

Direct Visualization of the Hydrolysis Kinetics of Titanium(IV) Alkoxides on Functionalized Gold Surfaces

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The hydrolysis kinetics of titanium(IV) alkoxides coordinated on functionalized gold surfaces was monitored with video-based contact angle measurements, and the experimental data were further modeled to evaluate pseudo-first-order reaction rate constants. In particular, titanium(IV) isopropoxide molecules were attached to dithiothreitol monolayers on gold from dilute 2-propanol solution to form titanium-coordinated surfaces. The side view of a sessile drop of aqueous solution on the titanium-coordinated surface changed significantly as a function of time (corresponding to an apparent decrease in the contact angles), indicating that the surface became more hydrophilic as a result of its reaction with aqueous solution (i.e., the hydrolysis and polycondensation). The kinetics of this surface reaction was modeled, for the first time, based on the observed changes in the time-dependent contact angles. Pseudo-first-order kinetic parameters obtained showed an interesting two-step reaction feature when water was used ($k_1 = 0.91 \times 10^{-3} \text{ s}^{-1}$ and $k_2 = 2.1 \times 10^{-3} \text{ s}^{-1}$), while the experiments using acid and base solutions displayed a clear enhancement effect and were better modeled with only one rate constant ($k_{\text{overall}} = 2.3 \times 10^{-3} \text{ s}^{-1}$ for 0.10 M HCl and $k_{\text{overall}} = 5.0 \times 10^{-3} \text{ s}^{-1}$ for 0.10 M NaOH).

Introduction

Titanium dioxide (TiO₂) has attracted considerable attention during the past three decades because of its semiconductor-based photocatalytic properties and its potential applications to energy renewal, energy storage, and environmental cleanup (e.g., the complete destruction of organic contaminants in polluted air, in wastewater, and on surfaces).^{1–5} Because nanocrystalline TiO₂ particles and/or thin films offer very high surface areas and enhanced catalytic activity, the study of these advanced materials has become a very active research topic recently.^{6–21} For catalytic applications, TiO₂ is usually prepared by means of precipitation (or hydrolysis) using titanium oxysulfate, sulfate, or tetrachloride as the starting material.^{8,9} However, a number of studies have shown that hydrolysis and condensation of titanium(IV) alkoxides yield thermally stable, nanocrystalline, and contamination free TiO₂ particles and/or thin films.^{7,15–17} This approach was particularly successful when it was combined with sol–gel and/or Langmuir–Blodgett techniques.^{11,12,14} Meanwhile, novel synthetic routes to TiO₂ thin films were also explored based on the hydrolysis of titanium(IV) complexes on functionalized self-assembled monolayers (SAMs) on solid substrates.^{9,10,13,19–21} There is no doubt that a better understanding of the mechanism(s) for the hydrolysis of titanium complexes, particularly at interfaces, would be beneficial to this expanding research area. We report herein the first study that explores the hydrolysis kinetics of titanium(IV) alkoxides on functionalized gold surfaces with video-based contact angle measurements.

Experimental measurement of contact angles is one of the most convenient methods to characterize solid/liquid interfaces.^{22,23} In particular, it has been extensively used to explore the wetting property and structure of alkanethiolate SAMs on gold by Whitesides and co-workers.²⁴ With considerable sensitivity, contact angle measurements were also used by a number of other research groups to study the formation kinetics of SAMs on gold,^{25–27} the ionization equilibrium of SAMs with terminal ionizable groups,^{28–30} and the step-by-step modification of surfaces.³¹ Recently, contact angle measurements have been employed to examine the alkaline hydrolysis of a polyimide surface and the oxidation kinetics of pyrite surfaces.^{32,33}

In the present study, titanium(IV) isopropoxide (referred to as TTIP hereafter) was attached to dithiothreitol (DTT) monolayers on gold via a ligand-exchange reaction. The titanium-coordinated gold surface was then hydrolyzed by exposure to a sessile drop of aqueous solution. By means of capturing the side view of the liquid drop using a video-based contact angle analyzer, the change in surface wetting properties could be followed in real time. Analysis of the recorded images provided the dependence of contact angle on reaction time, from which the hydrolysis kinetics of the titanium-coordinated surface was evaluated.

