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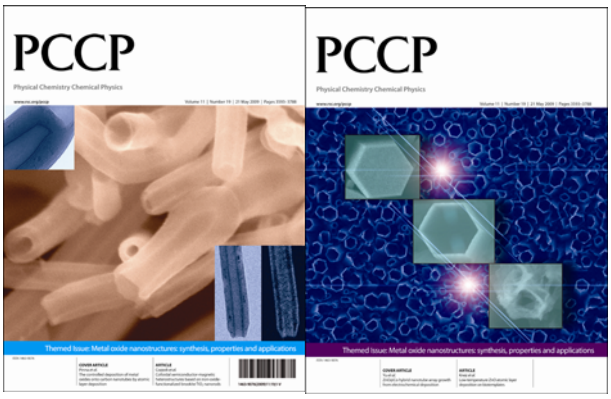

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Wettability conversion of colloidal TiO_2 nanocrystal thin films with UV-switchable hydrophilicity

Gianvito Caputo,[ab] Roberto Cingolani,[ac] Pantaleo Davide Cozzoli*[ab] and Athanassia Athanassiou*[ac]

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Under pulsed laser UV irradiation, thin-film coatings made of close-packed TiO_2 nanorods individually coated with surfactants can exhibit a temporary increase in their degree of surface hydroxylation without any apparent photocatalytic removal of the capping molecules. This mechanism provides a basis for achieving light-driven conversion from a highly hydrophobic to a highly hydrophilic, metastable state, followed by extremely slow recovery of the original conditions under dark ambient environment. A deeper insight into the wetting dynamics is gained by time-dependent water contact-angle and infrared spectroscopy monitoring of the film properties under different post-UV storage conditions. Our study reveals that, for reversible switchability between extreme wettability excursions and long-term repeatability of such changes to be achieved, specific modifications in the polar and nonpolar components of the TiO_2 films need to be guaranteed along with preservation of the original geometric arrangement of the nanocrystal building blocks. The application of moderate vacuum is found to be an effective method for accelerating the post-UV hydrophilic-to-hydrophobic conversion, thereby enabling fast and cyclic hydrophilization/hydrophobicization alternation without any detrimental signs of significant fatigue.

1. Introduction

The ability to engineer surfaces with dynamically modifiable wetting properties represents an actively pursued research area in materials science due to its implications in disparate technological fields, including sensing, microelectronics, cell manipulation, food technology, microfluidics, and design of smart multifunctional coatings and membranes.[1–6] There are two widely exploited classes of strategies for realizing surfaces that can display tailored and switchable wettability upon application of external stimuli. One approach involves surface functionalization with selected organic molecules that exhibit reversible changes in their dipole moment following structural transitions induced by either light irradiation, electric fields, pH or solvent changes.[7–11] The typical degree interval over which excursions in water contact angle (WCA) are achievable by these methods is, however, limited to about $\sim$10–15° only, which can be only slightly extended by enhancing the roughness of the solid surface underneath.[1–4,6–11] An alternative and more powerful strategy relies on the capability of some transition-metal oxides, namely ZnO,[12] WO_3,[13] V_2O_5[14] and TiO_2,[3,15–18] to increase their hydrophilicity under band-gap photoexcitation, and to revert back to the initial condition upon storage in the dark. Besides offering long-term reproducible performances due to their inherent chemical resistance, such oxide materials can exhibit WCA variations as large as $\sim$30–70° already in the form of smooth substrates, which can be ultimately amplified up to the 180° limit (*i.e.*, corresponding to superhydrophobic-to-superhydrophilic transitions) upon controlled introduction of extra micro- and nano-scale surface structuring.[1–6,9–17]

Among the aforementioned materials, TiO_2 represents an exclusive platform on which UV-light-stimulated wettability changes are triggered concertedly with the semiconductor photocatalytic activity. Joint exploitation of these two processes has indeed enabled development of unique multifunctional coatings simultaneously exhibiting self-cleaning, antibacterial, and antifogging properties.[5,15,16] Despite such technological potential, the understanding of the reversible photoswitchable wettability of TiO_2 remains a subject of intense debate. In one mechanistic picture, TiO_2 hydrophilicization has been rationalized as arising from sequential surface photocorrosion and reconstruction processes, which would involve hole-driven creation of surface oxygen vacancy defects on one side, and their healing upon molecular and/or dissociative adsorption of atmospheric water, on the other side.[3,15–17,19–21] Slow recovery of the starting surface condition then occurs under ambient storage in the dark due to atmospheric oxygen replacing the newly implanted hydroxyl moieties. Alternatively, it has been proposed that UV-driven hydrophylicization results from photocatalytic removal of adsorbed hydrophobic alkyl compounds (*e.g.* hydrocarbons), following which a new contaminating organic layer is

[a] *National Nanotechnology Laboratory of CNR-INFM, Unità di Ricerca IIT, Distretto Tecnologico ISUFI, via per Arnesano km 5, 73100, Lecce, Italy. E-mail: athanassia.athanassiou@unile.it, davide.cozzoli@unile.it*
[b] *Scuola Superiore ISUFI, University of Salento, Distretto Tecnologico, Via per Arnesano km 5, 73100, Lecce, Italy*
[c] *IIT-Italian Institute of Technology, Via Morego 30, 16152, Genova, Italy*

deposited upon prolonged dark storage.[22–26] However, discrepancies among main mechanistic conclusions should not necessarily be considered contradictory or mutually exclusive, owing to the broad variety of TiO_2 surfaces that have been probed by vastly different techniques under diverse measurement conditions.

