Current-less photoreactivity catalyzed by functionalized AFM tips†

Vasiliki Zorbas,‡,§[a] Mandakini Kanungo,§[a] Sukhmine A. Bains,¶[a] Yuanbing Mao,[b]
Tirandai Hemraj-Benny,[b] James A. Misewich[a] and Stanislaus S. Wong*[ab]

Received (in Cambridge, UK) 3rd May 2005, Accepted 7th July 2005
First published as an Advance Article on the web 11th August 2005
DOI: 10.1039/b506110e

A spatially confined photocatalytic oxidation of a thin film of synthetic textile azo dye (Procion Red MX-5B) using TiO_2-functionalized AFM probes is described.

The ability to conduct controlled photochemical reactions in a highly localized region is critical to the field of semiconductor technology. Scanning probe microscopy (SPM) techniques, especially atomic force microscopy (AFM), offer a good prospect towards fulfilment of this goal. Many photochemical reactions utilize titania (TiO_2), which has been considered as components of batteries, photovoltaic cells, pigments, photonics, optoelectronic devices, and gas sensors, partly due to their low cost, chemical stability, and robustness under UV illumination.[1–3]

AFM has been used to monitor the photocatalytic decomposition of octadecyltrichlorosilane based self assembled monolayers[4] on a TiO_2 substrate as well as to investigate the possible bactericidal activity of TiO_2 thin films.[5] In both cases, AFM was primarily a characterization tool, probing topographical changes of the relevant surfaces on the TiO_2 after irradiation with UV. Recently, Kobayashi *et al.* have applied voltage through a conductive AFM tip to decompose stearic acid films as well as adsorbed oxygen molecules deposited on TiO_2 surfaces upon scanning at 10 V under ultraviolet irradiation.[6,7]

In the present study, we have used a chemically-modified AFM probe to actively carry forth a highly localized photochemical reaction of a synthetic dye. In particular, by placing the TiO_2 powder catalyst onto the end of an AFM tip, we have been able to initiate a localized photochemical reaction of a synthetic textile dye within the spatially confined region where the tip traverses, leaving the rest of the sample surface unreacted. In other words, this procedure transforms an important, generalizable, and bulk photocatalytic reaction in solution into a highly localized, site-selective surface chemical modification.

As such, this experiment is a natural and logical extension of analogous efforts by a number of laboratories[8–15] in carrying out *in situ* surface reactions using SPM. Specifically, we investigate the UV-mediated photocatalytic oxidation of a common textile monoazo dye, Procion Red MX-5B (Aldrich), a reaction catalyzed by TiO_2 semiconductor particles.[16,17] Hence, Procion Red dye molecules undergo a series of oxidation processes, which lead to decolorization and formation of a number of aromatic and aliphatic intermediates that are produced as a result of the initial cleavage in the vicinity of the azo bond.[18,19] These photocatalytic oxidation processes are accelerated by the presence of hydrogen peroxide, which yield reactive hydroxyl radicals.

To evaluate the efficacy of the photooxidation process, we performed two sets of bulk experiments. First, we prepared a 10 ml aliquot of a 40 mg L^{-1} aqueous dye solution containing 100 mg L^{-1} TiO_2 and 1 mM H_2O_2. The absorbance of the dye was recorded at various time intervals from 1 to 8 h. Secondly, we coated glass wafers in air with an identical solution mixture to prove that the reaction could occur on surfaces containing the necessary reactive constituents. In each case, we subsequently irradiated both the solution samples and wafers with UV irradiation at 254 nm. We confirmed from optical microscopy images as well as from UV-visible spectroscopy results that Procion Red MX-5B in the presence of aqueous dispersions of TiO_2 did indeed experience photodegradation.

