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TiO_2-CeO_2 Based Composite Materials and Their Application in Photocatalysis: A Short Review

Marija Vasić Jovev[1*], Aleksandra Krstić[1], Marjan Ranđelović[1], Radomir Ljupković[1], Katarina Stepić[1], Aleksandra Zarubica[1]

1-University of Niš, Faculty of Science and Mathematics, Department of Chemistry, Višegradska 33, 18000 Niš, Serbia

[*]Corresponding author: marija.vasic@pmf.edu.rs

ABSTRACT

In light of the ever-increasing problem of environmental pollution, photocatalysis represents one of the most promising solutions for the remediation/decomposition of wastewater pollutants. Among the materials used for the photocatalytic degradation of organic pollutants, titanium dioxide has been widely investigated due to its unique and favourable properties. On the other hand, its limitation in absorbing only about 5% of solar light and its relatively wide band gap and rapid recombination of electron-hole pairs restricts its practical application. In order to overcome this drawback and improve photocatalytic ability, various methods have been investigated. Some of the significant methods that have been extensively studied over the past decades involve the preparation of binary oxides, mixed oxide systems, composite materials, etc. This short review provides a comprehensive summary of scientific reports of titania-ceria composite materials and their applications in photocatalytic reactions reported in the literature.

Keywords: *TiO_2-CeO_2, composite materials, photocatalysis*

Introduction

The problem of environmental pollution is continuously increasing due to the constant development of industry in the growing world. Wastewater from industry often contains carcinogenic, toxic and mutagenic compounds/pollutants. These pollutants present a great threat/concern to the environment/ecosystem and all living world (plants, animals and humans) (Kumari et al., 2023; Kusmierek, 2020). One of the most studied methods used to remove environmental pollutants is photocatalysis. It is considered ecologically friendly and can be applied to degrading a broad spectrum of pollutants in water treatments (Kumari et al., 2023; Kusmierek, 2020; Malekkiani et al., 2022).

TiO_2 is one of the most investigated versatile materials in photocatalysis as it is considered a non-toxic, chemically stable, inert, and relatively inexpensive material. It is known for efficiently deleting various organic pollutants from water systems under relatively mild conditions (Kumari et al., 2023; Kusmierek, 2020; Malekkiani et al., 2022). In addition to TiO_2 being characterised by numerous favourable characteristics, the main problem for practical and commercial use of titania is its relatively wide band gap (3.0 to 3.2 eV) and limitation to use only 3-5% of the entire solar radiation spectrum for its activation (Kumari et al., 2023; Malekkiani et al., 2022; Stefa et al., 2020).

Various methods have been used to overcome these limitations- such as metal doping, synthesis of composites (TiO_2-CeO_2, Cu_2O-TiO_2, ZnO-TiO_2, Bi_2O_3-TiO_2) (Bessekhouad et al., 2005; Bian et al., 2008; Malekkiani et al., 2022; Qu et al., 2014; Topkaya 2014; Yang et al., 2007), binary oxides (TiO_2-SiO_2, TiO_2-ZnO, SnO_2-TiO_2 etc.), (Luo et al., 2015; Siwińska-Stefańska et al., 2018; Tricoli et al., 2009), multi mixed oxides (CuO-ZnO-Al_2O_3-ZrO_2) (Kumari et al., 2023; Kusmierek, 2020; Luo et al., 2015; Qu et al., 2014; Siwińska-Stefańska et al., 2018; Velu et al., 2002) etc.

The TiO_2-CeO_2-based composites have been broadly investigated due to ceria's distinct features, especially its Ce^{3+}/Ce^{4+} redox couple, easy transition between these oxidation states, high UV absorption ability, and remarkable oxygen storage capacity (Malekkiani et al., 2022; Qu et al., 2014).

Similar to TiO_2, CeO_2 has found a broad application in the photocatalytic processes of organic pollutants degradation, and it is one of the most investigated materials in literature, following TiO_2 (Kusmierek, 2020). This can be attributed to numerous favourable characteristics possessed by CeO_2, such as high thermal and chemical stability, a high oxygen storage capacity, high hardness, relatively low cost, etc. (Kumari et al., 2023; Kusmierek, 2020; Stefa et al., 2020; Vita 2020). CeO_2 is a rare-earth metal oxide that has a band gap in the range of 2.6 to 3.4 eV and can absorb a somewhat larger portion of the solar spectrum compared to TiO_2 (Kumari et al., 2023; Kusmierek, 2020; Malekkiani et al., 2022; Vita 2020). However, the position of its conduction band (CB) and valence (VB) band restricts its application, as it has low photonic effectiveness of solar energy (Kumari et al., 2023; Kusmierek, 2020).

