
II.K.10 Fundamental Investigations of Water Splitting on Model TiO₂ Photocatalysts Doped for Visible Light Absorption

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Objectives

The objectives of this project are to provide fundamental understanding into how doping influences the visible-light absorption properties of TiO₂, to characterize how charge carriers from visible light absorption events participate in surface redox processes, and to determine what is the overall mechanism of the visible light initiated water splitting. Research components of the project include: (1) controlled doping of single crystal TiO₂ substrates and films (anatase and rutile) via molecular beam epitaxy and ion beam implantation, (2) dopant characterization using a wide variety of state-of-the-art techniques (e.g., scanning probe microscopy, photoemission, diffraction and electron paramagnetic resonance spectroscopies), (3) theoretical modeling of the physical and electronic structures of the doped and undoped surfaces using DFT methodologies, and (4) UHV surface science methods to probe the thermal and non-thermal (photon- and electron-initiated processes) of the reaction mechanism, kinetics, wavelength/energy dependence and surface specificity of the visible-light promoted splitting of water. These efforts contribute to long-term objectives of DOE BES toward development of new and improved concepts for solar energy conversion, specifically through the photocatalytic production of hydrogen.

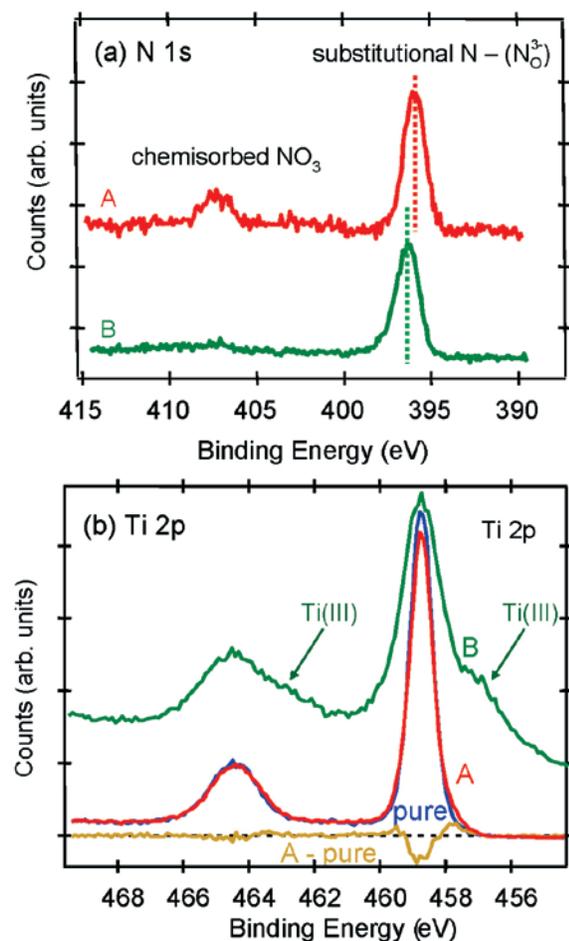
Technical Barriers

Development of new energy sources is a major need for the 21st century. Hydrogen has considerable potential as an alternative fuel, especially if it can be generated inexpensively from an abundant raw material such as water. However, the efficient photocatalytic splitting of water to generate hydrogen using sunlight remains an as yet unachieved goal from a technological standpoint.

New fundamental knowledge is needed regarding how potential photocatalyst materials can be made (more) active in the visible. Similarly, new insights are needed into the water splitting mechanism, particularly with regards to identification of thermodynamic and kinetic bottlenecks, in order to facilitate design of the most effective photocatalytic systems.

