Probing UV photo-oxidation on oxide surfaces

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UV light directly oxidizes carbon monoxide on rutile titanium dioxide surfaces.

Photochemistry at oxide surfaces is important for solar-energy conversion. The most promising candidate for solar-powered water splitting (i.e., hydrogen production) and, thus, benign energy production is titania (TiO$_2$)-based photocatalysis. Since the initial work of Fujishima and Honda, numerous improvements related to water splitting have been reported. However, even after nearly 40 years of research, major issues concerning the photoactivity of this important oxide are still debated. For example, a convincing explanation as to why the anatase polymorph of TiO$_2$ shows much more photocatalytic activity than its rutile form, by an order of magnitude, is unavailable.

Even simple reactions, such as carbon monoxide (CO) oxidation, are not understood because of the almost exclusive focus on oxide-powder samples. Such samples are structurally undefined, while all possible surface orientations—often with a high defect density—are probed simultaneously.

The surface-science approach to understanding heterogeneous catalysis has been quite successful. Consequently, progress toward unraveling fundamental principles governing oxide-surface chemistry urgently necessitates detailed experimental and theoretical studies on model systems.

Especially for TiO$_2$, surface-oxide research within the past two decades has proceeded along a different direction than that of metal surfaces. Primarily driven by the tremendous success of microscopic interrogation, particularly by scanning-tunneling microscopy (STM), a wealth of structural information has become available about processes on the atomic scale, e.g., reactions occurring at defect sites on rutile and, to a lesser extent, anatase. By employing density functional theory (DFT), many STM observations have been explained.

However, identification of chemical intermediates by STM/DFT is subject to some pitfalls (e.g., reliable identification of hydroxyl species at TiO$_2$ surfaces remains a challenge). It has become clear that spectroscopic methods, and in particular IR vibrational spectroscopy, are indispensable for establishing a reliable foundation of chemistry on oxide surfaces, as has been demonstrated with respect to chemistry on metal surfaces through the surface-science approach.

Unfortunately, specific optical properties of oxides lead to severe problems for applications of reflection-absorption IR spectroscopy (IRRAS), the standard experimental method in this field. Sensitivity to molecular vibrations within adsorbates on oxides is reduced by two orders of magnitude with respect to metals. Consequently, despite the availability of a large set of IR data recorded in transmission mode for powders, data for well-defined oxide model systems is virtually unavailable. This is one of the primary reasons why our understanding of chemistry and photochemistry on oxide surfaces is still relatively limited.

We recently overcame these intensity problems by employing a novel, carefully optimized apparatus, where an IR

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lengthier lifetimes of electronic excitations (electron-hole pairs) of anatase are predicted to be reduced to the values characteristic of rutile, since the indirect band gap will no longer reduce the electron-hole recombination rate. We next plan to look at other photochemical reactions on TiO$_2$ and zinc oxide surfaces, with particular emphasis on doping effects.

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References


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