It has been reported in the literature that titania's ability to absorb in the visible region can be achieved by coupling (integrating) titania with rare-earth metal oxides such as CeO_2 (Kumari et al., 2023; Malekkiani et al.; 2022 Vita 2020). The presence of ceria ions can facilitate the transfer of pollutant molecules onto the surface of the TiO_2 catalyst since Ce ions can form complexes with organic pollutants (Kumari et al., 2023). Furthermore, replacing Ti with Ce ions in the TiO_2 lattice introduces impurity levels in the band gap. This process increases the absorption capability of TiO_2, shifting its absorption towards the visible region, and provides better charge carrier separation (h^+/e^- pairs), thus enhancing the photocatalytic activity/efficiency of the TiO_2 catalyst (Kumari et al., 2023; Malekkiani et al., 2022). Additionally, CeO_2 can store oxygen from a water solution, increasing the amount of chemisorbed oxygen on the TiO_2 surface and consequently enhancing the degradation rate of pollutants, as oxygen plays a key role in oxidation reactions (Malekkiani et al., 2022). It has been reported in the literature that the TiO_2-CeO_2 composite has improved physico-chemical properties compared to pure titania when ceria is incorporated into TiO_2 (Kumari et al., 2023; Moongraksathum & Chen, 2017). In addition to causing the absorption edge to shift toward the visible region of the spectrum, the presence of ceria has an impact on the textural and structural characteristics of titania, stabilises the anatase crystal phase by suppressing the anatase to rutile phase transformation at elevated temperatures, thus consequently improving the photocatalytic activity (Kumari et al., 2023; Moongraksathum & Chen, 2017).

This short review provides a broad summary of scientific reports detailing the different synthesis methods, their optimisation and their influence on the physicochemical properties of prepared TiO_2-CeO_2-based composite materials. Furthermore, it will observe/discuss the impact of these characteristics on the photocatalytic performance investigated in various pollutant degradation reactions published in scientific literature.

Synthesis methods for the preparation of TiO_2-CeO_2-based composite

Various methods for synthesising TiO_2-CeO_2-based composite materials have been reported in scientific literature, including sol-gel (Moongraksathum & Chen, 2017; Qu et al., 2014; Wandre et al., 2016), hydrothermal (Stefa et al., 2020), co-precipitation (Zhang et al., 2018), electrodeposition, flame spray pyrolysis etc. (Kusmierek, 2020; Qu et al., 2014). It is well known that processing parameters and synthesis/preparation routes significantly affect the physicochemical characteristics of catalytic materials (such as textural, structural, morphological, etc.), consequently determining their photocatalytic performances (Kusmierek, 2020). In this paper, selected methods for synthesising titania-ceria composites will be discussed, as well as their influence on physical-chemical properties.

A group of authors, T. M. Wandre et al., reported (Wandre et al., 2016) the simple and economical sol-gel method using a cationic surfactant for preparing a series of TiO_2-CeO_2 composites. Titanium (IV) isopropoxide was used as the titania precursor, while cerium nitrate hexahydrate was used as the ceria precursor. Firstly, CeO_2 nanoparticles (NPs) were prepared and used later in the sol-gel synthesis of the TiO_2-CeO_2 nanocomposite. Cetyl trimethyl ammonium bromide (CTAB) was used as a capping agent, and ammonia facilitated the precipitation of the material. After the precipitation was finished, the precipitate was washed, filtered and dried, after which calcination was performed at a temperature of 500° C. Similarly, the authors prepared pure TiO_2 without adding CeO_2 for comparison (Wandre et al., 2016).

N. Zhang et al. (Zhang et al., 2018) reported the preparation/synthesis of sulfur-resistant TiO_2-CeO_2 composite material via the co-precipitation method. The authors used $TiOSO_4 \cdot 2H_2O$ and $Ce(NO_3)_3 \cdot 9H_2O$ as precursors for TiO_2 and CeO_2, respectively, to obtain TiO_2-CeO_2 catalyst powder with a molar ratio Ti: Ce=9:1. After the precipitation was completed, with the use of $NH_3 \cdot H_2O$ solution, the obtained residue was washed, dried and calcined for 3 hours at a temperature of 500 °C. The authors also prepared pure TiO_2 and CeO_2 using the same procedure (Zhang et al., 2018).

S. Stefa et al. (2020) reported using four different methods to prepare CeO_2/TiO_2 nanostructured oxides/composites. They used the hydrothermal method in one and two steps, precipitation and the Stöber method. The $TiOSO_4$ and $Ti(OBu)_4$, and $Ce(NO_3)_3{\cdot}6H_2O$ were used as a precursors for preparing CeO_2/TiO_2 materials with a Ce/Ti atomic ratio 4. The chemicals used by the authors were of analytical grade. Moreover, they studied the effect of these methods on the physico-chemical properties of as-synthesised materials. Furthermore, the authors used the CO oxidation performance for the catalytic evaluation of prepared catalysts (Stefa et al., 2020).

S. Ameen et al. (2014) synthesised CeO_2-TiO_2 nanocomposite material via facile solution-processed method. They used a Teflon-beaker autoclave, which was kept at 120° C for 48 hours. After the process, the autoclave was rested to cool down to room temperature. The resulting material was filtered, washed, and dried at a mild temperature overnight. This procedure was followed by a calcination process at 450° C (Ameen et al., 2014).

