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Ceria doping boosts methylene blue photodegradation in titania nanostructures

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Ceria-doped titania photocatalysts (ceria loading 0.25-5.0 wt.%) were synthesized by hydrothermal methods for water remediation. Nanotubes (CeTNTx) and nanoparticles (CeTNPx) were obtained. Ceria doping was applied to tune the electronic properties of nanostructured titania, boosting its photocatalytic activity. CeTNT nanostructure contained anatase as the only titania phase, whereas CeTNP series consisted of both anatase and rutile polymorphs. Ce addition induced a decrease in the energy gap, allowing to enhance the visible light harvesting. The photodegradation of methylene blue, MB, in aqueous solution was studied to assess the influence of the morphology and the ceria loading on the photocatalytic response, under UV and solar light. Both CeO₂-TiO₂ nanoparticles and nanotubes were found to be active under UV light. The highest MB degradation rates were obtained for the 0.25 wt% CeO₂ doping, for both nanotubes and nanoparticles (0.123 and 0.146 min⁻¹, respectively), able to photodegrade completely the dye after 120 min and being stable after a 3-cycle reusability test. The photo-response under simulated solar light confirmed that doping titania with ceria allows to match visible light absorption, enhancing the photoactivity. Maximum efficiency (85%) under simulated sunlight, at a degradation rate of 0.054 min⁻¹ was obtained. Transient photoluminescence confirmed that MB acts as a charge scavenger for the composite system. These results pointed out ceria-doped titania nanostructures as a promising class of photocatalysts for the degradation of dyes and other hazardous organic compounds in wastewater.

Introduction

Water pollution constitutes an issue of major concern worldwide that not only affects the environment, but also jeopardizes human health. Moreover, it is a long-term problem since water pollution occurs in superficial water bodies but also reaches groundwater. This fact, together with its properties as a universal solvent, ease the degradation of water quality due to hazardous substances contained in wastewater effluents, such as heavy metals or organic compounds that can be non-biodegradable, highly toxic or even carcinogenic. Among all the anthropogenic sources of water pollution, it is estimated that more than 20% comes from the textile industry, which releases between 1000 and 3000 m³ of wastewater effluents for the processing of less than 20 tons of textiles per day[1]. These effluents usually contain high concentration of organic and inorganic compounds due to the incomplete fixation of dyes onto the fabrics, which leads to synthetics dye contents in effluents up to 10-15% that negatively affect both the ecosystem and human health[1]. On the other hand, as well as colouring water even at concentrations below 1 mg/L, they totally or partially block sunlight penetration, thus hindering the appropriate functioning of microbiological processes in the aquatic ecosystem. They can also interfere with photosynthesis, competing for oxygen with living species [2,3].

Conventional technologies for water purification of organic contaminants such as trickling filters, flocculation or electrodialysis are highly energy-demanding processes with considerable operation and maintenance costs that are not effective for dyes removal [1]. Adsorption is usually used in the removal of dyes from wastewater effluents and it has shown remarkable results, especially when using nanostructured materials [4]. Nevertheless, adsorptive processes are based on the transfer of pollutants from one phase to another, so eventually dyes are not destroyed. As an alternative to achieve the complete degradation or mineralization of these compounds, advanced oxidation processes (AOPs) arise as a low waste generation technology consisting of chemical treatments to remove organic compounds in wastewater effluents by oxidation, taking advantage of chemical species with short lifetime but high oxidation power, such as hydroxyl radicals. As short-lived species, OH radicals must be produced during the process through oxidizing agents such as H₂O₂ or O₃, catalysts like Fe³⁺ (Fenton process) or irradiation with UV light [5].

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In the presence of oxidants or catalysts, OH· radicals can be initiated by photons produced by light irradiation. Titania, TiO$_2$, an n-type semiconductor, is the most largely employed catalyst for UV-based AOPs operating at mild conditions (atmospheric pressure and room temperature), thanks to its outstanding photocatalytic properties, as well as its low cost, non-toxicity, great chemical and thermal stability and remarkable oxidation power [6,7]. Titania’s photocatalytic performance strongly depends on several parameters such as crystallinity, nanostructures’ morphology, specific surface area and pore size distribution [8–10]. Thus, different strategies to modify and tune these parameters in order to obtain superior photocatalytic TiO$_2$-based materials have been largely investigated.

Morphology plays a key role in the transport and recombination of photogenerated charge carriers. One-dimensional nanostructures like nanotubes or nanorods present low charge carriers recombination due to the short distance for their diffusion to the surface where the reaction takes place [11]. Likewise, three-dimensional materials have emerged as promising candidates for degradation of organic compounds. Nanoparticles show outstanding performance thanks to their large surface to volume ratio, which provides efficient diffusion pathways for pollutant molecules with the advantage that properties such as pore size, pore volume and specific surface area can be easily tuned by changes in the hydrothermal synthesis conditions used for obtaining titania nanoparticles [12]. Besides, microspheres present also high pore volume and pore size and avoid the formation of slurries after reaction in aqueous media, easing the catalyst recovery [13].

Considering that more than 40% of the total incident solar spectrum consists of visible light and only 4-5% of UV irradiation [14], great attention has been paid to broadening titania’s applications as a photocatalyst under visible light irradiation through doping, with the aim of narrowing its wide band gap (3.2 eV for anatase and 3.0 eV for rutile) [15], that does not allow to significantly exploit sunlight irradiation, and diminishing its high electron-hole pair recombination rate. Doping with metal or non-metal elements can help to increase the charge carrier lifetime by forming shallow traps slightly below (above) the conduction (valence) band. The photogenerated charge carrier recombination rate is decreased and visible light absorption is possible thanks to the defect states created in the band gap or to the introduction of energy levels in it [16,17]. Dopant efficiency towards charge carriers trapping depends on several parameters like dopant concentration and distribution, light intensity or stability of titania crystalline phase [18].

Figure 1. Undoped and Ce-doped TNT series. (a) XRD patterns, including benchmarking Anatase, Rutile and P25. (b) (αhν)$^{1/2}$ plot against photo energy (eV). TEM/HAADF for sample CeTNT025 (c/d) and CeTNT5 (e/f). Insets in (c) and (e) collect the EDS mapping for Ce overlapping the STEM images.
Rare earth elements have been extensively studied as dopants to modify titania crystal structure, thanks to their 4f electronic configuration [19]. When incorporated into a host matrix, the influence of this matrix over 4f optical transitions is negligible, as electrons in this level are shielded by the crystal field of neighbouring ions with electrons in 5s² and 5p⁶ orbitals.

