Review

A CeO₂ Semiconductor as a Photocatalytic and Photoelectrocatalytic Material for the Remediation of Pollutants in Industrial Wastewater: A Review

Elzbieta Kusmierek

Institute of General and Ecological Chemistry, Faculty of Chemistry, Lodz University of Technology,
Zeromskiego 116 St., 90-924 Lodz, Poland; elzbieta.kusmierek@p.lodz.pl

Received: 22 November 2020; Accepted: 4 December 2020; Published: 8 December 2020

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 (CeO₂) is one of the photocatalysts most commonly applied in pollutant degradation. CeO₂ exhibits promising photocatalytic activity. Nonetheless, the position of conduction bands (CB) and valence bands (VB) in CeO₂ 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 CeO₂ application as a single or composite photocatalyst in the treatment of various pollutants. The photocatalytic characteristics of CeO₂ and its composites are described. The main photocatalytic reactions with the participation of CeO₂ 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 CeO₂ 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 (CeO_2) is one of the semiconductors most often applied, with the exception of titanium dioxide (TiO_2). 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. TiO_2 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. TiO_2 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].

CeO_2 is another semiconductor photocatalyst with various applications and similar properties to TiO_2 . However, its band gap is in the wide range of 2.6 to 3.4 eV, depending on the preparation method [22,23]. Furthermore, CeO_2 exhibits promising photocatalytic activity. Nonetheless, the position of CB and VB limits its application as an efficient photocatalyst utilizing solar energy, even though CeO_2 can absorb a larger fraction of the solar spectrum than TiO_2 [24]. The photocatalytic and photoelectrocatalytic activity of CeO_2 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 CeO_2 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 CeO_2 which should be mentioned include its high thermal stability, high hardness, oxygen ion conductivity, special redox features, and easy conversion between Ce^{3+} and Ce^{4+} oxidation states [30,42,43].

The above-mentioned properties indicate the possible practical application of CeO_2 as a photocatalyst or photoelectrocatalyst in wastewater treatment. CeO_2 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 CeO_2 semiconductor materials applied as photocatalysts and photoelectrocatalytic materials in the treatment of various pollutants present in industrial wastewater. The characteristics of CeO_2 semiconductors, as well as parameters characterizing the treatment process, are presented. They are followed by examples of CeO_2 applied in the photocatalytic and photoelectrocatalytic treatment of different kinds of pollutants, in order to prove the extraordinary properties of CeO_2 . 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 (CeO_2) is an n-type semiconductor material characterized by a relatively high dielectric constant value ($\epsilon = 23\text{--}52$) [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 Ce^{4+} oxidation state is regarded as more stable than Ce^{3+} due to Ce^{4+} 's electronic structure ($[\text{Xe}]4f^0$), which is more stable than that of Ce^{3+} ($[\text{Xe}]4f^1$). Cerium oxide also exists in two forms, with ongoing transformation between the oxygen-rich CeO_2 and the oxygen-poor Ce_2O_3 [64].

Generally, CeO₂ 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-x). Oxide defects play an important role in the catalytic and photocatalytic properties of CeO₂ [68].

In bulk materials, both forms of cerium oxide are present, i.e., CeO₂ and Ce₂O₃. In the case of Ce₂O₃, 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 Ce³⁺ to Ce⁴⁺, may generate neutral oxygen vacancies in ceria according to the following reaction [46]:

The transition between Ce³⁺ and Ce⁴⁺ 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]:

where O_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 Ce³⁺ ions. Furthermore, a reduction of the ceria particle size results in the formation of oxygen vacancies related to an increase in the levels of Ce³⁺ [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 CeO₂ 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 CeO₂ 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 Ce³⁺ in ceria means the formation of more defects, a higher concentration of Ce⁴⁺ ions results in a narrower bandgap of CeO₂ and photocatalytic activity of ceria under visible light can be enhanced [87]. Cerium oxide exhibits strong absorption in the UV region, and high transparency in the VIS region and near IR region. In comparison with TiO₂, the CeO₂ 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 TiO₂.

CeO₂ 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]:

$$E_{\text{CB}}^0(\text{CeO}_2) = \chi(\text{CeO}_2) - E_{\text{c}} - \frac{1}{2}E_{\text{g}}(\text{CeO}_2), \quad (3)$$

$$E_{\text{VB}}^0(\text{CeO}_2) = E_{\text{g}}(\text{CeO}_2) - E_{\text{CB}}(\text{CeO}_2), \quad (4)$$

where E_{CB} and E_{VB} denote conduction and valence band potentials, respectively; χ 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.

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_2O .

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]:

$$E_F = -eE + \text{const.}, \quad (5)$$

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. Energy of a CeO₂ 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 ($1/C^2$ vs. E) by its extrapolation to $1/C^2 = 0$ resulting from the Mott–Schottky equation [22,23,101,109]:

$$\frac{1}{C^2} = \left(\frac{2}{e\epsilon_0\epsilon_s A^2 N_D} \right) \left(E - E_{fb} - \frac{k_B T}{e} \right), \quad (6)$$

where C denotes the space-charge capacitance, N_D (cm^{−3}) is the donor density, e represents the electronic charge (1.602×10^{-19} C), ϵ denotes the relative permittivity of the semiconductor, A (cm²) is the active geometric surface area, ϵ_0 represents the vacuum permittivity (8.854×10^{-12} F m^{−1}), E (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 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. 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. 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]:

$$\text{QY} = \frac{\text{Rate of pollutant degradation (molecules per second)}}{\text{Flux of absorbed photons (photons per second)}}. \quad (7)$$

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:

$$\text{FOM} = \frac{\text{Product obtained (L)}}{\text{Catalyst dosage (g/L)} \cdot \text{Time (h)} \cdot \text{Energy consumption (Wh/}\mu\text{mole)} \left(\frac{\text{Wh}}{\mu\text{mole}} \right)}. \quad (8)$$

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 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]:

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 ($\text{OH}^\bullet$), as well as superoxide anion radicals ($\text{O}_2^{\bullet-}$), 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 ($\text{HO}_2^\bullet$), 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 $\text{OH}^\bullet$; 1.78 V for H_2O_2 ; 1.68 V for $\text{HO}_2^\bullet$; 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 CeO₂ 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	AO7, 70 mg/L	1000 W halogen lamp (>420 nm)	AO7—97% (11 h), TOC—60% (12 h)	[127]
Crystal phase	Precipitation followed by calcination		1.0 g/L	AO7, 70 mg/L, pH = 6.8	1000 W halogen lamp (>420 nm)	AO7—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 × 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]

Table 1. Cont.

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) MB NPs—36%, 30 kGy—65%, 90 kGy—75% (6 h)	[131]
CeO ₂ X-architecture particles	Hydrothermal route assisted by polyvinyl pyrrolidone		1 g/L	MB, 40 mg/L	500 W Hg lamp	98% (120 h)	[132]
CeO ₂ NPs	Microwave-assisted hydrothermal method	2.54 eV—rods, 2.75 eV—beams, 2.76 eV—rods/cubes, 2.95 eV—hexagons	0.3 g/L	RhB, 0.01 mM, Ciprofloxacin (CIP)—0.01 mM	15 W Philips lamps, 9.55 mW/cm ²	RhB Hexagons—20.6%, Rods/cubes (in the presence of ammonia oxalate)—86%, CIP Rods/cubes—53% (60 min)	[133]
CeO ₂ /SCB Sugarcane bagasse	Heterogeneous precipitation	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)	[134]

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 CeO₂ doping with metals (Me) on enhanced photogenerated hole (h⁺)/photoexcited electron (e⁻) pair separation.

CeO₂ 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 CeO₂ 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, F-CeO ₂ —2.88 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, N-CeO ₂ —2.83 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 hexamethylenetetramine			AO7, 0.2 mM, pH = 3	100 W Hg lamp (HML), 10 W fluorescent lamp (CFL)	HML TiO 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, Y-CeO ₂ —2.62 eV	0.2 g/L	Carmine indigo (CI)—15.55 mg/L, RhB, 5 mg/L	450 W Hg lamp	CI 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, Y-CeO ₂ —2.96 eV	1 g/L	RhB, 1 g/L	250 W halogen lamp (532 nm)	99% (3 h)	[139]

Table 2. Cont.

Photocatalyst	Preparation Method	Band Gap, eV	Catalyst Dose	Pollutant, Concentration	Light Source	Degradation Efficiency (Process Time)	Ref.
Y-CeO ₂ Hedgehog-like hierarchical structure	Hydrothermal process	CeO ₂ —3.20 eV, Y-CeO ₂ —3.35 eV	20 mg spread on glass dish	Acetylaldehyde, 500 ppm	LED diode (365 nm)	CO ₂ evolution CeO ₂ —~55 ppm, Y-CeO ₂ —~350 ppm (24 h)	[140]
CeO ₂ (CP) Mg-CeO ₂ (CM) Ca-CeO ₂ (CC) Sr-CeO ₂ (CS) Ba-CeO ₂ (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]
CeO ₂ Ag-CeO ₂ Bi-CeO ₂ Cd-CeO ₂ Pb-CeO ₂	Facile one-step precipitation method	CeO ₂ —2.84 eV, Ag-CeO ₂ —1.86 eV, Bi-CeO ₂ —2.60 eV, Cd-CeO ₂ —2.70 eV, Pb-CeO ₂ —2.25 eV	0.05 g/L	MB, 30 mg/L	Direct sunlight irradiation	CeO ₂ —10%, Ag-CeO ₂ —99.6%, Bi-CeO ₂ —~90%, Cd-CeO ₂ —~90%, Pb-CeO ₂ —~80% (90 min)	[142]
Fe-CeO ₂	Flame spray pyrolysis	CeO ₂ —3.18 eV, Fe(5%)-CeO ₂ —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-CeO ₂	Solvothermal method followed by thermal annealing	CeO ₂ —2.92 eV, Fe-CeO ₂ —2.63 eV	1 cm × 1 cm thin film	MB, 0.5 mM	UV light source (365 nm), 2 mW/cm ²	CeO ₂ —57%, Fe-CeO ₂ —80% (180 min)	[144]
Fe-CeO ₂ Hollow microspheres (HMs)	Co-precipitation route	CeO ₂ (HMs)—3.21 eV, Fe-CeO ₂ (NPs)—3.37 eV, Fe-CeO ₂ (HMs)—3.10 eV	0.2 g/L, with H ₂ O ₂ (1 mM)	AO7, 20 mg/L	Xe lamp (320–1100 nm)	CeO ₂ (HMs)—~81%, Fe-CeO ₂ (NPs)—~63%, Fe-CeO ₂ (HMs)—~93% (80 min)	[145]
Fe-CeO ₂	Homogeneous precipitation with homogeneous/impregnation method	CeO ₂ —~2.98 eV, Fe(1.5%)-CeO ₂ —~2.64 eV	thin film	MO, 0.025 mM	50 W halogen lamp, 185 mW/cm ²	CeO ₂ —~55%, Fe-CeO ₂ —~14% (120 min)	[26]

Table 2. Cont.

Photocatalyst	Preparation Method	Band Gap, eV	Catalyst Dose	Pollutant, Concentration	Light Source	Degradation Efficiency (Process Time)	Ref.
Co-CeO ₂	Co-precipitation method	CeO ₂ —3.13 eV, Co(6%)-CeO ₂ —2.84 eV	1 g/L	MB, 15 ppm	30 W lamp (365 nm), sunlight (~900 lm/cm ²)	UV CeO ₂ —34.5%, Co(6%)-CeO ₂ —98.7%, Sunlight CeO ₂ —34.5% Co(6%)-CeO ₂ —88.9% (7 h)	[27]
Co-CeO ₂	Hydrothermal technique		3.3 g/L	AO7, 0.02 M	UV light (2 mW) source (365 nm)	96% (8 h)	[146]
La-CeO ₂	Co-precipitation route		0.25 g/L, In the presence of NaBH ₄	MB, 0.25 mM	500 W halogen lamp (400–600 nm)	La(10%)-CeO ₂ —99.99% (180 min)	[147]
In-CeO ₂ Nanocrystals	Facile, green hydrothermal method	CeO ₂ —2.9 eV, In(10%)-CeO ₂ —2.7 eV	0.15 g/L	MO, 15.5 mg/L, MB, 15.5 mg/L	110 W UV light source	MO CeO ₂ —~53%, In-CeO ₂ —~92%, MB CeO ₂ —~38%, In-CeO ₂ —~65% (100 min)	[96]
Ag-CeO ₂	Co-impregnation and co-precipitation method		0.5 g/L	Tributyltin, 12 mg/L	10 W LED lamp (390 nm)	CeO ₂ —~20%, Ag-CeO ₂ —~60% (30 h)	[97]
Ag-CeO ₂ Au-CeO ₃	Co-precipitation route	CeO ₂ —3.12 eV, Ag(2%)-CeO ₂ —2.90 eV, Au(0.4%)-CeO ₂ —3.04 eV	0.25 g/L	RhB, 1 mg/L	Uv-Vis light	CeO ₂ —80%, Ag-CeO ₂ —97.7% (5 h) CeO ₂ —36%, Au-CeO ₂ —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: $\text{Ce}(\text{Co})\text{-NP} > \text{Ce}(\text{Mn})\text{-NP} > \text{Ce}(\text{Ti})\text{-NP} > \text{Ce}(\text{Fe})\text{-NP} > \text{Ce-NP}$. 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 ($\text{Ce}(\text{Co})\text{-NP}$), 2.77 eV ($\text{Ce}(\text{Ti})\text{-NP}$), 2.78 eV ($\text{Ce}(\text{Mn})\text{-NP}$), and 2.81 eV ($\text{Ce}(\text{Fe})\text{-NP}$) 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_2O_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].

CeO₂ heterojunctions with other semiconductors usually belong to n–n and p–n heterojunctions, e.g., CeO₂/TiO₂ [156] and CeO₂/CuO [157], respectively. Furthermore, CeO₂ can form Z-scheme heterojunctions, e.g., Mn₃O₄/CeO₂ [158] and g-C₃N₄/CeO₂ [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 CeO₂ composites applied in the photodegradation of different pollutants are presented in the next three subsections.

3.3.1. CeO₂ Coupled with TiO₂

CeO₂ is often coupled with TiO₂ due to its oxygen storage ability and photocatalytic activity. The presence of Ce⁴⁺ and Ce³⁺ oxidation states results in excellent CeO₂ characteristics manifesting themselves in transferring electrons and enhancement of the light absorption capability in near ultraviolet and ultraviolet ranges [161]. CeO₂ composites with TiO₂ also show a higher thermal stability and higher electrical conductivity [162]. In addition to these advantages, CeO₂/TiO₂ 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 CeO₂/TiO₂ 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 CeO₂/TiO₂ composites in the form of nanofilms or nanotube arrays, which are characterized by a large surface area and more convenient separation of the suspensions.

