Observation of a photochemical reaction on the TiO$_2$ (110) surface by atomic force microscopy

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A photocatalytic surface reaction—the decomposition of a submonolayer of stearic acid mediated by a rutile TiO$_2$ (110) single crystal—is examined by atomic force microscopy and the results reveal that the reaction occurs at substantially distinct rates at randomly distributed nanoscale surface sites.

The photocatalytic properties of TiO$_2$ are very interesting and are utilised in many situations. For example, ultraviolet irradiation of TiO$_2$ produces an amphiphilic surface with both antifogging and self-cleaning properties.[1–3] TiO$_2$ photocatalytic reactions, like many other surface reactions, have been studied for many years by macroscopic techniques such as vibrational spectroscopy. However, in the last decade, scanning probe techniques such as atomic force microscopy (AFM) have brought new insight on the morphology and molecular structure and periodicity of surfaces. In the present study, we examine the surface reactivity of rutile TiO$_2$ (110) during the photodecomposition of monolayer islands of stearic acid (C$_{17}$H$_{35}$COOH) using the AFM.

The submonolayer film of stearic acid was deposited onto a clean and polished rutile TiO$_2$ (110) single crystal substrate by way of the Langmuir–Blodgett (LB) technique. Film transfer was performed at 15 mN m^{-1} (area $\approx$ 0.201 nm^2 molecule^{-1}) at 20 °C in a clean room. The obtained film was imaged by contact-mode AFM (Seiko Instruments: SPA300 AFM system with a SPI3700 controller) under ambient conditions ($T \approx$ 20 °C, relative humidity = 40%) using a commercially available triangular Si$_3$N$_4$ sharpened cantilever. The force between the tip and sample was typically 1 nN. The UV light source was a Hypercure 200 UV lamp (Yamashita Denso, long wave UV $\lambda_{max} \approx$ 365 nm) equipped with a light guide. Incident UV light intensity (measured using a UV radiometer: Topcon UVR-1) at the sample surface was *ca.* 2.5 mW cm^{-2}. In a typical experiment, the tip was withdrawn from the sample before UV light irradiation. After irradiating for a predetermined period, the light was switched off and the tip re-engaged for image recording. A representative AFM image before irradiation is shown in Fig. 1(a). A notable feature is the perfectly circular nature of the islands. In two-dimensional phase separated systems, circular domains are thermodynamically favourable and are formed as a result of the minimisation of surface energy through a reduction in interfacial length and curvature.[4,5]

The surface morphological changes upon UV light irradiation are depicted in Fig. 1(b)–(e). The reactivity pattern and reaction trends are very intriguing. Fig. 1(b) imaged at 5 min reaction shows the inhomogeneous pitting or etching of the island as stearic acid molecules photodecomposed. Typical hole diameters were in the range of 24 nm to 100 nm, with an average depth of *ca.* 0.9 nm (hole-depth range $\approx$0.0–2.25 nm, *cf.* a fully extended stearic acid molecule[6] has a chain length of $\approx$2.5 nm), corresponding to an estimated 2250 to 40000 stearic acid molecules having undergone photodecomposition, respectively. It should be noted that at this stage of the reaction the organic

film comprises a mixture of adsorbed stearic acid as well as possible oxygenated alkyl intermediate molecules.[7] Likewise, we note that imaging of the island edges at higher resolutions revealed no clear trends in bulk island contraction. An island
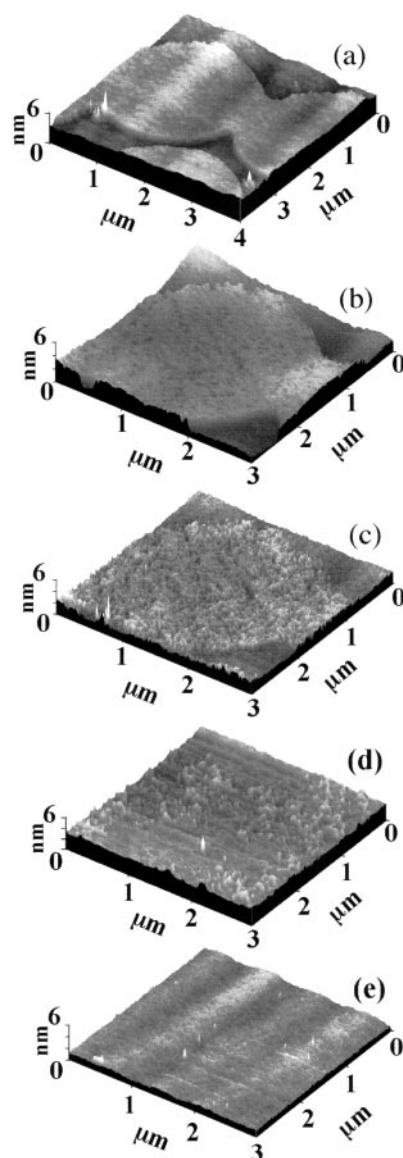

Fig. 1 Sequential 3-D AFM images of the rutile TiO$_2$ (110) mediated photodecomposition of stearic acid islands. Image (a) is 4 × 4 µm in size whereas all the other images are 3 × 3 µm. The images were obtained after: (a) 0, (b) 5, (c) 10, (d) 20, and (e) 60 min of UV light irradiation, respectively. Incident light intensity at the sample surface $\approx$ 2.5 mW cm^{-2}.

contraction scenario would arise if molecules at the edges photodecomposed at a faster rate than those in the interior. However, inhomogeneous decomposition at the edges as well as the interior suggests that the distribution of surface active sites governs surface reactivity. On analysing numerous other islands, we obtained the same randomisation phenomenon. With further irradiation, an even more peculiar reactivity pattern unfolds as depicted in Fig. 1(c) and (d). The surface morphology after irradiating for 10 min reveals a startling merging of holes to generate a mosaic, which eventually disappears with progress of reaction. At 20 min reaction [Fig. 1(d)], the island structure is no longer discernible. Prolonged irradiation resulted in the complete photodecomposition of the stearic acid molecules to CO_2 and H_2O.[8,9] That the reaction goes to completion was corroborated by parallel FT-IR experiments. Further control experiments in which monolayers of stearic acid were deposited onto CaF_2 substrates revealed that TiO_2 is essential for the photodecomposition of stearic acid.

The photodecomposition process is considered to proceed *via* two main oxidative routes, direct hole oxidation and ˙OH oxidation.[10–12] The observed inhomogeneous reactivity pattern appears to mirror the momentary distribution of the surface active sites. Thus, the spatial localisation of the reaction appears to be largely influenced by the nature and composition of the photocatalyst. Spatially localised electrochemical reactions on TiO_2 surfaces have also been observed by scanning electrochemical microscopy.[13,14] In conclusion, this study reveals that a TiO_2 photocatalytic reaction is spatially localised and occurs at different rates at randomly distributed surface sites.

Notes and References

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