Doping with cerium ions containing 4f electrons into the TiO₂ lattice can decrease significantly the recombination of electron–hole pairs and result in the extension of their wavelength response toward the visible region [20,21]. Among lanthanides, cerium is the most interesting element in the field of catalysis and photocatalysis. In particular, the wide use of ceria, CeO₂, and ceria-based mixed oxides as active components for catalytic reactions, especially oxidation reactions, has been traditionally associated with its unique excellent ability to shuttle between Ce(III) and Ce(IV) states, the well-known oxygen storage capacity (OSC), allowing CeO₂-based catalysts and photocatalysts to act as oxygen buffers and thus promoting reductive and oxidative activity [22–24]. The ability of Ce³⁺ to oxidize to Ce⁴⁺ states leads to high oxygen mobility, which in turn leads to a strong catalytic potential [17,25,26]. The theoretical band gap of CeO₂ is about 6.0 eV, nevertheless its experimental band gap is around 3.0-3.4 eV, a value very close to that of TiO₂ and ZnO [27], the two most employed semiconductors in photocatalysis. Most probably this is due to the O 2p→Ce 4f transition, even though the origin of this reduced band gap is still controversial [28].

Introduction of metal ions into the CeO₂ lattices can increase the density of oxygen vacancies and potentially improve the catalytic performance of CeO₂-supported metal catalysts, through changing the physical and chemical properties of the supports [29,30]. The preparation of CeO₂-TiO₂ systems could reduce the band gap of pure titania, improve charge separation and/or hinder the e⁻/h⁺ recombination due to the novel structures and interfacial charge transfer, resulting in a potentially enhanced photocatalytic degradation efficiency [31,32]. In fact, previous research carried out by Xu et al. [33] associated the enhancement in the photocatalytic activity of cerium doped titania in formaldehyde degradation with the suppression of electron-hole recombination by means of electron trapping at Ce⁴⁺ sites. Likewise, Li et al. [34] also demonstrated the improved photocatalytic performance of sol-gel synthesized Ce³⁺-TiO₂ catalysts in the photodegradation of 2-mercaptobenzothiazole in aqueous suspension with significant absorption in the visible region, suggesting that the existence of sub-energy levels in these structures may eliminate electron-hole pairs and therefore enhance the photocatalytic activity.

![Figure 2](image_url)
In the present work, nanostructured TiO$_2$ samples containing different CeO$_2$ loadings (ranging from 0.25 to 5.0 wt%) were synthesized by using hydrothermal methods in order to obtain two different nanoscale morphologies: nanotubes and nanoparticles. Their activity was evaluated in the methylene blue (MB) photodegradation at R.T. and atmospheric pressure, both under UV and solar light irradiation, and correlations between photocatalytic activity and physicochemical and optical properties of the nanomaterials were made.

### Results and discussion

**Physicochemical and optical characterization**

Phase identification of pure and ceria-titania nanotubes, pure and ceria-titania nanoparticles and commercial P25 titania (used for comparison purposes) was performed by X-ray diffraction and diffraction patterns are displayed in Figure 1 a) and Figure 2 a).

For all the CeTNTx (ceria-titania nanotubes) samples, the characteristic peaks of anatase phase emerged at 2θ = 25.5°, 38.0°, 48.1° and 54.7°, in agreement with the values of the standard card (database PDF 73-1764). No cerium-based phases were detected, neither in the samples with a very low CeO$_2$ content (0.25, 0.5, 1.0 wt%), undetectable as below the XRD detection limit, nor in the samples with a higher ceria loading (2.5 and 5.0 wt%), most probably due to a very highly homogeneous dispersion of cerium species in the titania matrix, or formation of very small ceria particles decorating titania structures. This result is confirmed also by Raman spectroscopy (Figure S1a), in which no ceria phase is detected and peaks only from anatase are visible.[35][Ref] Even though the ionic radius of Ce$^{4+}$ (0.97 Å) is much larger than that of Ti$^{4+}$ (0.68 Å) [36], the introduction of cerium ions into TiO$_2$ lattice, with some deformations on the lattice, and the formation of Ce-Ti solid solution, Ce$_x$Ti$_{1-x}$O$_2$, cannot be discarded. It has been suggested that, for quite low Ce concentration, the incorporation of Ce$^{4+}$ into the anatase lattice could take place, while at higher Ce loadings (usually ≥ 5 mol %, corresponding to ca 13 wt%) the anatase lattice is saturated and the formation/separation of amorphous ceria and/or ceria nucleation can occur, accompanied by the increase of TiO$_2$ anatase crystallite size and the limitation of value of anatase cell volume [37]. The highest Ce concentration studied (5.0 wt.%), is below the threshold for separation of amorphous ceria and/or nucleation of microcrystalline ceria. As for TNP and CeTNPx nanoparticle samples, well resolved reflections at 2θ values of 25.5°, 38.0°, 48.1° and 54.7°, corresponding to the characteristic pattern of anatase polymorph (PDF 73-1764), and less intense peaks related to rutile polymorph at 36.0° and 54.1° of 28 (PDF 21-1276), were observed for all the investigated systems. No peaks related to cerium-based phases were detected, most probably due to a high dispersion of cerium species into the titania matrix even with a 5.0 wt% CeO$_2$ loading. Semi-quantitative analysis indicates that about 80% of TiO$_2$ present in these samples is as anatase phase and the remaining 20% as rutile polymorph, comparable with the crystalline composition of the commercial P25 titania benchmark. These results are confirmed by Raman spectroscopy (Figure S1b), which indicate the presence of both anatase and rutile phases.[35][Ref]

