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.

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 photocactivity 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