

# Towards the understanding of structure-properties relationships in N,Nb doped TiO<sub>2</sub> nanopowders: a multidisciplinary experimental and DFT approach

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The photocatalytic activity of doped TiO<sub>2</sub> nanopowders in the visible region strongly depends on the close, yet not fully understood, interplay among local lattice distortions, nature and concentration of point defects and bulk electronic states. [1] Besides, also the mesoscale morphology is crucial, as pore volume and surface area determine the effective suitability of the material for industrial and environmental applications. [2]

We provide here a multidisciplinary experimental (HR-XRPD, EXAFS, EDX, BET, SEM, EPR, DRS) and quantum-mechanical (DFT, DFT+U) exploration of the structural, morphological and electronic properties of differently doped (N, Nb and N/Nb) TiO<sub>2</sub> materials. Overall, we disclose rather subtle correlations among (i) the electronic structure and the nature of the point defects and (ii) the chemical nature of the precursor and the dopant-induced lattice distortions.

First, we demonstrate that substitutional doping is preferred for both N and Nb guests at low concentrations, whereas higher N concentrations are invariably associated to a significant increase in the number of oxygen vacancies. The latter in turn might act as recombination sites for the photogenerated  $e^-h^+$  carriers, [3] accounting for the reduction of the photocatalytic efficiency at high dopant loadings. In co-doped N, Nb materials, Nb acts as a bulk reducing center towards nitrogen. This intrinsic charge compensation mechanism implies that shallow mid-gap states due to N atoms near the conduction band are more populated than in single-doped N-TiO<sub>2</sub> powders. This provides a possible explanation for the synergistic enhancement of the visible-light absorption showed by N, Nb co-doped nanopowders with respect to their single-doped analogues.

We also show that, upon selecting the proper chemical nitrogen precursor and the desired nominal N/Ti concentration, it is possible to tailor crucial microscopic and mesoscopic parameters, such as phase composition, surface area, morphology, and crystallographic cell distortions.

Synergism among experimental and theoretical techniques is here decisive to provide a sensible interpretative model for the observed photoelectrochemical activity in titania-based photocatalysts. In this context, access to large-scale X-ray and neutron facilities is foreseen to become more and more important in the next future to allow a complete and accurate understanding of the structure-properties relationships in these materials.

[1] Lo Presti *et al.*, *J. Phys. Chem. C* **2014**, 118, 4797; Marchiori *et al.*, *J. Phys. Chem. C* **2014**, 118, 24152; Spadavecchia *et al.*, *Chin. J. Chem.* **2014**, 32, 1195; Ceotto *et al.*, *J. Phys. Chem. C* **2012**, 116, 1764.

[2] Praseda Rao, Murali Dhar, *Recent Advances in Basic and Applied Aspects of Industrial Catalysis*, **1998**, Studies in Surface Science and Catalysis 113, Elsevier; ISBN: 0-444-82920-2

[3] Katoh *et al.*, *J. Phys. Chem. Lett.* **2010**, 1, 3261; Irie *et al.*, *J. Phys. Chem. B* **2003**, 107, 5483