

# **Supporting Information**

**for**

## **Surface Functionalization of Grown-on-Tip ZnO Nanopyramids: From Fabrication to Light-Triggered Applications**

Alberto Gasparotto,<sup>\*a</sup> Chiara Maccato,<sup>a</sup> Giorgio Carraro,<sup>a</sup> Cinzia Sada,<sup>b</sup>  
Urška Lavrenčič Štangar,<sup>c,d</sup> Bruno Alessi,<sup>e</sup> Conor Rocks,<sup>e</sup> Davide Mariotti,<sup>e</sup>  
Andrea La Porta,<sup>f</sup> Thomas Altantzis,<sup>f</sup> and Davide Barreca<sup>g</sup>

<sup>a</sup> Department of Chemical Sciences, Padova University and INSTM, 35131 Padova, Italy. E-mail: [alberto.gasparotto@unipd.it](mailto:alberto.gasparotto@unipd.it).

<sup>b</sup> Department of Physics and Astronomy, Padova University and INSTM, 35131 Padova, Italy.

<sup>c</sup> Faculty of Chemistry and Chemical Technology, University of Ljubljana, 1000 Ljubljana, Slovenia.

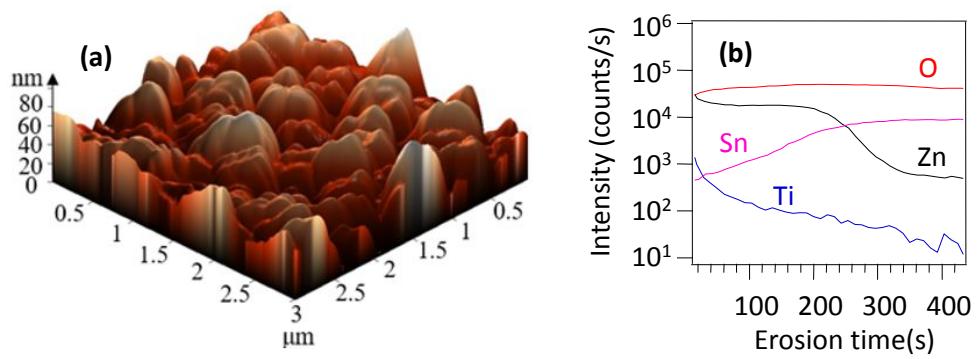
<sup>d</sup> Laboratory for Environmental and Life Sciences, University of Nova Gorica, 5000 Nova Gorica, Slovenia.

<sup>e</sup> Nanotechnology & Integrated Bio-Engineering Centre (NIBEC), Ulster University, BT37 0QB, UK.

