



# Article Photocatalytic Dye Decomposition over $CaMnO_{3-\delta}$ and $Pr_{0.5}Ca_{0.5}MnO_3$ : A Combined XPS and DFT Study

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**Abstract:** In the field of environmental sustainability, the development of highly efficient photocatalytic under a wide wavelength range with band engineering is regarded as a promising strategy to enhance photocatalytic dye degradation. Here, we report on  $CaMnO_{3-\delta}$  and  $Pr_{0.5}Ca_{0.5}MnO_3$  perovskite materials prepared by a sol-gel combustion method. From X-ray photoelectron spectroscopy (XPS), the particle surfaces of both compounds are oxygen deficient, while the surface hydroxyl and carbonyl groups' adsorption on the surface of  $Pr_{0.5}Ca_{0.5}MnO_3$  particles is more pronounced. FT-FIR spectroscopy has been used to investigate the covalent bonds and oxygen vacancy characteristics. Photocatalytic activities were investigated by the degradation of methylene blue and methyl orange under UV light. It was observed that both dye molecules are more degraded over  $CaMnO_{3-\delta}$ . The underlying mechanisms behind the photoexcitation and degradation process are established via the Spin-polarized Density Functional Theory (DFT).

Keywords: photocatalyst; perovskite; dye degradation; CaMnO3



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## 1. Introduction

Today, the serious environmental problems due to the growth of fossil fuel consumption have attracted special attention to developing efficient and nontoxic materials to assist in solving these issues. Photocatalysis is a promising technology in the field of clean energy applications to prevent organic pollutants from potentially causing environmental degradation. Many efforts have been made on various materials to develop new semiconductor photocatalysts [1,2] and find out the photocatalytic mechanism. Among the studied materials, rare earth ABO<sub>3</sub> perovskite compounds with unusual physical and chemical properties have shown photophysical properties due to the polaron formations inside the crystal lattice [3,4]. The effects of doping and nanosized crystalline are effective parameters in these physical and chemical properties. The perovskite structure consists of oxygen octahedra, where the B cation (Mn ion) is the atom in the center of the octahedron, and the A cation (Pr and Ca ions) is the atom outside the octahedron. The position of oxygen atoms around the transition metal cations B in the ABO<sub>3</sub> perovskites determines the exciting properties. The transfer of electrons between the B-sites is not direct transfer but through the intervention of the oxygen atoms surrounding the transition metal atoms in the B-site [5,6]. The electronic and magnetic properties of the perovskite change by the distortion of the octahedral reflects the importance of the mixed-valence states of the transition metal at B-site and the corner-shared octahedral  $BO_6$  in these materials [7–9]. Moreover, the small ionic radii of the A cations cause  $BO_6$  octahedral tilting. This tilting turns the cubic lattice structure to the lower symmetry orthorhombic crystal structure [10,11]. In perovskite compounds, octahedral tilting influences the electronic structure, electron or hole transport, and dielectric properties [12,13].

The perovskite-like materials such as tantalate, titanate, ferrite, and manganites have exhibited visible light photocatalytic activity because of the exclusive electronic properties correlated with the crystal structures [14–16]. The optimized bandgap in such materials, the doping concentration of the divalent element, explains and enhances photocatalytic performance and the separation of charge carriers. These compounds represent the bandgap values of the produced visible-light absorption as well as the UV region [17]. The potentials of optimizing the bandgap and the lattice distortion to capture charge carriers presented in such materials affect the efficiency of photocatalysts [18]. A simple member of the manganite compounds, CaMnO<sub>3</sub>, represents the bandgap of about 1.6 eV between the O 2p valence band and Mn 3d conduction bands. The Mn 3d orbitals split into the triply degenerated Mn t<sub>2g</sub> and doubly degenerated Mn e<sub>g</sub> states originating from the crystal field splitting [6,19]. Hence, there are two relative electron transitions in the energy range of 1 eV to 6 eV. The UV transition at the higher energies of 4–5 eV corresponds to the transitions between the O 2p states and the minority-spin states, while the lower energies are assigned to the transitions between the O 2p and majority-spin states. These transitions are of interest to the polaron physics of manganites. In addition, manganese-containing compounds can be considered promising candidates for functional water oxidation [20–23] inspired by the natural photosynthesis process in which the  $Ca_2Mn_3O_8$ ,  $CaMn_2O_4$ , and  $CaMnO_3$  clusters are identified as the catalytic site for the four-electron involved water oxidation [24].

