

Shape-control of Zinc Oxide nanoparticles: enhancing photocatalytic activity under UV irradiation

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Abstract: Zinc oxide (ZnO) nanostructures with different sizes and morphologies were synthesized using the Controlled Precipitation Method. It follows a standard process, but with different synthesis and washing solvents to modify the features related to the photocatalytic activity. The solid phase evolution during aging step was followed using Infrared Spectroscopy (FTIR) and the solids obtained, after the washing process, were characterized using X-ray diffraction (XRD). The Rietveld refinement indicates a Wurtzite phase (space group P6₃mc) as majority phase with lattice parameters $a = 3.2530 \text{ \AA}$ and $c = 5.2125 \text{ \AA}$. Scanning electron microscopy (SEM) image shows a sponge-like morphology for the sample synthesized with ethylene glycol as solvent, acidified with nitric acid and washed with water. The sample synthesized and washed with water shows a needle-like morphology; and the sample synthesized in acetic acid and washed with water shows particles with undefined morphology. The optical properties of the as-prepared ZnO samples were investigated by UV-vis absorption spectroscopy. Finally, the photocatalytic activity of ZnO powders was studied from the initial rate of decomposition of H₂O₂ in aqueous solution. The best results were obtained with samples synthesized and washed with water; the influence of all the solvents on the morphology of ZnO samples and the effect of the morphologies on the photocatalytic activity are discussed.

1. Introduction.

Zinc oxide semiconductor, a wide direct band gap (3.37 eV) with large excitation binding energy (60 meV), is an excellent material with multifunctional properties and applications in electronics, photoelectronics, sensors and photocatalysts [1-2]. The optical and electronic properties of ZnO particles can be modulated by changing their size and morphology. Then, the control over these properties will represent a great challenge to realize novel functional devices. Up to now, a large quantity of ZnO nano and microstructures with various specific shapes have been successfully synthesized by different techniques; chemical methods such as: sol-gel, hydrothermal, precursor polymeric (Pechinni) and controlled precipitation [3-4] and physical methods such as: thermal evaporation, chemical vapor deposition (CVD), and molecular beam epitaxy (MBE). Specifically, N. Morales et al. [5], fabricated ZnO nanostructures with different morphologies through ultrasound-assisted hydrolysis of zinc acetate at room temperature. They study the effects of morphology and other parameters like specific surface area, defect content, and surface contamination on photocatalytic activity, using methylene blue (MB) degradation under UV light, evidencing that all the above mentioned parameters seen to affect the photocatalytic performance of ZnO nanostructures. Linping Xu et al. synthesized ZnO materials with different morphologies via solvothermal method, with different solvents, exhibiting different activities to phenoldegradation. They indicate that there was no



correlation between the surface areas and the catalytic activity data for the studied samples suggesting that there are other more important factors that govern the photocatalytic activity, such as crystal habits [6].

In this work, ZnO particles were synthesized by the controlled precipitation method using zinc acetate and different synthesis and washing solvents. The powder obtained was washed (or chemically attacked) to modify and control the initial features such as morphology, particle size and surface area in order to study and improve the photocatalytic activity of ZnO structures.

2. Experimental

2.1 Materials

Zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COOH})_2$) (ACS reagent $\geq 98\%$, Sigma Aldrich), acetic acid (ACS reagent $\geq 99.7\%$, Sigma Aldrich), Ethylene glycol (anhydrous $\geq 99.8\%$, Sigma-Aldrich), nitric acid (ACS 70%, Sigma-Aldrich), and ammonium hydroxide solution (28-30% NH_3 basis, Sigma-Aldrich) were commercially available and used as received. Deionized water (18.2 $\text{M}\Omega\cdot\text{cm}$) was obtained from a Milli-Q water purification system (Millipore, Billerica, MA, USA)

2.2. Synthesis

ZnO nanoparticles were synthesized by the controlled precipitation method (controlled precipitation method: formation mechanics of ZnO nanoparticles), for this purpose, zinc acetate was dissolved in different solvents: 200 mL of water, ethylene glycol acidified with nitric acid and acetic acid in a concentration of 0.3M. The mixture was stirred for 20 minutes until reach a completely transparent solution. Then the NH_4OH solution was added at a rate of 1ml/min, in constant stirring, until the previously determinate pH value with the titration curve; pH 8.8 for the sample synthesized with water, pH 9.0 for the sample synthesized with ethylene glycol acidified with nitric acid and pH 7.0 for the sample synthesized with acetic acid.

