO$_2$ photocatalyst and resulted in a 44% degradation efficiency during a 4 h process. The results obtained in the presence of Cu$_2$S/CeO$_2$ were compared with the results of the process carried out in the presence of an n–n-type photocatalyst—Ag$_2$S/CeO$_2$. Under the same conditions, the photodegradation of Rh 6G was lower and totaled only 30% [213].

The photodegradation efficiency of a BiOI/CeO$_2$ composite in the degradation process of MO was significantly higher (94%) in a 50 min process [204], while the lower removal of Orange II dye (55%) in the presence of Bi$_2$O$_3$/CeO$_2$ required a process duration of 5 h [203]. However, it is worth noting that the concentration of Orange II was at least 3.5-times higher than the MO concentration and could limit the penetration of visible light inside the solution.

A CeO$_2$/ZrO$_2$ composite photocatalyst was tested in Congo red (CR) photodegradation of Congo red dye under UV, VIS, and sunlight irradiation. This photocatalyst exhibited a comparable degradation efficiency in the process under UV and sunlight irradiation, while the process under VIS irradiation resulted in a slightly higher efficiency (68%) [98]. The authors proved the possibility of simultaneous hydrogen generation.

The Z-scheme heterojunction seems to be an interesting alternative to n–n and p–n heterojunctions. The coupling of CeO$_2$ with Mn$_3$O$_4$, Ag$_2$CO$_3$, AgBr, ZnO, Ag$_3$PO$_4$, or Bi$_2$WO$_6$ can result in the formation of a Z-scheme heterojunction under specific conditions. Z-scheme system photocatalysts with CeO$_2$ were applied under visible light irradiation (Table 5) in the photodegradation of dyes and pharmaceuticals, in the photoreduction of CO$_2$, and in hydrogen photocatalytic generation. The comparison of Z-scheme junction application in photodegradation processes indicates its higher photodegradation efficiency in comparison with pristine photocatalysts due to the better separation of $h^+$/e$^-$ pairs and the presence of electrons with a higher redox potential and holes with a higher oxidation ability. RhB dye photodegradation proceeded with almost a two-times higher efficiency in the presence of ZnO/CeO$_2$ [158] and Mn$_3$O$_4$/CeO$_2$ photocatalysts [222] in comparison with pristine CeO$_2$, ZnO, and Mn$_3$O$_4$. Levofloxacin, which is a pharmaceutical, and Bisphenol A, which is a compound applied in the production of plastics and epoxy resins, were also photodegraded with a higher efficiency with the application of Ag$_2$CO$_3$/CeO$_2$/AgBr and Tm$^{3+}$-CeO$_2$/palygorskite [212,223]. A high photodegradation
efficiency was achieved in the process lasting about 1 h, except for Tm\(^{3+}\)-CeO\(_2\)/palygorskite and Mn\(_2\)O\(_4\)/CeO\(_2\) photocatalysts, which required a 3 h process to achieve about a 90% efficiency.

CeO\(_2\) composites are not only applied in the photodegradation of organic pollutants. Hollow magnetic microcapsules—CeO\(_2@\)Bi\(_2\)WO\(_6\)—were applied in the photodegradation of Cr(VI) and cyanides [200]. The photocatalyst dose of 0.5 and 1 g/L was enough to achieve a 99.6% removal of Cr(VI) and 98.3% removal of cyanide, respectively, during a process lasting 1 h. CeO\(_2@\)Bi\(_2\)MoO\(_6\) was applied in the photoreduction of CO\(_2\) into CH\(_3\)OH and C\(_2\)H\(_5\)OH [202]. The yield of CH\(_3\)OH and C\(_2\)H\(_5\)OH was 32.5 and 25.9 \(\mu\)mol/g\(_{catal.}\), respectively. A higher yield (40 and 30 \(\mu\)mol/g\(_{catal.}\)) was achieved in the case of the Ag/Ag\(_3\)PO\(_4\)/CeO\(_2\) photocatalyst used in CO\(_2\) photoreduction lasting 4 h, similar to the case of the previous composite material [209].

