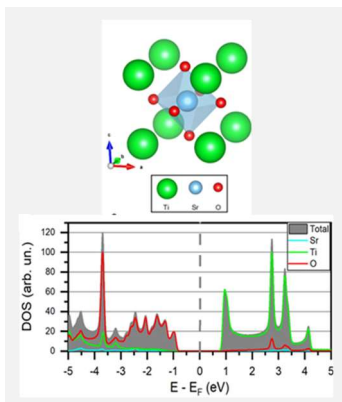


Imidacloprid photocatalytic degradation under visible light at Bi-doped SrTiO₃ perovskite

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The objective of this work was to study the influence of Bi content on the photocatalytic properties Sr_{1-x}Bi_xTiO₃ perovskites. Prepared materials were structurally, morphologically, chemically, and optically characterized. Electronic properties were depicted by calculating the density of states and evaluating the effects of Bi doping on the material band-gap energy. Density Functional Theory was utilized to describe the electron-ion interactions. The oxide Sr_{0.95}Bi_{0.05}TiO₃ was selected for imidacloprid (IMD) degradation under visible light irradiation, in aqueous solution and in a water-matrix collected from a river (RW), being the best IMD degradation attained in the RW. The calculated electronic properties of Bi-doped SrTiO₃ demonstrate the potential of Bi doping as a viable approach for optimizing its performance as photocatalyst. The saturation of the band gap widening at higher concentrations of Bi suggests an optimal doping level.

Introduction

Environmental pollution is a concern for today's society, requiring effective ways for real mitigation of this problem. A possible solution may involve photocatalysis with suitable catalytic materials, preferably activated by sunlight [1]. These advanced oxidation processes have received significant attention as an ecological and sustainable technology that takes advantage of a cheap and renewable energy source to initiate chemical reactions, improving the degradation of pollutants and increasing the efficiency of wastewater treatment [2].

Perovskite oxides are materials with adequate properties to be utilized in photocatalysis, being strontium titanate (SrTiO₃) among those suitable as photocatalytic materials, with high thermal and chemical stabilities, a good cost-benefit ratio, and ease of synthesis [3,4]. Although undoped SrTiO₃ exhibits photocatalytic activity, its effectiveness as a photocatalyst can be significantly improved through bismuth-doping in particular. This enhancement is attributed to the n-type doping effect induced by Bi, which effectively narrows the band gap and facilitates light absorption, thereby increasing the material responsiveness to visible light. Thus, Bi-doped SrTiO₃ emerges as a promising oxide for environmental remediation applications of persistent contaminants, such as imidacloprid (IMD), which represents a challenge due to its structural complexity and resilience in different environmental settings [5].

In this work, the synthesis and characterization of Bi-doped SrTiO₃ perovskites was carried out. The oxide

Sr_{0.95}Bi_{0.05}TiO₃ was selected for a detailed study on its photocatalytic effectiveness in the decomposition of IMD under visible light irradiation, in aqueous solution and in a water matrix collected from a river. The stability and reusability of the catalyst in successive degradation cycles was evaluated. Electronic properties were characterized by calculating the density of states (DOS) and evaluating the effects of Bi doping on the material band-gap energy. Density Functional Theory (DFT) was utilized to describe the electron-ion interactions.

Material and Methods

The Sr_{1-x}Bi_xTiO₃ (x = 0 and 0.05) perovskite powders were synthesized via the solid-state method [4]. In this process, stoichiometric amounts of SrCO₃, Bi₂O₃, and TiO₂ were ground together in an agate mortar. Mixtures were then heated in a tubular furnace at 900 °C (x = 0) or 750 °C (x = 0.05) for 24 h. Resulting samples were reground and reheated at 1200 °C (x = 0) or 750 °C (x = 0.05) for additional 24 h. The synthesized powders were structurally, morphologically, chemically, and optically characterized, by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray scattering spectroscopy (EDX), and diffuse reflectance spectroscopy (DRS), respectively. Quantum mechanical calculations were performed within the DFT framework utilizing the Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional, and the Projector Augmented Wave (PAW) [6]. Electronic properties were characterized by calculating the DOS and evaluating the effects of Bi on the energy gap.