In order to boost the technological potential of the reversibly photoinduced TiO_2 wettability, research activities have been intensively devoted to enhance the rate and the ultimate degree of hydrophilic conversion of TiO_2-based substrates by carefully engineering surface roughness,[3,15–18,27] applying anodic polarization,[28] doping,[29] and/or creating composite heterostructures whereby TiO_2 sections are intimately connected to other semiconductor domains with suitably staggered band gaps (*e.g.* WO_3).[29–31] On the other hand, although it would be highly desirable to devise strategies for affecting post-irradiation recovery of the pristine hydrophobicity status, earlier attempts have been limited to the use of either thermal or ultrasound treatments,[21,32–34] oxygenation[21] and visible irradiation,[35] albeit the relevant mechanistic implications have not yet been conclusive. The ability of reverting the wettability conditions of TiO_2 surfaces in a deliberate and fast way remains one of the most important goals that need to be achieved for enabling practical exploitation of such materials, for example, in microfluidics.

So far, the UV-switchable wettability of TiO_2 has been studied on micro-/nano-structured films grown directly onto substrates *via* sputtering, chemical vapour deposition, or sol–gel reaction/calcination, which are economically restrictive for large-scale applications. As a valuable alternative route, the assembly of preformed wet-chemically synthesized organic-free nanocrystals on substrates has been proposed for the fabrication of nanoporous coatings with superhydrophilic properties that, however, do not necessarily require UV irradiation to maintain their stability.[31,36,37]

More recently, we have demonstrated for the first time the feasibility of exploiting anatase TiO_2 nanorods (NRs) provided with an organic surfactant capping for the creation of close-packed thin-film coatings on a variety of inorganic and polymeric substrates with pre-engineered microroughness, which showed a reversible transition from a highly hydrophobic to a very hydrophilic state (with excursions in WCA values larger than $\sim 100^\circ$) upon 355 nm pulsed laser photoexcitation.[38–40] The intense and intermittent irradiation regime triggers a peculiar hydrophilicization mechanism, according to which the degree of surface hydroxylation increases selectively at the organic-free domains of the TiO_2 NR facets, while the pre-existing anchored surfactants are not subjected to any noticeable photocatalytic degradation. Prolonged sample storage in the dark under ambient conditions allows the initial hydrophobicity to be fully restored.[38–40] The convenience of using such NRs for building UV-responsive oxide films stands within their peculiar structure and shape anisotropy. Actually, the preferential NR elongation along the *c*-axis direction of the anatase lattice can favour delocalization of photoexcited charge carriers, and hence their efficient utilization in the creation of surface vacancies. Additionally, the dominant (011)/(101)-type facets at the NR surface are known to be particularly effective in the light-induced hydrophilicization mechanism of TiO_2.[38,41]

In this contribution we investigate the kinetics of the post-irradiation dehydrophilicization of such type of colloidal TiO_2 NR based coatings following application of different external stimuli. Surfactant-coated TiO_2 thin films can be conveniently regarded as model platforms to study the mechanism of hydrophobicity recuperation of UV-treated organic-capped nanocrystals, since any impact on the organic (*i.e.*, related to the surfactant coating) and/or inorganic components (*i.e.*, associated with TiO_2 lattice and surface chemistry) in such systems can be clearly recognized and discriminated, as previously demonstrated for the forward hydrophilicization process.[38–40] In particular, the effects of applying either vacuum, combined visible/infrared laser illumination, and substrate heating on the ultimate wettability changes of the films have been examined by time-dependent WCA and Fourier transform infrared spectroscopy (FT-IR) measurements, and comparatively discussed with respect to their otherwise natural evolution under ambient dark condition taken as the reference. Our study reveals that, for reversible switchability between extreme wetting conditions and long-term repeatability of such changes to be guaranteed, dynamic changes in the polar and nonpolar components of the TiO_2 films need also to be guaranteed along with preservation of the original geometric arrangement of the nanocrystal building blocks. In contrast to previous findings,[21,32–35] we have observed that the application of moderate vacuum conditions is the most effective method for remarkably accelerating the post-UV hydrophilic-to-hydrophobic conversion, thereby enabling cyclic hydrophilicization/hydrophobicization alternation without any significant fatigue.

2. Experimental

Materials

All chemicals were of the highest purity available and were used as received. Titanium tetraisopropoxide ($Ti(OPr^i)_4$ or TTIP, 97%), trimethylamine *N*-oxide dihydrate ($(CH_3)_3NO{\cdot}2H_2O$ or TMAO, 98%), oleic acid ($C_{17}H_{33}CO_2H$ or OLAC, 90%) were purchased from Aldrich. All solvents used were of analytical grade and were also purchased from Aldrich. Water was bidistilled (Millipore Q). Silicon (100) p-type slabs were purchased from Jocam.

Synthesis of TiO_2 nanorods (NRs)

The synthesis carried out using a standard Schlenk line setup. Organic-capped anatase TiO_2 NRs with an average diameter of 3–4 nm and a mean length of 25–30 nm were obtained by TMAO-catalyzed hydrolysis of TTIP in OLAC acting as both solvent and stabilizing ligand.[41] In a typical synthesis, 15 mmol of TTIP dissolved in 70 g of degassed OLAC was reacted with 4 mL of an aqueous 2 M TMAO solution at 100 °C for 70 h under ambient atmosphere in a close vessel. The NRs were separated from their growing mixture upon 2-propanol addition and were subsequently subjected to repeated purification cycles of re-dispersion in toluene and precipitation with 2-propanol to wash out unreacted precursor

and excess surfactant molecules. At this point, the NRs were provided with a fresh OLAC capping layer by a ligand-exchange procedure, which involved stirring the NRs for 12 h at 80 °C in OLAC under N_2 atmosphere. Finally, the NRs were extracted and purified, as described above. An optically clear TiO_2 stock dispersion in toluene was prepared, whose concentration was determined by inductively coupled plasma atomic emission (ICP-AES) measurements performed with a Varian Vista AX spectrometer.

