Supporting Information

Photocatalytic production of vanillin over CeO_x and ZrO_2 modified biomass-templated titania

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Abstract

Walnut shell residues have been used as sacrificial template in the synthesis of TiO_2-based materials, via mechanochemical synthesis. In order to improve the photocatalytic efficiency of the synthesized titania, functionalization with cerium and zirconium was also investigated. The samples were characterized using a multitechnique approach, including XRD, XPS, UV-visible spectroscopy and SEM. The synthesized materials have been used as catalysts in the photooxidation reaction of vanillyl alcohol towards vanillin, a compound of great interest due to its organoleptic properties. Such photocatalytic experiments were carried out in a batch-type photoreactor using a LED 12 V efficient emission lamp with a wavelength of 395 nm. The results pointed out that the use of walnut shell allows obtaining nanostructured materials based. The incorporation of Ce and Zr in the titania surface gave rise to an increased absorption of visible light, together with the improvement of electronic properties, therefore enhancing photocatalytic efficiency in comparison with pure TiO_2. The best catalytic behavior was observed for (1-5)Ce/TiO_2-BS and 5Zr/TiO_2-BS samples, with a maximum conversion of 39.7% and 52.4% for cerium and zirconium modified samples, respectively. Selectivity values of 99% towards vanillin and carbon balance of 98% were achieved in all the cases.

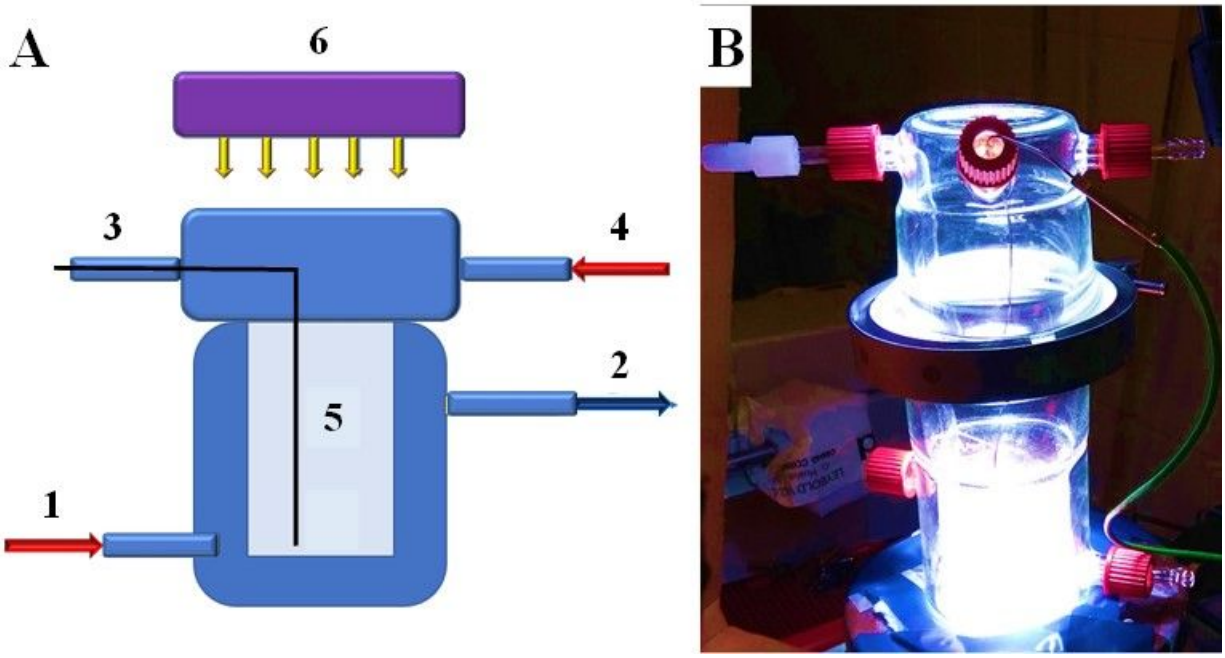

Figure S1. A. Schematic representation of the photoreactor setup. 1. Cooling water inlet; 2. Cooling water outlet; 3. Air entry; 4. Syringe entry (sampling); 5. Reaction tank; 6. LEDs lamp, B. Photoreactor image.