| Sample         | CeO$_2$ loading (wt%) | $^a$S$_{\text{BET}}$ (m$^2$g$^{-1}$) | $^b$Pore volume (cm$^3$g$^{-1}$) | $^c$TiO$_2$ phases \(X_a\) (wt%) | $^d$E$_{\text{g}}$ (eV) | $^e$K$_{\text{UV light}}$ (min$^{-1}$) | $^f$K$_{\text{Solar light}}$ (min$^{-1}$) |
|----------------|----------------------|------------------------------------|---------------------------------|---------------------------------|----------------|----------------------------|----------------------------|
| TNT            | -                    | 27                                 | 0.13                            | 100                             | -              | 3.20                      | 0.011                     |
| CeTNT025       | 0.25                 | 26                                 | 0.15                            | 100                             | -              | 3.10                      | 0.123                     |
| CeTNT05        | 0.5                  | 26                                 | 0.16                            | 100                             | -              | 3.05                      | 0.036                     |
| CeTNT1         | 1.0                  | 26                                 | 0.15                            | 100                             | -              | 3.03                      | 0.046                     |
| CeTNT2.5       | 2.5                  | 21                                 | 0.14                            | 100                             | -              | 2.90                      | 0.055                     |
| CeTNT5         | 5.0                  | 20                                 | 0.18                            | 100                             | -              | 2.65                      | 0.004                     |
| TNP            | -                    | 118                                | 0.55                            | 73                              | 27             | 3.00                      | 0.069                     |
| CeTNP025       | 0.25                 | 99                                 | 0.45                            | 79                              | 21             | 3.00                      | 0.146                     |
| CeTNP05        | 0.5                  | 98                                 | 0.44                            | 81                              | 19             | 3.00                      | 0.134                     |
| CeTNP1         | 1.0                  | 92                                 | 0.41                            | 81                              | 19             | 2.95                      | 0.105                     |
| CeTNP2.5       | 2.5                  | 71                                 | 0.36                            | 85                              | 15             | 2.75                      | 0.097                     |
| CeTNP5         | 5.0                  | 65                                 | 0.35                            | 79                              | 21             | 2.75                      | 0.056                     |
| P25            | -                    | 55                                 | 0.06                            | 83                              | 17             | 3.15                      | 0.079                     |

$^a$ N$_2$ physisorption data calculated with BET method by N$_2$ physisorption at -196°C.

$^b$ Cumulative pore volume calculated at relative pressure $p/p_0=0.98$ by N$_2$ physisorption at -196°C.

$^c$ TiO$_2$ crystalline phases determined with X-Pert High Score Program.

$^d$ Band gap determined by DRUV-Vis spectroscopy.

$^e$ Kinetics constants under UV and solar light irradiation, respectively.

### Table 1. Textural, structural, optical parameters and kinetic constants of MB degradation in aqueous solution under UV and simulated solar light irradiation for pure titania samples (TNT and TNP) and ceria-titania systems (CeTNTx and CeTNPx series).
The estimated anatase mean crystal size, calculated by Scherrer equation, was approximately 18 nm for all the samples of CeTNTx series and 32 nm for CeTNPx series. The porosity nature of the prepared materials was evaluated by N₂ physisorption at -196 °C and the textural properties (specific surface area, S_{BET}, and total pore volume, Vₚ) are summarized in Table 1. In order to compare the samples with a benchmark titania, Degussa P25 was also analyzed. The synthesized nanostructures, both nanoparticles and nanotubes, present type IV isotherms with H3 hysteresis loop (not shown), characteristic of mesoporous materials. While CeTNTx series shows a quite low specific surface area, ranging between 20-27 m²g⁻¹, CeTNPx series displays higher S_{BET} values, much higher than that of the commercial P25 titania (55 m²g⁻¹). Pure titania nanoparticles, TNP sample, show a BET specific surface area of 118 m²g⁻¹, with a cumulative pore volume of 0.55 cm³g⁻¹. Mixed oxide nanoparticles, CeTNPx, display textural properties very close to each other, with relatively lower BET values, ranging between 65 and 99 m²g⁻¹ and a slight decrease of the total pore volume in the range 0.35-0.45 cm³g⁻¹ (Table 1), indicating that although some CeO₂ species are blocking titania’s pores, titania nanoparticles are not significantly affected by changes in the sample composition.

The surface atomic compositions of CeO₂-TiO₂ materials as well as the chemical state of the elements were estimated by X-ray photoelectron spectroscopy (XPS). O 1s, Ti 2p, and Ce 3d core level spectra were recorded to determine the species present on the catalysts surface. The binding energies of core level electrons for ceria-titania nanotubes series (CeTNTx) and nanoparticle (CeTNPx) systems are listed in Table S1. The Ti 2p core level spectra for all the samples (Figure 3a-b) showed asymmetric doublets at 463.4 eV and 583.3 eV, ascribed to core levels of Ti 2p₁/₂ and Ti 2p₃/₂, respectively, characteristic of Ti⁴⁺ ions and very similar to that reported for pure TiO₂ nanosystems [38]. The peak separation Ti 2p₁/₂-Ti 2p₃/₂ was about 5.7 eV in all cases, indicating that Ti ions were present in Ti⁴⁺ oxidation state coordinated octahedrally. By comparing both families of compounds the Ti 2p₁/₂ BE values are slightly higher in the case of TNT family where the titania polymorph phase present was anatase; instead, TNP samples possess both anatase and rutile polymorphs. The BE values for anatase have been reported at 458.4 eV [39]; for rutile 458.7 eV [40]: the expected tendency is just the opposite found experimentally, suggesting that the morphology of titania, rather than its crystalline phase, determines the lability of the electrons in the core level. After cerium ions incorporation, a slight shift of the signal towards lower binding energy was observed in the case of CeTNT family. This effect is much more significant at higher Ce loadings, indicating a greater contribution of titanium in lower oxidation state due to the interaction with Ce species on the catalysts surface. However, the doublet separation (5.7 eV) indicates that titanium is in its (IV) oxidation state. The interaction with Ce on the surface could explain the observed shift due to the close interaction of ceria and titania species that ease oxygen mobility in the Ce-O-Ti system, leading to the formation of oxygen vacancies that are believed to be more reactive in redox processes [41], thus improving the photocatalytic activity. The opposite tendency is obtained for CeTNP family. A shift to higher BE values has been reported to be due to ion incorporation in the substitutional site of TiO₂ lattice or the formation of Ti-O-Me bonds, that in this case could be related to Ce insertion into TiO₂ matrix as observed before in mixed Ce-Ti oxides containing different Ce and Ti loadings, where similar shift in Ti signal happened [42]. Another possible reason for the peaks shift could be the existence of oxygen vacancies in the catalyst structure [43].
presence to surface oxygen: (O\textsuperscript{2-}, OH\textsuperscript{-}, CO\textsubscript{3}\textsuperscript{2-}, CO\textsubscript{2}\textsuperscript{2-}) [44]. By incorporating ceria, as in the case of Ti 2p signal, it was observed a shift to lower BE values, indicating an increase in the oxygen mobility [43]. In the case of CeTNPx family, O 1s main signal was located at lower BE values than CeTNTx one, 529.6 eV. TNP bare titania also showed the contribution at 531.6 eV, characteristic of surface oxygen. Ce incorporation shifted the main signal to slightly higher values, (Table S1), suggesting that, taking into account the decrease in electronic density due to Ce presence, the formation of CeTiO mixed solution cannot be discarded. The most striking results come from the appearance of a third contribution after Ce incorporation into pure TNP. This contribution appears at ca 533.5 eV, which is reported in the literature to be due to chemisorbed oxygen, respectively [45].

