

Influence of silver doping in CaTiO₃ on the removal of Rhodamine B from wastewater

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Dyes used in various industries represent a growing environmental concern. The study introduces a ceramic material designed as a solution to this problem through advanced oxidative processes (AOP). This investigation focuses on exploring the photocatalytic capabilities of Ca(1-x)Ag(x)TiO₃, where x varies between 0% and 3% in terms of Ag molar fraction. Ceramic powders were synthesized using the microwave-assisted hydrothermal method (MAH). The catalysts were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopy. In the photocatalysis experiments, the materials were immersed in a RhB solution and exposed to UV light. Aliquots of the solution were collected for UV-Vis absorption analysis. Characterization confirmed the crystalline phase of CT and the incorporation of silver into the CT3% structure. Results from the RhB photocatalysis experiments revealed that the sample containing 3% Ag achieved effective dye degradation.

Introduction

Recent years have witnessed a growing concern over the contamination of wastewater with dyes, largely originating from industries like textiles, leather, paper, and clothing [1]. These dyes present significant challenges due to their persistence and potential harm to ecosystems and human health. Consequently, there's an increasing demand for effective wastewater treatment methods capable of degrading or removing these pollutants. AOPs usually deal with the generation of oxygen-reactive species have emerged as a promising solution for addressing dye contamination in wastewater [2]. This process utilizes semiconductor photocatalysts to generate reactive oxygen species under light irradiation, facilitating the degradation of organic pollutants into harmless byproducts. While titanium dioxide (TiO₂) has been extensively studied for its photocatalytic properties, alternative materials like calcium titanate (CaTiO₃) have garnered attention for their unique characteristics and potential application in wastewater treatment [3].

However, despite the promising properties of CaTiO₃, there's still a gap in the literature regarding its use as a photocatalyst for dye removal, especially when doped with silver (Ag) to enhance its performance. Therefore, this study aims to investigate the photocatalytic activity of Ag-doped CaTiO₃ synthesized via the microwave-assisted hydrothermal method. By evaluating the dye degradation efficiency and morphological characteristics of the photocatalysts, this research aims to contribute to the development of sustainable and efficient wastewater treatment technologies.

Material and Methods

The CaTiO₃ (CT) was prepared using the

microwave-assisted hydrothermal method. Additionally, samples of Ag-doped CT were prepared at concentrations of 3% mol, by adding proportions of silver nitrate (AgNO₃) to the solution containing CT precursors immediately after the addition of CaCl₂·H₂O, before undergoing microwave heating. These samples were labeled as CT3%. The resulting CT was characterized by X-ray diffraction (Shimadzu, model XRD-6000), Raman spectroscopy (Renishaw, inVia), and FTIR spectroscopy (Perkin Elmer Frontier).

For investigating the photocatalytic degradation process, control experiments were conducted: adsorption and photolysis. Adsorption experiments involved solutions containing 10 mg L⁻¹ of Rhodamine B (RhB) and 1 g L⁻¹ of photocatalyst (CaTiO₃, CaTiO₃(Ag3%)) incubated in the dark at 25°C for 120 minutes. Photolysis experiments utilized an experimental setup with UVC lamps emitting radiation at 254 nm. Photocatalysis experiments employed solutions of 10 mg L⁻¹ of RhB and 1 g L⁻¹ of photocatalyst, which were irradiated for 120 minutes. Samples were taken at specific time points and analyzed for RhB concentration using a UV-vis spectrophotometer.

Results and Discussion

Regarding the X-ray diffraction results of the titanate samples, the orthorhombic phase of CaTiO₃ (JCPDS 89-8033) was identified in all samples. The residual phase of TiO₂ (anatase, tetragonal) was also observed, and its presence is associated with the lower crystallinity of the main CT phase, characterized by reduced intensities of characteristic peaks. Silver (Ag) was not detected in the diffractograms due to its low doping content. However, a slight shift of the peak around 2θ = 33°

to lower angles was observed, potentially indicating the presence of Ag in the CT host lattice. Similar results were reported [4], where Ag⁺ added via photoreduction may have been uniformly distributed on the surface of CaTiO₃.

