

Chemistry and Molecular Sciences and Technologies

COST Action CM1104

Reducible oxide chemistry, structure and functions

Working Groups

1-Fundamentals and 2- Synthesis and Characterisation

April 28-30, 2014



Universidad
Zaragoza

Zaragoza Scientific Center for Advanced Modeling, Zaragoza, Spain

Organizers

- **M. Verónica Ganduglia-Pirovano – WG1 coordinator**
Institute of Catalysis and Petrochemistry-CSIC, Madrid
- **Rubén Pérez**
Universidad Autonoma de Madrid, Madrid
- **Sergio Valeri – WG2 coordinator**
CNR-NANO, S3, Modena, Italy
Università di Modena e Reggio Emilia, Modena, Italy
- **Paola Luches**
CNR-NANO, S3, Modena, Italy

Program

Day 1 – April 28, 2014

13:00 to 15:15: Registration and light lunch at the ZCAM

Opening:

- 15:15 to 15:30 – **Welcome by the Organizers**

Session I: Metal/oxide systems – Chair: Michael Reichling

- 15:30 to 15:50 – **David C. Grinter**
Gold Supported on Ultrathin Ceria: Microspectroscopy of a model catalyst system
- 15:50 to 16:10 – **András Berkó**
Gold on TiO₂-decorated Rh(111) facets: exchange and competitive processes between Au and TiO₂ atomic layers studied by STM, LEIS, XPS
- 16:10 to 16:30 – **Željko Šljivančanin**
A novel mechanism for diffusion of gold clusters at defected MgO(100) and CaO(100)

surfaces

16:30 to 17:10: Coffee Break

Session II: Oxide/metal systems – Chair: Paola Luches

- 17:10 to 17:30 – **Falko P. Netzer**
Ceria nanostructures on Cu(110)
- 17:30 to 17:50 – **Alex Walton**
Cobalt oxide nanoparticles on Au(111): structure, composition and dynamics
- 17:50 to 18:10 – **Jacek Goniakowski**
Active sites at a realistic model of SMSI catalysts: the case of Pt(111)-supported iron oxide film
- 18:10 to 18:30 – **Svetlozar Surnev**
Reaction of (WO₃)₃ clusters with metal-supported FeO(111) films: Formation of ordered two-dimensional iron tungstate nanolayers

19:00 to 21:30: Poster Session (including dinner/buffet)

Day 2 – April 29, 2014

Session III: Oxide formation, defects and characterization – Chair: Sergio Valeri

- 9:30 to 10:10 – Invited speaker: **Wolf Widdra**
Surface-driven topological oxide quasicrystals
- 10:10 to 10:30 – **Juan José Delgado**
Recent contributions of electron microscopy to the characterization of reducible oxides based catalysts
- 10:30 to 10:50 – **Jan Ingo Flege**
Growth, structure, and morphology of CeO₂(111) and CeO₂(100) islands on Ru(0001)

10:50 to 11:30: Coffee Break

Session IV: Reactivity and Fundamentals – Chair: Rubén Pérez

- 11:30 to 11:50 – **Gianfranco Pacchioni**
Redox properties of MgO and CaO films doped by transition metal ions
- 11:50 to 12:10 – **David López-Durán**
Ni/CeO₂: a monofunctional model catalyst for the water-gas shift reaction
- 12:10 to 12:30 – **Svatopluk Civiš**
Room temperature spontaneous conversion of OCS to CO₂ on the anatase TiO₂ surface
- 12:30 to 12:50 – **Hannes Jónsson**
ODD energy functionals for improved accuracy of calculations scaling as third power of system size

13:00 to 15:00: Lunch Break

Session V: Defects and doping – Chair: Michael Nolan

- 15:00 to 15:20 – **Ulrike Diebold**
Small and Large Polarons in TiO₂ rutile and anatase
- 15:20 to 15:40 – **Milica Todorović**
Simulated NC-AFM and STM characterisation of surface defects and molecular adsorbates on the (101) surface of TiO₂ anatase
- 15:40 to 16:00 – **Maria Cristina Paganini**
Defects and photochemical properties of bare and cerium-doped zirconium dioxide

16:00 to 16:50: Coffee Break

- 16:50 to 18:20 – **Round Table: Theory**
Computational modeling of reducible oxides: Challenges and perspectives
Moderator: M. Verónica Ganduglia-Pirovano
Speakers: Gianfranco Pacchioni, Hannes Jónsson
- 16:50 to 18:20 – **Round Table: Experiment**
Experimental challenges, controversial topics and exciting perspectives in the synthesis and analysis of reducible oxides
Moderator: Sergio Valeri
Speakers: Falko Netzer, Zbigniew Sojka, Michael Reichling, Jan Ingo Flege

21:00: Conference Dinner

Day 3 – April 30, 2014

Session VI: Metal/oxides and Reducibility – Chair: Francesc Illas

- 09:30 to 09:50 – **Monica Calatayud**
Measuring reducibility of metal oxides from DFT calculations
- 09:50 to 10:10 – **Sergio Tosoni**
Effects of interstitial doping with alkali metals on structural and electronic properties of WO_3
- 10:10 to 10:30 – **Jeppe V. Lauritsen**
Thermally induced Cu wetting on $\text{ZnO}(0001)\text{-Zn}$
- 10:30 to 10:50 – **Jacques Jupille**
Metallic and oxidized zinc at the surface of $\alpha\text{-Al}_2\text{O}_3(0001)$

10:50 to 11:30: Coffee Break

Session VII: Nanocrystals – Chair: Javier Fernández-Sanz

- 11:30 to 11:50 – **Emile Maras**
Simulation of TiO_2 surfaces with the second-moment tight-binding Qeq model
- 11:50 to 12:10 – **Stefan Bromley**
Approaching the nanocluster-to-bulk structural transition in CeO_2 , TiO_2 and SiO_2
- 12:10 to 12:30 – **Joanna Grybos**
Insights into structure and morphology of zirconium oxide nanocrystals by HR TEM techniques combined with DFT molecular modelling and images simulations.
- 12:30 to 12:50 – **Witold Piskorz**
DFT+U modeling of charge transfer processes and redox properties of nano- Co_3O_4 crystals
- 12:50 to 13:00 – **Closing**

13:00: Lunch

Talks

Gold Supported on Ultrathin Ceria: Microspectroscopy of a Model Catalyst System

David C. Grinter¹, Bobbie-Jean Shaw¹, Chi-Ming Yim¹, Chi L. Pang¹, Chris Muryn², Benito Santos³, Tefvik O. Montes³, Andrea Locatelli³ and Geoff Thornton¹

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With varied applications across a number of fields, ceria-based materials are the focus of intense study. The suitability of ceria as a heterogeneous catalyst support due to its excellent oxygen storage and release characteristics is well-known. In particular, gold nanoparticles supported on ceria have displayed high catalytic activity towards the low temperature water-gas-shift reaction.[1] In this work we describe the preparation and characterisation of model systems employed to study such catalysts. To overcome the charging problems resulting from the application of electron-based spectroscopy and microscopy to insulating materials such as ceria, we form ultrathin epitaxial films of CeO_{2-x}(111) on a number of conducting substrates including Pt(111),[2] Rh(111), and Re(0001).[3]

To characterise the morphology and oxidation state of these films we have employed a combination of techniques including scanning tunnelling microscopy (STM), low energy electron microscopy (LEEM) and synchrotron-based x-ray photoemission electron microscopy (XPEEM). The growth and structure of the ceria films have been followed in-situ with bright- and dark-field LEEM. We have analysed the defect structure of the CeO_{2-x}(111) surface using atomically-resolved STM imaging and identified oxygen vacancy structures which may play important roles in their reactivity. High-resolution XPEEM imaging using resonant photoemission of Ce 4f has permitted us to interrogate the local oxidation state of individual ceria islands. The adsorption of gold clusters ranging in size from single atoms to ~5 nm diameter nanoparticles has been investigated with STM and their chemical state probed using XPEEM imaging of the Au 4f. Shifts to higher binding energies are observed for gold supported on the ceria with the magnitude of the shift inversely related to the size of the gold clusters.

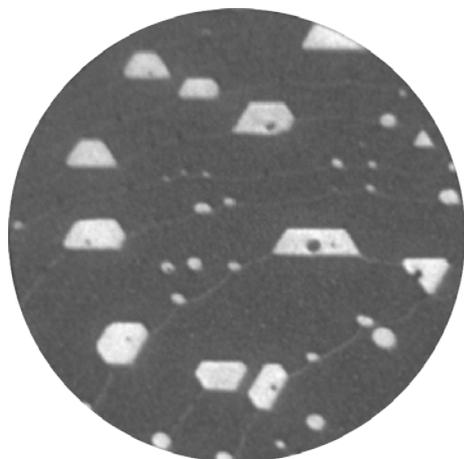


Figure 1. Darkfield LEEM of a 1.1 MLE CeO_{2-x}(111) film on Rh(111). Bright ceria islands are observed to decorate the substrate with a clear preference for nucleation at the rhodium step edges. E = 16 eV, FOV = 2 μm.

