

# NANOSTRUCTURED OXIDES: NEW MATERIALS FOR ENERGY AND ENVIRONMENT



*Quantum Chemistry Laboratory  
Dipartimento di Scienza dei Materiali  
Università Milano-Bicocca*



<http://www2.mater.unimib.it/utenti/pacchioni/index.htm>



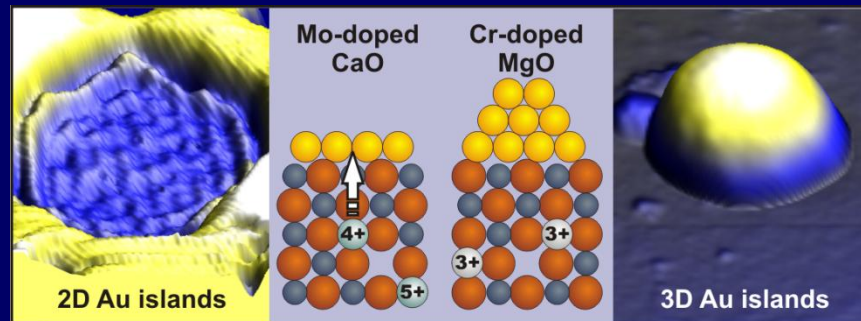
# THE GROUP AT UNIMIB



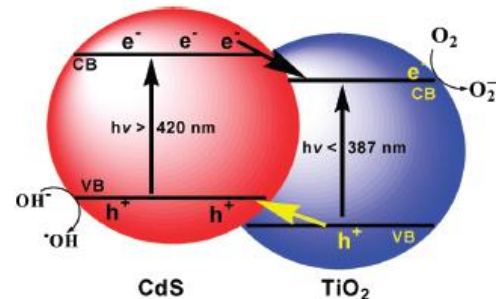
# Quantum Chemistry Laboratory

## THREE MAIN RESEARCH LINES

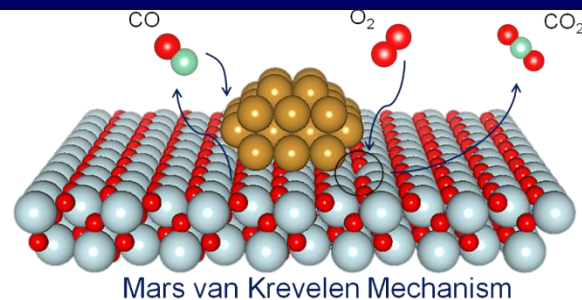
Nanostructured oxides and thin films as model catalysts  
(UHV, surface science)



Semiconducting oxides in photocatalysis  
Band gap engineering

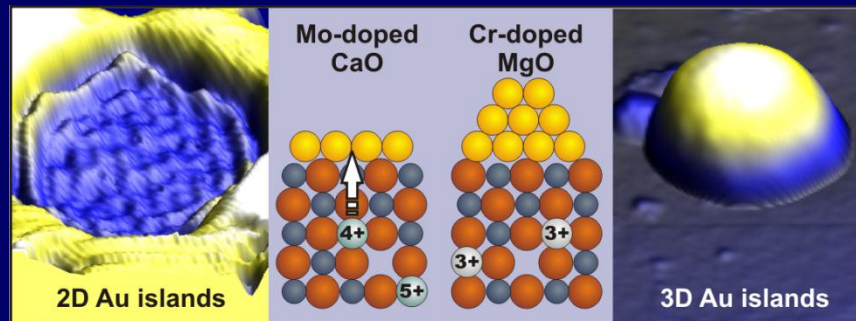


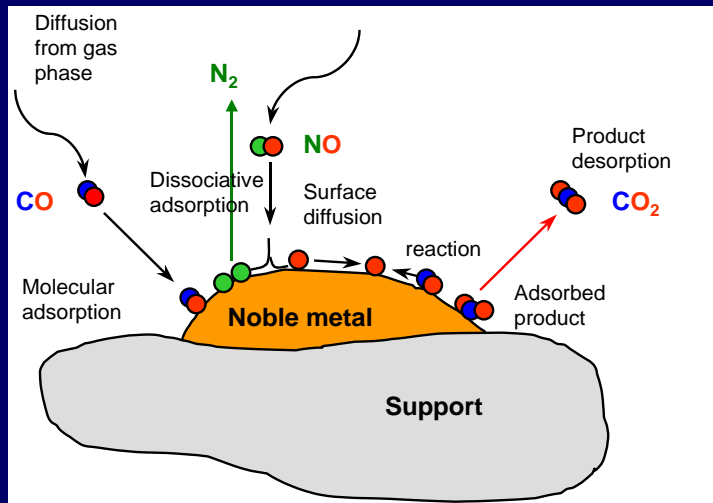
Nanoparticles in catalysis  
Concepts and interpretations



# Nanostructured oxides and thin films

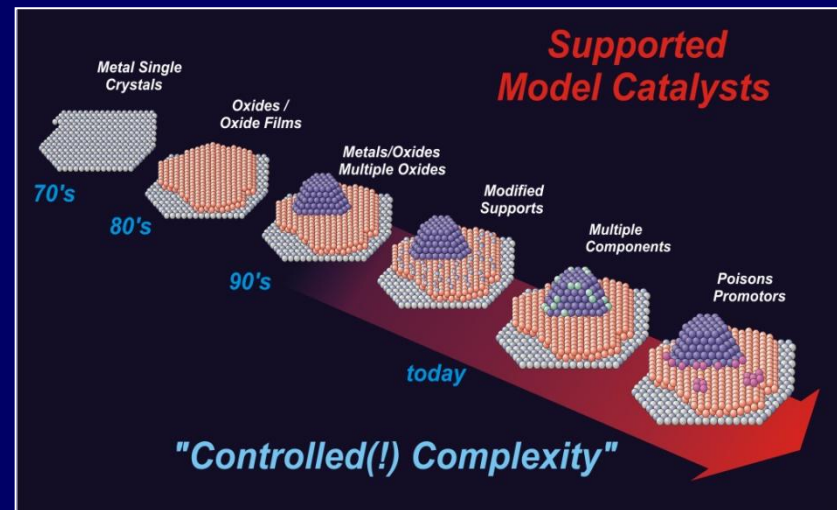
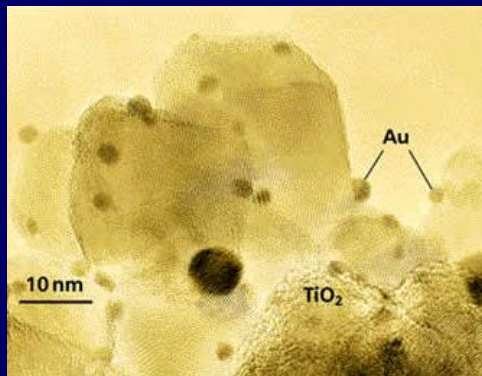
## Model catalysts





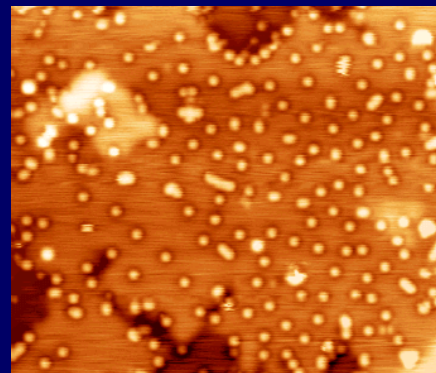
*Real systems:*

Au nano-catalyst on TiO<sub>2</sub>  
TEM



*Model systems:*

Au nano-clusters on MgO/Ag(100)  
STM



# PRACTICAL SOLUTION OF THE SCHRÖDINGER EQUATION: DFT


$$i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} = \left[ -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) \right] \Psi(\vec{r}, t)$$

Second Series      December, 1926      Vol. 28, No. 6

THE  
**PHYSICAL REVIEW**


AN UNDULATORY THEORY OF THE MECHANICS  
 OF ATOMS AND MOLECULES  
 BY E. SCHRÖDINGER  
 ABSTRACT

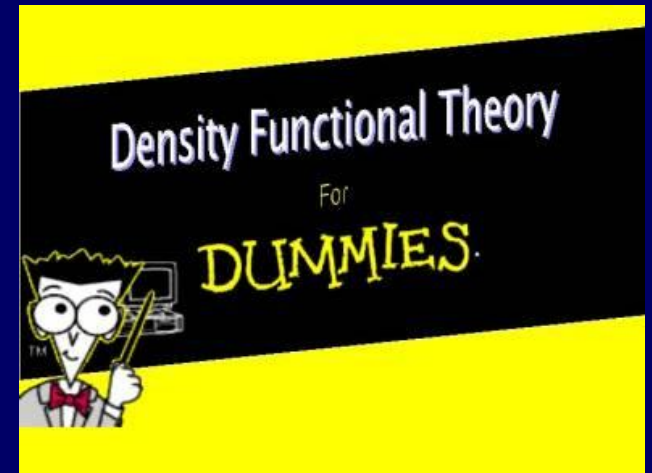
The paper gives an account of the author's work on a new form of quantum theory. §1. The Hamiltonian analogy between mechanics and optics. §2. The analogy is to be extended to include real "physical" or "undulatory" mechanics instead of mere geometrical mechanics. §3. The significance of wave-length;



The Nobel Prize in Physics 1933  
 Erwin Schrödinger, Paul A.M. Dirac

The Nobel Prize in Physics 1933 was awarded jointly to Erwin Schrödinger and Paul Adrien Maurice Dirac "for the discovery of new productive forms of atomic theory."