Photocatalytic experiments were conducted in batch mode, at controlled temperature of 25 °C, using 100 mL of perovskite suspension (0.2 g L⁻¹), containing IMD (Ci = 5 mg L⁻¹), under visible light radiation (300 W). Suspensions were prepared with distilled water (DW) or river water (RW - dissolved organic and inorganic carbon of 2.14 and 3.02 mg L⁻¹; pH of 7.02). During experiments, samples were collected every hour, being analyzed for IMD concentration, determined by RP-HPLC, with a reverse phase column (Merck Millipore, Purosphere STAR RP-18 endcapped, 250 mm × 4 mm (i.d.), 5 μm particles), at 35 °C. A mixture of 10 mM oxalic acid aqueous solution (Fluka, 0.1 M) (component A) and acetonitrile (Fisher Chemical, ≥99%) (component B) was used as the mobile phase. The elution was performed isocratically, at a flow rate of 0.7 mL min⁻¹, with a relative percentage of B of 20% (v/v). IMD detection was carried out at 270 nm.

Results and Discussion

Figure 1 presents the XRD diffractograms of the Sr_{1-x}Bi_xTiO₃ (x = 0 and 0.05) perovskite powders. Both spectra show pronounced peaks corresponding to the perovskite symmetry documented in the ICDD file PDF#35-0734. A minor phase was identified for the Sr_{0.95}Bi_{0.05}TiO₃ sample, corresponding to bismuth titanate, Bi₄Ti₃O₁₂ (ICDD file PDF#47-0398). Figure 2 shows IMD concentration decay during photolysis, and photocatalysis with Sr_{0.95}Bi_{0.05}TiO₃ suspensions. Both photolytic experiments, under visible light, were able to achieve concentration removals of 18.0% and 21.5%, after 3 h, for the assays performed in DW and in RW, respectively. The addition of the photocatalyst resulted in higher degradation rates, under both experimental conditions. This

improvement is more significant for the photocatalytic experiment performed in RW, where a IMD concentration removal of 59.5% was achieved, after 3 h. Matrix composition (i.e. ionic composition and pH) had a positive influence on IMD photocatalytic degradation profile.

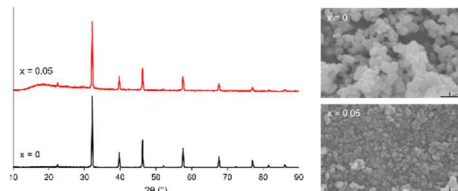


Figure 1. XRD patterns and micrographs of Sr_{1-x}Bi_xTiO₃ samples (x=0; 0.05).

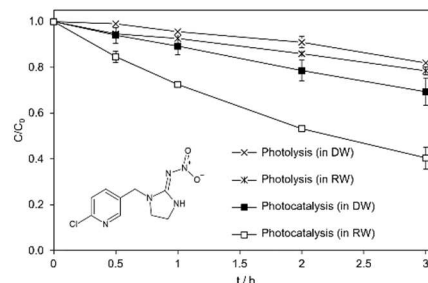


Figure 2. Variation of [IMD] during photolysis and photocatalysis in Sr_{0.95}Bi_{0.05}TiO₃ (0.2 g L⁻¹) suspensions, under visible light. [IMD]₀ = 5 mg L⁻¹.

The computational studies showed an increase in the energy gap with Bi concentration until a saturation level, beyond which the photocatalytic efficiency does not improve with Bi content.

Conclusions

The Sr_{1-x}Bi_xTiO₃ (x = 0 and 0.05) perovskite oxides were successfully prepared and for x=0.05 a minor phase of Bi₄Ti₃O₁₂ was identified.

Photocatalysis with Sr_{0.95}Bi_{0.05}TiO₃, under visible light, was able to degrade IMD in DW and in RW, being the best results obtained in RW.

The saturation of the band gap widening at higher concentrations of Bi suggests an optimal doping level.

Knowledge of electronic properties of Bi-doped SrTiO₃ demonstrate the potential of Bi doping as a viable approach for optimizing its performance as photocatalyst.

Acknowledgments

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