Fig. 1 depicts the experimental protocol that was subsequently used to transform the reaction performed on the wafer in bulk into a localized site-selective surface reaction initiated by the AFM tip in ambient air. To immobilize the catalyst particles on the tip to create a functionalized probe, we attached 120 nm-sized chunks

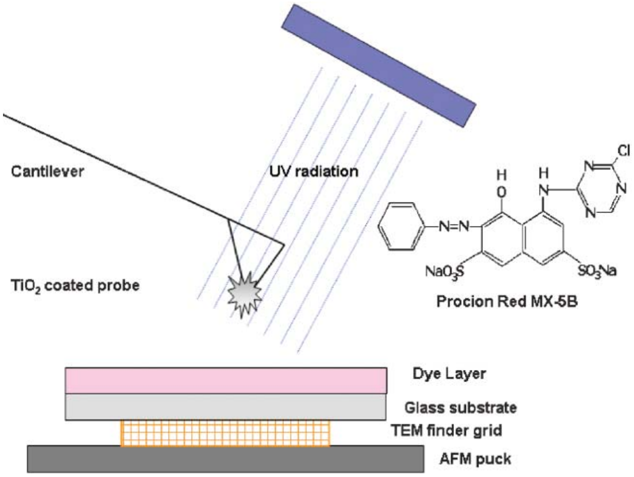

Fig. 1 Schematic of experimental protocol used for AFM tip initiation of a highly localized surface photocatalytic reaction in air. TiO_2 nanoparticles attached to an AFM probe were used to degrade Procion Red MX-5B dye in the presence of UV radiation, within a spatially defined region.

---

[a] *Materials and Chemical Sciences Department, Brookhaven National Laboratory, Building 480, Upton, NY 11973, USA*
[b] *Department of Chemistry, SUNY at Stony Brook, Stony Brook, NY 11794-3400, USA. E-mail: sswong@notes.cc.sunysb.edu; sswong@bnl.gov; Tel: 631-632-1703; 631-344-3178*

† Electronic supplementary information (ESI) available: Experimental methods. See http://dx.doi.org/10.1039/b506110e

‡ Current address: Department of Chemistry, University of Texas at Dallas, Richardson, TX 75080, USA.

§ These authors contributed equally to this work.

¶ Current address: Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720, USA.

(based on scanning electron microscopy measurements) of the anatase TiO_2 powder (Aldrich) to conventional silicon pyramids (force modulation etched silicon probes, Nanoworld, k = 3–6 N m^{-1}) using a thin film of UV-curable glue (Norland Products). This task was facilitated by using an inverted optical microscope (Nikon Epiphot 200) with an in-house micromanipulation setup.

Full experimental details concerning the sample preparation and reaction conditions are given in the ESI†. The photochemical oxidation reaction was performed under ambient conditions using a Multimode Nanoscope IIIa AFM (Veeco Inc., Santa Barbara, CA) operated in TappingMode™. As a control experiment, an uncoated conventional silicon tip was scanned over a dye surface in the presence of UV radiation and in addition, a TiO_2-coated tip in the absence of UV radiation was scanned over a separate dye surface. All other experimental conditions were maintained.

The optical micrograph taken after AFM scanning and tip-catalyzed reactivity (Fig. 2) reveals a well-defined, tip-reacted area, measuring 30 × 30 μm. The degraded region, outlined by the dotted rectangle, is clearly evident due to surface modification and decolorization. The slight asymmetry of the feature can be attributed to scanner drift over the 8 h period of raster scanning. Conversely, optical images taken upon completion of the two control experiments exhibited no visible topographical or color change and yielded an unpatterned, homogeneous result.

AFM height images taken before and after scanning with a TiO_2-coated AFM tip under UV radiation provide further evidence of dye degradation (Fig. 3). Fig. 3a is a typical AFM height image of the deposited Procion Red MX-5B dye, exhibiting crystal-like features ranging in length from 0.2 to 1.0 μ m with an average length of 0.5 ± 0.1 μm and varying in height from 56.2 to 114.4 nm with an average height of 79.6 ± 14.1 nm. Features of these length and height dimensions as well as general shape and morphology are no longer present in the AFM height images of the identical region after tip-catalyzed reactivity (Fig. 3b). In fact, AFM height images of the identical reacted region show very few features and these range in length from 0.1 to 0.6 μm with an average length of 0.2 ± 0.1 μm and height from 10.8 to 47.7 nm with an average height of 22.6 ± 7.6 nm.

