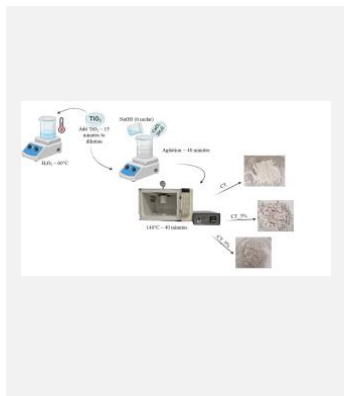


## CaTiO<sub>3</sub>: Impact of Ag Doping on the Efficiency of •OH Radical Generation under UV Radiation

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This study investigates the photocatalytic activity of pure and Ag-doped CaTiO<sub>3</sub>, focusing on OH radical generation under UV radiation. It explores how Ag doping influences the perovskite structure and enhances photocatalytic performance. CaTiO<sub>3</sub> and Ag-doped CaTiO<sub>3</sub> were synthesized using a microwave-assisted hydrothermal method. OH radical generation was quantified using pCBA as a probe compound under UV irradiation. CT3 exhibited superior OH radical generation compared to CT and CT5, with concentrations of  $4.07 \times 10^{-11}$  mol L<sup>-1</sup>,  $2.2 \times 10^{-11}$  mol L<sup>-1</sup>, and  $2.25 \times 10^{-11}$  mol L<sup>-1</sup>, respectively. The enhanced performance of CT3 is attributed to its reduced band gap energy, facilitating better photocatalytic activity.

### Introduction

Heterogeneous photocatalysis is a widely used advanced oxidation process. Its extensive use is due to the fact that this process is superior to homogeneous photocatalysis for practical applications. This is because it is easier to separate the catalyst from the reaction mixture, which reduces contamination and provides both environmental and economic benefits. Therefore, heterogeneous photocatalysis is closely related to the characteristics of the catalyst material, such as its crystalline structure and electronic states. In terms of materials, photocatalysts can be grouped into metal oxides, metal sulfides, metal nitrides, metal hydroxides, bismuth-based salts, carbon-based polymers, silver halides (Ag), perovskites, and other new materials such as metal-organic frameworks and covalent organic frameworks [1].

Among photocatalytic materials, semiconductors have received special attention due to their band gap characteristics, which can generate excitons capable of participating in the redox reactions of pollutants. Photocatalysis studies have been conducted with pure TiO<sub>2</sub>, doped forms, composites, and heterostructures [2-4].

Calcium titanate (CaTiO<sub>3</sub>), an n-type semiconductor with a perovskite structure (ABO<sub>3</sub>), is cited in the literature as a promising photocatalyst alternative to TiO<sub>2</sub> due to its wider band gap energy (~3.6 eV) and unique properties that favor its use in heterogeneous photocatalysis. The band gap of TiO<sub>2</sub> is around 3.2 eV according to the literature [5]. Furthermore, dopants can also be accommodated in the perovskite structure,

promoting desired defects or oxygen excess, significantly contributing to its catalytic performance [6].

There are studies evaluating the photocatalytic potential of pure and modified CaTiO<sub>3</sub> prepared by various synthesis methods [6]. However, there are no previous studies on CaTiO<sub>3</sub> doped exclusively with Ag at the A-site of its perovskite structure. The introduction of Ag as a dopant, as explored in this study, induces the formation of local defects within the perovskite lattice. These defects result in distortions within the electronic structure of the lattice ions, creating intermediate states within the band gap. The emergence of these interband states effectively reduces the band gap energy, a beneficial outcome for photocatalytic processes [1]. Essentially, this modification can enhance the production of reactive species during the photocatalytic process.

In this context, this work presents results from a study on the photocatalytic activity of pure CaTiO<sub>3</sub> and Ag-doped CaTiO<sub>3</sub> prepared by the microwave-assisted hydrothermal method. We aim to investigate the influence of the dopant on the perovskite structure in •OH generation under UV radiation.