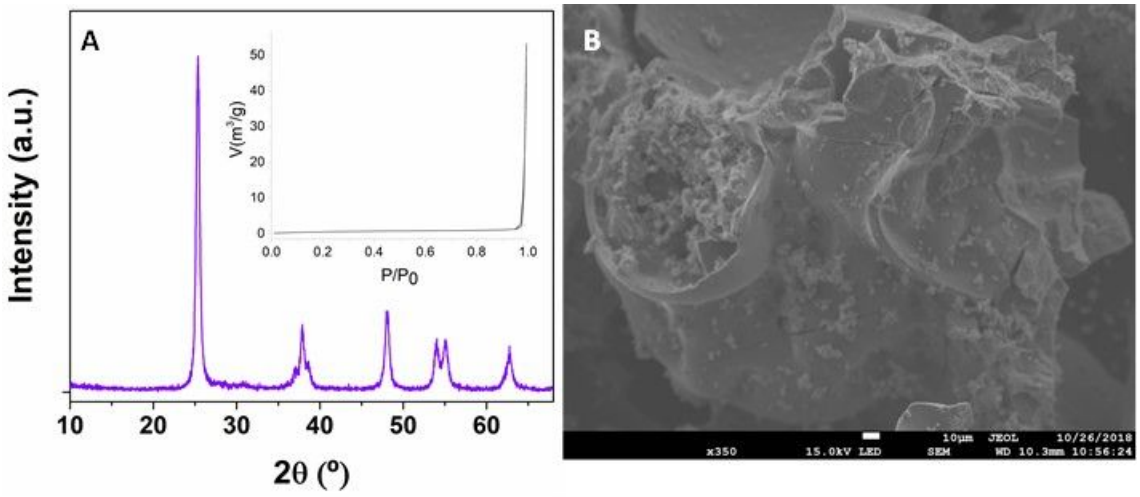

Figure S2. A. XRD pattern (Inset: N_2-physisorption isotherm) and **B.** SEM image of TiO_2 sample, prepared in absence of walnut shell as sacrificial template.

N_2-physisorption measurements of the obtained titania, by performing the same experimental procedure in absence of the walnut shell, displayed low surface area (< 5 m^2g^{-1}), which in turn prevent the efficient cerium or zirconium deposition and therefore affect the catalytic performance. In addition, the crystallinity of the obtained material was studied by XRD analysis, displaying the presence of anatase.

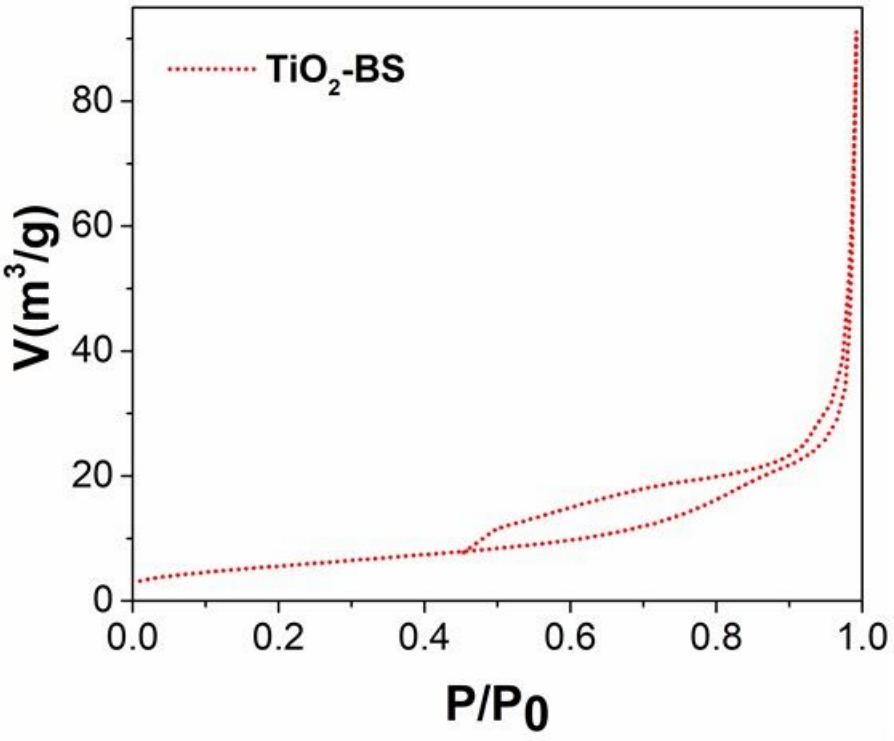

Figure S3. N_2 adsorption-desorption isotherms of TiO_2-BS.