

Microwave-Assisted Hydrothermal Synthesis of Zn₂SnO₄ Nanostructures for Photocatalytic Dye Degradation †

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Abstract: Zinc-tin oxide (ZTO) nanostructures appear as one of the most promising material systems for a new generation of nanodevices. In this work, a microwave-assisted hydrothermal synthesis to produce different shapes of Zn₂SnO₄ nanostructures (nanoparticles, octahedrons and nanoplates) is presented. Reproducible and homogeneous results were obtained with the advantage of reducing up to 20 h the synthesis time when compared to using a conventional oven. Furthermore, the photocatalytic activity of the Zn₂SnO₄ nanostructures in the degradation of rhodamine B under UV light was studied. Zn₂SnO₄ nanoparticles demonstrated better performance with >90% of degradation being achieved in 2.5 h.

Keywords: Zn₂SnO₄; ZTO; octahedrons; nanoparticles; nanoplates; microwave-assisted hydrothermal synthesis; photocatalysis; rhodamine B

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1. Introduction

The zinc-tin oxide (ZTO) material system possesses a wide range of attractive properties for a new generation of multifunctional nanodevices. It can crystallize in Zn₂SnO₄ and ZnSnO₃ phases, with different types of nanostructures possible for each phase. Each has unique properties suitable for applications in catalysis, sensors, transistors, memories, or energy harvesting devices [1–5].

Hydrothermal synthesis is one of the best methods to obtain complex oxides due to its characteristic pressure and temperature conditions. These processes are commonly performed using conventional ovens; nevertheless, microwave-assisted synthesis is an interesting alternative for the inorganic nanostructures' fabrication, due to its faster reactions and consequences of its heating process. This contributes to an enhancement of the product purity and yield [6–9]. Several ZnO and SnO₂ nanostructures have been reported by microwave-assisted synthesis [7,10–15], however, the advantageous multicomponent ZTO is significantly more difficult to obtain. Nevertheless, ZTO nanostructures synthesized in microwave systems have already been reported [8,16–18]. A simple method to produce quantum dots using a conventional microwave was demonstrated by Lehnen et al. [8], while Nehru et al. produced Zn₂SnO₄ nanostructures in a microwave system by using a urea-based combustion process [16]. Recently, Jain et al. reported a microwave-assisted hydrothermal synthesis of Zn₂SnO₄ nanorods using a power of 600 W for 15 min, and an annealing treatment at 700 °C for 5 h [18]. In this work, a seed-layer free microwave-assisted hydrothermal synthesis of Zn₂SnO₄ nanostructures with different morphologies (nanoparticles, octahedrons and nanoplates) is presented. The Zn₂SnO₄ nanostructures were obtained in ≤60 min without employing any annealing treatment. The photocatalytic performance of these nanostructures in degradation of rhodamine B (RhB) under

UV light is also shown, with better performance being observed when using the Zn_2SnO_4 nanoparticles.

2. Materials and Methods

The Zn_2SnO_4 octahedrons and nanoplates were synthesized through the hydrothermal process described in reference [19]. The Zn_2SnO_4 nanoparticles were synthesized based on the synthesis of Annamalai et al. [20]. After its preparation, the solutions were kept in the microwave (CEM Focused Microwave Synthesis System Discover SP), in a dynamic mode at 200 °C, establishing a maximum pressure of 270 PSI and a maximum power of 100 W for the nanoparticles and 80 W for the octahedrons and the nanoplates. The nanostructures were washed several times alternately with IPA and H_2O , and then dried at 60 °C for 2 h in a vacuum [21]. A PANalytical's X'Pert PRO MRD diffractometer (with Cu Ka radiation) was used to determine the crystalline structure of the Zn_2SnO_4 nanostructures. The data was acquired in the 10–90° 2θ range with a step size of 0.033°. The morphology of the nanostructures was carried out by a Carl Zeiss AURIGA CrossBeam (FIB-SEM) workstation. The photocatalytic performance of the ZTO nanostructures in the degradation of rhodamine B (RhB) was evaluated at room temperature. For each experiment, 40 mg of each powder containing the different nanostructures was dispersed in 50 mL of the RhB solution (5 mg/L). The RhB used is from Sigma Aldrich (Lisbon, Portugal). The photocatalysis tests were performed under UV light using 3 lamps (Osram, HNS L 95 W 2G11, Munich, Germany) with an emission wavelength range of 200–280 nm (ozone free), aligned in parallel at a distance of 10 cm from the solutions with the nanostructures.