Ce 3d signals from CeTNTx series were not detected, associated to the low Ce quantity and probably its low dispersion. Nonetheless, Ce core-level photoelectron spectra were observed for CeTNPx samples and represented in Figure 3d. The spectra were very noisy and the different contributions were only noticeable for Ce loadings higher than 0.5%. Thus, four spin-orbit doublets were present and indicated as v(n) and u(n): three due to Ce\textsuperscript{4+} species (v (∼882.2 eV) and u (∼900.7 eV); v’ (∼888.8 eV) and u’ (∼907.2 eV); v” (∼892.8 eV), u” (∼916.5 eV)) and one due to Ce\textsuperscript{3+} ones (v’’ (∼884.5) and u’’ (∼903.3 eV)). [46]. The presence of Ce\textsuperscript{4+} was dominant, although great proportion of Ce\textsuperscript{3+} can be observed for samples containing 2.5 and % of Ce.

HR-TEM micrographs in Figure 1 c-f show that CeTNTx series presents randomly distributed titania nanotubes as the main structure, with nanometric ceria particles hosted inside titania nanotubes as demonstrated in HAADF images. In the case of CeTNT5, although the majority of titania is in the form of nanotubes, the presence of some nanosphere structures can also be noticed in Figure S2, suggesting an incomplete transformation of the nanopowder, from the sol-gel process (first step of synthesis) to the reaction with a basic solution at autogenous pressure (second step) [47]. The analysis of nanotubes and nanoparticles sizes was performed with ImageJ software. On the one hand, it reveals that CeTNT2.5 nanotubes present a uniform length of approximately 122 nm and diameter of 6 nm, whereas those in samples with the highest Ce contents have an average length of 97 nm and diameter of 8 nm. On the other hand, it was found that Ce nanoparticles had a mean diameter of just 2 nm in samples with 2.5 wt% Ce and 1.6 nm in CeTNT5 sample, which supports the fact that, as previously reported [48], ceria nanoparticles grow inside titania nanotubes, assuring a close contact between both phases and promoting the formation of an intermixing of ceria and titania oxides, which would favor the formation of Ce\textsuperscript{3+} cations. The small size of ceria particles may also explain the absence of reflections from ceria phases in XRD. For comparison purposes, HR-TEM micrographs of pure titania samples, both TNP and TNT, are reported in Figure S3.

EDX-STEM mapping was performed in order to study the dispersion of Ce on the catalysts, resulting in high dispersion of Ce nanoparticles in titania nanostructures, as observed in insets of Figure 1c and e. EDX spectrum’s quantification (see Figure S4) showed that Ce nanoparticles count up to 3 wt% and 3.5 wt% of Ce in CeTNT2.5 and CeTNT5 systems, respectively, which is close to the theoretical values expected considering the local analyses carried out. The EDX spectrum also showed a contribution attributed to Na from the synthetic method employed.

Regarding CeTNPx series, HR-TEM micrographs in Figure 2 c-f and Figure S5 revealed that titania nanoparticles were mainly square-shaped, with diameters between 20 and 25 nm, being the largest ones found in the samples with higher Ce content. Although different cerium loadings seem not modifying the general morphology of titania nanostructures, EDX mapping in Figure 2d showed that in the case of CeTNP2.5, despite the good dispersion of ceria, also some agglomerates can be observed that are not present in the sample with 5 wt% Ce in Figure 2f. As in the case of CeTNTx series, the EDX spectrum quantification of 3.85 wt% and 5 wt% of Ce for CeTNP2.5 and CeTNP5, respectively, which is in good agreement with the theoretical value, suggesting a great dispersion of ceria in the titania matrix. The small NPs in Figure 2d and Figure S5 seem being Ce-rich. Such phenomenon is most likely due to the fact that Ce atoms tend to concentrate mainly at the surface of titania structures. This is in agreement with XRD and Raman results, in which no ceria phases are detected and (in XRD) no distortion of crystal lattice is recorded, even at the highest Ce concentration. Since the small particles exhibit the highest specific surface, it is reasonable that Ce concentration is higher than for large NPs.

The photo-responsive behavior of both nanostructured systems was explored by DRUV-Vis spectroscopy, to determine the energy gap, E\textsubscript{g}. The DRUV-Vis spectra of CeTNTx and CeTNPx series are shown in Figure 1b and Figure 2b, respectively, and optical band gap values, estimated from the intercept of the extrapolated linear fit for the plotted experimental data of (ahv)\textsuperscript{1/2} (the exponent ½ was chosen for the indirect bandgap in titania) versus incident photon energy (hv) near the absorption edge, are listed in Table 1. The intrinsic interband absorption of pure titania sample TNT was observed at wavelengths shorter than 400 nm (in the UV region) with E\textsubscript{g} values of 3.20 eV. Conversely, the CeO\textsubscript{2} doped-TiO\textsubscript{2} nanotubes showed a red shift in absorbance, as highlighted in Figure 2b. This narrower band edge has been speculated to arise from the formation of Ce\textsuperscript{3+} ions that can induce some localized mid-gap states in the band gap [49,50].

By increasing the loading of ceria in the titania matrix for TNT series, a significant decrease of the band gap was in fact obtained. The E\textsubscript{g} values of samples containing a low amount of ceria, CeTNT025, CeTNT05 and CeTNT1, are slightly lower, in the 3.10-3.03 eV range. CeTNT2.5 and CeTNT5 samples (containing 2.5 and 5.0 wt% of ceria, respectively) display an E\textsubscript{g} value of 2.90 and 2.65 eV, respectively, much lower than that of pure titania sample. The doping of ceria with Ce ions produced a red shift in the absorption edges, increasing the available spectral region that could be used in photocatalytic processes, allowing to harvest visible light and generating a greater number of electrons and holes under visible-light irradiation that could
actively participate in oxidation and reduction reactions. A significant decrease of the band gap by increasing the Ce loading, even though less marked than in CeTNT family, was also obtained in the CeTNPx series (Figure 2b), passing from 3.00 eV for the pure titania, TNP, to 2.75 eV for the 5.0 wt% ceria-doped sample, CeTNT5.