The wet solid obtained was washed (or chemically attacked). In this process was used 100 mL of water and re-dispersed using a high shear equipment (Ultraturrax-T50) for 10 minutes at 10000 rpm, then the system was allowed to stand for 24 hours and proceeded to remove the liquid phase by decanting. This process was repeated by four times. After the fourth wash, the liquid phase was removed and the solid dried at a temperature of 100 °C. The resulting product was macerated in an agate mortar until a fine powder which was subjected for 2 hours heat treatment at temperature of 300 °C, respectively, using an oven (Termolyne).

3. Results and Discussion

XRD was used to investigate the crystalline structure of the as-prepared ZnO particles, as shown in Figure 1(a). From the XRD patterns, it has been observed that the ZnO structures exhibit single-phase Wurtzite structure with average crystallite size of about 7, 36 and 16 nm for the sample synthesized with ethylene glycol acidified with nitric acid, water and acetic acid, respectively. The average crystallite size has been calculated using the Scherrer formula. Figure 1(b) shows FTIR spectra of ZnO samples within 400–4000 cm^{-1} . These results revealed that the peak at 3437 cm^{-1} comes from the stretching mode vibrations of OH, while the peak at 1639 cm^{-1} is attributed to the bending vibrations of adsorbed H_2O molecules. The small peak at 1397 cm^{-1} is due to asymmetric stretching modes COO^- which probably comes from the residues of preparation processes. It indicates the presence of small amount of organic residues absorbed on the surface of nanoparticles in the samples, especially in the synthesized with ethylene glycol with nitric acid. The strong peak at 525 and 463 cm^{-1} can be ascribed to the vibration of Zn–O bond as shown in the literature (J.E. Rodriguez – Páez, 2001) [7-8]. The displacement of these absorption bands can be justified based on the morphology of the particles.

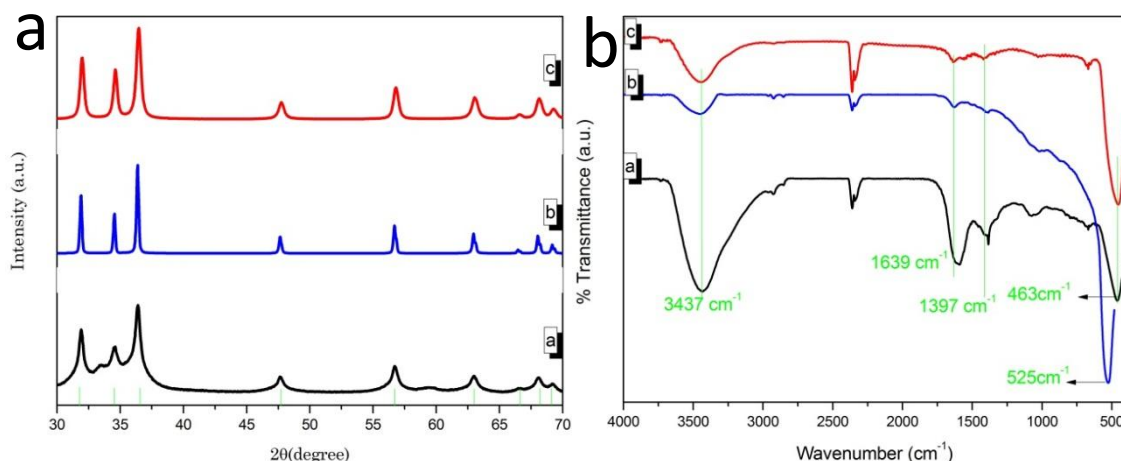


Figure 1. XRD and FTIR patterns of the as-prepared samples; (a) ethylene glycol acidified with nitric acid, (b) water and (c) acetic acid.

The optical characterization of the samples was recorded on UV-Vis absorption spectrophotometer. Figure 2(a) shows the UV-Visible absorption spectra of ZnO particles as a function of wavelength. The presence of a single slope in the plot suggests that the nanoparticles have direct and allowed transition for the sample synthesized with water and acetic acid, attributed to the band edge absorption of wurtzite hexagonal ZnO; it is clearly seen that the absorbance decreases with an increase in wavelength, and a sharp decrease in absorbance near the band edge (390 nm) indicating the better crystallinity of the samples.

Energy band gap studies of these materials have been reported using Tauc plot, this intrinsic band gap is given as the intercept with the energy axis of a linear fit to the square of the absorption data in a energy interval slightly above the band gap, where the data is linear. An illustration of this procedure is shown in figure 2(b). The band gap values of ZnO are 3.19 eV for the samples synthesised with water and acetic acid and 2.72 eV for the sample synthesized with ethylene glycol.