Determine the time-independent Schrödinger equation using the more general time-dependent equation.

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = U(x) \Psi(x,t) - \frac{\hbar^2 k^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2}$$

① In mathematics, it is sometimes possible to express a function of two variables as the product of two different functions:  
 $f(x,y) \Rightarrow f(x,y) = g(x) \cdot h(y)$

$\Psi(x,t) = \psi(x) \cdot f(t)$

② Let us now substitute equation (1) into the Schrödinger equation:

$$i\hbar \frac{\partial \psi(x)f(t)}{\partial t} = U(x) \psi(x)f(t) - \frac{\hbar^2 k^2}{2m} \frac{\partial^2 \psi(x)f(t)}{\partial x^2}$$

③ Now we can divide both sides by  $\psi(x) \cdot f(t)$ :

$$i\hbar \frac{1}{f(t)} \frac{\partial f(t)}{\partial t} = U(x) - \frac{\hbar^2 k^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2}$$

In mathematics, this is known as the separation of variables.

④ Notice that the left side is strictly in terms of time while the right side is strictly in terms of position. This implies that both sides are equal to some constant, let's call it  $E$ .

$$U(x) - \frac{\hbar^2 k^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} = E$$

⑤ and multiply both sides by  $\psi(x)$

$$U(x) \psi(x) = E \psi(x)$$

We see that the time-independent Schrödinger equation!



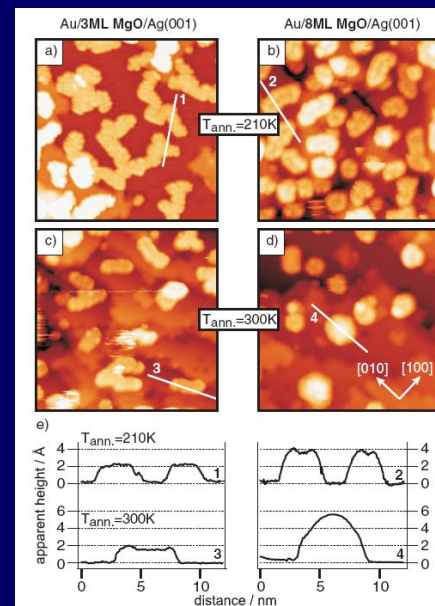
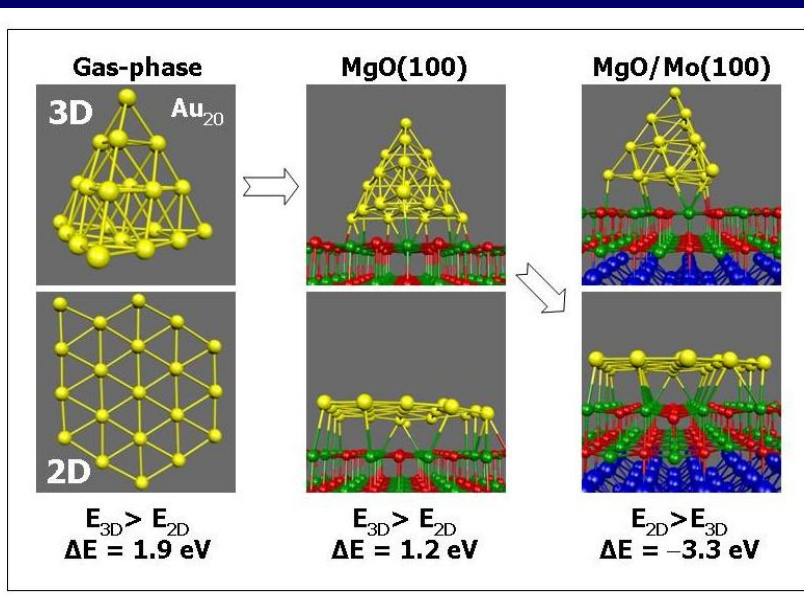
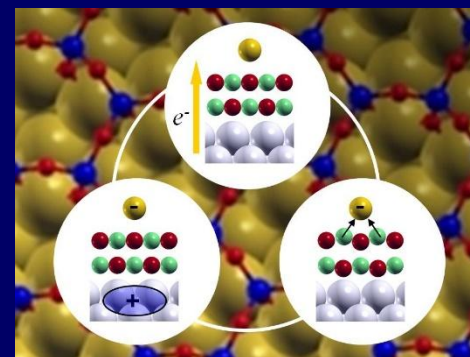
## Oxide Films at the Nanoscale: New Structures, New Functions, and New Materials

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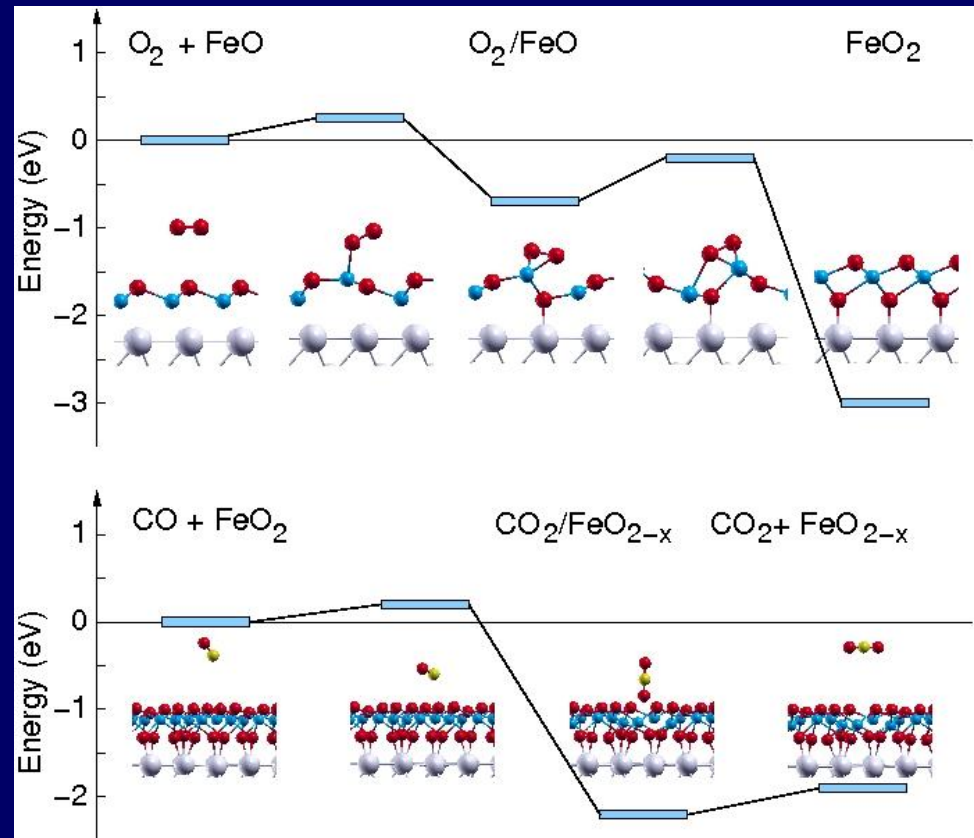
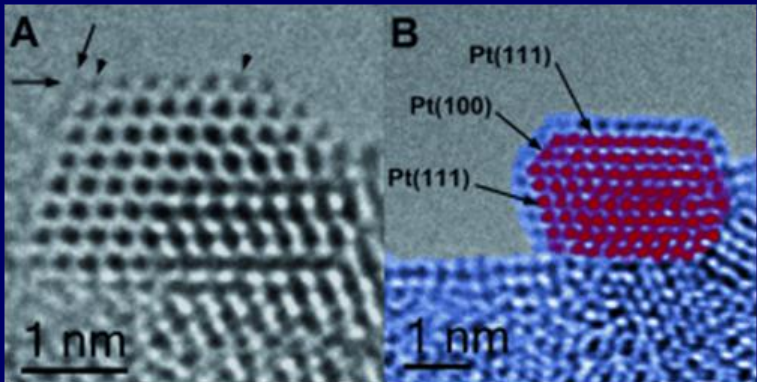
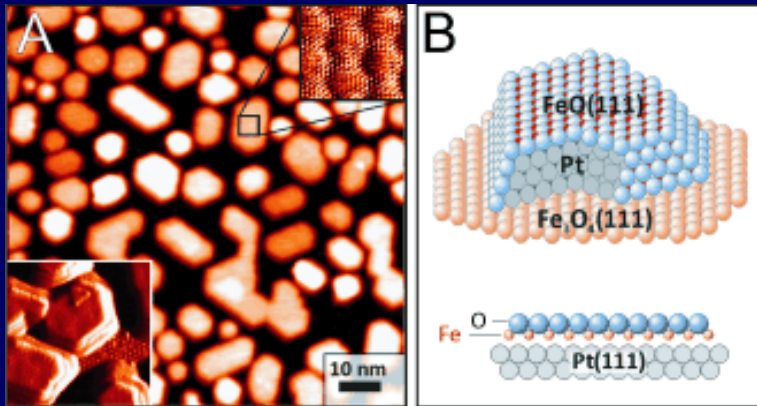
ACCOUNTS OF CHEMICAL RESEARCH ■ 1244–1252 ■ 2011 ■ Vol. 44, No. 11

Electron transfer from oxide films to adsorbates  
(metal clusters, molecules) by electron tunneling