Another application of CeO\(_2\) composites occurs in the photocatalytic generation of hydrogen with the utilization of renewable resources. A CeO\(_2\)/CdS composite photocatalyst was applied in the process performed under UV and VIS irradiation [224]. The hydrogen evolution rate was 3.5-times higher when CeO\(_2\)/CdS was irradiated with visible light (\(\lambda > 420\) nm). A significantly higher hydrogen evolution rate was observed in a process with the application of CeO\(_2\)/CdS-DETA (DETA—diethylenetriamine) under visible irradiation [79] and was attributed to large active sites of oxygen vacancies in CeO\(_2\), excellent electron transfer between CdS-DETA and CeO\(_2\), and anti-photocorrosion. The possibility of hydrogen generation is important because this process is plausible in a performance with the simultaneous degradation of pollutants.

The examples of CeO\(_2\) composite materials applied in the photodegradation of various pollutants show a relatively high photocatalytic efficiency estimated as the degradation of a pollutant, but not the mineralization of a solution. Only in a few cases was the mineralization of a pollutant solution presented by the determination of TOC. The photodegradation efficiency of levofloxacin performed with the application of a ternary photocatalyst—Ag\(_2\)CO\(_3\)/CeO\(_2\)/AgBr—resulted in an 88% degradation of the pollutant achieved in a 40 min process, while a 61% decrease in TOC required a process lasting two-times longer [212]. Furthermore, CeO\(_2\) composite materials were mainly tested in model solutions of different pollutants and not in real industrial wastewater, with a few exceptions. In the case of ZnO/CeO\(_2\) photocatalyst applied in the photodegradation of industrial textile effluent, a 90% decrease in TOC required a 6 h process, while the degradation of MO, MB, and phenol was above 96% in 2.5 h photodegradation [220]. Similarly, the application of CeO\(_2\)/CuO composite material in the photodegradation of industrial textile effluent resulted in its 86% degradation, determined as a change in UV-VIS absorbance spectra during a 5 h process [214]. These examples show that the photodegradation of pollutant mixtures present in industrial wastewater is more difficult than in a model solution of a single pollutant, and mineralization (not only the removal of a pollutant) requires a significantly higher duration in terms of the treatment process.

### 3.4. CeO\(_2\) as a Photoelectrocatalyst Applied in Pollutant Degradation

Photocatalytic (PC) treatment techniques are tested in the degradation of model solutions of various inorganic and organic pollutants, but also in the case of industrial effluents. As was presented in the previous sections, the photocatalytic degradation of pollutants can be performed with the application of a pristine CeO\(_2\) photocatalyst or composite photocatalysts including CeO\(_2\). However, PC treatment requires a relatively long process duration in order to achieve a high removal efficiency. Usually, total removal of a pollutant does not mean its total degradation, but only its transformation to other less toxic or sometimes more toxic compounds in photocatalytic treatment. This effect is especially related to the PC degradation of synthetic dyes. Their PC treatment leads to the decolorization of wastewater, but not to complete mineralization. Complete mineralization is achieved when a significant decrease in TOC is observed. A TOC decrease requires a significantly longer duration in terms of the treatment process than decolorization. Furthermore, PC treatment requires an additional post-treatment process for photocatalyst removal. The duration of the process and the necessity of photocatalyst removal are the two main factors leading to the combination of PC with an electrocatalytic (EC) treatment.
The combination of these two processes should result in the higher efficiency of pollutant degradation and the elimination of post-treatment removal of the photocatalyst. Photocatalysts can be immobilized on the surface of an electrode—an anode or cathode applied in the process.

Electrocatalytic techniques have been tested in industrial wastewater treatment containing organic and inorganic pollutants in the past several years. EC oxidation of pollutants seems to be more common than electroreduction and can be performed directly or indirectly [225]. The direct electrooxidation of pollutants usually results in a poor efficiency. Therefore, indirect electrooxidation by electrochemically generated oxidants, i.e., reactive oxygen species (ROS), especially hydroxyl radicals, is applied more often [226–228]. The EC treatment is also characterized by several disadvantages. The complete degradation of pollutants requires the so-called “deep electrooxidation” with the application of high voltages or current densities, resulting in high treatment costs [229]. Hence, it seems to be purposeful to combine the EC process with PC treatment. The photoelectrocatalytic (PEC) treatment of wastewater can be performed with a photoanode or photocathode—a photocatalyst (semiconductor) immobilized on a conducting support—and the concurrent application of UV or VIS irradiation simultaneously with the bias potential [230–234]. The treatment efficiency can also be increased by the application of commonly used electrode materials and the suspension of photocatalysts in wastewater. However, in this case, the post-treatment removal of photocatalysts is not eliminated.