Fabrication of TiO_2 NR based thin film coatings

Before use, the Si substrates (1 cm^2) were immersed into 2-propanol for 10 min, then repeatedly rinsed with acetone, and, finally, dried with a nitrogen flow. A 500-μL volume of a 0.1 M TiO_2 NR stock dispersion was uniformly spread onto the surface of liquid water that half-filled a 250-mL beaker. After the organic solvent was evaporated, a slightly opaque floating TiO_2 film could be recognized on the water surface. At this point, the substrate was gently dipped into the solution and subsequently withdrawn at a rate of $\sim$1 cm min^{-1}. This sequence was repeated a few times (up to five), as needed. Finally, the TiO_2–covered substrates were dried with a gentle nitrogen flow and kept under vacuum for 3 h prior to further use in the irradiation/storage experiments (see below). The thickness of the coating films was typically less than 0.5 μm, as measured by a profilometer (Alpha-Step 500, Tencor Instruments).

Characterization of the films

The size-morphological characterization of as-prepared NRs were routinely checked by low-resolution transmission electron microscopy (TEM) analysis performed with a Jeol Jem 1011 microscope operating at an accelerating voltage of 100 kV. The TiO_2 NR coatings deposited onto silicon substrates were imaged by scanning transmission microscopy (SEM) inspection carried out with FEI Nova NanoSEM 200 instrument operating in high-resolution mode at accelerating voltage 5 kV.

The surface chemistry of the films was investigated by Fourier transform infrared spectroscopy (FT-IR) measurements in the 4000–400 cm^{-1} spectral range, which were carried out on TiO_2-coated silicon substrates using a Bruker Equinox 70 FT-IR apparatus in transmission mode at a resolution of 4 cm^{-1}. To compensate for possible changes in the positioning of the samples as well as in the thickness of the films, all the spectra were normalized to the TiO_2 absorption at 800 cm^{-1}, which was previously verified to be insensitive to any UV or post-UV storage treatments.[38,39] A peak deconvolution procedure was applied to the spectra using the Levenberg–Marquardt method, as described previously.[38] The accuracy of the fit was estimated by the goodness-of-fit statistical indicator of the software.

The wettability of the TiO_2 films was evaluated by water contact angle (WCA) measurements performed by the sessile drop method using a CAM200-KSV instrument (equipped with a digital camera for taking magnified images of the microdroplets). The tests were typically conducted by dispensing the droplets of bidistilled water (3 μL) by means of a microsyringe. For each sample, the contact angle value was obtained as an average of 5 measurements recorded on different neighbouring surface locations on the basis of shape analysis performed by a CAM200-KSV software.

Irradiation/storage experiments

To induce hydrophilicity, the TiO_2 coatings were irradiated with the third harmonic wavelength (355 nm) of a pulsed Nd:YAG laser, with a pulse duration of 3 ns, a repetition rate of 10 Hz, and fluence of 7 mJ cm^{-2} (measured by a Tektronik oscilloscope coupled with an energy meter). The laser spot had a 0.5 cm diameter and was always positioned in the center of the substrate slides to allow for the reproducible identification of the illuminated area. The total duration of the UV irradiation experiments was 120 min, corresponding to 72 000 laser pulses, and hence, to an actual interaction time of UV photons with the TiO_2 samples of only 0.216 ms.[38]

After UV irradiation, the TiO_2 films were subjected to different sets of storage conditions/stimulation, as follows: (i) storage in the dark under ambient environment (with relative humidity of 30–40%); (ii) heating in the dark by contacting the underlying Si substrate with a hot plate kept at 50–150 °C; (iii) irradiation of the film surfaces with laser pulses at λ_{ex} = 532 nm and λ_{ex} = 1064 nm (with repetition rate = 10 Hz, total fluence = 15 mJ cm^{-2}) using simultaneously the second and the first harmonics of a Nd-YAG laser; (iv) sample storage under vacuum at a pressure of 3×10^{-3} mbar achieved by a rotary pump. Conditions (ii)–(iv) were hold for 40 h, following which further storage was allowed under ambient dark.

3. Results

3.1 Morphological characterization of the TiO_2 films

In this work, we have carefully examined the wetting behaviour of TiO_2 NR thin-films with UV-switchable hydrophilicity. In order to circumvent extra wettability effects induced by micron-size structuring[40] and, hence, to simplify rationalization of the detectable effects, we have considered TiO_2 coatings with nanometer-scale roughness realized on flat silicon substrates. To this aim, OLAC-capped anatase (tetragonal) TiO_2 NRs have been synthesized by a low-temperature base-catalyzed hydrolysis of titanium tetra-isopropoxide in OLAC as both solvent and promoter of anisotropic growth.[41] The representative low-magnification TEM image in Fig. 1a demonstrates that the NRs actually consist of uniformly sized and shaped nanocrystals with a rod-like profile and average short-/long-axis dimensions of $\sim$3 nm/$\sim$25 nm, respectively. Prior to their utilization in film fabrication, the as-prepared NRs have been provided with fresh OLAC capping by means of a ligand-exchange procedure carried out under inert atmosphere, which allows the inner –C═C– double to be preserved from possible oxidative damages.[47–48] TiO_2 coatings (typically $\sim$300–500 nm in thickness) made of NRs arranged in laterally close-packed assemblies have been fabricated at room temperature by transferring NR films floating at a water/air interface to Si substrates by a sequential dipping/withdrawal procedure carried out at controlled rate. The representative SEM overview in Fig. 1b