Ricci, Bongiorno, GP, Landman, Phys. Rev. Lett. 97, 036106 (2006)  
Sterrer, Risse, Heyde, Rust, Freund, Phys. Rev. Lett. 98, 206103 (2007)

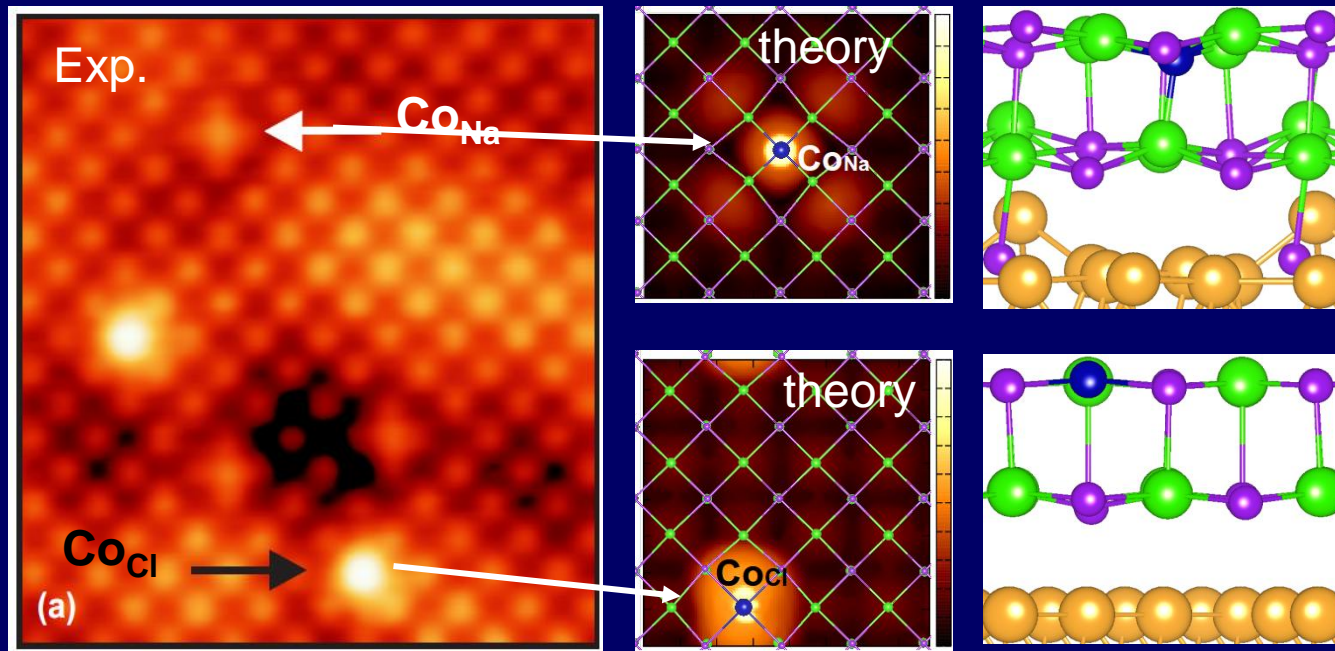
# STRUCTURAL CHANGE OF FeO/Pt(111) FILM UNDER O<sub>2</sub> PRESSURE



Giordano, Goniakowski, Shaikutdinov, GP, Freund et al. Angew. Chemie 49, 4418 (2010)

# ATOMS AND CLUSTERS DEPOSITION ON NaCl/Au(111) THIN FILMS

## STM of $\text{Co}_{\text{Na}}$ and $\text{Co}_{\text{Cl}}$ in NaCl/Au



Li, Chen, Schouteden, Lauwaet, Giordano, Trioni, Janssens, Iancu, Van Haesendonck, Lievens, GP, *Phys. Rev. Lett.*, **112**, 026102 (2014)

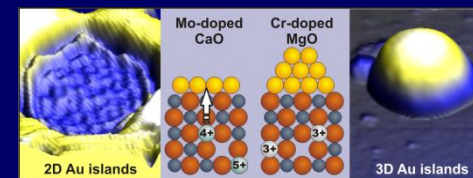
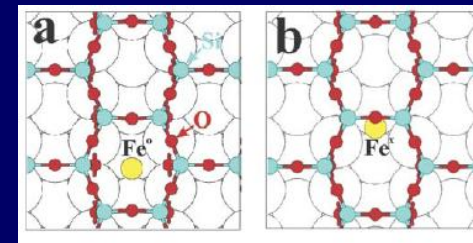
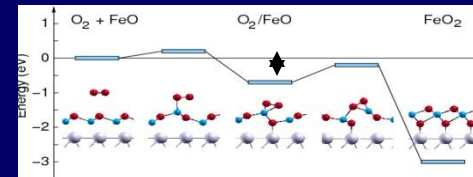
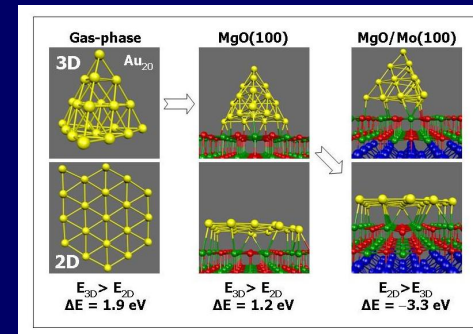
# MAIN RESULTS

■ on ultrathin films spontaneous charging of supported clusters possible by direct tunneling; role of the metal/oxide work function

■ structural flexibility may lead to enhanced reactivity

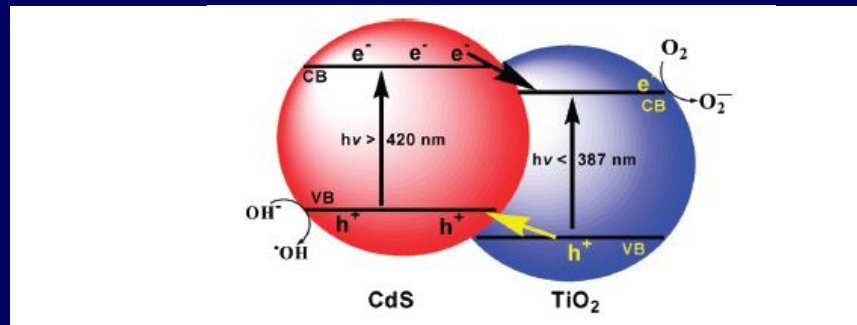
■ Exploit nano-porosity to modify properties and generate assembly of ad-atoms and clusters

■ Doping of oxide films - charging can be induced by selective doping with TM atoms