The PEC treatment of pollutants present in industrial wastewater includes heterogeneous photocatalysis and simultaneous electrocatalysis with a biased potential or current applied to a photoelectrode. The pollutant removal depends on the different radicals formed in both photocatalytic and electrocatalytic processes. Therefore, the efficiency of the photoelectrocatalytic degradation process depends on the operation parameters affecting both photochemical and electrochemical processes. In addition to the photoelectrode type, these parameters include the (1) light source and its intensity, (2) external bias potential or current, (3) solution pH, (4) supporting electrolyte related to the solution conductivity, (5) concentration of a pollutant, (6) type of counter electrode, and (7) design of the photoelectrochemical reactor [102,105,235,236].

The degradation of various pollutants from industrial wastewater observed in a photoelectrocatalytic process can be monitored by control parameters, including [105,235]

1. The decolorization degree determined by UV/VIS spectrophotometry:

\[
\text{Decolorization(\%)} = \frac{A_0 - A_t}{A_0} \times 100, \quad (30)
\]

where \(A_0\) and \(A_t\) represent the initial and final absorbance determined in a treated solution, respectively;

2. Pollutant removal:

\[
\text{Removal(\%)} = \frac{C_0 - C_t}{C_0} \times 100, \quad (31)
\]

where \(C_0\) and \(C_t\) represent the initial and final concentration of a pollutant, respectively;

3. TOC and COD removal:

\[
\text{TOC(\%)} = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_t} \times 100, \quad (32)
\]

\[
\text{COD(\%)} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_t} \times 100, \quad (33)
\]

where \(\text{TOC}_0\) and \(\text{TOC}_t\) represent the initial and final values of total organic carbon, respectively, and \(\text{COD}_0\) and \(\text{COD}_t\) represent the initial and final values of the chemical oxygen demand, respectively;

4. The electrical energy consumption per mass, which constitutes the main part of the operating costs:

\[
E_{EM} = \frac{P \times t \times 10^6}{V \times (C_0 - C_t)}, \quad (34)
\]
where $P$ is the rated power (kW) of the system; $V$ is the volume of treated wastewater (L); $t$ is the treatment time (h); and $C_0$ and $C_t$ represent the initial and final mass concentrations of a pollutant in mg/L, respectively. The decolorization degree is a parameter applied in the case of colored pollutant solutions, especially dye solution. Sometimes, absorbance values are used in the determination of the pollutant concentration. TOC and COD parameters are applied in the assessment of the mineralization of organic pollutant solution, which means pollutant conversion to CO$_2$. The electrical energy consumption constitutes the main part of the operating costs.

Some operational and control parameters of photoelectrocatalytic processes performed with the application of CeO$_2$ composites applied as photoelectrodes are presented in Table 6.
Table 6. Application of CeO$_2$ composites as photoelectrodes in photoelectrocatalytic (PEC) processes.