Abstract

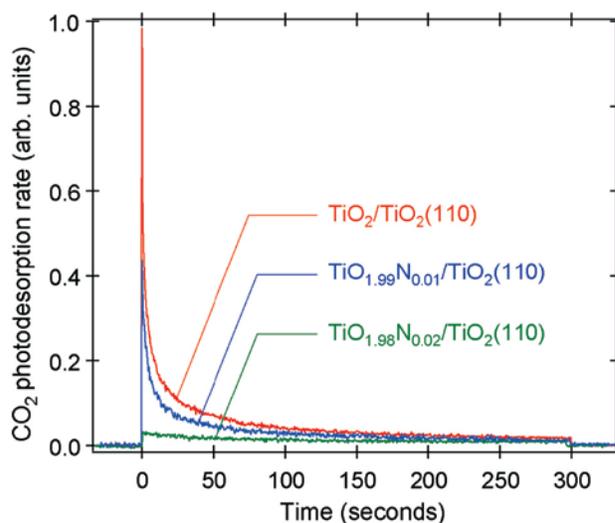
One of the major needs for the 21st century is the development of alternative energy sources to fossil fuels that do not contribute to greenhouse gas emissions. Hydrogen has considerable potential as an alternative fuel because it is carbon-free, facilitates use of more efficient power generation systems (e.g., fuel cells), and can be used to chemically reduce carbon oxides (CO, CO₂) to chemical fuels. Solar-to-chemical energy conversion of water to H₂ is especially attractive given the abundance of water and of the ‘free’ energy available in sunlight. For this reason, the discovery of Fujishima and coworkers in 1969 that water could be catalytically split using electrical energy generated at titanium dioxide (TiO₂) photoelectrodes continues to motivate photochemical research toward H₂ as an alternative fuel, and in turn has revolutionized the field of heterogeneous photocatalysis. While TiO₂ absorbs little of the solar spectrum, doping may red-shift the TiO₂ absorption spectrum into the visible. However, a link between doping and increased photoactivity for water splitting in the visible has not been well-established. As such, there is a specific need for basic science to provide a solid foundation of understanding of how doping influences the visible-light photocatalytic properties of TiO₂. There is also a general need for a better understanding of the heterogeneous photocatalytic water splitting reaction. In this project, we examine the fundamental properties of heterogeneous photocatalytic water splitting on undoped and ion-doped TiO₂ single crystal surfaces. We also examine the structure and chemical/photochemical activities of water layers on model doped and undoped TiO₂ surfaces. These studies focus on determining the water splitting mechanism with emphasis on the fundamental surface chemistry of key intermediates (such as Ti³⁺-OH and HO₂ groups) generated by non-thermal means. These tasks provide important fundamental information lacking in understanding photocatalytic water splitting, and directly address two key elements (“Design of Catalysts on the Nanoscale” and “Solar Hydrogen Production”) of the Hydrogen Fuel Initiative.



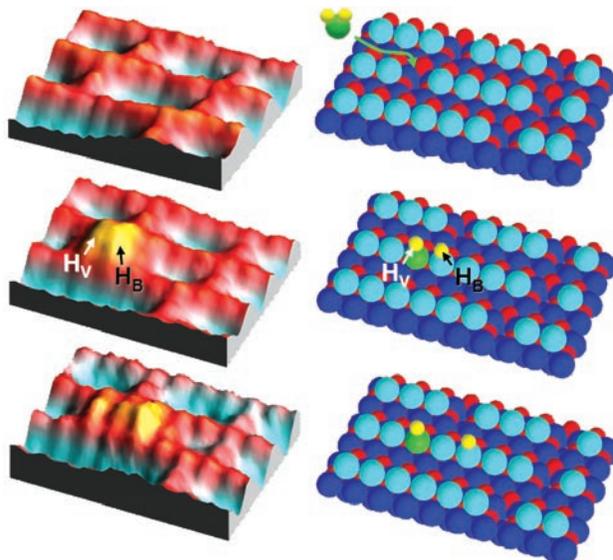
High-resolution N 1s (a) and Ti 2p (b) core-level spectra for the two $\text{TiO}_{2-x}\text{N}_x/\text{TiO}_2(110)$ films. A: 2% N; B: 6% N.

Progress

- We have successfully grown epitaxial films of N-doped anatase and rutile on lattice matched oxide single crystal surfaces. The substitutional solubility of N in TiO_2 is limited to $\sim 2\%$, above which a separate TiN_x surface phase forms. Substitutional anion dopants in anatase and rutile are accompanied by an equivalent (or greater) concentration of Ti^{3+} donors. Films exhibit new absorption feature in the visible at ~ 2.8 eV resulting from substitutional N doping.
- Using a prototypical organic (trimethyl acetic acid - TMAA) as a probe molecule for photogenerated holes, we have shown that substitutional N doped in $\text{TiO}_2(110)$ readily scavenges holes generated during band-to-band excitation with UV light.
- STM studies on $\text{TiO}_2(110)$ reveal that bridge bonding OH groups resulting from water dissociation at an oxygen vacancy site on $\text{TiO}_2(110)$ are electronic inequivalent. The deposited proton diffuses with a higher probability than the proton



CO_2 photodesorption spectra from TMAA photodecomposition on pure and N-doped TiO_2 rutile.



STM images and ball models of the clean $\text{TiO}_2(110)$ (top), $\text{TiO}_2(110)$ after adsorption and dissociation of a single water molecule (center), and after a single along-row hop of hydrogen (bottom).

retained on the water molecule's O atom. Similar studies with O_2 adsorption reveal dissociation with one O atom filling the vacancy, but the other atom being hyperthermally excited and diffusing several unit cells across the surface.

- Using low energy electrons as both sources of electronic excitation and as probes, we have shown that the redox state of fragments generated from water activation depends critically on the thickness of the irradiated water layer. Oxidized water surface products (e.g., O atoms) accumulate for water coverages below 1 ML, whereas reduced water

products (e.g., H atoms) populate the bridging O rows for water coverages above 1 ML. This indicates that the redox state of water is sensitive to proximity of the molecule to the surface. There is also a stronger thermodynamic tendency for electronically excited water to dissociate at the $\text{TiO}_2(110)$ interface than in a water film away from the interface.