[1] Fu, Q. et al. *Science* **301**, 935, (2003).

[2] Grinter, D.C. et al. *J. Phys. Chem. C* **114**, 17036, (2010).

[3] Grinter, D. C. et al. *J. Phys. Chem. C* **117**, 16509, (2013).

Gold on TiO_{-1,2}-decorated Rh(111) facets: exchange and compatitive processes between Au and TiO_{1,2} atomic layers studied by STM, LEIS, XPS

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Deposition and thermal stability of Au were studied on a TiO_{-1,2} "pinwheel" type ordered decoration ultrathin oxide film (w-TiO-UTO) grown on extended Rh nanoparticles (showing flat (111) top facets) supported on TiO₂(110) surface. STM, XPS and LEIS methods were applied in this study. The (111) top facets of the Rh nanoparticles were uniformly and completely covered by the w-Ti-UTO film [1, 2]. Regarding that the free (interparticle) regions of the support have clearly shown a structure characteristic of clean terraces of a TiO₂(110) surface, it was possible to follow concurrently the Au particle formation on both the encapsulation w-TiO-UTO layer and the atomic terraces of the clean TiO₂ support. The deposition of different amounts of Au at 300 K revealed that the ordered w-Ti-UTO layer becomes strongly disturbed and the Au adlayer exhibits 3D growth. No sign of an ordered templating effect of the oxide film was observed even at the lowest coverage studied in this work (0.02 ML). It was found that the 3D (2-3 monolayer thick) Au nanoparticles of 2-3 nm diameter formed at 300 K sinter gradually in the temperature range of 500-800 K, probably as a result of thermally activated Ostwald-ripening process. The lateral extension of these particles increased upon the raise of the temperature and their top facets suggested an atomic arrangement of Au(111) surface as revealed by STM. The results obtained by LEIS measurements strongly suggest a replacement process between the w-TiO-UTO layer and the deposited Au. Interestingly the nearest neighbor distance of the Au atoms was measured to be 0.26(±0.1) nm, which is characteristic of a Rh-Rh distance on a Rh(111) surface. It means that the first and second layers of Au grows in a homomorph way on a Rh(111) surface. In the temperature range of 800-900 K, the 2D gold nanoparticles exhibited characteristically a double layer height. Note that the Au nanoparticles formed on the TiO₂ support exhibit clearly a 3D growth mode. Above 900 K, the thickness of the Au particles sitting on the extended Rh particles covered by w-TiO-UTO layer tend to become a single layer, while they spread out and form a continuous layer if the coverage is sufficiently high. Surprisingly, in several cases the gold nanoparticles exhibited a reconstruction of (2 × 1) structure consisting of limited size (2-3 nm) domains. The replacement of the w-TiO-UTO film by Au was corroborated by XPS measurements showing a strong attenuation of the Ti²⁺ component, characteristic of the encapsulation layer. The formation of Rh-supported one-dimensional Au/w-TiO-UTO interface regions will also be analyzed in this work.

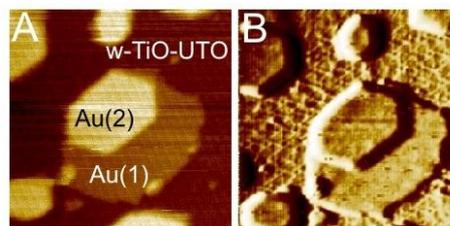


Figure 1: (A) Constant current and (B) constant height images of 20 x 20 nm² recorded after deposition of Au on a w-TiO-UTO film at 500 K followed by annealing at 900 K.

[1] Z. Majzik, N. Balázs, A. Berkó, J. Phys. Chem. C, **115**, 9535, (2012).

[2] A. Berkó, R. Gubó, L. Óvári, L. Bugyi, I. Szenti, Z. Kónya, Langmuir **29**(51), 15868, (2013).

A novel mechanism for diffusion of gold clusters at defected MgO(100) and CaO(100) surfaces

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Using computational modeling based on density functional theory (DFT) we revealed a new, low energy path for diffusion of Au nanoclusters deposited on MgO(100) and CaO(100) surfaces. This diffusion mechanism enables aggregation of metal particles bound to the F-centers at the temperatures considerable lower than previously thought. According to our calculations the joint diffusion of the clusters and the oxygen vacancies proceeds with the activation energies up to 0.9 eV smaller than the energy barriers corresponding to the detachment of the clusters from the F-centers, since it does not require energetically costly breaking of the stable complexes formed by the clusters and the point defects. For Au dimers and trimers at the CaO(100) this diffusion route, accompanied with the activation energy of only 1.0 eV, is effective already at the room temperature.

Ceria Nanostructures on Cu(110)

Liyang Ma, Nassar Doudin, Svetlozar Surnev, Falko P. Netzer

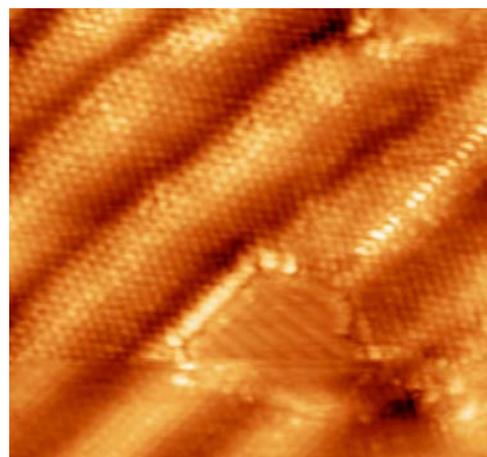
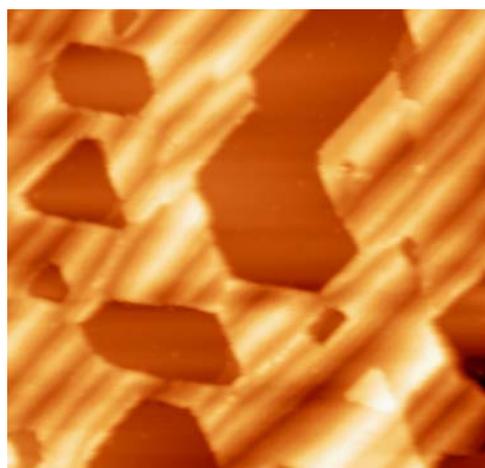
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The growth of ceria nanostructures on Cu(110) has been investigated by STM, LEED and XPS. Well-ordered epitaxial ceria monolayer phases have been obtained, however the ceria develops a highly corrugated nanoscopic stripe pattern (see the figure, left panel). This morphological peculiarity is caused by the frustration of the overlayer-substrate bonding produced by the epitaxial mismatch and by the competition between local substrate-overlayer and intralayer interactions [1]. The chemically induced topographic modulation supports a well-defined heteroepitaxial relationship of the oxidic ceria layer and the metal surface. As a function of the preparation conditions, different surface morphologies can be generated, with different Cu-O surface oxide phases (displaying Cu-O(2x1), Cu-O c(6x2) reconstructions) coexisting with the ceria nanostructures. The so-created surfaces constitute a kind of mixed oxide nanostructured monolayer catalyst, with high structural order (see figure, right panel), tunability of the Cu-O phase and different chemical reactivities.

[1] M. Wagner, F.R. Negreiros, L. Sementa, G. Barcaro, S. Surnev, A. Fortunelli, F.P. Netzer, *Phys. Rev. Lett.* 110, 216101 (2013)

Work supported by the ERC Advanced Grant SEPON and by COST CM1104



Left panel: STM image of a ceria monolayer phase on Cu(110) (80x80 nm); the vacancy islands with hexagonal symmetry contain the Cu-O(2x1) surface oxide. Right panel: High resolution STM image of the ceria monolayer (14.4x14.4 nm); the hexagonal atomic lattice and the stripe pattern following the [110] direction is clearly resolved.