TiO₂/CeO₂ 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 CeO₂/TiO₂ composites under UV and VIS irradiation is presented in Figure 4.

Figure 4. A schematic diagram of CeO₂/titanium dioxide (TiO₂) composite photoexcitation under UV and VIS light irradiation.

When a CeO₂/TiO₂ composite is irradiated by UV light, then both CeO₂ and TiO₂ 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 TiO₂, photogenerated electrons in CB of CeO₂ are easily transferred to the CB of TiO₂ and form superoxide anion radicals (O₂^{•−}) which react with pollutant molecules. Simultaneously, photogenerated holes in the VB of TiO₂ are moved to the VB of CeO₂ 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]:

Ce⁴⁺ species scavenge the excited photoelectrons in TiO₂ 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 CeO₂ is predicted to absorb light and generate photoexcited h⁺/e[−] pairs. The photogenerated electrons are transferred to the CB of TiO₂ (Figure 4) [156,167]. This limits the recombination of h⁺/e[−] pairs and improves the photocatalytic properties of the composite material.

Exemplary applications of CeO₂/TiO₂ 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 CeO₂ composites with TiO₂ 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 —3.18 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) VIS (CeO ₂ /TiO ₂) p-CP—57.5%, TOC—48.9% (6 h)	[168]
CeO ₂ /TiO ₂	Hydrothermal method	TiO ₂ —3.18 eV, CeO ₂ /TiO ₂ —2.67 eV		Bromophenol dye	300 W Xe lamp (>400 nm)	TiO ₂ —6%, CeO ₂ /TiO ₂ —72% (180 min)	[156]
CeO ₂ /TiO ₂ NTAs	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	CeO ₂ —35%, TiO ₂ —42%, CeO ₂ /TiO ₂ —90% (5 h—desulfurization)	[169]
CeO ₂ @TiO ₂ Core-shell	Hydrothermal route with the Stöber 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 —55%, CeO ₂ /TiO ₂ —82% (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	350 W solar simulator (300–2500 nm)	TiO ₂ —38%, CeO ₂ -TiO ₂ /SiO ₂ —96.5% (180 min)	[161]

Table 3. Cont.

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	1 g/L	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% (5 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	Diisopropanolamine (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.

CeO₂/TiO₂ composites belong to n–n heterojunctions and can also be classified as staggered gap (type II) heterojunctions. Usually, the band gap of the composite material displays a lower energy than TiO₂ or CeO₂ (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 CeO₂/TiO₂ 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. CeO₂-Based Carbon Materials

Although CeO₂ 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-C₃N₄) [176–178]. In the case of CeO₂, graphene oxide or reduced graphene oxide is often applied as a supporting material.

Graphene containing single layers of sp²-bonded carbon atoms packed into a 2D structure exhibits unique properties, such as a large specific surface area (~2600 m²/g), high adsorption ability, significant mobility of charge carriers (200,000 cm²/(V·s) at room temperature), high electrical conductivity (106 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-C₃N₃) is another carbon compound which can be combined with CeO₂. Its structure is similar to graphite and composed of hexagonal rings of carbon atoms with sp² hybrid bonds [184]. The g-C₃N₄ 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 TiO₂, g-C₃N₄ 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 CeO₂

and g-C₃N₄ 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 CeO₂ composites with graphitic carbon nitride (g-C₃N₄) in a type II heterojunction.

The application of CeO₂ composites with GO, rGO, and g-C₃N₄ 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-CeO ₂	Hydrothermal method	CeO ₂ NPs—2.94 eV, rGO-CeO ₂ —2.91 eV	1 g/L	MB, 0.01 mM	Direct sunlight	rGO—3.5%, CeO ₂ NPs—35%, rGO-CeO ₂ —~72% (50 min)	[87]
rGO/CeO ₂	In-situ growth and self-assembly approach		0.3 g/L	MB, 20 mg/L, with addition of 1 mL 30% H ₂ O ₂	500 W tungsten lamp	RGO—7.8%, CeO ₂ —10%, RGO/CeO ₂ —74.8% (140 min)	[187]
CeO ₂ HS/rGO HS—hollow nanospheres	Hydrothermal method		0.5 g/L	MO, 30 mg/L pH = 6.5	800 W Hg lamp	CeO ₂ HS—16%, rGO—22%, GO—25%, CeO ₂ HS/rGO—97% (50 min)	[177]
ZnO-CeO ₂ -rGO Possible H ₂ generation in PEC	Hydrothermal process	ZnO-rGO—3.04 eV, ZnO-CeO ₂ -rGO—2.20 eV	1 g/L	MB, 100 mM, pH = 3	Xe lamp (AM 1.5G filter), 100 mW/cm ²	MB ZnO-rGO—20%, ZnO-CeO ₂ -rGO—90%, TOC ZnO-rGO—11%, ZnO-CeO ₂ -rGO—72% (90 min)	[188]
rGO-CeO ₂ NCs	Hydrothermal process	CeO ₂ NWs—2.88 eV, CeO ₂ NCs—2.76 eV	0.375 g/L	MB, 0.01 mM	500 W Hg lamp, 40 mW/cm ²	CeO ₂ NWs—58%, CeO ₂ NCs—65%, RGO-CeO ₂ NCs—87% (90 min)	[33]
CeO ₂ /Graphene NPs	Hydrothermal method	CeO ₂ NPs—3.16 eV, CeO ₂ -Graphene—2.69 eV	0.08 g/L	CR, 5 mg/L MB, 5 mg/L	400 W lamp, (>500 nm)	CR Graphene—~16%, CeO ₂ -Graphene—~94.5% MB Graphene—~20%, CeO ₂ -Graphene—~98% (180 min)	[119]
UCNCs@SiO ₂ @CeO ₂ :Tm/GN GN-graphene Core/shell structure upconversion nanocrystals—UCNCs	Two-step wet-chemical route		0.4 g/L	RhB, 20 mg/L	500 W Xe lamp (300–2500 nm)	CeO ₂ —46%, CeO ₂ :Tm—55%, UCNCs@SiO ₂ @CeO ₂ :Tm—82%, UCNCs@SiO ₂ @CeO ₂ :Tm/GN—95%, (210 min)	[24]

Table 4. Cont.

Composite	Preparation Method	Band Gap, eV	Catalyst Dose	Pollutant, Concentration	Light Source	Degradation Efficiency (Process Time)	Ref.
CuO-CeO ₂ /GO GO—graphene oxide	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/GO—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 core-shell structure	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 ATP—attapulgite	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 /g-C ₃ N ₄ —83%, CeO ₂ /ATP/g-C ₃ N ₄ —98% (3 h)	[194]

Table 4. Cont.

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	g-C ₃ N ₄ —2.7 eV, α-Fe ₂ O ₃ —1.98 eV, CeO ₂ —2.81 eV, g-C ₃ N ₄ /α-Fe ₂ O ₃ —2.51 eV, g-C ₃ N ₄ /α-Fe ₂ O ₃ /CeO ₂ —2.34 eV	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-C₃N₄—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]:

The superoxide and hydroxyl radicals can react with pollutant molecules and mineralize solutions with the formation of simple inorganic products, such as CO₂, H₂O, SO₄^{2−}, 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]:

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.

CeO₂ heterojunctions include n–n and p–n semiconductor heterojunctions belonging to the typical type II heterojunctions, and to more effective Z-scheme heterojunctions. Ag₂O/CeO₂ and CuO/CeO₂ 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 way, 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 CeO₂'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.

CeO₂ 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 CeO₂ 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)	RhB CeO ₂ —7.7%, Bi ₂ WO ₆ —9.7%, CeO ₂ /Bi ₂ WO ₆ —54.1% MB CeO ₂ —8.2%, Bi ₂ WO ₆ —10.7%, CeO ₂ /Bi ₂ WO ₆ —15.6% (75 min)	[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 Hollow magnetic microcapsules	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 [−] CeO ₂ —6%, Bi ₂ WO ₆ —8%, CeO ₂ @Bi ₂ WO ₆ —98.3% (1 h)	[200]
CeO ₂ /Bi ₄ Ti ₃ O ₁₂ (C-BTO)	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 Hierarchical heterostructure microspheres	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]

Table 5. Cont.

Composite	Preparation Method	Band Gap, eV	Catalyst Dose	Pollutant, Concentration	Light Source	Degradation Efficiency (Process Time)	Ref.
Bi ₂ O ₃ /CeO ₂	Hydrothermal method	CeO ₂ —3.1 eV, Bi ₂ O ₃ —2.84 eV, Bi ₂ O ₃ /CeO ₂ —2.39 eV		Orange II dye, 0.1 mM	150 W Xe lamp (>400 nm)	CeO ₂ —~26%, Bi ₂ O ₃ —~27%, Bi ₂ O ₃ /CeO ₂ —~55% (5 h)	[203]
BiOI/CeO ₂	In-situ chemical bath method	CeO ₂ —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)	MO CeO ₂ —11.9%, BiOI—55.1%, BiOI/CeO ₂ —93.8%, (50 min) BPA CeO ₂ —28.1%, BiOI—55.8%, BiOI/CeO ₂ —92.0% (90 min)	[204]
CeO _x /BiVO ₄	Hydrothermal and ion-impregnation method	BiVO ₄ —2.52 eV, CeO _x (5.7%)/BiVO ₄ —2.48 eV	1 g/L	MB, 0.03 mM	100 W lamp (>420 nm)	BiVO ₄ —24%, CeO _x /BiVO ₄ —61% (150 min)	[205]
BiVO ₄ /CeO ₂	Homogeneous precipitation coupled with the hydrothermal method	CeO ₂ —2.76 eV, BiVO ₄ —2.51 eV, BiVO ₄ /CeO ₂ —2.46 eV	1 g/L	MB, 0.02 mM	Halogen lamp (>400 nm), 185 mW/cm ²	CeO ₂ —~20%, BiVO ₄ —~50% BiVO ₄ /CeO ₂ —80% (30 min)	[206]
Ag ₃ PO ₄ /CeO ₂	Low-temperature solution combustion followed by annealing	CeO ₂ —3.2 eV, Ag ₃ PO ₄ —2.45 eV	0.375 g/L	MB, 10 mg/L with addition of H ₂ O ₂	300 W UV lamp, 55 W fluorescent lamp (>400 nm)	UV CeO ₂ —40.6%, Ag ₃ PO ₄ —92.4%, Ag ₃ PO ₄ /CeO ₂ —98.9% (6 min) VIS CeO ₂ —20.8%, Ag ₃ PO ₄ —82.1%, Ag ₃ PO ₄ /CeO ₂ —98% (60 min)	[207]
Ag ₃ PO ₄ /CeO ₂	Ultrasound-assisted method	CeO ₂ —2.98 eV, Ag ₃ PO ₄ —2.45 eV, Ag ₃ PO ₄ /CeO ₂ —2.20 eV	1 g/L	MB, 10 mg/L	300 W Xe lamp	CeO ₂ —20%, Ag ₃ PO ₄ —88%, Ag ₃ PO ₄ /CeO ₂ —95% (40 min)	[208]

Table 5. Cont.

Composite	Preparation Method	Band Gap, eV	Catalyst Dose	Pollutant, Concentration	Light Source	Degradation Efficiency (Process Time)	Ref.
Ag/Ag ₃ PO ₄ /CeO ₂	Solvothermal method combined with co-precipitation and photoreduction	CeO ₂ —2.54 eV, Ag ₃ PO ₄ —2.42 eV	1 g/L	CO ₂ bubbled in ultrapure water	300 W Xe lamp (>420 nm)	Production CH ₃ OH—40 µmol/g _{catal.} , C ₂ H ₅ OH—30 µmol/g _{catal.} (4 h)	[209]
AgI/CeO ₂	Sol-gel auto-combustion method	CeO ₂ —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 CeO ₂ —20%, AgI 48%, AgI/CeO ₂ —98% (20 min) TC CeO ₂ —46%, AgI—74%, AgI/CeO ₂ —94% (1 h)	[210]
Ag ₂ O/CeO ₂	Hydrolysis and calcination followed by thermal decomposition	CeO ₂ —2.72 eV, Ag ₂ O—1.30 eV	1 g/L	Enrofloxacin (EFA), 10 mg/L	300 W Xe lamp (>420 nm)	EFA CeO ₂ —11.7%, Ag ₂ O—43%, Ag ₂ O/CeO ₂ —87.1% (120 min) TOC Ag ₂ O/CeO ₂ —66.8% (120 min)	[211]
Ag ₂ CO ₃ /CeO ₂ /AgBr	Hydrolysis and calcination followed by hydrobromic acid corrosion	CeO ₂ —2.72 eV, Ag ₂ CO ₃ —2.43 eV, AgBr—2.58 eV	0.4 g/L	Levofloxacin, 10 mg/L	300 W Xe lamp (>420 nm)	CeO ₂ —~11%, Ag ₂ CO ₃ —46%, Ag ₂ CO ₃ /CeO ₂ —~69% (60 min) AgBr—~45%, CeO ₂ /AgBr—~53%, Ag ₂ CO ₃ /CeO ₂ /AgBr—88% (40 min) TOC—60.98% (80 min)	[212]
Fe ₂ O ₃ -CeO ₂	Precipitation method	CeO ₂ —2.82 eV, Fe ₂ O ₃ -CeO ₂ —2.1 eV	2 g/L	CR, 25 mg/L	100 W tungsten lamp (>400 nm)	CeO ₂ —89%, Fe ₂ O ₃ -CeO ₂ —96% (adsorption—91%)	[34]

Table 5. Cont.

