

Crystallization time in ZnO: The role of surface OH groups in its photoactivity

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EXPERIMENTAL SECTION

Characterization

Thermogravimetry (TG) analysis was performed in a TA Instruments Q500 thermogravimetric analyzer in a temperature range of 20 to 700 °C under synthetic airflow, applying a heating rate of 10°C.min⁻¹. The crystalline nature of the samples was analyzed by X-ray diffraction (XRD) applying *Cu Kα* radiation ($\lambda=1,5406\text{\AA}$) in the 2θ range from 10 to 60° employing a Shimadzu XRD-6000 diffractometer. Raman spectra were obtained in an FT-Raman spectrometer (Bruker RAM II with a Ge detector) equipped with an Nd:YAG. It was applied an excitation wavelength of 1064 nm, generating a power of 100 mW at a resolution of 2 cm⁻¹. Infrared (FTIR) spectra of the materials were obtained in a Spectrum 1000 spectrophotometer (Perkin Elmer) in the range from 400 to 4000 cm⁻¹ with 32 scans and resolution of 4 cm⁻¹. The Near Infrared (NIR) analyses were carried out in triplicate, on a Büchi NIRFlex N-500 FT-NIR spectrometer (Flawil, Switzerland), equipped with a diffuse reflectance accessory in the range from 4000 to 10000 cm⁻¹ with 64 scans and resolution of 4 cm⁻¹. The indirect detection of OH radicals by fluorescence was conducted using terephthalic acid (TPA) 5.10⁻⁴ mol L⁻¹ solution prepared in NaOH 2.10⁻³ mol L⁻¹. The catalyst samples were added in the same proportion of photocatalysis tests. The samples were exposed to UVC radiation per 3 hours and the 2-hydroxyterephthalic acid reaction product was measured by a Perkin Elmer LS 50B equipment. Differential scanning calorimetry (DSC) was performed with a Q Series DSC Q800 TA Instruments. Samples were weighed (8.0 ± 1.0 mg) in aluminum pans, which were sealed and heated at a rate of 10 °C min⁻¹ until 300 °C and stabilized at this temperature per 2 hours. An empty aluminum pan was used as a reference. The zeta potential of the prepared ZnO samples was recorded in a suspension (0.1 mg/L) using a Zetasizer Nano ZS analyzer (Malvern Instruments, Great

Britain). The measurements were performed in a U-shaped cell with gold-plated electrodes at 25°C and pH ~7.4 in ultrapure water obtained from a Milli-Q purifier system (Millipore Corp., Bedford, MA USA). Because of the ZnO solubility, the particles are unstable at high and low pH values, so different pH solutions were not tested.^{1,2} Also, the main purpose of this measurement was to observe and compare the surface potential of the samples in a pH value near to the applied in the photocatalytic tests. The morphologies of the samples were verified by field emission scanning electron microscopy (FESEM) using a JSM 6701 F microscope (JEOL) operated at 5 kV. The specific surface area of the materials was obtained using nitrogen physisorption at 77 K (ASAP-2020, Micromeritics) and applying the data in the BET model. Before the analyses, the samples were degassed by heating at 70°C under vacuum until reaching a pressure of less than 20 mmHg.

RESULTS AND DISCUSSIONS

XRD measures were conducted on ZnO samples calcinated under 200, 300, 400, and 500 °C temperature (Figure S1). It is possible to observe that the sample calcinated under 200 °C presented lower peaks intensity. No significant variations are shown among the samples calcinated under 300 °C to 500 °C.

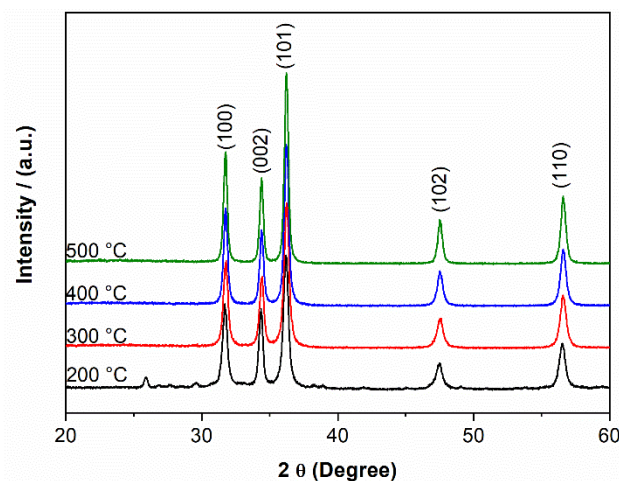


Figure S1: XRD of samples calcinated under 200, 300, 400, and 500°C.

