



TAILORING THE STRUCTURAL AND ELECTRONIC FEATURES OF N-DOPED TiO₂/SnO₂ PHOTOCATALYSTS FOR POLLUTANT DEGRADATION

S. Clerici^a, C. Cionti^{a,b}, L. Lo Presti^{a,c,d}, D. Meroni^{a,b}, S. Ardizzone^{a,b}

^a Department of Chemistry, Università degli Studi di Milano, via Golgi 19, 20133, Milan, Italy;

^b Consorzio INSTM, via Giusti 9, 50121, Florence, Italy;

^c CNR-ISTM, Via Golgi 19, Milano, Italy

^d CMC, Aarhus University, Langelandsgade 140, DK-8000, Aarhus, Denmark

TiO₂/SnO₂ composites hold promise in numerous cutting-edge research fields, such as gas sensors (Chen 2015), fuel cells (An 2013) and photocatalysis (Toloman 2019). Thanks to the near isomorphism of TiO₂ rutile ($P4_2/mnm$, $a=4.5937$ Å, $c=2.9587$ Å) and SnO₂ cassiterite ($P4_2/mnm$, $a=4.7382$ Å, $c=3.1871$ Å), stable heterojunctions between the two semiconductors can be obtained. Furthermore, SnO₂ and TiO₂ present different work functions (4.4 and 4.2 eV, respectively). The Fermi energy of TiO₂ is higher than that of SnO₂, which can promote electron transfer from the TiO₂ conduction band to the SnO₂ one, with the ensuing formation of an interface contact potential (Floriano 2014). These electron transfer phenomena can be exploited to promote the separation of charge carriers in photocatalytic applications, leading to more efficient materials. Extending the lifetime of photo-generated charges is a crucial aspect particularly for N-doped TiO₂, as in these materials visible-light activity is generally achieved at the expense of faster charge carriers recombination (Asahi 2014; Rimoldi 2015). We have recently shown that addition of Sn species can promote the photocatalytic activity under solar irradiation of N-doped TiO₂ (Rimoldi 2018).

In this work, N-doped TiO₂/SnO₂ materials are investigated as photocatalyst for the light activated degradation of both water and gas phase pollutants. N-doped TiO₂/SnO₂ and TiO₂/SnO₂ samples were synthesized in a broad range of Sn:Ti molar ratios (up to 20%) adopting three different methods (mechanical mixing, co-synthesis and seeded growth) followed by calcination at 400°C. Commercial and *ad hoc* synthesized TiO₂ and SnO₂ samples were also analyzed as references. The structural, morphological, electronic and surface features of each set of samples were investigated in detail. The local structure, defectivity and charge transfer phenomena were also studied via *in situ* X-ray absorption spectroscopy experiments.

High resolution X-ray diffraction and X-ray absorption curves at the Sn L1-edge and Ti K-edge showed that the adopted synthetic strategies control the microstructure in terms of both phase composition and concentration of defects, which in turn imply significant changes in both the long- and short-range structures. In particular, the coprecipitation route gives rise to notable differences with respect to the other two methods, showing no peaks due to SnO₂ cassiterite and promoted growth of TiO₂ rutile (**Fig. 1b**) as well as a different Sn coordination geometry (**Fig. 1a**). Furthermore, the *operando* measurements provided evidence of electron transfer mechanisms taking place upon UV light irradiation. The distinctive character of samples from coprecipitation route is also appreciable in terms of light absorption features (**Fig. 2**), where the copromotion with Sn and N gives rise to synergistic effects.