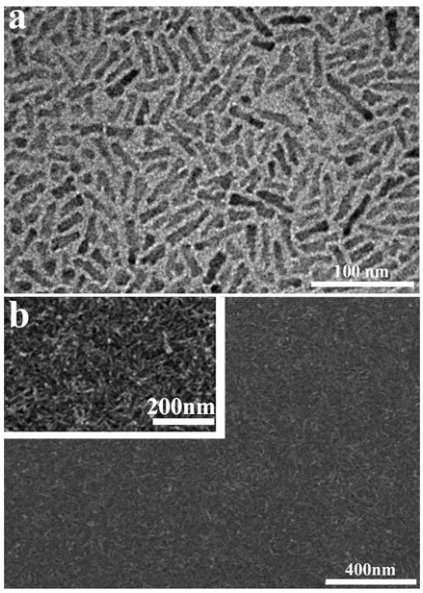

Fig. 1 (a) Low-magnification TEM image of the as-synthesized TiO_2 nanorods (NRs). (b) SEM overview at different magnifications of a typical TiO_2 NR film on a silicon substrate.

shows that continuous, crack-free compact NR films are achieved on the substrates over areas as large as several squared micrometers without formation of micron-sized aggregates.

3.2 WCA characterization

In order to induce hydrophilicity, the TiO_2-coated substrates have been excited with laser pulses at λ_{ex} = 355 nm for 120 min, corresponding to a net photon-TiO_2 interaction time of 0.216 ms. The employed irradiation wavelength guarantees maximized absorption by the TiO_2 component, while the low repetition rate ensures negligible heat production within the films.[38] Fig. 2 summarizes the typical evolution of the WCA values for samples subjected to UV irradiation/storage cycles. The as-prepared TiO_2 NR coatings display a WCA of about $\sim$100° (Fig. 2b) that is considerably higher than the values reported in literature for both polycrystalline TiO_2 films and single-crystalline surfaces (50–60°).[3,15–34] Such an elevated degree of hydrophobicity is ascribable to the synergistic contributions from the nonpolar character of the OLAC molecules capping individual NRs and from the nanometer-scale roughness of the film surface, which is naturally imparted by the attained organization of the NR building blocks in compact multilayers lying approximately parallel to the substrate underneath (*cf.* Fig. 1b).[38,39] Pulsed UV irradiation for 120 min is sufficient to convert the wettability of the substrates to a very hydrophilic state featured by a WCA close to less than $\sim$20° (Fig. 2b).[38–40] The post-UV wettability changes exhibited by the films have been then monitored by applying the following sets of storage conditions/stimulation for 40 h, while taking the corresponding recovery kinetics under ambient laboratory environment in the dark as a reference:

(a) sample storage under vacuum;

(b) heating by contacting the underlying Si substrate with a hot plate (as a representative case of study, we report on the results of heating at 100 °C, *i.e.*, close to the boiling point of water);

(c) irradiation of the film surfaces with laser pulses at λ_{ex} = 532 nm and λ_{ex} = 1064 nm (such double-wavelength illumination conditions was selected in order to mimic qualitatively the irradiation regime used in previously reported light-assisted recovery experiments).[35]

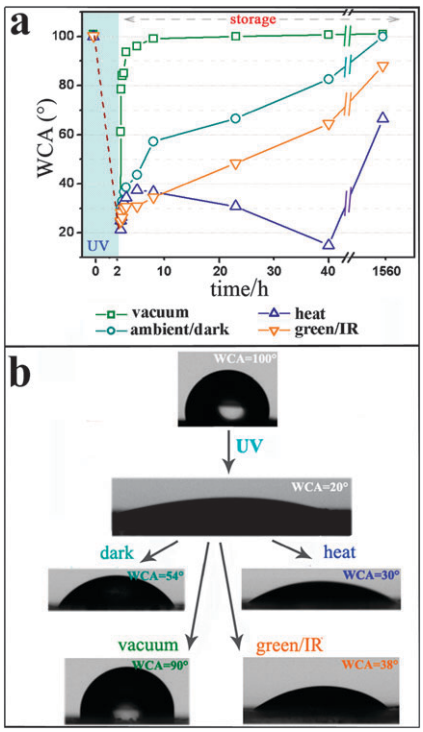

Fig. 2 (a) Water contact angle (WCA) measurements performed on distinct TiO_2 NR film samples at scheduled time intervals following pulsed UV irradiation and prolonged storage under: (i) ambient laboratory atmosphere in the dark; (ii) vacuum; (iii) hot-plate heating; (iv) green/IR laser irradiation. Conditions (ii)–(iv) were kept for 40 h, following which further storage was allowed under ambient dark conditions. (b) Optical images of a water droplet in contact with TiO_2 NR films before UV irradiation, and after UV irradiation followed by 5 h storage under different conditions.

The comparative overview in Fig. 2a highlights that the wettability changes exhibited by the NR films after their UV-induced hydrophilicization depend strongly on the specific storage conditions applied. From the collected data, it clearly emerges that the WCA increases abruptly only upon vacuum application. For example, it can be appreciated that the coatings kept under vacuum exhibit an increase in the WCA up to about 60° in less than 1 h. In contrast, a similar wetting status is achieved after $\sim$14 h, $\sim$35 h, or $\sim$1500 h for films stored in the dark, or subjected to green/IR irradiation or heating, followed by dark storage, respectively. Vacuum storage ultimately allows complete recuperation of the pristine pre-UV hydrophobicity in about 5 h, after which no further changes can be noticed (Fig. 2b). As opposed, the dehydrophilicization process proceeds at a remarkably slower rate with all of the other alternative methods (Fig. 2a). In particular, while only a slight variation in the slope of the time-dependent wettability curves is identifiable at around 6–10 h both for the