The photocatalytic performance of ZnO samples with calcination temperatures of 200, 300, 400, and 500 °C was evaluated for Methylene Blue (MB) and Rhodamine B (RhB) dyes degradation, the results can be seen in the Figure S2. The study confirms that the sample calcinated under 300 °C shows superior photodegradation efficiency than samples calcinated under higher temperatures. Although the sample calcinated under 200 °C presented comparable results, TG-DTG data shows thermic variations occurring below 300 °C, disqualifying the sample for further studies.

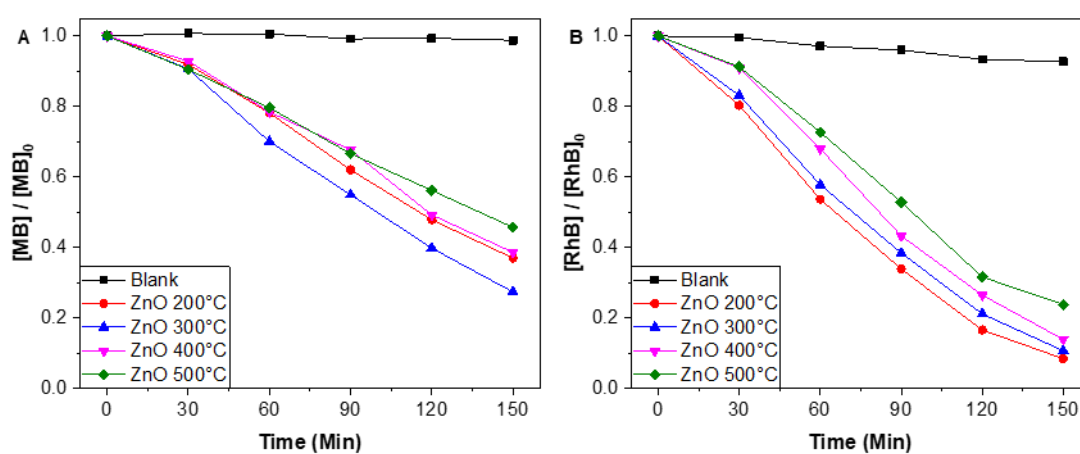


Figure S2: Removal of dye: Methylene Blue 5 mg L⁻¹ (A) and Rhodamine B 2,5 mg L⁻¹ (B); with different calcination temperatures.

DSC information was also collected to observe thermal events occurring in the studied temperature conditions. Figure S3 exhibits the heat flow of the precursor sample heated under 300 °C per 2hours after the ramp stabilization. In the graph, we can observe an exothermic event ending at 300 °C. After that, no changes are perceived. Therefore, we can state that no other phase transformation events took place in the samples annealed at 300 °C, which means that all the Zn(OH)₂ were transformed into ZnO, in accordance with XRD and Raman spectroscopy.

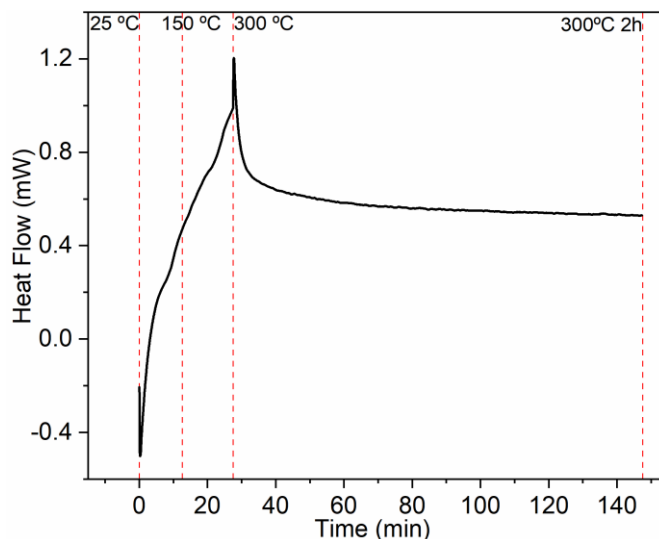


Figure S3: DSC spectrum of precursor sample in a ramp from 25 to 300 °C followed by 2 hours temperature stabilization.