F. K. Dokan and Kuru (Dokan & Kuru, 2021) reported preparing an ultrafine composite material based on TiO_2-CeO_2 using the following procedure. Firstly, TiO_2 microspheres were prepared using the hydrothermal method. Afterwards, CeO_2 nanoparticles were loaded in different ratios/proportions onto the mentioned TiO_2 microparticles via the sol-gel method, using Pluronic 123 surfactant. Titanium (IV) butoxide ($Ti(OBu)_4$) was used as the precursor for TiO_2. The hydrothermal treatment was performed in a stainless steel autoclave at 240 °C for 2 hours. After the reaction, the precipitate was filtered and washed with water and ethyl alcohol. The next step was drying the material at 80 °C, and to obtain microspheres of TiO_2, the calcination was performed at 500 °C for 4 hours. Cerium nitrate (($Ce(NO_3)_3{\cdot}6H_2O$) was used as a precursor for the preparation of ultrafine nano-spherical TiO_2-CeO_2 composites. The preparation of composites was achieved by the surfactant-supported sol-gel method, as mentioned above (Dokan & Kuru, 2021).

The proposed schematic diagram of TiO_2-CeO_2-based material under UV and Visible light

The preparation method of the composite can significantly influence the position of the valence and conduction bands, affecting the photocatalytic performance of the prepared composite materials (Kusmierek, 2020). A heterojunction can form after coupling CeO_2 with TiO_2 (Jiang et al., 2018; Kumari et al., 2023;). Figure 1. (Kusmierek, 2020), presented/reported by E. Kusmierek, shows the possible photo-excitation mechanism of CeO_2/TiO_2-based composites.

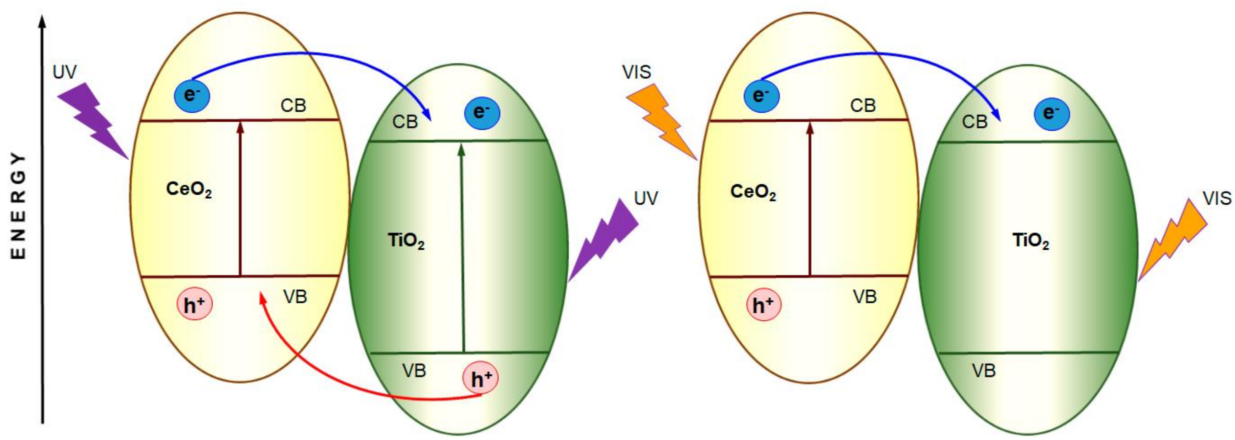

Figure 1. The proposed diagram of CeO_2/TiO_2 composite photo-excitation under UV and Visible light irradiation (Kusmierek, 2020)

After illumination by UV light, a CeO_2/TiO_2-based composite exhibits the formation of electron vacancies (holes) in the valence band (VB) and electrons in the conduction band (CB) of both semiconductors, resulting in the creation of h^+/e^- pairs. Electrons move from the valence band to the conduction band, generating electron vacancies (h^+) in the valence band. This phenomenon is depicted in Fig. 1 and reported by E. Kusmierek (Kusmierek, 2020). Ceria's VB and CB possess higher energy levels compared to titania, initiating photogenerated electrons to transfer from the CB of CeO_2 to the lower energy CB of TiO_2 (Ameen et al., 2014; Kusmierek, 2020; Tuyen et al., 2018). At the same time, photogenerated holes transfer from the VB of Titania to the VB of Ceria. This way, with the presence of O_2 and water, the formation of superoxide anion radicals ($O_2^{\bullet -}$) and hydroxyl radicals ($OH^{\bullet}$) occurs, as presented by the following reaction mechanism (Dokan & Kuru, 2021; Kusmierek, 2020):

$TiO_2 + h\nu \rightarrow e^{-}_{CB} + h^{+}_{VB}$

$Ce^{4+} + e^{-}_{CB} \rightarrow Ce^{3+}$

$Ce^{3+} + O_2 \rightarrow Ce^{4+} + O_2^{\bullet-}$

$H_2O + h^{+}_{VB} \rightarrow OH^{\bullet} + H^{+}$

$O_2^{\bullet-} + 4H^{+} \rightarrow 2OH^{\bullet}$

Ce^{4+} ions scavenge the photoexcited electrons, thus suppressing the recombination of h^{+}/e^{-} species and enhancing the photocatalytic efficiency of the composite materials (Kusmierek, 2020; Tuyen et al., 2018).