Doping CaMnO<sub>3</sub> by the trivalent ions (Pr) inserts the extra electrons into the antibonding  $e_g$  states of the Mn 3d orbitals. These electrons form polarons and cause octahedral distortion [10]. Therefore, octahedral distortion affects the conduction band distributions as well as the valance band top [25]. Oxygen vacancy is another approach to modifying the conduction band distribution of electronic states [26]. Water oxidation and O<sub>2</sub> reduction depend on the photoinduced reactions and potential levels of the valence and conduction bands with respect to the oxidation and reduction of potential levels. Thus, doping and deficiencies in the lattice offer great potential for band structure engineering and consequently designing new photocatalysts. The photocatalytic properties and the relative mechanism for the transitions, particularly at lower energies (visible region), draw the attention to sunlight. The effects of UV transitions in perovskites corresponded to the transition between the O 2p states and minority-spin states of the conduction band are still missing. Here, oxygen deficiencies, as well as doping agents, have been used to prepare the CaMnO<sub>3</sub> manganite structure with Mn<sup>3+</sup> and Mn<sup>4+</sup> coexistence to investigate the mechanism of the photocatalytic activities in the UV radiation region.

In this work, nanosized CaMnO<sub>3- $\delta$ </sub> (CMO) and Pr<sub>0.5</sub>Ca<sub>0.5</sub>MnO<sub>3</sub> (PCMO) were characterized by FT-FIR spectroscopy and XPS and the photocatalytic activity in the UV region for the decomposition of methyl orange (MO) and methylene blue (MB) was investigated. To better understand the photocatalytic behavior of ABO<sub>3</sub> perovskites, the band structures of the compounds were discussed concerning the photocatalytic activities. To shed light on the experimental finding, first-principle calculations based on the density functional theory (DFT) were carried out to assess the influences of oxygen vacancy on the electronic density of states (DoS).

## 2. Materials and Methods

## 2.1. Preparation of Samples

The CMO and PCMO nanoparticles were prepared by gel combustion method. Calcium nitrate tetrahydrate Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (99%), manganese nitrate tetrahydrate Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (99.5%), praseodymium nitrate hexahydrate Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99.9%) and gelatin were used. In order to prepare the primary sol, appropriate amounts of nitrates were dissolved in distilled water, stirring at room temperature for 20 min. Then, the gelatin solution was added to the sol and stirred at 60 °C for 2 h. The final gel was obtained by heating the sol at 90 °C. Finally, the brownish gel was dried at 200 °C for 5 min. The nanoparticles were prepared after calcining the samples at 900 °C for 5 h. The preparation methods, as well as the structural analysis by X-ray diffraction and Rietveld refinement, have been published recently [27].

## 2.2. Characterizations and Photocatalysis Experiments

The structural, microstructural, electrocatalytic, and in situ investigations of CMO and PCMO nanopowders have been previously reported [27,28]. Here, the infrared optical density  $O_d$  for both compounds was obtained in the 150–700 cm<sup>-1</sup> using a far-infrared Fourier spectrometer (FT-FIR). The powders were pressed into pellets under a vacuum followed by finely milling and mixing with CsI in the ratio of 1:100 in weight.

X-ray Photoelectron Spectroscopy (XPS) was performed in a custom-designed system with an Al-K $\alpha$  X-ray source (1486.6 eV), steps of 0.1 eV and 20 eV pass energy. Chemical compositions of particles have been investigated using core-level photoemission spectra from Ca 2p, Pr 3d, Mn 2p, and O 1s regions collected in normal emission at room temperature. The binding energies were referenced to Au-4f at 84 eV.

In order to collect the photoemission spectra, the monochromator and exit slit was set to  $c_{\rm ff} = 2.25$  and 111  $\mu$ m, respectively. The step size for Ca 2p and O 1s spectra was 20 meV. All spectra were collected using pass energy of 20 eV and a dwell time of 100 ms. The intensities have been scaled and normalized with reference to impinging photon flux. A blend of linear and Shirley-type backgrounds was subtracted. Experiments have been conducted according to the protocol given in Ref. [29].

The photocatalytic reaction in the ultraviolet region was performed with a 200 W HBO Mercury short-arc lamp as an ultraviolet light source with a peak irradiance at 365 nm and intensity of 50 mW/cm<sup>2</sup> at the sample position. The concentration of MB and MO dyes was chosen as 5 ppm. The amount of photocatalyst was 50 mg in 50 mL of deionized water. The solution was stirred in darkness for 30 min to complete the adsorption–desorption equilibrium between the dye and the catalyst. The solution temperature was kept at 25 °C throughout the experiment. After darkness, solutions were exposed to light. Aliquots were taken at the time interval of 20 min. The solution was then centrifuged, and its absorption spectrum was recorded by UV-Visible spectrometer.