### Material and Methods

#### Sample preparation

CaTiO<sub>3</sub> (CT) was synthesized using the microwave-assisted hydrothermal method. Calcium chloride (CaCl<sub>2</sub>·H<sub>2</sub>O) and titanium dioxide (TiO<sub>2</sub>) were used as precursors. These were diluted in 15 mL of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), heated to 60°C, and stirred for approximately 15 minutes in a 100 mL Teflon® cup.

The synthesis involved a heating ramp of 10°C per minute, reaching 140°C for 40 minutes.

This procedure was also followed for the preparation of Ag-doped CaTiO<sub>3</sub>. In these cases, 3% and 5% mol of silver nitrate (AgNO<sub>3</sub>) were added to the solution containing the CT precursors immediately after the addition of CaCl<sub>2</sub>·H<sub>2</sub>O, prior to microwave heating. These samples were designated as CT3% and CT5%, respectively. Graphical abstract shows the schematic representation of the CaTiO<sub>3</sub> and Ag-containing CaTiO<sub>3</sub> preparation.

### Hydroxyl radical quantification

The concentration of hydroxyl radicals can be indirectly determined by the rate of consumption of a probe compound. In this research, pCBA was used for this purpose. The concentration of OH can be estimated using Equation (1).

$$-\frac{d[pCBA]}{dt} = k_{OH,pCBA}[OH]_{ss}[pCBA] \quad (1)$$

where,  $k_{OH,pCBA}$  is the rate constant of pCBA with OH, ( $5 \times 10^9 \text{ mol L}^{-1} \text{ s}^{-1}$ ) at ambient temperature and pressure; and  $[OH]_{ss}$  and  $[pCBA]$  are the steady state concentration of hydroxyl radicals, and the concentration of pCBA, respectively.

## Results and Discussion

The OH radical is the most frequently involved reactive intermediate species in photocatalytic processes.

### Conclusions

This work presents results from a study on the photocatalytic activity of pure CaTiO<sub>3</sub> and Ag-doped CaTiO<sub>3</sub> prepared by the microwave-assisted hydrothermal method. The investigation of the influence of the dopant on the perovskite structure in OH radical generation under UV radiation shows that CT3 exhibits superior performance. The superior performance of CT3 in OH radical generation aligns with the dye degradation reported in literature [6]. The better performance of CT3 could be attributed to the decreased band gap energy values, which were found to be lower than those of pure CT and CT5.

### Acknowledgments

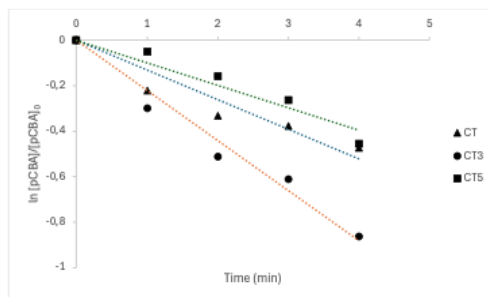
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Consequently, we investigated the formation of OH radicals from the photocatalysts developed by our research group. We quantified the generation of OH radicals from CT, CT3, and CT5 when irradiated by UV light. Using a probe compound with a known OH radical rate of reaction allows for the indirect quantification of these species.

Figure 1 shows the depletion of pCBA promoted by UV-irradiated CT, CT3, and CT5. The slope of each degradation curve ( $\ln([pCBA]/[pCBA]_0)$  vs. time), divided by  $k_{OH,pCBA}$ , results in the concentration of OH radicals produced during irradiation. The continuous generation of OH radicals was found to be  $2.2 \times 10^{-11} \text{ mol L}^{-1}$  for the CT sample,  $4.07 \times 10^{-11} \text{ mol L}^{-1}$  for CT3, and  $2.25 \times 10^{-11} \text{ mol L}^{-1}$  for CT5. These results indicate that the concentration of OH radicals is highest in the CT3 sample.



**Figure 1.** Depletion of pCBA under UV irradiation of CT, CT3 and CT5.