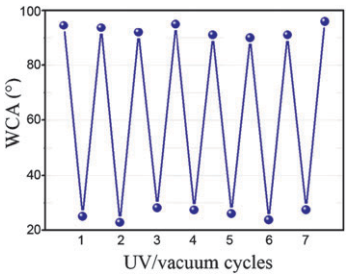

Fig. 3 Reversible wettability changes of TiO_2 NR coatings during cyclic alternations of 120 min pulsed UV illumination and 5 h storage in vacuum the repeated UV-vacuum storage. No significant fatigue can be noted.

green/IR treated and the naturally stored samples, the use of heating leads to a more complex three-stage behaviour. Actually, the WCA slightly increases during the first 3–5 h, after which it steadily declines approaching a hydrophilic degree even slightly higher than that observed after UV irradiation (WCA $\approx$ 15° at $\sim$40 h). Subsequently, a renewed WCA increase is detected. As a matter of fact, it is observable that the full hydrophobicity recovery (*i.e.*, WCA $\sim$100°) is reached after a period as long as 1560 h (65 days) exclusively under dark ambient conditions, whereas only partial recuperation is ultimately achieved by assisting the initial 40 h storage with green/IR or heat (WCA $\approx$ 90 °C and $\approx$65°, in the respective cases).

For the specific type of colloidal TiO_2 films investigated here, it appears clear that application of post-UV vacuum is an extremely efficient strategy permitting fast and full recovery of the original wettability responses. In order to check the suitability of such systems for practical applications, the repeatability of the switchable WCA values TiO_2 has been examined. Fig. 3 demonstrates that the process of hydrophilicization/hydrophobicization within the $\sim$100°–20° WCA interval can be safely carried out over several cycles of alternating 120 min pulsed UV irradiation and vacuum storage periods as short as 5 h (*cf.* Fig. 2). The data prove that the NR coatings indeed exhibit excellent reversibility in their wettability properties without being detrimentally affected by any apparent fatigue, as similarly assessed for samples that are allowed to recuperate (although comparatively more slowly) under dark ambient conditions.[38–40] In contrast, corresponding repeatability assessment experiments, in which the post-UV recovery was assisted by either green/IR or hot plate heating showed progressive attenuation of the ultimate wettability excursions with increasing the number of cycles (data not shown), which actually suggests the occurrence of irreversible degradation phenomena under such storage modes.

3.3 FT-IR characterization

In order to elucidate the mechanism responsible for the diverse recovery dynamics, the temporal evolution of the main vibrational modes associated with the organic components TiO_2 NR films have been monitored by means of FT-IR spectroscopy over 40 h of post-UV storage. At the end of such periods (*cf.* Fig. 2), the vacuum-treated films have reverted back to the initial WCA $\approx$ 100° since long, the sample stored under ambient conditions and subjected to green/IR stimulation have attained only partial WCA restoration to $\approx$83° and 65°, respectively, whereas the heated samples have instead become more hydrophilic with WCA $\approx$ 15°. The results are summarized in Fig. 4, in which the evolution of the full FT-IR spectra is reported, and in Fig. 5, in which the relative time-dependent changes of the most informative sets of stretching (ν) and bending (δ) vibrations, obtained by peak deconvolution analysis, are shown (note that, in order to allow for a comparative evaluation, the peak areas relative to the O–H vibrations in Fig. 4a–b were normalized to their respective values recorded *immediately after* UV irradiation, while the peak areas relative to the C–H vibrations in Fig. 4c were normalized to their respective initial values *prior to* UV irradiation).

In the 3600–1000 cm^{-1} interval, the as-prepared (*i.e.* unirradiated) TiO_2 NR films (black traces in all of the panels of Fig. 4) show the characteristic bands of OLAC molecules bound to the surface of the NRs,[38] including the olefinic and methyl/methylene groups in the alkyl chain (with ν(=C–H) at $\sim$3005 cm^{-1} and $\nu(CH_3/CH_2)$ between 2900–2800 cm^{-1}, respectively), carboxylate anions of OLAC coordinated to surface Ti atoms in chelating bidentate binding mode (a double band peaking at $\nu(-CO_2^-) \approx$ 1520 and $\approx$1430 cm^{-1}, respectively), carbonyl moieties of protonated carboxylic heads of OLAC, which form unidendate surface complexes *via* their alkyl oxygen atom (ν(C=O) $\approx$ 1710 cm^{-1}). The broad and weak stretching band of hydroxyl groups at ν(O–H)=3600–2800 cm^{-1} suggests that a few titanol groups, TiO–H (commonly referred to as dissociatively adsorbed H_2O) and/or molecularly physisorbed H_2O already contaminate the NR surface.[41] The broad featureless ν(Ti–O) signature of the TiO_2 lattice vibrations can be clearly observed below $\sim$1000 cm^{-1}. Taken together, these FT-IR analyses are fully consistent with the fact that the colloidal NRs composing the films are individually enwrapped within a surface shell of OLAC molecules that are directly anchored to the exposed TiO_2 facets *via* their carboxylic heads while exposing the alkyl chains outwards. Such surfactant surface protection on the NR building blocks attributes a pronounced hydrophobic character to films, as authenticated by a WCA value of the order of $\sim$100° (Fig. 2).[38]

Following pulsed UV-treatment the films attain a generally higher degree of the TiO_2 surface hydroxylation that is corroborated by a considerable increase in the ν(O–H) vibrations due to the convoluted contributions from growing TiO–H species and physisorbed H_2O at $\sim$3400 cm^{-1} and $\sim$3200 cm^{-1}, respectively (*cf.* light blue traces in Fig. 4 and Fig. 5a–b). The latter attributions are in agreement with the strong enhancement of the δ(O–H) vibration at $\sim$1640 cm^{-1} which is indeed a signature of the presence of molecularly adsorbed (*i.e.*, undissociated) H_2O (Fig. 4). Concomitantly, the UV irradiation causes a moderate attenuation for the ν(C–H) and $\nu(CO_2^-)$ bands of the OLAC ligands (*cf.* Fig. 4 and Fig. 5c). As a coherent macroscopic result of a renovated surface environment embodying a rich density of O–H species and OLAC ligands, the UV-irradiated TiO_2 films exhibit a highly hydrophilic state featured by WCA as low as 20° (Fig. 2).