## 2.3. Theoretical Method

Calculations were performed based on the Spin-polarized Density Functional Theory (DFT) [30]. The exchange-correlation functional is approximated with the HSE06 functional [31] to obtain a proper description of the Mn 3d orbitals, as implemented in the Vienna Ab initio Simulation Package (VASP) [32,33]. The typical value of 0.2 is employed as a mixing factor. We used  $2 \times 2 \times 2$  supercells of the primitive perovskite cell for CaMnO<sub>3</sub>, corresponding to 20 atoms. The total energy was sampled on a well-converged  $4 \times 4 \times 4$  k-point grid together with projector-augmented wave theory [34] and a 520 eV plane-wave cutoff. The total energy is converged within  $1 \times 10^{-5}$  eV per supercell. For Pr<sub>0.5</sub>Ca<sub>0.5</sub>MnO<sub>3</sub>, a larger supercell has been considered with the CE-type order, corresponding to 80 atoms, sampled on a  $2 \times 2 \times 2$  k-point grid. Oxygen vacancy in the perovskite is assessed in the low-vacancy limit, one O vacancy per supercell. The structures were allowed to relax until the convergence of the forces on the atom were lower than  $1 \times 10^{-2}$  eV Å<sup>-1</sup>. The minimum distance between O vacancies considered as at least 10 Å minimized the fictitious interactions across periodic boundaries [6].

## 3. Results and Discussion

#### 3.1. Structural and Microstructural Properties

The XRD patterns of the single CMO and PCMO are shown in Figure 1. We identified the orthorhombic space group of Pnma (no. 62) for the crystal structure. While the ionic radius of  $Pr^{3+}$  (1.13 Å) is close to that of  $Ca^{2+}$  (1.12 Å), the lattice constants enlarge with an increase in Pr content, as has already been published [27]. The lattice expansion is because of the Mn–O bond length increases caused by electron insertion into the antibonding Mn e<sub>g</sub> orbitals. The surface morphology has been investigated by scanning electron microscopy

(SEM), and a representative SEM image for the micrographs of undoped and Pr-doped Ca $MnO_3$  is shown in Figure 2. The samples were composed of nanoparticles with an average particle size of 70 nm. Phase identification, lattice parameters, and microstructural analysis were published in previous work [27].



**Figure 1.** XRD patterns of CaMnO<sub>3</sub> (CMO) and  $Pr_{1-x}Ca_xMnO_3$  (PCMO). The indices correspond to the space group Pnma.



**Figure 2.** SEM micrographs of (**a**)  $CaMnO_3$  (CMO) and (**b**)  $Pr_{1-x}Ca_xMnO_3$  (PCMO). The average particle size was 70 and 64 nm for CMO and PCMO, respectively.

## 3.2. Spectroscopic Analysis

In our previous work [27], X-ray absorption spectroscopy of the Mn-L edge gave the Mn valence of the undoped calcium manganite about 2.95, confirming the oxygen deficiency in the structure, which is very common in Ca-rich manganites. The structural properties of the samples obtained by Rietveld refinement indicated that Mn–O bond length increases with the increase of  $e_g$  electron occupation of the antibonding Mn ( $e_g$ )–O (2p) levels. Here, FT-FIR spectroscopy has been used to investigate the covalent bond characteristics and the position of oxygen vacancies. The infrared optical densities of polycrystalline  $Ca_{1-x}Pr_xMnO_3$  (x = 0.00 and 0.50) at 300 K are shown in Figure 3. The numerous peaks in the spectra relating to the infrared active transverse optical TO modes show strong deviations from a cubic symmetry to orthorhombic in both compounds. Two strong, broad peaks are contributing several smaller peaks at 414 cm<sup>-1</sup> and 596 cm<sup>-1</sup> have been observed for  $Pr_{0.5}Ca_{0.5}MnO_3$ . This is due to the lifting of the  $e_g$  degeneracy (Jahn–Teller distortion) because of the strong elongation of the Mn–O(1) bond and consequently splitting one IR absorption band into two adjacent bands [35]. The spectra shown in Figure 3 appear qualitatively similar in structure, exhibiting three main groups centered around 200, 400, and 600  $cm^{-1}$ . The low-energy modes are the bending band and are expected to be

sensitive to the  $MnO_6$  octahedra tilting distortions. On the other hand, the high-energy modes (centered around 600 cm<sup>-1</sup>) are thought to involve mainly stretching vibrations of  $MnO_6$  octahedra. The frequencies of these modes are expected to be directly related to the interatomic distances of Mn–O bonds. Therefore, the structure of the bending band and Mn–O bonds in CMO with oxygen vacancies should appear significantly reduced compared to the fine structure of PCMO.



