Modeling TiO$_2$ surfaces for hydrogen generation from water

Karin Larsson

Photo-induced decomposition of water on TiO$_2$ electrodes offers the prospect of sustainable hydrogen production, but the underlying character of adsorption remains a matter of controversy.

Titanium dioxide (TiO$_2$), versatile and widely used for photocatalysis, is a promising material for air and water remediation with broad applications in coating technologies and maintenance-free surfaces. Using both experimental approaches and theoretic modeling, we investigated the prospects of using Niobium (Nb)-doped TiO$_2$ as an active photocatalytic. At fairly high doping concentrations (10-20 mol %), we showed that this material is a poor solar-active photocatalyst compared to TiO$_2$, despite the fact that Nb doping extends optical absorption into the visible spectrum and uses a larger portion of sunlight.

Using the interplay between measurements by Fourier transform spectroscopy (FTIR) and density functional theory (DFT) calculations, we also investigated in detail the importance of cation coordination and bonding of intermediate reaction products for the total photocatalytic oxidation rate.

Cost-effective and sustainable hydrogen production makes photo-induced decomposition of water on TiO$_2$ electrodes a topic of special interest. The possibility that water can be photoelectrochemically split by illuminating TiO$_2$ was first demonstrated thirty-five years ago. However, the high intrinsic band gaps of the two different structures of TiO$_2$ (the anatase and rutile bandgaps are 3.2 eV) allow only absorption of the ultraviolet part of the solar irradiation. Doping with anionic species (e.g., N, C, S, F) or cationic species (transition metals), has shown promise in reducing the TiO$_2$ band gap, which would thereby extend optical absorption to the visible light region of the solar spectrum.

Although water adsorption on TiO$_2$ has been been extensively investigated in both theory and experiment, the type of adsorption remains a matter of controversy. Experiments suggest that, for the most part, H$_2$O adsorbs associatively. Dissociation may occur at low coverages (<15%) associated with defective sites.

Figure 1. Adsorption of water molecules to (a) a non-doped and (b) Nb-doped rutile (110) surface.

By contrast, theoretical modeling predicts various degrees of both associative and dissociative water adsorption.

The effect of cationic and anionic dopants on the water adsorption process for both anatase and rutile structures of TiO$_2$, has also been investigated on a theoretic basis by our research group (see Figure 1). For non-doped surfaces, we found anatase to be more reactive towards water adsorption than rutile. This tendency was greater when using nearby N substituents within the surface. However, neighboring H$_2$O adsorbates were required in order to to improve the probability of disrupting the water bond. The situation was totally different when using Nb dopants. Here Nb was found to largely affect H$_2$O adsorption on rutile, and to clearly affect the tendency for H$_2$O dissociative adsorption at higher surface coverages.

Author Information

Karin Larsson
Angstrom Laboratory
Materials Chemistry
Uppsala, Sweden
http://www.mkem.uu.se

Karin Larsson is a Professor in Inorganic Chemistry at the University of Uppsala. Her major research focus is theoretical investigation of surface processes on semiconducting materials.

Continued on next page
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