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Dark Photocatalysis

Voltage-Induced Payload Release and Wettability Control on TiO_2 and TiO_2 Nanotubes**

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Since the first report of Fujishima and Honda in 1972,[1] the outstanding photocatalytic properties of TiO_2 have built the basis for over 5000 publications[2–4] targeting fundamental aspects and applications, such as photoinduced water splitting,[5,6] self-cleaning,[7] and organic pollutant degradation.[3] Most recently, the development of high-aspect-ratio self-organized TiO_2 nanotube layers[8] has even further widened the use of TiO_2 as a very efficient catalyst system[9] that provides a highly defined three-dimensional nanoarchitecture. Some interesting applications of photocatalysis are based on the scission of organic monolayers attached to the TiO_2 surface. For example, we recently reported the photoinduced cut of organic monolayers on TiO_2 nanotubes for a precise adjustment of the surface wettability[10,11] and for controlled drug release.[12,13] The underlying principle of all these photocatalytic reactions is that UV light produces electron–hole pairs in the semiconductive TiO_2. The generated charge carriers are ejected to the surrounding electrolyte and create highly reactive redox species; namely, valence-band holes (h^+) transferred to water electrolytes have a sufficient energy to produce $OH^{\bullet}$ radicals. These radicals can be used to trigger chain scission in attached hydrocarbon chains, and thus liberate terminal payloads.

Herein we show that a pseudo photocatalytic reaction, and in particular chain scission, can be initiated in the absence of light by using an applied voltage that is expected to lead to valence-band hole generation. This may be achieved for sufficiently doped semiconductors under depletion conditions if a bias voltage is applied that is larger than the band gap.[14–17] Such voltage-induced carrier generation has been reported for silicon, where it was exploited for electrochemical etching or metal deposition reactions.[14,15] To transfer the principle to TiO_2 layers, a requirement is that a sufficiently defined and highly doped semiconductive nature of the material can be established (10^{18}–10^{19} cm^{-3}).[16] For this we used anodically formed TiO_2 nanotube layers (and for reference anodically formed compact layers) that were annealed to an anatase structure with a doping level of approximately 1.0×10^{19} cm^{-3}.[18] Onto these TiO_2 structures we either grafted OPDA (octadecylphosphonic acid) for wettability control experiments, or attached an enzyme, namely horseradish peroxidase (HRP), via a vitamin C linker to demonstrate payload release. Details on sample preparation and characterization are given in the Supporting Information. With these samples, voltage-induced chain scission experiments were carried out in the dark at different anodic voltages in two- and three-electrode electrochemical cells.

Figure 1 shows an example for OPDA grafted on a TiO_2 surface. For OPDA-modified TiO_2 nanotube surfaces, a superhydrophobic wetting behavior is obtained (Figure 1 b; non-modified TiO_2 nanotube surfaces are superhydrophilic).[10,11] By immersing the superhydrophobic samples in an aqueous electrolyte and applying a sufficient anodic polarization, significant alterations in the contact angle can be triggered (Figure 1 b). The voltage has to be sufficiently anodic (more than 3 $V_{Ag/AgCl}$) to obtain a significant effect. To properly study voltage-induced surface chemistry alterations by XPS, we additionally carried out similar experiments on OPDA-grafted flat (compact) TiO_2 surfaces (Figure 1 c). To show how crucial the electronic properties and crystallinity of TiO_2 are to successfully trigger the reaction, we carried out identical experiments on an amorphous TiO_2 surface. From