**Figure 3.** Optical density of polycrystalline CaMnO<sub>3- $\delta$ </sub> and Pr<sub>0.5</sub>Ca<sub>0.5</sub>MnO<sub>3</sub>. The indices (1) and (2) indicate the bands corresponding to the vibrations of apical and in-plane oxygens, respectively.

The phonon modes below 270 cm<sup>-1</sup> for all samples correspond to mixed vibrations of Ca/Pr atoms and octahedral [35]. Because the strong orthorhombic lattice is strongly distorted, none of the modes observed above 280 cm<sup>-1</sup> can be considered as purely bending or stretching, as these modes considerably depend on the changes of both the Mn–O–Mn bond angles and the Mn–O bond lengths [36]. The phonon modes between 280 and  $350 \text{ cm}^{-1}$  correspond to the motions in which the Mn displacements are comparable with O atoms. For higher frequencies, the displacements of Mn and Ca/Pr atoms and phonons involve mostly the motions of oxygen atoms [35,36]. As shown in Figure 3 for CaMnO<sub> $3-\delta$ </sub>, the peaks relating to the vibration of apical and in-plane oxygen are indexed with (1) and (2), respectively. For the modes at 354, 368, 396, 514, and 560  $\text{cm}^{-1}$ , the in-plane oxygen vibrations dominate. For those at 430, 460, and 640  $\rm cm^{-1}$ , the motions of the oxygen atoms in apical sites play the main role [35]. The infrared absorption spectrum of polycrystalline  $CaMnO_3$  reported and thoroughly discussed by Fedorov et al. [35] is similar to our results for CaMnO<sub>3- $\delta$ </sub> with a significant difference. The absorption bands corresponding to the vibration of apical oxygen atoms are so close to the results reported, while the vibration of Mn–O(2) considerably shifts compared to the results obtained for CaMnO<sub>3</sub> which was free from oxygen vacancies. This may be due to the fact the oxygen vacancies are more or less localized in in-plane sites and consequently can affect the ion conductivity and the photocatalytic properties.

Figure 4a shows the survey XPS spectra obtained for CaMnO<sub>3- $\delta$ </sub> and Pr<sub>0.5</sub>Ca<sub>0.5</sub>MnO<sub>3</sub>. As shown in this figure, no other impurity elements were observed. Figure 4b,c show the doublet XPS spectrum of Ca 2p at binding energies around 345.5 and 349 eV assigning to Ca 2p<sub>3/2</sub> and Ca 2p<sub>1/2</sub>, respectively. Ca<sup>2+</sup> exhibits a binding energy (BE) shift toward higher energies with increasing Pr content due to the changes in the nearest neighbors of Ca atoms and, consequently, the electronic structure of the Ca atoms. In the case of the Ca 2p<sub>3/2</sub> component, it can be seen that the peak is broadened in Pr<sub>0.5</sub>Ca<sub>0.5</sub>MnO<sub>3</sub> compared to undoped CaMnO<sub>3- $\delta$ </sub>. This can be due to the formation of CaCO<sub>3</sub> and/or CaO at the oxide surface due to Ca segregation [37]. The narrow scan spectrum of the oxygen 1s core level of samples is shown in Figure 4d,e. The oxygen peaks corresponding to O 1s can be resolved into two components at around 529 and 532.1 eV. This doublet peak of O 1s agrees with the earlier reports on perovskite oxides [37–39]. This doublet peak corresponds to

the chemical shifts in the oxygen core level arising out of two kinds of chemical bonding. The lower binding energy component is assigned to the oxygen in the perovskite lattice (metal-oxygen bonds). The next component at around 531.9 eV can be associated with CaO and/or CaCO<sub>3</sub> formed at the surface due to Ca segregation. In PCMO, the peak at BE energies of 532 eV has a higher intensity than the 529 eV line compared to CMO, indicating that Pr substitution in Ca sites helps to more occurrence probability of surface Ca/Pr–O bonds and Ca segregation [37].