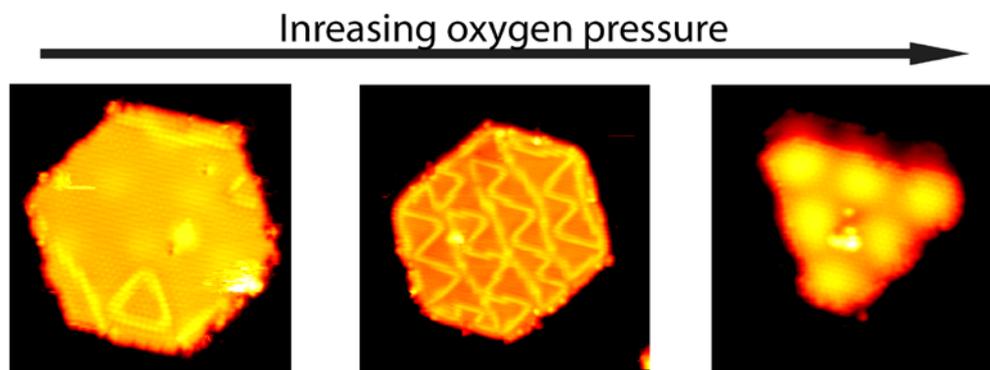
Cobalt oxide nanoparticles on Au(111): Structure, composition and dynamics

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Cobalt oxide shows great promise as an oxidation catalyst, shown to be highly active for CO oxidation at low temperatures[1]. It has also been demonstrated as an effective catalyst for water oxidation[2]. Its catalytic properties have been shown to improve dramatically when promoted with gold[3]. We used atom-resolved Scanning Tunneling Microscopy and X-Ray Photoelectron Spectroscopy to investigate the nature of the cobalt – gold interaction by studying cobalt oxide (CoO) nanoparticles synthesized on a single crystal gold substrate, Au(111). We find that the structure of the nanoparticles is determined by the interplay between substrate interaction and surface polarity compensation – leading to a complex mixed rocksalt-wurtzite crystal structure.

Furthermore, we find that the coordination and valency of the cobalt species in the nanoparticles can be tuned by variation of oxygen chemical potential during synthesis, with nanoparticles synthesized at low pressure containing Co^{2+} in octahedral and tetrahedral coordinations and those at higher pressure a mixture of tetrahedral Co^{2+} and octahedral Co^{3+} , much like Co_3O_4 .

At intermediate pressures, oxygen adatom line defects form on the surface of the nanoparticles, leading to rows of over-coordinated cobalt atoms. These structures are reactive and mobile. We investigated the dynamics and reactivity of these structures using STM movies.



1. Xie, X., et al., Nature, 2009. **458**(7239), 746-749.
2. Liao, L., et al., Nat Nano, 2014. **9**(1), 69-73.
3. Ma, C.Y., et al., Journal of the American Chemical Society, 2010. **132**(8), 2608-2613.

Active sites at a realistic model of SMSI catalysts: the case of Pt(111)-supported iron oxide film

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Oxide ultra-thin films can be formed under reaction conditions on active metals used in heterogeneous catalysis and alter considerably the catalytic activity of the metal phase. For example, Pt nanoparticles encapsulated by iron oxide film are more active than the bare Pt(111) surface under the same conditions and a similar activity has been reported for FeO layers grown on Pt(111) [1-3]. The proposed reaction mechanism involves oxygen incorporation by the FeO film in oxygen rich-conditions with formation of FeO₂ islands which easily react with CO [1,2,4,5].

In the present study we report computational results on oxygen adsorption and extraction characteristics obtained for a realistic model of the Pt(111)-supported FeO_x ultra-thin film [6]. Derived directly from the experimental results, the model enables a coherent analysis of the activity towards oxygen at a large variety of sites, ranging from FeO and FeO₂ oxide terraces to different oxide/metal and oxide/oxide boundaries. We show that the trends in calculated adsorption and desorption energetics are to a large extent specific to the small thickness of the supported oxides, and are mainly driven by the electron exchange with the underlying metal substrate. The thorough mapping of the activity of different local surface environments enables the identification of the sites, which are most likely responsible for the observed low-temperature activity of FeO_x/Pt films in CO oxidation. Beyond the oxide/metal boundaries known for their larger activity compared to the separated materials, we find that also the sites at boundaries between the co-existing oxide phases of different composition can easily adsorb and release oxygen.

- [1] Y. N. Sun, Z. H. Qin, M. Lewandowski, E. Carrasco, M. Sterrer, S. Shaikhutdinov, H.-J. Freund, *J. Catal.* **266**, 359 (2009).
- [2] Y. N. Sun, L. Giordano, J. Goniakowski, M. Lewandowski, Z. H. Qin, C. Noguera, S. Shaikhutdinov, G. Pacchioni, H.-J. Freund, *Angew. Chem. Int. Ed.* **49**, 4418 (2010).
- [3] M. Lewandowski, Y. N. Sun, Z. H. Qin, S. Shaikhutdinov, H.-J. Freund, *Applied Catalysis A: General* **391**, 407 (2011).
- [4] M. Lewandowski, I. M. N. Groot, S. Shaikhutdinov, H.-J. Freund, *Catal. Today* **181**, 52 (2012).
- [5] L. Giordano, M. Lewandowski, I. M. N. Groot, Y.-N. Sun, J. Goniakowski, C. Noguera, S. Shaikhutdinov, G. Pacchioni, H.-J. Freund, *J. Phys. Chem. C* **114**, 21504 (2010).
- [6] L. Giordano, G. Pacchioni, C. Noguera, J. Goniakowski, *ChemCatChem* **6**, 185 (2014).

Reaction of $(\text{WO}_3)_3$ clusters with metal-supported FeO(111) films: Formation of ordered two-dimensional iron tungstate nanolayers

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Iron tungstate (FeWO_4 , ferberite) is a promising material for applications in the catalysis, photoluminescence, microwave technology and gas sensing. These materials have been synthesized mostly in a bulk form, but with the advance of nanotechnologies there is a growing interest in preparing FeWO_4 structures at the nanoscale, whose physical and chemical properties are unexplored yet. Here, we investigate the possibility of fabricating two-dimensional (2-D) FeWO_x layers via a 2-D solid-state reaction of $(\text{WO}_3)_3$ clusters with structurally well-defined FeO(111) bi-layers supported on Pd(100) and Pt(111) surfaces. The FeO(111) layer on Pd(100) exhibits a $c(8 \times 2)$ coincidence structure, similar to that reported for FeO(111) layers on a Pt(100) surface [1], whereas the structure of the FeO(111) layer on Pt(111) has been established previously [2]. Following the deposition of $\sim 1\text{ML}$ $(\text{WO}_3)_3$ clusters at 300 K and subsequent annealing to elevated temperatures in UHV well-ordered 2-D phases have been detected in the STM and LEED (Fig. 1) on both Pd(100) and Pt(111) surfaces, whose structure will be discussed. The formation of these phases has been investigated by XPS: the W 4f core level spectra reveal sharp fingerprints, characteristic of ordered 2-D ternary oxide phases of FeWO_x type.

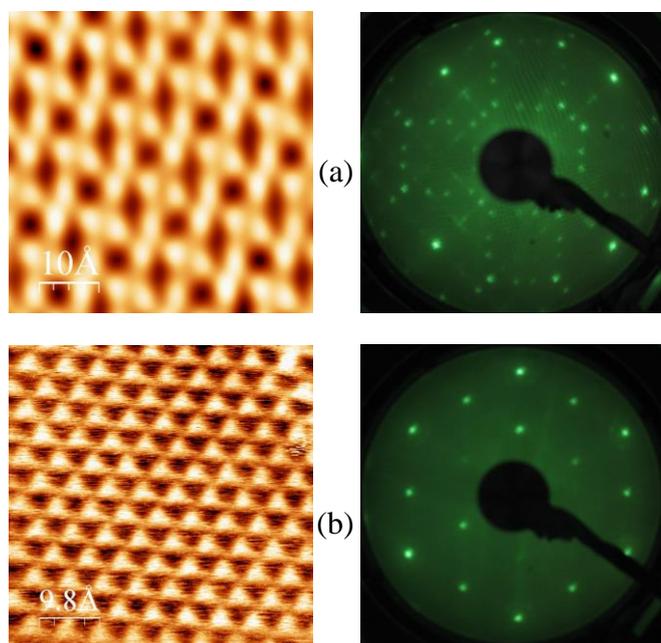


Fig. 1: STM images and corresponding LEED patterns of FeWO_x phases on (a) Pd(100) and (b) Pt(111) surfaces.