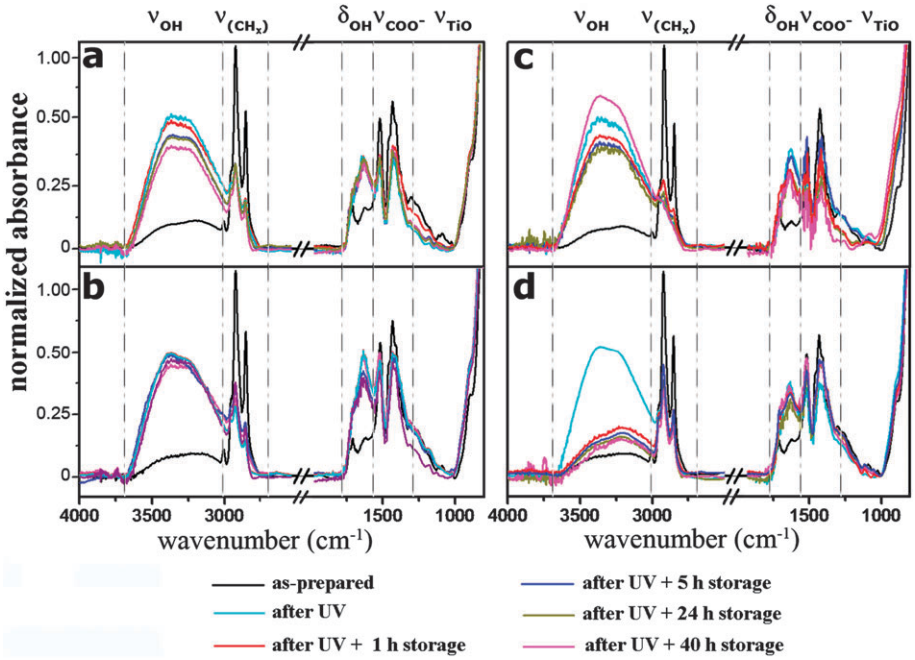

Fig. 4 FT-IR time evolution of the surface chemistry of distinct TiO_2 NR films after 120 min pulsed UV irradiation and varying storage periods under different conditions: (a) under ambient laboratory atmosphere in the dark; (b) under pulsed green/IR laser irradiation; (c) on a hot plate heated up to 100 °C; (d) under vacuum produced by a rotary pump. To compensate for possible changes in the positioning of the samples as well as in the thickness of the films, all the spectra were normalized to the TiO_2 absorption at 800 cm^{-1}.

Comparative examination of the time-dependent data in Fig. 4 and Fig. 5 reveals that the investigated storage conditions impact on the evolution of the film chemistry to a strongly variable extent. As for what concerns the spectral evolution associated with the samples subjected to either ambient storage and vacuum treatment, it is noted that the most prominent alterations in ν(O–H) and δ(O–H) bands (of the order of 80% and 20%, respectively) occur over the first 10 h of storage, along with moderate enhancement in C–H vibrations of the OLAC ligands (by 25% and 5%, respectively), after which further evolution occurs steadily, although at reduced rate. The minor non-monotonic changes in the $\nu(CO_2^-)$ features could be presumably ascribed to rearrangements of the binding configuration of carboxylic heads on the TiO_2 surfaces.[38]

By comparison, the application of green/IR irradiation to the hydrophilized is accompanied by a slower ν(O–H)/δ(O–H) removal process and almost negligible ν(C–H) recuperation (Fig. 5).

In the case of the heat-assisted recovery, the vibrational bands do not follow any monotonic behaviour. Actually, the ν(O–H)/δ(O–H) intensities decrease during the first 20 h by about 40%, reaching a minimum, after which they even recuperate to value obtained immediately after UV irradiation (Fig. 5a–b). Concomitantly, minor ν(C–H) recuperation (by less than 5%) takes place over the first 20 h, after which the related signals are permanently depressed well below the intensity level attained immediately after the UV irradiation (Fig. 5c).

Finally, it deserves emphasizing that control experiments carried out on unirradiated NR films have not evidenced any significant variations in their WCA and/or in the associate vibrational features after being subjected to either of the concerned storage conditions. In addition UV-hydrophilicization/storage experiments conducted on organic-free TiO_2 NR films (from which the OLAC coating has been photocatalytically removed under continuous illumination with a conventional cw 500 W Xe lamp[38]) have not been accompanied by emergence of any detectable ν(C–H)/$\nu(CO_2^-)$ signals over time. These facts discredit the hypothesis that the inherent wettability and/or the surface features of the as-prepared NR films could be modified upon adsorption/desorption of atmospheric hydrocarbon and/or water.

4. Discussion

Upon pulsed UV irradiation, the TiO_2 NR coatings can convert from a highly hydrophobic to a highly hydrophilic state, a transition that is accompanied by an increased degree of TiO_2 surface hydroxylation. On the other side, except for the heat-treated samples, the recovery behaviour of the film hydrophobicity, as marked by corresponding variations in the WCA values (*cf.* Fig. 2 and Fig. 4,5), generally correlates well with a gradual abatement of the O–H signals (which indicates progressive dehydroxylation), concomitant to slow recuperation of the C–H bands.

