Photocatalytic Activity of Bulk TiO_2 Anatase and Rutile Single Crystals Using Infrared Absorption Spectroscopy

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A systematic study on the photocatalytic activity of well-defined, macroscopic bulk single-crystal TiO_2 anatase and rutile samples has been carried out, which allows us to link photoreactions at surfaces of well-defined oxide semiconductors to an important bulk property with regard to photochemistry, the life time of *e-h* pairs generated in the bulk of the oxides by photon absorption. The anatase (101) surface shows a substantially higher activity, by an order of magnitude, for CO photo-oxidation to CO_2 than the rutile (110) surface. This surprisingly large difference in activity tracks the bulk *e-h* pair lifetime difference for the two TiO_2 modifications as determined by contactless transient photoconductance measurements on the corresponding bulk materials.

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The quest for new and renewable energy sources without harmful environmental effects has become a key human objective. One of the most promising technologies for environmentally benign energy production involves the solar-powered splitting of water to generate hydrogen, and presently the most promising candidate for this solar-to-hydrogen conversion process is titania-based photocatalysis. Since the seminal work of Fujishima and Honda published in 1972 [1], numerous speculations about the underlying mechanisms and suggestions for the improvement of the water splitting process by the addition of doping agents to TiO_2 have been reported [1–3]. Even after nearly 40 years of work, major issues concerning the photoactivity of this important oxide are still under debate. The reasons behind the differences in activity between the two most important polymorphs of titania, rutile, and anatase are still not resolved [2]. In general, anatase powders display photocatalytic activities that are an order of magnitude higher than that of rutile [3–5]. Research to examine the surprising differences in activity between anatase and rutile thus far has focused exclusively on comparing the powdered forms of these two titania modifications. Powder studies are important, but by their nature, powdered forms of TiO_2 are poorly defined and information obtained from them to examine the intrinsic electronic properties of this oxide is not reliable. Nevertheless, a number of hypotheses have been proposed to explain the high catalytic efficiency of anatase [6] and they include invoking special surface active sites specific to the crystal structure of anatase (I), the presence of differently oriented facets on anatase powder particles (II), the higher specific surface of anatase powder particles (III), a difference in the band gap of anatase (3.2 eV) [7] relative to rutile (3.0 eV) [8] [Fig. 3] (IV), and differences in the photoexcited electron-hole (*e-h*) lifetimes (V).

In principle, such fundamental questions about surface photochemistry at oxide surfaces could be addressed using a surface science approach to understanding heterogeneous catalysis [9]. This approach, which has been successfully applied to metals, relies on experimental input obtained for well-defined model systems, i.e., surfaces of differently oriented single-crystalline substrates. From this experimental input—under active involvement of theory—a database has been constructed which, in turn, has allowed us to model and to explain fundamental processes governing surface chemistry.

For oxides, and especially for titania, research has proceeded along a different direction and has been driven by the tremendous success of microscopic methods. Scanning tunneling microscopy (STM) can be applied to TiO_2 surfaces in a straightforward fashion and has provided a wealth of information about processes on the atomic scale, e.g., reactions occurring at defect sites on rutile [10–17] and, to a lesser extent, on anatase [18–20]. By employing density functional theory, many of the STM observations have been explained and have established a high level of understanding (see the review by Diebold [11]).

However, the identification of chemical intermediates by STM and density functional theory is subject to some pitfalls (e.g., the reliable identification of OH species at titania surfaces is a challenge [21–24]) and it has become clear that spectroscopic methods are indispensable for

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establishing a reliable foundation for understanding the chemistry on oxide surfaces. In particular, vibrational spectroscopy data, which have provided key contributions within the surface science approach, are urgently required. Unfortunately, the application of the two standard experimental methods in this field, electron energy loss spectroscopy and reflection-absorption infrared spectroscopy (RAIRS) have been severely hampered by technical problems. Although a large set of IR data recorded in transmission for powders is available (see Refs. [25–27] for TiO_2), there is virtually no database containing experimental results for well-defined model systems (i.e., single-crystal surfaces). This lack of information is particularly pressing for titania-based photochemistry and investigations on the importance of the electronic excitation lifetimes in rutile vs anatase urgently require single-crystal data.

