Reduction of TiO\textsubscript{2} by a low-temperature degradation of adsorbed organic solvents

V. Gargiulo,\textsuperscript{1} M. Alfè,\textsuperscript{1} M. Amati,\textsuperscript{2} P. Zeller,\textsuperscript{2} V. -A. Maraloiu,\textsuperscript{3} P. Maddalena,\textsuperscript{4} S. Lettieri,\textsuperscript{5}

\textsuperscript{1}Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili, Consiglio Nazionale delle Ricerche (CNR-STEMS), Piazzale V. Tecchio 80, 80125 Napoli, Italy.

\textsuperscript{2}Elettra-Sincrotrone Trieste S.C.p.A di interesse nazionale, SS14 Km 163,5, I-34149 Trieste, Italy.

\textsuperscript{3}National Institute of Materials Physics, 405A Atomistilor St, 077125 Magurele, Romania.

\textsuperscript{4} Dipartimento di Fisica, Università degli Studi di Napoli “Federico II”, Complesso Universitario di Monte S. Angelo, Via Cintia 21, 80126 Napoli, Italy.

\textsuperscript{5} Istituto per le Scienze Applicate e i Sistemi Intelligenti, Consiglio Nazionale delle Ricerche (CNR-ISASI), U.r.T UNINA, Complesso Universitario di Monte S. Angelo, Via Cupa 21, 80126 Napoli, Italy.

(*) corresponding author. E-mail: Stefano.lettieri@isasi.cnr.it

We discuss how employing a refluxing solvothermal treatment of TiO\textsubscript{2} in organic solvents at mild temperature (120 °C) allows producing blue-colored and reduced titanium dioxide (TiO\textsubscript{2-\textit{x}}). The treatment, tested for different organic solvents, increases the density of Ti(III) species and the appearance of two optical absorption features: a broad absorption band responsible for the blue coloration and a subgap absorption tail close to the band gap energy.

Experimental analyses based on X-ray photoemission spectroscopy and excitation-resolved photoluminescence suggests that the solvothermal process at 120°C leads to formation of surface and subsurface oxygen vacancies (V\textsubscript{O}). Different solvents have been tested, where ethanol is found to be the most effective. Improved photocatalytic degradation by the processed TiO\textsubscript{2} under VIS illumination is demonstrated, and the possible mechanism involved in the formation of surface V\textsubscript{O} is discussed. The method outlines a very simple, low-cost, and fast procedure to target the formation of V\textsubscript{O} in the TiO\textsubscript{2} surface region.

\textbf{Figure 1:} Image P25 powder before (left column) and immediately after (center and right columns) a 24 hours refluxing treatment in three different alcohols (Top row: ethanol; center row: methanol; bottom row: 2-propanol) and at two different oil bath temperatures: T\textsubscript{1}=T\textsubscript{b}+10°C (center column) and T\textsubscript{2}= 120°C. Here T\textsubscript{b} indicates the boiling temperature of the different alcohols.