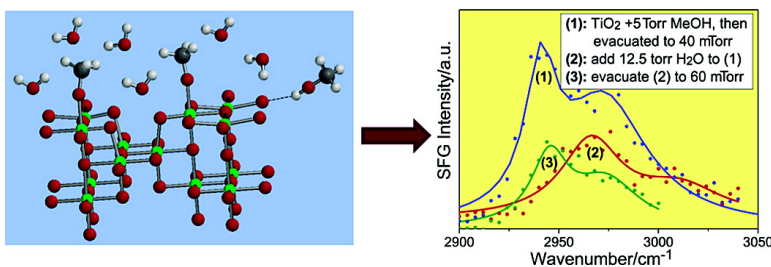Communication

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Direct Observation of Competitive Adsorption between Methanol and Water on TiO$_2$: An in Situ Sum-Frequency Generation Study

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Materials based on TiO$_2$ are finding applications in many important fields such as catalysis, wetting, sensors, corrosion, coatings, and solar cells.[1−4] To improve the usefulness of the materials, it is essential to understand TiO$_2$ surface chemistry on a molecular level. In this context, methanol and water have proven to be effective molecular probes.[5,6] A large body of work has been devoted to either water or methanol adsorption on TiO$_2$.[6−8] However, molecular-level information on competitive adsorption between these two molecular probes on the TiO$_2$ surface has remained elusive, regardless of its practical significance. Water, a ubiquitous substance, is generally already present in systems at ambient conditions studied by a methanol probe. To obtain information about competitive adsorption, it is necessary to differentiate trace surface adsorbents, including adsorbed water and methanol, from each other and to separate them from the molecules in the bulk environment. This is a challenge to traditional spectroscopic methods such as IR due to the limited surface sensitivity. In this communication, we present an approach to interrogate the competitive adsorption process between water and methanol on TiO$_2$ through in situ use of sum frequency generation (SFG), a nonlinear spectroscopic technique.

The theoretical background for SFG is well established in the literature.[9−11] Within the electric dipole approximation, the sum-frequency signal can only be generated where inversion symmetry is broken. Inversion symmetry is necessarily broken at a surface or interface. This inherent advantage renders SFG a prime candidate to probe any surface process, including adsorption, where interference from the bulk phase is undesirable.[12]

TiO$_2$ films employed in the present work were fabricated by evaporation-driven self-assembly of colloidal anatase TiO$_2$ nanoparticles from an aqueous solution. The films are ca. 500 nm thick, as monitored by a profilometer (SLOAN DEK TAK). On a macroscopic scale, the film surfaces are flat with a root-mean-square (RMS) roughness of ±0.5 nm, enabling efficient collection of the SFG signal.[5]

Considering that the TiO$_2$ film is grown "bottom-up" on a substrate, isotropic symmetry is broken at the top layer of the film. Furthermore, due to the asymmetric environment, molecules adsorbed on the film surface adopt a preferred polar orientation with respect to the surface normal. This preferred orientation gives rise to a characteristic SFG signal.

In the reported experiments, the TiO$_2$ film on a CaF$_2$ substrate is mounted on a vacuum cell. The substrate, which also serves as a window, is mounted on the glass cell with an O-ring seal. The TiO$_2$ film faces the inside of the cell. The visible and infrared beams used to generate SFG come from the top side through the window/substrate and the film. Beam polarizations are: *s, s, p* for sum frequency, visible, and infrared, respectively. The cell is attached to a vacuum line and evacuated by a diffusion pump. After evacuation the cell is filled with the desired pressure of methanol

or water vapor. Details of the SFG experimental setup have been previously described.[13]

The strategy to get information on competitive adsorption between methanol and water on the TiO$_2$ surface involves in situ SFG measurements in the following order: (1) introduction of 5 Torr methanol into an evacuated SFG cell covered with TiO$_2$ film for 20 min with subsequent evacuation of the cell to 40 mTorr; (2) introduction of 12.5 Torr water vapor; (3) evacuation of the cell to 60 mTorr.

The corresponding SFG spectra in the region of 2900−3000 cm^{-1} are shown in Figure 1(a−c). According to the basic principles of SFG, the spectral data shown in Figure 1 are fitted to Lorentzian distributions, and information about mode strength and peak position is thus extracted.