By employing a state-of-the-art infrared (IR) spectrometer modified to fit an ultrahigh vacuum (UHV) chamber [28], we recently confirmed earlier findings from mass spectroscopy on the cross section for photooxidation of CO on rutile $TiO_2(110)$ and demonstrated that the photooxidation proceeds without any intermediates [29]. Herein, we present results which strongly suggest that the higher photochemical activity of anatase as compared to rutile results from the lifetimes of the electronic excitations being an order of magnitude larger for anatase.

The RAIRS measurements were carried out in a novel UHV apparatus which combines a state-of-the-art vacuum Fourier-transform IR spectrometer (Bruker, VERTEX 80v) with an UHV system (PREVAC) as described in detail in Ref. [28]. The single-crystalline rutile $TiO_2(110)$ and anatase $TiO_2(101)$ surfaces were cleaned by several cycles of Ar ion sputtering (2.5 kV, 10 mA) and annealing at 850 K in the presence of O_2. Previous work has shown that this annealing and sputtering procedure provides well-defined substrates with a comparable defect density for both rutile and anatase [18,30]. In addition, recent work has demonstrated that on rutile TiO_2 surface defects do not have a pronounced effect on surface photochemistry [31]. The contactless transient photoconductance measurements were carried out in the microwave frequency range at 30 GHz as described in detail previously [32].

The structures of the rutile (110) and anatase (101) surfaces are presented in Fig. 1. The differences in the cross section for CO photooxidation on these surfaces are demonstrated by the RAIRS data [Fig. 2]. Exposure of anatase (101) to CO at 100 K leads to the appearance of an IR peak at 2180 cm^{-1} which is assigned to CO adsorbed on fivefold coordinated Ti^{4+} cations. When the $TiO_2(101)$ surface is further exposed to both molecular oxygen gas and UV photons with energy of 3.40 eV, the photo-induced oxidation of CO occurs as confirmed by the significant decrease of the CO band intensity. Simultaneously, a new peak shows up at 2340 cm^{-1} being characteristic for physisorbed CO_2. The fact that the two peaks at 2180 and 2340 cm^{-1} show a different sign results from the different orientation of the adsorbed species, CO and CO_2, relative to the substrate. For a more thorough discussion of this interesting effect affecting grazing incidence IR spectroscopy, see the recent paper by Xu *et al.* [33]. Based on the IR data shown in Fig. 2(b) the photoreaction cross section Q is determined to 2.0×10^{-17} cm^2 for anatase, an order of magnitude larger than that for the different titantia pseudomorph, rutile (2.0×10^{-18} cm^2). The dark reaction ($CO + O_2$) does not yield any CO_2 on either of the substrates. Also, in the presence of UV but the absence of O_2, no reaction was observed. The absence of any additional vibrational bands in the IR data for anatase shows that like rutile, CO photooxidation occurs without the formation of intermediates (e.g., carbonate), thus allowing us to obtain direct information about the underlying photophysical processes.