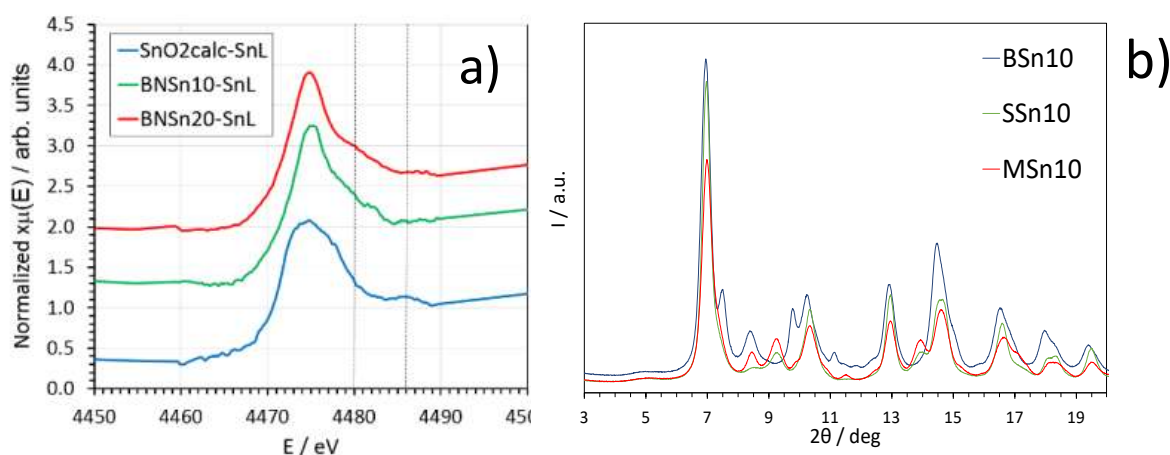


Figure 1. a) Normalized absorption coefficient $\mu(E)$ curves for the Sn L-edge of samples from coprecipitation route compared to the one of SnO₂; b) Diffraction patterns for the samples from different synthetic procedures with same Sn content.

Samples were tested under UV and solar irradiation towards the remediation of an emerging pollutant (tetracycline) in water and of a model VOC (ethanol) in the gas phase. Both the molecule disappearance, the reaction intermediate and final mineralization were monitored, showing promising results in terms of photocatalytic activity of the copromoted samples (**Fig. 2**). The photocatalytic performances were correlated with the structural and spectroscopic results also on the grounds of the reaction pathways.

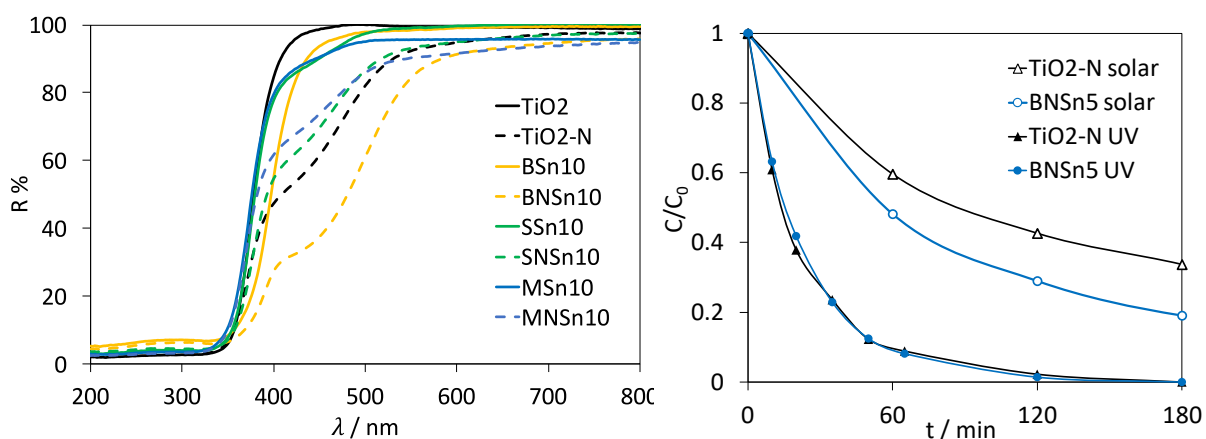


Figure 2. Diffuse reflectance spectra of samples with same Sn content with and without N doping (left); tetracycline disappearance curves under UV and solar irradiation for N-doped TiO₂ and a sample promoted with 5% Sn (right).

References

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