



|   |  |                                     |
|---|--|-------------------------------------|
|   | <b>Experiment title:</b><br>CHARGE TRAPPING IN V-N-DOPED TiO <sub>2</sub><br>NANOSTRUCTURED THIN FILMS | <b>Experiment number:</b><br>HC2263 |
| <b>Beamline:</b><br>ID26  | <b>Date of experiment:</b><br>from: 24/2/16 to: 1/3/16   | <b>Date of report:</b><br>7/9/17    |
| <b>Shifts:</b><br>18  | <b>Local contact(s):</b><br>L. Amidani   | <i>Received at ESRF:</i>            |
| <b>Names and affiliations of applicants</b> (* indicates experimentalists):<br>G. Rossi, M. Calizzi, L. Pasquini and F. Boscherini <sup>#</sup> , Univ. of Bologna<br>L. Amidani, ESRF<br><sup>#</sup> also with CNR-IOM, Italy |  |                                     |

## Report:

The objective of this experiment was to probe element specific signatures of the visible light excitation of V-doped TiO<sub>2</sub> nanoparticles. In fact, doping is a well-known tool to modify the physical properties of semiconductors and insulators. Dopants can change the optical properties by introducing states in or near the forbidden energy gap and can modify the transport properties by releasing charge carriers and/or giving rise to traps which reduce the carrier lifetime. The modification of the optical properties may be due to various phenomena, including excitation of electrons from dopant states in the gap to the host conduction band and/or excitation of host electrons from the valence band to defect gap states induced by the dopants. A physical description and understanding of these aspects is crucially important.

Titanium dioxide (TiO<sub>2</sub>), especially in the form of nanoparticles (NPs), is one of the most studied oxide semiconductors for photocatalysis. However, because of its wide band gap, only a small fraction of the solar spectrum is harvested, i.e., UV light (3%–5% of total). The incorporation of 3d transition metals is an effective approach to decrease the band gap and to improve the photoactivity under visible light. For example, it is known that the incorporation of V in TiO<sub>2</sub> creates an intra-gap state near the bottom of the conduction band, increasing both the photoabsorption and the photocatalytic activity under solar irradiance. However, it is unclear whether the enhanced photoactivity is due to electron excitation from dopant states in the gap to the host conduction band or to transitions from the host valence band to defect states in the gap, possibly also related to oxygen vacancies induced by the presence of dopants, or both. The open questions are: (i) Does light absorption lead to the release of an electron from V or the opposite? (ii) If an electron is, in fact, released from V, what is its fate, that is, is it transferred to the TiO<sub>2</sub> matrix on a particular atomic site (Ti or O, bulk or surface)?

In this experiment, we shed light on the above issues by using high-energy-resolution fluorescence detected x-ray absorption near edge structure (HERFD-XANES) under differential visible light illumination. HERFD-XAS can be used to study charge-transfer processes, as shown by the recent study by our group of plasmon induced charge transfer in Au:TiO<sub>2</sub> nanostructures [1]. As for the specific system here investigated, we have recently demonstrated that V dopants in TiO<sub>2</sub> NPs are found in both 4+ and 5+ oxidation states in bulk and surface sites, respectively, and occupy substitutional sites irrespective of whether the matrix has an atomic structure similar to rutile or anatase [2].

The main experimental result is highlighted in Fig. 1 in which we report Ti and V HERFD-XANES spectra. Briefly, we detected a clear light – induced shift to higher (lower) energies of the V (Ti) edges (top row insets). Moreover, the differential signals (middle and bottom rows) could be reproduced with an empirical edge shift approach (best fit red curves). These results lead us to conclude that visible light absorption predominantly induces an electron transfer from V to long-lived Ti-related traps. It was also possible to roughly estimate the lifetime of the electrons in the trapped states as 0.8 ms.

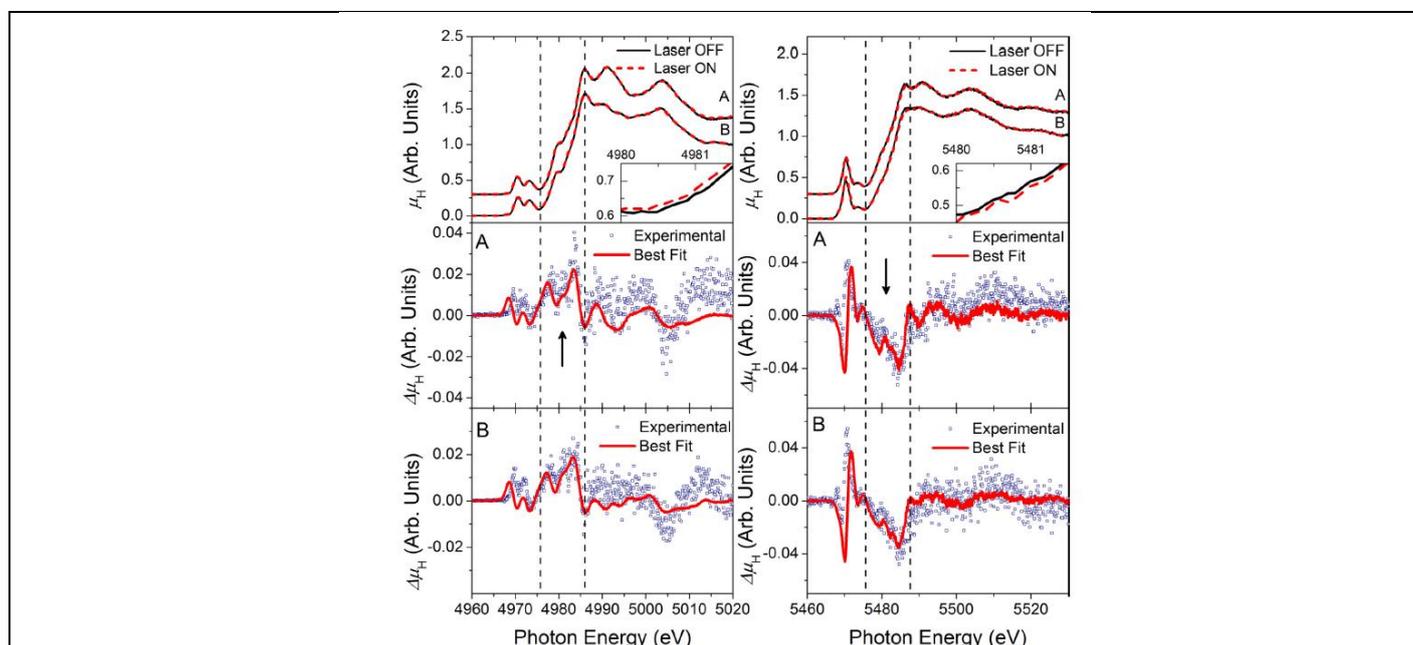


Fig. 1: Top row: HERFD-XANES spectra for samples A and B with and without laser illumination; the inset is a zoom on the rising edge, highlighting the edge shift. Middle and bottom panels: differential HERFD-XANES spectra and best fits. In all cases, left column Ti  $K\beta$  HERFD-XANES, right column V  $K\alpha$  HERFD-XANES.

[1] L. Amidani et al., *Angew. Chem. Int. Ed.* **54**, 5413 (2015).

[2] G. Rossi et al., *J. Phys. Chem. C* **120**, 7457 (2016).

These results have been published as Rossi et al., *Phys. Rev. B* **96**, 05303 (2017), DOI: 10.1103/PhysRevB.96.045303.

This research was funded by the Italian Ministry of Research (MIUR) within PRIN-2015 Project No. NEWLI-2015CL3APH.