3. Results and Discussion

3.1. Microwave-Assisted Synthesis of Zn_2SnO_4 Nanostructures

In a previous work, Zn_2SnO_4 octahedrons were synthesized by a hydrothermal method in a conventional oven at 200 °C for 24 h [19]. A posteriori, a shorter duration of 12 h was also studied and it was found that this is not enough time to purely produce the Zn_2SnO_4 phase, leading instead to the predominance of Zn_2SnO_4 nanoplates, which are an intermediate structure in the formation of the Zn_2SnO_4 octahedrons [22]. Following these results, Zn_2SnO_4 octahedrons and nanoplates were synthesized replacing the conventional oven with a microwave system. Figure 1 shows the XRD patterns and the SEM images for the ZTO nanostructures obtained with these microwave-assisted syntheses. The same trend observed for the oven syntheses is verified for microwave syntheses even if employing significantly shorter times, i.e., longer synthesis leads to the achievement of pure phase Zn_2SnO_4 octahedrons, while some mixture of phases is achieved for shorter syntheses, producing mainly Zn_2SnO_4 nanoplates [22].

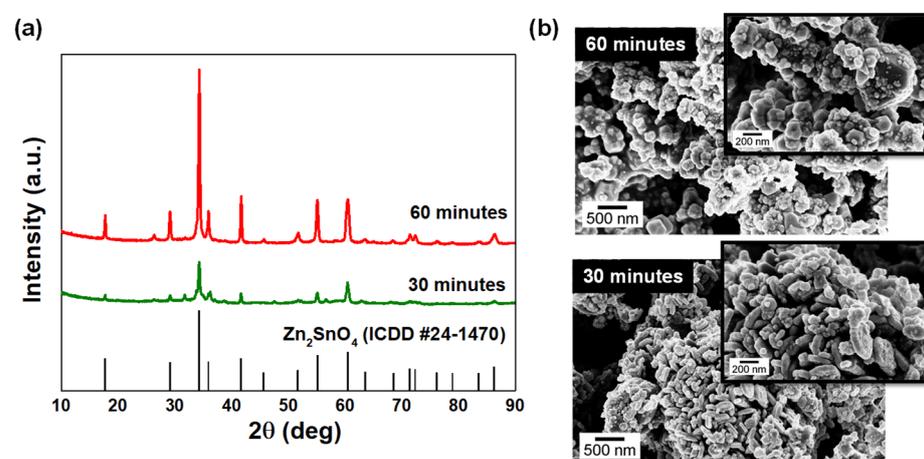


Figure 1. (a) XRD pattern and (b) SEM images of the Zn_2SnO_4 nanoplates and octahedrons synthesized in the microwave system (for 30' and 60').

Based on the synthesis described by Annamalai et al. [20] in a conventional oven, and aiming to reduce the synthesis time, Zn_2SnO_4 nanoparticles were also synthesized using the microwave system. This synthesis was performed at 200 °C, establishing a maximum power of 100 W and a maximum pressure of 270 PSI. Two synthesis durations were considered, 20 min and 60 min.

In Figure 2, the SEM images and the XRD patterns are presented, showing that in both cases small nanoparticles with a pure Zn_2SnO_4 phase were obtained. This shows that it is possible to reduce at least 5 h of synthesis time, compared to the synthesis reported by Annamalai et al. [20], and still produce Zn_2SnO_4 nanoparticles with good quality.