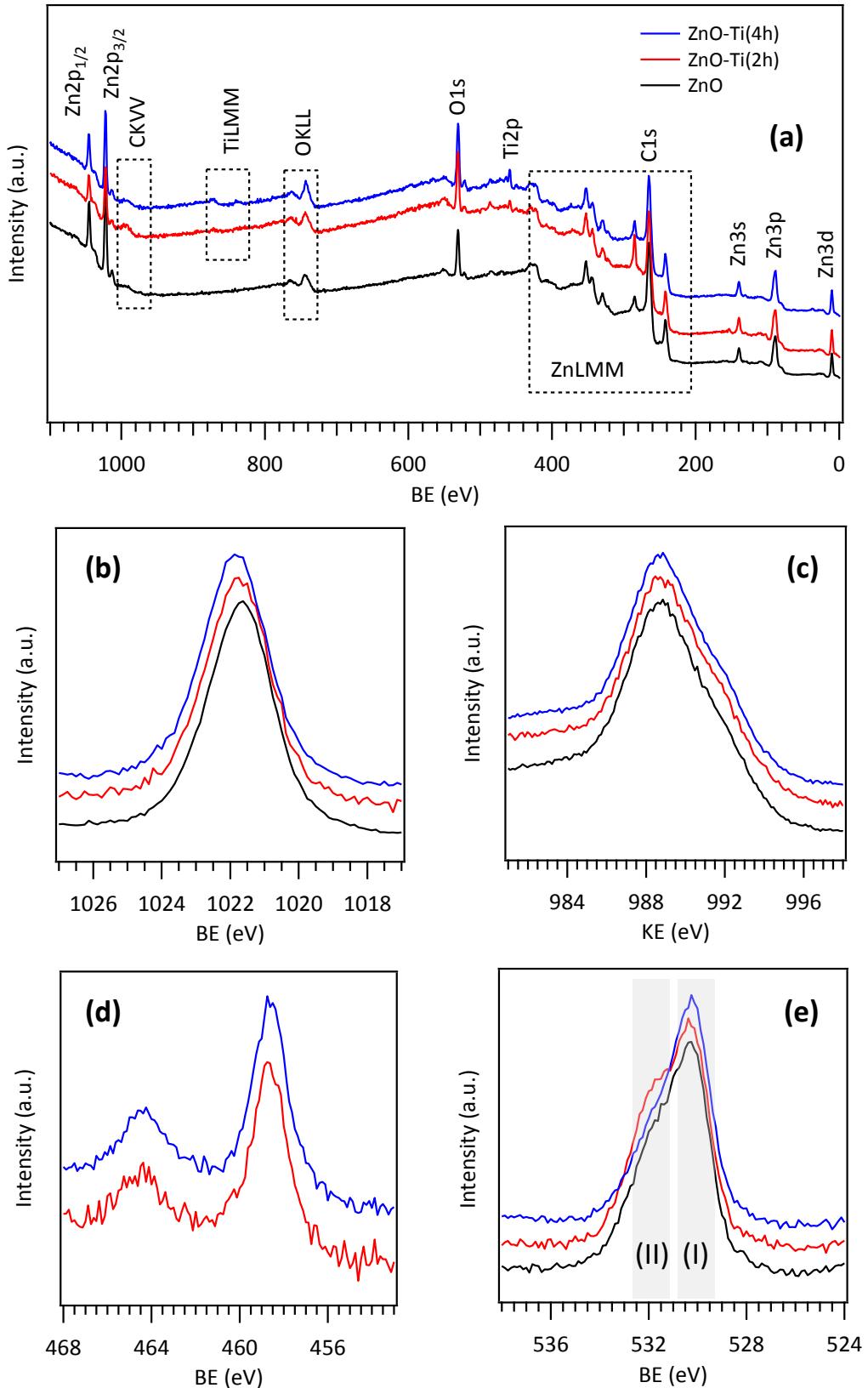
<sup>f</sup> EMAT, University of Antwerp, 2020 Antwerpen, Belgium.

<sup>g</sup> CNR-ICMATE and INSTM, Department of Chemical Sciences, Padova University, 35131 Padova, Italy.

\* Corresponding author; phone: +39-0498275192; e-mail: [alberto.gasparotto@unipd.it](mailto:alberto.gasparotto@unipd.it)  
(A.G.).