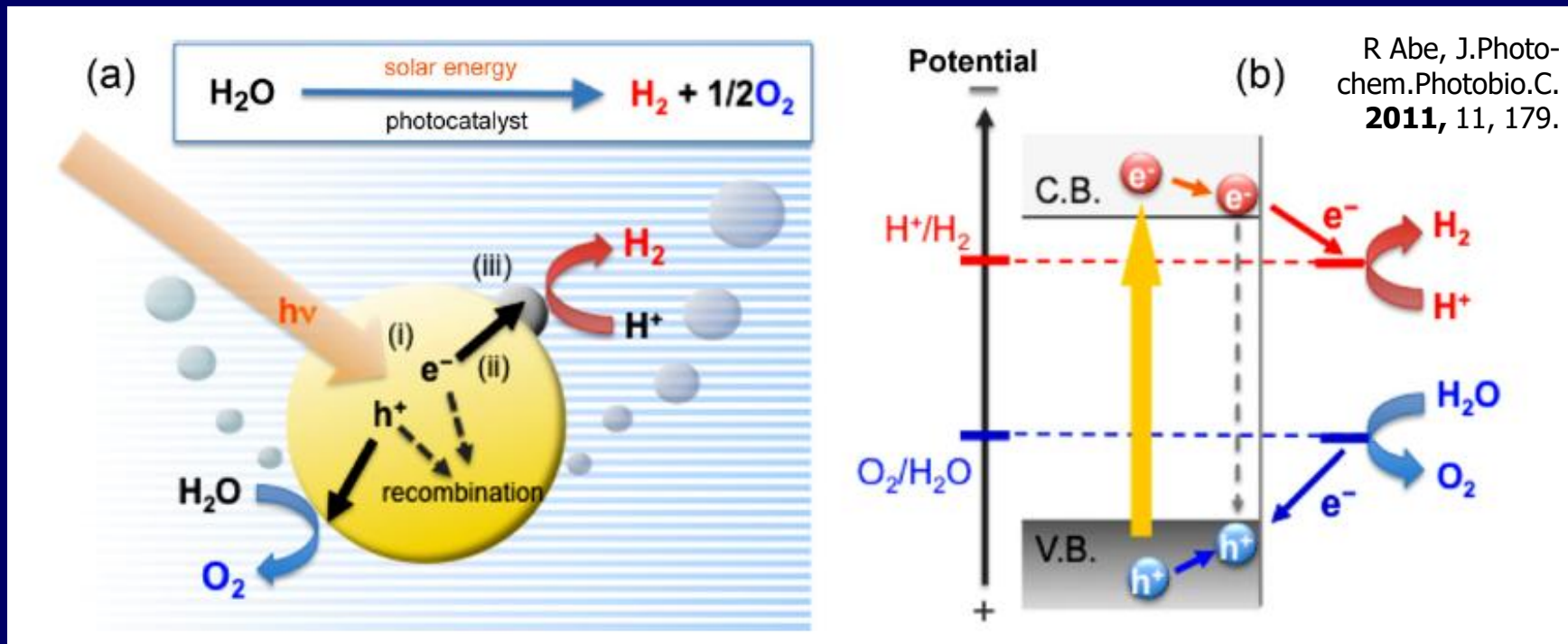


# Semiconducting oxides in photocatalysis

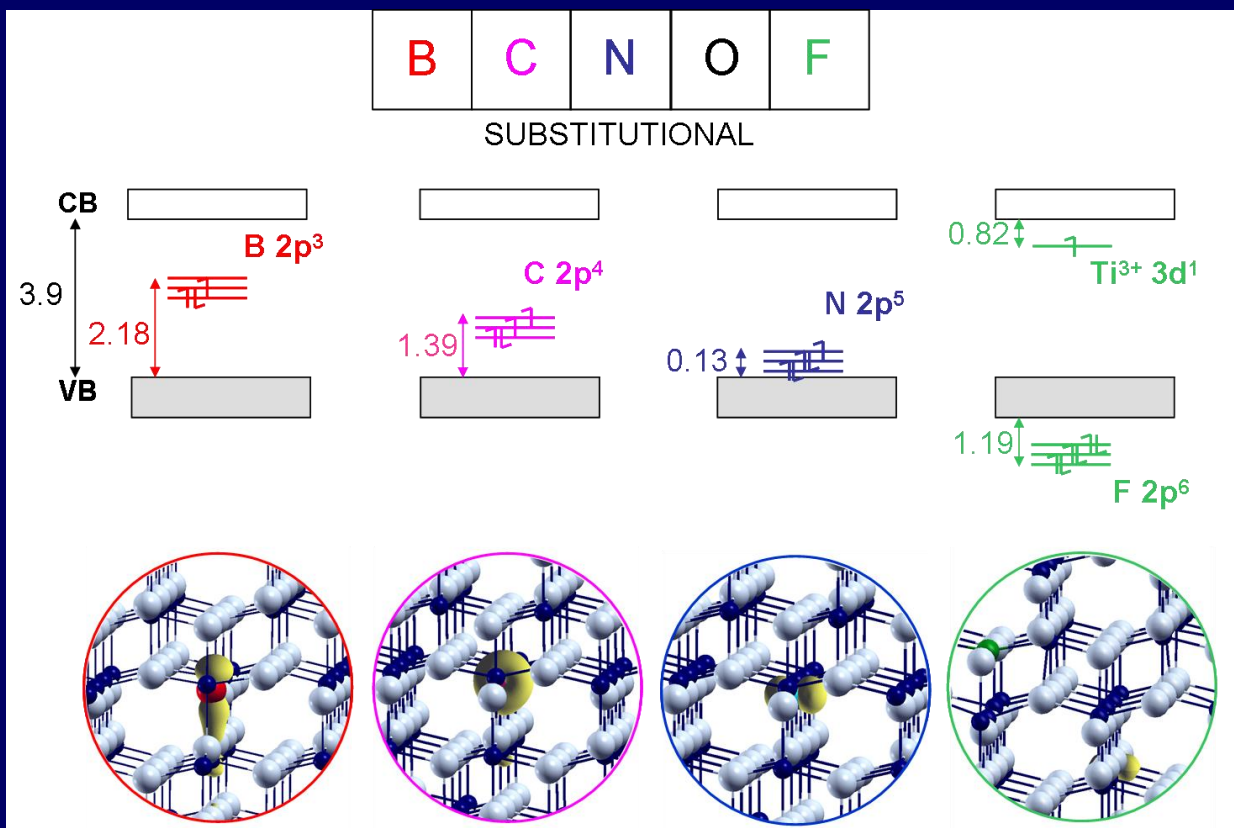
## Band gap engineering



# Photoactivity: the mechanism



# DOPED TiO<sub>2</sub>: B, C, N, F SUBSTITUTIONAL TO O



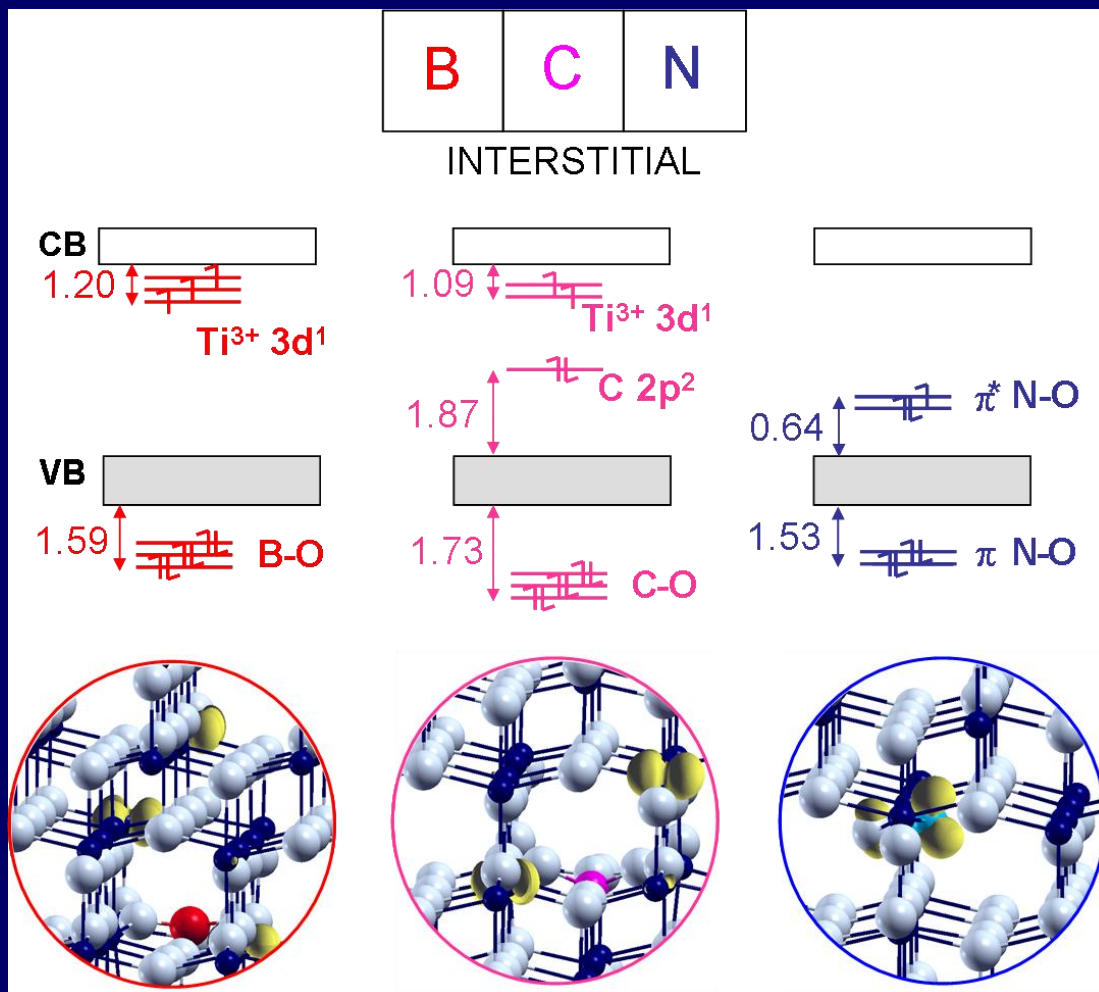
Paramagnetic defects

states in the gap  
move down along the  
series

F substitutional:  
formation of Ti<sup>3+</sup>(3d<sup>1</sup>)

States are localized!

# DOPED $\text{TiO}_2$ : B, C, N INTERSTITIALS



Interstitials more stable than substitutional

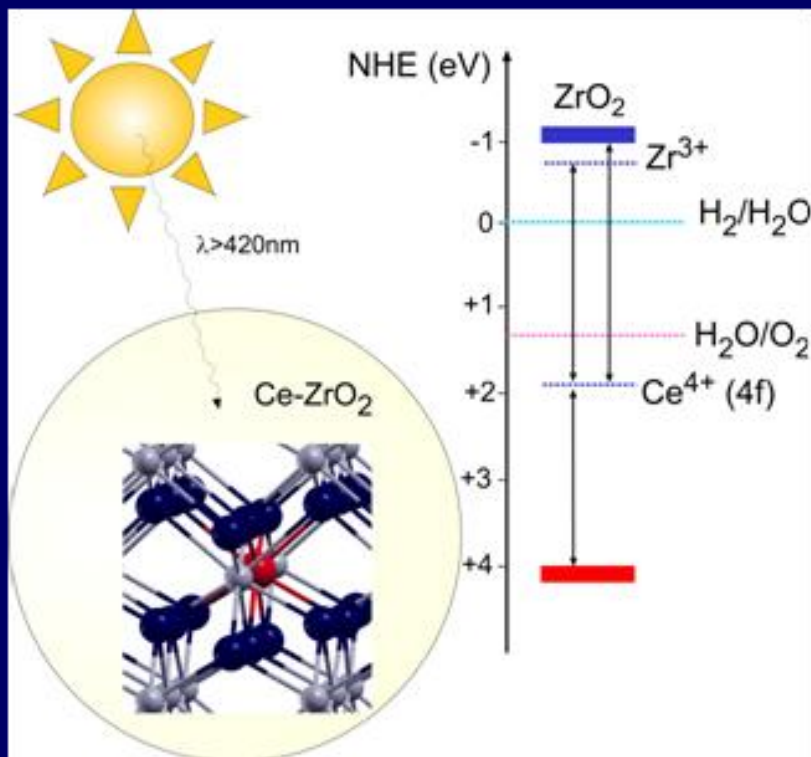
B and C interstitials act as electron donors: formation of  $\text{Ti}^{3+}(3d^1)$

N forms "NO" interstitials (proven by EPR and XPS)

Defect states are localized!