With only methanol vapor in contact with the TiO$_2$ film (Figure 1a), two kinds of species, molecular methanol and methoxy that is produced by dissociative chemisorption of methanol, are detected on the TiO$_2$ surface. This is evident from the two SFG peaks located at 2940 and 2970 cm^{-1}, respectively. The assignment of the two peaks is supported by the change of SFG signals with both temperature and pressure.[5] The methoxy and methanol SFG signatures remaining after evacuation correspond to a submonolayer coverage, as inferred by comparing the present SFG intensities with those at monolayer.[5] Details of the adsorption modes and spectral features of methanol on TiO$_2$ are reported elsewhere.[5]

When a relatively large amount of water vapor is introduced into the system (the ratio between water and methanol is ca. 300), as seen in Figure 1b, the surface methoxy signal drops below the SFG detection limit, but physisorbed methanol remains as evidenced by an appreciable SFG signal. In addition, a new broad peak beyond 3000 cm^{-1} corresponding to H-bonding OH groups appears. The disappearance of the methoxy SFG peak, in conjunction with the appearance of the H-bonding OH peak, indicates that methoxy species on TiO$_2$ is hydrolyzed by water addition.[14]

Evacuating the system containing a large amount of water and a relatively small amount of methanol causes the water SFG peak to drop below the SFG detection limit. The methanol peak remains. Interestingly, a substantial methoxy SFG peak reappears (Figure 1c). The disappearance of water, but not of methanol, indicates that methanol is much more strongly adsorbed to the TiO$_2$ surface than is water. The reappearance of the methoxy SFG peak suggests the following: (1) Methoxy species is hydrolyzed when adding water, and the produced methanol remains as an adsorption layer close to the TiO$_2$ surface. If the produced methanol entered the gas phase it would vanish permanently upon evacuation. (2) Surface dehydroxylation by methanol occurs when evacuation of the system reduces the relative water concentration, restoring the chemisorbed methoxy species on the TiO$_2$ surface.

Combining both observations, a reversible reaction model is proposed (Scheme 1) to explain the methoxy SFG peak change in Figure 1a → 1b → 1c. Note that surface dehydroxylation by
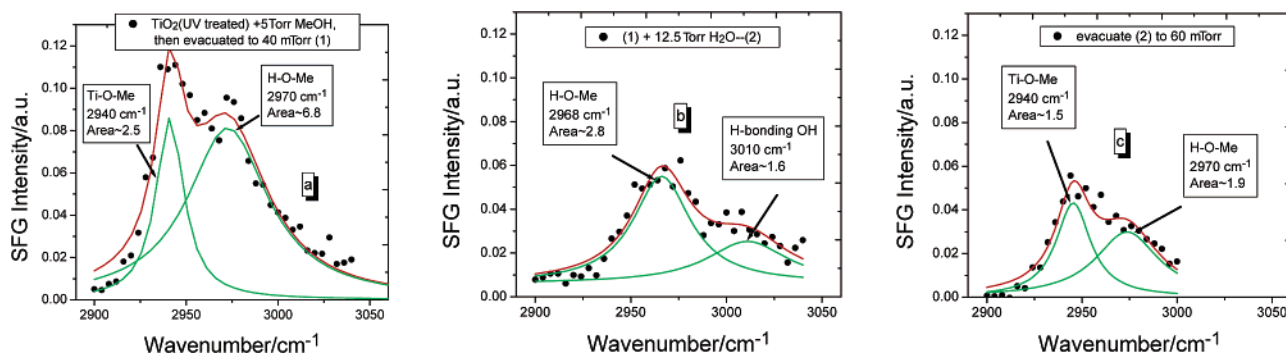
Figure 1. SFG spectral evolution of methanol on TiO_2 with introduction of water vapor and subsequent evacuation. Note: (1) the pretreatment by UV irradiation is conducted to clean the sample film of any potential organic contaminants; (2) experimental error is within ±5%; and (3) instrumental resolution is 4 cm^{-1}.

Scheme 1. Reversible Hydroxylation/Dehydroxylation at the TiO_2 Surface
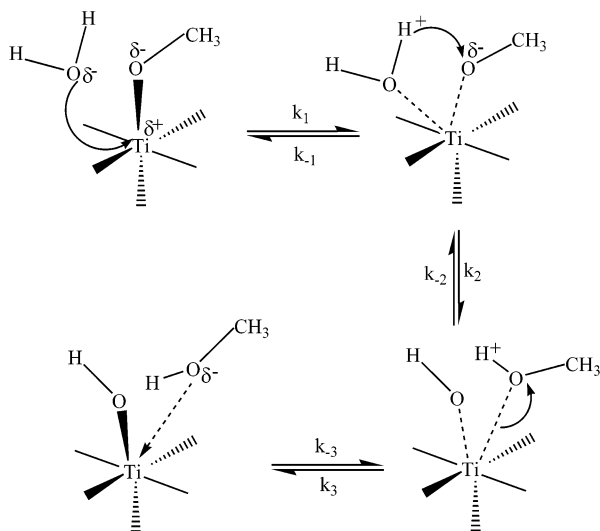
methanol, the reverse reaction, is favored thermodynamically, but an excess of water shifts the equilibria toward the hydrolysis of the surface methoxy species.