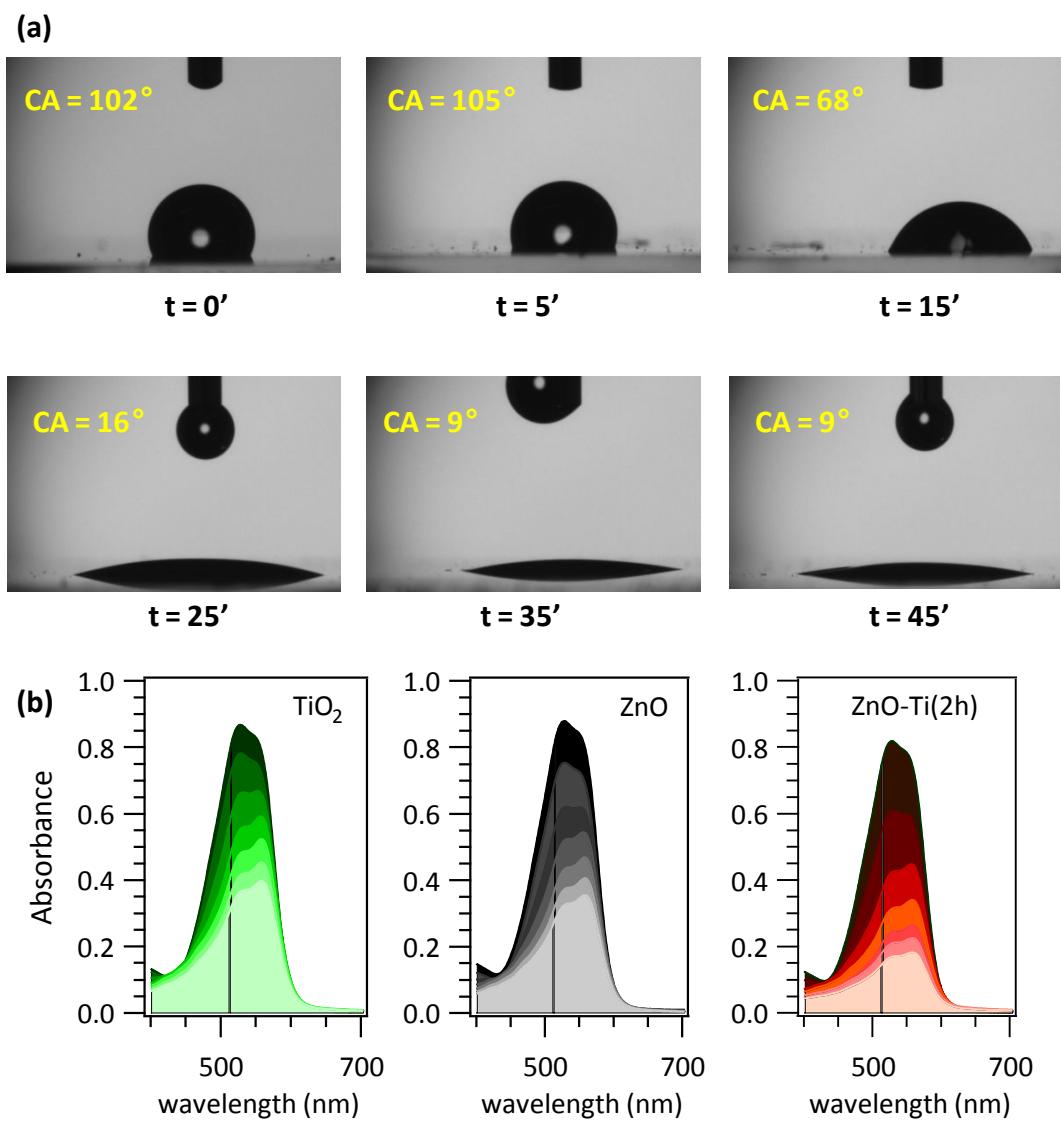


**Figure S1.** (a) Representative AFM micrograph and (b) SIMS depth profile of sample ZnO-Ti(4h).

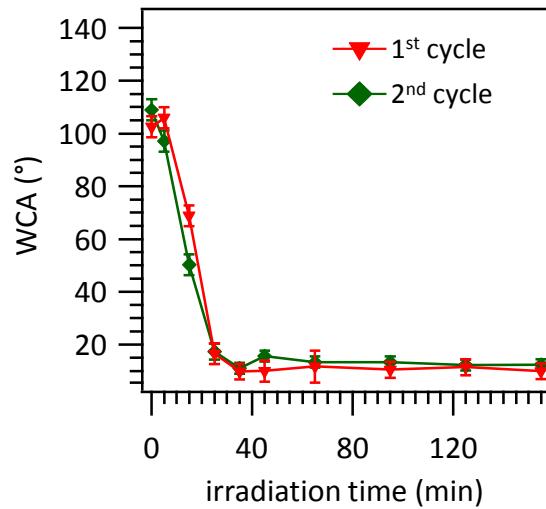


**Figure S2.** (a) Surface XPS survey spectra of ZnO, ZnO-Ti(2h) and ZnO-Ti(4h) samples. (b) Zn2p, (c) ZnLMM, (d) Ti2p, and (e) O1s lines for the same specimens. Color codes as in panel (a).