| Photoelectrode                  | Preparation Method | Counter Electrode | Pollutant, Concentration | Supporting Electrolyte | Light Source, Applied Voltage/Current | Degradation Efficiency (Process Time) | Ref. |
|---------------------------------|--------------------|-------------------|--------------------------|------------------------|--------------------------------------|--------------------------------------|------|
| CeO$_2$/TiO$_2$ NTAs            | Electrodeposition method | Pt                | MO, 5 mg/L               | 0.1 M Na$_2$SO$_4$     | 350 W Xe lamp, 2.0 V vs. SCE        | EC—23.2%, PC—56.5%, PEC—98.1% (60 min) | [237] |
| EG-CeO$_2$                      | Impregnation ultrasonic agitation  | Pt foil           | 2,4-DCP, 50 mg/L         | 0.1 M Na$_2$SO$_4$, pH = 6.2 | 350 W Xe lamp (AM 1.5G filter), 0.1 W/cm$^2$, 8 mA/cm$^2$ | PEC—98.7%, TOC—92.6% (3 h, 8 mA/cm$^2$), PC—43.9%, PEC—85.7% (3 h, 2 mA/cm$^2$) | [238] |
| rGO-CeO$_2$-TNAs                | Galvanostatic method | Pt foil           | BPA, 10 mg/L             | 0.05 M Na$_2$SO$_4$    | 500 W Xe lamp (>365 nm), 110 mW/cm$^2$, 9 V | Fenton—30%, EC-Fenton—30%, P-Fenton—55%, PC-Fenton—72%, PEC-Fenton—82% (120 min) | [239] |
| rGO-CeO$_2$-TiO$_2$ NTAs        | Galvanostatic method | Pt foil           | Tetrabromobisphenol A, 10 mg/L | 0.05 M Na$_2$SO$_4$    | 500 W Xe lamp, simulated solar light—110 mW/cm$^2$, 9 V vs. SCE | TiO$_2$—85.3%, CeO$_2$/TiO$_2$—90.3%, PANI/CeO$_2$/TiO$_2$—86.8%, PANI/TiO$_2$—94.0% (2 h) | [240] |
| PANI/CeO$_2$/TiO$_2$ NTAs PANI—polyaniline | Electrochemical method | Pt foil           | Tetrabromobisphenol A, 10 mg/L | 0.05 M Na$_2$SO$_4$    | 500 W Xe lamp, 120 mW/cm$^2$, 9 V vs. SCE | TiO$_2$—85.3%, CeO$_2$/TiO$_2$—90.3%, PANI/CeO$_2$/TiO$_2$—86.8%, PANI/TiO$_2$—94.0% (2 h) | [241] |
| CeO$_2$ QDs/Ag$_2$Se            | Precipitation route | Pt plate          | Tetracycline, 0.02 g/L   | 0.1 M Na$_2$SO$_4$     | 8 W halogen lamp (400–790 nm), 80 lm/W, 0.5 V vs. SCE | EC—27.7%, PC—92.3% (90 min), PEC—95.8% (75 min) | [242] |
| CeO$_2$@α-Fe$_2$O$_3$ NTAs      | Electrodeposition method | Pt foil           | Tetracycline, 30 mg/L, pH = 13 | 0.1 M NaOH            | 300 W Xe lamp (AM 1.5G filter), 100 mW/cm$^2$, 1.5 V vs. Ag/AgCl | PC—15.6%, PEC—88.6% (1 h) | [243] |
| Photoelectrode                        | Preparation Method | Counter Electrode | Pollutant, Concentration | Supporting Electrolyte | Light Source, Applied Voltage/Current | Degradation Efficiency (Process Time) | Ref.  |
|-------------------------------------|-------------------|------------------|---------------------------|------------------------|--------------------------------------|--------------------------------------|-------|
| Ti/SnO$_2$-Sb-CeO$_2$@TiO$_2$-SnO$_2$ | Sol-gel route     | Pt               | MB, 20 ppm                | 10 g/L Na$_2$SO$_4$    | 500 W Xe lamp, 60.2 mW/cm$^2$, 1.5 V | EC—63.1%, PC—84.2%, PEC—95.8% (2 h) | [244] |
| Ce/Ce$_2$O$_2$/CeO$_2$/TiO$_2$ TNAs | Electrochemical anodization | Pt grid          | 0.1 M Na$_2$SO$_4$ + 10vol% ethylene glycol | 450 W Xe lamp, 100 mW/cm$^2$, 0.7 V vs. OCP | H$_2$ generation UV TNTs—2.6 mL (h·cm$^2$), TNTs-Ce-CeO$_x$—5.0 mL/(h·cm$^2$) VIS TNTs—1.2 mL/(h·cm$^2$), TNTs-Ce-CeO$_x$—2.9 mL/(h·cm$^2$) | | [109] |
| ns-TiO$_2$/CeO$_2$/Ti ns-nanostructured | Sol-gel process    | Pt               | H$_2$SO$_4$ + K$_2$SO$_4$ | 100W Xe lamp, 450 mW/cm$^2$ | H$_2$ generation ns-TiO$_2$—8.2 l/(h·m$^2$), ns-TiO$_2$-Ce-CeO$_x$—13.8 l/(h·m$^2$) | | [245] |
| CeO$_2$/CuO/Cu                     | Electrochemical method | Pt               | CO$_2$, Flow rate—40 mL/min | 0.1 M KHCO$_3$ | 500 W Xe lamp (420–800 nm), 100 mW/cm$^2$, −1.0 V vs. SCE | Methanol yield in µmol/(cm$^2$) | [246] |
| CeO$_2$/Cu$_2$O                   | Deposition route   | Pt gauze         | 0.1 M NaOH                | 150 W Xe lamp, 0.7 V vs. SCE | H$_2$ generation 3.62 mL/h | | [23] |