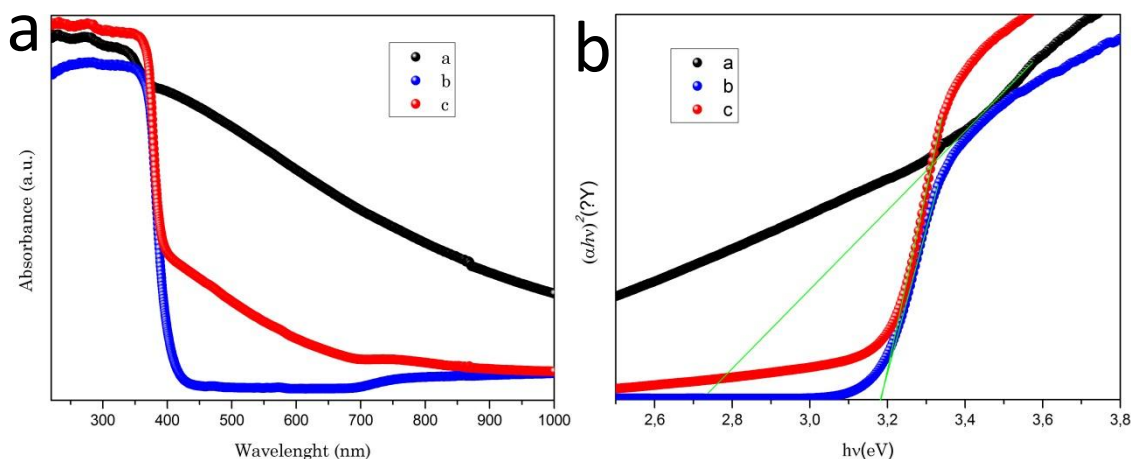


Figure 2. UV-visible spectra of as-synthesized ZnO samples at different synthesis solvents; (a) ethylene glycol acidified with nitric acid, (b) water and (c) acetic acid.

The morphology of samples was examined by Scanning electron microscopy (SEM) and Transmission Electronic Microscopy (TEM) as shown in Figure 3.

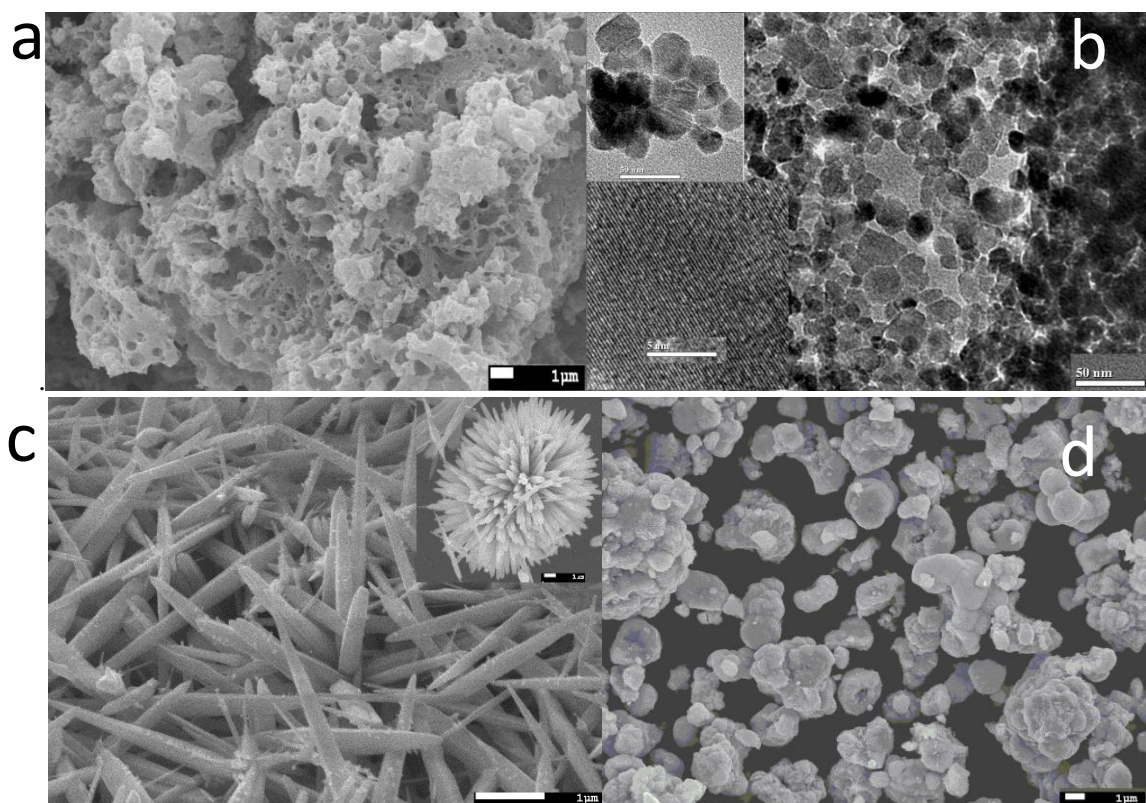


Figure 3. SEM and TEM images of as-synthesized ZnO samples at different synthesis solvents; (a,b) ethylene glycol acidified with nitric acid, (c) water and (d) acetic acid.