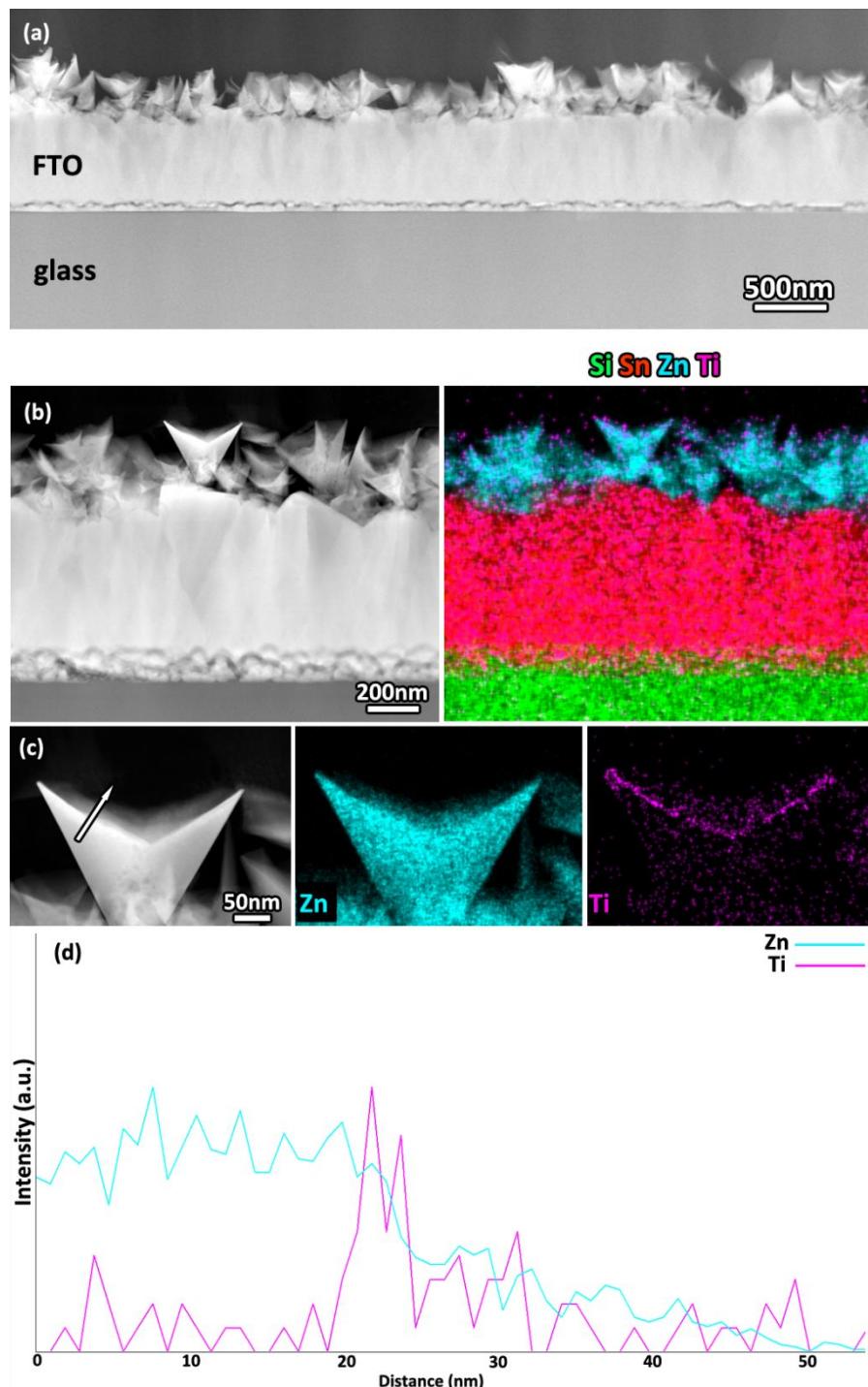
Survey spectra revealed the presence of zinc, oxygen, and eventually titanium signals, along with carbon arising from atmospheric exposure. Evaluation of the zinc Auger parameter, defined as  $\alpha = BE(Zn2p_{3/2}) + KE(ZnLMM)$ ,<sup>1</sup> yielded values of 2010.4, 2010.6 and 2010.7 eV for specimens ZnO, ZnO-Ti(2h), and ZnO-Ti(4h) respectively. For all samples, the O1s peak displayed a similar spectral shape, resulting from the concurrent contribution of lattice oxygen ( $BE = 530.2$  eV, component (I) in Fig. S2e) and adsorbed hydroxyl/carbonate groups ( $BE = 531.8$  eV, component (II)).<sup>2-5</sup>