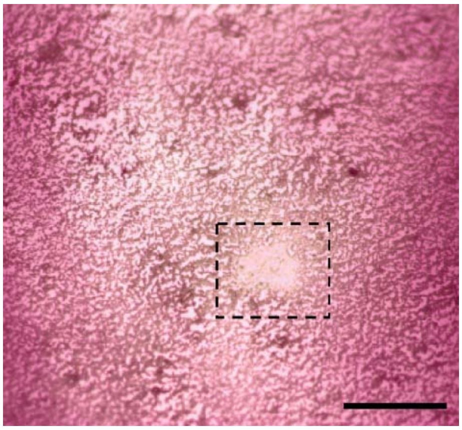

Fig. 2 The outlined, dotted region in the optical micrograph depicts the highly localized nature of the photocatalytic degradation of Procion-Red MX-5B after controlled raster scanning with a TiO_2 coated AFM probe in the presence of UV radiation. The scale bar represents 50 μm. The image was taken at 200× magnification with a Nikon Epiphot 200 inverted microscope under bright-field illumination.

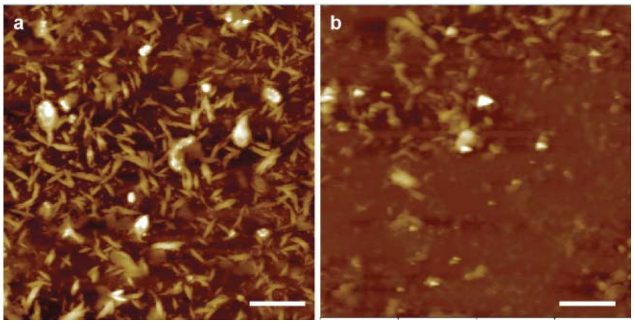

Fig. 3 TappingMode™ AFM height images of Procion Red MX-5B (a) before and (b) after reaction under UV irradiation with a scanning TiO_2-coated AFM probe for 8 h. Scale bars in both images represent 1.0 μm. The z data scale in both images is 250.0 nm.

Nanoscope offline software was utilized to perform statistical roughness analysis on the AFM height images acquired before and after the surface photocatalytic degradation reactions at varying reaction times from 1 to 8 h, as well as for the two previously described control experiments. AFM images were plane-fitted and flattened prior to the roughness analysis. The morphology of the surface changed dramatically after reaction under UV radiation with a scanning TiO_2-coated AFM probe. Fig. 4 shows the percentage of decrease in average surface roughness (R_a) values from the original, pre-reacted values as a function of irradiated, reaction time. Average roughness is defined as the average of surface height deviations taken from the mean data plane. It is apparent that the average surface roughness decreases continuously with increasing reaction time. Though all data were collected for 5 × 5 μm^2 area regions, similar results were noted, irrespective of the sample size analyzed in the roughness calculations. For example, the R_a value was lowered by almost 50% after scanning for 4 h and by nearly 70% after scanning for 8 h with a TiO_2-coated AFM probe under UV irradiation, observations consistent with dye degradation and an accompanying formation of photo-oxidation products of progressively lower molecular weight.

By contrast, we observed no significant change in surface roughness upon scanning with a TiO_2-coated AFM probe in the absence of UV radiation (Control 1), eliminating the possibility

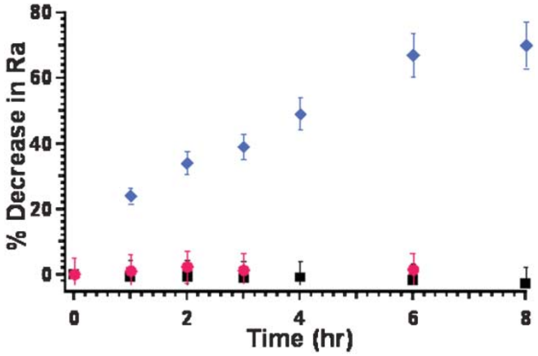

Fig. 4 Plot of percentage decrease in the mean surface roughness value (R_a) of 0.65 mM Procion Red dye films *vs.* reaction times in the presence of a scanning TiO_2-modified tip under UV irradiation (blue). Changes in the corresponding R_a for Control 1 (red) and Control 2 (black), respectively, are also shown for comparison.

