REVERSIBLY UV-LIGHT-INDUCED HYDROPHOBIC/OLEOFILIC TO AMPHIPHILIC SURFACE TRANSITION IN THIN FILMS OF ORGANIC-CAPPED TiO_2 NANORODS

Gianvito Caputo,[1] Athanassia Athanassiou,[1] Concetta Nobile,[1] Tobias Kipp,[2] Roman Krahne,[1]*

Elvio Carlino,[2] Liberato Manna,[1] Roberto Cingolani,[1] and P. Davide Cozzoli[1]

[1] National Nanotechnology Laboratory of CNR-INFM, Unità di Ricerca IIT, Distretto Tecnologico ISUFI, via per Arnesano km 5, I-73100 Lecce, Italy.
[2] Institut für Angewandte Physik und Zentrum für Mikrostrukturforschung, Universität Hamburg, Jungiusstrasse 11, 20355 Hamburg
[2] TASC-INFM-CNR National Laboratory, Area Science Park - Basovizza, Bld MM, SS 14, Km 163.5, I-34012 Trieste, Italy
* To whom all correspondence should be addressed: Phone:+39-0832-298271. Fax: +39-0832-298238. E-mail: gianvito.caputo@unile.it

Nanocrystalline TiO_2 is among the most studied semiconductor oxides, owing to its low-cost widespread applications in light-assisted environmental clean-up, in solar energy conversion, in sensing, and in the photodynamic deactivation of micro-organisms and of malignant cells. More recently, it has been discovered that UV-irradiation of TiO_2 surfaces rapidly converts them from an initially hydrophobic state to a highly amphiphilic one, followed by a slow back-recovery of the starting properties under ambient conditions.[1-4] These findings have stimulated the fabrication and the study of inorganic coatings which exhibit simultaneous self-cleaning and antifogging behaviour.[5, 6] However, the understanding the mechanism leading to light-induced wettability modification on TiO_2 surfaces remains elusive yet and the ability to control them has to be developed further.

In this contribution we will present a novel approach to engineer TiO_2 surfaces with UV-switchable wettability, which relies on the use of organic-capped TiO_2 nanorods (NRs)[7] for the fabrication of thin films made of close-packed laterally aligned arrays of TiO_2 crystalline domains exposing well-defined light-active crystal facets. As opposed to conventional polycrystalline or single-crystal TiO_2 surfaces, such NR-based films exhibit a reversible surface transition from a highly hydrophobic/oleofilic state (water and octadecene contact angles of 110° and 8°, respectively) to a highly amphiphilic state (water and octadecene contact angles of 20° and 3°, respectively) under remarkably milder UV-irradiation conditions (energy density as low as 1-2 mJ/cm^2). By using a combination of techniques (XRD, HRTEM, SEM, UV-vis, FTIR and Raman spectroscopy, and contact angle measurements), we will demonstrate that the observed light-driven wettability changes are accomplished by progressive hydroxylation of the TiO_2 surface irrespective of the presence of the native shell of surfactant molecules, which simultaneously undergo conformational changes without suffering for significant photocatalytic degradation.

References

1. R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe *Nature* **1997,** 388, 431-432.
2. R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe *Adv. Mater.* **1998,** 10, (2), 135-138.
3. N.Sakai, A. Fujishima, T. Watanabe, K. Hashimoto *J. Phys. Chem. B* **2003,** 107, (4), 1028-1035.
4. X. Feng, J. Zhai, L. Jiang *Angew. Chem. In. Ed* **2005,** 44, (32), 5115-5118.
5. K. Qi, W. A. Daoud, J. H. Xin, C. L. Mak, W. Tang, W. P. Cheung *J. Mater. Chem.* **2006,** 16, (47), 4567-4574.
6. E. Allain, S. Besson, C. Durand, M. Moreau, T. Gacoin, J.-P. Boilot *Adv. Func. Mater.* **2007,** 17, (4), 549-554.
7. P. D. Cozzoli, A.Kornowski, H. Weller *J. Am. Chem. Soc.* **2003,** 125, (47), 14539-14548.