**Figure 4.** XPS survey spectra (**a**), Ca 2p (**b**,**c**), and O 1s (**d**,**e**) photoemission spectra of CaMnO<sub>3- $\delta$ </sub> and Pr<sub>0.5</sub>Ca<sub>0.5</sub>MnO<sub>3</sub> taken in normal emission using an Al K $\alpha$  X-ray source. The peaks in the O 1s region were assigned to lattice oxygen and surface hydroxyl groups, carbonyl groups, and CaO/CaCO<sub>3</sub>.

The mixed-valence of surface manganese in perovskite manganites can be determined by analyzing the manganese doublet spectra corresponding to the spin-orbit split of manganese 2p peaks (Mn  $2p_{3/2}$  and Mn  $2p_{1/2}$ ) around 642.1 eV and 653.5 eV, respectively (Figure 5). Quantitative deconvolution and curve fitting results for Mn  $2p_{3/2}$  give evidence for the existence of mixed-valence states of manganese. Here, the higher binding energy component at 642.6 eV relates to Mn<sup>4+</sup>, and the other component at 641.5 eV is assigned to Mn<sup>3+</sup> [40]. The mixed-valence Mn ratios of Mn<sup>4+</sup>/Mn<sup>3+</sup> of all samples are approximately determined as 1.37 and 0.92 for CaMnO<sub>3- $\delta$ </sub> and Pr<sub>0.5</sub>Ca<sub>0.5</sub>MnO<sub>3</sub>, respectively. By comparing this ratio obtained by XPS from the surface of CaMnO<sub>3- $\delta$ </sub> nanoparticles from one side and Mn valence estimated from XAS [27], it is observed that the surface of particles is more oxygen-deficient than the bulk. However, the ratio of Mn<sup>4+</sup>/Mn<sup>3+</sup> for both surface and bulk of Pr<sub>0.5</sub>Ca<sub>0.5</sub>MnO<sub>3</sub> particles is near one, which is consistent with the Mn valence obtained by XAS. These shreds of evidence indicate that the surface of Pr<sub>0.5</sub>Ca<sub>0.5</sub>MnO<sub>3</sub> particles is more stable than CaMnO<sub>3- $\delta$ </sub>, consistent with in-situ HRTEM investigations reported before [28]. The third peak in Figure 5 (green line) corresponds to the satellite structure observed in about 5 eV higher binding energy than the Mn 2p<sub>3/2</sub> clearly associated with ligand 2p to Mn 3d charge transfer [41]. Note that the satellite component comes from Mn<sup>4+</sup>, as shown in Figure 5b. In the case that the interaction between the 2p core hole and the correlated 3d valence electrons is sufficiently strong, satellites are present in the photoemission spectra accompanying the main lines.



**Figure 5.** Energy spectroscopies of Mn 2p recorded for (a)  $CaMnO_{3-\delta}$  and (b)  $Pr_{0.5}Ca_{0.5}MnO_3$  nanoparticles. The peaks in the  $2p_{3/2}$  region are assigned to the binding energies of  $Mn^{3+}$  and  $Mn^{4+}$ .

## 3.3. Photocatalytic Degradation Analysis

The photodegradation of MB and MO is given in Figure 6, which was carried out by degrading MB and MO in an aqueous solution under irradiation of a 200W HBO Mercury short-arc lamp as an ultraviolet light source. The decoloration rate of MB in the presence of CMO reached 43% at 180 min, which was close to 41% obtained for PCMO. However, the MO degradation performance of CMO and PCMO was limited to 23% and 21% within three hours, respectively.

Photocatalytic oxidation of organic pollutants follows Langmuir–Hinshelwood kinetics in which only the first-order form  $(-\ln(C_0/C) = k_{app}t)$  is accounted for when the reactant concentration is very small [42]. In this equation,  $k_{app}$  is the apparent first-order reaction constant, and  $C_0$  and C are the reactant concentrations at the initial and later times, respectively. The photocatalytic activities of CMO and PCMO were evaluated by comparing the  $k_{app}$  obtained from the plots of  $-\ln(C_0/C)$  against irradiation time (insets of Figure 5) and listed in Table 1.

**Table 1.** Apparent first-order reaction constants obtained for MO and MB, and the band structure parameters determined by ab initio studies.

Material	Particle Size (nm) [27]	Specific Surface Area (cm <sup>2</sup> /mg)	k <sub>app</sub> for MB (10 <sup>-3</sup> min <sup>-1</sup> )	k <sub>app</sub> for MO (10 <sup>-3</sup> min <sup>-1</sup> )
СМО	70	81.63	3.98	2.56
РСМО	64	49.96	3.42	1.81



**Figure 6.** Photocatalytic decomposition of methylene blue (**left**) and methyl orange (**right**) over CMO and PCMO catalysts. The insets are the plots of  $Ln(C_0/C)$  versus time. The slopes of these linear plots are used to obtain the values of  $k_{app}$  summarized in Table 1.