Composite	Preparation Method	Band Gap, eV	Catalyst Dose	Pollutant, Concentration	Light Source	Degradation Efficiency (Process Time)	Ref.
<i>p</i> -CuO/ <i>n</i> -CeO ₂	Combination of ribbon-ignition and calcination methods	CeO ₂ —2.94 eV, CuO—1.54 eV, CuO/CeO ₂ —2.59 eV	0.5 g/L	RhB, 10 mg/L, with addition of 2 mL 30% H ₂ O ₂	350 W Xe lamp (>420 nm)	CeO ₂ —~70%, CuO—~77%, CuO/CeO ₂ —86.2% (12 min)	[157]
Cu ₂ S/CeO ₂ Ag ₂ S/CeO ₂	Precipitation method	CeO ₂ —3.39 eV, Ag ₂ S—2.00 eV, Ag ₂ S/CeO ₂ —2.51 eV Cu ₂ S—1.75 eV, Cu ₂ S/CeO ₂ —2.62 eV	1 g/L	Rhodamine 6G—0.01 mM	natural sunlight	CeO ₂ NPs—25%, Cu ₂ S/CeO ₂ —44%, Ag ₂ S/CeO ₂ —30% (240 min)	[213]
CeO ₂ /V ₂ O ₅ , CeO ₂ /CuO	Thermal decomposition method	CeO ₂ —3.28 eV, V ₂ O ₅ —2.66 eV, CuO—1.83 eV, CeO ₂ /V ₂ O ₅ —2.62 eV, CeO ₂ /CuO—2.59 eV	1 g/L	MB, 0.03 mM, Textile effluent	250 W Philips lamp (532 nm)	MB CeO ₂ —6.1%, V ₂ O ₅ —27.5%, CuO—33.4%, CeO ₂ /V ₂ O ₅ —64%, CeO ₂ /CuO—70.1% (210 min) Textile effluent CeO ₂ /V ₂ O ₅ —76.9%, CeO ₂ /CuO—85.7% (300 min)	[214]
CuBi ₂ O ₄ /CeO ₂	Solid state method	CeO ₂ —3.18 eV, CuBiO ₄ —1.38 eV CuBiO ₄ (30%)/CeO ₂ (70%)—3.14 eV	0.5 g/L	CR, 20 mg/L, pH = 7	6 W UV lamp (365 nm)	CeO ₂ —14.92%, CuBi ₂ O ₄ —3.13%, CuBi ₂ O ₄ /CeO ₂ —83.05% (100 min)	[215]
CeO ₂ /MgAl	Dispersion of insoluble metal oxides	CeO ₂ /MgAl—3.2eV	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/cm ²	Ph—50% (7 h), 4-CP—96% (5 h), 2,4,6-TCP—90% (2 h)	[216]
CeO ₂ /Al ₂ O ₃	Wet-chemical method	CeO ₂ —3.0 eV, CeO ₂ /Al ₂ O ₃ —2.85 eV	50 mg in 5 ppm dye solution	CR, 5 ppm, MO, 5 ppm pH = 11	300 W tungsten lamp	CR—90% (120 min) MO—92%, TOC—92% (90 min)	[217]

Table 5. Cont.

Composite	Preparation Method	Band Gap, eV	Catalyst Dose	Pollutant, Concentration	Light Source	Degradation Efficiency (Process Time)	Ref.
NiO/CeO ₂	Electrospinning technique	CeO ₂ —3.2 eV, NiO—3.5 eV	0.375 g/L	MB, 10 mg/L	300 W UV lamp	NiO—47.3%, CeO ₂ —69.2%, NiO/CeO ₂ —96% (40 min)	[218]
CeO ₂ -ZrO ₂ 3DOM—3 dimensionally ordered microporous structure	Sol-gel method combined with the decompression filling method	CeO ₂ —2.73 eV, ZrO ₂ —3.25 eV, CeO ₂ -ZrO ₂ —2.44 eV	1.7 g/L	CR, 50 mg/L	400W Xe lamp (>410 nm), 1000 W Xe lamp—simulated sunlight	CeO ₂ VIS—55%, Sunlight—53%, UV—55%, ZrO ₂ VIS—24%, Sunlight—52%, UV—40%, CeO ₂ -ZrO ₂ VIS—72%, Sunlight—68%, UV—68% (120 min)	[98]
CeO ₂ /SnO ₂	Wet-chemical method	CeO ₂ -SnO ₂ —3.4 eV	0.1 g/L	MB, 0.03 mM	250 W lamp (532 nm)	80% (150 min)	[219]
ZnO/CeO ₂	Thermal decomposition method	ZnO—3.2 eV, CeO ₂ —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 MO—4.0%, MB—4.7%, Ph—1.9% CeO ₂ MO—4.2%, MB—5.5%, Ph—2.9% ZnO/CeO ₂ MO—95.9%, MB—97.4%, Ph—96.2% (150 min) Ite—ZnO/CeO ₂ TOC—90.2% (6 h)	[220]
ZnO/CeO ₂	Wet chemistry method with the calcination technique	ZnO—3.13 eV, CeO ₂ —2.86 eV	0.5 g/L	RhB, 10 mg/L	300 W Xe lamp (>400 nm), 0.95 mW/cm ²	CeO ₂ —56%, ZnO—38%, ZnO/CeO ₂ —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 Pal—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 DETA—diethylenetriamine	Two-step hydrothermal method	CeO ₂ —3.07 eV, CdS-DETA—2.35 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.

CeO₂ composites with Bi₂WO₆, Bi₂MoO₆, BiVO₄, Bi₄Ti₃O₁₂, ZnO, and Ag₂S belong to n–n heterojunctions which are prepared with the application of hydrothermal, solvothermal, or precipitation methods (Table 5). CeO₂/Bi₂WO₆ 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., CeO₂ and BiWO₆ in the composite photocatalysts. The method of preparation also plays an important role in the composite photocatalyst activity. CeO₂/Bi₂WO₆ 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.

CeO₂ composites with ZrO₂, Cu₂S, CuO, CuBi₂O₄, Bi₂O₃, BiOI, Ag₂O, 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 CuBi₂O₄/CeO₂ 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 Cu₂S/CeO₂ photocatalyst and resulted in a 44% degradation efficiency during a 4 h process. The results obtained in the presence of Cu₂S/CeO₂ were compared with the results of the process carried out in the presence of an n–n-type photocatalyst—Ag₂S/CeO₂. Under the same conditions, the photodegradation of Rh 6G was lower and totaled only 30% [213].

The photodegradation efficiency of a BiOI/CeO₂ 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 Bi₂O₃/CeO₂ 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 CeO₂/ZrO₂ 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 CeO₂ with Mn₃O₄, Ag₂CO₃, AgBr, ZnO, Ag₃PO₄, or Bi₂WO₆ can result in the formation of a Z-scheme heterojunction under specific conditions. Z-scheme system photocatalysts with CeO₂ were applied under visible light irradiation (Table 5) in the photodegradation of dyes and pharmaceuticals, in the photoreduction of CO₂, 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/CeO₂ [158] and Mn₃O₄/CeO₂ photocatalysts [222] in comparison with pristine CeO₂, ZnO, and Mn₃O₄. 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 Ag₂CO₃/CeO₂/AgBr and Tm³⁺:CeO₂/palygorskite [212,223]. A high photodegradation

efficiency was achieved in the process lasting about 1 h, except for $\text{Tm}^{3+}:\text{CeO}_2/\text{palygorskite}$ and $\text{Mn}_3\text{O}_4/\text{CeO}_2$ 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— $\text{CeO}_2@\text{Bi}_2\text{WO}_6$ —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.

$\text{CeO}_2/\text{Bi}_2\text{MoO}_6$ was applied in the photoreduction of CO_2 into CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ [202]. The yield of CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ was 32.5 and 25.9 $\mu\text{mol/g}_{\text{catal.}}$, respectively. A higher yield (40 and 30 $\mu\text{mol/g}_{\text{catal.}}$) was achieved in the case of the $\text{Ag}/\text{Ag}_3\text{PO}_4/\text{CeO}_2$ 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 $\text{CeO}_2/\text{CdS-DETA}$ (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— $\text{Ag}_2\text{CO}_3/\text{CeO}_2/\text{AgBr}$ —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:

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

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

where TOC_0 and TOC_t represent the initial and final values of total organic carbon, respectively, and COD_0 and 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 CeO₂ 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) P—11.2%, EC—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	EC—~42%, PC—~65%, PEC—87% (100 min)	[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/TiO ₂ —86.8%, PANI/CeO ₂ /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]

Table 6. Cont.

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 ₃ /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 -CeO ₂ —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) PC—5.53, EC—9.51, PEC—22.32 (6.5 h)	[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—TiO₂ nanotube arrays; rGO—reduced graphene oxide; P—photolysis; PC—photocatalysis; EC—electrocatalysis; and PEC—photoelectrocatalysis.

CeO₂ 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 H₂ generation. Ce/Ce₂O₃/CeO₂/TiO₂ TiO₂ nanotube arrays (TNAs) and TiO₂/CeO₂/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 CeO₂/Cu₂O 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—CeO₂/CuO—deposited on the Cu substrate was used in CO₂ 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 CeO₂ 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 CeO₂ with exfoliated graphite (EG) and reduced graphene oxide co-modified with TiO₂ 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-CeO₂-TiO₂ 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—CeO₂@ α -Fe₂O₃ and CeO₂ QDs/Ag₂Se—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 CeO₂@ α -Fe₂O₃ photoelectrode, its photocorrosion was inhibited, resulting in an enhancement of its photocatalytic stability. The PEC degradation of methyl orange with the application of the CeO₂/TiO₂ 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 CeO₂ 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 CeO₂ 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 CeO₂ in the photocatalytic and photoelectrocatalytic treatment of industrial wastewater requires further investigations, which should focus on the following aspects:

- (1) The development of CeO₂ 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 CeO₂-based photocatalyst manufacturing, with special attention given to morphology control, an increase in the active surface area, and CeO₂ immobilization on a substrate in order to remove it from wastewater easily and ensure electrical conductivity in the case of photoelectrodes;
- (3) CeO₂ 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 CeO₂ 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 CeO₂ 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 CeO₂-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 CeO₂ 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 CeO₂-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, CeO₂ and its composites seem to be promising photocatalytic materials.

Funding: This research received no external funding.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Chen, X.; Chen, R.; Zhu, X.; Liao, Q.; Zhang, Y.; Ye, D.; Zhang, B.; Yu, Y.; Li, J. A solar responsive cubic nanosized CuS/Cu₂O/Cu photocathode with enhanced photoelectrochemical activity. *J. Catal.* **2019**, *372*, 182–192. [[CrossRef](#)]
2. Nadarajan, R.; Bakar, W.A.W.A.; Ali, R.; Ismail, R. Photocatalytic degradation of 1,2-dichlorobenzene using immobilized TiO₂/SnO₂/WO₃ photocatalyst under visible light: Application of response surface methodology. *Arab. J. Chem.* **2018**, *11*, 34–47. [[CrossRef](#)]

3. Trandafilović, L.V.; Jovanović, D.J.; Zhang, X.; Ptasinska, S.; Dramićanin, M.D. Enhanced photocatalytic degradation of methylene blue and methyl orange by ZnO: Eu nanoparticles. *Appl. Catal. B Environ.* **2017**, *203*, 740–752. [[CrossRef](#)]
4. Intarasuwan, K.; Amornpitoksuk, P.; Suwanboon, S.; Graidist, P. Photocatalytic dye degradation by ZnO nanoparticles prepared from $X_2C_2O_4$ ($X = H, Na$ and NH_4) and the cytotoxicity of the treated dye solutions. *Sep. Purif. Technol.* **2017**, *177*, 304–312. [[CrossRef](#)]
5. Zhang, A.-Y.; Wang, W.-K.; Pei, D.-N.; Yu, H.-Q. Degradation of refractory pollutants under solar light irradiation by a robust and self-protected ZnO/CdS/TiO₂ hybrid photocatalyst. *Water. Res.* **2016**, *92*, 78–86. [[CrossRef](#)] [[PubMed](#)]
6. Liu, X.; Jin, A.L.; Jia, Y.S.; Xia, T.L.; Deng, C.X.; Zhu, M.H.; Chen, C.F.; Chen, X.S. Synergy of adsorption and visible-light photocatalytic degradation of methylene blue by a bifunctional Z-scheme heterojunction of WO₃/g-C₃N₄. *Appl. Surf. Sci.* **2017**, *405*, 359–371. [[CrossRef](#)]
7. Munoz-Batista, M.J.; Fernandez-Garcia, M.; Kubacka, A. Promotion of CeO₂-TiO₂ photoactivity by g-C₃N₄: Ultraviolet and visible light elimination of toluene. *Appl. Catal. B Environ.* **2015**, *164*, 261–270. [[CrossRef](#)]
8. Munoz-Batista, M.J.; Nasalevich, M.A.; Savenije, T.J.; Kapteijn, F.; Gascon, J.; Kubacka, A.; Fernandez-Garcia, M. Enhancing promoting effects in g-C₃N₄-Mnⁿ⁺/CeO₂-TiO₂ ternary composites: Photo-handling of charge carriers. *Appl. Catal. B Environ.* **2015**, *176–177*, 687–698. [[CrossRef](#)]
9. Yu, Y.; Zhong, Q.; Cai, W.; Ding, J. Promotional effect of N-doped CeO₂ supported CoO_x catalysts with enhanced catalytic activity on NO oxidation. *J. Mol. Catal. A Chem.* **2015**, *398*, 344–352. [[CrossRef](#)]
10. Xiao, F.-X.; Hung, S.-F.; Miao, J.; Wang, H.-Y.; Yang, H.; Liu, B. Metal-cluster-decorated TiO₂ nanotube arrays: A composite heterostructure toward versatile photocatalytic and photoelectrochemical applications. *Small* **2015**, *11*, 554–567. [[CrossRef](#)]
11. Fernandez-Domene, R.M.; Rosello-Marquez, G.; Sanchez-Tovae, R.; Lucas-Granados, B. Photoelectrochemical removal of chlorfenvinphos by using WO₃ nanorods: Influence of annealing temperature and operation pH. *Sep. Purif. Technol.* **2019**, *212*, 458–464. [[CrossRef](#)]
12. Huda, A.; Suman, P.H.; Torquato, L.D.M.; Silva, B.F.; Handoko, C.T.; Gulo, F. Visible light-driven photoelectrocatalytic degradation of acid yellow 17 using Sn₃O₄ flower-like thin films supported on Ti substrate (Sn₃O₄/TiO₂/Ti). *J. Photochem. Photobiol. A* **2019**, *376*, 196–205. [[CrossRef](#)]
13. Wang, X.; Wu, Q.; Ma, H.; Ma, C.; Yu, Z.; Fu, Y.; Dong, X. Fabrication of PbO₂ tipped Co₃O₄ nanowires for efficient photoelectrochemical decolorization of dye (reactive brilliant blue KN-R) wastewater. *Sol. Energy Mater. Sol. Cells* **2019**, *191*, 381–388. [[CrossRef](#)]
14. Goulart, L.A.; Alves, S.A.; Mascaro, L.H. Photoelectrochemical degradation of bisphenol A using Cu doped WO₃ electrodes. *J. Electroanal. Chem.* **2019**, *39*, 123–133. [[CrossRef](#)]
15. Fernandez-Domene, R.M.; Sanchez-Tovar, R.; Lucas-Granados, B.; Munoz-Portero, M.J. Elimination of pesticide atrazine by photoelectrocatalysis using a photoanode based on WO₃ nanosheets. *Chem. Eng. J.* **2018**, *350*, 1114–1124. [[CrossRef](#)]
16. Chang, K.-L.; Sun, Q.; Peng, Y.-P.; Lai, S.-W.; Sung, M.; Huang, C.-Y.; Kuo, H.-W.; Sun, J.; Lin, Y.-C. Cu₂O loaded titanate nanotube arrays for simultaneously photoelectrochemical ibuprofen oxidation and hydrogen generation. *Chemosphere* **2016**, *150*, 605–614. [[CrossRef](#)]
17. Kasinathan, K.; Kennedy, J.; Elayaperumal, M.; Henini, M.; Malik, M. Photodegradation of organic pollutants RhB dye using UV simulated sunlight on ceria based TiO₂ nanomaterials for antibacterial applications. *Sci. Rep.* **2016**, *6*, 38064. [[CrossRef](#)]
18. Yan, H.; Wang, X.; Yao, M.; Yao, X. Band structure design of semiconductors for enhanced photocatalytic activity: The case of TiO₂. *Prog. Nat. Sci.* **2013**, *23*, 402–407. [[CrossRef](#)]
19. Nakata, K.; Fujishima, A. TiO₂ Photocatalysis: Design and applications. *J. Photochem. Photobiol. C* **2012**, *13*, 169–189. [[CrossRef](#)]
20. Kang, X.; Liu, S.; Dai, Z.; He, Y.; Song, X.; Tan, Z. Titanium dioxide: From engineering to applications. *Catalysts* **2019**, *9*, 191. [[CrossRef](#)]
21. Shen, L.; Xing, Z.; Zou, J.; Li, Z.; Wu, X.; Zhang, Y.; Zhu, Q.; Yang, S.; Zhou, W. Black TiO₂ nanobelts/g-C₃N₄ nanosheets laminated heterojunctions with efficient visible-light-driven photocatalytic performance. *Sci. Rep.* **2017**, *7*, 41978. [[CrossRef](#)] [[PubMed](#)]
22. Sharma, D.; Mehta, B.R. Nanostructured TiO₂ thin films sensitized by CeO₂ as an inexpensive photoanode for enhanced photoactivity of water oxidation. *J. Alloys Compd.* **2018**, *749*, 329–335. [[CrossRef](#)]