Abbreviations: MO—methyl orange; MB—methylene blue; BPA—bisphenol A; TOC—total organic carbon; DCP—dichlorophenol; NTAs—nanotube arrays; OCP—open circuit potential; TNAs—TiO$_2$ nanotube arrays; rGO—reduced graphene oxide; P—photolysis; PC—photocatalysis; EC—electrocatalysis; and PEC—photoelectrocatalysis.
CeO\textsubscript{2} composite materials immobilized on fluorine-doped tin oxide glass (FTO), indium tin oxide glass (ITO), or other substrates can be applied as photoelectrodes in the PEC process of hydrogen evolution. This process is important considering the possible simultaneous degradation of pollutants and \(\text{H}_2\) generation. Ce/\(\text{CeO}_2\)/\(\text{CeO}_2\)/\(\text{TiO}_2\) \(\text{TiO}_2\) nanotube arrays (TNAs) and \(\text{TiO}_2\)/\(\text{CeO}_2\)/\(\text{Ti}\) photoelectrodes were applied in hydrogen generation from different electrolytes under UV and VIS irradiation \([109,245]\). A higher hydrogen evolution rate was observed at the composite electrodes in contrast to single component electrodes. This effect was attributed to the better charge separation and improved light absorption ability. The CeO\textsubscript{2}/CuO composite (p–n heterojunction) deposited on ITO was also successfully applied in hydrogen evolution from 0.1 M NaOH solution in the PEC process \([23]\) with the hydrogen evolution rate of 3.62 mL/h. The p–n composite—CeO\textsubscript{2}/CuO—deposited on the Cu substrate was used in \(\text{CO}_2\) photoelectrocatalytic reduction and methanol generation \([246]\). In this case, the PEC process exhibited a 4- and 2.4-times higher yield in comparison to the PC and EC process, respectively.

The CeO\textsubscript{2} composite materials were also applied in the PEC degradation of different pollutants, even though PEC processes are not as common as PC degradation. Composites of CeO\textsubscript{2} with exfoliated graphite (EG) and reduced graphene oxide co-modified with TiO\textsubscript{2} were used in the PEC degradation of 2,4-dichlorophenol, bisphenol A, and tetrabromobisphenol A. The PEC degradation of 2,4-dichlorophenol exhibited a clear synergic effect of EC and PC, resulting in a high photodegradation degree of 99% being achieved in a 3 h process \([238]\). It is worth noting that the TOC decrease was only slight lower and totaled 93%, while such a high decrease in the TOC value observed in the PC process required a significantly longer duration for the PC process, as was presented in the previous section. An RGO-CeO\textsubscript{2}-TiO\textsubscript{2} photoanode was applied in the PEC process combined with a Fenton reaction \([239]\). The EC process or Fenton reaction as a separate process resulted in a degradation efficiency of bisphenol A that was not higher than 30%. However, the combination of EC, PC, and the Fenton reaction increased the degradation efficiency to 82%. A similar composite photoelectrode was used in tetrabromobisphenol A treatment and the degradation efficiency was even higher (87%) without a Fenton reaction, in a process 20 min shorter than in the previous case \([240]\). The higher degradation efficiency was attributed to improved hole-electron separation by applying bias potential. Tetracycline was degraded in the PEC process with two novel photoelectrodes—Ce\textsubscript{2}O\textsubscript{3}@\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} and CeO\textsubscript{2} QDs/Ag\textsubscript{2}Se—both representing a Z-scheme heterojunction \([242,243]\). The Z-scheme band structure in both composite materials promoted the separation and transfer of photogenerated charges and accelerated the surface redox reaction of tetracycline molecules. Furthermore, in the case of the CeO\textsubscript{2}@\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} photoelectrode, its photocorrosion was inhibited, resulting in an enhancement of its photocatalytic stability. The PEC degradation of methyl orange with the application of the CeO\textsubscript{2}/TiO\textsubscript{2} photoelectrode confirmed that the PC process combined with EC degradation results in a higher efficiency of pollutant removal achieved in a shorter time. A degradation efficiency higher than 98% was achieved during the photoelectrocatalytic oxidation of methyl orange in the process lasting 1 h.