# Third generation photocatalysts

## Multi-photon excitations?



$\text{ZrO}_2$ , inert material as photocatalyst due to high band gap

Ce-doped  $\text{ZrO}_2$ : under visible light material becomes active

$e^-/h^+$  pairs generated by irradiation with visible light ( $\lambda > 420 \text{ nm}$ )

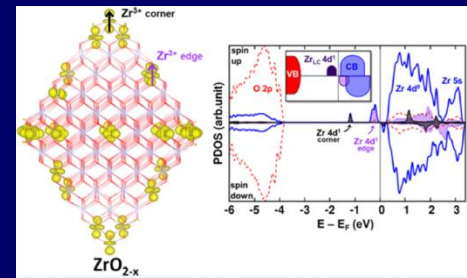
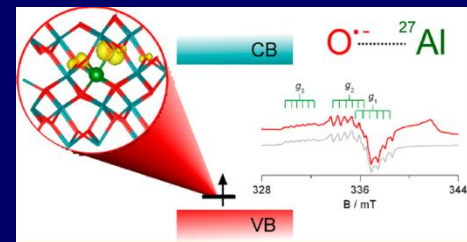
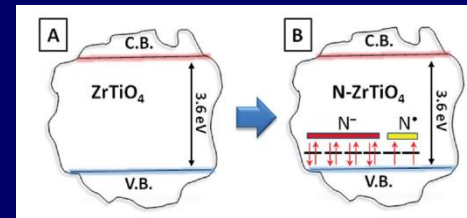
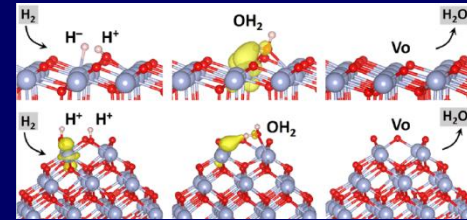
$e^-/h^+$  pairs migrate to the surface

Ce introduces new states in the gap

Double excitation possible explanation

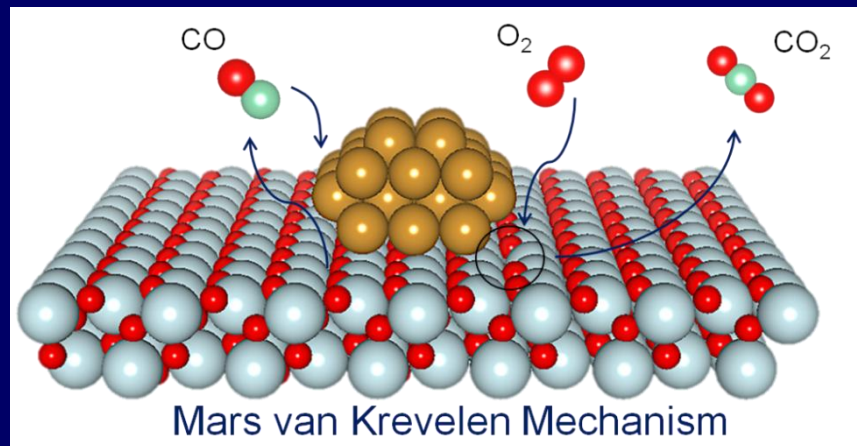
# MAIN RESULTS

- role of oxygen vacancies in oxide surfaces and nanostructures; oxide reducibility
- doping and nanostructuring, heterojunctions, effects on band gap engineering
- electron localization, comparison with EPR studies, electron-hole formation
- magnetic properties of doped and defective oxides

