Poster Presentation

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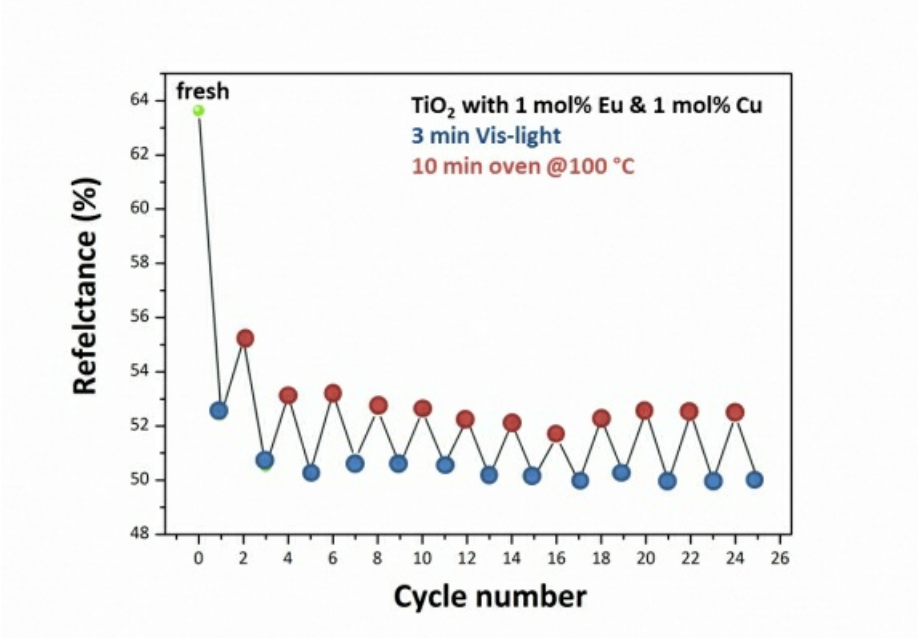
Copper and rare earths TiO_2 nano-heterostructure as a bifunctional material

Maria Paula Seabra[1], David Maria Tobaldi[1], Rute A. S. Ferreira[2], Luís D. Carlos[2], João A. Labrincha[1]
[1]*Department Of Materials And Ceramic Engineering/CICECO-Aveiro Institute Of Mater, Aveiro, Portugal,* [2]*Physics Department and CICECO-Aveiro Institute of Materials, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal, Aveiro, Portugal*
E-mail: pseabra@ua.pt

Titanium dioxide (TiO2) nanomaterials are attracting increasing interest, mostly because of their superior photocatalytic and antibacterial properties, as well as their use for solar cells and energy materials. We previously reported that copper modification gave the first ever purely inorganic nanoparticles (10 nm diameter) to show photochromism under UV and visible light irradiation [1]. Furthermore, we have also shown that doping of TiO2 with rare earths (RE), in particular Nd–TiO2, gave a multifunctional material, having photocatalytic activity and NIR photoluminescence emission induced by the same excitation UV source – the first result of its kind [2]. In this work, we report the synthesis, by a "green" aqueous sol–gel route, of nano-TiO2 modified with copper (1, 2, and 5 mol%), and doped with Eu and Nd (1, 2, and 5 mol%), in order to achieve a bifunctional photochromic/photoluminescent material. The products of the synthesis were fired at 450 °C / 2h, and their mineralogical composition was revealed via semi-quantitative phase analysis (QPA) using the Rietveld method on the XRPD data. Microstructural features of the produced nanopowders were also evaluated by means of XRPD, with the novel yet state-of-the-art whole powder pattern modelling (WPPM). Photochromism was thoroughly investigated via diffuse reflectance spectroscopy (DRS), whilst the photoluminescence (PL) spectra were recorded in the UV-Vis and NIR spectral ranges with a modular double grating excitation spectrofluorimeter. XRPD QPA showed that the addition of Cu and RE greatly delayed the anatase-to-rutile phase transition; from unit cell parameters, RE seemed to enter the TiO2 lattice, while copper clustered around TiO2 NPs. XRPD WPPM microstructural data revealed that addition of Cu and RE greatly retarded anatase's crystal growth, and also narrower size distributions compared to the unmodified TiO2. As per the functional properties, all the specimens were shown to be photochromic, their colour changed from pale green to dark brown upon visible-light irradiation (a lamp having irradiance in the visible equal to 50 W m–2, and nil in the UVA was used). Furthermore, with the addition of REs, especially for 1 mol% addition, that photochromic effect was greatly reduced, if compared with that experienced using copper only, most likely because of up-conversion effects. Moreover, the photochromic effect of the specimens was also shown to be reversible, and switchable, by simply storing them in a dark oven at 100 °C, and then re-irradiating them. From PL spectra, specimens also showed emission in the visible and NIR spectral regions, this likely having a role in their enhanced photochromic property.

[1] Tobaldi, D.M., Rozman, N., Leoni, M., Seabra, M.P., Škapin, A.S., Pullar, R.C. & Labrincha, J.A. (2015). J. Phys. Chem. C. 119, 23658–23668.
[2] Tobaldi, D.M., Ferreira, R.A.S., Pullar, R.C., Seabra, M.P., Carlos, L.D. & Labrincha, J.A. (2015). J. Mater. Chem. C. 3, 4970–4986.



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