Although PEC processes represent a promising method of pollutant removal from industrial wastewater, they still require improvement in order to increase the stability of photoelectrodes, facilitate natural solar light utilization instead of UV or VIS light irradiation, and decrease process costs.

4. Conclusions and Future Perspectives

An overview of the CeO\textsubscript{2} photocatalyst and its composites with other materials applied in the photocatalytic and photoelectrocatalytic treatment of various pollutants present in industrial wastewater has been presented. The characteristics of ceria as a photocatalyst have also been described. Examples of CeO\textsubscript{2} and its composite materials with the main experimental conditions and results of pollutant degradation were included in the presentation of the advantages and disadvantages of photocatalytic and photoelectrocatalytic processes.

Photocatalysis and photoelectrocatalysis seem to be promising options for solving environmental pollution and energy shortage issues. Nonetheless, these processes require further enhancements.
One of the possible development directions is associated with the application of properly selected photocatalytic or photoelectrocatalytic material. The application of CeO$_2$ in the photocatalytic and photoelectrocatalytic treatment of industrial wastewater requires further investigations, which should focus on the following aspects:

(1) The development of CeO$_2$ composites which are highly efficient, stable, and visible light- or sunlight-active, and are characterized by a proper band gap structure and energy for redox reactions, a high photostability during long-term utilization, and scalability, making their commercial implementation possible;

(2) The development of simple and low-cost procedures for CeO$_2$-based photocatalyst manufacturing, with special attention given to morphology control, an increase in the active surface area, and CeO$_2$ immobilization on a substrate in order to remove it from wastewater easily and ensure electrical conductivity in the case of photoelectrodes;

(3) CeO$_2$ application in combination with the photocatalytic or electrocatalytic treatment of wastewater with simultaneous electricity and hydrogen generation.

During the last two decades, many studies on the possible application of CeO$_2$ and its composites in pollutant treatment have been reported. However, the concentrations of pollutants which have been considered have been relatively low and have not reflected the real concentrations observed in industrial wastewater. An increase in pollutant concentrations usually results in a degradation efficiency decrease. Furthermore, wastewater with a strong color, e.g., containing dyes, hinders the penetration of UV or VIS light irradiation inside solutions. These issues also need attention and problem-solving.

The optimization of photocatalytic and photoelectrocatalytic processes with CeO$_2$ applied in wastewater treatment should involve not only the removal of pollutants, but also a COD and/or TOC decrease in the treated effluent containing organics. Toxicity control and the enhancement of wastewater biodegradability during treatment processes should also be considered.

The coupling of heterogeneous photocatalysis with electrocatalysis presents advantages over single processes. The photoelectrocatalytic treatment of pollutants proceeds with a higher efficiency in comparison to photocatalytic and electrocatalytic degradation performed under similar conditions. The proper choice of composition of CeO$_2$-based photoelectrode materials is very important in order to achieve the optimal degradation of pollutant under mild conditions. The development of these photoelectrode materials should lead to a higher stability and extended lifetime. Furthermore, the strong adherence of CeO$_2$ photocatalysts to conductive supports should be guaranteed.

The composition of industrial wastewater may vary, and some pollutants can poison photocatalysts and photoelectrocatalysts. Therefore, regeneration methods for CeO$_2$-based photocatalyst surfaces must be taken under consideration.

Although there are many issues that should be overcome in photocatalytic and photoelectrocatalytic processes in wastewater treatment before these processes can be commercially implemented, CeO$_2$ and its composites seem to be promising photocatalytic materials.

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