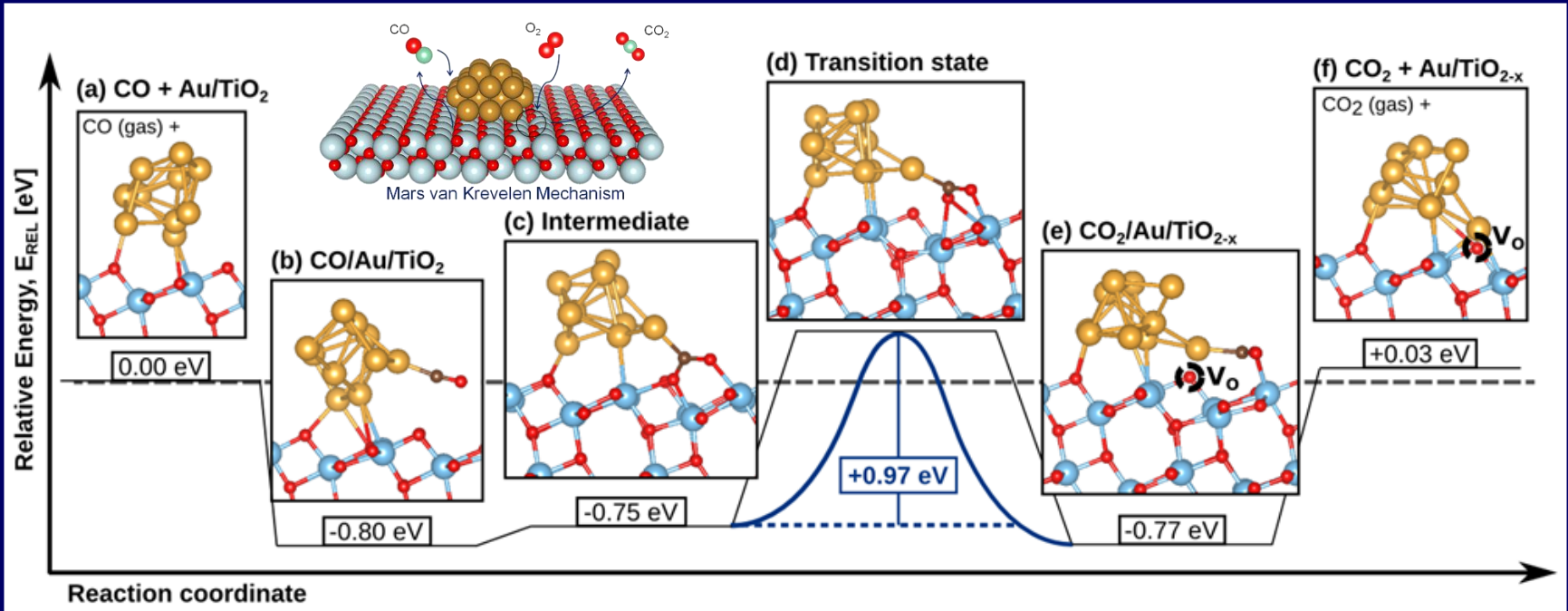


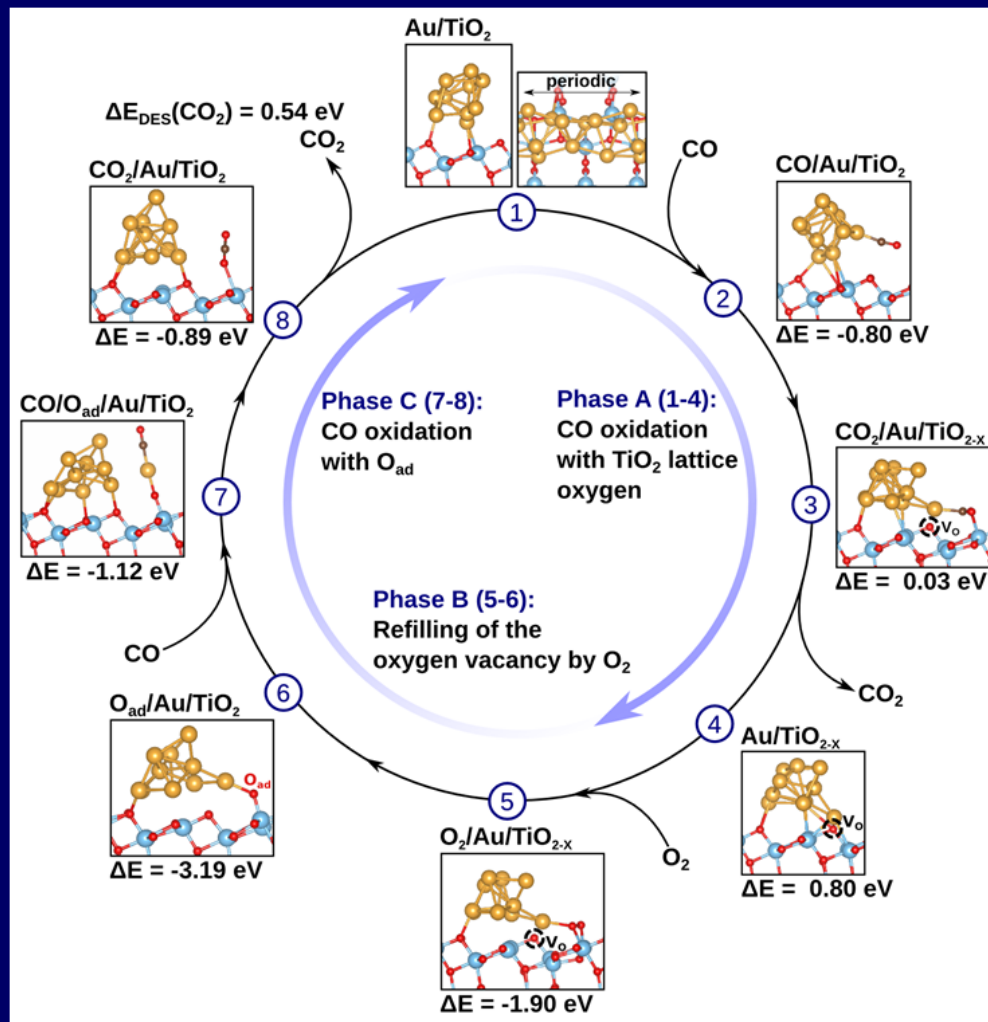
# Nanoparticles in catalysis

## Concepts and interpretations

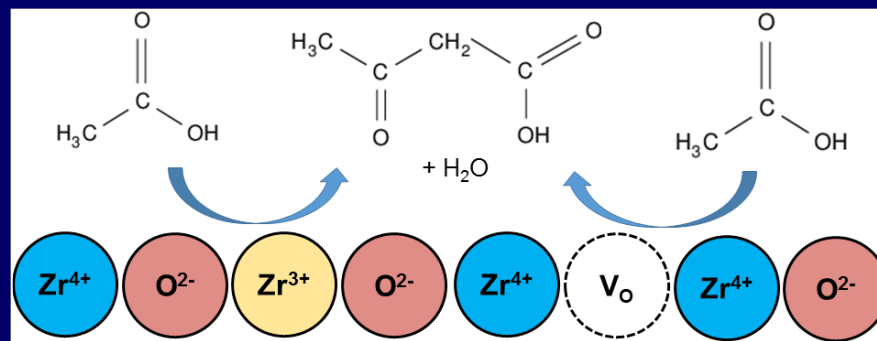


# Au/TiO<sub>2</sub> in CO oxidation at high temperature: role of metal/oxide interface

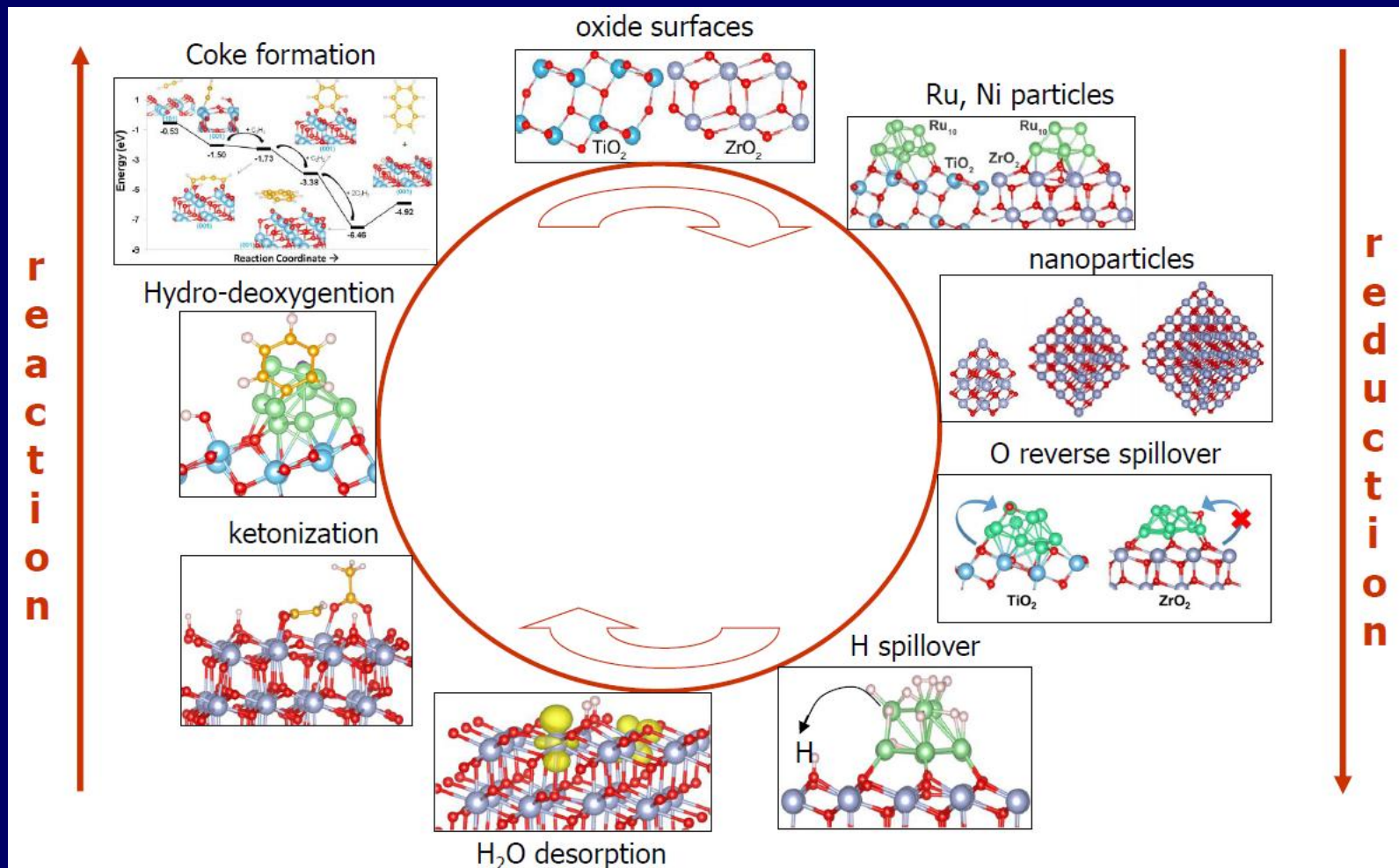




## Oxide catalysts in biomass conversion

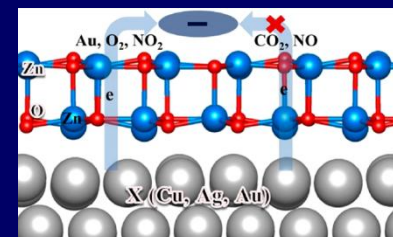
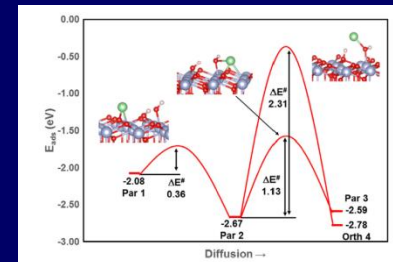
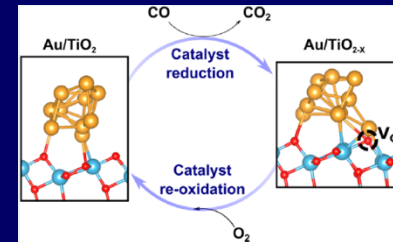


# Titania and zirconia in biomass conversion



# MAIN RESULTS

- role of metal/oxide interface in determining reactivity of supported metal particles
- mechanism leading to sintering of supported nanoclusters
- dependence of properties on size and shape of nanoclusters
- charging effects on metal nanoparticles deposited on oxides



# EXTERNAL COLLABORATIONS AND PROJECTS



**HJ Freund**  
Fritz Haber MPI Berlin



**N Nilius**



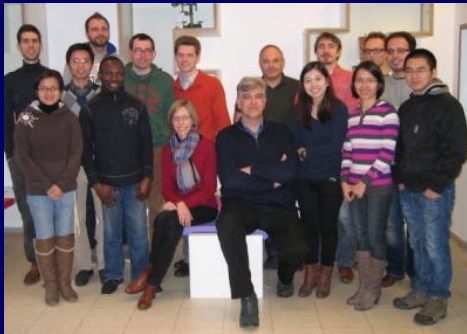
**E Giamello**  
Univ. Torino



**G Granozzi**  
Univ. Padova



**J Behm**  
Univ. Ulm



**P. Lievens**  
Univ. Leuven

## Recent projects:

MIUR PRIN 2016-2019 – New materials for CO<sub>2</sub> and H<sub>2</sub> cataysis

MIUR FIRB 2011-2016 – Nanostructured oxides

Cariplo Foundation 2014-2017 – Oxides photocatalysis

DECORE – FP7 2012-2015 – Oxidecarbides for fuel cells

CASCATBEL – FP7 2014-2018 – Oxide catalysts for biofuels

CATSENSE – FP7 2014-2018 – Metal clusters on oxides

COST CM1104 – 2013-2017 - Reducible oxides

# REVIEW ARTICLES

## ACCOUNTS of chemical research

### Oxide Films at the Nanoscale: New Structures, New Functions, and New Materials

LIVIA GORDANO AND GIANFRANCO PACCHIONI<sup>1</sup>  
Dipartimento di Scienza dei Materiali, Università Milano Bicocca, via R. Cozzi  
55-20123 Milano, Italy

RECEIVED JANUARY 16, 2011

#### CONCEPTS

We all make use of oxide ultrathin films, even if we are unaware of doing so. They are essential components of many common devices, such as mobile phones and laptops. The films in these ubiquitous electronics are composed of silicon dioxide, an unprocessed material in the design of transistors. But oxide films at the nanoscale (typically just 10 nm or less in thickness) are integral to many other applications. In some cases, they form under normal reactive conditions and confer new properties to a material; one example is the corrosion protection of stainless steel, which is the result of a passive film. A new generation of devices for energy production and communication technology, such as ferroelectric ultrathin film capacitors, tunneling magnetoresistance sensors, solar energy materials, solid oxide fuel cells, and many others, are being specifically designed to exploit the unusual properties afforded by reduced oxide thickness.