Experimental Section

Titanium(IV) isopropoxide (TTIP) (Aldrich Chemical Co., Milwaukee, WI) and dithiothreitol (DTT) (Diagnostic Chemicals Ltd., PEI, Canada) were used as received. Gold substrates (2.5 × 7.5 cm) were purchased from Evaporated Metal Films (EMF), Inc. (Ithaca, NY) and consisted of regular glass slides coated first with about 10 nm of titanium followed by 150 nm gold. Water was deionized with a Milli-Q purification system (Millipore products, Bedford, MA). The absolute ethanol,

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TABLE 1: Wetting Properties of Gold Substrates before and after Modification with Dithiothreitol (DTT) and Further Coordination of Titanium(IV) Isopropoxide (TTIP)

	contact angles (H ₂ O), deg
bare Au	50 ± 7
DTT-Au	31 ± 2
Ti-DTT-Au	45 ± 2 ^a
HO(CH ₂) ₁₁ S-Au	22 ± 6 ^b

^a At time zero, see text for details. ^b A 0° contact angle (<15°) was determined and widely accepted for very polar OH surfaces,^{35,37} but nonzero contact angles have been reported previously.³⁶ This is probably due to the rapid contamination of these surfaces in air.³⁷

2-propanol, H₂O₂ (30% w/w), H₂SO₄ (95.0–98.0%), HCl (36.5–38.0%), and NaOH were of ACS reagent grade and used without further purification.

DTT monolayers on gold (DTT-Au) were prepared according to a standard procedure reported previously.^{22,34,35} Reflection–absorption FTIR has been used to show that various derivatives of oxidized DTT form SAMs on gold surfaces.³⁴ In this study the formation of DTT monolayers on gold was confirmed by using wetting measurements, electrochemistry, and Auger spectroscopy (see Results and Discussion below for details). Gold substrates were cleaned by immersion in “piranha” solution (3:1 mixture of concentrated H₂SO₄ and 30% H₂O₂ heated to about 90 °C) for 5 min (**CAUTION: “piranha” solution reacts violently with organic materials, it must be handled with extreme care**). DTT monolayers were formed on gold by immersing freshly cleaned gold substrates into a dilute solution (~1.0 mM) of DTT in absolute ethanol for at least 12 h. The gold substrates modified with DTT monolayers were rinsed sequentially with absolute ethanol and water, and then dried under N₂. To coordinate TTIP to functionalized gold surfaces, the DTT-Au substrates were immersed into a 5.0 mM TTIP solution in 2-propanol for 1 h. The prepared Ti-DTT-Au samples were finally rinsed several times with pure 2-propanol and dried under N₂ before characterization. Contact angles were determined on a First Ten Angstroms Model 125 static contact angle and surface tension analyzer (Portsmouth, VA). Static contact angles of water, 0.10 M HCl, and 0.10 M NaOH on the titanium-coordinated gold surfaces were derived from the analysis of images that showed the side view of liquid drops with the software provided by the manufacturer. All measurements were carried out at room temperature and ambient humidity and were repeated at least three times.

Results and Discussion

The formation of dithiothreitol (DTT) monolayers on gold was monitored by the change of surface wetting properties. Gold substrates modified with DTT monolayers are more hydrophilic compared to bare gold substrates, as revealed by much smaller contact angles obtained with H₂O (Table 1). This indicates that hydroxyl groups are exposed on the outer surface of the DTT monolayers on gold (Figure 1), which is essentially the same as when ω -hydroxyalkanethiols (e.g., HS(CH₂)₁₁OH) are coordinated to gold surfaces.^{24,36,37} However, the average contact angle for DTT-Au is still noticeably larger than that of 11-mercapto-1-undecanol SAMs on gold (HO(CH₂)₁₁S-Au), indicating that DTT monolayers on gold are not as compact and ordered as the HO(CH₂)₁₁S-Au SAMs. This is consistent with our results of heterogeneous electron-transfer measurements (a typical method to examine the quality of SAMs³⁵), which showed negligible difference between a bare gold substrate and one modified with DTT.³⁸