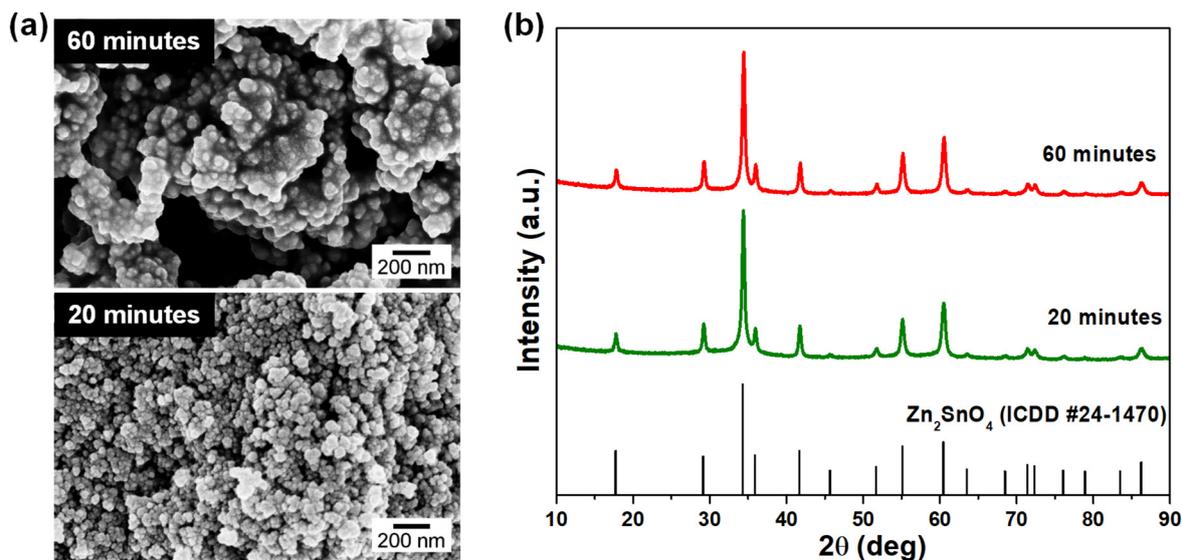


Figure 2. (a) XRD patterns and (b) SEM images of the Zn_2SnO_4 nanoparticles synthesized by microwave-assisted synthesis for 20 min and 60 min.

In general, these studies showed the efficiency of the microwave heating method to produce high-quality Zn_2SnO_4 nanoplates, octahedrons and nanoparticles, without post-processing annealing treatment and with the advantage of allowing for much shorter syntheses than usually needed when using conventional ovens.

3.2. Photocatalytic Activity of Zn_2SnO_4 Nanostructures

The photocatalytic activity of the Zn_2SnO_4 octahedrons, nanoplates and nanoparticles produced by microwave-assisted hydrothermal synthesis in only 60 min was studied in the degradation of RhB under UV light. Figure 3 shows the absorbance spectra variation of the RhB solution with the UV light exposure time in the presence of each ZTO nanostructure. It is possible to observe that the nanoparticles have a much higher degradation rate (0.01659 min^{-1}) compared to octahedrons (0.01069 min^{-1}) and the nanoplates (0.01097 min^{-1}). This could be due to the higher surface area of the nanoparticles compared with the other two nanostructures, which also could explain the smaller degradation rate of the octahedrons compared with the nanoparticles and the nanoplates. The degradation rate was obtained through the pseudo-first-order reaction kinetic model, which is represented by $\ln(C_0/C) = kt$, where C_0 is the initial concentration ($\text{mg}\cdot\text{L}^{-1}$) [18,23,24].