Oxide ultrathin films also have tremendous potential in catalysis, representing a rich new source of catalytic materials. About 20 years ago, researchers began to prepare model systems of truly heterogeneous catalysts based on thin oxide layers grown on single crystals of metal. Only recently, however, was it realized that these systems may behave quite differently from their corresponding bulk oxides. One of the phenomena uncovered is the occurrence of a spontaneous charge transfer from the metal support to an adsorbed species through the thin insulating layer (see verse). The importance of this property is clear: consequently, the activation and bond breaking of adsorbed molecules begins with precisely the same process, electron transfer into an antibonding orbital. But electron transfer can also be harnessed to make a supported metal particle more chemically active, increase its adsorption energy, or change its shape. Most importantly, the basic principles underlying electron transfer and other phenomena (such as structural flexibility, electronic modifications, and nonperiodicity) are now largely understood, thus paving the way for the rational design of new catalytic systems based on oxide ultrathin films. Many of the mechanisms involved (electron tunneling, work function changes, defects engineering, and so forth) are typical of semiconductor physics and allow a direct link between the two fields.

A related conceptual framework, the "electronic theory of catalysis", was proposed a long time ago but has been largely neglected by the catalytic community. A renewed appreciation of this catalytic framework, together with spectacular advances in modeling and electron structure methods, now makes it possible to combine theory with advanced experimental setups and meet the challenge of designing new materials with tailored properties. In this Account, we discuss some of the recent advances with nanoscale oxide films, highlighting contributions from our laboratory. Once mastered, ultrathin oxide films on metals will provide vast and unforeseen opportunities in heterogeneous catalysis as well as in other fields of science and technology.

#### Introduction

Oxide ultrathin films are essential components of several modern technologies. For instance, ultrathin silicon dioxide films represent an unprocessed material in the design of metal oxide field effect transistors, and the microelectronic revolution would have not been the same without the excellent properties of thin SiO<sub>2</sub> films grown on silicon. But oxides at the nanoscale (typically up to 10 nm in

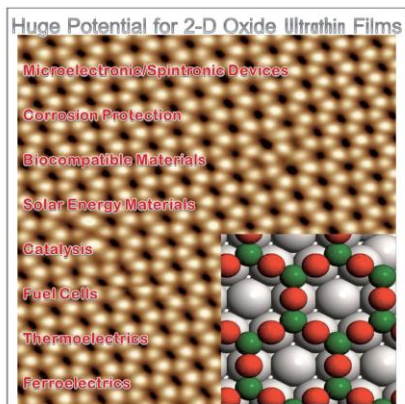
thickness) are used also in many other systems and devices: corrosion protection of metals by passive films,<sup>1</sup> ferroelectric ultrathin film capacitors,<sup>2</sup> tunneling magnetoresistance sensors,<sup>3</sup> and solar energy materials.<sup>4</sup> Sometimes, the possibility to grow ultrathin films is essential to improve performances: for instance, for solid oxide fuel cells to operate at low temperature ultrathin films of yttria-stabilized zirconia would be needed.<sup>5</sup>

CHEMISTRY  
A EUROPEAN JOURNAL

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### Two-Dimensional Oxides: Multifunctional Materials for Advanced Technologies

Gianfranco Pacchioni<sup>1,2†</sup>



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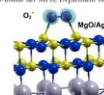
Chem. Eur. J. 2011, 17, 10044–10058

## CHEMICAL REVIEWS

### Electron Transfer at Oxide Surfaces. The MgO Paradigm: from Defects to Ultrathin Films

Gianfranco Pacchioni<sup>1\*</sup> and Hajo Freund<sup>2</sup>

<sup>1</sup>Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Via R. Cozzi, 55, 20123, Milano, Italy  
<sup>2</sup>Fritz-Haber Institut der MPG, Department of Chemical Physics, Faradayweg 4-6, 14195 Berlin, Germany



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Author Information  
Corresponding Author  
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#### 1. INTRODUCTION

Electron transfer (ET) is a fundamental process in physics, chemistry, and biology. Charge transfer transitions phenomena like oxidation and reduction, bond activation and bond breaking in chemical reactions, formation of radical species, and charge transport and charge trapping in nanoelectronic devices, just to mention a few examples, ET processes are the basis of technologically relevant fields such as electrochemistry, homogeneous, heterogeneous and enzymatic catalysis, photocatalysis, energy production, dye-sensitized solar cells, photocatalysis, sensors, information storage, molecular electronics, etc.<sup>1</sup> ET may involve donors and acceptors at the molecular level, but often one of the components is a solid state, a semiconductor, or an insulator. In this latter case the donor or acceptor state usually corresponds to a specific site on the surface of the material, for example a defect, a morphological irregularity, an exposed atom, or a functional group. A well-defined orbital energy is associated to each of these sites, and the overlap and interaction with the occupied or empty states of incoming molecules, clusters of atoms, or extended systems determines the extent and the direction of charge exchange. The theoretical foundations of ET processes in condensed phases have been addressed in dedicated articles and reviews, and the reader is referred to these studies for a more thorough treatment.<sup>2</sup>

There are situations where it is possible to follow the ET process in detail by looking at the fate of the transferred electron. This is when paramagnetic centers or paramagnetic species form during the ET process. In this case electron paramagnetic resonance (EPR) spectroscopy may be used to monitor the reaction. This is a powerful technique that provides direct information on the nature of the reactants and products involved in ET.<sup>3</sup> It is only applicable and thus very sensitive to the presence of unpaired electrons, being able to reveal 10<sup>3</sup> spins. This means that for a high surface area polycrystalline oxide sample of, say, 200 m<sup>2</sup> g<sup>-1</sup> the lower limit of sensitivity is

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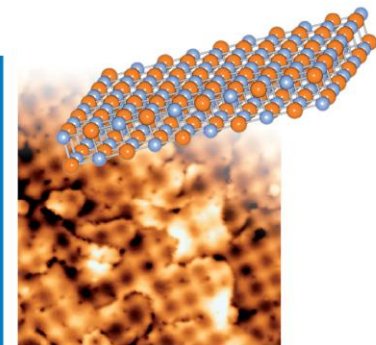
doi:10.1002/chem.201100117 Chem. Eur. J. 2011, 17, 10044–10058

Edited by Gianfranco Pacchioni  
and Sergio Valeri

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## Oxide Ultrathin Films

Science and Technology



## FEATURE ARTICLE

### Reduced and n-Type Doped TiO<sub>2</sub>: Nature of Ti<sup>3+</sup> Species

Cristiana Di Valentin\* and Gianfranco Pacchioni

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Defect states in reduced and n-type doped titania are of fundamental importance in several technologically important applications. Still, the exact nature of these states, often referred to as “Ti<sup>3+</sup> centers”, is largely unclear and a matter of debate. The problem is complicated by the fact that electronic structure calculations based on density functional theory (DFT) in the local density approximation (LDA) or semilocal generalized gradient approximation (GGA) provide results that do not account for many of the experimentally observed fingerprints of the formation of Ti<sup>3+</sup> centers in reduced TiO<sub>2</sub>. Here, we investigate the properties of at least four different types of Ti<sup>3+</sup> centers in bulk anatase: (1) 6-fold-coordinated Ti<sub>6c</sub><sup>3+</sup> ions introduced by F- or Nb-doping, (2) Ti<sub>5c</sub><sup>3+</sup>–OH species associated with H-doping, (3) undercoordinated Ti<sub>5c</sub><sup>3+</sup> species associated with oxygen vacancies, and (4) interstitial Ti<sub>4c</sub><sup>3+</sup> species. The characterization of these different kinds of Ti<sup>3+</sup> centers is based on DFT+U and/or hybrid functional calculations, which are known to (partially) correct the self-interaction error of local and semilocal DFT functionals. We found that strongly localized solutions where an excess electron is on a single Ti<sup>3+</sup> ion are very close in energy and sometimes degenerate with partly or highly delocalized solutions where the extra charge is distributed over several Ti ions. The defect states corresponding to these different energies in the band gap of the material. This has important implications for the conductivity mechanism in reduced or n-type doped titania and suggests a significant role of temperature in determining the degree of localization of the trapped charge.