In particular, it emerges that the spectral evolution associated with the samples subjected to either ambient storage and vacuum treatment closely adheres to an inverted behaviour as compared to that observed during the forward UV-driven hydrophilicization. The latter observations allow us to deduce that the UV-driven wetting properties of the TiO_2 films that are reversed either naturally or under vacuum storage should be directly traced back to the flexible, concerted

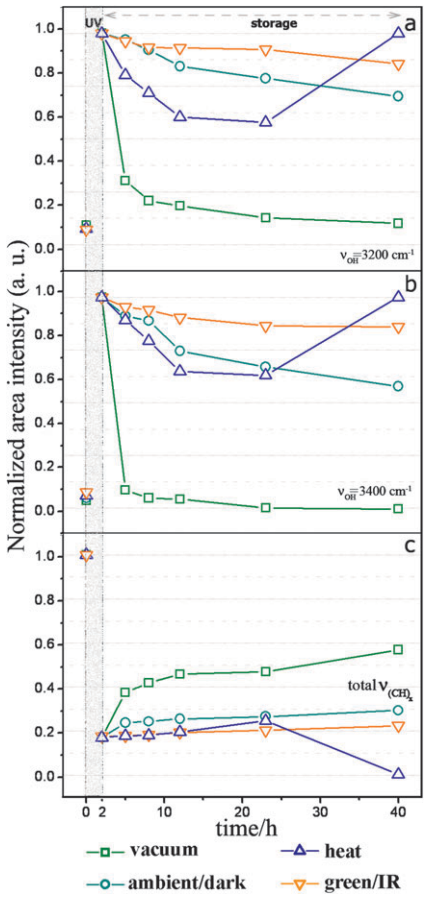

Fig. 5 Temporal evolution of the peak area for relevant vibrations: O–H stretching at 3200 cm^{-1} (a) and 3400 cm^{-1} (b), respectively; total C–H stretching bands at 2960 cm^{-1}, 2920 cm^{-1} and 2860 cm^{-1} (c), respectively, determined by Levenberg–Marquadt deconvolution analysis of FT-IR spectra recorded at scheduled time intervals (as shown in Fig. 4). The peak areas relative to the O–H vibrations in panels (a)–(b) were normalized to their respective values recorded *immediately after* UV irradiation, while the peak area values relative to the C–H vibrations in panel (c) were normalized to their respective initial values *prior to* UV irradiation.

changes in the polar and nonpolar components of the TiO_2 surface chemistry, as pointed out earlier.[38] On the other side, the finding that the original hydrophobicity of the samples can be ultimately recovered upon removal of O–H species despite the intensity of the C–H bands is not fully recuperated, supports our previously proposed mechanistic picture, according to which the surfactants could indeed respond to the hydroxylation/dehydroxylation processes by rearranging conformationally without being necessarily degraded.[38]

Similar arguments can be invoked to interpret the effects of green/IR light in assisting the post-UV recovery period. Under these circumstances, the slower ν(O–H)/δ(O–H) removal process and almost negligible ν(C–H) recuperation can be correlated with the observable decelerated dehydrophilicization and the incomplete recovery of the pre-UV hydrophobicity degree (Fig. 2). This finding therefore suggests that the extended lifetime of the hydrophilic state upon green/IR irradiation results from the TiO_2 surfaces retaining a moderately high polar character while also undergoing partial deactivation/elimination of the nonpolar components.

Differently, the impact of heating appears to be less straightforward to rationalize, as the associate vibrational band changes follow a non-monotonic three-phase behaviour. Among the various observations reported, the fact that the ν(C–H) signal intensity is decreased well below the post-UV value in spite of minor recuperation in the first 20 h of storage (Fig. 5c), clearly points to irreversible loss of nonpolar surface species. Such loss can account for the trend toward enhanced hydrophilicity which culminates at 40 h storage with WCA $< 15^\circ$ that is even lower than the value induced by UV treatment itself. Additionally, it is noted that the sole convolution of the time-dependent changes of the polar and nonpolar components of the surfaces does not satisfactorily fit to three-phase changing behaviour of the WCA. Major discrepancies can be identified at the latest storage stages ($\gg$40 h), at which renovated dominance of the O–H species coincides with hydrophobicity recuperation up to WCA $\approx 60^\circ$. Such unusual behaviour is likely to originate from structural heat-induced modifications in the TiO_2 films taking place along OLAC removal, such as reorganization of the NR packing mode and/or introduction of different surface geometries, which could complicate the ultimate wetting behaviour due to transition though diverse wetting regimes.[1,2,40]

The detailed pathways the hydrophilicization/dehydrophilicization processes underlying the investigated wettability changes deserve further discussion. Our experiments are mostly consistent with previous mechanistic explanations.[3,15–17,19–21] Band-gap TiO_2 photoexcitation would induce formation of oxygen vacancies on TiO_2 surfaces, at which ambient H_2O could compete kinetically with O_2 for adsorption, eventually dissociating into TiO–H groups. As ligand coverage on colloidal nanocrystals is usually incomplete, the NRs can be expected to carry surfactant-free surface regions of nanometer-scale extension. Such domains are believed to serve as a primary ground for molecular and/or dissociative adsorption of atmospheric H_2O, thereby initiating TiO_2 hydrophilicization.[38] An increasing density of such newly introduced O–H species could, in turn, promote adhesion of H_2O multilayers, leading to the formation of highly hydrophilic surface regions on the NR facets. Overall, UV irradiation would produce an alternating distribution of nanoscale surface region with either hydrophilic (related to the newly implanted O–H moities) or hydrophobic character (associated with surfactant-passivated areas of the NRs) throughout the porous NR films, which could give rise to a two- and three-dimensional nanocapillary infiltration effect, allowing water droplets to spread out over the TiO_2 coatings.[15,16,38]