Characterisation of TiO_2-CeO_2-based composite materials

Numerous techniques and methods have been used by scientists for thorough characterisation of TiO_2-CeO_2-based composite materials such as X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), Brunauer–Emmett–Teller (BET) by N_2 adsorption-desorption measurements, Fourier-transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), photoluminescence (PL) spectroscopy, field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), H_2 temperature-programmed reduction (H_2-TPR), high-resolution transmission electron microscopy (HRTEM) and others (Ameen et al., 2014; Dokan & Kuru, 2021; Stefa et al., 2020; Wandre et al., 2016; Zhang et al., 2018;).

As detailed above, T. M. Wandre et al. reported synthesising and comprehensively characterising TiO_2-CeO_2 nanocomposites (Wandre et al., 2016). Various methods were used for detailed characterisation by the authors, including XRD with EDS attachment, UV–Vis diffuse reflectance spectra, FTIR spectra, PL spectra, XPS, and SEM. In this short review, the XRD and SEM methods will be discussed, as well as the photocatalytic activity of the samples prepared and reported by T. M. Wandre et al. (Wandre et al., 2016).

The authors (Wandre et al., 2016) used the X-ray diffraction method for crystallinity and phase determination. XRD results revealed that in the TiO_2-CeO_2 composite, the transformation from anatase phase to rutile was suppressed. Hence, the presence of ceria secured the stabilisation of the anatase phase. Furthermore, they noted that with an increase in CeO_2 content, the intensity of the peak characteristic for the anatase phase decreased (Wandre et al., 2016).

The authors (Wandre et al., 2016) investigated the morphological properties using SEM imaging. As the authors (Wandre et al., 2016) discussed, SEM micrographs revealed a similar fine particle structure of all samples that differed in particle sizes. They noted and reported that an increase in CeO_2 content led to a decrease in TiO_2 particle sizes; thus, the presence of CeO_2 restricted particle growth. In addition, the authors suggested that even/homogeneous dispersion of CeO_2 nanoparticles onto the TiO_2 surface was observed (Wandre et al., 2016).

N. Zhang et al. (Zhang et al., 2018) reported a thorough characterisation of the composite based on TiO_2-CeO_2 they prepared, as mentioned before. The methods they used were XRD, Raman spectra, BET XPS, H_2-TPR and oxygen storage capacity (OSC) technique. The XRD results reported and presented by the authors N. Zhang et al. are shown in Figure 2. (Zhang et al., 2018).

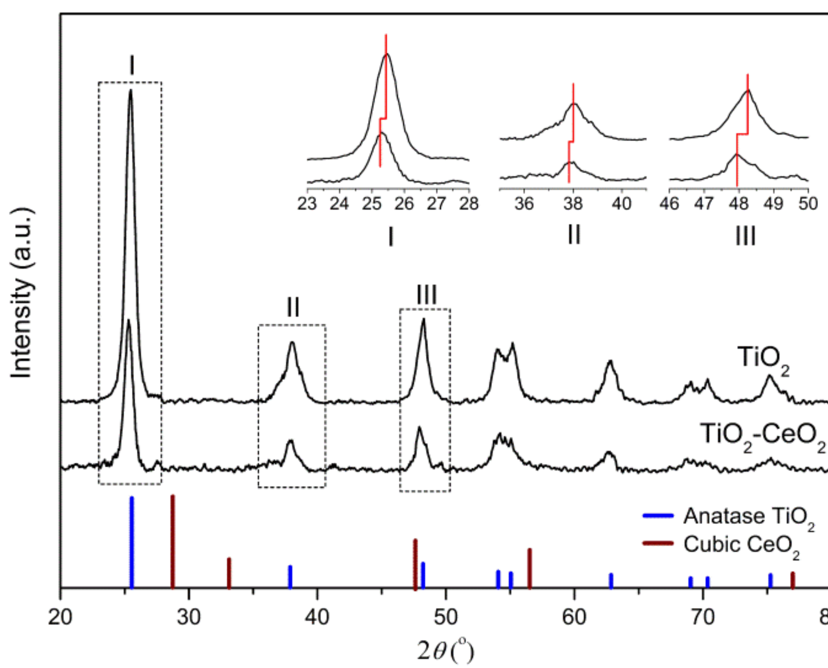

Figure 2. XRD patterns of the TiO_2 and TiO_2-CeO_2 catalysts (Zhang et al., 2018)