Photodegradation of methylene blue under UV and simulated solar light irradiation

Methylene blue, a heterocyclic aromatic compound, was taken as the photocatalytic probe molecule in this work since it is used as a textile, leather and paper dye that contributes to water pollution. It is well known that the amount of organic molecule adsorbed on the catalyst surface is affected by the pH value of the solution and depends on both the specific surface area and the point of zero charge (PZC) of the material. Ceria typically shows a PZC around pH 7.2 [51], while that of titania is around 6.0-6.5 [52]. The adsorption of MB via coulombic attraction is likely to be negligible at solution pH values below the PZC of the semiconductor, but increasingly significant at pH above the PZC value with an electrostatic absorption between the cationic dye [26] and the negatively charged surfaces of CeO₂ or TiO₂ [43,44,45]. A value of pH around 5.5 is generally recommended for the degradation of methylene blue in an aqueous medium [53].

The pathway for MB degradation under UV light irradiation on TiO₂-based materials is well known, based on the conversion of the organic dye into harmless CO₂, nitrate, ammonium, and sulfate ions and it has been deeply investigated through LC/MS and GC/MS analyses of the intermediate compounds [54]. In this work, UV-visible spectra were recorded and monitored in the range 300-900 nm at different photoreaction times (after 5, 10, 15, 20, 40, 60, 90 and 120 min), also investigating the potential presence of leuco methylene blue (LMB) in solution. It is in fact known that MB can be reduced to colorless LMB, stable in vacuum or under inert atmosphere, that can be rapidly reduced back to MB [55] and both methylene blue and its reduced form exhibit their characteristic and strong absorbance bands in the 250-800 nm range. At the pH used to perform the catalytic test, no color change of MB solution was noticed, which was also confirmed by the absorption profile of the dye in the visible region. This marks the stability of MB solution in an acidic pH range as no absorption peak appeared around 520 nm [55], the characteristic wavelength of the LMB peak.

Figure 4. (a, b) UV-Visible spectra recorded at different times, from 30 min in dark conditions (30D) to 120 min under UV light irradiation (120L) of the two 5.0 wt% CeO₂-TiO₂ nanostructures: a) CeTNT5 sample; b) CeTNP5 sample. (c-f) MB photodegradation test in aqueous solution: c) CeTNTx under UV light irradiation and d) under simulated solar light; d) CeTNPx under UV light irradiation and f) under simulated solar light.

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Figure 4a and b shows the MB UV-vis absorption spectra in dark mode and under UV light for the two nanostructures with the highest CeO$_2$ loading (5 wt%), taken as examples. The decrease in absorption at 664 nm has been ascribed to the degradation of benzene rings and heteropoly-aromatic linkage [54]. Since no other absorption bands were detected, it can be stated that LMB form was not present in the reaction environment neither for nanotube samples nor for nanoparticle ones and that the sample solution bleaching was completely due to dye degradation. Figure 4c-f presents the photocatalytic performance of nanotube and nanoparticle series in the methylene blue decomposition in aqueous solution under UV and simulated solar light irradiation, while the corresponding pseudo-first order kinetic constant values, $k$, calculated using the data from non-stationary regime during the light phase, are listed in Table 1. A comparison with the commercial P25 Degussa TiO$_2$, usually employed as a standard benchmark photocatalyst, was also made since it shows a high activity in the investigated reaction.

Figure 4c and e presents the photocatalytic activity of CeTNTx series in the monitored period of 120 minutes. After 30 min of equilibration in the dark (switching off light), a certain amount of MB is adsorbed on the surface of the samples, with a 35%-45% decrease in dye concentration in the solution when increasing CeO$_2$ loading from 0.25 up to 5.0 wt%.

Under UV light, all the CeTNTx photocatalysts show a very interesting catalytic performance, except the CeTNT5 sample, being the CeTNT025 (0.25 wt% ceria-containing nanosystem) the most photoactive one, with a kinetic constant for MB degradation rate of 0.123 min$^{-1}$, and able to photodegrade almost completely (99%) the dye after 120 minutes. As to the pure titania sample, TNT, its performance is lower than that of P25 benchmark, which could be ascribed to the lower surface area of TNT in comparison with the commercial titania (27 m$^2$g$^{-1}$ and 55 m$^2$g$^{-1}$, respectively). Regarding the Ce-containing samples, the presence of ceria seems to improve the photocatalytic activity with respect to pure nanotubes at low loadings, while the catalytic performance worsens for a 5 wt% ceria loading. As suggested by TEM and EDX measurements, the relatively high coverage of the surface by ceria nanoparticles could be hindering pollutants molecules’ access to TiO$_2$ actives sites, thus lessening the photocatalytic activity.
These materials were also tested in the same operating conditions under standard simulated solar light irradiation. CeTNT2.5 sample displayed the highest reaction rate ($k = 0.019$ $\text{min}^{-1}$), as well as the best performance, both in comparison with the other Ce-containing nanotubes and the pure titania samples (TNT and P25). The catalytic behaviour of these systems is in accordance with the $E_C$ values obtained (Table 1): the lower the band gap of the sample, the higher its activity under simulated sunlight. Although also the sample containing 5 wt% of ceria displayed a band gap (2.65 eV) suitable to harvest the visible portion of the solar spectrum, its catalytic activity is quite lower in comparison to the sample containing 2.5 wt% of ceria, probably due to the weak interaction between TiO$_2$, the most photoactive phase, and CeO$_2$ in this sample as a consequence of the high Ce loading covering the photocatalyst’s surface, as confirmed by HRTEM. As expected, both pure TiO$_2$ samples, the fresh synthesized TNT and the commercial P25 chosen for comparison purposes, showed a kinetic constant higher under UV than solar light irradiation, due to their wide energy gap values (3.20 and 3.15 eV, respectively). As for the CeTNPx series (Figure 4d-f), under UV light irradiation all the samples displayed a high activity towards the desired reaction, reaching an almost complete dye photodegradation in the monitored time. In particular, the results suggest that the presence of small amounts (< 2.5 wt%, best performance for 0.25 wt.%) of ceria in this kind of nanostructure is highly beneficial for the kinetics of the reaction.