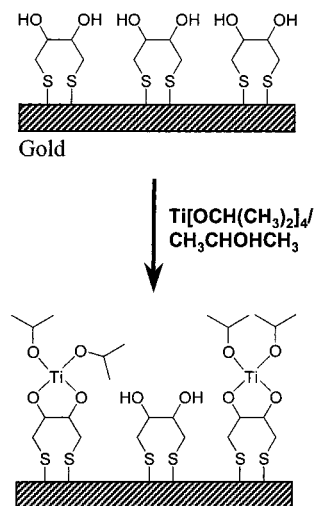


Figure 1. Schematic representations of possible structures of dithiothreitol (DTT) monolayers on gold and titanium-coordinated gold surfaces.

The water contact angles showed an increase (i.e., more hydrophobic surface) after immersion of the DTT modified gold substrates into dilute TTIP/2-propanol solutions (Table 1). This indicates that titanium(IV) alkoxide molecules were anchored to the OH-terminated monolayers via a ligand exchange reaction of the SAM's terminal alcohols with alkoxide ligands (Figure 1).³⁹ The remaining titanium coordination sites were still occupied by isopropoxides with their hydrocarbon tails exposed on the surface (Figure 1); therefore, an increase in hydrophobicity was expected. The coordination of titanium(IV) alkoxides onto OH-functionalized surfaces was reported in the previous study by Shin et al.¹⁰ The formation of DTT monolayers on gold and the further coordination of the titanium complex were also confirmed by our preliminary data with Auger spectroscopy.⁴⁰

Once placed on the titanium-coordinated surface, the contact angle of the water drop decreased significantly as a function of time. This effect was even more significant when a drop of either dilute acid (0.10 M HCl) or base (0.10 M NaOH) was used. Figure 2 displays a series of images captured by a video-based contact angle analyzer for a set of three experiments using neutral, acidic, and basic solutions, respectively. The corresponding contact angle changes as a function of time are shown graphically in Figure 3. Besides the advantage of monitoring the surface reaction in a straightforward manner (i.e., “direct visualization”), the video-based contact angle measurements also provide a higher degree of accuracy for time-dependent contact angle determination. The video-based contact angle analyzer avoids the time delay of reading the contact angles that would be associated with a traditional contact angle goniometer.

A change in contact angle as a function of time is generally attributed to either evaporation of liquid from the sessile drop or a change in surface wetting properties (as a result of surface reaction or reconstruction). It could also be a combination of both. Evaporation would effectively decrease the drop size as a function of time, however, contact angles on low-energy solid surfaces vary only a few degrees for a change of a few millimeters in drop size.²³ Therefore, conventional contact angle measurements with an accuracy of one or two degrees would probably fail to detect such a dependence. In our measurements, the drop size did not change discernibly, and the variations in terms of the observed contact angles were more significant than either experimental uncertainties or the possible drop size dependence as mentioned above (see Figure 3). Furthermore,

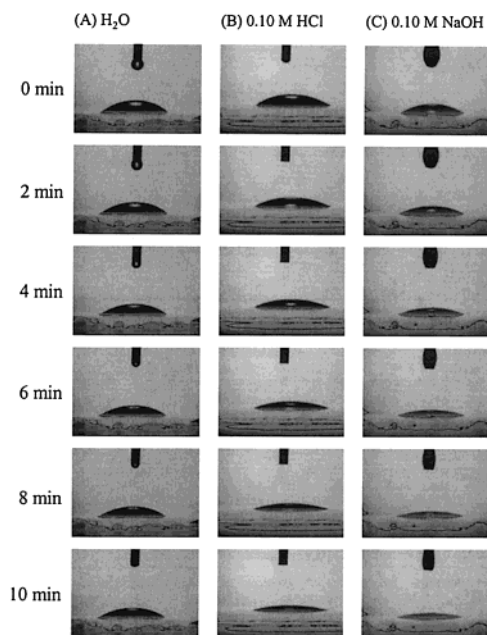


Figure 2. Side view of sessile drops of water, 0.10 M HCl, and 0.10 M NaOH on titanium-coordinated gold surfaces as a function of time.