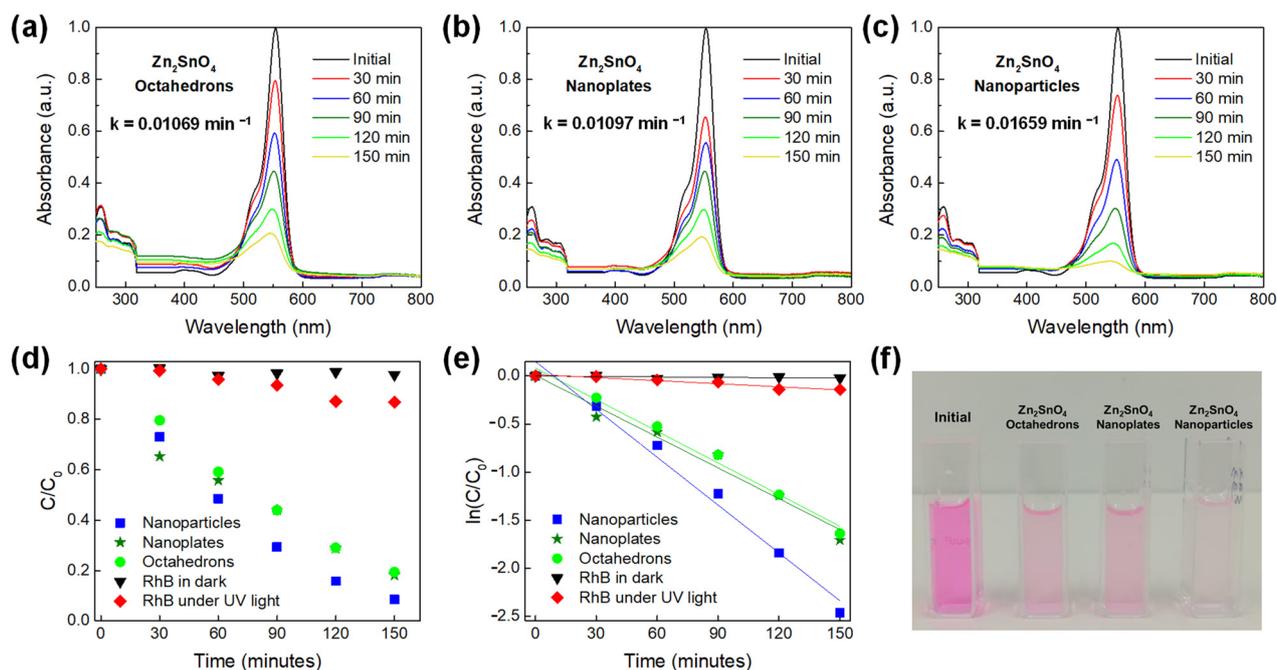


Figure 3. Absorbance spectra of the photocatalytic degradation of rhodamine B (RhB) under UV light using as photocatalyst Zn_2SnO_4 (a) octahedrons, (b) nanoplates and (c) nanoparticles. (d) C/C_0 comparison of the photocatalytic degradation between zinc-tin oxide (ZTO) nanostructures. (e) Kinetic parameters of the RhB degradation under UV of each Zn_2SnO_4 nanostructure. (f) Photograph image of the initial RhB solution and after its degradation under UV light during 150 min using each of the Zn_2SnO_4 nanostructures as photocatalyst.

4. Conclusions

While Zn_2SnO_4 nanostructures such as octahedrons, nanoplates and nanoparticles present great interest for different applications, sometimes the reaction times and/or yield are not practical, especially when considering devices that require a high volume of particles. Thus, microwave-assisted synthesis was explored in this work due to its faster and more uniform heating rate. This method has shown to be able to result in different ZTO nanostructures (Zn_2SnO_4 octahedrons, nanoplates and nanoparticles), allowing to decrease the synthesis time up to 20 h, when comparing with the conventional oven. Furthermore, the photocatalytic activity of the ZTO nanostructures synthesized in only 60 min was studied in the degradation of rhodamine B under UV light, revealing a higher degradation rate using the nanoparticles (0.01659 min^{-1}) as photocatalyst rather than using the nanoplates (0.01097 min^{-1}) and the octahedrons (0.01069 min^{-1}).

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