23. Sharma, D.; Sastsangi, V.R.; Shrivastav, R.; Waghmare, U.V.; Dass, S. Understanding the photoelectrochemical properties of nanostructured CeO₂/CuO₂ heterojunction photoanode for efficient photoelectrochemical water splitting. *Int. J. Hydrog. Energy* **2016**, *41*, 18339–18350. [\[CrossRef\]](#)
24. Yin, D.; Zhao, F.; Zhang, L.; Zhang, X.; Liu, Y.; Zhang, T.; Wu, C.; Chen, D.; Chen, Z. Greatly enhanced photocatalytic activity of semiconductor CeO₂ by integrating with upconversion nanocrystals and graphene. *RSC Adv.* **2016**, *6*, 103795–103802. [\[CrossRef\]](#)
25. Zhang, C.; Zhang, X.; Wang, Y.; Xie, S.; Liu, Y.; Lu, X.; Tong, Y. Facile electrochemical synthesis of CeO₂ hierarchical nanorods and nanowires with excellent photocatalytic activities. *New J. Chem.* **2014**, *38*, 2581–2586. [\[CrossRef\]](#)
26. Channei, D.; Inceesungvorn, B.; Wetchakun, N.; Ukritnukun, S.; Nattestad, A.; Chen, J.; Phanichphant, S. Photocatalytic degradation of methyl orange by CeO₂ and Fe-doped CeO₂ films under visible light irradiation. *Sci. Rep.* **2014**, *4*, 5757. [\[CrossRef\]](#)
27. Saranya, J.; Ranjith, K.S.; Saravanan, P.; Mangalaraj, D.; Kumar, R.T.R. Cobalt-doped cerium oxide nanoparticles: Enhanced photocatalytic activity under UV and visible light irradiation. *Mater. Sci. Semicond. Process.* **2014**, *26*, 218–224. [\[CrossRef\]](#)
28. Li, R.; Li, C.; Yin, S.; Fu, C.; Satom, T. Synthesis of C-N Co-doped nano-CeO₂ and dye degradation under compact fluorescent lamp irradiation. *J. Nanosci. Nanotechnol.* **2012**, *12*, 2797–2801. [\[CrossRef\]](#)
29. Mittal, M.; Gupta, A.; Pandey, O.P. Role of oxygen vacancies in Ag/Au doped CeO₂ nanoparticles for fast photocatalysis. *Sol. Energy* **2018**, *165*, 206–216. [\[CrossRef\]](#)
30. Xiu, Z.; Xing, Z.; Li, Z.; Wu, X.; Yan, X.; Hu, M.; Cao, Y.; Yang, S.; Zhou, W. Ti³⁺-TiO₂/Ce³⁺-CeO₂ nanosheet heterojunctions as efficient visible-light-driven photocatalysts. *Mater. Res. Bull.* **2018**, *100*, 191–197. [\[CrossRef\]](#)
31. Qu, X.; Xie, D.; Gao, L.; Du, F. Synthesis and photocatalytic activity of TiO₂/CeO₂ core-shell nanotubes. *Mater. Sci. Semicond. Process.* **2014**, *26*, 657–662. [\[CrossRef\]](#)
32. Issarapanacheewin, S.; Wetchakun, K.; Phanichphant, S.; Kangwansupamokon, W.; Wetchakun, N. A novel CeO₂/Bi₂WO₆ composite with highly enhanced photocatalytic activity. *Mater. Lett.* **2015**, *156*, 28–31. [\[CrossRef\]](#)
33. Huang, K.; Li, Y.H.; Liang, C.; Xu, X.; Zhou, Y.F.; Fan, D.Y.; Yang, H.J.; Lang, P.L.; Zhang, R.; Wang, Y.G.; et al. One-step synthesis of reduced graphene oxide-CeO₂ nanocubes composites with enhanced catalytic activity. *Mater. Lett.* **2014**, *124*, 223–226. [\[CrossRef\]](#)
34. Aboutaleb, W.A.; El-Salamony, R.A. Effect of Fe₂O₃-CeO₂ nanocomposite synthesis method on the Congo red dye photodegradation under visible light irradiation. *Mater. Chem. Phys.* **2019**, *236*, 121724. [\[CrossRef\]](#)
35. Wang, B.; Zhu, B.; Yun, S.; Zhang, W.; Xia, C.; Afzal, M.; Cai, Y.; Liu, Y.; Wang, Y.; Wang, H. Fast ionic conduction in semiconductor CeO_{2-δ} electrolyte fuel cells. *NPG Asia Mater.* **2019**, *11*, 51. [\[CrossRef\]](#)
36. Wang, W.; Zhu, Q.; Dai, Q.; Wang, X. Fe doped CeO₂ nanosheets for catalytic oxidation of 1,2-dichloroethane: Effect of preparation method. *Chem. Eng. J.* **2017**, *307*, 1037–1046. [\[CrossRef\]](#)
37. Zhang, N.; Zhang, G.; Chong, S.; Zhao, H.; Huang, T.; Zhu, J. Ultrasonic impregnation of MnO₂/CeO₂ and its application in catalytic sono-degradation of methyl orange. *J. Environ. Manag.* **2018**, *205*, 134–141. [\[CrossRef\]](#)
38. Toro, R.G.; Malandrino, G.; Fragala, I.L. Relationship between the nanostructures and the optical properties of CeO₂ thin films. *J. Phys. Chem. B* **2004**, *108*, 16357–16364. [\[CrossRef\]](#)
39. Avellaneda, C.O.; Berton, M.A.C.; Bulhões, L.O.S. Optical and electrochemical properties of CeO₂ thin film prepared by an alkoxide route. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 240–244. [\[CrossRef\]](#)
40. Wongkaew, A. Effect of cerium oxide and zirconium oxide to activity of catalysts. *Chiang Mai J. Sci.* **2008**, *35*, 156–162.
41. Chen, H.-I.; Chang, H.-Y. Synthesis and characterization of nanocrystalline cerium oxide powders by two-stage non-isothermal precipitation. *Solid State Commun.* **2005**, *133*, 593–598. [\[CrossRef\]](#)
42. Munoz-Batista, M.J.; Gomez-Cerezo, M.N.; Kubacka, A.; Tudela, D.; Fernandez-Garcia, M. Role of interface contact in CeO₂-TiO₂ photocatalytic composite materials. *ACS Catal.* **2014**, *4*, 63–72. [\[CrossRef\]](#)
43. Lei, W.; Zhang, T.; Gu, L.; Liu, P.; Rodriquez, J.A.; Liu, G.; Liu, M. Surface-structure sensitivity of CeO₂ nanocrystals in photocatalysis and enhancing the reactivity with nanogold. *ACS Catal.* **2015**, *5*, 4385–4393. [\[CrossRef\]](#)
44. Ramezanzadeh, B.; Bahlakeh, G.; Ramezanzadeh, M. Polyaniline-cerium oxide (PAni-CeO₂) coated graphene oxide for enhancement of epoxy coating corrosion protection performance on mild steel. *Corros. Sci.* **2018**, *137*, 111–126. [\[CrossRef\]](#)

45. Zhang, W.; Wang, H.; Lv, C.; Chen, X.; Zhao, Z.; Qu, Y.; Zhu, Y. Effects of CeO₂ geometry on corrosion resistance of epoxy coatings. *Surf. Eng.* **2020**, *36*, 175–183. [\[CrossRef\]](#)
46. Younis, A.; Chu, D.; Li, S. Cerium oxide nanostructures and their applications. Chapter 3. In *Functionalized Nanomaterials*; Farukh, M.A., Ed.; IntechOpen: London, UK, 2016; pp. 53–68.
47. Melchionna, M.; Fornasiero, P. The role of ceria-based nanostructured materials in energy applications. *Mater. Today* **2014**, *17*, 349–357. [\[CrossRef\]](#)
48. He, Q. Experimental study on polishing performance of CeO₂ and nano-SiO₂ mixed abrasive. *Appl. Nanosci.* **2018**, *8*, 163–171. [\[CrossRef\]](#)
49. Porqueras, I.; Person, C.; Corbella, C.; Vives, M.; Pinyol, A.; Bertran, E. Characteristics of e-beam deposited electrochromic CeO₂ thin films. *Solid State Ion.* **2003**, *165*, 131–137. [\[CrossRef\]](#)
50. Parwaiz, S.; Khan, M.M.; Pradhan, D. CeO₂-based nanocomposites: An advanced alternative to TiO₂ and ZnO₂ in sunscreens. *Mater. Express* **2019**, *9*, 185–202. [\[CrossRef\]](#)
51. Li, Y.; Hou, X.; Yang, C.; Pang, Y.; Li, X.; Jiang, G.; Liu, Y. Photoprotection of cerium oxide nanoparticles against UVA radiation-induced senescence of human skin fibroblasts due to their antioxidant properties. *Sci. Rep.* **2019**, *9*, 2595. [\[CrossRef\]](#)
52. Pislaru-Danescu, L.; Telipan, G.; Ion, I.; Marinescu, V. Prototyping a gas sensors using CeO₂ as a matrix or dopant in oxide semiconductor systems. Introductory Chapter; In *Cerium Oxide—Applications and Attributes*; Khan, S.B., Akhtar, K., Eds.; IntechOpen: London, UK, 2019; pp. 1–34.
53. Hu, J.; Sun, Y.; Xue, Y.; Zhang, M.; Li, P.; Lian, K.; Zhuiykov, S.; Zhang, W.; Chen, Y. Highly sensitive and ultra-fast gas sensor based on CeO₂-loaded In₂O₃ hollow spheres for ppb-level hydrogen detection. *Sens. Actuators B Chem.* **2018**, *257*, 124–135. [\[CrossRef\]](#)
54. Li, C.; Lu, Z. Effect of CeO₂ and CuO sintering additives on the properties of KNN-based piezoelectric ceramics. *Mater. Technol.* **2018**, *33*, 474–478. [\[CrossRef\]](#)
55. Souza, J.V.C.; de Macedo Silva, O.M.; do Carmo Andrade Nono, M.; Machado, J.P.B.; Pimenta, M.; Ribeiro, M.V. S₃N₄ ceramics cutting tool sintered with CeO₂ and Al₂O₃ additives with AlCrN coating. *Mater. Res.* **2011**, *14*, 514–518. [\[CrossRef\]](#)
56. Gong, Q.; Gao, T.; Huang, H.; Wang, R.; Cao, P.; Zhou, G. Double-shelled CeO₂@C hollow nanospheres as enhanced anode materials for lithium-ion batteries. *Inorg. Chem. Front.* **2018**, *5*, 3197–3204. [\[CrossRef\]](#)
57. Di Monte, R.; Kaspar, J. On the role of oxygen storage in three-way catalysis. *Top. Catal.* **2004**, *28*, 47–57. [\[CrossRef\]](#)
58. Machida, M.; Fujiwara, A.; Yoshida, H.; Ohyama, J.; Asakura, H.; Hosokawa, S.; Tanaka, T.; Haneda, M.; Tomita, A.; Miki, T.; et al. Deactivation mechanism of Pd/CeO₂-ZrO₂ three-way Catalysts analysed by chassis-dynamometer tests and *in situ* diffuse reflectance spectroscopy. *ACS Catal.* **2019**, *9*, 6415–6424. [\[CrossRef\]](#)
59. Jiang, L.; Wei, M.; Xu, X.; Lin, Y.; Lu, Z.; Song, J.; Duan, X. SO_x oxidation and adsorption by CeO₂/MgO: Synergistic effect between CeO₂ and MgO in the fluid catalytic cracking process. *Ind. Eng. Chem. Res.* **2011**, *50*, 4398–4404. [\[CrossRef\]](#)
60. Ramamoorthy, R.; Dutta, P.K.; Akbar, S.A. Oxygen sensors: Materials, methods, designs and applications. *J. Mater. Sci.* **2003**, *38*, 4271–4282. [\[CrossRef\]](#)
61. Wu, T.; Vegge, T.; Hansen, H.A. Improved electrocatalytic water splitting reaction on CeO₂(111) by strain engineering: A DFT+U study. *ACS Catal.* **2019**, *9*, 4853–4861. [\[CrossRef\]](#)
62. Umale, S.V.; Tambat, S.N.; Sontakke, S.M. Combustion synthesized CeO₂ as an anodic material in dye sensitized solar cells. *Mater. Res. Bull.* **2017**, *94*, 483–488. [\[CrossRef\]](#)
63. Chiu, F.-C.; Lai, C.-M. Optical and electrical characterizations cerium oxide thin films. *J. Phys. D Appl. Phys.* **2010**, *43*, 075104. [\[CrossRef\]](#)
64. Skorodumova, N.V.; Ahuja, R.; Simak, S.I.; Abrikosov, I.A.; Johansson, B.; Lundqvist, B.I. Electronic, bonding, and optical properties of CeO₂ and Ce₂O₃ from first principles. *Phys. Rev. B* **2001**, *64*, 115108. [\[CrossRef\]](#)
65. Schwarz, K. Materials design of solid electrolytes. *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 3497. [\[CrossRef\]](#) [\[PubMed\]](#)
66. Zhang, D.; Du, X.; Shi, L.; Gao, R. Shape-controlled synthesis and catalytic application of ceria nanomaterials. *Dalton Trans.* **2012**, *41*, 14455–14475. [\[CrossRef\]](#)
67. Sun, C.; Li, H.; Chen, L. Nanostructured ceria-based materials: Synthesis, properties, and applications. *Energy Environ. Sci.* **2012**, *5*, 8475–8505. [\[CrossRef\]](#)