The highest $k$ constant under UV light (0.146 $\text{min}^{-1}$) was obtained for CeTNP025 sample, able to reach a residual $C/C_0$ value of 5 % just after 20 min and photodegrade completely MB after 2 h. Under simulated sunlight irradiation, the catalytic behavior of the nanoparticle-based series showed what was already observed for the CeTNTx series, with the trend following the increasing amount of ceria in the titania matrix and, as expected, the decreasing band gap values. Samples with 2.5 and 5.0 wt% of ceria exhibit a much higher activity in degrading the organic dye under solar light with respect to their congeners, with a $k$ value of 0.054 and 0.052 $\text{min}^{-1}$, respectively. Charge dynamics in the two series of samples was investigated through time-resolved photoluminescence (TRPL), by monitoring the modification of the PL decay spectra upon MB addition in suspensions containing CeTNTx and CeTNPx. Similar analysis was already proposed for other luminophores to investigate the PL quenching properties of electron scavengers during photocatalytic processes [56]. The emission and excitation wavelengths were selected as: $\lambda_{em}=400$ nm and $\lambda_{ex}=250$ nm ($-4.96$ eV) aiming at studying the evolution of the 4f-5d transition of Ce$^{3+}$ [57]. The PL emission at 400 nm is also observed in the as-prepared TiO$_2$ (TNP) sample, which is similar to the PL of ultrafine TiO$_2$ powder reported by S. Kanjanaka and co-workers [58]. The presence of MB in solution, as already highlighted from the photocatalytic measurements in both the series of samples, induces a fast charge transfer from the photoexcited electrons in the conduction band of the mixed oxide to the lower unoccupied molecular orbital (LUMO) of MB. Such recombination path competes with the radiative recombination originating the PL under investigation, affecting its time decay behavior. In Figure 5 the time resolved PL at 400 nm emission is reported for a series of selected samples in solution with and without MB from both the series. In all the samples, the TRPL intensity curve is characterized by the presence of two time constant decays, the first one with characteristic decay time in the range of few ns (falling into the limit of the instrument), the second one in the order of around 110 $\mu$s. The presence of MB modifies the TRPL spectra. The relative intensity of fast decay increases while the slow decay decreases. However, the long decay constant of around 110 $\mu$s keeps the same in both Ce-TNT (TNP) and Ce-TNT (TNP)/MB, which is in agreement with the hypothesis that the MB acts as a carrier scavenger to Ce-TiO$_2$. It also indicates that uptake (and degradation) of MB did not introduce any new excited state around 400 nm. Among all the five measured samples as shown in Figure 5, the Ce-TNT25 sample presents most significant drop on the intensity of the slow decay component after mixing with MB, which can be correlated and is in agreement with the results on MB degradation presented in Figure 6.

Since the recyclability of a catalyst is very important for its practical use, a stability and reusability test of the best performing photocatalysts under UV light irradiation, CeTNT025 and CeTNP025 (both containing 0.25 wt% CeO$_2$ in TiO$_2$), was carried out using the same operating conditions as before. As shown in Figure 6, a slight decrease in the activity of the catalyst during repeated cycles was observed. Adsorption of MB (initial dark period) is slightly reduced, probably due to a partial blockage of the active sites by the degradation products. However, after three recycling processes, both the Ce-doped nanotubes and nanoparticles resulted still active in the MB dye degradation under UV light, with a slightly lower efficiency, suggesting a very good physico-chemical stability of these samples.

The best performing samples were recovered after a 3-cycle reusability test, washed, dried at 110 °C in air flow and then analyzed by X-ray diffraction. As expected, in both the diffractograms (Figure S6) the size of titania crystallites did not change, and no new peaks related to cerium- or titanium-based phases were detected after the reaction. Used CeTNT025 and CeTNP025 systems were also analyzed by N$_2$ physisorption at -196 °C. The BET specific surface area of the samples slightly decreased after the recyclability test, passing from 26 to 22 m$^2$g$^{-1}$ for CeTNT025 and from 99 to 91 m$^2$g$^{-1}$ for CeTNP025, attributed to a partial pore blocking by the degradation by-products. Regarding the catalytic activity, a slight diminution of MB absorption at the initial dark period can be noticed by comparing the profiles of the first and third cycles, both for nanoparticles and nanotubes (Fig. 6a-b), most probably due to the above mentioned surface area decrease. According to the obtained results, it could be assumed that the formation of a ceria-titania composite can led to the formation of a heterojunction structure, with synergistic effects for harvesting the visible light, and beneficial to the separation and transfer of photogenerated charge carriers.
titania-based nanostructure seems to have a significant effect on the photo-activity. CeTNPx series showed a lower dye performance of a TiO$_2$ matrix. Moreover, a very small amount of ceria, 0.25 wt%, has been found optimal to cover enough TiO$_2$ surface with ceria ions and leaving enough uncovered titania surface where the organic pigment can get adsorbed and degraded under UV light. Such a loading can allow ceria to produce electrons immediately leaving enough uncovered titania surface where the organic pigment can get adsorbed and degraded under UV light. Such a loading can allow ceria to produce electrons immediately leaving enough uncovered titania surface where the organic pigment can get adsorbed and degraded under UV light. However, under sunlight irradiation the doping of titania with Ce ions seems to have produced a red shift in the absorption edges (Table 1), increasing the available spectral region that could be used in photocatalytic processes, allowing to harvest visible light and generating a greater number of electron and hole pairs under this less energetic radiation. From the experimental results, it seems that a ceria amount about 2.5 wt% is the optimum for enhancing the photocatalytic performance of a TiO$_2$ matrix. Besides the doping with ceria, also the morphology of the titania-based nanostructure seems to have a significant effect on the photo-activity. CeTNPx series showed a lower dye adsorption after 30 min of equilibration in the dark, and higher MB photodegradation activity and $k$ values, both under UV and simulated sunlight irradiation, with respect to the CeTNTx series. As previously reported, this suggests that a less ordered nanostructure, like nanoparticles, are more photoactive than nanotubes or nanosheets in dyes photodegradation (see Table 2). Under similar reaction conditions (but with lower performances, see Table 2), Bonfanti-Vieira et al. [59] reported that Ce-doped titania with combined morphologies, such as nanotubes, nanosheets and nanoparticles, attained almost a complete degradation of both MB and polyvinylpyrrolidone (PVP) pollutants, over 90% both under UV and simulated solar light irradiation. In this work it was also suggested that it is in fact ceria addition that induces the disorder in the nanostructures. Not only is the less ordered structure morphology that enhances the catalytic activity, but also the surface to volume ratio of the nanostructures. Three-dimensional nano-architectures with large surface to volume ratios and high light absorbance, have currently emerged as particularly promising candidates for the degradation of organic pollutants.