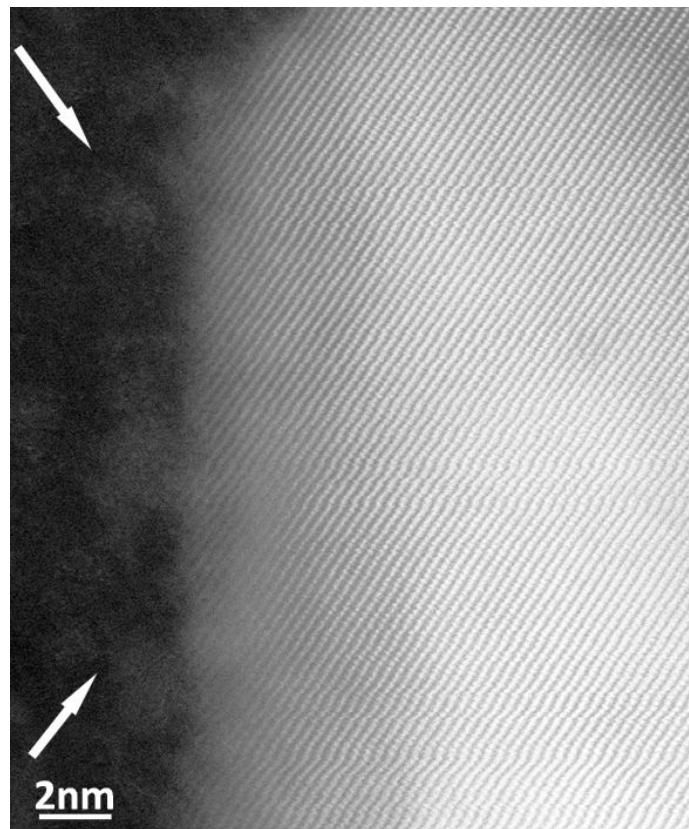
**Figure S3.** (a) Digital photographs showing the evolution of WCA with irradiation time on sample ZnO-Ti(2h). (b) Optical absorption spectra of Plasmocorinth B aqueous solutions (concentration = 12 mg/L) as a function of UV irradiation time. The black vertical line marks the dye absorbance maximum ( $\lambda_{\text{max}} = 527 \text{ nm}$ ) that was sampled at regular time intervals (30 min).