68. Zhang, J.; Kumagai, H.; Yamamura, K.; Ohara, S.; Takami, S.; Morikawa, A.; Shinjoh, H.; Kaneko, K.; Adschiri, T.; Suda, A. Extra-low-temperature oxygen storage capacity of CeO₂ nanocrystals with cubic facets. *Nano Lett.* **2011**, *11*, 361–364. [\[CrossRef\]](#)
69. Charbgoon, F.; Ramezani, M.; Darroudi, M. Bios-sensing applications of cerium oxide nanoparticles: Advantages and disadvantages. *Biosens. Bioelectron.* **2017**, *96*, 33–43. [\[CrossRef\]](#)
70. Charbgoon, F.; Ahmad, M.B.; Darroudi, M. Cerium oxide nanoparticles: Green synthesis and biological applications. *Int. J. Nanomed.* **2017**, *12*, 1401–1413. [\[CrossRef\]](#)
71. Campbell, C.T.; Peden, C.H.F. Oxygen vacancies and catalysis on ceria surfaces. *Science* **2005**, *309*, 713–714. [\[CrossRef\]](#)
72. Gogoi, A.; Navgire, M.; Sarma, K.C.; Gogoi, P. Fe₃O₃-CeO₂ metal oxide nanocomposite as a Fenton-like heterogeneous catalyst for degradation of catechol. *Chem. Eng. J.* **2017**, *311*, 153–162. [\[CrossRef\]](#)
73. Wu, Z.; Li, M.; Overbury, S.H. On the structure dependence of CO oxidation over CeO₂ nanocrystals with well-defined surface planes. *J. Catal.* **2012**, *285*, 61–73. [\[CrossRef\]](#)
74. Sayle, T.X.T.; Cantoni, M.; Bhatta, U.M.; Parker, S.C.; Hall, S.R.; Möbus, G.; Molinari, M.; Reid, D.; Seal, S.; Sayle, D.C. Strain and architecture-tuned reactivity in ceria nanostructures; Enhanced Catalytic oxidation of CO to CO₂. *Chem. Mater.* **2012**, *24*, 1811–1821. [\[CrossRef\]](#)
75. Liu, L.; Cao, Y.; Sun, W.; Yao, Z.; Liu, B.; Gao, F.; Dong, L. Morphology and nanosize effects of ceria from different precursors on the activity for NO reduction. *Catal. Today* **2011**, *175*, 48–54. [\[CrossRef\]](#)
76. Fernandez-Garcia, S.; Jiang, L.; Tinoco, M.; Hungria, A.B.; Han, J.; Blanco, G.; Calvino, J.J.; Chen, X. Enhanced hydroxyl radical scavenging activity by doping lanthanum in ceria nanocubes. *J. Phys. Chem. C* **2016**, *120*, 1891–1901. [\[CrossRef\]](#)
77. Doornkamp, C.; Ponc, V. The universal character of the Mars and Van Krevelen mechanism. *J. Mol. Catal. A Chem.* **2000**, *162*, 19–32. [\[CrossRef\]](#)
78. Mora-Briseno, P.; Jimenez-Garcia, G.; Castillo-Araiza, C.O.; Gonzales-Rodriguez, H.; Huirache-Acuna, R.; Maya-Yescas, R. Mars van Krevelen Mechanism for the selective partial oxidation of ethane. *Int. J. Chem. React. Eng.* **2018**, *7*, 20180085. [\[CrossRef\]](#)
79. Li, Z.; Zhang, J.; Lv, J.; Lu, L.; Liang, C.; Dai, K. Sustainable synthesis of CeO₂/CdS-diethylenetriamine composites for enhanced photocatalytic hydrogen evolution under visible light. *J. Alloys Compd.* **2018**, *758*, 162–170. [\[CrossRef\]](#)
80. Wang, J.; Liu, P.; Fu, X.; Li, Z.; Han, W.; Wang, X. Relationship between oxygen defects and the photocatalytic property of ZnO nanocrystals in Nafion membranes. *Langmuir* **2009**, *25*, 1218–1223. [\[CrossRef\]](#)
81. Tachikawa, T.; Yamashita, S.; Majima, T. Evidence for crystal-face-dependent TiO₂ photocatalysis from single-molecule imaging and kinetic analysis. *J. Am. Chem. Soc.* **2011**, *133*, 7197–7204. [\[CrossRef\]](#)
82. Liyanage, A.D.; Perera, S.D.; Tan, K.; Chabal, Y.; Balkus, K.J. Synthesis, characterization, and photocatalytic activity of Y-doped CeO₂ nanorods. *ACS Catal.* **2014**, *4*, 577–584. [\[CrossRef\]](#)
83. Chen, H.; Zhang, C.; Pang, Y.; Shen, Q.; Yu, Y.; Su, Y.; Wang, J.; Zhang, F.; Yang, H. Oxygen vacancy regulation in Nb-doped Bi₂WO₆ for enhanced visible light photocatalytic activity. *RSC Adv.* **2019**, *9*, 22559–22566. [\[CrossRef\]](#)
84. Pu, Z.-Y.; Liu, X.-S.; Jia, A.-P.; Xie, Y.-L.; Lu, J.-Q.; Luo, M.-F. Enhanced activity of CO oxidation over Pr- and Cu-doped CeO₂ catalysts: Effect of oxygen vacancies. *J. Phys. Chem. C* **2008**, *112*, 15045–15051. [\[CrossRef\]](#)
85. Heydari, H.; Elahifard, M.; Behjatmanesh-Ardakani, R. Role of oxygen vacancy in the adsorption and dissociation of the water molecule on the surfaces of pure and Ni-doped rutile (110): A periodic full-potential DFT study. *Surf. Sci.* **2019**, *679*, 218–224. [\[CrossRef\]](#)
86. Varilla, L.A.A.; Seriani, N.; Montoya, J.A. Molecular adsorption and dissociation of CO₂ on TiO₂ anatase (001) activated by oxygen vacancies. *J. Mol. Model.* **2019**, *25*, 231. [\[CrossRef\]](#)
87. Kumar, S.; Kumar, A. Enhanced photocatalytic activity of rGO-CeO₂ nanocomposites driven by sunlight. *Mater. Sci. Eng. B* **2017**, *223*, 98–108. [\[CrossRef\]](#)
88. Özer, N. Optical properties and electrochromic characterization of sol-gel deposited ceria films. *Sol. Energy Mater. Sol. Cells* **2001**, *68*, 391–400. [\[CrossRef\]](#)
89. Corma, A.; Atienzar, P.; Garcia, H.; Chane-Ching, J.-Y. Hierarchically mesostructured doped CeO₂ with potential for solar-cell use. *Nat. Mater.* **2004**, *3*, 394–397. [\[CrossRef\]](#)
90. Schmitt, R.; Nenning, A.; Kraynis, O.; Korobko, R.; Frenkel, A.I.; Lubomirsky, I.; Haile, S.M.; Rupp, J.L.M. A review of defect structure and chemistry in ceria and its solid solutions. *Chem. Soc. Rev.* **2019**. [\[CrossRef\]](#)

91. Castleton, C.W.M.; Kullgren, J.; Hermansson, K. Tuning LDA+*U* for electron localization and structure at oxygen vacancies in ceria. *J. Chem. Phys.* **2007**, *127*, 244704. [\[CrossRef\]](#)
92. Keating, P.R.L.; Scanlon, K.D.O.; Morgan, B.J.; Galea, N.M.; Watson, G.W. Analysis of intrinsic defects in CeO₂ using a Koopmans-like GGA+*U* approach. *J. Phys. Chem. C* **2012**, *116*, 2443–2452. [\[CrossRef\]](#)
93. Song, Y.Q.; Zhang, W.W.; Yang, Q.H.; Liu, Y.L.; Li, Y.X.; Shah, L.R.; Zhu, H.; Xiao, J.Q. Electronic structure and magnetic properties of Co-doped CeO₂: Based on first principle calculation. *J. Phys. Condens. Matter* **2009**, *21*, 125504. [\[CrossRef\]](#) [\[PubMed\]](#)
94. Zacherle, T.; Schriever, A.; De Souza, R.A.; Martin, M. Ab initio analysis of the defect structure of ceria. *Phys. Rev. B* **2013**, *87*, 134104. [\[CrossRef\]](#)
95. Nolan, M.; Grigoleit, S.; Sayle, D.C.; Parker, S.C.; Watson, G.W. Density functional theory studies of the structure and electronic structure of pure and defective low index surfaces of ceria. *Surf. Sci.* **2005**, *576*, 217–229. [\[CrossRef\]](#)
96. Younis, A.; Chu, D.; Kaneti, Y.V.; Li, S. Tuning the surface oxygen concentration of {111} surrounded ceria nanocrystals for enhanced photocatalytic activities. *Nanoscale* **2016**, *8*, 378–387. [\[CrossRef\]](#) [\[PubMed\]](#)
97. Raudonyte-Svirbutaviciene, E.; Neagu, A.; Vickackaite, V.; Jasulaitiene, V.; Zarkov, A.; Tai, C.-W.; Katelnikovas, A. Two-step photochemical inorganic approach to the synthesis of Ag-CeO₂ nanoheterostructures and their photocatalytic activity on tributyltin degradation. *J. Photochem. Photobiol. A* **2018**, *351*, 29–41. [\[CrossRef\]](#)
98. Hao, Y.; Li, L.; Zhang, J.; Luo, H.; Zhang, X.; Chen, E. Multilayer and open structure of dendritic crosslinked CeO₂-ZrO₂ composite: Enhanced photocatalytic degradation and water splitting performance. *Int. J. Hydrog. Energy* **2017**, *42*, 5916–5929. [\[CrossRef\]](#)
99. Li, H.; Cui, Y.; Hong, W. High photocatalytic performance of BiOI/Bi₂WO₃ toward toluene and Reactive Brilliant Red. *Appl. Surf. Sci.* **2013**, *264*, 581–588. [\[CrossRef\]](#)
100. Issarapanacheewin, S.; Wetchakun, K.; Phanichphant, S.; Kangwansupamonkon, W.; Wetchakun, N. Photodegradation of organic dyes by CeO₂/Bi₂WO₆ nanocomposite and its physicochemical properties investigation. *Ceram. Int.* **2016**, *42*, 16007–16016. [\[CrossRef\]](#)
101. Berger, T.; Monllor-Satoca, D.; Jankulovska, M.; Lana-Villarreal, T.; Gomez, R. The electrochemistry of nanostructured titanium dioxide electrodes. *ChemPhysChem* **2012**, *13*, 2824–2875. [\[CrossRef\]](#)
102. Kusmirek, E. Semiconductor electrode materials applied in photoelectrocatalytic wastewater treatment—An overview. *Catalysts* **2020**, *10*, 439. [\[CrossRef\]](#)
103. Peter, L.M. Photoelectrochemistry from basic principles to photocatalysis. Chapter 1. In *Photocatalysis: Fundamentals and Perspectives*; Schneider, J., Bahnemann, D., Ye, J., Puma, G.L., Dionysiou, D.D., Eds.; Royal Society of Chemistry: London, UK, 2016; pp. 3–28.
104. Guijarro, N.; Prevot, M.S.; Sivula, K. Surface modification of semiconductor photoelectrodes. *Phys. Chem. Chem. Phys.* **2015**, *17*, 15655–15674. [\[CrossRef\]](#) [\[PubMed\]](#)
105. Bessegato, G.G.; Guaraldo, T.T.; de Brito, J.F.; Brugnera, M.F.; Zannoni, M.V.B. Achievements and trends in photoelectrocatalysis: From environmental to energy applications. *Electrocatalysis* **2015**, *6*, 415–441. [\[CrossRef\]](#)
106. Bessegato, G.G.; Guaraldo, T.T.; Zannoni, M.V.B. Enhancement of photoelectrocatalysis efficiency by using nanostructured electrodes. Chapter 10. In *Modern Electrochemical Methods in Nano, Surface and Corrosion Science*; Aliokhazraei, M., Ed.; IntechOpen: London, UK, 2014; pp. 271–319.
107. Brugnera, M.F.; de Araujo Souza, B.C.; Zannoni, M.V.B. Advanced oxidation processes applied to actinobacterium disinfection. Chapter 15. In *Antibacteria—Basics and Biotechnological Applications*; Dhanasekaran, D., Ed.; IntechOpen: London, UK, 2016; pp. 353–376.
108. Paramasivam, I.; Jha, H.; Liu, N.; Schmuku, P. A review of photocatalysis using self-organized TiO₂ nanotubes and other ordered oxide nanostructure. *Small* **2012**, *8*, 3073–3103. [\[CrossRef\]](#)
109. Tan, Y.; Zhang, S.; Shi, R.; Wang, W.; Liang, K. Visible light active Ce/Ce₂O/CeO₂/TiO₂ nanotube arrays for efficient hydrogen production by photoelectrochemical water splitting. *Int. J. Hydrog. Energy* **2016**, *41*, 5437–5444. [\[CrossRef\]](#)
110. Chaudhary, P.; Ingole, P.P. In-situ solid-state synthesis of 2D/2D interface between Ni/NiO hexagonal nanosheets supported on g-C₃N₄ for enhanced photo-electrochemical water splitting. *Int. J. Hydrog. Energy* **2020**, *45*, 16060–16079. [\[CrossRef\]](#)