The SFG observations have direct implications for understanding the mechanism of TiO_2-based photocatalysis, a most promising technology for environmental remediation.[4] Two possible mechanisms are proposed for the TiO_2 photooxidation of organic contaminants: (1) direct oxidation by photogenerated holes[15,16] and (2) indirect oxidation via interfacial •OH radicals that are products of trapping valence holes by surface OH groups or adsorbed water.[17] It is still a challenge to distinguish the two mechanisms in practice due to the lack of suitable probe techniques. The oxidation pathway, direct or indirect, depends on the molecular species adsorbed on the TiO_2 surface. For photooxidation of methanol at TiO_2, a prototype reaction toward understanding the mechanism of TiO_2 photcatalysis, these SFG results clearly suggest that indirect oxidation by •OH radicals is the mechanism when water is the dominant species; the critical mole ratio between water and methanol for the •OH radical mechanism is ca. 300. Such a high

ratio applies to photooxidation of methanol by TiO_2 in aqueous systems. If the water content is lower than the critical one, direct oxidation of methanol by photogenerated holes occurs at the TiO_2 surface.

In conclusion, the competitive adsorption between water and methanol, as well as reversible hydroxylation/dehydroxylation on the TiO_2 surface, is unambiguously resolved for the first time by an in situ SFG study.

Supporting Information Available: Full SFG spectrum in the region of 2900−3800 cm^{-1} for the case of adding water. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Oregan, B.; Grätzel, M. *Nature* **1991**, *353*, 737−740.
(2) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T. *Nature* **1997**, *388*, 431−432.
(3) Brown, G. E.; Henrich, V. E.; Casey, W. H.; Clark, D. L.; Eggleston, C.; Felmy, A.; Goodman, D. W.; Gratzel, M.; Maciel, G.; McCarthy, M. I.; Nealson, K. H.; Sverjensky, D. A.; Toney, M. F.; Zachara, J. M. *Chem. Rev.* **1999**, *99*, 77−174.
(4) Hoffmann, M. R.; Martin, S. T.; Choi, W. Y.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69−96.
(5) Wang, C. Y.; Groenzin, H.; Shultz, M. J. *J. Phys. Chem. B* **2004**, *108*, 265−272.
(6) Zhang, C. J.; Lindan, P. J. D. *J. Chem. Phys.* **2003**, *118*, 4620−4630.
(7) Wu, W. C.; Chuang, C. C.; Lin, J. L. *J. Phys. Chem. B* **2000**, *104*, 8719−8724.
(8) Finnie, K. S.; Cassidy, D. J.; Bartlett, J. R.; Woolfrey, J. L. *Langmuir* **2001**, *17*, 816−820.
(9) Shen, Y. R. *Nature* **1989**, *337*, 519−525.
(10) Hirose, C.; Akamatsu, N.; Domen, K. *Appl. Spectrosc.* **1992**, *46*, 1051−1072.
(11) Bain, C. D. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1281−1296.
(12) Shultz, M. J.; Baldelli, S.; Schnitzer, C.; Simonelli, D. *J. Phys. Chem. B* **2002**, *106*, 5313−5324.
(13) Wang, C. Y.; Groenzin, H.; Shultz, M. J. *Langmuir* **2003**, *19*, 7330−7334.
(14) The full SFG spectrum in the OH region for the case of adding water is available in the Supporting Information.
(15) Chen, J.; Ollis, D. F.; Rulkens, W. H.; Bruning, H. *Water Res.* **1999**, *33*, 669−676.
(16) Bahnemann, D. W.; Hilgendorff, M.; Memming, R. *J. Phys. Chem. B* **1997**, *101*, 4265−4275.
(17) Wang, C. Y.; Rabani, J.; Bahnemann, D. W.; Dohrmann, J. K. *J. Photochem. Photobiol., A* **2002**, *148*, 169−176.

JA048165L