Li et al. [60] studied the degradation of ciprofloxacin pollutant under UV-Vis irradiation using eco-friendly produced TiO$_2$ with two different morphologies, rod-like and tripyramid-like, demonstrating that the three dimensional architecture achieved 90% degradation after 60 minutes of reaction, while rod-like one attained just 50% of degradation, which could be attributed to the improved surface area by the special tri-dimensional structures. Likewise, Bergamonti et al. [61] investigated the photocatalytic performance of TiO$_2$-supported chitosan scaffolds in amoxicillin photodegradation under UV-Vis irradiation, with total degradation even with large quantities of the pollutant. The advantage in the use of these scaffold titania structures lies on the possibility of modulating their shape and size, which provides a high area to volume ratio, as well as improving the stability and handling of the titania photocatalyst. This could be also ascribed to a higher specific surface area that allows a better dispersion of ceria on the catalyst surface and a higher interaction between the dye and the active sites of the inorganic matrix.

### Experimental

#### Synthesis of TiO$_2$ nanotubes

TiO$_2$ nanotubes were prepared by a two-step hydrothermal route, where titania nanopowder was firstly obtained by sol-gel process, and then nanotubes were prepared by a dehydration reaction using TiO$_2$ nanopowder as the starting material. In the sol-gel process, 5 mL of titanium tetraisopropoxide (TTIP) (Sigma-Aldrich, 97%) were added to 15 mL of 2-propanol (Sigma-Aldrich, 99.5%) and 250 mL of milliQ water into a flask under vigorous stirring and aged at 70 °C for 10 h. Then the pH of the reaction was set at 2 by adding 0.6 M hydrochloric acid (Sigma-Aldrich, 37%). The product was separated by centrifugation, washed with absolute ethanol (Sigma-Aldrich, > 99%) and dried at 80 °C overnight. An amount of 0.5 g of product was then dissolved in 30 mL of 10 M NaOH (VWR Chemicals) aqueous solution, placed in a Teflon autoclave and kept at 130 °C and autogenous pressure for 24 h. The obtained product was recovered by centrifugation, filtered and washed with MilliQ water, 0.1M...
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HNO₃ (VWR Chemicals, ≥90.0%) aqueous solution and finally hot MilliQ water until neutral pH.

| Photocatalyst | Dopant loading (wt%) | Dye concentration (mg L⁻¹) | Catalyst loading (g L⁻¹) | Irradiation source | Irradiation time (min) | Dye degradation (%) | k (min⁻¹) | Reference |
|---------------|-----------------------|-----------------------------|---------------------------|--------------------|------------------------|---------------------|------------|-----------|
| TiO₂-CeO₂ nanosheet | 1.56 | 10 | 1 | λ > 420 nm | 180 | 70 | 0.0073 | [62] |
| CeO₂/TiO₂ nanotubes | 15 | 15 | 0.8 | λ > 400 nm | 150 | >99 | 0.032 | [63] |
| WO₃/TiO₂ | 10 | 10 | 0.6 | UV | 180 | 98.92 | 0.017 | [64] |
| ZnS/TiO₂ | 0.2 | 20 | 0.5 | UV-Vis | 120 | 100 | - | [65] |
| Gd-Si-TiO₂ | 0.06- | 10 | 0.3 | Solar light | 120 | 100 | - | [66] |
| Ce-TiO₂ | 0.85 | 20 | 0.5 | Visible | 160 | 90 | 0.021 | [59] |
| TiO₂-CeO₂ nanoparticles (CeTNP025) | 0.25 | 19.2 | 0.68 | Solar light | 120 | 60 | 0.029 | This work |

The sample was dried at 80 °C overnight and annealed at 400 °C for 2 h (heating rate 1 °C min⁻¹) in air flow to obtain titania nanotubes. The sample was identified as TNT, where T = titania, NT = NanoTubes.

Synthesis of TiO₂ nanoparticles

Titania nanoparticles were prepared by a hydrothermal reaction following a procedure reported in literature [67] with some modifications. 1.0 g of titanium dioxide P25 (Aeroxide Evonik Industries) was dispersed in 80 mL of a 10 M KOH (VWR Chemicals) aqueous solution under vigorous stirring for 1 h. Then the suspension was transferred into a Teflon-lined autoclave and heated at 160 °C for 6 h. The product was separated by centrifugation and washed with MilliQ water, 0.1 M HNO₃ aqueous solution and hot MilliQ water until neutral pH. The product was dried at 80°C for 48 h and then thermally treated at 400 °C for 2 h (heating rate 1 °C min⁻¹) in air flow to obtain titania nanoparticles. The sample was identified as TNP where T=titania, NP=NanoParticles.

Synthesis of CeO₂-TiO₂ photocatalysts

Ceria-containing nanotubes and nanoparticles were prepared by following the procedures reported in sections 2.1 and 2.2, respectively, adding the required amount of Ce(NO₃)₂·6H₂O (Sigma-Aldrich) to the solution of TTIP, 2-propanol and MilliQ water and to the aqueous solution of KOH to obtain ceria-titania nanotubes (CeTNTx series) and ceria-titania nanoparticles (CeTNPx series), respectively.

The samples were referred to by the acronyms CeTNTx and CeTNPx, where Ce=ceria, T=Titania, NT=NanoTubes, NP=NanoParticles and x= 0.25, 0.5, 1.0, 2.5, 5.0 wt% CeO₂.

Characterization of Catalysts

X-ray powder diffraction (XRPD) patterns were collected on a Philips PW 1139 diffractometer with the voltage of 40kV and a Bragg-Brentano reflection configuration and a Cu anode (Kα1 = 1.5406 Å). The measures were recorded in the range from 10° to 80° of 2θ, with a step size of 0.05° (2θ).

N₂ physisorption measurements were performed at -196 °C with an ASAP 2010 apparatus of Micromeritics. After outgassing at 130 °C for 12 h at 0.67 Pa, the N₂ isotherms were acquired to determine the specific surface areas through the BET equation (S_BET), the specific pore volume (Vₚ) calculated at P/P₀ = 0.98, and pore size distribution by BJH (Barrett-Joyner-Halenda) method, taking the data of the desorption branch and assuming a cylindrical pore model.

Raman spectra were recorded using WiTec CRM-200 microRaman system equipped Olympus LMPPlanFL 20x/0.40 objective. The excitation laser is 633nm and laser power on the samples was kept at 1mW.

