On the possibility of photocatalytic water splitting on the rutile TiO$_2$(110) surface
a theoretical study

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CCP 2014, Boston
Photoelectrochemical cells

TiO$_2$ photocatalysis

R. Su et al. ACS Nano 8, 3490 (2014)
TiO$_2$ photocatalysis

Au co-catalyst

Au/Pd

systematic improvement?

R. Su et al. ACS Nano 8, 3490 (2014)
Water splitting on rutile TiO$_2$

bulk

Wulff construction

(110) surface

Water splitting on rutile TiO$_2$

Entirely light-driven?

Develop a computational strategy for the study of photocatalyzed reactions on semiconductor surfaces using (time-dependent) density functional theory.

Investigate the possibility of photocatalytic water splitting on the rutile TiO$_2$ (110) surface.
Structural model of the rutile TiO$_2$ (110) surface

DFT+$U$ (PBE), $U(Ti_{3d}) = 4.2$ eV
Kohn-Sham band gap: 2.2 eV

\[
\left[ -\frac{1}{2} \nabla^2 + V_{\text{ion}} + V_H + V_{\text{xc}}^{\text{DFT}} \right] \psi_{n\mathbf{k}}^{\text{DFT}} = E_{n\mathbf{k}}^{\text{DFT}} \psi_{n\mathbf{k}}^{\text{DFT}}
\]

Software: GPAW (grid-based)
Excited-state molecular dynamics

Time evolution: Ehrenfest dynamics within time-dependent-DFT

\[ i \frac{\partial \phi_n}{\partial t} = \hat{H}_{KS} \phi_n \]
\[ \rho(r, t) = \sum_{i=1}^{N} |\phi(r, t)|^2 \]

Electronic subsystem: Quantum mechanical treatment

overlap matrix

due to ion motion

\[
\begin{bmatrix}
S + i \frac{\Delta t}{2} (H_{1/2} + P)
\end{bmatrix}
\begin{bmatrix}
c_n(t + \Delta t)
\end{bmatrix}
\]

\[
= \begin{bmatrix}
S - i \frac{\Delta t}{2} (H_{1/2} + P)
\end{bmatrix}
\begin{bmatrix}
c_n(t)
\end{bmatrix} + O(\Delta t^3)
\]

KS Hamiltonian

basis function coefficients

Excited-state molecular dynamics
Time evolution: Ehrenfest dynamics within time-dependent-DFT

\[ i \frac{\partial \phi_n}{\partial t} = \hat{H}_{KS} \phi_n \]
\[ \rho(r, t) = \sum_{i=1}^{N} |\phi(r, t)|^2 \]

Ionic subsystem: Classical treatment (velocity Verlet)

\[ \mathbf{F}_{a}^{EC} = -\frac{\partial E_{el}}{\partial \mathbf{R}_a} + \sum_n f_n c_n^* \left( \text{HS}^{-1} \mathbf{D}_a + \text{c. c.} \right) c_n \]

Excited-state molecular dynamics
Vertical excitation: Linear expansion Delta Self-Consistent Field

\[ n(r) = \sum_n f_{N-1}(T, \varepsilon_n) |\psi_n(r)|^2 + |\psi_a(r)|^2. \]

\[ |\psi_a\rangle = \sum_n c_{na} |\psi_n\rangle, \quad c_{na} = \langle \psi_n | \psi_a \rangle \]

\[ \varepsilon_a = \sum_n |c_{na}|^2 \varepsilon_n. \]

High-energy excitation

Vertical excitation energy: 9.60 eV (EUV, 130 nm), 100 K

non-bonding orbital of molecular water

light green for less charge with respect to the ground state (h⁺)
orange for more charge (e⁻)
High-energy excitation

Vertical excitation energy: 9.60 eV (EUV, 130 nm), 100 K

light green for less charge
orange for more charge
Chemical bonding at the surface

Maximally-localized Wannier functions

bulk DOS (scaled)

$w(\epsilon)$

$\epsilon(\text{eV})$

$10^{-3}$
Low-energy excitation

Vertical excitation energy: 3.93 eV (UV, 315 nm), 100 K

light green for less charge
orange for more charge
Water splitting on defected surface

Vertical excitation energy: 1.00 eV

100 K
Thermally driven

60 K
Not observed

80 K
Photon-induced, phonon-assisted

80 K
0 fs
1.24 Å

15 fs
1.10 Å

light green for less charge
orange for more charge
Charge-carrier transport

stoichiometric

9.60 eV

http://tinyurl.com/ccp2014gtm
Alignment of energy levels in TiO$_2$/methoxy

Work by G. Kolesov
On the possibility of photocatalytic water splitting on the rutile TiO$_2$(110) surface

A framework was developed for the study of photocatalysis on semiconductors. We found that the completeness of the first step of water dissociation on the surface depends sensitively on the local atomic environment and external parameters such as temperature. Thermal and photon-induced effects can act in a complementary manner during dissociation on defect-containing surfaces that leave an ambiguity in the causal sequence.

People
Till Cremer and Fanny Hiebel at the Department of Chemistry & Chemical Biology, Harvard University

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thank you