NIR spectroscopy was conducted to confirm the presence of the hydroxyl groups on the solid surface, the results are presented in Figure S4. NIR spectrum exhibits bands at 4461 and 7112 cm^{-1} assigned to hydroxyl groups and a band at 5188 cm^{-1} corresponding to the presence of water molecules. Accordingly, the samples showed a similar tendency compared to FTIR regarding the occurrence of OH groups onto the surface.

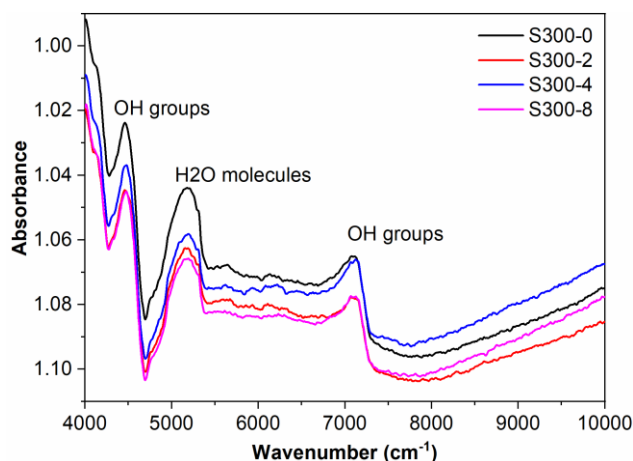


Figure S4: NIR spectra of the samples annealed at 300 °C.

The photocatalytic reaction kinetic of MB and RhB degradation followed the model:

$$r = -\frac{dC}{dt} = k \cdot \text{SSA} \cdot [C] \quad (\text{Equation S1})$$

where r is the degradation rate of reactant, k is the rate constant, SSA the specific surface area from SSA analysis, and $[C]$ is the dye concentration in a given time. Since there is no solubilization, we can suppose that SSA remains constant in time during photocatalysis. Therefore, we can assume $k' = k \cdot \text{SSA}$. Therefore, equation S1 can be linearized as follow:

$$\ln\left(\frac{C}{C_0}\right) = -k't \quad (\text{Equation S2})$$

where C_0 is the initial reactant concentration and t is the time reaction. The pseudo-first-order kinetic of dyes degradation within 120 minutes can be found in Figure S5.

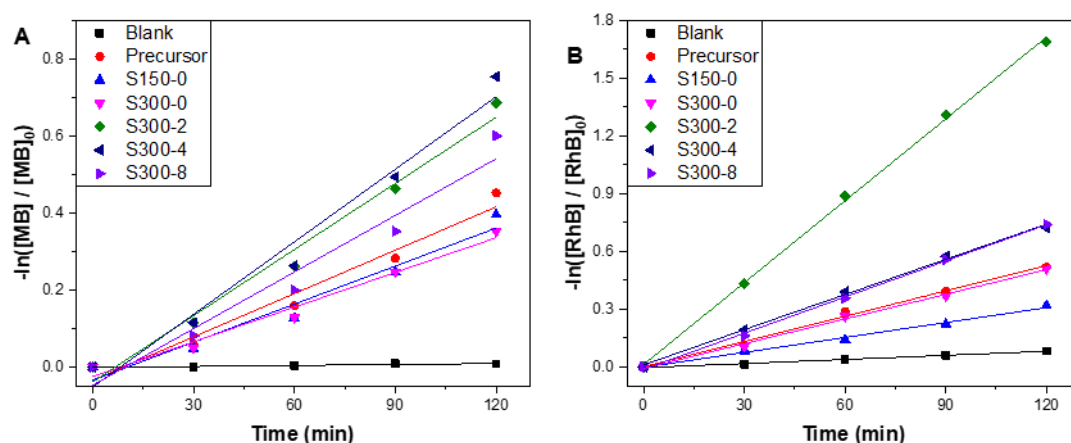


Figure S5: Pseudo-first-order kinetic of dyes degradation within 120 minutes time variation for Methylene Blue 10 mg L⁻¹ (A), and Rhodamine B 5 mg L⁻¹ (B).