#### 1. Introduction

Titania (TiO<sub>2</sub>) samples in the form of single crystals, powders, or thin films are often reduced and electrically conducting.<sup>1–3</sup> Chemical reduction is associated with a change in the oxidation state of the transition metal ion, formally Ti<sup>3+</sup> in stoichiometric TiO<sub>2</sub>, with the formation of Ti<sup>3+</sup> species. These species are believed to be responsible for the electronic conductivity, important for many applications of TiO<sub>2</sub>, especially photocatalysis,<sup>4,5</sup> photochemical water splitting,<sup>6</sup> and dye-sensitized solar cells.<sup>7,8</sup> Ti<sup>3+</sup> ions in TiO<sub>2</sub> are also formed through classical n-type doping, that is, by introduction of donor species in the material; for example, Nb-doped TiO<sub>2</sub>, obtained via substitution of tetravalent Ti by pentavalent Nb, is a transparent conducting oxide (TCO) whose conductivity is attributed to the presence of Ti<sup>3+</sup> ions.<sup>9</sup>

The formation of Ti<sup>3+</sup> species upon TiO<sub>2</sub> reduction is supported by several pieces of experimental evidence: (i) the sample blue color, whose intensity increases with the level of reduction, is assigned to d–d transitions<sup>10</sup> (ii) the occurrence of a gap state at ~2 eV above the valence band (VB) maximum and ~1 eV below the conduction band (CB) minimum, which is observed by photoelectron spectroscopy<sup>10–12</sup> and electron

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energy loss experiments;<sup>13</sup> (iii) the EPR-measured g-factor typical of a Ti 3d<sup>1</sup> state;<sup>14–16</sup> (iv) the shift in the core level binding energies of the reduced Ti atoms;<sup>17</sup> (v) the population of Ti-3d states as probed by resonant Auger electron spectroscopy<sup>18</sup> or resonant photoemission<sup>19</sup> and (vi) resonant photoelectron diffraction patterns recorded for photoelectrons from Ti-3d defect states.<sup>20</sup> It is often assumed that the different experimental techniques mentioned above probe the same type of Ti<sup>3+</sup> species. However, this is not necessarily true; for instance, some techniques mainly probe bulk-like Ti<sup>3+</sup> ions, while others are more sensitive to surface-like Ti<sup>3+</sup> ions. The idea that different types of Ti<sup>3+</sup> species might exist and even coexist in the same sample is corroborated by early experiments by Ghosh et al.,<sup>21</sup> who detected a large number of defect energy levels in the TiO<sub>2</sub> band gap using various spectroscopies, as well as by more recent EPR studies by M. Li et al.<sup>22</sup> on reduced rutile single crystals.

Despite the interest and importance of Ti<sup>3+</sup> species, the understanding of their specific chemical and structural characteristics is still incomplete. Various issues are under debate, and conflicting views are found in the literature. First of all, there is not yet a general consensus on whether oxygen vacancies or titanium interstitials (or both) are the prominent species formed upon reduction.<sup>23,24</sup> A clear answer to this question is complicated by the existence of two major polymorphs, anatase and rutile (which can even be mixed in powder samples, such as

### Trends in non-metal doping of anatase TiO<sub>2</sub>: B, C, N and F

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#### ABSTRACT

Anatase TiO<sub>2</sub> doping with boron, carbon, nitrogen, and fluorine atoms has been considered in a systematic study by performing periodic DFT calculations with the hybrid B3PW functional and large supercells. The effect on the electronic structure of replacing lattice O atoms with B, C, N, or F dopants, or to include the same atoms in interstitial positions has been considered. Clear trends emerge as a function of the atomic number of the doping element: B, C, and N atoms in substitutional positions result in magnetic impurities whose energy levels fall in the energy gap of the material. The position of these gap states closely follows the effective nuclear charge of the dopant, with B that gives states high in the gap and N which introduces states just above the top of the valence band. Fluorine, being very electronegative, has filled states below the O 2p valence band and leads to the formation of Ti<sup>3+</sup> ions due to charge compensation. Interstitial impurities have a quite different electronic structure, which again depends on the nuclear effective charge. B acts as a net electron donor with formation of B<sup>3+</sup> and three Ti<sup>3+</sup> ions; C donates only two electrons to the lattice with formation of a C<sup>2+</sup> ion. N forms a direct bond with a lattice O, and does not donate electrons to the host lattice. We also discuss possible internal charge transfers between high-lying electronic states in the gap (Ti<sup>3+</sup> 3d<sup>1</sup> states) and low-lying acceptor states of the dopant. The interplay between substitutional and interstitial dopants, between dopants and oxygen vacancies or titanium interstitials, and between co-dopants (B/N, N/F) are discussed in view of their beneficial effects for photocatalytic processes.

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#### 1. Introduction

Non-metal doping has been considered for about ten years [1] as a promising way to change the photo-absorption properties of TiO<sub>2</sub> for harvesting solar light with applications in photocatalysis and photoelectrochemistry [2–5]. The time is ripe for the scientific community working in the field of doped TiO<sub>2</sub> [6] to analyze achievements, successes and failures, in order to define a sensible and rational track for the future research. Non-metal doped TiO<sub>2</sub> has also been subject of an intense computational work [5]. The theoretical modeling has fundamentally contributed to the comprehension of these systems with reference to the possible configurations and the details of their electronic structure [7]. The introduction of the dopant in the lattice may affect the band edges or introduce impurity states in the band gap of the system [8]. The description of these effects is very delicate from the theoretical point of view, especially concerning the localized or delocalized

nature of the impurity states [9]. A paradigmatic example of this problem is the degree of band mixing of the additional N 2p states with the O 2p valence band (VB) in the widely studied N-doped TiO<sub>2</sub> system. In the pioneering work by Kaki et al. [1], the authors proposed, based on non spin-polarized LDA (Local Density Approximation) calculations with small supercell models, that the effect of N-doping is a rigid shift of the top of the VB to higher energies. This picture however is not correct as it was shown, few years later, by means of more accurate hybrid functionals, spin polarized calculations and larger supercell models, that the N 2p impurity states are almost fully localized on the N atom; they lie few tenths of an eV above the valence band [6,10]. This theoretical result is fully consistent with electron paramagnetic resonance (EPR) measurements in terms of hyperfine coupling of the unpaired electrons with the <sup>14</sup>N nucleus [7]. In a more general context, hybrid functionals are presently considered a good compromise between computational cost and results accuracy and reliability. Compared to standard LDA or GGA (Generalized Gradient Approximation) functionals, they provide improved band position, band width, and band gap values [11]. This is due to the fact that hybrid functionals partly correct the self-interaction problem of standard functionals, an effect that results in unphysical or overestimated delocalization of electrons and holes.

In this work we present a systematic comparative study of the non-metal doping of bulk anatase TiO<sub>2</sub> by some elements of the

### Tungsten Oxide in Catalysis and Photocatalysis: Hints from DFT

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**Abstract** Despite the importance of tungsten oxide in various areas of materials science including catalysis and photocatalysis, relatively few systematic theoretical studies have been devoted to this system. In this review we report the results of first principle density functional theory calculations based on a hybrid functional that properly reproduces the band gap and other fundamental properties of WO<sub>3</sub>. We briefly describe the dependence of the band gap on the crystalline phase of WO<sub>3</sub>. Then, we address the nature of defects and dopants in bulk WO<sub>3</sub>. As WO<sub>3</sub> can be easily reduced to WO<sub>3-x</sub>, we first discuss the nature of isolated O vacancies showing that three different situations arise from the removal of one O atom along each of the three crystallographic directions of RT monoclinic WO<sub>3</sub>. The data provide insight into the origin of electrochromism of this material. Then we discuss the role of doping of WO<sub>3</sub> with substitutional atoms in order to increase the activity for water splitting and we show that Hf is a promising dopant. The redox properties of WO<sub>3</sub> are discussed also in relation to H<sub>2</sub> adsorption on the WO<sub>3</sub>(001) surface. Finally, the role of nanostructuring is analyzed by studying the properties of (WO<sub>3</sub>)<sub>n</sub> cyclic chains deposited on the rutile TiO<sub>2</sub>(110) surface. Charge transfers at the (WO<sub>3</sub>)<sub>n</sub>/TiO<sub>2</sub> interface and their role on the activity of this heterogeneous catalyst are discussed.

**Keywords** Semiconducting oxides · Defects · Dopants · DFT · Electronic structure · Reduction · Nanostructuring

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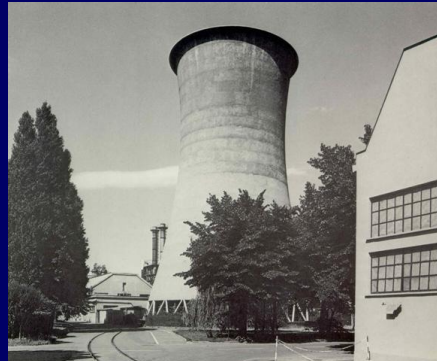
#### 1 Introduction

Tungsten oxide (WO<sub>3</sub>) is a key material in several important applications which range from smart windows technology to dye-sensitized solar cells, from sensors to photoelectrochemical water splitting, from high T<sub>c</sub> superconductivity to heterogeneous catalysis, etc. [1–4]. Despite the spectacular progress reached by some of these technologies, a corresponding deep understanding of the underlying physico-chemical mechanisms is still lacking.

Experimentally, the band gap of WO<sub>3</sub> from optical, photocurrent and photoemission measurements varies from 2.5 to 3.2 eV [1, 5–10], but most of the results are from 2.6 to 3.0 eV [11]. The geometrical structure has an important effect on the electronic properties, including the band gap. The simplest structure of WO<sub>3</sub> is cubic, and is composed of corner sharing regular octahedra, but occurs only with incorporation of impurities [12]. Several distortions are possible in pure WO<sub>3</sub> as a function of temperature. Fig. 1: low-temperature (LT) monoclinic structure from ~140 to ~50 °C [13, 14], triclinic from ~50 to 17 °C [15–17], followed by a room-temperature (RT) monoclinic structure from 17 to 330 °C [18]. Above 330 °C up to 740 °C, WO<sub>3</sub> becomes orthorhombic [19–21], and above 740 °C it assumes a tetragonal structure [21, 22].

Density functional theory (DFT) calculations provide an important complement to experiment in studying the structural and electronic properties of oxide semiconductors. Recently, there have been numerous theoretical studies on WO<sub>3</sub>, including DFT and Hartree-Fock (HF) calculations [23–29]. However, most of these studies are normally limited to the simple cubic phase.

It is common practice to estimate the semiconductor band gap and the energy levels introduced in the gap by defect centers using the single-particle Kohn-Sham eigenvalues.



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