[1] S. Shaikhutdinov, M. Ritter, and W. Weiss, Phys. Rev. B 62 (2000) 7535

[2] H.C. Galloway, J.J. Benitez, and M. Salmeron, Surf. Sci. 298 (1993) 127

Surface-driven Topological Oxide Quasicrystals

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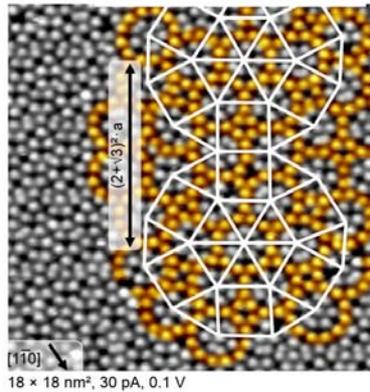
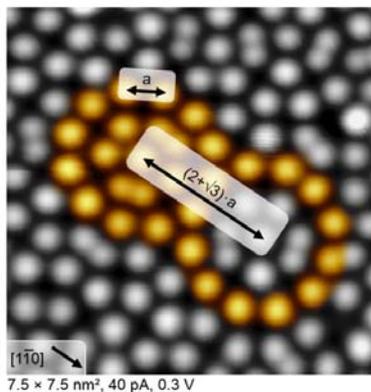
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Two-dimensional materials - like graphene, hexagonal boron nitride, or topological insulators - have recently pioneered a new field of materials science. Their peculiar properties are often related to their lower dimensional periodic structure. Here we report on the discovery of a new member in the family of 2D materials: A two-dimensional oxide quasicrystal (QC) [1].

The QC is derived from BaTiO₃ thin films on a hexagonal Pt(111) substrate. Low-energy electron diffraction (LEED) reveals a twelve-fold rotational symmetry. Scanning tunneling microscopy allows to resolve the atomic structure in details. The aperiodic structure is formed by surface atoms which are arranged in forms of squares, triangles, and rhombi with a universal edge length of 0.69 nm. The characteristic self-similarity of an ordered QC is clearly visible in high-resolution STM images: In addition to the dodecagonal atomic arrangement, building blocks of squares, triangles, and rhombi are also found in a $(2\sqrt{3})a$ and $(2 + \sqrt{3})2$ larger scale [1]. The observed formation of a 2D QC from a perovskite oxide in contact with a hexagonal substrate is expected to be a general phenomenon which is driven by the interface or topological frustration between a threefold and a fourfold system.

The preparation and the growth of these the QC films are discussed and compared with the growth of epitaxial, pseudomorphic 2% strained BaTiO₃(111) and BaTiO₃(100) films on Pt(111) and Pt(100) substrates [2-4].



STM images of the dodecagonal oxide ultrathin film on Pt(111). The fundamental length scale of $a = 0.685$ nm is marked.

- [1] S. Förster, K. Meinel, R. Hammer, M. Trautmann, and W. Widdra, *Nature* 502, 215 (2013).
- [2] S. Förster, K. Meinel, K.-M. Schindler, and W. Widdra, *Surf. and Interf. Analysis* 44, 628 (2012).
- [3] S. Förster, M. Huth, K.-M. Schindler, and W. Widdra, *J. Chem. Phys.* 135, 104701 (2011).
- [4] S. Förster and W. Widdra, *Surf. Sci.* 604, 2163 (2010).

RECENT CONTRIBUTIONS OF ELECTRON MICROSCOPY TO THE CHARACTERIZATION OF REDUCIBLE OXIDES BASED CATALYSTS

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It is unquestionable that one of the most important challenges of our society is the development of new energy strategies to tackle global warming and exhaustion of fossil fuels. In this context, catalysis has been proven as a critical enabling science for developing the use of alternative feedstocks, such as biomass or hydrogen, and increasing energy production efficiency [1].

Real catalysts commonly are complex multicomponent systems whose characterization usually demands an insight at the atomic level, and they are continuously posing new challenges and calling for further improvements in Electron Microscopy techniques. On the other hand, real catalysts contain morphological, structural and compositional heterogeneities and it is also obvious the need of developing new methodologies, based in statistical studies, that will give us a real picture of our catalyst. This point is really crucial for the rationalization of structure-activity relationships and understanding the deactivation processes.

The major goal of this contribution will be to review, using a number of examples from our most recent work, the possibilities of (Scanning) Transmission Electron Microscopy to reveal the ultimate details of the structure of nanostructured catalysts and how this information allow us gaining some understanding of how they work as catalysts. The lecture will focus on understanding the interaction of CO with gold catalysts [2] and the use of bimetallic catalyst and core shell nano-structured catalysts [3] in the sustainable energy production.

Acknowledgements

This work has received financial support from Spanish MICINN/FEDER-EU (Project MAT2008-00889-NAN).

[1] G.M. Whitesides and G.W. Crabtree, *Science*, 315 (2007), 796.

[2] M. Lopez-Haro, J.J. Delgado, J.M. Cies, E. del Río, S. Bernal, R. Burch, M.A. Cauqui, S. Trasobares, J.A. Perez-Omil, P. Bayle-Guillemaud and J.J. Calvino, *Angew. Chem. Int. Ed.*, 49(2010), 1981. J. van der Geer, J.A.J. Hanraads, R.A. Lupton, *J. Sci. Commun.* 163 (2010) 51–59.

[3] M. Cargnello, J. J. Delgado, J. C. Hernández, K. Bakhmutsky, T. Montini, J. J. Calvino Gámez, R. J. Gorte, P. Fornasiero, *Science*, 337 (2012), 713-717.

Growth, structure, and morphology of CeO₂(111) and CeO₂(100) islands on Ru(0001)

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On many transition metal surfaces, the deposition of cerium oxide usually results in the formation of (111)-oriented CeO₂ islands, representing conditions near thermodynamic equilibrium. On ruthenium(0001), and at temperatures of about 1000 K or higher, single-crystalline ceria(111) islands emerge at step edges, which subsequently adopt a triangular shape. Depending on substrate temperature and terrace width, these islands exhibit a typical height of 2-3 nm and may easily grow to micrometer dimensions [1]. However, near significant substrate step bunches and other defects, both square- and rectangular-shaped islands may also be observed for deposition at 1100 K using in-situ low-energy electron microscopy (LEEM). Different from the (111) majority phase, these objects almost always appear dark in contrast compared to the oxygen-covered Ru surface and the ceria(111) phase. Employing a suite of experimental tools comprising both in-situ and ex-situ microscopy, micro-diffraction, and synchrotron-based microspectroscopic techniques, the square islands are identified as CeO₂(100) islands that are about 7 to 10 nm tall, typically between about 50 and 500 nm in lateral diameter, and terminated with a c(2x2) O-deficient surface reconstruction. This structural identification is corroborated by local intensity-voltage ($I(V)$) analysis in comparison with results from *ab initio* electron scattering calculations, which were performed in analogy to (111)-oriented cerium oxide [2] and which successfully reproduce both the shape of the $I(V)$ curve and the unusually low electron reflectivity in the very-low-energy range [3].

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Redox properties of MgO and CaO films doped by transition metal ions

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We will present recent DFT results on the effect of doping MgO and CaO thin films by substituting Mg²⁺ cations with atoms like Li, Al, Ni, Cr and Mo. While on bare MgO the dopants affect the oxide electronic structure by creating holes in the valence band (low-valent dopants) or excess electrons (high-valent dopants), on metal supported ultrathin films the metallic support provides a reservoir to compensate charges via electron transfer through the oxide layer. The charge transfer has direct consequences on the work function (ϕ) of the combined oxide/metal system. Doping the films with monovalent Li atoms results in an increase of ϕ while a reduction of ϕ can be obtained with low-concentration of trivalent Al dopants. In the case of Ni, the impurity atoms can assume different oxidation states, Ni²⁺, Ni⁺ and Ni⁰, depending on the position in the film but for all configurations considered substitutional Ni leads to an increase of the work function. These effects are suppressed for thicker films due to the low tunneling probability. For thicker films, the surface properties can be altered by including in the lattice transition metal (TM) cations like Cr (MgO) or Mo (CaO). The TM species replacing the di-valent Mg cation can assume higher oxidation states, e.g. Cr³⁺ or Mo⁴⁺ and the charge imbalance is compensated via formation of cation vacancies. The impurity ions introduce states in the gap of the oxide that can deeply modify the electronic properties of the films. In particular, charge transfer from the d states of the TM impurity to gold atoms or particles deposited on the surface results in a complete change in adsorption properties.

Ni/CeO₂: a monofunctional model catalyst for the water-gas shift reaction

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Nanoparticles of late transition metals adsorbed on oxide surfaces form the basis for many catalysts important in energy technology. In the case of the water-gas shift (WGS) reaction, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$, ceria (CeO_2) supported noble metals like Pd, Pt, and Au were reported to be highly active. The nature of the active metal, the role of both the metal and the oxide as well as that of the metal/support interaction in the catalytic activity, and the actual reaction mechanism are matters of considerable debate. Yet, it is clear that WGS involves the adsorption and activation of both CO and H₂O. It is generally accepted that neither the metal nor the oxide can catalyze the reaction by themselves and that metal/oxide catalysts are bifunctional: CO adsorbs molecularly on the metal and H₂O dissociatively on the oxide [1]. The latter is, in principle, the rate-limiting step. The main drawback of noble metals is their cost. In contrast, Ni is cheaper and represents an alternative, as recently suggested [2]. However, the activity of Ni/CeO₂ strongly depends on the metal coverage; only small and dispersed Ni nanoparticles are efficient for the WGS reaction, whereas larger ones favor CO methanation.