The diffusive reflectance UV-vis (DRUV-vis) spectra were collected with a Perkin Lambda 35 UV-vis spectrophotometer, equipped with integrating sphere accessory, with the wavelength ranging from 300 to 800 nm. The absorption coefficient (α) was calculated as follows: α=ln(1/T)/d, where T is the measured transmittance and d is the optical path length.

Band gap energy, Eₚ, was determined thorough the α value (m⁻¹) from a plot of (αhv)ⁿ versus photon energy (hv), where h is Planck’s constant, v is the frequency (s⁻¹) and the exponent n is the power factor of the optical transition mode, depending on the nature of the electronic transitions responsible for the absorption and which is equal to 2 for allowed indirect transitions. The intercept of the tangent to the absorption curves was used to estimate the band gap (Eₚ) values.

The time resolve PL was recorded using FLS980 photoluminescence spectrometer from Edinburgh instrument which is equipped with a highspeed photomultiplier tube. The samples were excited with 250 nm UV light from a microseconds Xe flashlamp and the decay spectra of sample emission at 400 nm were collected in CeTNTx-water dispersion both before and after mixing with MB.

High resolution transmission electron microscopy (HR-TEM) was performed by using a ZEISS EM10c electron microscope. TEM analysis was performed at 200 kV and 5.5 µA and scanning transmission electron microscopy (STEM) with a HAADF detector was carried out at 200 kV and 200 pA. Imagei software (Imagej 1.51K) was used to estimate the average particle size distribution.

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X-ray Photoelectron spectra (XPS) were collected using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg Kα radiation (300 W, 15 kV, 1253.6 eV) for the analysis of the core level signals of C 1s, O 1s, Ti 2p, and Ce 3d, and with a multichannel detector. Binding energy (BE) values were referenced to the C 1s peak (284.8 eV) from the adventitious contamination layer. The spectrometer energy scale was calibrated using Cu 2p3/2, Ag 3d3/2, and Au 4f7/2 photoelectron lines at 932.7, 368.3, and 84.0 eV, respectively. The PHI ACCESS ESCA-V6.0 F software package and Multipak v8.2b were used for acquisition and data analysis, respectively. A Shirley-type background was subtracted from the signals, recorded spectra were always fitted using Gauss-Lorentz curves, in order to determine the binding energy of the different element core levels more accurately. The error in BE was estimated to be ca. 0.1 eV.

Photocatalytic Activity

The degradation of methylene blue, MB, was chosen as a test reaction to evaluate the photocatalytic activity of the synthesized materials both under UV and simulated solar light irradiation. A 300 mL Pyrex photochemical reactor was used, with an initial concentration of the target molecule of $6.0 \times 10^{-5}$ M at pH=5.0. All the degradation experiments were carried out at 20 °C. The amount of the photocatalyst was fixed at 0.68 g L$^{-1}$. Under UV light, a 125 W high pressure mercury lamp, operating at wavelengths between 180 and 420 nm with a peak at 366 nm, was used. When samples were tested under simulated solar light irradiation, a Sunlight Solar Simulator, AM1.5G filter, 100 watt Xenon arc lamp (Abet Technologies) was used. Before the catalytic measurements under simulated sunlight, a reference cell was used to set the intensity of the light source to standard illumination conditions. The photon flux was measured by using a Delta OHM radiometer HD2302.0, equipped with a multichannel detector. A Shimadzu UV-2450 UV-Vis spectrometer was used for the determination of the dye concentration, after calibration. The absorbance at the maximum (664 nm) of the UV-vis spectrum, during the degradation experiments. The degradation processes were monitored by measuring the absorbance at the maximum (664 nm) of the UV-vis spectrum of the target molecule. Since the degradation pathway for the selected dye is known with high reliability [54], the eventual formation of by-products was checked, monitoring the overall UV-vis spectrum of the solutions recovered at different times during the degradation experiments.

The rate constant was calculated according to (1):

$$\ln \frac{C}{C_0} = -kt$$

Where $C$ is concentration after time $t$, $C_0$ represents the initial concentration and $k$ is the pseudo-first order rate constant (min$^{-1}$), calculated as (2):

$$k = 2.303 \times \text{slope (2)}$$

To evaluate the stability and reusability of the photocatalysts, a 3-cycle recycling test was performed. The powder sample was collected by centrifugation, washed with deionized water and dried overnight after each photocatalytic cycle for the recycling test.

Conclusions

In the present work, nanostructured TiO$_2$ samples with different CeO$_2$ loadings in the range 0.25-5.0 wt% were hydrothermally synthesized to obtain nanotubes (TNT series) and nanoparticles (TNP series). These two Ce-doped titania series were used as photocatalysts in the degradation of methylene blue in aqueous solution, both under UV and simulated solar light irradiation at room temperature and atmospheric pressure. It was demonstrated that morphology plays a crucial role in the photocatalytic activity: the less ordered structure, CeTNP nanoparticle series, displayed a greater catalytic performance, most probably due to a higher surface to volume ratio and a better dispersion of ceria nanoparticles, together with a high specific surface area. The photoresponse confirmed that a suitable $E_p$ obtained by tuning the amount of ceria in the framework of titania and consequently lowering the band gap to harvest visible light, can enhance the catalytic activity. Containing samples showed in fact a higher MB degradation rate than the corresponding pure titania nanosystems, both under simulated solar light and UV irradiation, which could be attributed to both $E_p$ decrease and to oxygen vacancies supplied by Ce redox pair. It was also observed that Ce acts like a promoter, as samples with high ceria contents showed worse conversions, probably due to several factors such as low specific surface area due to pore blockage or hindering of active titania sites by ceria nanoparticles. In fact, the sample that showed the best catalytic performance was Ce-doped titania nanoparticles with 0.25 wt% Ce, that was able to degrade more than 90% of MB in less than 20 minutes of reaction and presented a great stability after 3 reutilisation cycles. These results pave the way for the development of highly efficient titania-based photocatalysts with low dopant concentration, whose structural, optical and electronic properties can be controlled through dopant concentration and suitable preparation conditions.

Author Contributions

CA, IB-M, AI-M, SY, AT, HG investigation, and formal analysis. ER-C, AV, AI-M, EM conceptualization, funding acquisition, providing resources. EM, AV, AI-M supervision and writing original draft. All the authors reviewed and approved the manuscript.

Conflicts of interest

There are no conflicts to declare.
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