Regarding Raman microscopy, for the CT sample, all Raman modes were attributed to the orthorhombic perovskite phase, consistent with previous literature. Some of these bands were also observed in the CT3% sample, indicating the presence of vibrational modes of the orthorhombic phase of CaTiO₃. Additionally, vibrational modes corresponding to TiO₂ in the anatase phase were observed in the CT3% sample, consistent with X-ray diffraction results. The presence of calcium carbonate (CaCO₃ - calcite) in the CT sample was indicated by a peak at 1084 cm⁻¹.

In general, the FTIR spectra of titanates with perovskite structure exhibit peaks between 500 and 900 cm⁻¹ corresponding to metal-oxygen bonds. Peaks at 529 cm⁻¹ and 882 cm⁻¹ in the CT sample may characterize stretching and bending vibrational modes of the Ti-O bond within the octahedron [TiO₆] of the perovskite structure. With Ag doping, a slight shift in the frequency corresponding to the bending vibrational mode at 882 cm⁻¹ was observed, possibly indicating partial substitution of Ca by Ag in the perovskite lattice.

The control experiments (adsorption and photolysis assays) demonstrated that there was no variation in the concentration of RhB throughout the experiments. This outcome reveals that the photocatalysts under study do not adsorb the rhodamine B dye. Additionally, it was revealed that the RhB dye does not undergo photolysis within two hours under UV radiation at 254 nm. These findings indicate that the degradation of the dye in the photocatalysis experiments results exclusively from the reactions initiated by the photocatalysts. Figure 1 presents the results of the photocatalysis experiments with CT. Photodegradation using CaTiO₃ proved incapable of removing the RhB dye after 120 minutes of UV irradiation at 254 nm. The observed result can be attributed to the limitation in the overall photocatalytic effectiveness of CaTiO₃, despite its high photoactivity, due to its wide bandgap and low quantum efficiency. An important factor contributing to this limitation is the ultrafast recombination of photoexcited electron-hole pairs. The performance of CT3% is consistent with that presented through XRD, which reveals the simultaneous presence of the TiO₂ phase, which may assist in altering the E_g of this sample if there is a CaTiO₃-TiO₂ heterojunction. Results also observed superior photocatalytic performance with CaTiO₃ modified with 3% Ag. They attributed this to the decrease in band gap energy values, which were found to be lower than those of pure CT. The experimental results suggest that the degradation capacity of CaTiO₃ is significantly enhanced by depositing Ag on its surface, with higher RhB removal percentages for CT3% compared to pure

CT. These metallic deposits act as electron accumulation sites, effectively capturing photoexcited electrons from the surface of CaTiO₃ and transferring them to oxygen molecules, consequently generating more reactive intermediate species, such as highly reactive hydroxyl radicals ($\cdot\text{OH}$) and superoxide radical anions ($\cdot\text{O}_2^-$), which can react with RhB, resulting in increased degradation.

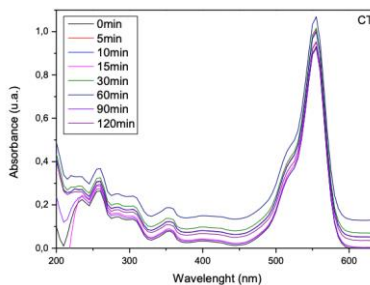


Figure 1. The variation in UV–visible absorption spectra of RhB dye solution as a function of irradiation time in the presence of CT as a catalyst under UV light radiation.

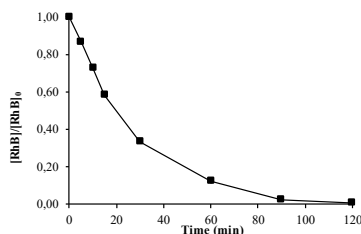


Figure 2. Concentration variation of the RhB during photocatalysis experiment for [RhB]₀=100mg L⁻¹ and [CT3%]₀=1 gL⁻¹.

Conclusions

The employed method proved to be effective in synthesizing CT and CT3% photocatalysts. Through XRD analysis, the presence of the orthorhombic phase of CaTiO₃ was confirmed in all samples, along with the residual phase of TiO₂ (anatase, tetragonal) in the sample containing Ag. Micro-Raman spectra confirmed the presence of TiO₂ in the anatase phase for CT3%, as well as Ti-O vibrations of the TiO₂ phase. Photocatalysis experiments demonstrated enhanced performance in RhB degradation with Ag-doped CaTiO₃ compared to pure CT, as supported by material characterization.

Acknowledgments

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