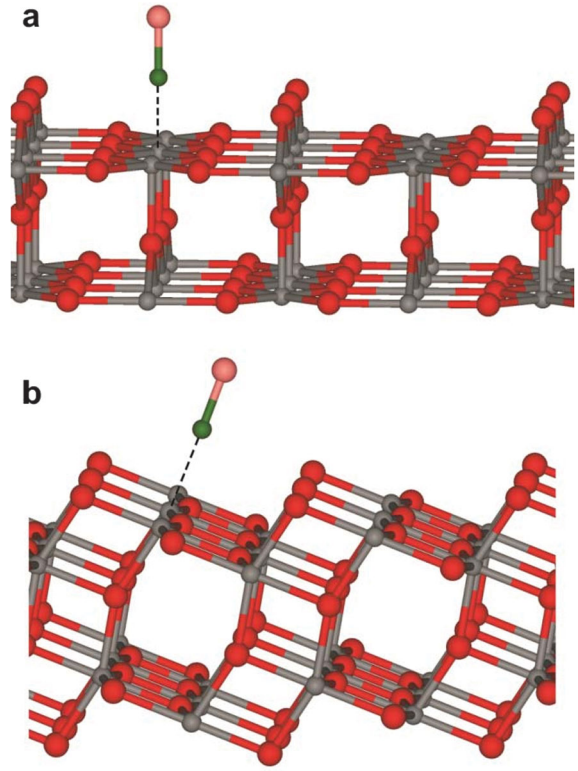

FIG. 1 (color). Ball-and-stick models of different titania surfaces. (a) Rutile $TiO_2(110)$. (b) Anatase $TiO_2(101)$. CO binds via the C-atom to a surface Ti ion. Note the very similar binding geometry on the two different titania pseudomorphs. Red or pink ball: O; grey ball: Ti; green ball: C.

The effects that we observe for well-defined anatase and rutile cannot be attributed to the presence of significantly more surface defects in anatase. It is a general consensus that the preparation procedures employed here yields well-defined surfaces of reproducible quality, with the rutile (110) surface containing 3% to 5% surface oxygen

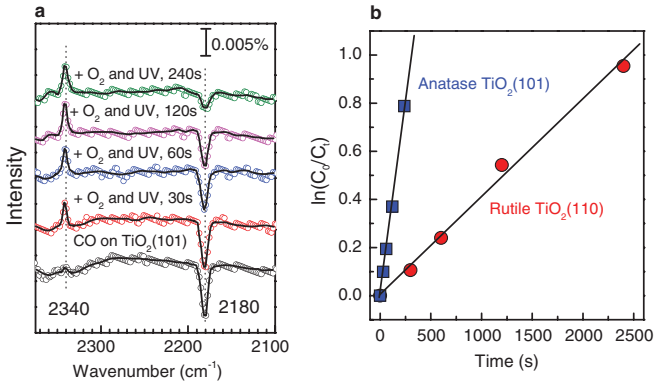

FIG. 2 (color). Photooxidation of CO on TiO_2 monitored by RAIRS. (a) RAIRS data of CO and CO_2 during photo-induced CO oxidation reaction on the anatase $TiO_2(101)$ single-crystal surface at 100 K. The sample was first exposed to CO (10^{-7} mbar) and then exposed to O_2 (10^{-7} mbar) and UV light (3.4 eV, 2×10^{14} photons/(cm^2 s)) for different times. (b) Comparison of the reaction cross section Q of CO photo-oxidaton on rutile $TiO_2(110)$ and anatase $TiO_2(101)$. Plotted is the $\ln(C_0/C_t)$ as a function of the UV irradiation time. C_0 is the initial CO coverage before UV irradiation, and C_t is the CO coverage after irradiation at time t. The blue squares are the data for CO on anatase $TiO_2(101)$ as shown in Fig. 2(a). The red circles denote data for CO on rutile TiO_2 (110).

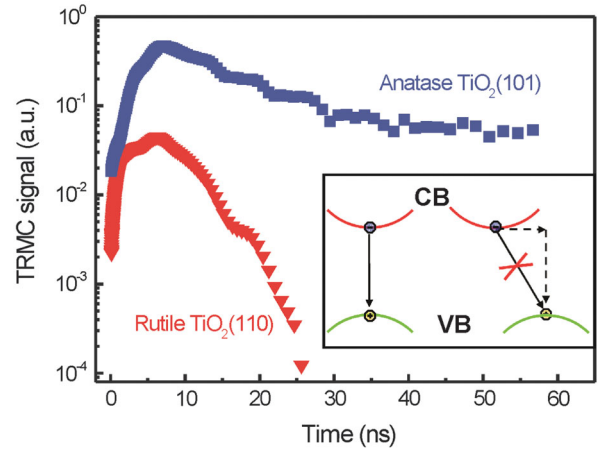

FIG. 3 (color). Transient photoconductance measurements at 30 GHz induced by 355 nm laser pulses (10 ns FWHM) in a rutile (red) and in an anatase (blue) TiO_2 single crystal. The inset shows the schematic model of the band gap of rutile (left) and anatase (right). The indirect band gap in anatase makes direct transitions of excited electrons from the bottom of the conduction band (CB) to the top of the valence band (VB) impossible.