To further investigate the Ni/ceria systems, computational model catalysts have been created, namely, Ni₁/CeO₂(111) and Ni₄/CeO₂(111), and the adsorption of C and CO have been studied employing density-functional theory (DFT) with the DFT+U approach [3]. Furthermore, the adsorption and dissociation of H₂O have been considered. The results are compared to those for Ni(111) and the clean and reduced CeO₂(111) support. We find evidence of a strong metal-support interaction; small Ni particles are in the +2 oxidation state. We provide computational evidence that ceria supported isolated particles [Ni₁/CeO₂(111)] behaves *monofunctional* with (i) the least decrease in the CO bond strength upon adsorption on the metal and (ii) a fairly low H₂O dissociation barrier *also* on the metal, as compared to larger Ni₄ particles and extended Ni(111). The H₂O dissociation barrier is comparable to that on the reduced CeO_{2-x}(111) support, but on the latter, the resulting OH species are too strongly bound for any further reaction.

The origin of the dependence on Ni coverage of the activity for WGS and CO methanation reactions of Ni/CeO₂ catalysts and the role played by both the metal and the oxide have been revealed. The effect of the ceria support is, in fact, to modify the electronic structure of the metal, and in turn its chemisorptive and reactive properties.

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Room Temperature Spontaneous Conversion of OCS to CO₂ on the Anatase TiO₂ Surface

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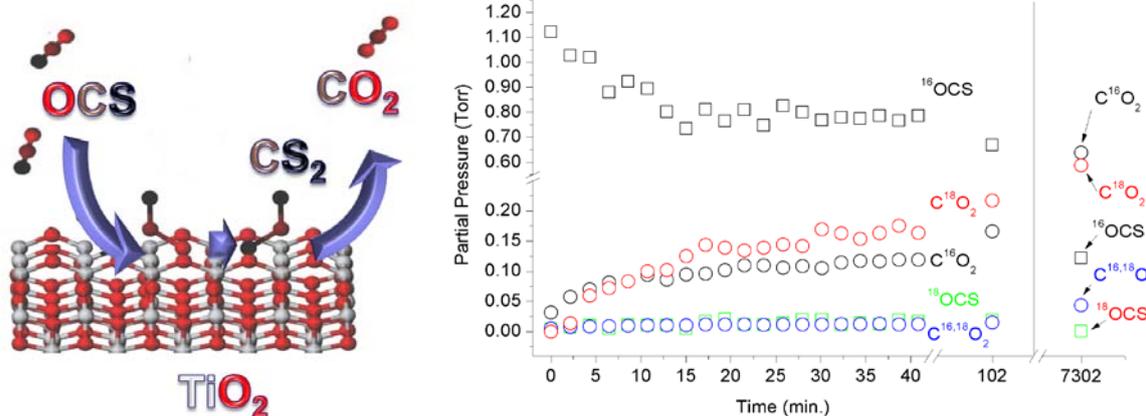
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High-resolution FT-IR spectroscopy combined with quantum chemical calculations was used to study the chemistry of ¹⁶OCS-disproportionation over the reduced surface of isotopically labelled, nanocrystalline Ti¹⁸O₂. Analysis of the isotopic composition of the product gases has revealed that the reaction involves solely OCS molecules from the gas-phase.

Using quantum chemical calculations we propose a plausible mechanistic scenario, in which two reduced Ti³⁺ centres mediate the reaction of the adsorbed OCS molecules.

Our recent research^{1,2,3,4} is related to the question of how molecules can be spontaneously converted on the reduced titania catalytic surfaces. The quantum chemical mechanism is also a subject of this exploration.



Scheme of the sulphur – oxygen exchange on the titania surface together with an evolution of the composition of the reaction mixture in the reaction of Ti¹⁸O₂(s) + ¹⁶OCS(g).

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ODD energy functionals for improved accuracy of calculations scaling as third power of system size

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Abstract

While Kohn-Sham density functional theory using generalized gradient approximation (GGA) for the energy functional has been remarkably successful and widely used to calculate properties of materials, there are several, systematic shortcomings which limit its applicability. These include: (1) Instability of localized electronic defect states with respect to delocalized states, (2) inaccurate orbital energies, which for example give large underestimates of band gaps and absence of Rydberg states, (3) underestimation of energy barriers for atomic rearrangements, and (4) overestimation of bond dissociation energies. All of these shortcomings can be traced to the incorrect estimate of the Coulomb energy which in Kohn-Sham theory is based on the total electron density, thus introducing self-interaction of the electrons. Many elaborate schemes for improved estimates of the exchange-correlation energy have been devised to help cancel out this self-interaction. However, since orbitals have already been introduced to estimate the kinetic energy, the question arises why orbitals are not also used to estimate the Coulomb energy without introducing self-interaction? A more accurate estimate would include only Coulomb repulsion between distinct pairs of orbital densities. Such an approach is, however, mathematically more challenging as the energy and electron density are no longer unitary invariant, i.e. independent of which linear combination of orbitals is chosen. Then the minimization of the energy of the system cannot be written as a set of one electron eigenvalue problems for the ‘canonical’ orbitals. On the other hand, minimization of such a functional yields a unique set of ‘optimal’ orbitals which can correspond well to chemical intuition where repelling, localized electron pairs have become the basis for understanding molecular structure and chemical reactivity. Some progress has been made recently on the implementation of orbital density dependent (ODD) functionals but good exchange and correlation functional to go with self-interaction free Coulomb energy remains to be developed. The Perdew-Zunger self-interaction correction to LDA or GGA functionals is one approach, which has been shown to lead to significant improvements in many cases, but higher accuracy could be obtained by developing a new, optimal exchange correlation functional to complement the self-interaction free Coulomb energy.

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Small and Large Polarons in TiO₂ Rutile and Anatase

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When excess electrons are added to the conduction band of an oxide, the electron-phonon interaction may result in electron trapping – the formation of either localized (small) or delocalized (large) polarons [1]. Electron localization in TiO₂ rutile has been the topic of intense investigations, see e.g., [2].

We have used a combination of STM, STS and DFT+*U* to investigate the nature of electron polarons in rutile and anatase. In agreement with many previous studies, we find that the excess electrons in rutile can localize at any lattice Ti atom, forming a small polaron. The polarons in rutile can easily hop to neighboring sites. Electrons in a perfect anatase lattice prefer a delocalized (band-like) solution, while small polarons can only be formed at defects such as O vacancies or step edges. These then act as preferential adsorption sites for electron scavengers such as O₂ [3]. Large polarons were observed in Nb-doped anatase in vicinity of subsurface Nb dopants.

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Simulated NC-AFM and STM characterisation of surface defects and molecular adsorbates on the (101) surface of TiO₂ anatase

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The (101) surface of TiO₂ anatase is a technologically important reducible oxide material where the mechanisms of surface reactivity and their modification with surface defects are not fully understood. There are still very few atomic-scale studies of this surface system, mainly using scanning tunnelling microscopy [1], and recently this surface has been also explored using simultaneous NC-AFM and STM [2]. Our computational study is designed to aid experimental data interpretation for this multi-channel SPM technique and develop its capacity for functional imaging of metal-oxide surfaces and their defects.

We present a systematic DFT+U study of the changes in geometry and electronic properties of the clean anatase (101) surface induced by the creation of common surface defects such as the O vacancy and H defect and with surface adsorption of water. Using a realistic TiO₂ cluster tip model [3], we investigate tip-surface interactions in simulated AFM force spectroscopy characterisations of the clean anatase surface, its defects, and the adsorbed water molecule. Lastly, we explore the contrast mechanisms of simple STM imaging on the clean anatase surface and analyse the simulated STM images for the O vacancy, the H defect and the adsorbed water. Our findings are matched with extensive simultaneous AFM/STM measurements at atomic scale recently obtained for the (101) anatase surface to gain a deeper understanding of its chemical and electronic response [2].