111. Anwer, H.; Mahmood, A.; Lee, J.; Kim, K.-H.; Park, J.-W.; Yip, A.C.K. Photocatalysts for degradation of dyes in industrial effluents: Opportunities and challenges. *Nano Res.* **2019**, *12*, 955–972. [\[CrossRef\]](#)
112. Zangeneh, H.; Zinatizadeh, A.A.L.; Habibi, M.; Akia, M.; Isa, M.H. Photocatalytic oxidation of organic dyes and pollutants in wastewater using different modified titanium dioxides: A comparative study. *J. Ind. Eng. Chem.* **2015**, *26*, 1–36. [\[CrossRef\]](#)
113. Kuhn, H.J.; Braslavsky, S.E.; Schmidt, R. Chemical actinometry (IUPAC Technical Report). *Pure Appl. Chem.* **2004**, *76*, 2105–2146. [\[CrossRef\]](#)
114. Sun, L.; Bolton, J.R. Determination of the quantum yield for the photochemical generation of hydroxyl radicals in TiO₂ suspension. *J. Phys. Chem.* **1996**, *100*, 4127–4134. [\[CrossRef\]](#)
115. Ling, L.; Tugaoen, H.; Brame, J.; Sinha, S.; Li, C.; Schoepf, J.; Hristovski, K.; Kim, J.-H.; Shang, C.; Westerhoff, P. Coupling light emitting diodes with photocatalyst-coated optical fibers improves quantum yield of pollutant oxidation. *Environ. Sci. Technol.* **2017**, *51*, 13319–13326. [\[CrossRef\]](#)
116. Anwer, H.; Park, J.-W. Near-infrared to visible photon transition by upconverting NaYF₄: Yb³⁺, Gd³⁺, Tm³⁺ @ Bi₂WO₆ core@ shell composite for bisphenol A degradation in solar light. *Appl. Catal. B* **2019**, *243*, 438–447. [\[CrossRef\]](#)
117. Goharshadi, E.K.; Samiee, S.; Nancarrow, P. Fabrication of cerium oxide nanoparticles: Characterization and optical properties. *J. Colloid Interface Sci.* **2011**, *356*, 473–480. [\[CrossRef\]](#) [\[PubMed\]](#)
118. Dong, B.; Li, L.; Dong, Z.; Xu, R.; Wu, Y. Fabrication of CeO₂ nanorods for enhanced solar photocatalysts. *Int. J. Hydrog. Energy* **2018**, *43*, 5275–5282. [\[CrossRef\]](#)
119. Khan, M.E.; Khan, M.M.; Cho, M.H. Ce³⁺-ion, surface oxygen vacancy, and visible light-induced photocatalytic dye degradation and photocapacitive performance of CeO₂-graphene nanostructures. *Sci. Rep.* **2017**, *7*, 5928. [\[CrossRef\]](#) [\[PubMed\]](#)
120. Wang, J.; Han, A.; Jaenicke, S.; Chuah, G.-K. Advances in sorbents and photocatalytic materials for water remediation. Chapter 6. In *New and Future Developments in Catalysis—Catalysis for Remediation and Environmental Concerns*; Suib, S.L., Ed.; Elsevier: Amsterdam, The Netherlands, 2013; pp. 127–153.
121. Capodaglio, A.G. Contaminants of emerging concern removal by high-energy oxidation-reduction processes: State of the art. *Appl. Sci.* **2019**, *9*, 4562. [\[CrossRef\]](#)
122. Armstrong, D.A.; Huie, R.E.; Lymar, S.; Koppenol, W.H.; Merenyi, G.; Neta, P.; Stanbury, D.M.; Steenken, S.; Wardman, P. Standard electrode potentials involving radicals in aqueous solution: Inorganic radicals (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1139–1150. [\[CrossRef\]](#)
123. Zamiri, R.; Ahangar, H.A.; Kaushal, A.; Zakaria, A.; Zamiri, G.; Tobaldi, D.; Ferreira, J.M.F. Dielectrical properties of CeO₂ nanoparticles at different temperatures. *PLoS ONE* **2015**, *10*, e0122989.
124. Renu, G.; Rani, V.V.D.; Nair, S.V.; Subramanian, K.R.V.; Lakshmanan, V.-K. Development of cerium oxide nanoparticles and its cytotoxicity in prostate cancer cells. *Adv. Sci. Lett.* **2012**, *5*, 1–9. [\[CrossRef\]](#)
125. Tarnuzzer, R.W.; Colon, J.; Patil, S.; Seal, S. Vacancy engineered ceria nanostructures for protection from radiation-induced cellular damage. *Nano Lett.* **2005**, *5*, 2573–2577. [\[CrossRef\]](#) [\[PubMed\]](#)
126. Phuruangrat, A.; Thongtem, S.; Thongtem, T. Microwave-assisted hydrothermal synthesis and characterization of CeO₂ nanowires for using as a photocatalytic material. *Mater. Lett.* **2017**, *196*, 61–63. [\[CrossRef\]](#)
127. Ji, P.; Zhang, J.; Chen, F.; Anpo, M. Study of adsorption and degradation of acid orange 7 on the surface of CeO₂ under visible light irradiation. *Appl. Catal. B Environ.* **2009**, *85*, 148–154. [\[CrossRef\]](#)
128. Ji, P.; Tian, B.; Chen, F.; Zhang, J. CeO₂ mediated photocatalytic degradation studies of C.I. acid orange 7. *Environ. Technol.* **2012**, *33*, 467–472. [\[CrossRef\]](#) [\[PubMed\]](#)
129. Tambat, S.; Umale, S.; Sontakke, S. Photocatalytic degradation of Milling Yellow dye using sol-gel synthesized CeO₂. *Mater. Res. Bull.* **2016**, *76*, 466–472. [\[CrossRef\]](#)
130. Aslam, M.; Qamar, M.T.; Soomro, M.T.; Ismail, I.M.I.; Salah, N.; Almeelbi, T.; Gondal, M.A.; Hameed, A. The effect of sunlight induced surface defects on the photocatalytic activity of nanosized CeO₂ for the degradation of phenol and its derivatives. *Appl. Catal. B Environ.* **2016**, *180*, 391–402. [\[CrossRef\]](#)
131. Khan, M.M.; Ansari, S.A.; Pradhan, D.; Han, D.H.; Lee, J.; Cho, M.H. Defect-induced band gap narrowed CeO₂ nanostructures for visible light activities. *Ind. Eng. Chem. Res.* **2014**, *53*, 9754–9763. [\[CrossRef\]](#)
132. Zheng, X.; Huang, S.; Yang, D.; Zhai, H.; You, Y.; Fu, X.; Yuan, J.; Zhou, X.; Wen, J.; Liu, Y. Synthesis of X-architecture CeO₂ for the photodegradation of methylene blue under UV-light irradiation. *J. Alloys Compd.* **2017**, *705*, 131–137. [\[CrossRef\]](#)

133. Amoresi, R.A.C.; Oliveira, R.C.; Marana, N.L.; de Almeida, P.B.; Prata, P.S.; Zaghe, M.A.; Longo, E.; Sambrano, J.R.; Simoes, A.Z. CeO₂ nanoparticle morphologies and their corresponding crystalline planes for the photocatalytic degradation of organic pollutants. *ACS Appl. Nano Mater.* **2019**, *2*, 6513–6526. [\[CrossRef\]](#)
134. Channei, D.; Nakaruk, A.; Phanichphant, S. Photocatalytic degradation of dye using CeO₂/SCB composite catalysts. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2017**, *183*, 218–224. [\[CrossRef\]](#)
135. Yang, K.; Huang, W.-Q.; Xu, L.; Luo, K.-W.; Yang, Y.-C.; Huang, G.-F. Insights into enhanced visible-light photocatalytic activity of CeO₂ doped with nonmetal impurity from the first principles. *Mater. Sci. Semicond. Process.* **2016**, *41*, 200–208. [\[CrossRef\]](#)
136. Miao, H.; Huang, G.-F.; Liu, J.-H.; Zhou, B.-X.; Pan, A.; Huang, W.-Q.; Huang, G.-F. Origin of enhanced photocatalytic activity of F-doped CeO₂ nanocubes. *Appl. Surf. Sci.* **2016**, *370*, 427–432. [\[CrossRef\]](#)
137. Wu, C. Solvothermal synthesis of N-doped CeO₂ microspheres with visible light-driven photocatalytic activity. *Mater. Lett.* **2015**, *139*, 383–384. [\[CrossRef\]](#)
138. Mao, C.; Zhao, Y.; Qiu, X.; Zhu, J.; Burda, C. Synthesis, characterization and computational study of nitrogen-doped CeO₂ nanoparticles with visible-light activity. *Phys. Chem. Chem. Phys.* **2008**, *10*, 5633–5638. [\[CrossRef\]](#)
139. Akbari-Fakhrabai, A.; Saravanan, R.; Jamshidijam, M.; Mangalaraja, R.V.; Gracia, M.A. Preparation of nanosized yttrium doped CeO₂ catalyst used for photocatalytic application. *J. Saudi Chem. Soc.* **2015**, *19*, 505–510. [\[CrossRef\]](#)
140. Xu, B.; Zhang, Q.; Yuan, S.; Zhang, M.; Ohno, T. Morphology control and photocatalytic characterization of yttrium-doped hedgehog-like CeO₂. *Appl. Catal. B Environ.* **2015**, *164*, 120–127. [\[CrossRef\]](#)
141. Murugan, R.; Kashinath, L.; Subash, R.; Sakthivel, P.; Byrappa, K.; Rajendran, S.; Ravi, G. Pure and alkaline metal ion (Mg, Ca, Sr, Ba) doped cerium oxide nanostructures for photo degradation of methylene blue. *Mater. Res. Bull.* **2018**, *97*, 319–325. [\[CrossRef\]](#)
142. Murugadoss, G.; Ma, J.; Ning, X.; Kumar, M.R. Selective metal ions doped CeO₂ nanoparticles for excellent photocatalytic activity under sun light and supercapacitor application. *Inorg. Chem. Commun.* **2019**, *109*, 107577. [\[CrossRef\]](#)
143. Channei, D.; Inceesungvorn, B.; Wetchakun, N.; Phanichphant, S.; Nakaruk, A.; Koshy, P.; Sorrell, C.C. Photocatalytic activity under visible light of Fe-doped CeO₂ nanoparticles synthesized by flame spray pyrolysis. *Ceram. Int.* **2013**, *39*, 3129–3134. [\[CrossRef\]](#)
144. Arul, N.S.; Mangalaraj, D.; Han, J.I. Enhanced photocatalytic property of self-assembled Fe-doped CeO₂ hierarchical nanostructures. *Mater. Lett.* **2015**, *145*, 189–192. [\[CrossRef\]](#)
145. Zhao, B.; Shao, Q.; Hao, L.; Zhang, L.; Liu, Z.; Zhang, B.; Ge, S.; Guo, Z. Yeast-template synthesized Fe-doped cerium oxide hollow microspheres for visible photodegradation of acid orange 7. *J. Colloid Interface Sci.* **2018**, *511*, 39–47. [\[CrossRef\]](#)
146. Arul, N.S.; Mangalaraj, D.; Chen, P.C.; Ponpandian, N.; Viswanathan, C. Self assembly of Co doped CeO₂ microspheres from nanocubes by hydrothermal method and their photodegradation activity on AO7. *Mater. Lett.* **2011**, *65*, 3320–3322. [\[CrossRef\]](#)
147. Singh, K.; Kumar, K.; Srivastava, S.; Chowdhury, A. Effect of rare-earth doping in CeO₂ matrix: Correlations with structure, catalytic and visible light photocatalytic properties. *Ceram. Int.* **2017**, *43*, 17041–17047. [\[CrossRef\]](#)
148. Chen, X.; Mao, S.S. Titanium dioxide materials: Synthesis, properties, modifications, and applications. *Chem. Rev.* **2007**, *107*, 2891–2959. [\[CrossRef\]](#)
149. Jorge, A.B.; Fraxedas, J.; Cantarero, A.; Williams, A.J.; Rodgers, J.; Attfield, J.P.; Fuertes, A. Nitrogen doping ceria. *Chem. Mater.* **2008**, *20*, 1682–1684. [\[CrossRef\]](#)
150. Yue, L.; Zhang, X.-M. Structural characterization and photocatalytic behaviours of doped CeO₂ nanoparticles. *J. Alloys Compd.* **2009**, *475*, 702–705. [\[CrossRef\]](#)
151. Vinodkumar, T.; Rao, B.G.; Reddy, B.M. Influence of isovalent and aliovalent dopants on the reactivity of cerium oxide for catalytic applications. *Catal. Today* **2015**, *253*, 57–64. [\[CrossRef\]](#)
152. Wang, H.; Zhang, L.; Chen, Z.; Hu, J.; Li, S.; Wang, Z.; Liu, J.; Wang, X. Semiconductor heterojunction photocatalyst: Design, construction, and photocatalytic performances. *Chem. Soc. Rev.* **2014**, *43*, 5234–5244. [\[CrossRef\]](#)
153. Peleyeju, M.G.; Arotiba, O.A. Recent trend in visible-light photoelectrocatalytic systems for degradation of organic contaminants in water/wastewater. *Environ. Sci. Water Res. Technol.* **2018**, *4*, 1389–1411. [\[CrossRef\]](#)