defects, while the anatase (101) surface contains less than 2% defects [18,20,34]. An independent proof of the quality of the rutile surface is provided by IR spectroscopy, where CO adsorbed close to defects shows a redshift of 10 cm^{-1} [35]. In addition, the almost exact agreement of the CO stretching frequencies for both substrates, 2183 and 2180 cm^{-1} for rutile and anatase, respectively, provides strong evidence that the nature of the chemical interaction binding CO to these two different titania pseudomorphs must be very similar. We thus conclude that the chemical reactivity related explanations I–IV (see above) proposed previously to account for differences in photocatalytic activity do not appear to be supported by our experimental findings on well-defined single-crystal substrates. We thus have to consider hypothesis V, which suggests a correlation with different lifetimes of the photogenerated electron-hole pairs in the two titania pseudomorphs.

Unfortunately, experimental information of the lifetime of *e-h* pairs in bulk titania single crystals is available only for rutile [36], but not for anatase. Therefore, we have determined the *e-h* lifetime in bulk TiO_2 single crystals using contactless transient photoconductance measurements. A comparison of the data for the two titania pseudomorphs [Fig. 3] clearly demonstrates a dramatic difference: the *e-h* lifetime is about an order of magnitude larger for anatase than for rutile. From the shape of the curve for the signal in rutile, it can be concluded that the decay is very fast (< 1 ns) and already active during the excitation phase. Such a short lifetime also accounts for the much smaller signal amplitude in rutile. For anatase, in contrast, the decay is much slower and reveals a lifetime of photo-excited carriers of larger than 10 ns. Since these data are recorded for high-quality single crystals with macroscopic dimensions, extrinsic effects arising from bulk defects and impurities, interparticles effects, particle size effects, or surface effects (e.g., OH-groups acting as hole traps, adventitious surface carbon, etc.) can be largely ruled out.

Although not directly relevant for our main conclusions, we will briefly speculate about the origin of the huge difference in *e-h* lifetimes between rutile and anatase. Previous theoretical work has clearly demonstrated that the band structure of anatase exhibits a special topological feature, namely, an indirect band gap [see inset in Fig. 3] [37]. When electrons relax (on a fs time scale) to the bottom of the conduction band (CB) after they have been photoexcited (vertically) into unoccupied states, they will not be able to recombine directly with holes, thus increasing the *e-h* lifetime relative to a situation with a direct band gap. As a result, the diffusion length of *e-h* pairs excited in the bulk will increase also, thus enhancing the chance of photoexcited *e-h* pairs to drive surface chemical reactions. For rutile, so far no general consensus on the presence or absence of a direct band gap has been obtained yet. Earlier experimental data from Kavan *et al.* [38] pointed towards an indirect gap for rutile. Some recent theoretical works have indicated the presence of a direct gap in rutile [37], but even the most recent and most advanced electronic structure calculations [39,40] do not completely agree on this point. We take our result as a strong indication that the rutile band gap might indeed be a direct one, allowing for a much faster recombination of photoexcited *e-h* pairs in rutile than in anatase.

Taken together, the results from the surface cross section and the bulk lifetime experiments provide us with a consistent picture explaining the larger activity for photooxidation of CO on anatase vs rutile. We argue that the longer lifetime of *e-h* pairs in anatase facilitates the translocation of the photon-excited electrons and holes from the bulk to the surface, where the photochemical reactions take place [41].

The present studies have important consequences with regard to the fundamental understanding of photochemical energy conversion in general and the high performance of anatase, in particular. Disturbing the band structure of anatase, e.g., through dopants, will reduce the lifetimes by making *e-h* recombinations at localized defects possible. The latter effect will at some point overcompensate for the dopant-induced gain in the photochemical cross section that results from a reduction of the band gap. For nanoparticle sizes in the 1 nm region the electronic structure of particles cannot be described well with a band structure model [42], and the longer *e-h* lifetimes of anatase are predicted to approach those of rutile since the indirect band gap will no longer reduce the recombination rate.

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