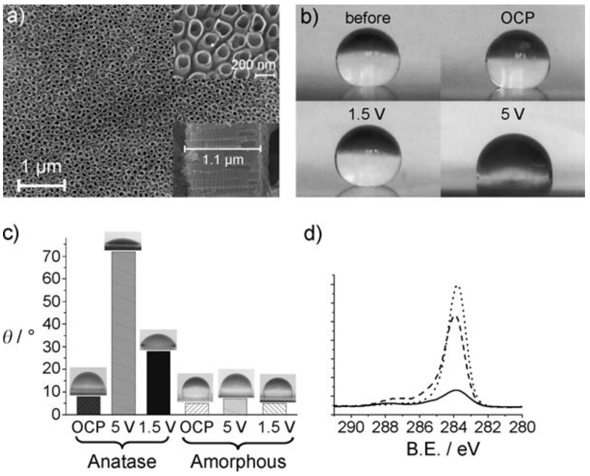

Figure 1. Wettability control. a) SEM images of the TiO_2 nanotube layers used in this work (top inset: closer view, lower inset: side view). b) Optical images of a water droplet on anatase TiO_2 nanotube layers modified with OPDA before anodization, at the OCP (open circuit potential), and at 1.5 V and 5 V. A significant change in contact angles can be triggered at above 3 V. c) Contact-angle change on flat anatase and an amorphous TiO_2 surface after applying different voltages on an OPDA monolayer. d) XPS characterization of the C 1s peak for an OPDA-modified flat TiO_2 (anatase) surface (•••••) and after applying difference voltages (----- 1.5 V, —— 5 V). B.E.: binding energy.

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the results in Figure 1 c, it can be seen that contact angles can be altered strongly for voltages of over 3 V if we use anatase TiO_2 surfaces, whereas hardly any change occurs on an amorphous TiO_2 surfaces, regardless of the applied voltage. This effect may be ascribed to the different state distribution in amorphous materials. XPS analysis of all the samples before and after the experiments strongly support the concept of a voltage-induced chain scission. Figure 1 d shows the C 1s peak for the flat anatase surface after holding the surface at different voltages (the XPS peaks for O 1s, Ti 2p, and P 2p are shown in the Supporting Information). The results demonstrate that for voltages of more than 3 V, a strong loss of the C 1s signal is obtained, whilst the area of the P signal remains nearly unchanged and the substrate Ti and O peaks increase. This indicates that the phosphonate monolayer is cut, leaving the phosphate head group still attached to TiO_2, which is entirely in line with findings commonly observed for photocatalytic chain scission.[10–13] The XPS results for the amorphous layers (Supporting Information, Figure S4) indeed show that for these layers, no chain scission could be observed. In other words, the findings clearly show that not only a sufficiently high applied voltage is needed, but also a suitable electronic structure of the substrate must be provided to achieve a successful cut of the hydrocarbon chain. To verify that even after longer anodization experiments changes in pH (O_2 evolution) were not affecting the results, additional experiments were carried out (see the Supporting Information).

In Figure 2, it can bee seen that the chain scission principle can be used for voltage-induced payload release. A protein (horseradish peroxidase; HRP) was covalently attached to nanotubes and compact TiO_2 surfaces by a 3-aminopropyltriethoxysilane (APTES)/vitamin C monolayer linker.[19,20] The different TiO_2 layers with the grafted protein were then subjected to different anodic voltages. We took samples of the surrounding electrolyte at regular time intervals and tested for the release of the protein. When liberated, HRP can easily be detected in solution by an enzymatic color reaction (see the Supporting Information).[20] Blue-green coloration of the solution (Figure 2) for a HRP-modified TiO_2 nanotube layer held at 5 V thus indicates the release of the free and functional protein (that is, the color change not only indicates the release of organic species but also shows that the enzyme is still active). Figure 2 b shows solution spectra for the release from tubular and compact TiO_2 anatase layers held at potentials higher and lower than 3 V. If the maximum spectral response at $\lambda = 747$ nm is plotted against time, release kinetics (Figure 2 c) can be obtained. It is clear from Figure 2 that a significant release can only be achieved for voltages of more than 3 V, and that higher release kinetics are achieved for tubular than for flat structures, which is due to the higher surface area and possibly a field amplification effect owing to the curvature at the bottom of the nanotube. The release of the protein was additionally verified by XPS measurements (Supporting Information, Figure S5). The results are again in line with a voltage-induced cut of the linker chain behind the head coupling group for voltages above 3 V.

