Microwave-Assisted Synthesis and Characterization of Ag–ZnO Core–Shell Nanostructures for Antimicrobial Biomedical Applications

Miriam Roldán Matilla[1], Silvia Pérez Pérez [2], María Fuencisla Gilsanz[2], Javier Pérez-Piñeiro[2], Isabel Lado-Touriño[3*], Arisbel Cerpa-Naranjo[3*]

[1]Professional Formation Centre. European University of Madrid, Villaviciosa de Odón, Madrid, Spain.
[2]Department of Science, Architecture, Engineering and Design Faculty. European University, Villaviciosa de Odón, Madrid, Spain.
[3]Department of Engineering. Architecture, Engineering and Design Faculty. European University, Villaviciosa de Odón, Madrid, Spain.

miriam.roldan@universidadeuropea.es

Core–shell Ag–ZnO nanostructures integrate the plasmonic and antibacterial behaviour of silver (Ag) with the semiconducting and biocompatible properties of zinc oxide (ZnO), forming hybrid systems of great interest in nanobiomedicine due to their antimicrobial, photocatalytic, and biosensing potential [1]. The combination of both components generates a synergistic multimodal action, based on the release of Ag^+ ions, the generation of reactive oxygen species (ROS) under ZnO excitation, and the photoinduced damage to bacterial cellular structures [2]. However, obtaining these nanostructures with controlled morphology, high crystallinity, and good colloidal stability remains a key challenge for their biomedical development [3].

In this work, two complementary synthesis routes were optimized for the preparation of Ag–ZnO nanocomposites, differing in the method of core formation: a hydrothermal route [4], where a silver core coated with carbon (Ag-C) was produced via glucose reduction at 160 °C, and a chemical reduction route [5], based on the reduction of $AgNO_3$ in the presence of CTAB, ascorbic acid (AA), and NaOH. In both approaches, the formation of the ZnO shell was carried out by controlled precipitation ($Zn(NO_3)_2$/HMT), incorporating microwave-assisted heating as an alternative to conventional thermal treatment (85–86 °C, 8 h).

Microwave processing (120 °C, 28 min, magnetic stirring) accelerated the homogeneous hydrolysis of HMT, responsible for the gradual release of OH^-, and promoted the heterogeneous nucleation of $Zn(OH)_2$/ZnO directly on the core surface. This modification drastically reduced the reaction time, prevented the formation of free ZnO particles in the bulk solution, and improved the uniformity, adhesion, and thickness of the coating. In both routes, the resulting products were subsequently washed and calcined at 500 °C for 2 h, a process that removed organic residues (CTAB, AA, carbon) and promoted ZnO crystallization in the wurtzite phase, as well as the development of surface porosity in the shell layer.

Structural and morphological characterization by SEM and TEM, complemented by EDX mapping and selected area electron diffraction (SAED), confirmed the formation of the core–shell architecture, revealing a metallic Ag core coated with a polycrystalline ZnO shell. The hydrodynamic radius and colloidal stability were determined by dynamic light scattering (DLS) and zeta potential measurements. Additionally, zeta potential measurements as a function of pH were performed to determine the isoelectric point (pI) and to correlate colloidal stability with surface charge distribution and its influence on electrostatic interactions with biomolecules and cell membranes under different physiological conditions [6].

UV–Visible spectroscopy revealed two main absorption bands: one around 430 nm, attributed to the localized surface plasmon resonance (LSPR) of silver, and another near 370 nm, corresponding to the ZnO band-edge transition ($E_9 \approx 3.3$ eV), confirming the plasmon–semiconductor optical coupling characteristic of these hybrid nanostructures. To correlate the photophysical properties with the potential antimicrobial activity of the nanocomposite, photoluminescence (PL) and photoluminescence excitation (PLE) measurements were performed. PL spectra were used to identify the emissive centers associated with ZnO defects and the Ag/ZnO interface, and to analyze the radiative recombination processes and the dynamics of electron–hole (e^-/h^+) pair separation. PLE spectra, in turn, were used to determine the optical absorption energies and evaluate the plasmon–semiconductor coupling, evidencing the energy transfer between silver and ZnO that promotes the generation of ROS involved in the antimicrobial mechanism [7].

Overall, the microwave-assisted synthesis emerges as a reproducible, efficient, and potentially scalable strategy for producing core–shell Ag–ZnO nanostructures with high crystallinity, porosity, and stability, exhibiting optical, photocatalytic, and interfacial properties that support their great potential as antimicrobial systems and functional platforms for advanced biomedical applications.

