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Reduced and Doped TiO2: what is the nature of the defect states?

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# Reduced and doped TiO<sub>2</sub>: what is the nature of the defect states?



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#### TiO<sub>2</sub>: very important role of defects

Color change in TiO<sub>2</sub> samples induced by incresing level of defects

Defects change electronic properties of the material

Defect engineering of TiO<sub>2</sub> for photocatalytic applications



Main defects: oxygen vacancies, Ti<sup>3+</sup> ions

# OUTLINE

## Part I : intrinsic defects

O vacancies and Ti interstitials

### Part II : extrinsic defects

N impurities and their interplay with other defects



Experimental proofs of formation of reduced bulk titania: (1) UV-vis (2) UPS (3) XPS (4) EPR

Every theoretical method dealing with reduced TiO<sub>2</sub> should be able to reproduce these features... (1) absorption bands in the visible region responsible for the change in color (assigned to d-d transitions)

(2) occurrence of a new
state in the gap at about
0.8 eV below the
conduction band attributed
to the reduced Ti<sup>3+</sup> ions

(3) shift in the core level binding energies of the reduced Ti atoms from Xray photoemission (XPS)

(4) presence of more than one EPR signal associated to various kinds of paramagnetic Ti<sup>3+</sup> ions in the lattice



Aponetic field B (10)

#### **DFT** calculations

#### QUANTUM EXPRESSO (pure DFT, DFT+U)

plane-wave-pseudopotential approach PBE functional – spin polarized calculations 96-atoms supercells



#### CRYSTAL06 (hybrid DFT)

atomic gaussian basis set approach Hybrid DFT functionals – spin polarized calculation hyperfine coupling constants (EPR)



#### O vacancy in bulk anatase: standard DFT





No states in the gap, electrons fully delocalized, no major geometrical distortion around the defect

Problem due to self-interaction in DFT

### Pragmatic ways to improve the model

#### **DFT+U** methods

Systems where atomic-like features are persistent in the solid: explicit description of correlation by an on-site correlation term U for a few selected localized orbitals Add a Hubbard-like E<sub>Hub</sub> term to the standard functional:

$$E_{\text{LDA+U}}[n(\mathbf{r})] = E_{\text{LDA}}[n(\mathbf{r})] + E_{\text{Hub}}[\{n_m^{I\sigma}\}] - E_{\text{DC}}[\{n^{I\sigma}\}]$$

Anisimov et al., Phys. Rev. B 44, 943 (1991)

Hybrid functionals

Use of hybrid functionals where HF-like exchange is mixed in with the DFT exchange: B3LYP (20%), H&H LYP (50%)

$$E_{xc}^{B3LYP} = a \ E_x^{LSDA} + (1-a) \ E_x^{HF} + b \ \Delta E_x^{Becke} + (1-c) \ E_c^{LSDA} + c \ E_c^{LYP}$$

Becke J. Chem. Phys. 98, 5648 (1993)

O vacancy in bulk anatase: B3LYP and DFT+U

 Remove an O atom: 2e left on the system. Quantities of interest:

 (1) Energy gap (E<sub>g</sub>)
 (2) Distance of impurity levels from bottom of conduction band (ΔE<sub>1</sub>, ΔE<sub>2</sub>)





Finazzi, Di Valentin, Selloni, GP, J. Chem. Phys. 128, 182505 (2008)

#### Similar results for rutile (110) surface

B3LYP xc functional, c(4x2) surface cell, AO Gaussian basis sets, spin polarized calculations, CRYSTAL03



 O vacancy: two electrons localized on two nonequivalent Ti ions
 triplet ground state (magnetic)
 Two states in the gap at 1.2 and 0.9 eV below conduction band (as in the experiment)

Di Valentin, GP, Selloni, Phys. Rev. Lett. 97, 166803 (2006)

#### Polaronic nature of O vacancy



Geometry: B3LYP DOS: B3LYP localization

Geometry: B3LYP DOS: PBE localization

Geometry: PBE DOS: B3LYP no localization

Geometry: PBE DOS: PBE no localization

Di Valentin et al. Chem. Phys. 339, 44 (2007)

### Reduced titania: a problem for theory

Pure functionals fail to reproduce the correct band structure

DFT+U or hybrid functionals improve the description but suffer from the use of "empirical" parameters

Need to compare different approaches

Need for clean experimental data (often missing)

Generate defects in controlled way and characterize them by various spectroscopies (central role of EPR)

#### In summary ...

F and Nb doping of stoichiometric TiO<sub>2</sub> leads to lattice Ti<sup>3+</sup> ions in pseudo-octahedral enviornment

H doping of stoichiometric TiO<sub>2</sub> leads to the same lattice Ti<sup>3+</sup> ions

Reduction of stoichiometric TiO<sub>2</sub> in mild conditions leads mainly to lattice Ti<sup>3+</sup> ions

Strong evidence from comparison of measured and computed EPR spectra of localized Ti 3d states at low T

Only hybrid or DFT+U functionals lead to electron localization

Localized and delocalized states are very close in energy and can depend on external conditions (T, P, etc.)