that large masses of TiO_2 were falling off the tip and peeling away the surface layers of dye. Likewise, the statistical roughness characteristics of the dye surface remain relatively constant upon scanning with an unmodified AFM tip in the presence of UV radiation (Control 2). These results are important in demonstrating that the changes in surface roughness observed are indeed due to reproducible, tip-induced chemical changes and not due to a physical flattening or mechanical removal of features.

The photocatalytic oxidation reaction with Procion Red MX-5B dye, as with other azo dyes and similar aromatic organic compounds, follows first-order kinetics with a pseudo first-order rate constant, k'. For the calculation of k' in this study, we made a reasonable assumption that the decrease in the percentage of the R_a value was directly proportional to the percentage decrease in the dye concentration. As such, we computed k' for the AFM-catalyzed surface reaction to be 0.0024 per min. This value was compared with the rate constant computed from the bulk solution experiment. In this case, the absorbance peak value at 539 nm, proportional to the dye concentration, of the reaction solution measured by spectrophotometry was used. The k' value thereby determined for the bulk reaction in solution using the same dye concentration was found to be 0.0054 per min. Our non-optimized data are in the same general range as other pseudo-first-order rate constants previously reported.[16] For example, it has been noted that under optimal conditions, Procion Red MX-5B can be essentially fully decolorized in 20 min.[16]

Surface FT-mid-IR spectroscopy (ESI) showed significant changes in the chemical composition between the unreacted and reacted areas portrayed in Fig. 2. While the spectral features from 2000–1000 cm^{-1} were masked by the intense band interference of the SiO_2 glass substrate, spectral changes in the 3500–2000 cm^{-1} region were clearly evident before and after reaction. This span of the IR spectrum of a typical unreacted Procion Red MX-5B region agrees with the standard reference spectrum. Specifically, this higher wavenumber region shows (a) a weak shoulder located at 2800–2750 cm^{-1}, attributable to an asymmetrical aromatic C–H stretching vibration of the conjugated moiety attached to the N=N group, (b) a medium intensity band at 2460 cm^{-1}, ascribed to a N^+=C stretch, and (c) overlapping hydroxyl stretching vibration bands from 3500–3200 cm^{-1}. The other significant band is in the region of 3445 cm^{-1}, which is typical of an aromatic N–H stretch. All of these spectral features representative of the pristine dye compound significantly diminish or disappear in the spectrum taken of the localized reacted region. Additionally, a new absorption band appeared in the 2900–2650 cm^{-1} region, originating from CH_3 stretching vibrations or from OH stretching vibrations of carboxylic acids, consistent with the expected formation of aliphatic carboxylic acid degradation intermediates such as 1-propene-1,2,3-tricarboxylic acid, propanoic acid, propanedioic acid, malic acid, butanedioic acid, oxalic acid, and acetic acid.[18]

These spectral changes provide chemical corroboration for the other AFM and optical microscopy evidence, implying site-selective photocatalytic degradation of the dye induced by a functionalized catalytic tip. We have additionally confirmed the feasibility of the reaction by replicating the photodegradation experiments in bulk. UV-visible data showed a pronounced decrease in the dye peak absorption as a function of irradiation time, while solution mid-infrared results yielded specifically the appearance of an exceedingly broad O–H stretch in the 2900 to 3300 cm^{-1} range, consistent with the postulated formation of carboxylic acids as byproducts (see ESI†).