The XRD spectra obtained by the authors (Zhang et al., 2018) indicated the presence of the anatase TiO_2 crystal phase in both samples, pure TiO_2 and TiO_2-CeO_2. The authors N. Zhang et al. discussed that the position of peaks characteristic of the anatase TiO_2 crystal phase shifted to smaller angles in the TiO_2-CeO_2 composite compared to pure TiO_2 and suggested that this shift could be due to the possible entry of Ce^{4+} ions into the TiO_2 lattice, so complete CeO_2 crystals were not formed. Moreover, the authors reported the restriction of crystal growth in the TiO_2-CeO_2 composite material (Zhang et al., 2018). Also, no characteristic peaks for CeO_2 were observed. For the catalyst evaluation, the authors studied the oxidation test of the diesel-soluble organic fraction and noted an enhancement in the catalytic performances of the TiO_2-CeO_2 composite (Zhang et al., 2018).

S. Stefa et al. provided an extensive characterisation of the series of the materials they prepared, including BET, XRD, SEM/EDX, TEM, H_2-TPR (Stefa et al., 2020).

The textural characteristics presented by the S. Stefa et al. demonstrated that the sample synthesised by the one-step hydrothermal method (CeO_2/TiO_2-H1) had the highest value for BET surface area, followed by bare CeO_2 nanorods (CeO_2 NRs), CeO_2/TiO_2-S (sample prepared by the Stöber method), CeO_2/TiO_2-H2 (prepared by the two-step hydrothermal method), and the CeO_2/TiO_2-P sample (prepared by the precipitation), which demonstrated the lowest BET surface area value in the series of the prepared materials (Stefa et al., 2020).

S. Stefa et al. examined the structural characteristics of the XRD method (Stefa et al., 2020). Their results revealed the presence of the cubic fluorite structure of ceria in all samples. However, the small intensity of the peak characteristic for the anatase phase at around 25° was hardly noticed only in the sample prepared by the Stöber method (CeO_2/TiO_2- S), which was ascribed to the low loading of titania, as well as its high dispersion, by the authors (Stefa et al., 2020).

The authors discussed the morphological properties obtained by TEM and SEM-EDS methods (Stefa et al., 2020). TEM and HRTEM images obtained by S. Stefa et al. are shown in Figure 3. (Stefa et al., 2020). They noticed that the bare CeO_2 sample displayed a rod-like morphology and the samples prepared by the hydrothermal method in both one and two steps. In contrast, the sample obtained by the precipitation method showed irregular shapes. Furthermore, in the TEM images of the sample prepared by the one-step hydrothermal method, they discussed that no separated TiO_2 nanoparticles were identified. In contrast, in the sample prepared by the two-step hydrothermal method, TiO_2 nanoparticles were clearly observed (Stefa et al., 2020). The sample prepared by the Stöber method (CeO_2/TiO_2- S) displayed a rod-like morphology without separated TiO_2 particles, but the uniform distribution of TiO_2 around CeO_2 nanorods, as discussed by the authors S. Stefa et al. (Stefa et al., 2020).

These results clearly indicated that the choice of the preparation method and synthesis conditions/parameters significantly influenced the physicochemical properties of prepared samples (Stefa et al., 2020).