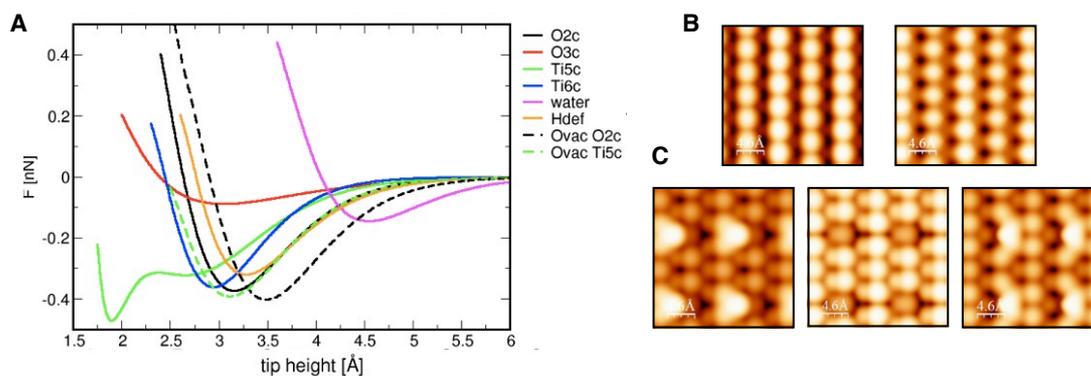


Figure 1: A. Computed forces of AFM tip-surface interactions on anatase (101) TiO₂ surface. B. Simulated STM images of the clean surface at negative and positive bias voltages (imaging O and Ti atoms respectively). C. Simulated STM images of the H defect, subsurface O vacancy and adsorbed water molecules in the positive bias regime.

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Defects and photochemical properties of bare and Cerium-doped Zirconium dioxide

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Zirconium dioxide has been studied in the last decades because of its large range of applications as ceramic material, in optical devices, gas sensors and catalysts (both as catalyst and catalyst support) [1]. On the other hand also Cerium oxide has attracted researchers attention because of its redox properties related to the oxygen storage capacity (OSC) and release. [2,3] As bare oxide, CeO₂ is not stable even at low temperature, but its most important disadvantage is the sintering process that occurs starting at that temperature and consequently the drastic reduction of surface area.

In the last few years the mixed system CeO₂-ZrO₂ based materials have been widely employed as catalysts for the conversion of automotive and industrial plants emissions into non-toxic compounds. The application of such system is based on the easy Ce^{III}→Ce^{IV} switching (and viceversa) influencing the oxygen storage capacity of ceria, and on the improvement of thermal stability and redox properties featured by ceria-zirconia mixed oxides with respect to pure CeO₂. [4,5].

Recently zirconia based mixed oxides have been used for photocatalysis processes. The high zirconia band gap (more than 5 eV) implies the use of UV light in the photoactivation but also the presence of particularly attractive reduction and oxidation potentials.

In our study we synthesized ZrO₂-CeO₂ mixed oxides with different CeO₂ loading (0.5-1-5 wt%) via sol-gel process. From structural (XRPD) and spectroscopic (DR-UV-Vis and EPR) systematic characterization we derived important information about the nature of defects in the lattice of the material and we checked also the photo-activity of the mixed oxides with visible light. Preliminary photo-catalytic experiments have been performed to test reductive and oxidative properties of these mixed oxides. Encouraging results have been obtained especially with the sample having lower ceria loading (0.5%). Both reduction and oxidation activity of the sample have been verified through paramagnetic resonance technique. The photoformation of both electrons (reacting with oxygen and producing superoxide anions) and holes necessary to entail photocatalytic processes has been demonstrated irradiating with visible light (lamp cut off at 420nm). This phenomenon, which is not observed for bare ZrO₂, is due to the presence of empty Ce⁴⁺ states in the zirconia band gap.

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Measuring reducibility of metal oxides from DFT calculations

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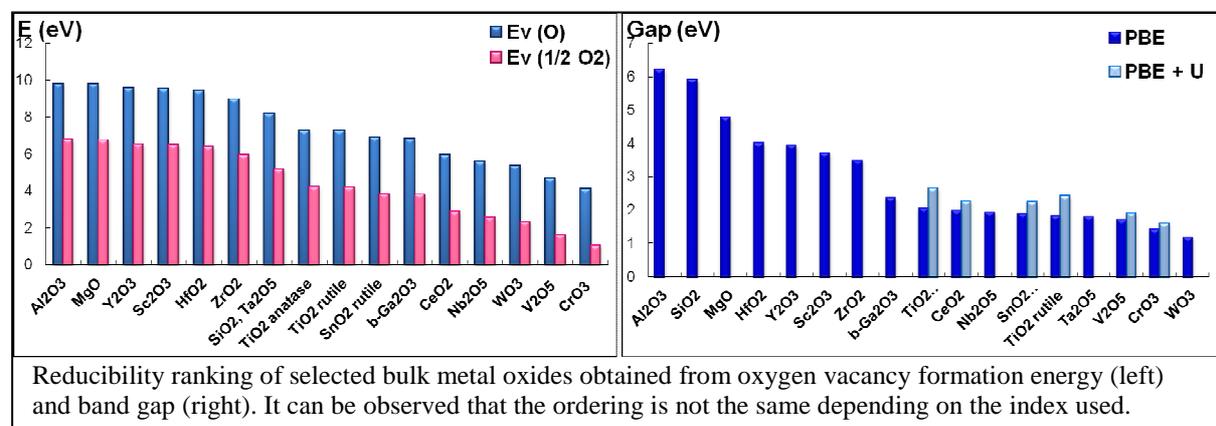
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Reducibility is one of the main properties determining the oxide chemical behaviour. If the meaning of “reducible metal oxide” is clear for both chemists and physicists, the term is far from being unambiguous.

From the theoretical point of view, some reactivity descriptors have been used to understand the nature and the extent of reducibility in a variety of materials. Among the most widely used, the oxygen vacancy formation energy E_v allows measuring the cost of removing an oxygen out of the lattice. The electronic description of the reduced system is also a critical index to understand reducibility: the band gap is correlated with the ability of a system to be reduced. Also, the localization of the electrons left by the removal of a lattice oxygen can be used as index: they may be transferred to the cation if it is reducible, or may stay at the lattice point if it is not.

In the present work we perform periodic density functional theory based calculations on a series of bulk metal oxides to establish a ranking of reducibility based on two criteria: the E_v value and the electronic structure. We will show that the two criteria do not lead to the same ordering, and we will discuss case examples of reducible, irreducible and intermediate behaviour.



Effects of Interstitial Doping with Alkali Metals on Structural and Electronic Properties of WO₃

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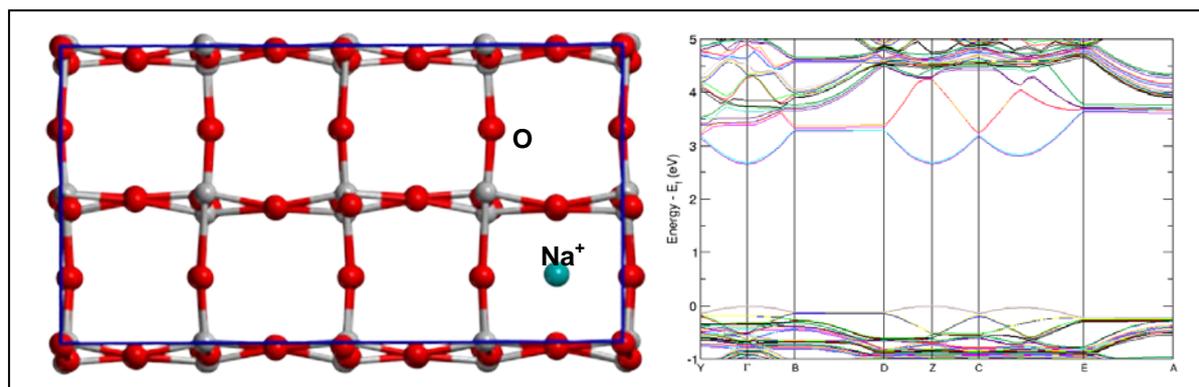
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In the last few years, electronic structure modifications which improve the visible light absorption of semiconducting oxides, such as WO₃, have been the subject of an intense research with the final goal of a more efficient harvesting of solar light for photochemical and photocatalytic applications. In particular, WO₃ is widely used in tandem or Z-scheme photocatalysts for the O₂ evolution in water splitting.

Following former studies on the different phases of bulk WO₃[1] and on its substitutional doping,[2,3] we now focus on interstitial doping and its effect on the electronic structure of the most stable polymorph at RT, namely the monoclinic one. It is already known that insertion of N₂ molecules in very high concentrations in the cavities of the monoclinic lattice of WO₃ induces a radical modification of its electronic structure, with a reduction of the band gap of 0.7 eV.[4] In the present work, we explore interstitial doping with alkali ions at lower and more sustainable concentrations, evaluating the induced modification of the electronic band gap by means of hybrid density functional calculations on periodic models.

We study the insertion of first-group cations from Li⁺ to Cs⁺ in a monoclinic-(WO₃)₃₂ supercell, relaxing both internal coordinates and lattice parameters, and calculate the band structure. The results show a trend of remarkable reduction of the band gap induced by the positive doping on the oxide (from 3.1 to 2.5 eV), with larger cations inducing stronger band gap reduction. The cavities of the monoclinic WO₃ structure undergo a remarkable distortion upon interstitial doping. The intrinsic structural flexibility of this oxide allows to host also very large cations, such as Rb⁺ or Cs⁺, at low concentration.