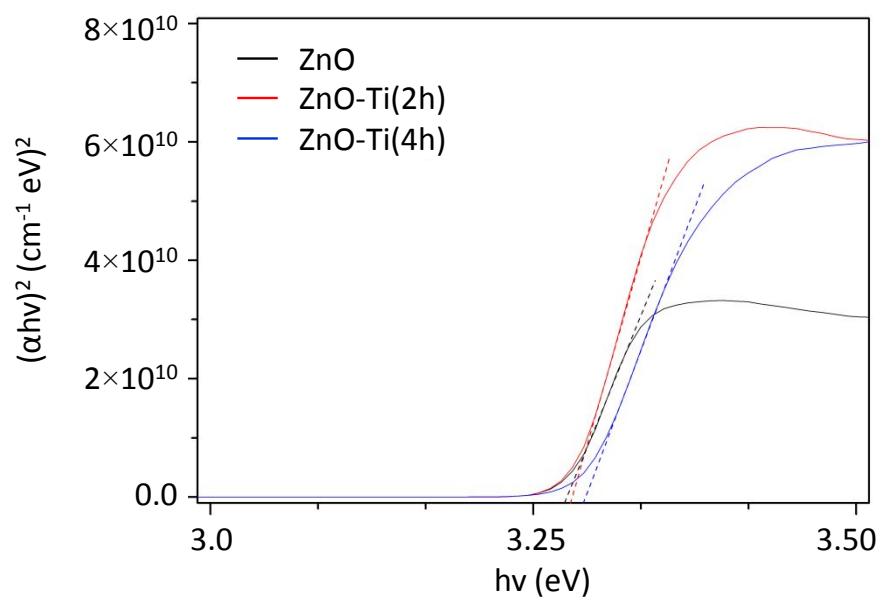
**Figure S4.** WCA evolution as a function of irradiation time during the first and second cycle of utilization for sample ZnO-Ti(2h).



**Figure S5.** (a) Cross-sectional HAADF-STEM overview of the ZnO-Ti(4h) sample. (b) HAADF-STEM image of a sample region, and corresponding EDXS elemental maps. (c) HAADF-STEM micrograph and EDXS maps of an individual ZnO nanopyramid, showing the surface presence of a discontinuous TiO<sub>2</sub> layer. (d) Zn and Ti EDXS line-scans collected along the arrow indicated in (c).



**Figure S6.** High resolution cross-sectional HAADF-STEM micrograph of the surface region of specimen ZnO-Ti(4h). Arrows indicate the TiO<sub>2</sub> deposit, while the brighter image region corresponds to ZnO.



**Figure S7.** Tauc plots of bare and Ti-modified ZnO-based samples.

## References

- (1) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray photoelectron spectroscopy*, Perkin Elmer Corporation, Eden Prairie, MN, USA 1992.
- (2) Fittipaldi, M.; Gombac, V.; Gasparotto, A.; Deiana, C.; Adami, G.; Barreca, D.; Montini, T.; Martra, G.; Gatteschi, D.; Fornasiero, P. Synergistic Role of B and F Dopants in Promoting the Photocatalytic Activity of Rutile TiO<sub>2</sub>. *ChemPhysChem* **2011**, *12*, 2221-2224.
- (3) Balbuena, J.; Carraro, G.; Cruz, M.; Gasparotto, A.; Maccato, C.; Pastor, A.; Sada, C.; Barreca, D.; Sánchez, L. Advances in Photocatalytic NO<sub>x</sub> Abatement through the Use of Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> Nanocomposites. *RSC Adv.* **2016**, *6*, 74878-74885.
- (4) Gasparotto, A.; Carraro, G.; Maccato, C.; Sada, C.; Balbuena, J.; Cruz-Yusta, M.; Sánchez, L.; Vodišek, N.; Lavrenčič Štangar, U.; Barreca, D. WO<sub>3</sub>-Decorated ZnO Nanostructures for Light-Activated Applications. *CrystEngComm* **2018**, *20*, 1282-1290.
- (5) Kwiatkowski, M.; Bezverkhyy, I.; Skompska, M. ZnO Nanorods Covered with a TiO<sub>2</sub> Layer: Simple Sol-Gel Preparation, and Optical, Photocatalytic and Photoelectrochemical Properties. *J. Mater. Chem. A* **2015**, *3*, 12748-12760.