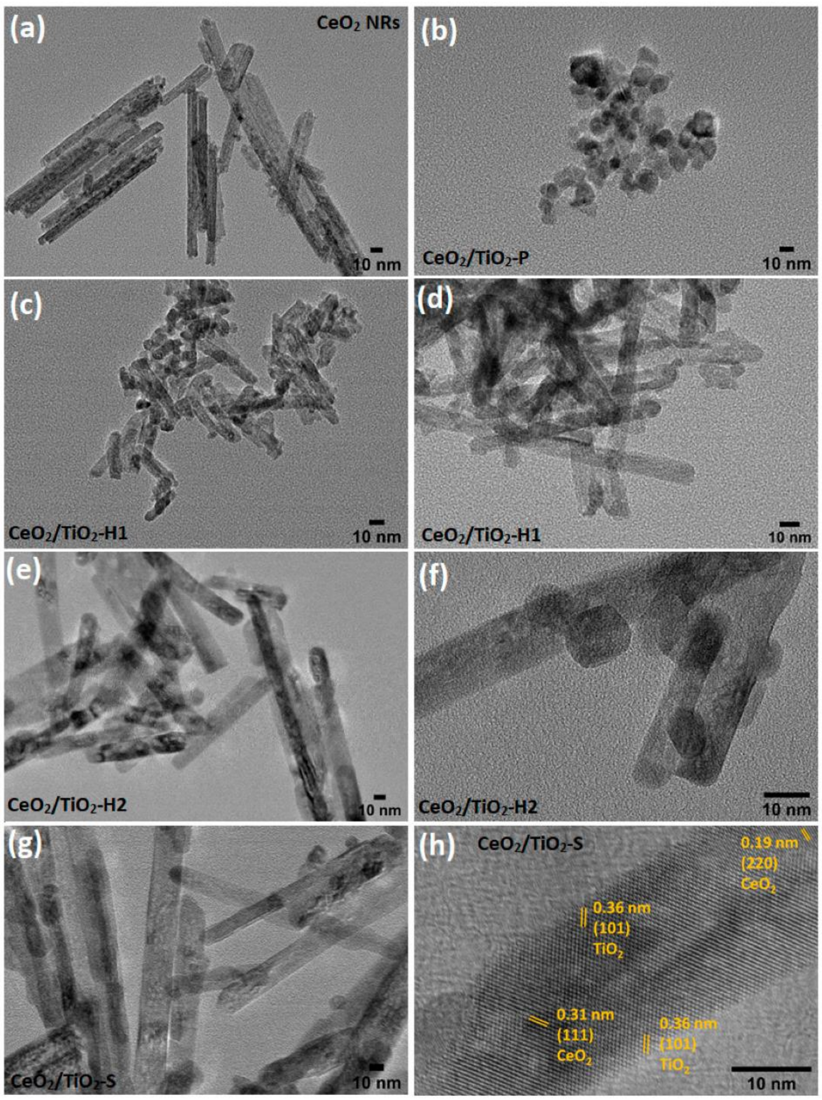

Figure 3. TEM images of the samples: (a) CeO_2 nanorods; (b) CeO_2/TiO_2-P; (c,d) CeO_2/TiO_2-H1; (e,f) CeO_2/TiO_2-H2; (g) CeO_2/TiO_2-S; (h) HRTEM images of CeO_2/TiO_2-S obtained by S. Stefa et al. (Stefa et al., 2020)

S. Ameen et al. (Ameen et al., 2014) published XRD results for structural characterisation, and they used FESEM and TEM for the determination of morphological properties. The FESEM and TEM images obtained by the authors showed that the large CeO_2 particles were uniformly embedded into small TiO_2 nanoparticles, which indicated/proved an excellent interaction and good mixing of CeO_2 into the TiO_2 in CeO_2-TiO_2 composite material (Ameen et al., 2014). Furthermore, the XRD spectra revealed the presence of diffraction peaks characteristic of anatase TiO_2 and cubic fluorite CeO_2 structure at 25,3° and 28,3°, respectively. These results revealed a significant red shift in the CeO_2/TiO_2 composite, indicating a shift to higher wavelength, which indicated the incorporation of Ce cations into the lattice of TiO_2 in TiO_2-CeO_2 composite material as discussed by the authors (Ameen et al., 2014).

F. K. Dokan and Kuru (Dokan & Kuru, 2021) thoroughly characterised the physicochemical properties of the TiO_2-CeO_2 prepared materials described earlier, which included techniques such as XRD, EDX, FE-SEM, BET, FTIR, etc. The BET results provided data on the textural properties of the materials prepared by authors F. K. Dokan and Kuru (Dokan & Kuru, 2021). The results obtained and presented by the authors revealed that the surface area increased with the increase in CeO_2 content (Dokan & Kuru, 2021). It has been reported that a high surface area is a favourable parameter, as it facilitates/promotes the adsorption of pollutant molecules on the catalytic surface, therefore improving/enhancing photocatalytic ability (Dokan & Kuru, 2021, Wang et al., 2013).

Application/testing of (photocatalytic) activity of TiO_2-CeO_2-based composite materials

A wide spectrum of hazardous pollutants has been investigated in photocatalytic degradation by titania-ceria composite materials under UV and/or Visible light.

The T. M. Wandre et al. (Wandre et al., 2016) reported investigating the photocatalytic application in the degradation reaction of methyl orange (MO) under UV irradiation (applied wavelength of 365 nm using a mercury lamp) and sunlight. Before UV irradiation, an adsorption-desorption equilibrium was secured. To estimate the photocatalytic activity, they utilised/used the UV-Vis-NIR spectrophotometer to observe the changes in the concentration of the tested solution.

The authors (Wandre et al., 2016) published that in the series of TiO_2-CeO_2 composite materials, all samples prepared with different ceria content showed improved photocatalytic activity compared to pure TiO_2. They discussed that as the CeO_2 content increased up to 30 %, the degradation rate increased and then decreased when the CeO_2 content was 50 %. It was concluded that the composite sample TiO_2-CeO_2 (7:3) exhibited the highest degradation rate of MO in the observed photocatalytic reactions and also showed outstanding performance in sunlight (Wandre et al., 2016).

S. Stefa et al. studied the CO oxidation performance order to investigate the catalytic activity of the samples they prepared based on CeO_2/TiO_2, CeO_2-NRs, and commercial TiO_2 that was used for comparison (Stefa et al., 2020). Their results showed that the oxygen storage capacity significantly impacted catalytic activity. The authors concluded that with an increase in oxygen storage capacity, the activity was improved. The sample prepared by the Stöber method (CeO_2/TiO_2-S) displayed the highest reaction rate (CO conversion), followed by the sample prepared by the one-step hydrothermal method. Their results clearly indicated that the synthesis method and preparation route significantly impacted the prepared ceria-titania materials' structural, morphological and other properties and that oxygen storage capacity was crucial for their catalytic performance (Stefa et al., 2020).