154. Ge, J.; Zhang, Y.; Heo, Y.-J.; Park, S.-J. Advanced design and synthesis of composite photocatalyst for the remediation of wastewater: A review. *Catalysts* **2019**, *9*, 122. [\[CrossRef\]](#)
155. Low, J.; Jaroniec, M.; Wageh, S.; Al-Ghamdi, A.A. Heterojunction photocatalysts. *Adv. Mater.* **2017**, *29*, 1601694. [\[CrossRef\]](#)
156. Ameen, S.; Akhtar, M.S.; Seo, H.-K.; Shin, H.-S. Solution processed CeO₂/TiO₂ nanocomposite as potent visible light photocatalyst for the degradation of bromophenol dye. *Chem. Eng. J.* **2014**, *247*, 193–198. [\[CrossRef\]](#)
157. Wang, N.; Pan, Y.; Lu, T.; Li, X.; Wu, S.; Wu, J. A new ribbon-ignition method for fabricating p-CuO/n-CeO₂ heterojunction with enhanced photocatalytic activity. *Appl. Surf. Sci.* **2017**, *403*, 699–706. [\[CrossRef\]](#)
158. Zhu, L.; Li, H.; Xia, P.; Liu, Z.; Xiong, D. Hierarchical ZnO decorated CeO₂ nanoparticles as the direct Z-scheme heterojunctions for enhanced photocatalytic activity. *ACS Appl. Mater. Interfaces* **2018**, *10*, 39679–39687. [\[CrossRef\]](#) [\[PubMed\]](#)
159. Qiao, Q.; Yang, K.; Ma, L.-L.; Huang, W.-Q.; Zhou, B.-X.; Pan, A.; Hu, W.; Fan, X.; Huang, G.-F. Facile in situ construction of mediator-free direct Z-scheme g-C₃N₄/CeO₂ heterojunctions with highly efficient photocatalytic activity. *J. Phys. D Appl. Phys.* **2018**, *51*, 275302. [\[CrossRef\]](#)
160. Li, H.; Tu, W.; Zhou, Y.; Zou, Z. Z-Scheme photocatalytic systems for promoting photocatalytic performance: Recent progress and future challenges. *Adv. Sci.* **2016**, *3*, 1500389. [\[CrossRef\]](#)
161. Hao, C.; Li, J.; Zhang, Z.; Ji, Y.; Zhan, H.; Xiao, F.; Wang, D.; Liu, B.; Su, F. Enhancement of photocatalytic properties of TiO₂ nanoparticles doped with CeO₂ and supported on SiO₂ for phenol degradation. *Appl. Surf. Sci.* **2015**, *331*, 17–26. [\[CrossRef\]](#)
162. Li, G.; Zhang, D.; Yu, J.C. Thermally stable mesoporous CeO₂/TiO₂ visible light photocatalysts. *Phys. Chem. Chem. Phys.* **2009**, *11*, 3775–3782. [\[CrossRef\]](#)
163. Liriano-Jorge, C.F.; Sohmen, U.; Özkan, A.; Gulyas, H.; Otterpohl, R. TiO₂ photocatalyst nanoparticle separation: Flocculation in different matrices and use of powdered activated carbon as a precoat in low-cost fabric filtration. *Adv. Mater. Sci. Eng.* **2014**, 602495.
164. Szabo, T.; Veres, A.; Cho, E.; Khim, J.; Varga, N.; Dekany, I. Photocatalyst separation from aqueous dispersion using graphene oxide/TiO₂ nanocomposites. *Colloids Surf. A Physicochem. Eng. Asp.* **2013**, *433*, 230–239. [\[CrossRef\]](#)
165. Moongraksathum, B.; Chen, Y.-W. CeO₂-TiO₂ mixed oxide thin films with enhanced photocatalytic degradation of organic pollutants. *J. Sol-Gel Sci. Technol.* **2017**, *82*, 772–782. [\[CrossRef\]](#)
166. Eskandarloo, H.; Badiel, A.; Behnajady, M.A. TiO₂/CeO₂ hybrid photocatalyst with enhanced photocatalytic activity: Optimization of synthesis variables. *Ind. Eng. Chem. Res.* **2014**, *53*, 7847–7855. [\[CrossRef\]](#)
167. Tuyen, L.T.T.; Quang, D.A.; Toan, T.T.T.; Tung, T.Q.; Hoa, T.T.; Mau, T.X.; Khieu, D.Q. Synthesis of CeO₂/TiO₂ nanotubes and heterogeneous photocatalytic degradation of methylene blue. *J. Environ. Chem. Eng.* **2018**, *6*, 5999–6011. [\[CrossRef\]](#)
168. Liu, H.; Wang, M.; Wang, Y.; Liang, Y.; Cao, W.; Su, Y. Ionic liquid-templated synthesis of mesoporous CeO₂-TiO₂ nanoparticles and their enhanced photocatalytic activities under UV or visible light. *J. Photochem. Photobiol. A* **2011**, *223*, 157–164. [\[CrossRef\]](#)
169. Lu, X.; Li, X.; Qian, J.; Miao, N.; Yao, C.; Chen, Z. Synthesis and characterization of CeO₂/TiO₂ nanotube arrays and enhanced photocatalytic oxidative desulfurization performance. *J. Alloys Compd.* **2016**, *661*, 363–371. [\[CrossRef\]](#)
170. Chen, F.; Ho, P.; Ran, R.; Chen, W.; Si, Z.; Wu, X.; Weng, D.; Huang, Z.; Lee, C. Synergistic effect of CeO₂ modified TiO₂ photocatalyst on the enhancement of visible light photocatalytic performance. *J. Alloys Compd.* **2017**, *714*, 560–566. [\[CrossRef\]](#)
171. Yuan, B.; Long, Y.; Wu, L.; Liang, K.; Wen, H.; Luo, S.; Huo, H.; Yang, H.; Ma, J. TiO₂@h-CeO₂: A composite yolk-shell microsphere with enhanced photodegradation activity. *Catal. Sci. Technol.* **2016**, *6*, 6396–6405. [\[CrossRef\]](#)
172. Zhang, L.; Zhang, J.; Jiu, H.; Zhang, X.; Xu, M. Preparation of hollow core/shell CeO₂@TiO₂ with enhanced photocatalytic performance. *J. Mater. Sci.* **2015**, *50*, 5228–5237. [\[CrossRef\]](#)
173. Liu, Y.; Li, T.; Chen, W.; Guo, Y.; Liu, L.; Guo, H. Hierarchical hollow TiO₂@CeO₂ nanocube heterostructures for photocatalytic detoxification of cyanide. *RSC Adv.* **2015**, *5*, 11733–11737. [\[CrossRef\]](#)
174. Sivalingam, J.R.; Kait, C.F.; Wilfred, C.D. CeO₂-TiO₂ photocatalyst: Ionic liquid-mediated synthesis, characterization, and performance for diisopropanolamine visible light degradation. *Bull. Chem. React. Eng. Catal.* **2018**, *13*, 170–178. [\[CrossRef\]](#)

175. Vieira, G.B.; Jose, H.J.; Peterson, M.; Baldissarelli, V.Z.; Alvarez, P.; Moreira, R.F.P.M. CeO₂/TiO₂ nanostructures enhanced adsorption and photocatalytic degradation of organic compounds in aqueous suspension. *J. Photochem. Photobiol. A* **2018**, *353*, 325–336. [\[CrossRef\]](#)
176. Velasco, L.F.; Parra, J.B.; Ania, C.O. Role of activated carbon features on the photocatalytic degradation of phenol. *Appl. Surf. Sci.* **2010**, *256*, 5254–5258. [\[CrossRef\]](#)
177. Wang, M.Y.; Zhu, W.; Zhang, D.E.; Li, S.A.; Ma, W.X.; Tong, Z.W.; Chen, J. CeO₂ hollow nanospheres decorated reduced graphene oxide composite for efficient photocatalytic dye-degradation. *Mater. Lett.* **2014**, *137*, 229–232.
178. Lam, S.-M.; Sin, J.-C.; Mohamed, A.R. A review on photocatalytic application of g-C₃N₄/semiconductor (CNS) nanocomposites towards the erasure of dyeing wastewater. *Mater. Sci. Semicond. Process.* **2016**, *47*, 62–84. [\[CrossRef\]](#)
179. Xiang, Q.; Yu, J.; Jaroniec, M. Graphene-based semiconductor photocatalysts. *Chem. Soc. Rev.* **2011**. [\[CrossRef\]](#) [\[PubMed\]](#)
180. Gusain, R.; Kumar, P.; Sharma, O.P.; Jain, S.L.; Khatri, O.P. Reduced graphene oxide-CuO nanocomposites for photocatalytic conversion of CO₂ into methanol under visible light irradiation. *Appl. Catal. B Environ.* **2016**, *181*, 352–362. [\[CrossRef\]](#)
181. Chang, H.; Wu, H. Graphene-based nanocomposites: Preparation, functionalization, and energy and environmental applications. *Energy Environ. Sci.* **2013**, *6*, 3483–3507. [\[CrossRef\]](#)
182. Alberio, J.; Mateo, D.; Garcia, H. Graphene-based materials as efficient photocatalysts for water splitting. *Molecules* **2019**, *24*, 906. [\[CrossRef\]](#)
183. Dreyer, D.R.; Ruoff, R.S.; Bielawski, C.W. From conception to realization: An historical account of graphene and some perspectives for its future. *Angew. Chem. Int. Ed.* **2010**, *49*, 9336–9344. [\[CrossRef\]](#)
184. Inagaki, M.; Tsumura, T.; Kinumoto, T.; Toyoda, M. Graphitic carbon nitrides (g-C₃N₄) with comparative discussion to carbon materials. *Carbon* **2019**, *141*, 580–607. [\[CrossRef\]](#)
185. Darkwah, W.K.; Oswald, K.A. Photocatalytic applications of heterostructure graphitic carbon nitride: Pollutant degradation, hydrogen gas production (water splitting), and CO₂ reduction. *Nanoscale Res. Lett.* **2019**, *14*, 234. [\[CrossRef\]](#)
186. Samsudin, M.F.R.; Bacho, N.; Sufian, S. Recent development of graphitic carbon nitride-based photocatalyst for environmental pollution remediation. Chapter 3. In *Nanocatalysts*; Sinha, I., Shukla, M., Eds.; IntechOpen: London, UK, 2018; pp. 1–15.
187. Ji, Z.; Shen, X.; Li, M.; Zhou, H.; Zhu, G.; Chen, K. Synthesis of reduced graphene oxide/CeO₂ nanocomposites and their photocatalytic properties. *Nanotechnology* **2013**, *24*, 115603. [\[CrossRef\]](#)
188. Murali, A.; Sarswat, P.K.; Free, M.L. Minimizing electron-hole pair recombination through band-gap engineering in novel ZnO-CeO₂-rGO ternary nanocomposite for photoelectrochemical and photocatalytic applications. *Environ. Sci. Pollut. Res.* **2010**, *27*, 25042–25056. [\[CrossRef\]](#) [\[PubMed\]](#)
189. Huang, T.; Wu, J.; Zhao, Z.; Zeng, T.; Zhang, J.; Xu, A.; Zhou, X.; Qi, Y.; Ren, J.; Zhou, R.; et al. Synthesis and photocatalytic performance of CuO-CeO₂/graphene oxide. *Mater. Lett.* **2016**, *185*, 503–506. [\[CrossRef\]](#)
190. Huang, L.; Li, Y.; Xu, H.; Xu, Y.; Xia, J.; Wang, K.; Li, H.; Cheng, X. Synthesis and characterization of CeO₂/g-C₃N₄ composites with enhanced visible-light photocatalytic activity. *RSC Adv.* **2013**, *3*, 22269–22279. [\[CrossRef\]](#)
191. Tian, N.; Huang, H.; Liu, C.; Dong, F.; Zhang, T.; Du, X.; Yu, S.; Zhang, Y. In situ co-pyrolysis fabrication of CeO₂/g-C₃N₄ n-n type heterojunction for synchronously promoting photo-induced oxidation and reduction properties. *J. Mater. Chem. A* **2015**, *3*, 17120–17129. [\[CrossRef\]](#)
192. Liu, W.; Zhou, J.; Hu, Z. Nano-sized g-C₃N₄ thin layer @ CeO₂ sphere core-shell photocatalyst combined with H₂O₂ to degrade doxycycline in water under visible light irradiation. *Sep. Purif. Technol.* **2019**, *227*, 115665. [\[CrossRef\]](#)
193. Jourshabani, M.; Shariatnia, Z.; Badiei, A. Facile one-pot synthesis of cerium oxide/sulfur-doped graphitic carbon nitride (g-C₃N₄) as efficient nanophotocatalysts under visible light irradiation. *J. Colloid Interface Sci.* **2017**, *507*, 59–73. [\[CrossRef\]](#)
194. Li, X.; Zhu, W.; Lu, X.; Zuo, S.; Yao, C.; Ni, C. Integrated nanostructures of CeO₂/attapulgite/g-C₃N₄ as efficient catalyst for photocatalytic desulfurization: Mechanism, kinetics and influencing factors. *Chem. Eng. J.* **2017**, *326*, 87–98. [\[CrossRef\]](#)