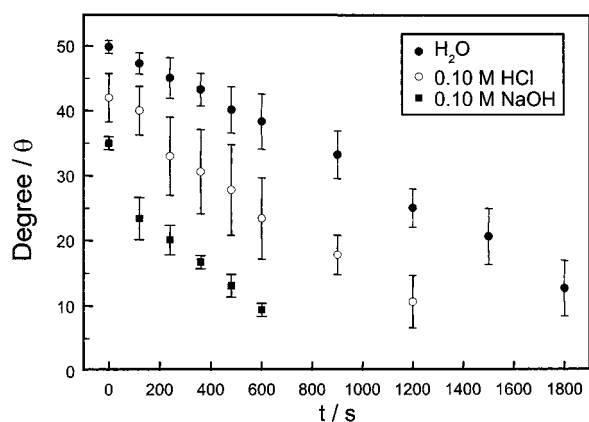


Figure 3. Apparent contact angles of water (●), 0.10 M HCl (○), and 0.10 M NaOH (■) on titanium-coordinated surfaces as a function of time. The experimental uncertainties were determined from the reproducibility of at least three sets of independent measurements.

there were striking differences in the rates of contact angle changes when different solutions were used (Figure 2 and Figure 3). As noted by Raichur et al.,³³ the evaporation of water solution at constant temperature is mainly determined by the partial pressure of water vapor (i.e., the relative humidity). If this were the case, the evaporation rate would have been the same (within experimental error) at all different pH values as long as the humidity remained relatively constant during the course of experiments (30 min or shorter). Therefore, it is more likely the decrease in the contact angle is due to the change of surface wetting properties. Hydrolysis (followed by polycondensation) of the surface-coordinated titanium(IV) complex to form more hydrophilic species such as titanium(IV) polyoxoalkoxides and/or titanium dioxide (TiO₂),^{41,42} would certainly account for the change in surface wetting properties, because a number of newly formed hydroxyl groups would have been exposed to the surface instead of the hydrophobic isopropoxides (Figure 1). This interpretation is also consistent with the enhancement effect on the contact angle changes found when either dilute acid (0.10 M HCl) or base (0.10 M NaOH) was used in the measurements, as mentioned above.

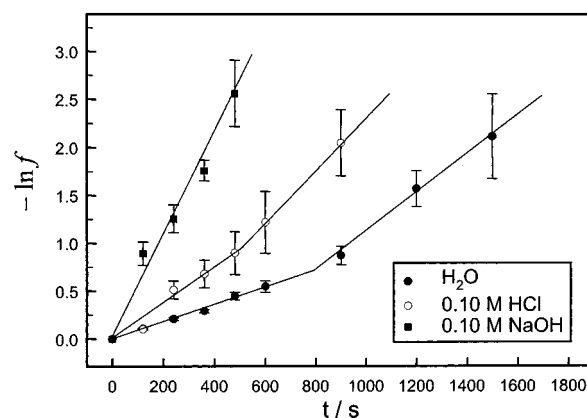


Figure 4. Negative natural logarithmic fraction of titanium alkoxide as a function of the contact time with water (●), 0.10 M HCl (○), and 0.10 M NaOH (■). The solid lines are least-squares fits to the experimental data, from which pseudo-first-order reaction rate constants were calculated (see text for details).