As detailed above, S. Ameen et al. (2014) reported the results of testing the CeO_2-TiO_2 composite they prepared for the photodegradation of bromophenol (Bph) dye under visible light. The results revealed outstanding efficiency of the CeO_2-TiO_2 composite, with 72% dye degradation after 3 hours, compared to only 6% when bare TiO_2 was used. This was attributed to enhanced charge separation (e-/h+ pairs) and higher adsorption capacity. The authors also provided mass results that indicated the degradation of Bph dye into less harmful chemicals under light illumination (Ameen et al., 2014).

The F. K. Dokan and Kuru (Dokan & Kuru, 2021) examined the photocatalytic activity of TiO_2 and TiO_2-CeO_2 nanocomposites in the photocatalytic degradation of Methylene blue dye under 365 nm UV light. The TiO_2-CeO_2 composite showed a higher degradation rate compared to TiO_2 microspheres. However, the authors discussed a phenomenon that with an increase in CeO_2 content, the surface area increased, and the degradation rate decreased. This decrease resulted from the increased coverage of the TiO_2 surface by CeO_2 microns, making it difficult for UV to stimulate/activate the TiO_2 catalyst surface. Therefore, it was concluded that for photocatalytic efficiency, it was fundamental/crucial to optimise the CeO_2 content, proving that only 0.1% was sufficient for achieving excellent photocatalytic performance (Dokan & Kuru, 2021).

Conclusion

Environmental contamination presents a challenging global issue, with industrial development constantly contributing to increasing the need for the improvement of methods and techniques used in combating pollution. This methods should be environmentally friendly, inexpensive and should not have a harmful impact on the environment during their application.

Recently, composite materials based on TiO_2 and other metal oxides have attracted significant attention from scientists, particularly the TiO_2-CeO_2-based composite materials that was the focus of this short review. The scientific reports discussed clearly indicate the existence of a synergistic effect between TiO_2 and CeO_2 that are reflected on the characteristics of the TiO_2-CeO_2-based composite material and significantly improves its activity. The presence of CeO_2 extended the light absorption towards the visible spectrum, enhanced charge separation and improved the overall photocatalytic performance of TiO_2-CeO_2 composite material compared to pure TiO_2.

Within the scope of this short review, different synthesis methods, characterization methods/techniques, and the catalysts' activities of TiO_2-CeO_2-based materials published in scientific papers were observed. Based on the discussed scientific papers, the synthesis method, together with optimising experimental conditions, has a crucial role in obtaining favourable physicochemical characteristics that further influence these materials' (photo)catalytic activity in the degradation of organic pollutants to less harmful or completely benign to the environment.

The composite materials based on TiO_2-CeO_2 exhibit unique physico-chemical properties that exceed the limitations/restrictions of individual components, thus offering a promising solution to environmental challenges regarding the green chemistry approach.

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Conflict-of-Interest Statement

None.

References

Ameen, S. Akhtar, M. S., Seo, H.-K., & Shin, H.-K. (2014). Solution-processed CeO_2/TiO_2 nanocomposite as potent visible light photocatalyst for the degradation of bromophenol dye. Chemical Engineering Journal, 247, 193–198.

Bessekhouad, Y., Robert, D., & Weber, J.-V. (2005). Photocatalytic activity of Cu_2O/TiO_2, Bi_2O_3/TiO_2 and $ZnMn_2O_4/TiO_2$ heterojunctions. Catalysis Today, 101, 315−321.

Bian, Z., Zhu, J., Wang, S., Cao, Y., Qian, X., & Li, H. (2008). Self-assembly of active Bi_2O_3/TiO_2 visible photocatalyst with ordered mesoporous structure and highly crystallised anatase. The Journal of Physical Chemistry C, 112, 6258−6262.

Dokan, F. K., & Kuru, M. (2021). A new approach to optimise the synthesis parameters of TiO_2 microsphere and development of photocatalytic performance. Journal of Materials Science: Materials in Electronics, 32, 640-655.

Jiang, H., Li, M., Liu, J., Li, X., Tian, L., & Chen, P. (2018). Alkali-free synthesis of a novel heterostructured CeO_2-TiO_2 nanocomposite with high performance to reduce Cr(VI) under visible light. Ceramics International, 44, 2709–2717.

Kumari, V., Sharma, A., Kumar, N., Sillanpaa, M., Makgwane, P. R., Ahmaruzzaman, Md., Hosseini-Bandegharaei, A., Manju Rani, M., & Chinnamuthu, P. (2023). TiO_2-CeO_2 assisted heterostructures for photocatalytic mitigation of environmental pollutants: A comprehensive study on band gap engineering and mechanistic aspects. Inorganic Chemistry Communications, 151, 110564.