CMO and PCMO exhibited apparent rate constants of  $3.98 \times 10^{-3} \text{ min}^{-1}$  and  $3.42 \times 10^{-3} \text{ min}^{-1}$  for MB decomposition, respectively, showing higher activities than the values of  $2.56 \times 10^{-3} \text{ min}^{-1}$  and  $1.81 \times 10^{-3} \text{ min}^{-1}$  obtained for MO degradation. In addition, the photocatalytic activity of nanosized CMO is slightly better than PCMO.

Here, the main factors, including specific surface area, amount of chemisorbed oxygen at the surface of the particles, band structure, and electron-hole pair recombination rate, play significant roles in the photocatalytic activities of CMO and PCMO samples. The specific surface area has been obtained in our previous report [27] and given in Table 1. The higher specific surface area of CMO in comparison with PCMO, can provide a higher density of active sites [43,44]. In addition, the diffusion rate of the photogenerated electron-hole pair must be longer than the particle size to avoid recombination [45]. It should be noted that the recombination rate depends on the crystal phase and doping level. Nevertheless, enhanced photo-catalytic performance through the high surface-area-to-volume ratio of nanostructured PCMO can be achieved without detriment to the rates of charge carrier recombination in the composites. Consequently, the recombination rate of the carriers on the surface of the photocatalyst decreases with the decrease in particle size.

In addition to the surface area, the amount of chemisorbed oxygen usually associated with the mixed-valence states of the transition metal ion B is correlated with the photocatalytic activity [46–48]. It should be noted that the surface measured under UHV conditions can be restored by annealing at about 120 °C in 0.1 mbar  $O_2$ .

Molecular oxygen has a great tendency to be adsorbed on a surface vacancy site, and consequently, a surface-adsorbed O ad-atom is formed. As shown in Figure 4b, the content of chemisorbed oxygen observed on the surface of PCMO particles is considerably higher than CMO, while the amount of oxygen vacancies created on the surface and bulk of CMO is much more pronounced. This may be due to the fact that in the ABO<sub>3</sub> perovskites, the AO-terminated facets showed stronger binding to the adsorbed oxygen [49]. In addition, our FT-FIR results about CMO show that the oxygen vacancies are more or less localized in BO<sub>2</sub> sites rather than AO. Thus, the amount of chemisorbed oxygen more constructively affects the photocatalytic activity of PCMO in comparison with CMO.

While all parameters play a role in photocatalytic activities, the activity can be described dominantly through the factors such as geometry and the electronic structure of the perovskites. The potential levels configuration of the reduced conduction band and the oxidized valence band have to be compared with the  $O_2/O_2^-$  and the OH/H<sub>2</sub>O potential levels, respectively [50].

To clarify the photodegradation mechanism of MB by CMO under UV light, several scavengers were used. Generally, during the photodegradation of dyes, different reactive species, such as OH and  $O_2^-$ , are generated in addition to the  $e^-/h^+$  pair. For example, the

free electrons reduce the dissolved oxygen, resulting in the formation of superoxide ions, while the holes may react with  $H_2O$  and  $OH^-$  to produce hydroxyl radicals [51]. The scavengers used in this work are EDTA for holes, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and AgNO<sub>3</sub> as electron scavengers, sodium azide (NaN<sub>3</sub>) for singlet oxygen (<sup>1</sup>O<sub>2</sub>), DMSO for OH<sub>bulk</sub>, sodium iodide (NaI) for OH<sub>ads</sub>, and tert-butanol as a free OH radical scavenger [52]. If the photodegradation of MB by the catalyst is performed because of any of the reactive species, the reaction is slowed down or inhibited in the presence of the corresponding scavenger [52]. For the sake of comparison, the MB degradation in the absence of a catalyst under light exposure was investigated for possible self-degradation of MB. Moreover, the MB degradation by CMO without using a scavenger was carried out. Figure 7 shows the variation of  $C/C_0$  for MB as a function of exposure time by adding different scavengers into the photocatalytic system. As this figure shows, no degradation in the absence of the photocatalyst for MB under light irradiation was observed. It means that MB is a photo-stable dye during our experiments. Moreover, this figure shows that the dye was degraded 43% within 180 min in the absence of any scavenger. Adding NaI, tert-butanol, DMSO, and EDTA had no considerable influence on the photodegradation process. Thus OH radicals and holes are not the main active species in MB photodegradation. As Figure 7 shows, the degradation efficiency of MB over CMO significantly decreases with the addition of NaN<sub>3</sub>, indicating that  ${}^{1}O_{2}$  is the main active species during the photocatalytic degradation process. Since the photocatalytic degradation efficiency decreases in the presents of  $K_2S_2O_8$  and AgNO<sub>3</sub>, electrons play a supplementary role. A possible mechanism for the degradation based on our radical scavenger results is as follows. Under light irradiation, electrons are excited from the valance band (VB) to the conduction band (CB) of CMO nanoparticles. Electrons react with dye and dissolved oxygen molecules. The excited electrons reduce the dissolved oxygen, resulting in the formation of singlet oxygen ions. These active singlet oxygen ions and electrons degrade MB dye, which was adsorbed on the surface of nanoparticles. Note that the interfacial modification and composition manipulation by coating provides an efficient way for stabilizing and improving photocatalytic activity [53,54].