As a matter of fact, OH-healed TiO_2 surfaces are known to be metastable. Therefore, it can be easily understood that, with the lack of oxygen vacancies being continuously regenerated exclusively under UV illumination, O_2 substitution for the previously implanted O–H moieties, which is indeed thermodynamically favoured, can dominate over H_2O adsorption during prolonged periods of air storage in the dark. Back-reconstruction proceeds at a comparatively faster rate in the initial period of dark storage, after which further relaxation is slowed down, indicating that the recovery kinetics depends on

the actual density of O–H moieties. Overall, establishment of the new near-equilibrium conditions at the TiO_2 surface is an extremely slow process, which could be in fact facilitated only supplying extra doses of O_2 under an artificially adjusted atmosphere.[21]

On the other hand, the temporary nature that characterizes the intensity alterations in the OLAC bands under natural storage conditions cannot be explained by the occurrence of irreversible photocatalytic degradation and/or abstraction of the capping OLAC shell, but most likely arises from the bound surfactants undergoing conformational changes in response to surface hydroxylation/dehydroxylation events.[38–40] Actually, substantial geometric rearrangements can be expected to lead to alterations in the characteristic intensity and frequency of their vibrational modes.[42–44] Changes in NR-to-NR hydrophobic interactions could, in turn, affect the back-conformational rearrangements in the dark, so that the vibrational behaviour that accompanies the forward and reverse processes may differ to some extent. Regardless of this, such a mechanism implies preservation of the nonpolar surface micro-environment associated with the alkyl chains of OLAC ligands.

The inherent metastability of the OH-healed TiO_2 surfaces is further manifested by the effect of applying vacuum to the hydrophilicized films. In the lack of oxygen at such reduced pressures, the most plausible mechanism that could be operative should involve continuous subtraction of surface bound O–H species from TiO–H, molecularly physisorbed H_2O, and H-bonded H_2O multilayers, in the form of gaseous H_2O and possibly H_2O_2 molecules.[45,46] However, vacuum-driven O–H removal may not necessarily result in formation of surface oxygen vacancies similar to those primarily induced by the forward UV photocorrosion. In fact, under such circumstances highly reactive surfaces would be produced, which could be expected to be susceptible to be suddenly hydroxylated again once put in contact with the ambient pressure atmosphere. However, the attained increase in WCA remains stable, therefore indicating that any hydroxylation is disfavoured on such vacuum-reconstructed surfaces.

For durable and reversibly switchable wettability to be achieved between hydrophobic/hydrophilic extremes, dynamic changes in the degree of TiO_2 hydroxylation, on one side, and preservation of the alkyl chains of the OLAC ligands, on the other side, should be ensured throughout a number of alternating UV/storage cycles. It has been previously established that the selective, pulsed UV irradiation conditions employed in our experiments meet both requirements in the forward UV-driven hydrophilicization stage.[38] The present experimental data demonstrate that vacuum application allows the pre-UV hydrophobicity state to be recovered by reverting back the UV-altered polar and nonpolar components of the TiO_2 surface chemistry to their original conditions. Although a similar reversible wettability can be observed upon storage under natural ambient conditions, however the overall vacuum-driven dehydrophilicization demonstrates to be a $\sim$250-times faster process.

The slower and incomplete wettability recovery under either green/IR illumination or heating should be related to the induced stimulation of vibrational modes of both the TiO_2 lattice and of OLAC surfactants. This could lead to two main effects. First, OLAC ligands may be driven to take configurations hindering the OH/H_2O desorption from the TiO_2 surface, thus imposing a hydrophilic character for a longer time. Second, some photodegradation pathways can come into play, for example, upon photodesorption and/or rupture of chemical bonds, followed by reaction of the resulting radicals with atmospheric oxygen.[47,48] Consequent depletion of O_2 availability in proximity of the TiO_2 surfaces would further contribute to slow down the dehydroxylation of the OH-healed surfaces. The slow decay of the ν(OH) vibrations under green/IR light, on one side, and their unexpected huge increase after prolonged heating on the other side, can be partly be rationalized on the basis of OLAC degradation into hydroxylated by-products with low molecular weight.[49,50] As highlighted by our data, the impact of direct hot-plate heating appears to be considerably pronounced, likely due to the broader spectrum of excitable vibrations, as compared to what can be achieved by the wavelength-selective green/IR stimulation. Actually, the susceptibility of the OLAC capping to be photo-oxidized is dramatically accentuated under the former circumstances.

5. Conclusions

We have examined the wettability evolution of compact TiO_2 thin films made of surfactant-capped nanocrystals, which can convert from a highly hydrophobic state to a highly hydrophilic and metastable one under UV irradiation. Combined FT-IR and WCA investigations have provided detailed mechanistic information on the impact of post-UV storage on the properties of such types of films. It has been understood that achieving switchability between extreme wettability excursions as well as long-term repeatability of such changes requires dynamic modifications in the polar and nonpolar components of the TiO_2 films, which are related to newly introduced OH moieties, on one side, and to alkyl chains of the capping molecules, on the other side. The relevant roles played by such pre-existing organic components explain why the responses of the as-hydrophilicized films to either visible/IR or heat stimulation diverge significantly from those reported for conventional organic-free polycrystalline TiO_2 surfaces.[21,32–35] The application of moderate vacuum is found to be an effective tool to accelerate the post-UV hydrophilic-to-hydrophobic conversion, thereby enabling cyclic hydrophilicization/hydrophobicization alternation without any detrimental fatigue.

Overall, the present study further highlights that largely varying mechanisms can concur to determine the ultimate TiO_2 wetting switchability, the relative extent of which can be expected to depend on the specific features of the concerned surfaces and on the particular irradiation/storage conditions applied. Our findings may be useful to suggest additional criteria to engineer light-responsive, TiO_2-based organic-inorganic functional surfaces with controllable wettability properties for tailored applications, *e.g.* in microfluidics.

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