There is a large excess of water in the liquid drop in comparison to the surface concentration of titanium(IV) alkoxides, it is reasonable to use pseudo-first-order reaction kinetics to analyze the dependence of contact angle as a function of time based on the formula⁴³

$$\ln \frac{\Gamma_t}{\Gamma_0} = -kt \quad (1)$$

where Γ_t is the surface concentration at time t , Γ_0 is the initial surface concentration of titanium(IV) alkoxides, and k is the pseudo-first-order rate constant for the hydrolysis of surface-coordinated titanium(IV) alkoxide. If we introduce the surface coverage f (the fraction of coordinated titanium(IV) alkoxide left on the surface with respect to the initial concentration), eq 1 can be simplified to

$$-\ln f = kt \quad (2)$$

If the partially hydrolyzed surface is considered to consist of two types of domains, i.e., surface-coordinated titanium alkoxide and the hydrolyzed species, the intrinsic contact angles with respect to a given liquid being θ_0 and θ_∞ , the surface coverage at any time t , can be determined from Cassie's law,⁴⁴

$$\cos \theta = f \cos \theta_0 + (1 - f) \cos \theta_\infty \quad (3)$$

Rearrangement of eq 3 gives

$$f = \frac{\cos \theta - \cos \theta_\infty}{\cos \theta_0 - \cos \theta_\infty} \quad (4)$$

Figure 4 shows the dependence of $-\ln f$ as a function of time t , in which f was derived from eq 4. The solid lines shown in Figure 4 represent linear least-squares fits to the experimental data with eq 2. Kinetic parameters for the hydrolysis/polycondensation of titanium-coordinated surfaces under neutral, acidic and basic conditions were determined accordingly and were summarized in Table 2.

Upon examination of the kinetic data (Figure 4 and Table 2), two characteristics are immediately apparent. First, the reaction was much faster under acidic and basic conditions. Second, the reaction of surface-confined titanium with water under neutral conditions could not be fit with a single rate constant, and only poorly fit with a single rate constant when dilute acid (0.10 M HCl) was used. However, a good fit with a

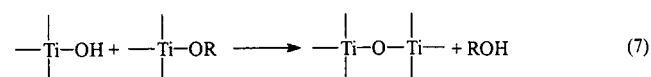
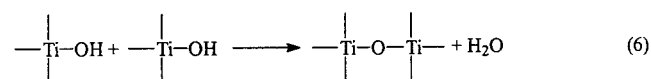
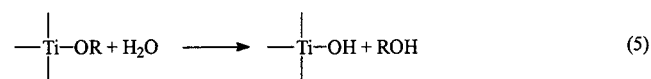
TABLE 2: Kinetic Data for Surface Hydrolysis of Titanium-Coordinated Dithiothreitol Monolayers on Gold (Ti-DTT-Au)

	first-order reaction rate constants	
	$k_1/10^{-3} \text{ s}^{-1}$	$k_2/10^{-3} \text{ s}^{-1}$
H ₂ O	0.91 ± 0.05	2.1 ± 0.4
0.10 M HCl	2.0 ± 0.2	2.8 ± 0.6^a
0.10 M NaOH	5.0 ± 0.5	N/A ^b

^a The kinetic data can also be fitted with a single first-order reaction rate constant ($k_{\text{overall}} = (2.3 \pm 0.5) \times 10^{-3} \text{ s}^{-1}$) that is within the uncertainties of the two rate constants. ^b No second rate constant is required to fit the data.

single rate constant was obtained when dilute base (0.10 M NaOH) was used.

To explain the unique kinetic behavior observed for the surface hydrolysis of titanium(IV) alkoxides on functionalized gold surfaces, it is necessary to recall the hydrolysis/polycondensation model for the formation of titanium dioxide from the reaction of titanium(IV) alkoxides with water in solution phase as shown in eq 5–7.^{7,45–49} The –OR represents an alkoxy-



group and ROH is the corresponding alcohol. The initial step, eq 5 is the sequential ligand exchange process in which alkoxy groups are replaced by hydroxyl groups. The following steps, eqs 6 and 7, are dehydrative polycondensation and dealcoholic polycondensation, respectively.