**Figure 7.** Effect of different radical scavengers (3 mmol/L) on the photodegradation of MB (5 ppm) CMO (1 mg/mL).  $C/C_0$  ratio ( $C_0$  is the initial concentration) vs. irradiation time.

## 3.4. Electronic Structure of CaMnO<sub>3- $\delta$ </sub> and Pr<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3</sub>

In order to obtain the potential levels of the conduction band  $Mn t_{2g}\downarrow$  and  $e_g\uparrow$ , the theoretical calculation of the electronic band structures of CMO and PCMO was carried out with the HSE06 functional. CaMnO<sub>3</sub> is the simple member of the  $Pr_{1-x}Ca_xMnO_3$  manganite. This compound has an orthorhombic perovskite structure. Mn and O ions form a network of corner-sharing MnO<sub>6</sub> octahedra with a formal valence of 4+ for the Mn cations. Thus, the Mn atoms have a  $3d^3$  configuration. It means three electrons in the  $t_{2g}$  orbitals and a strong crystal field splitting with the empty  $e_g$  states. Ca donates its two

valence electrons to the valence band of the O 2p character. In the CaMnO<sub>3</sub>, the size of the Ca ions is sufficiently small so that the MnO<sub>6</sub> octahedra tilt increases the ionic attraction. The orientation of the tilt axis is determined by a bond angle force at the oxygen bridge.

The calculated DoS of stoichiometric CaMnO<sub>3</sub> is shown in Figure 8a. The valance band is dominated by O p states (red) with the contribution of Mn d orbitals (green and yellow) at the bottom part of the valence band. Above the valence band, Mn d and Ca d states (blue) form the conduction band. The empty Mn d states are associated with different spin orientations according to their relative electron population, namely majority Mn e<sub>g</sub> states (yellow) from 2 eV to 4 eV and minority Mn t<sub>2g</sub> (green) and Mn e<sub>g</sub> stats (yellow) from 4 eV to 7 eV.



**Figure 8.** Total and projected DoS of (**a**) CaMnO<sub>3</sub>, (**b**) CaMnO<sub>3</sub> including O-vacancy, (**c**)  $Pr_{0.5}Ca_{0.5}MnO_3$ , and (**d**)  $Pr_{0.5}Ca_{0.5}MnO_3$  including O-vacancy. The graph shows the total DoS (grey) and the projected DoS for O p (red), Mn  $t_{2g}$  (green), Mn  $e_g$  (yellow), Ca d (blue), and Pr f (magenta). The arrows indicate the dipole-allowed optical transitions within the Mn d orbitals (A) and from O p states to the majority (B) and minority (C) Mn  $e_g$  states.

In CaMnO<sub>3</sub>, each O atom at apical and in-plane sites is surrounded by the two Mn atoms. The Mn–O bond lengths are similar in this structure, so O cages are not Jahn–Teller distorted.

The formation of an oxygen vacancy leaves two Mn ions under coordination, and as suggested by FT-FIR analysis, the O-vacancies are located at in-plane sites. The DoS for the supercell with the oxygen vacancy in the neutral charge state is shown in Figure 8b. As shown in this figure, the oxygen vacancy creates a deep level in the bandgap. This state is a vacancy-assisted polaron that originates from the majority spin direction of Mn e<sub>g</sub> states. The Fermi level shifts upward to the top part of the mid-gap states. More vacancy can separate more states from the bottom part of the Mn e<sub>g</sub> state in the conduction band to the top part of the valance band, as shown in Figure 8b.

