



## Synthesis of Nano-Sil1/TiO<sub>2</sub>NTs Composite photocatalyst

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### Significance and Relevance

In this work, we report the preparation of a ZSM-5/TiO<sub>2</sub>NTs composite obtained using an innovative synthesis approach in which nanocrystals of Silicalite-1 zeolite were growth directly on TiO<sub>2</sub> nanotubes<sup>1</sup> by modified Steam Assisted Crystallisation (SAC)<sup>2</sup>, leading to the incorporation of the zeolite inside the titania nanotube's structure. The resulting material was denoted as nano-Sil1/TiO<sub>2</sub>NTs.

The synthesized material represents a promising new heterogeneous catalyst in which selectivity can be modulated by modifying the properties of the nanozeolite confined in a well-ordered structure having a controlled geometry, like titania nanotubes.

- *Preferred and 2<sup>nd</sup> choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization / Green chemistry and biomass transformation, renewable resources conversion / Water treatment*

*Preferred presentation: Short Oral*

### Introduction and Motivations

TiO<sub>2</sub> in its anatase form is one of the most widely used photocatalytic active material, due to its high stability and low cost. In this approach, typically anatase nanocrystallites in tubular form are decorated with zeolites. The potential advantage of using TiO<sub>2</sub> nanotubes as a substrate for zeolites is that a very defined geometry for the photocatalytic decomposition can be established.<sup>3</sup> The aim is to combine the excellent photocatalytic functionality of the TiO<sub>2</sub> nanotubes with the selective capturing ability of zeolites to produce a new generation of 'trapping' photocatalyst. The resulting composite coupling the photocatalyst properties of titania with the decomposition ability for organics of zeolites can be used for traditional purpose like pollutant removal from wastewater or for the abatement of VOCs in gaseous effluents<sup>4</sup> thanks to the outstanding adsorbent capability of zeolite, but also for reactions of industrial interest (biomass conversion) exploiting the specific nature of the zeolite counterpart.

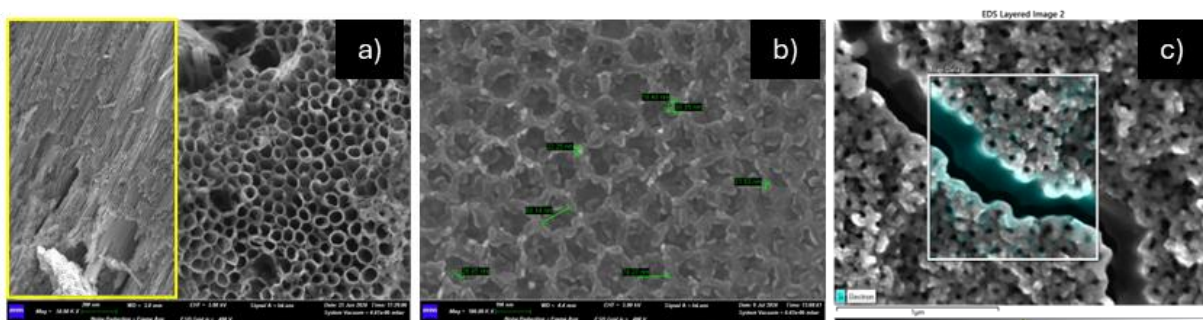
### Materials and Methods

A novel two-steps coating technique was used for composite preparation. Firstly, in a dip-coating step a zeolite synthesis gel, typically consisting of a source of silica (tetraethylortosilicate, TEOS), a templating agent (tetrapropylammonium hydroxide, TPAOH), and water was homogeneously dispersed on top of a TiO<sub>2</sub> substrate. A hydrothermal synthesis was then carried out. For the coating step the so treated substrate was transferred into a supported-Teflon covered steel autoclave, then heated up to 170 °C and the temperature was kept for 24 hours. This process facilitates the crystallization of the Silicalite-1 on the walls of the titanium nanotubes without affecting (clogging) the tubular structure.

The organic template was then removed, without affecting the anatase titania phase, by a following step involving the calcination of the composite in static air at 450 °C for 8 hours.

## Results and Discussion

The obtained composite was characterized by XRD, SEM, TEM, and N<sub>2</sub> physisorption<sup>3</sup>, to evaluate the physicochemical and structural properties, as well as the nanocrystals distribution on titania nanotubes.



**Figure 1.** a) SEM images of the top view and, in the yellow insert on the left, of the cross-section view of the TiO<sub>2</sub> nanotubes before SAC. b) SEM image of the prepared composite: nano-Si1/TiO<sub>2</sub>NTs showing the incorporation of the zeolite inside the titania nanotube's structure. c) EDS layered image of the sample post synthesis not calcined highlighting the presence of Si in light blue.

The composite is under consideration for further testing in reactions of industrial interest.

## References

1. R. Passalacqua, S. Perathoner, G. Centi, *Catalysis Today* **2015**, 251, 121.
2. H. Yang, P. Yang, X. Liu, Y. Wang, *Chemical Engineering Journal* **2016**, 299, 112.
3. I. Paramasivam, A. Avhale, A. Inayat, A. Bösmann, P. Schmuki, and W. Schwieger, *Nanotechnology*, **2009**, 20, 225607.
4. J. Fernández-Catalá, M. Sánchez-Rubio, M. Navlani-García, Á. Berenguer-Murcia, and D. Cazorla-Amorós, *ACS Omega* **2020**, 5(48), 31323.