It is not difficult to understand the enhancement effect in the overall hydrolysis kinetics when the pH value of the aqueous solution was changed, particularly when a base was used. Because of the high concentration of hydroxyl groups, the initial exchange of alkoxy group with hydroxyl group consequently became much faster. A similar effect was reported using aqueous ammonia as the base in the case of solution hydrolysis of titanium alkoxides.⁴⁸ It also has been found that both acid and base would be effective to accelerate the overall polycondensations.⁴⁷ The dehydrative polycondensation requires both deprotonation of one hydroxyl species and dehydroxylation of the other to form M–O–M oxospecies and water. In a similar manner, dealcoholic polycondensation requires both deprotonation of a hydroxyl species and dealkoxylation of an alkoxy group to form M–O–M oxo species and the corresponding alcohol. The deprotonation is accelerated by base while the dehydroxylation and the dealcoholation are accelerated by acid. Therefore, either base or acid would accelerate the overall surface hydrolysis process.

It is a challenge to explain the fact that the kinetics for the reaction of titanium-coordinated surface with water under neutral conditions has to be fit with two pseudo-first-order rate constants. At first, one might want to attribute it to the successive reactions, i.e., a hydrolysis followed by a polycondensation, as described above. However, it should be noted that the rate constant for the latter part is larger than that for the earlier part of the reaction. If it were simply a case of successive reactions, the second reaction could only be discernible kinetically if it

were the slower of the two. A more likely explanation may be the fact that the surface-bound titanium has to be released from surface before it can react completely (hydrolysis/polycondensation). Under acidic (and neutral) conditions the reaction is likely to proceed through protonation of the alkoxy oxygen followed by dissociation to give a positively charged titanium intermediate and a neutral alcohol. Nucleophilic attack of the cationic intermediate by water leads to the first hydrolysis product (this would be analogous to an S_N1 mechanism).⁵⁰ The DTT oxygen atoms may be less susceptible to protonation for steric reasons. Furthermore, dissociation of one of the DTT alkoxy moieties still leaves the other attached and neither the cationic titanium species nor the “neutral alcohol” is able to diffuse. Thus the surface-bound DTT hydroxyl oxygen re-attacks the metal more often than allowing a water molecule to diffuse in and displace it. At the moment there are enough “break points” for the solution phase nucleophiles to compete with the surface-bound DTT nucleophiles for the cationic titanium intermediates, and the overall reaction becomes much faster.

The kinetic data were reasonably fit with a single rate constant under basic conditions, which might simply be the fact that the two rate constants are very close to each other (as a result of the enhancement effect). However, the better explanation should involve a different reaction mechanism from that of acidic (and neutral) conditions. In general, under basic conditions the hydroxide anion is the nucleophile and can easily attack the exposed backside of the coordinated titanium. It may displace one of the two oxygens of the surface bound DTT as an alkoxide anion, while the other DTT oxygen is still bound to the metal. Rather than re-attack the metal center this alkoxide species must react as a base and deprotonate a nearby water molecule to form another hydroxide anion. The hydroxide in turn reacts as a nucleophile and displaces the other DTT oxygen and releases the titanium from the surface. According to such a mechanism, a “turning point” leading to two distinct reaction rate constants is not expected.

A few aspects of the present approach deserve further discussion. First, the postulated reaction mechanisms are consistent with the kinetic data but are difficult to be proved experimentally. Second, although the pseudo-first-order reaction rate constants for the hydrolysis of titanium-coordinated surfaces are in the same order as those obtained previously in solution at high temperatures (e.g., $0.076 \pm 0.008 \text{ min}^{-1}$ at 531 K),⁴⁹ a direct quantitative comparison cannot be made because of totally different experimental conditions. Nevertheless, the comparison of solution kinetic parameters and reaction mechanisms to our surface results are of primary importance for practical applications, for which controlled experiments are currently underway. Third, although the hypothetical scheme shown in Figure 1 is consistent with the experimental observations, the structure and chemical composition of titanium-coordinated surfaces, particularly after the hydrolyzation, require further clarification.

