Semiconductor Photocatalysis - DTU Orbit (27/07/2019)

**Semiconductor Photocatalysis: Electronic Hole Trapping in TiO$_2$**

Photocatalysis is presently used in large variety of applications and is one of the possible strategies for future sustainable fuel production from solar energy. A general picture of a photocatalytic process is well known: photogeneration of electron-hole pairs, excess carrier transport to distinct reactive sites and finally carrier utilization in a chemical reaction. For most photocatalyst a detailed understanding of these steps, however, is lacking yet it is crucial to elucidate photocatalyst limitations. Of particular importance is gaining insight into the nature of photogenerated carriers as they play a central role in all the basics steps of a photocatalytic process.

The main objective of this thesis is to elucidate the experimentally observed localized nature of photogenerated electron holes in titanium dioxide—most studied, yet poorly understood photocatalyst. By means of the density functional theory (DFT) and its simple extension, the linear expansion self-consistent field DFT, it is shown that in TiO$_2$ the photogenerated holes self-trap forming O$^-$ small polarons. Self-trapping strength is significantly modified in surface layers due to the variation of surface electrostatic potential. This finding explains differences in photooxidative properties among rutile and anatase TiO$_2$ facades.

Optical absorption spectra and hole hopping mobilities of the O$^-$ centers in TiO$_2$ have been calculated. Since time resolved optical spectroscopies are common techniques to study hole dynamics in TiO$_2$, these results should aid analysis of photocatalytic processes on TiO$_2$.

Apart from photocatalysis this thesis also deals with the problem of the localization/delocalization error in approximate DFT functionals—the effect of the incorrect, nonlinear description of fractional electron systems by approximate exchange-correlation functionals. It is shown that by removing the total energy nonlinearity a more consistent description of states with different degrees of localization can be achieved.

**General information**
Publication status: Published
Organisations: Department of Physics, Theoretical Atomic-scale Physics
Contributors: Zawadzki, P.
Number of pages: 138
Publication date: 2011

**Publication Information**
Place of publication: Kgs. Lyngby
Publisher: Technical University of Denmark, Center for Atomic-Scale Materials Physics
Original language: English
Electronic versions: Pawel_Zawadzki.pdf