SEM images show a sponge-like morphology for the sample synthesized with ethylene glycol solvent, acidified with nitric acid and washed with water (Figure 3a). It composed of primary particles of nanometric sizes that make up the secondary particle sponge (Figure 3b). The sample synthesized and washed with water shows a nanoneedles morphology (Figure 3c), with hexagonal cross section, forming nanoflowers and the sample synthesized in acetic acid and washed with water shows particles with undefined morphology (Figure 3d). The morphology of ZnO particles would be governed by the balance of the nucleation and crystal growth determined by the reaction route. Experimental data show that the variation of the synthesis conditions significantly affects the specific surface area (BET) and pore size distribution as shown in Figure 4a. According to the IUPAC classification, the hysteresis loops observed in samples synthesized with ethylene glycol acidified with nitric acid and the sample synthesized with and washing with water can be attributed to H3-type mesoporous material and isotherm of the sample synthesized with water corresponds to a microporous solid.

The catalytic and photocatalytic activities of ZnO samples were studied from the initial rate of decomposition of H_2O_2 in aqueous solution. The kinetic study was followed by the production of O_2 via gas pressure monitoring (O_2 – monitored method [9], under UV-visible light irradiation ($\lambda \geq 400$ nm), at 20 °C. Experimental data showed that the rate of H_2O_2 decomposition, under ultraviolet visible light irradiation, obeys the first order kinetic law. Under visible light irradiation the H_2O_2 decomposition rate achieved a maximal value of 9.5 mmol g⁻¹ s⁻¹ for ZnO2 sample, 5.8 mmol g⁻¹ s⁻¹ for sample ZnO3 and 3.74 mmol g⁻¹ s⁻¹ for sample ZnO1.

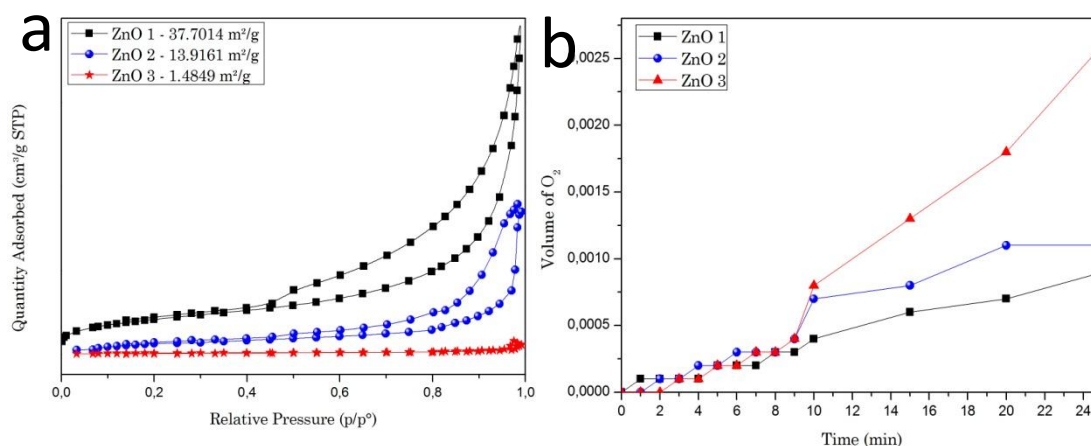


Figure 4. (a) Typical N₂ adsorption–desorption isotherms for ZnO nanostructures, (b) Photodecomposition of H₂O₂ catalyzed by ZnO compounds.

These results show that nanoparticles with well-defined morphology exhibit large activity in the photocatalytic photo-decomposition of H₂O₂ (Figure 4b) regardless of specific surface area. This indicates that a high surface reactivity of ZnO samples is not necessarily related to a high surface area. It seems that the abundance of specific sites, which strongly depends on the preparation route, is the most important feature for the active of the ZnO. Results indicate that ZnO nanoflowers showed significantly higher photocatalytic activity than others ZnO samples. The photocatalytic activities were found to be associated with their content of oxygen vacancy. The catalytic activity is related to defects created in the structure which allow a greater or lesser degree of vacancies affecting the electron-hole pair recombination. Additional measurements and studies are being developed in order to understand better the photocatalytic activity of these samples.

4. Conclusion

ZnO samples with diverse sizes and morphologies were prepared by the controlled precipitation method using different solvents and modifying the washing process. Comparing the photochemical test with the morphology and surface area results, it seems that the abundance of specific sites, directly related to the morphology of ZnO samples which strongly depends on the preparation route, is the most important feature for the active of the ZnO.

5. Acknowledgments

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6. References

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