Conclusions

The video-based contact angle measurements provide a simple and accurate method to monitor and quantify the hydrolysis/polycondensation kinetics of titanium(IV) alkoxides on OH-functionalized surfaces. In particular, this technique was used to study the hydrolysis kinetics of titanium-coordinated gold surfaces that were prepared by coordinating titanium(IV) isopropoxide molecules to dithiothreitol monolayers on gold. The conversion of surface-confined titanium alkoxides to more hydrophilic titanium(IV) polyoxoalkoxides and titanium dioxide (TiO₂) was followed as a function of time under acidic, neutral,

and basic conditions. Pseudo-first-order kinetic data obtained using water showed an interesting two-step reaction feature, while the experiments using dilute base and acid solutions displayed much faster reactions. The unique kinetic behavior observed for the surface reaction under neutral (and acidic) conditions may be understood in terms of an S_N1 reaction mechanism where surface bound intermediate electrophiles react faster with neighbor-attached nucleophiles than they do with water.

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References and Notes

- (1) Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37–38.
- (2) Heller, A. *Acc. Chem. Res.* **1995**, *28*, 503–508.
- (3) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49–68.
- (4) Linsebigler, A. L.; Lu, G.; Yates, J. T., Jr. *Chem. Rev.* **1995**, *95*, 735–758.
- (5) Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. *Science* **2001**, *293*, 269–271 and references therein.
- (6) Bahnemann, D.; Henglein, A.; Lilie, J.; Spanhel, L. *J. Phys. Chem.* **1984**, *88*, 709–711.
- (7) Barringer, E. A.; Bowen, H. K. *Langmuir* **1985**, *1*, 414–420 and references therein.
- (8) Kormann, C.; Bahnemann, D. W.; Hoffmann, M. R. *J. Phys. Chem.* **1988**, *92*, 5196–5201.
- (9) Shin, H.; Collins, R. J.; De Guire, M. R.; Heuer, A. H.; Sukenik, C. N. *J. Mater. Res.* **1995**, *10*, 692–698.
- (10) Shin, H.; Collins, R. J.; De Guire, M. R.; Heuer, A. H.; Sukenik, C. N. *J. Mater. Res.* **1995**, *10*, 699–703.
- (11) Doherty, S.; Fitzmaurice, D. J. *Phys. Chem.* **1996**, *100*, 10732–10738.
- (12) Moriguchi, I.; Maeda, H.; Teraoka, Y.; Kagawa, S. *Chem. Mater.* **1997**, *9*, 1050–1057.
- (13) Baskaran, S.; Song, L.; Liu, J.; Chen, Y. L.; Graff, G. L. *J. Am. Ceram. Soc.* **1998**, *81*, 401–408.
- (14) Puccetti, G.; Leblanc, R. M. *J. Phys. Chem. B* **1998**, *102*, 9002–9005.
- (15) Sakai, H.; Kawahara, H.; Shimazaki, M.; Abe, M. *Langmuir* **1998**, *14*, 2208–2212.
- (16) Kominami, H.; Kohno, M.; Takada, Y.; Inoue, M.; Inui, T.; Kera, Y. *Ind. Eng. Chem. Res.* **1999**, *38*, 3925–3931.
- (17) Kobayashi, S.; Hanabusa, K.; Hamasaki, N.; Kimura, M.; Shirai, H. *Chem. Mater.* **2000**, *12*, 1523–1525.
- (18) Kotani, Y.; Matoda, T.; Matsuda, A.; Kogure, T.; Tatsumisago, M.; Minami, T. *J. Mater. Chem.* **2001**, *11*, 2045–2048.
- (19) Kwak, S.-Y.; Kim, S. H.; Kim, S. S. *Environ. Sci. Technol.* **2001**, *35*, 2388–2394.
- (20) Masuda, Y.; Seo, W. S.; Koumoto, K. *Langmuir* **2001**, *17*, 4876–4880.
- (21) Niesen, T. P.; Bill, J.; Aldinger, F. *Chem. Mater.* **2001**, *13*, 1552–1559.
- (22) Ulman, A. *An Introduction to Organic Ultrathin Films, from Langmuir–Blodgett to Self-Assembly*; Academic Inc.: New York, 1991.
- (23) Li, D.; Neumann, A. W. In *Characterization of Organic Thin Films*; Ulman, A., Ed.; Butterworth-Heinemann: Stoneham, MA, 1994.