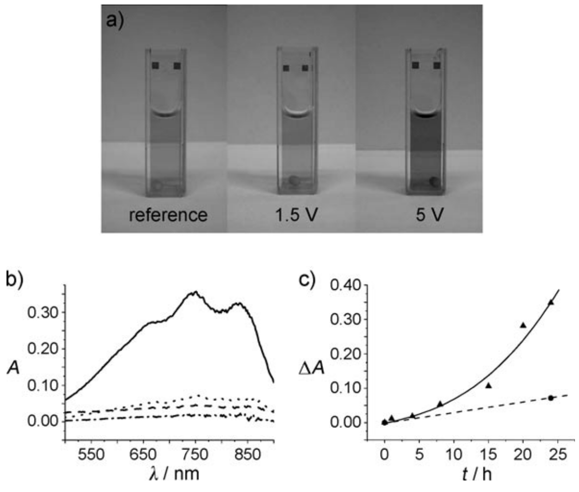

Figure 2. Protein release from a TiO_2 (anatase) surface modified with linked HRP. a) Detection of voltage-induced protein release using an enzymatic color reaction with ABTS and H_2O_2. Cuvettes show reagent for samples taken before HRP release and for HRP-TiO_2 nanotube surfaces after application of 1.5 V and 5 V. b) Spectrophotometric measurement of released HRP: tube, 5 V (——); flat, 5 V (••••); tube, 1.5 V (-----); flat, 1.5 V (–•–•). c) Absorption intensity change at 747 nm (▲ tubes; ● flat) after applying potentials for different times.

To gain more insight into the mechanism of the voltage-induced effect, we performed some additional experiments. In photocatalytic reactions on TiO_2, it is often perceived that $OH^{\bullet}$ radicals are formed that cause the degradation of C_xH_y molecules.[3] To test for $OH^{\bullet}$ radicals, we employed a fluorescence approach based on a terephalic acid (TA) reaction, which is frequently used in photocatalysis investigations.[21,22] The approach is based on a reaction of $OH^{\bullet}$ with TA to form 2-hydroxyterephthalic acid (TAOH), which has a characteristic blue fluorescence. Figure 3 a shows the fluorescence response for a solution of TA after a TiO_2 nanotube sample was held at different voltages for identical time periods. The results clearly indicate the formation of $OH^{\bullet}$ radicals (strong blue fluorescence) for the solution where TiO_2 nanotubes were held at 5 V, whereas virtually no fluorescence can be seen for open-circuit conditions or at a potential of 1.5 V. The fluorescence intensity is plotted as a function of the anodization time in Figure 3 b. With anodization time at a potential of 5 V, the amount of TAOH increases and reaches a high steady value. At lower voltages (< 3 V), even with extended anodization times, hardly any signal can be detected. Considering all these findings, it may thus be postulated that at 5 V, valence-band holes are generated that can react with their environment in a similar manner as photogenerated holes in TiO_2. All the examples in Figures 1–3 demonstrate that a certain threshold voltage has to be overcome to make the mechanism operative. This is in line with polarization curves (Figure 3 c) for a compact TiO_2 anatase layer, in which an onset of significant dark current is observed in a neutral electrolyte at about 2.8–3 $V_{Ag/AgCl}$. Considering that the flat-band potential of anatase TiO_2 in this solution is at about -0.4 $V_{Ag/AgCl}$ (from the Mott–Schottky plot in Figure 3 c), it may be concluded that the onset of current flow coincides with the Fermi level reaching the TiO_2 valence band edge at the surface. As the Fermi level reaches this position, band ionization, that is generation of holes (h^+),

