

Characterization of TiO₂ and ZnO nanoparticles and films generated by pulsed laser ablation: Application in photocatalysis of microplastics

Patricia Martínez-García^{1,2}, Carlos García-Arcos^{1,2}, Mikel Sanz^{1,2}, Rebeca de Nalda³, Esther Rebollar^{3*}, Oscar Gálvez^{1,2}

¹ Universidad Nacional de Educación a Distancia (UNED). Dept. Física Interdisciplinar, Fac. Ciencias Av. de Esparta s/n, 28232, Las Rozas, Madrid, Spain

² NANOesMAT, UNED, Unidad Asociada al CSIC por el IEM y el IQF, Av. de Esparta s/n, 28232, Las Rozas, Madrid, Spain

³ Instituto de Química Física Blas Cabrera (IQF-CSIC), Serrano 119, 28006 Madrid, Spain

*Corresponding author email: e.rebollar@csic.es

Pulsed laser technology, using techniques such as pulsed laser ablation in liquids (PLAL) and pulsed laser deposition (PLD), offers a green and versatile approach to produce nanoparticles (NPs) and thin films with tailored properties [1,2]. In this study, we used PLAL and PLD to fabricate titanium and zinc oxides NPs and thin films, and metal-doped samples with Pt and Au. For PLAL, a Q-switched Nd:YAG laser (Quantel Brilliant B) at 532 or 1064 nm with pulse duration (τ) of 4 ns and a repetition rate of 10 Hz was used to ablate metal targets (Ti or Zn). For PLD, a Q-switched Nd:YAG laser (LOTIS TII LS2147) at 532 nm, $\tau=15$ ns, repetition rate 10 Hz was used to ablate Ti, TiO₂, Zn and ZnO targets. Different laser fluences in the range 0.1–10 J/cm² were applied. NPs synthesis was conducted in different liquids (water, methanol, ethanol, isopropanol and ethylene glycol), with different thermal conductivities, viscosities, and chemical properties. Thin films were deposited by PLD at temperatures ranging from 25 to 780 °C. Comprehensive characterization of the NPs (Raman/IR, TEM, AFM, UV-Vis, DLS and X-Ray) and thin films (Raman/IR, AFM, SEM, and X-Ray) was performed to assess the impact of liquid environment, laser parameters, and deposition temperature on morphology, size, crystallinity and composition. Results indicate varying NP production rates and sizes depending on the liquid medium and laser wavelength, while thin films exhibit differing morphologies, crystallization degrees, and roughness influenced by both laser parameters and deposition temperature.

The final aim of this study is to assess the photoactivity of the synthesized NPs and films in degrading microplastics [3]. Thin films of polystyrene or polyethylene (approx. 1 μ m thick) were spin-coated onto infrared-transparent silicon substrate coated with TiO₂ and ZnO NPs and films. The plastics were exposed to solar lamp (Newport: Mercury-Xenon, 1000 W, Ozone free and equipped by an AM 1.5 global filter) irradiation for photolysis, and monitored primarily by FTIR spectroscopy. Initial findings suggest doped TiO₂ and ZnO samples are essential for significant microplastics photolysis, potentially due to enhanced light absorption.

Acknowledgements: The authors would like to thank the project TED2021-131914B-I00 funded by MCIN/AEI/10.13039/501100011033 and "ERDF A way of making Europe" and J.P. Sánchez for the technical assistance.

References: [1] M. Oujja, K. Tabakkouht, M. Sanz, E. Rebollar, M. Sánchez-Arenillas, et al, Appl. Phys. A128 (2022) 375; [2] D.E. Martínez-Tong, M. Sanz, T.A. Ezquerra, A. Nogales, J.F. Marco, et al., Appl. Surf. Sci. 418 (2017) 522-529; [3] I. Nabi, A.U.R. Bacha, K. Li, H. Cheng, T. Wang, et al., iScience 23 (2020) 101326