References

[1] K. Chatterjee, S. Sarkar, K. Jagajjanani Rao, and S. Paria, *Adv Colloid Interface Sci*, vol. 209, pp. 8–39, Jul. 2014.

[2] S. Anjum, K. Nawaz, B. Ahmad, C. Hano, and B. H. Abbasi, *RSC Adv*, vol. 12, no. 37, pp. 23845–23859, 2022.

[3] M. Laurenti, S. Stassi, G. Canavese, and V. Cauda, *Adv Mater Interfaces*, vol. 4, no. 2, Jan. 2017.

[4] W. Han, W. Wang, J. Fan, R. Jia, X. Yang, T. Wu, and Q. Wu, *Green Energy & Environment*, vol. 9, no. 2, pp. 366–377, Feb. 2024.

[5] A. N. Kadam, D. P. Bhopate, V. V. Kondalkar, S. M. Majhi, C. D. Bathula, A.-V. Tran, and S.-W. Lee, *Journal of Industrial and Engineering Chemistry*, vol. 61, pp. 78–86, May 2018.

[6] X. Wang, T. Sun, H. Zhu, T. Han, J. Wang, and H. Dai, *J Environ Manage*, vol. 267, p. 110656, Aug. 2020.

[7] S. Seong, I.-S. Park, Y. C. Jung, T. Lee, S. Y. Kim, J. S. Park, J.-H. Ko, and J. Ahn, *Mater Des*, vol. 177, p. 107831, Sep. 2019.

Figures

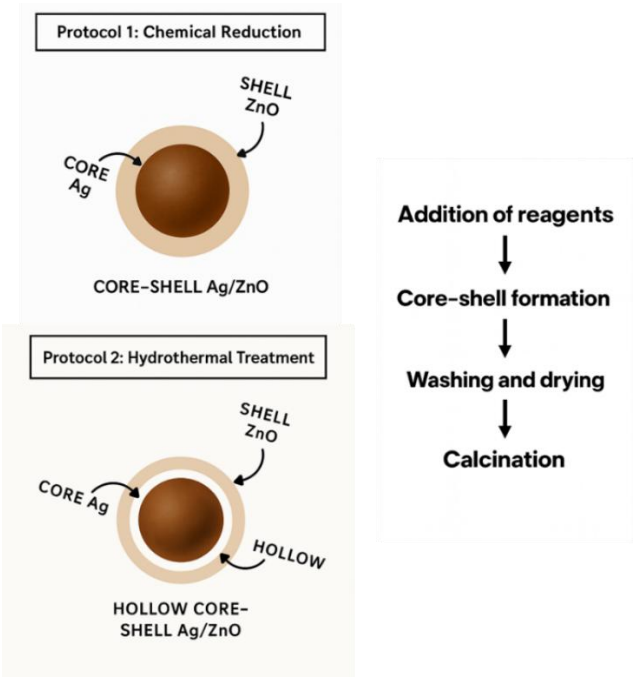

Figure 1. Schematic representation of two synthesis routes for Ag–ZnO core–shell nanostructures: compact structures from chemical reduction and hollow ones from hydrothermal treatment.

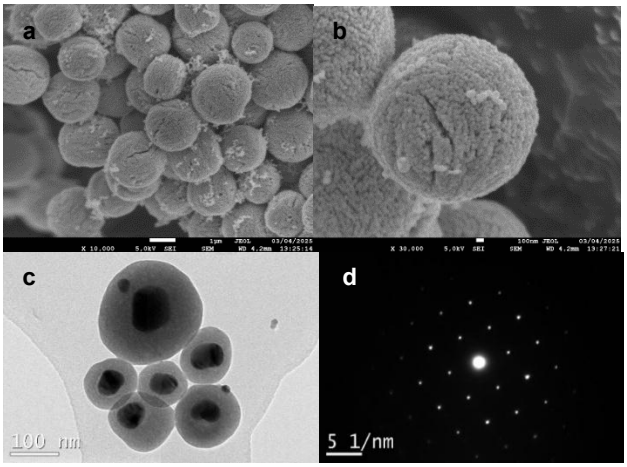

Figure 2. (a,b) SEM images of the ZnO core–shell nanostructure. (c) TEM images of the ZnO core–shell nanostructure. (d) Diffraction pattern showing sharp rings characteristic of the FCC structure of silver in the Ag-C sample.