Future Directions

- Hole mediated photochemistry on N-doped TiO_2 with x (in $\text{TiO}_{2-x}\text{N}_x$) above and below the critical concentration limit for pure substitution.
- Film thickness dependence studies where the N dopant is placed at various depths in the film.
- Epitaxial growth of C-doped anatase and rutile TiO_2 films.
- Epitaxial growth of Fe-doped TiO_2 and anion-codoped TiO_2 .
- Identification of probe molecules that are sensitive to electron-mediated photochemistry on TiO_2 .
- Investigation of the thermal and non-thermal chemistries of water films on well-characterized $\text{TiO}_2(110)$ including the diffusion of water monomers, and the photon- and electron-stimulated reactions at comparable photon energies.
- Studies of the adsorption, diffusion and chemical reactions of hydrogen and oxygen using STM, adsorption/desorption measurements and theory.
- Deposition of metal nanoparticles on $\text{TiO}_2(110)$, and examination of their thermal and non-thermal chemistry for water films.

Publications

1. Z. Zhang, O. Bondarchuk, B.D. Kay, J.M. White, Z. Dohnalek, "Imaging Water Dissociation on $\text{TiO}_2(110)$: Evidence for Inequivalent Geminate OH Groups," **Journal of Physical Chemistry B** 110 (2006) 21840. (Featured on journal cover.)
2. S.A. Chambers, S.H. Cheung, V. Shutthanandan, S. Thevuthasan, M.K. Bowman, A.G. Joly, "Properties of Structurally Excellent N-doped TiO_2 Rutile", invited review article for special issue of Chemical Physics entitled *Doping and Functionalization of Photoactive Semiconducting Metal Oxides*, ed. C. DiValentin, U. Diebold, A. Selloni, **Chemical Physics** 339 (2007) 27.



3. S.H. Cheung, P. Nachimuthu, A.G. Joly, M.H. Engelhard, M.K. Bowman, S.A. Chambers, "N Incorporation and Electronic Structure in N-doped $\text{TiO}_2(110)$ Rutile," **Surface Science** 601 (2007) 1754.
4. C.D. Lane, N.G. Petrik, T.M. Orlando, G.A. Kimmel, "Electron-stimulated oxidation of thin water films adsorbed on $\text{TiO}_2(110)$," **Journal of Physical Chemistry C** 111 (2007) 16319.
5. N.G. Petrik, G.A. Kimmel, "Hydrogen bonding, H/D exchange and molecular mobility in thin water films on $\text{TiO}_2(110)$," **Physical Review Letters** 99 (2007) 196103.
6. S.A. Chambers, "Advances in the Surface Science of TiO_2 - A Global Perspective", invited review article for **Journal of Surface Science, Japan** 28 (2007) 561.
7. O. Bondarchuk and I. Lyubintsky, "Preparation of $\text{TiO}_2(110)-(1 \times 1)$ surface via UHV Cleavage: An STM Studies," **Reviews of Scientific Instrumentation** 78 (2007) 113907.
8. C.D. Lane, N.G. Petrik, T.M. Orlando, G.A. Kimmel, "Site-dependent electron-stimulated reactions in water films on $\text{TiO}_2(110)$," **Journal of Chemical Physics** 127 (2007) 224706.
9. S.H. Cheung, P. Nachimuthu, M.H. Engelhard, C.M. Wang, S.A. Chambers, "N Incorporation, Composition and Electronic Structure in N-doped $\text{TiO}_2(001)$ Anatase Epitaxial Films Grown on $\text{LaAlO}_3(001)$," **Surface Science** 602 (2008) 133.
10. Z. Yu; C. Wang; Y. Du; S. Thevuthasan; I. Lyubintsky, "Reproducible tip fabrication and cleaning for UHV STM," **Ultramicroscopy** 78 (2008) 113907.
11. Y. Du, Z. Dohnálek, and I. Lyubintsky, "Transient Mobility of Oxygen Adatoms upon O_2 Dissociation on Reduced $\text{TiO}_2(110)$," **Journal of Physical Chemistry C** 112 (2008) 2649. (Featured on journal cover.)
12. S.A. Chambers, "Molecular Beam Epitaxial Growth of Doped Transition Metal Oxide Semiconductors", invited review article for **Journal of Physics: Condensed Matter** (2008) in press.
13. G.A. Kimmel and N.G. Petrik, "Tetraoxygen on reduced $\text{TiO}_2(110)$: Oxygen adsorption and reactions with oxygen vacancies," **Physical Review Letters**, submitted.