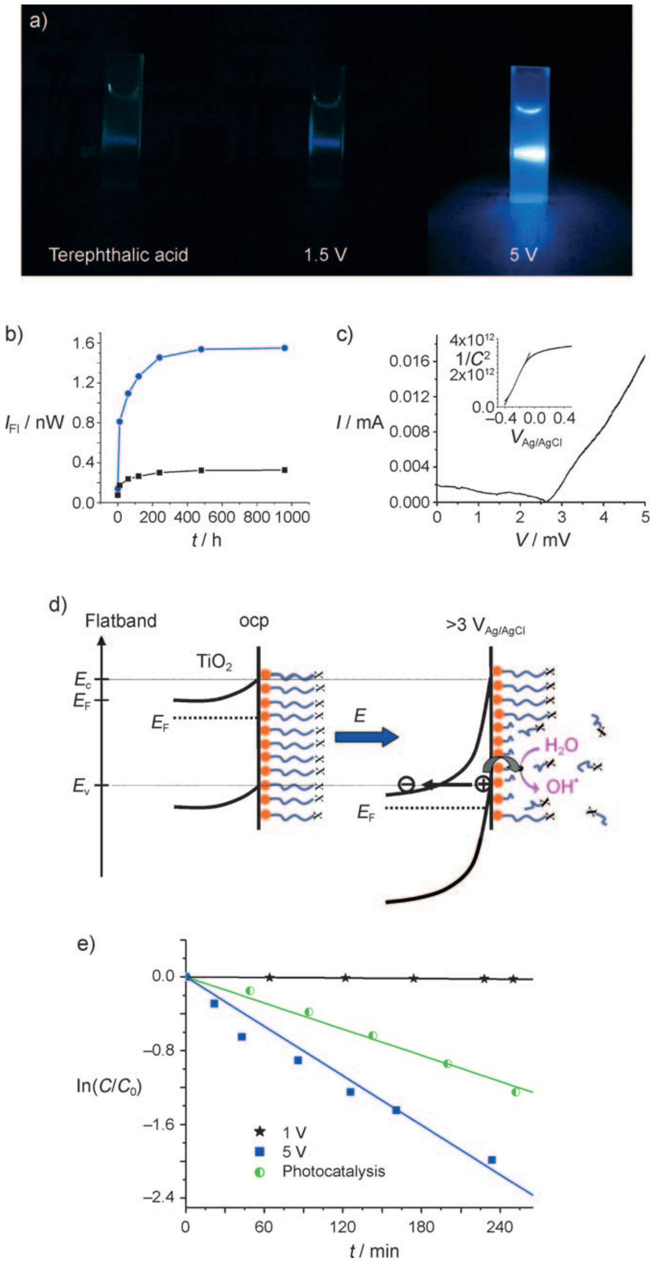

Figure 3. Radical mechanism. a) Fluorescence testing of radical formation by reaction of terephalic acid with anatase TiO_2 nanotubes before voltage application and after 1.5 V and 5 V. (For experimental details, see the Supporting Information). b) Fluorescence intensity as a function of time at 5 V (blue, ●) and 1.5 V (black, ■). c) Polarization curve for a compact anatase layer recorded from 0 to 5 V in 0.1 M Na_2SO_4 electrolyte. Inset: Mott–Schottky plot of compact anatase layers in 1 M Na_2SO_4 recorded with a frequency of 1 KHz. d) Reaction scheme for voltage-induced $OH^{\bullet}$ radical formation and payload release. e) Comparison of classical photocatalytic degradation of model pollutant AO7 (2.5×10^{-5} M + 0.1 M Na_2SO_4) with voltage-induced degradation on a flat anatase TiO_2 surface, showing comparable degradation kinetics.

and Schottky barrier breakdown can take place (Figure 3 d). Such hole generation in combination with tunneling or avalanche breakdown of the Schottky barrier requires comparably high fields to be established in the space-charge layer, otherwise deep depletion conditions may be favored.[17] This may explain why specific conditions (electronic properties) in the TiO_2 layers, typical for annealed TiO_2 anodic films or nanotubes at 450 °C in air,[18] are needed to allow suitable breakdown conditions to be established. For many applications, nanotube surfaces are more efficient than compact thin layers, as they have a high area and thus allow for higher filling capacity or superhydrophobic surfaces, thus making changes over the entire wettability spectrum of 180 °C possible. This principle also works for conventional degradation reactions of model dyes, such as acid orange 7 (AO7).

In summary, we have demonstrated that voltage-induced pseudo photocatalytic processes, and in particular chain scission reactions, can be achieved on TiO_2 surfaces most likely by a valence-band ionization mechanism. TiO_2 nanotubes can be particularly effective owing to their high surface area (high loading capacity) and the feasibility of establishing surface hydrophobic conditions. This can be of considerable practical significance, for example in biomedical, biochip, or microfluidic applications, as not only photocatalytic[3,12,23] but also voltage-induced control of self-cleaning, surface wetting, or payload release processes can be realized, which, in combination with microelectronic devices, may even be preferred.

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