This study demonstrates the principle that AFM probes, coated with photocatalyst nanoparticles, can be used to carry out controllable, *in situ* oxidation reactions. The experimental process used was designed to mimic an important photochemical reaction on a small, yet discernable scale. Work is currently underway to improve the spatial resolution and patterning ability of the procedure. Efforts involve decreasing the particle size of the semiconductor catalyst used as well as covalent attachment of the catalyst to the ends of sharper probes, such as single-walled carbon nanotube (SWNT) tips.[20,21]

We acknowledge support of this work through startup funds provided by SUNY Stony Brook as well as BNL. SSW acknowledges support from the National Science Foundation (DMR-0348239), the ACS Petroleum Research Fund, and 3 M. Partial support of this work, particularly the actual AFM studies, came through the US Department of Energy (DOE) under contract number DE-AC02-98CH10886. VZ acknowledges Department of Homeland Security Fellowship Program support for studies at BNL. SAB thanks the DOE Office of Science for SULI (Science Undergraduate Laboratory Internship) support. We thank Lisa M. Miller (BNL) for her assistance with the surface FT-IR analyses and Sarbajit Banerjee for helpful discussions.

Notes and references

1 M. Grätzel, *Nature*, 2001, **414**, 338.
2 M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chem. Rev.*, 1995, **95**, 69.
3 O. K. Varghese, D. Gong, M. Paulose, K. G. Ong, E. C. Dickey and C. A. Grimes, *Adv. Mater.*, 2003, **15**, 624.
4 J. P. Lee, H. K. Kim, C. R. Park, G. Park, H. T. Kwak, S. M. Koo and M. M. Sung, *J. Phys. Chem. B*, 2003, **107**, 8997.
5 Z. Lu, L. Zhou, Z.-L. Zhang, W.-L. Shi, Z.-X. Xie, H.-Y. Xie, D.-W. Pang and P. Shen, *Langmuir*, 2003, **19**, 8765.
6 K. Kobayashi, Y. Tomita and S. Yoshida, *Nano Lett.*, 2002, **2**, 925.
7 K. Kobayashi, Y. Tomita, K. Matsuhisa and Y. Doi, *Appl. Surf. Sci.*, 2005, **244**, 389.
8 Y. Okawa and M. Aono, *Nature*, 2001, **409**, 683.
9 H. Schönherr, V. Chechik, C. J. M. Stirling and G. J. Vancso, *J. Am. Chem. Soc.*, 2000, **122**, 3679.
10 J.-B. D. Green, M. T. McDermott and M. D. Porter, *J. Phys. Chem.*, 1996, **100**, 13342.
11 W. T. Müller, D. L. Klein, T. Lee, J. Clarke, P. L. McEuen and P. G. Schultz, *Science*, 1995, **268**, 272.
12 C. Blackledge, D. A. Engebretson and J. D. McDonald, *Langmuir*, 2000, **16**, 8317.
13 X. Wang, D. Zhou, T. Rayment and C. Abell, *Chem. Commun.*, 2003, 474.
14 S. Kramer, R. R. Fuierer and C. B. Gorman, *Chem. Rev.*, 2003, **103**, 4367.
15 L. K. Blasdel, S. Banerjee and S. S. Wong, *Langmuir*, 2002, **18**, 5055.
16 C. M. So, M. Y. Cheng, J. C. Yu and P. K. Wong, *Chemosphere*, 2002, **46**, 905.
17 N. M. Dimitrijevic, Z. V. Saponjic, D. M. Bartels, M. C. Thurnauer, D. M. Tiede and T. Rajh, *J. Phys. Chem. B*, 2003, **107**, 7368.
18 C. Hu, J. C. Yu, Z. Hao and P. K. Wong, *Appl. Catal., B*, 2003, **42**, 47.
19 K. Tanaka, K. Padermpole and T. Hisanaga, *Wat. Res.*, 2000, **34**, 327.
20 S. S. Wong, E. Joselevich, A. T. Woolley, C. L. Cheung and C. M. Lieber, *Nature*, 1998, **394**, 52.
21 S. S. Wong, J. D. Harper, P. T. Lansbury and C. M. Lieber, *J. Am. Chem. Soc.*, 1998, **120**, 603.