Figure S6 presents the chemical structure of the dye studied in this work. As can be seen, MB allows the positive charge to be dislocated over the N and S atoms. On the other hand, in RhB molecule the positive charge is strictly located over the N atom.

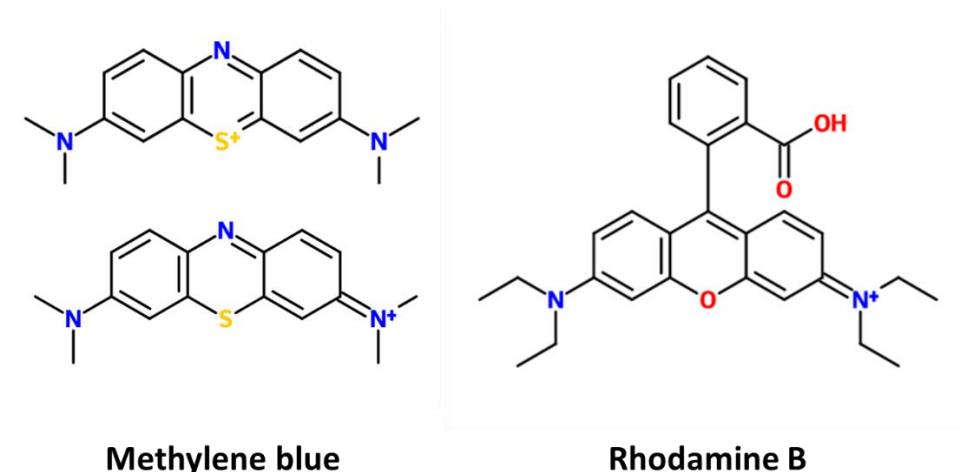


Figure S6: Methylene blue and rhodamine b dyes structures and its charge resonance.

Another approach used to verify the photocatalytic process was to track the OH radicals formed after UV incidence by applying the reaction of such radicals with terephthalic acid (TPA). The radicals produced by the samples react with TPA producing 2-hydroxyterephthalic acid, which is photoluminescent at 425 nm when excited at 315 nm. Figure S4B displays the spectrum obtained by fluorescence spectroscopy after 3 hours under UV incidence. It is shown that all the annealed samples were able to produce OH radicals. However, the sample annealed per 2 h showed a less intense spectrum. It occurred due to the polyhydroxylation of TPA, yielding in a non-luminescent compound. Therefore, it is shown that, in accordance with photocatalytic experiments, the samples showed different radicals generation capability.

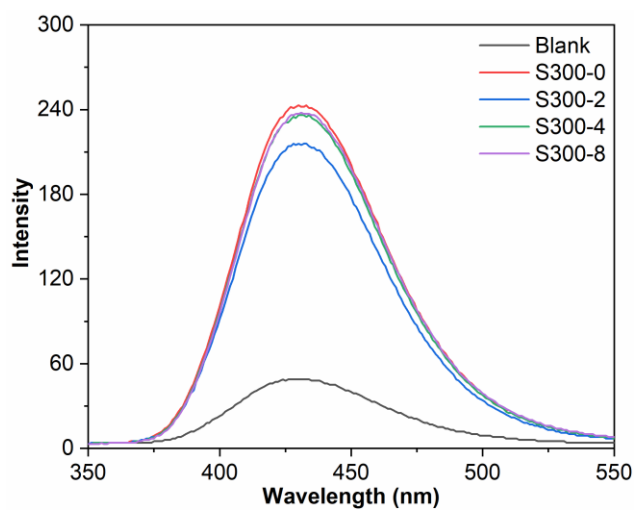


Figure S7: Fluorescence spectroscopy of 2-hydroxyterephthalic acid formed by the reaction between OH radicals generated on the ZnO surface and TPA.

References

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