Kusmierek, E. (2020). A CeO_2 Semiconductor as a Photocatalytic and Photoelectrocatalytic Material for the Remediation of Pollutants in Industrial Wastewater: A Review. Catalysts, 10 (12), 1435. https://doi.org/10.3390/catal10121435

Luo, S., Nguyen-Phan, T.-D., Johnston-Peck, A.C., Barrio, L., Sallis, S., Arena, D.A., Kundu, S., Xu, W., Piper, L.F.J., Stach, E.A., Polyansky, D.E., Fujita, E., Rodriguez, J.A., & Senanayake, S. D. (2015). Hierarchical Heterogeneity at the CeO_x−TiO_2 Interface: Electronic and Geometric Structural Influence on the Photocatalytic Activity of Oxide on Oxide Nanostructures. The Journal of Physical Chemistry C, 119, 2669−2679.

Malekkiani, M., Ravari, F., Magham, A. H. J., Dadmehr, M., Groiss, H., Hosseini, H. A., & Sharif, R. (2022). Fabrication of Graphene-Based TiO_2@CeO_2 and CeO_2@TiO_2 Core−Shell Heterostructures for Enhanced Photocatalytic Activity and Cytotoxicity. ACS Omega, 7, 30601−30621.

Moongraksathum, B. & Chen, Y.-W. (2017). CeO_2–TiO_2 mixed oxide thin films with enhanced photocatalytic degradation of organic pollutants. Journal of Sol-Gel Science and Technology, 82, 772–782.

Qu, X., Xie, D., Gao, L., & Du, F. (2014). Synthesis and photocatalytic activity of TiO_2/CeO_2 core–shell nanotubes. Materials Science in Semiconductor Processing, 26, 657–662.

Siwińska-Stefańska, K., Kubiak, A., Piasecki, A., Goscianska, J., Nowaczyk, G., Jurga, S., & Jesionowski, T. (2018). TiO_2-ZnO Binary Oxide Systems: Comprehensive Characterisation and Tests of Photocatalytic Activity. Materials, 11, 841.

Stefa, S., Lykaki, M., Fragkoulis, D., Binas, V., Pandis, P. K., Stathopoulos, V. N., & Konsolakis, M. (2020). Effect of the Preparation Method on the Physicochemical Properties and the CO

Oxidation Performance of Nanostructured CeO_2/TiO_2 Oxides. Processes, 8 (7), 847. https://doi.org/10.3390/pr8070847

Topkaya, E., Konyar, M., Yatmaz, H. C., & Öztürk, K. (2014). Pure ZnO and composite ZnO/TiO_2 catalyst plates: A comparative study for the degradation of azo dye, pesticide and antibiotic in aqueous solutions. Journal of Colloid and Interface Science, 430, 6−11.

Tricoli, A., Righettoni, M., & Pratsinis, S. E. (2009). Minimal Cross-Sensitivity to Humidity During Ethanol Detection by SnO_2-TiO_2 Solid Solutions. Nanotechnology, 20, 315502.

Tuyen, L. T. T., Quang, D.A., Toan, T. T. T., Tung, T.Q., Hoa, T. T., Mau, T. X., & Khieu, D.Q. (2018). Synthesis of CeO_2/TiO_2 nanotubes and heterogeneous photocatalytic degradation of methylene blue. Journal of Environmental Chemical Engineering, 6, 5999–6011.

Velu, S., Suzuki, K., Gopinath, C. S., Yoshida, H., & Hattori, T. (2002). XPS, XANES and EXAFS Investigations of $CuO/ZnO/Al_2O_3/ZrO_2$ Mixed Oxide Catalysts. Physical Chemistry Chemical Physics, 4, 1990−1999.

Vita, A. (2020). Catalytic Applications of CeO_2-Based Materials. Catalysts, 10, 576.

Wandre, T. M., Gaikwad, P. N., Tapase, A. S., Garadkar, K. M., Vanalakar, S. A., Lokhande, P. D., Sasikala, R., & Hankare, P. P. (2016). Sol–gel synthesised TiO_2–CeO_2 nanocomposite: an efficient photocatalyst for degradation of methyl orange under sunlight. Journal of Materials Science: Materials in Electronics 27, 825–833.

Wang, L., Wang, X., Cui, S., Fan, X., Zu, B., & Wan, C. (2013). TiO_2 supported on silica nanolayers derived from vermiculite for efficient photocatalysis. Catalysis Today, 216, 95-103.

Yang, H., Zhang, K., Shi, R.; & Tang, A. (2007). Sol−gel synthesis and photocatalytic activity of CeO_2/TiO_2 nanocomposites. Journal of the American Chemical Society, 90, 1370−1374.

Zhang, N., Yang, Z., Chen Z., Li, Y., Liao, Y., Li, Y., Gong, M., & Chen, Y. (2018). Synthesis of Sulfur-Resistant TiO_2-CeO_2 Composite and Its Catalytic Performance in the Oxidation of a Soluble Organic Fraction from Diesel Exhaust. Catalysts, 8 (6), 246. https://doi.org/10.3390/catal8060246