- (24) As an example see, Bain, C. D.; Whitesides, G. M. *Science* **1988**, *240*, 62–63.
- (25) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321–335.
- (26) Yu, H. Z.; Zhao, J. W.; Wang, Y. Q.; Liu, Z. F. *Mol. Cryst. Liq. Cryst. A* **1997**, *294*, 107–112.
- (27) Liao, S.; Shnidman, Y.; Ulman, A. *J. Am. Chem. Soc.* **2000**, *122*, 3688–3694.
- (28) Holmes-Farley, S. R.; Bain, C. D.; Whitesides, G. M. *Langmuir* **1988**, *4*, 921–937.
- (29) Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 1990–1995.
- (30) Creager, S. E.; Clarke, J. *Langmuir* **1994**, *10*, 3675–3683.
- (31) Yu, H. Z.; Zhao, J. W.; Wang, Y. Q.; Cai, S. M.; Liu, Z. F. *J. Electroanal. Chem.* **1997**, *438*, 221–224.
- (32) Stephans, L. E.; Myles, A.; Thomas, R. R. *Langmuir* **2000**, *16*, 4706–4710.
- (33) Raichur, A. M.; Wang, X. H.; Parekh, B. K. *Colloids Surf. A: Physicochem. Eng. Aspects* **2000**, *167*, 245–251.
- (34) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481–4483.
- (35) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559–3568.
- (36) Keller, H.; Schrepp, W.; Fuchs, H. *Thin Solid Films* **1992**, *210/211*, 799–802.
- (37) Evans, S. D.; Sharma, R.; Ulman, A. *Langmuir* **1991**, *7*, 156–161.
- (38) The cyclic voltammetric current–potential response of solution-diffused $\text{Fe}(\text{CN})_6^{3-}$ on DTT-modified gold electrodes is similar to that of a bare gold electrode, indicating that the monolayer is not very compact (figures not shown).
- (39) It should be noted that the structure of the DTT monolayer on gold and further coordination of titanium(IV) isopropoxide on the OH-terminated surface (Figure 1) are hypothetical. Further characterization is necessary to confirm the proposed structure. The anchored titanium submonolayer may not be densely packed, as depicted. There is no evidence to exclude the physically adsorbed second or third layer adsorption either. Nevertheless, the uncertainty in the microscopic structure of the system does not interfere with our monitoring and evaluation of the reaction kinetics as described.
- (40) Banks, J. T.; Cappello, M. L.; Hardy, K. A.; MacDairmid, A. R.; Gallagher, M. C. Unpublished results. The presence of DTT on the gold surface was verified by strong peaks at 153 eV (S), 275 eV (C), and 510 eV (O) in the Auger spectrum. After exposure of these SAMs to a dilute solution of TTIP, the peaks for titanium at 390 and 421 eV were evident in the Auger spectrum.
- (41) Day, V. W.; Eberspacher, T. A.; Chen, Y.; Hao, J.; Klemperer, W. G. *Inorg. Chim. Acta* **1995**, *229*, 391–405.
- (42) Boyle, T. J.; Schwartz, R. W.; Doedens, R. J.; Ziller, J. W. *Inorg. Chem.* **1995**, *34*, 1110–1120.
- (43) Levine, I. N. *Physical Chemistry*, 5th ed.; McGraw-Hill: New York, 1995; p 534–539.
- (44) Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *40*, 546–551.
- (45) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th Ed.; John Wiley & Sons: New York, 1999; p 702.
- (46) Terabe, K.; Kato, K.; Miyazaki, H.; Yamaguchi, S.; Imai, A.; Iguchi, Y. *J. Mater. Sci.* **1994**, *29*, 1617–1622.
- (47) Murakami, Y.; Matsumoto, T.; Takasu, Y. *J. Phys. Chem. B* **1999**, *103*, 1836–1840.
- (48) Klein, L. C. *Annu. Rev. Mater. Sci.* **1985**, *15*, 227–248.
- (49) Courtecuisse, V. G.; Chhor, K.; Bocquet, J.-F.; Pommier, C. *Ind. Eng. Chem. Res.* **1996**, *35*, 2539–2545.
- (50) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987.