In  $Pr_{0.5}Ca_{0.5}MnO_3$ , which is oxygen stoichiometric as reported previously, each Mn ion is sixfold coordinated with O atoms which form an octahedron cage around the Mn ion. However, in the half-doped system,  $Pr_{0.5}Ca_{0.5}MnO_3$ , the Zener polaron forms, which is characterized by an electron shared by two ferromagnetically coupled Mn neighbors. Characteristic of a Zener polaron are two neighboring Mn sites, both having a Jahn–Teller expansion along the axis of the pair. In  $Pr_{0.5}Ca_{0.5}MnO_3$ , the lower Jahn–Teller band is itself split into two, of which only one is occupied. The origin of the splitting of the lower Jahn–Teller band is due to the formation of an antibond with the bridging oxygen ion [55,56].

The DoS for the half-doped system is shown in Figure 8c. The filled majority  $Mn e_g$  states are located on top of the valence band, and the empty majority  $Mn e_g$  states are located at the bottom part of the conduction band. The oxygen vacancy adds electrons in the unoccupied majority  $Mn e_g$  states in the half-doped system and shifts them down to the top of the valence band. As shown in Figure 8d, the vacancy can separate more states from the majority  $Mn e_g$  state in the conduction band.

As shown in Figure 8, photoexcited electrons can be placed in the Mn 3d  $t_{2g}\downarrow$  conduction bands under UV light irradiation in both CaMnO<sub>3- $\delta$ </sub> and Pr<sub>0.5</sub>Ca<sub>0.5</sub>MnO<sub>3</sub>. The Mn 3d  $t_{2g}\downarrow$  conduction band level is more negative than the O<sub>2</sub>/O<sub>2</sub><sup>-</sup> reduction level, and the hybridized O 2p and Mn e<sub>g</sub>↑1valence band levels are more positive than H<sub>2</sub>O/OH<sup>-</sup> oxidation level [51].

The calculated absorption spectra for CaMnO<sub>3</sub> and  $Pr_{0.5}Ca_{0.5}MnO_3$  are shown in Figure 9. The  $Pr_{0.5}Ca_{0.5}MnO_3$  spectrum exhibits a considerable shift towards higher energies and a loss of absorption intensity between 2 eV and 4 eV compared to CaMnrO<sub>3</sub>. The intensity reduction in the  $Pr_{0.5}Ca_{0.5}MnO_3$  is attributed to the empty Mn e<sub>g</sub> states, which lower from CaMnO<sub>3</sub> to  $Pr_{0.5}Ca_{0.5}MnO_3$ . The Mn e<sub>g</sub> states become occupied by Pr doping, and they become unable to be used for optical excitation. Thus, this analysis sheds light on the experimentally obtained spectra of doped and undoped CaMnO<sub>3</sub>.



**Figure 9.** Calculated absorption spectra for CaMnO<sub>3</sub> (black) and  $Pr_{0.5}Ca_{0.5}MnO_3$  (red). The absorption edge from 2 eV to 4 eV is attributed to the occupation of the Mn eg states, which demonstrate the lowering of the absorption intensity due to doping in  $Pr_{0.5}Ca_{0.5}MnO_3$ , while they are empty and thus visible in the spectrum of CaMnO<sub>3</sub>.

## 4. Conclusions

In this work, the photocatalytic dye decomposition over the perovskites  $CaMnO_{3-\delta}$ and  $Pr_{0.5}Ca_{0.5}MnO_3$  under UV irradiation has been studied. The kinetics of photocatalytic oxidation of organic pollutants showed that  $CaMnO_{3-\delta}$  was slightly more active than  $Pr_{0.5}Ca_{0.5}MnO_3$ . The effects of surface oxygen vacancies and electronic structure on photocatalytic degradation have been investigated by XPS and DFT. The surface oxygen vacancies were found not to be a pivotal factor for improving the photocatalytic properties as long as the O-vacancies occupied the  $BO_2$  positions. The content of chemisorbed oxygen observed on the surface of PCMO particles is considerably higher than CMO, while the amount of oxygen vacancies created on the surface and bulk of CMO is much more pronounced. XPS studies showed the ratio of  $Mn^{4+}/Mn^{3+}$  for both surface and bulk of  $Pr_{0.5}Ca_{0.5}MnO_3$  particles. Based on the theoretical calculation of the electronic structure, the photoexcitation of the electrons from the hybridized O 2p and Mn  $e_g\uparrow$  valance band to the Mn  $e_g\uparrow$  and Mn  $e_g\downarrow$  were responsible for the  $O_2$  reduction under UV irradiation. This work may be useful for designing new Mn-based oxide photocatalysts.

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