#### New experiments: delocalization is a temperature effect?

PRL 100, 055501 (2008)

PHYSICAL REVIEW LETTERS

week ending 8 FEBRUARY 2008

#### **Defect States at the TiO<sub>2</sub>(110) Surface Probed by Resonant Photoelectron Diffraction**

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 (Received 30 May 2006; revised manuscript received 2 November 2007; published 4 February 2008)

The charge distribution of the defect states at the reduced  $TiO_2(110)$  surface is studied via a new method, the resonant photoelectron diffraction. The diffraction pattern from the defect state, excited at the Ti-2*p*-3*d* resonance, is analyzed in the forward scattering approach and on the basis of multiple scattering calculations. The defect charge is found to be shared by several surface and subsurface Ti sites with the dominant contribution on a specific subsurface site in agreement with density functional theory calculations.

Delocalization of trapped electron occurs at RT (but here good agreement for the wrong reason: DFT calculations done at 0 K!)

Barrier for e- migration from site to site <0.1 eV (see M. Dupuis lecutre). At RT e<sup>-</sup> is mobile on the time scale of experiment







#### Properties of sol-gel prepared anatase N-doped TiO<sub>2</sub>



UV-vis absorption spectra of pure and N-doped anatase Rate of methylene-blue degradation on N-doped (a) and pure (b) anatase





Both interstitial and substitutional N (paramagnetic) introduce localized states above the O 2p valence band

#### Substitutional versus interstital N-doping: EPR

N<sub>int</sub>

TiTi	EPR	A <sub>1</sub> (N), G	A <sub>2</sub> (N), G	A <sub>3</sub> (N), G	Ti 0
► N //	exp	2.4	4.2	32.5	N
	N <sub>int</sub>	0.2	1.8	33.4	$\sim$
Ti N <sub>sub</sub>	N <sub>sub</sub>	2.5	2.8	38.2	Ťi

EPR: confirms localized nature of N-induced states in the gap

Theory: PBE (Espresso) and B3LYP (Crystal03) calculations show similar level of localization. EPR properties computed at B3LYP level

Hyperfine coupling constants: interstitial  $N_{int}$  more likely than substitutional  $N_{sub}$  (consistent with XPS)

Di Valentin, Pacchioni, Selloni, Livraghi, Giamello, J. Phys. Chem. B 109 (2005) 11414

Messagge from EPR and theory:

Stable N-species exist in the bulk
 Most likely interestitial N is formed
 N-induced states are localized!

A conclusion of purely theoretical interest?

### Interplay between N-doping and oxygen vacancies



■  $N_s$ -doping stabilized by the presence of oxygen vacancies  $(N_{s-0}+V_0)$ 

most stable situation under oxygen-poor conditions



Di Valentin, Pacchioni, Selloni, Livraghi, Giamello, J. Phys. Chem. B 109, 11414 (2005) Di Valentin, Pacchioni, Selloni, Chem. Materials 17, 6656 (2005)



#### Experimental proof: reaction of TiO<sub>2</sub> with atomic N



TiO<sub>2</sub> single crystal: N implantation reduces peak due to Ti<sup>3+</sup>(3d)<sup>1</sup> states in UPS Batzill, Morales, Diebold, Phys. Rev. Lett. 96, 026103 (2006) Reduced TiO<sub>2</sub> powders exposed to atomic N: decrease of Ti<sup>3+</sup>(3d)<sup>1</sup> signal until it is completely quenched





#### An interesting experiment on N-doped samples



Livraghi, Paganini, Giamello, Selloni, Di Valentin, Pacchioni J. Am. Chem. Soc. 128, 15666 (2006)

### Generation of paramagnetic defects under irradiation



Process completely reversible by turning light off

#### Adsorbed O<sub>2</sub> as electron scavanger



■ EPR and DFT show unambiguously the localized nature of N-induces states in TiO<sub>2</sub>

■ N dopants favor formation of oxygen vacancies in the material (Ti<sup>3+</sup> states); vacacies can become hydroxilated (same behaviour)

■ Charge transfer occurs from Ti<sup>3+</sup> states (high in the gap) and singly occupied N-states (low in the gap): Ti<sup>3+</sup> +  $N_b^{\bullet} \rightarrow Ti^{4+} + N_b^{-}$ 

■ Visible light induces conversion of diamagnetic precursors into paramagnetic centers by excitation of electrons to the conduction band  $(N_b^- + h_V \rightarrow N_b^{\bullet})$ 

Excited electrons are captured by  $O_2$  adsorbed on the surface (formation of paramagnetic  $O_2^-$ )

N-states responsible for photo-activity of N-doped TiO<sub>2</sub>



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