Further investigation on the nature of the change in the electronic structure upon doping, reveals an interesting interplay of structural and electrostatic factors, where the former have a predominant role.



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Thermally induced Cu wetting on ZnO(0001)-Zn

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The Cu/ZnO/Al₂O₃ catalyst is industrially used for the synthesis of methanol and for the production of hydrogen via the water-gas shift reaction. An intriguing fact for the Cu/ZnO catalyst is that methanol activity of the freshly prepared industrial catalyst drops at steady-state to almost 30% of its initial value during the first short time of operation [1]. This seemingly inevitable deactivation is often ascribed to Cu sintering, but the transient has strong dependence of the gas composition and interesting wetting/dewetting phenomena and Zn-Cu alloy formation effects are observed for the system. The strong synergistic behaviour contained in the Cu/ZnO system and the relationship between catalytic activity and selectivity are not yet understood in sufficient detail. Most catalyst models consider the Cu as the active phase, but the role of ZnO in the catalyst is much more important than that of a support only, having a big impact on the structural, electronic and catalytic properties of the supported Cu nanoparticles. A second important factor for a fundamental description is the fact that the ZnO(0001)-Zn surface is polar, which means that the surface is very sensitive to reconstruction and forming new surface structures depending on the experimental conditions and influence of adsorbates [2].

Here we have used Scanning Tunneling Microscopy (STM), X-ray Photoelectron Microscopy (XPS) and Thermal Desorption Spectroscopy (TDS) to investigate the thermal effects on Cu nanoparticle dispersion and morphology on the Zn-terminated ZnO(0001) surface. STM images recorded after heat flashing in 50K intervals under UHV reveal that the Cu morphology develops in three different stages. In the first stage from 300K to 500K, initially 2D-like Cu islands undergo strong sintering into 3D Cu nanoparticles, in line with previous observations [3]. In the second stage above 500K, however, the Cu re-disperses and forms a completely wetting film, evidenced by loss of visible Cu particles in the STM data but an increased Cu signal in XPS. During the first two stages the ZnO surface remains atomically flat, but at higher temperatures, Cu in-diffusion is initiated, and the ZnO surface then adopts a stepped morphology where triangular pits dominate. In our tentative model for the observations of thermally induced Cu wetting we explain the phenomena by lattice exchange of Cu on the plain ZnO(0001) surface. In such a scenario, the Cu enters as a stabilizing adsorbate on the polar ZnO(0001)-surface in stage two, whereas in the third stage the effect is lost and the surface is then again stabilized by O-terminated triangular pits as seen for the pristine ZnO(0001)-Zn surface [4].

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Metallic and oxidized zinc at the surface of α -Al₂O₃(0001)

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Metal/ α -Al₂O₃(0001) interfaces are of particular interest because the basal plane of the corundum structure show polar terminations which can potentially lead to quite different interfacial structures and energies. A particular case is the zinc/alumina interface. The oxygen-induced segregation of aluminium at the surface of the steel grades involving aluminium prevents the wetting by zinc during galvanization, i.e. the common treatment of steel against corrosion. This has prompted us to mimic the system by exploring the Zn/ α -Al₂O₃(0001) surface. To represent the polar terminations, we have chosen to study the Al-terminated non polar (1 \times 1), the reconstructed $\sqrt{31} \times \sqrt{31}R9^\circ$ and the hydroxylated surfaces, by photoemission, thermal desorption and, to get insight into the wetting via the aspect ratio of the supported particles, surface differential reflectance spectroscopy in the UV-visible. Zinc can be adsorbed on α -Al₂O₃(0001) below 240 K in a weakly bound metallic form ($E_{\text{ads}} \sim 0.5 \text{ eV}\cdot\text{atom}^{-1}$ after the Redhead formula). Zinc clusters desorb above 450 K. However, a fraction of monolayer of the initially metallic zinc becomes oxidized at 550 K upon annealing, which indicates an activated process. This species desorbs above 1300 K ($E_{\text{ads}} \sim 3.5 \text{ eV}\cdot\text{atom}^{-1}$). The observation of the two Zn oxidation degrees is compared to numerical simulations of Zn adsorptions on the various α -Al₂O₃(0001) terminations and also to other metal/ α -Al₂O₃(0001) systems.

Simulation of TiO₂ surfaces with the second-moment tight-binding Qeq model

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Titania (TiO₂) is of great interest for a variety of applications such as photocatalysis and solar cells [1]. The physical properties of a system can vary greatly depending on its morphology. To understand those properties, it is crucial to be able to model the atomic structure. At relatively low temperature, the most stable atomic configurations are those with the lowest energy. Many methods such as genetic algorithms or basin hopping have been specifically designed in order to find low energy configurations. Of course, the reliability of these methods depends on the interaction potential used to calculate the energy of the system. One can use first-principle calculations such as density functional theory (DFT) but unfortunately those methods are computationally expensive and can only be used in global optimization of relatively small systems. To overcome this limitation, we use a less expensive Second-Moment Tight-Binding Qeq model (SMTB-Q) [2]. This is a variable-charge model in which the ionic-covalent metal-oxygen bond is described by means of the tight-binding formalism that takes into account the electronic structure of the oxide. In order to check the accuracy and improve on the model, we use extensive data from a paper by Martinez et al. [3]. They used a genetic algorithm with DFT to identify a stable reconstruction of the $\langle 1\bar{1}1 \rangle$ step edge on the rutile (110) surface. In the process they obtained many configurations, which we use as a benchmark to check and improve the accuracy of the empirical potential. We will then apply the potential in global optimization simulations of larger systems such as an island on a (110) rutile surface.

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Approaching the Nanocluster-to-Bulk Structural Transition in CeO₂, TiO₂ and SiO₂

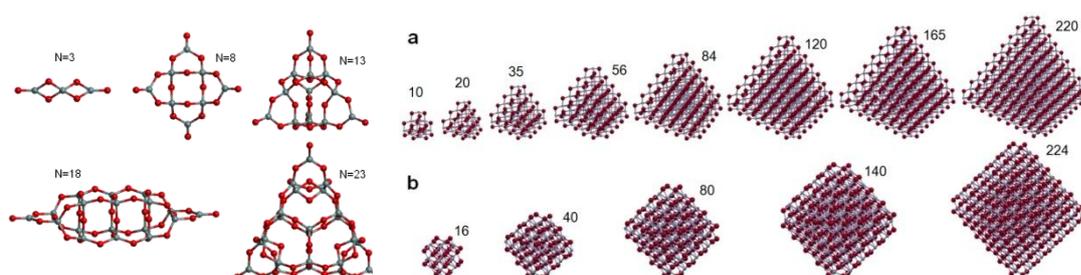
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Employing both global optimisation and density functional calculations, the structural transition from nanoscale clusters towards bulk materials is followed for two important reducible oxide materials (TiO₂, CeO₂) and a prototypical insulator (SiO₂). These three oxide materials have the same stoichiometry but different bonding tendencies, which is related to their ionicity/covalency. We examine how the latter affects the speed and manner in which these materials approach a bulk-like crystalline phase with increasing size from non-bulk-like nanoclusters. Although for ionic materials such as CeO₂ the cluster-to-bulk structural transition can be examined in detail by computational modelling, for low-ionicity/more-covalent materials (e.g. TiO₂, SiO₂) the space of low energy nanostructures is significantly richer, and the size at which a structural transition to the bulk occurs is difficult to estimate solely from a bottom-up theoretical approach.¹ We discuss how this fundamental nano-bulk crossover may be probed for materials such as TiO₂ and highlight the practical importance of the knowing how and at which size this transition occurs for practical applications.



Low energy cluster isomers resulting from global optimisation for: (SiO₂)_N clusters² (left), (CeO₂)_N clusters³ (right).

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[3] A. Migani, K. M. Neyman, S. T. Bromley, *Chem. Commun.*, 48 (2012) 4199.

Insights into structure and morphology of zirconium oxide nanocrystals by HR TEM techniques combined with DFT molecular modelling and images simulations.