195. Vignesh, S.; Suganthi, S.; Sundar, J.K.; Raj, V. Construction of α -Fe₂O₃/CeO₂ decorated g-C₃N₄ nanosheets for magnetically separable efficient photocatalytic performance under visible light exposure and bacterial disinfection. *Appl. Surf. Sci.* **2019**, *488*, 763–777. [[CrossRef](#)]
196. Yuan, Y.; Huang, G.-F.; Hu, W.-Y.; Xiong, D.-N.; Zhou, B.-X.; Chang, S.; Huang, W.-Q. Construction of g-C₃N₄/CeO₂/ZnO ternary photocatalysts with enhanced photocatalytic performance. *J. Phys. Chem. Solids* **2017**, *106*, 1–9. [[CrossRef](#)]
197. Stelo, F.; Kublik, N.; Ullah, S.; Wender, H. Recent advances in Bi₂MoO₆ based Z-scheme heterojunctions for photocatalytic degradation of pollutants. *J. Alloys Compd.* **2020**, *829*, 154591. [[CrossRef](#)]
198. You, L.; Gao, M.; Li, T.; Guo, L.; Chen, P.; Liu, M. Investigation of the kinetics and mechanism of Z-scheme Ag₃PO₄/WO₃ p-n junction photocatalysts with enhanced removal efficiency for RhB. *New. J. Chem.* **2019**, *43*, 17104. [[CrossRef](#)]
199. Issarapanacheewin, S.; Wetchakun, K.; Phanichphant, S.; Kangwansupamonkon, W.; Wetchakun, N. Efficient photocatalytic degradation of Rhodamine B by a novel CeO₂/Bi₂WO₆ composite film. *Catal. Today* **2016**, *278*, 280–290. [[CrossRef](#)]
200. Lv, Z.; Zhou, H.; Liu, H.; Liu, B.; Liang, M.; Guo, H. Controlled assemble of oxygen vacant CeO₂@Bi₂WO₆ hollow magnetic microcapsule heterostructures for visible-light photocatalytic activity. *Chem. Eng. J.* **2017**, *330*, 1297–1305. [[CrossRef](#)]
201. Liu, Y.; Zhu, G.; Gao, J.; Hojamberdiev, M.; Lu, H.; Zhu, R.; Wei, X.; Liu, P. A novel CeO₂/Bi₄Ti₃O₁₂ composite heterojunction structure with an enhanced photocatalytic activity for bisphenol A. *J. Alloys Compd.* **2016**, *688*, 487–496. [[CrossRef](#)]
202. Dai, W.; Hu, X.; Wang, T.; Xiong, W.; Luo, X.; Zou, J. Hierarchical CeO₂/Bi₂MoO₆ heterostructured nanocomposites for photoreduction of CO₂ into hydrocarbons under visible light irradiation. *Appl. Surf. Sci.* **2018**, *434*, 481–491. [[CrossRef](#)]
203. Hsieh, S.-H.; Manivel, A.; Lee, G.-J.; Wu, J.J. Synthesis of mesoporous Bi₂O₃/CeO₂ microsphere for photocatalytic degradation of Orange II dye. *Mater. Res. Bull.* **2013**, *48*, 4174–4180. [[CrossRef](#)]
204. Wen, X.-J.; Niu, C.-G.; Zhang, L.; Zeng, G.-M. Novel p-n heterojunction BiOI/CeO₂ photocatalyst for wider spectrum visible-light photocatalytic degradation of refractory pollutants. *Dalton Trans.* **2017**, *46*, 4982–4993. [[CrossRef](#)]
205. Gu, S.; Li, W.; Wang, F.; Wang, S.; Zhou, H.; Li, H. Synthesis of buckhorn-like BiVO₄ with a shell of CeO_x nanodots: Effect of heterojunction structure on the enhancement of photocatalytic activity. *Appl. Catal. B Environ.* **2015**, *170–171*, 186–194. [[CrossRef](#)]
206. Wetchakun, N.; Chaiwichain, S.; Inceesungvorn, B.; Pingmuang, K.; Phanichphant, S.; Minett, A.I.; Chen, J. BiVO₄/CeO₂ nanocomposites with high visible-light-induced photocatalytic activity. *ACS Appl. Mater. Interfaces* **2012**, *4*, 3718–3723. [[CrossRef](#)]
207. Yang, Z.-M.; Huang, G.-F.; Huang, W.-Q.; Wei, J.-M.; Yan, X.-G.; Liu, Y.-Y.; Jiao, C.; Wan, Z.; Pan, A. Novel Ag₃PO₄/CeO₂ composite with high efficiency and stability for photocatalytic applications. *J. Mater. Chem. A* **2014**, *2*, 1750–1756. [[CrossRef](#)]
208. Lin, W.; Zhang, S.; Wang, D.; Zhang, C.; Sun, D. Ultrasound-assisted synthesis of high-efficiency Ag₃PO₄/CeO₂ heterojunction photocatalyst. *Ceram. Int.* **2015**, *41*, 8956–8963. [[CrossRef](#)]
209. Xiong, W.; Dai, W.; Hu, X.; Yang, L.; Wang, T.; Qin, Y.; Luo, X.; Zou, J. Enhanced photocatalytic reduction of CO₂ into alcohols on Z-scheme Ag/Ag₃PO₄/CeO₂ driven by visible light. *Mater. Lett.* **2018**, *232*, 36–39. [[CrossRef](#)]
210. Wen, X.-J.; Niu, C.-G.; Ruan, M.; Zhang, L.; Zeng, G.-M. AgI nanoparticles-decorated CeO₂ microspheres photocatalyst for the degradation of organic dye and tetracycline under visible-light irradiation. *J. Colloid Interface Sci.* **2017**, *497*, 368–377. [[CrossRef](#)] [[PubMed](#)]
211. Wen, X.-J.; Niu, C.-G.; Zhang, L.; Liang, C.; Zeng, G.-M. A novel Ag₂O/CeO₂ heterojunction photocatalysts for photocatalytic degradation of enrofloxacin: Possible degradation pathways, mineralization activity and an in depth mechanism insight. *Appl. Catal. B Environ.* **2018**, *221*, 701–704. [[CrossRef](#)]
212. Wen, X.-J.; Niu, C.-G.; Guo, H.; Liang, C.; Zeng, G.-M. Photocatalytic degradation of levofloxacin by ternary Ag₂CO₃/CeO₂/AgBr photocatalyst under visible-light irradiation: Degradation pathways, mineralization ability, and an accelerated interfacial charge transfer process study. *J. Catal.* **2018**, *358*, 211–223. [[CrossRef](#)]

213. Madkour, M.; Allam, O.G.; Nazeer, A.A.; Amin, M.O.; Al-Hetlani, E. CeO₂-based nanoheterostructures with p-n and n-n heterojunction arrangements for enhancing the solar-driven photodegradation of rhodamine 6G dye. *J. Mater. Sci. Mater. Electron.* **2019**, *30*, 10857–10866. [\[CrossRef\]](#)
214. Saravanan, R.; Joicy, S.; Gupta, V.K.; Narayanan, V.; Stephen, A. Visible light induced degradation of methylene blue using CeO₂/V₂O₅ and CeO₂/CuO catalysts. *Mater. Sci. Eng. C* **2013**, *33*, 4725–4731. [\[CrossRef\]](#)
215. Elaziouti, A.; Laouedj, N.; Bekka, A.; Vannier, R.-N. Preparation and characterization of p-n heterojunction CuBi₂O₄/CeO₂ and its photocatalytic activities under UVA light irradiation. *J. King Saud Univ. Sci.* **2015**, *27*, 120–135. [\[CrossRef\]](#)
216. Valente, J.S.; Tzompantzi, F.; Prince, J. Highly efficient photocatalytic elimination of phenol and chlorinated phenols by CeO₂/MgAl layered double hydroxides. *Appl. Catal. B Environ.* **2011**, *102*, 276–285. [\[CrossRef\]](#)
217. Latha, P.; Prakash, K.; Karuthapandian, S. Enhanced visible light photocatalytic activity of CeO₂/alumina nanocomposite; Synthesized via facile mixing-calcination method for dye degradation. *Adv. Powder Technol.* **2017**, *28*, 2903–2913. [\[CrossRef\]](#)
218. Yang, Z.-M.; Hou, S.-C.; Huang, G.-F.; Duan, H.-G.; Huang, W.-Q. Electrospinning preparation of p-type NiO/n-type CeO₂ heterojunctions with enhanced photocatalytic activity. *Mater. Lett.* **2014**, *133*, 109–112. [\[CrossRef\]](#)
219. Usharani, S.; Rajendran, V. Optical, magnetic and visible light photocatalytic activity of CeO₂/SnO₂ nanocomposites. *Eng. Sci. Technol.* **2016**, *19*, 2088–2093. [\[CrossRef\]](#)
220. Rajendra, S.; Khan, M.M.; Gracia, F.; Qin, J.; Gupta, V.K.; Arumainathan, S. Ce³⁺-ion-induced visible-light photocatalytic degradation and electrochemical activity of ZnO/CeO₂ nanocomposite. *Sci. Rep.* **2016**, *6*, 31641. [\[CrossRef\]](#) [\[PubMed\]](#)
221. Prabhu, S.; Viswanathan, T.; Jothivenkatachalam, K.; Jeganathan, K. Visible light photocatalytic activity of CeO₂-ZnO-TiO₂ composites for the degradation of Rhodamine B. *Indian J. Mater. Sci.* **2014**, 536123. [\[CrossRef\]](#)
222. Ma, Y.; Jiang, J.; Zhu, A.; Tan, P.; Bian, Y.; Zeng, W.; Cui, H.; Pan, J. Enhanced visible-light photocatalytic degradation by Mn₃O₄/CeO₂ heterojunction: A Z-scheme system photocatalyst. *Inorg. Chem. Front.* **2018**, *5*, 2579–2586. [\[CrossRef\]](#)
223. Wang, Z.; Li, X.; Qian, H.; Zuo, S.; Yan, X.; Chen, Q.; Yao, C. Upconversion Tm³⁺: CeO₂/palygorskite as direct Z-scheme heterostructure for photocatalytic degradation of bisphenol A. *J. Photochem. Photobiol. A* **2019**, *372*, 42–48. [\[CrossRef\]](#)
224. Lu, X.-H.; Xie, S.-L.; Zhai, T.; Zhao, Y.-F.; Zhang, P.; Zhang, Y.-L.; Tong, Y.-X. Monodisperse CeO₂/CdS heterostructured spheres: One-pot synthesis and enhanced photocatalytic hydrogen activity. *RSC Adv.* **2011**, *1*, 1207–1210. [\[CrossRef\]](#)
225. Martinez-Huitle, C.A.; Ferro, S. Electrochemical oxidation of organic pollutants for the wastewater treatment: Direct and indirect processes. *Chem. Soc. Rev.* **2006**, *35*, 1324–1340. [\[CrossRef\]](#)
226. Brillas, E.; Martinez-Huitle, C.A. Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review. *Appl. Catal. B Environ.* **2015**, *166–167*, 603–643. [\[CrossRef\]](#)
227. Malpass, G.R.P.; Miwa, D.G.; Machado, S.A.S.; Motheo, A.J. SnO₂-based materials for pesticide degradation. *J. Hazard. Mater.* **2010**, *180*, 145–151. [\[CrossRef\]](#)
228. Peleyelu, M.G.; Umukoro, E.H.; Bablola, J.O.; Arotiba, O.A. Electrochemical degradation of an anthraquinone dye on an expanded graphite-diamond composite electrode. *Electrocatalysis* **2016**, *7*, 132–139. [\[CrossRef\]](#)
229. Jüttner, K.; Galla, U.; Schmieder, H. Electrochemical approaches to environmental problems in the process industry. *Electrochim. Acta* **2000**, *45*, 2575–2594. [\[CrossRef\]](#)
230. Umukoro, E.H.; Kumar, N.; Ngila, J.C.; Arotiba, O.A. Expanded graphite supported p-n MoS₂-SnO₂ heterojunction nanocomposite electrode for enhanced photo-electrocatalytic degradation of a pharmaceutical pollutant. *J. Electroanal. Chem.* **2018**, *827*, 193–203. [\[CrossRef\]](#)
231. Kusmierik, E.; Chrząscijanska, E. Application of TiO₂-RuO₂/Ti electrodes modified with WO₃ in electro- and photoelectrochemical oxidation of Acid Orange 7 dye. *J. Photochem. Photobiol. A* **2015**, *302*, 59–68. [\[CrossRef\]](#)
232. Tantis, I.; Bousiakou, L.; Karikas, G.-A.; Lianos, P. Photocatalytic and photoelectrocatalytic degradation of the antibacterial agent ciprofloxacin. *Photochem. Photobiol. Sci.* **2015**, *14*, 603–607. [\[CrossRef\]](#)
233. Xiao, S.; Song, Y.; Tian, Z.; Tu, X.; Hu, X.; Ruixia, L. Enhanced mineralization of antibiotic berberine by the photoelectrochemical process in presence of chlorides and its optimization by response surface methodology. *Environ. Earth Sci.* **2015**, *73*, 4947–4955. [\[CrossRef\]](#)

234. Li, J.; Lv, S.; Liu, Y.; Bai, J.; Zhou, B.; Hu, X. Photoelectrocatalytic activity of an n-ZnO/p-Cu₂O/n-TNA ternary heterojunction electrode for tetracycline degradation. *J. Hazard. Mater.* **2013**, *262*, 482–488. [[CrossRef](#)]
235. Garcia-Segura, S.; Brillas, E. Applied photoelectrocatalysis on the degradation of organic pollutants in wastewater. *J. Photochem. Photobiol. C* **2017**, *31*, 1–35. [[CrossRef](#)]
236. Zarei, E.; Ojani, R. Fundamentals and some applications of photoelectrocatalysis and effective factors on its efficiency: A review. *J. Solid State Electrochem.* **2017**, *21*, 305–336. [[CrossRef](#)]
237. Yu, Y.; Yu, X.; Yang, S. Preparation and characterization of CeO₂ decorated TiO₂ nanotube arrays photoelectrode and its enhanced photoelectrocatalytic efficiency for degradation of methyl orange. *J. Mater. Sci. Mater. Electron.* **2015**, *26*, 5715–5723. [[CrossRef](#)]
238. Mafa, P.J.; Mamba, B.B.; Kuvarega, A.T. Photoelectrocatalytic evaluation of EG-CeO₂ photoanode on degradation of 2,4-dichlorophenol. *Sol. Energy Mater. Sol. Cells* **2020**, *208*, 110416. [[CrossRef](#)]
239. Zhou, Q.; Xing, A.; Li, J.; Zhao, D.; Zhao, K.; Lei, M. Synergistic enhancement in photoelectrocatalytic degradation of bisphenol A by CeO₂ and reduced graphene oxide co-modified TiO₂ nanotube arrays in combination with Fenton oxidation. *Electrochim. Acta* **2016**, *209*, 379–388. [[CrossRef](#)]
240. Zhou, Q.; Xing, A.; Zhao, D.; Zhao, K. Tetrabromobisphenol A photoelectrocatalytic degradation using reduced graphene oxide and cerium dioxide comodified TiO₂ nanotube arrays as electrode under visible light. *Chemosphere* **2016**, *165*, 268–276. [[CrossRef](#)] [[PubMed](#)]
241. Chen, C.; Zhao, D.; Zhou, Q.; Wu, Y.; Zhou, X.; Wang, H. Facile preparation and characterization of polyaniline and CeO₂ co-decorated TiO₂ nanotube array and its highly efficient photoelectrocatalytic activity. *Nanoscale Res. Lett.* **2019**, *14*, 60. [[CrossRef](#)]
242. Li, L.; Feng, H.; Wei, X.; Jiang, K.; Xue, S.; Chu, P.K. Ag as cocatalyst and electron-hole medium in CeO₂ QDs/Ag/Ag₂Se Z-Scheme heterojunction enhanced the photo-electrocatalytic properties of photoelectrode. *Nanomaterials* **2020**, *10*, 253. [[CrossRef](#)]
243. He, S.; Yan, C.; Chen, X.-Z.; Wang, Z.; Ouyang, T.; Guo, M.-L. Construction of core-shell heterojunction regulating α -Fe₂O₃ layer on CeO₂ nanotube arrays enables highly efficient Z-scheme photoelectrocatalysis. *Appl. Catal. B Environ.* **2020**, *276*, 119138. [[CrossRef](#)]
244. Wang, Y.; Hu, B.; Hu, C.; Zhou, X. Fabrication of a novel Ti/SnO₂-Sb-CeO₂@TiO₂-SnO₂ electrode and photoelectrocatalytic application in wastewater treatment. *Mater. Sci. Semicond. Process.* **2015**, *40*, 744–751. [[CrossRef](#)]
245. Chawla, P.; Tripathi, M. Surface modification of semiconductor photoanode for photoelectrochemical water splitting. *Int. J. Hydrog. Energy* **2016**, *41*, 7987–7992. [[CrossRef](#)]
246. Pan, Z.; Han, E.; Zheng, J.; Lu, J.; Wang, X.; Yin, Y.; Waterhouse, G.I.N.; Wang, X.; Li, P. Highly efficient photoelectrocatalytic reduction of CO₂ to methanol by a p-n heterojunction CeO₂/CuO/Cu catalyst. *Nano-Micro Lett.* **2020**, *12*, 18. [[CrossRef](#)]

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© 2020 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).