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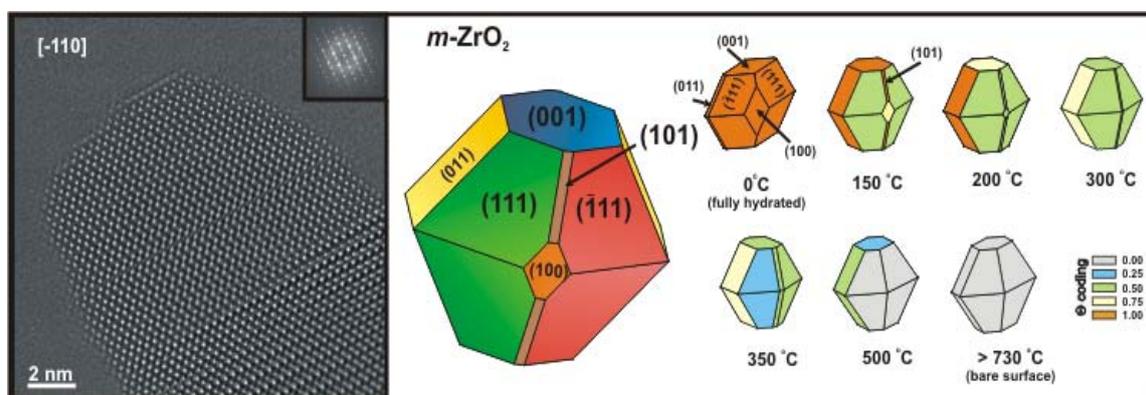
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Redox properties of oxide catalysts are determined by their structure and morphology. Nanostructured zirconium oxide catalysts are characterized by exposed facets, edges, corners and kinks that played crucial role their reactivity. In this contribution we combined HR TEM with DFT modelling to provide the morphological and structural description of monoclinic ZrO₂ surface at nano- and pico-scales. Equilibrium shape of the monoclinic zirconia nanocrystals with inclusions of entropy was predicted by means of plane wave periodic DFT/PW91 calculations combined with phonon structure calculations and Wulff construction. For modelling the VASP code and PHONON were applied. Atomic structure relaxation and reconstruction of the exposed zirconia planes were modeled and discussed in detail. The results were compared with HR TEM images (Fig. 1). The morphology predicted by the Wulff construction compares well with the experimental habit of the synthesized m-ZrO₂ nanocrystals. Small discrepancies in both shapes may be caused by the anisotropy in the rate of the crystal growth.

For experimental atomic-scale characterisation of the exposed planes, an aberration corrected HR TEM imaging at 300 keV was used. Quantitative measurements of the positions of the m-ZrO₂ atomic columns were performed by fitting the phase image areas to the two dimensional Gaussian function. To revealed the surface reconstruction, the space between the atomic planes was obtained by fitting the positions of the individual atomic columns to straight lines. The HR TEM images were simulated within the multislice approach, with inclusion of thermal vibrations of the crystal lattice, accounted for by the Debey-Waller factor. The calculated phonon structure of the bulk and the exposed facets of m-ZrO₂, helped to improve the accuracy of simulated images. The ab initio simulated images were validated against the experimental one. Furthermore the topographic irregularities of the exposed facets revealed by the picometric imaging were used to develop a complete picture of surface reconstruction.



DFT+U Modeling of Charge Transfer Processes and Redox Properties of nano-Co₃O₄ Crystals

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Remarkable ability for morphological tuning and high flexibility in modifying their electronic properties, make spinels excellent redox model catalyst of great theoretical and practical relevance. Depending on the synthesis method, faceted nanocrystals of cobalt spinel expose well-defined planes, allowing for sensible investigations into structure-reactivity relationships at both model and practical conditions. This allows for designing of redox-tunable catalytic materials of increased activity and selectivity by preferential development of the more active surface planes and enhancement of the active sites density. The redox properties of spinel oxides depend of intrinsic charge transport properties such as electron and hole transport, charge disproportionation and low spin – high spin transitions. These processes are controlled by the band structure of the spinel, defect states, inversion degree and doping.

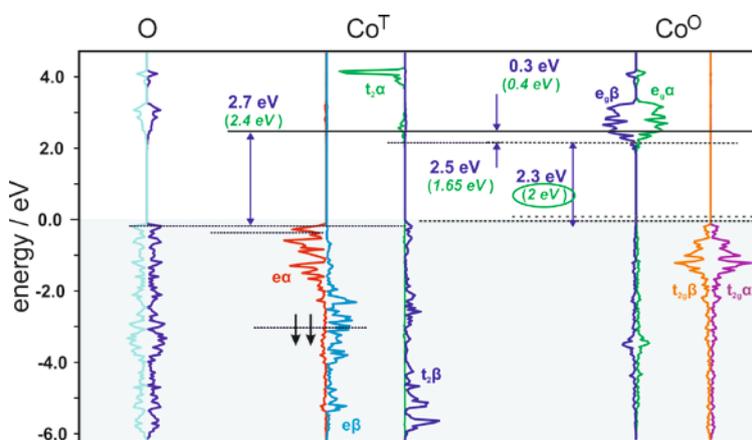


Figure 1. Spin resolved cobalt spinel DoS structure.

Herein, we present periodic plane wave DFT+U modeling of cobalt spinel electronic and magnetic structure. A gradient rPBE (with $U = 4.5$ and 6.5 eV for Co^{3+} and Co^{2+} respectively) and hybrid B3LYP functionals were used. The spin unrestricted band structure calculations for the bulk Co_3O_4 and the exposed (100), (110), and (111) planes were performed. These calculations were complemented by construction of the corresponding DOS and simplified energy level diagrams used for discussion of redox properties of Co_3O_4 and optical transitions. The results were compared with work function and conductivity measurements. Within the diabatic approximation a small polaron mechanism was proposed to model hole ($\text{Co}^{4+}/\text{Co}^{3+}$) and electronic ($\text{Co}^{3+}/\text{Co}^{2+}$) charge transfer processes occurring within the octahedral cobalt centers and between the octahedral and tetrahedral centers (spinel inversion). The activation barriers for the charge transfer processes were equal to 0.45 and 0.19 eV for electrons and holes, respectively. Two models of holes formation were taken into account - generation of oxygen vacancies and adsorption of atomic oxygen. An interfacial electron transfer from octahedral cobalt donor sites to suprafacial oxygen acceptor centers, as well as the stability of the resultant surface oxygen species were modeled and discussed.

Acknowledgement

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Simulated Mechanical Annealing Study for Cerium Oxide Nanostructures

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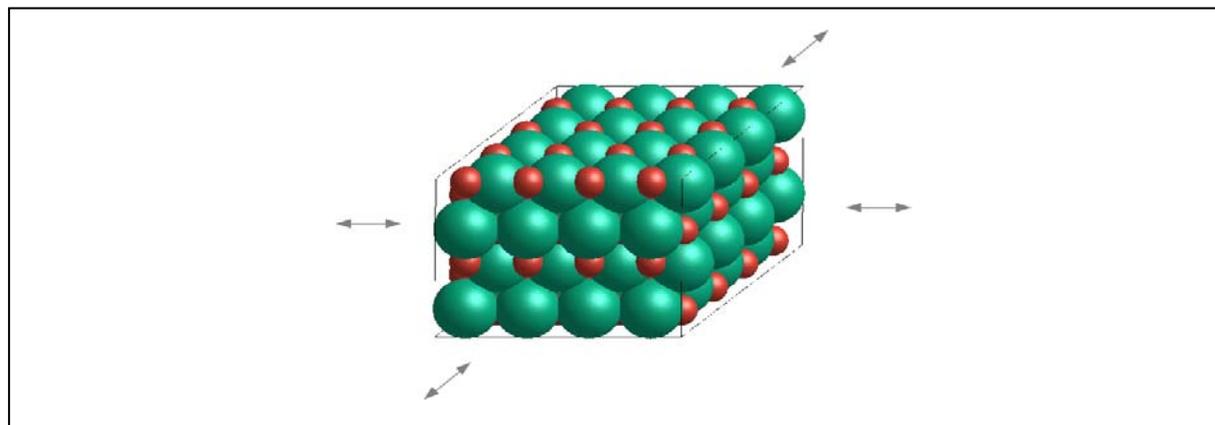
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Cerium Oxide (Ceria) is an important compound for a variety of applications including gas sensors, fuel cells and catalysis due to its high oxygen storage capacity and facile oxygen release feature. Reducing the size of ceria crystallites to the nanoscale commonly results in new or improved properties. [1] 2D nanofilms are thus important, which is applied as substrates in model studies of the chemical reactivity of ceria based catalysts.

Here we investigate the 2D nanostructures of cerium oxide by exploring configurational energy space by using interatomic potentials. For this purpose we used simulated mechanical annealing approach, which can be also extended to 1D or 3D structures. The approach mimicks mechanical annealing which is experimentally used to get rid of structural defects by iteratively introducing positive and negative strain on the structure. [2]



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Ordering of oxygen vacancies and excess charges in reduced bulk ceria

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The in-depth understanding and control of the density, and distribution of oxygen vacancies in ceria provide a means to influence the electronic structure and to tailor the systems' functionality. Using the DFT+U method we investigated the ordering of oxygen vacancies and excess charge localization driving the $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ reduction in bulk CeO_2 for defect concentrations ranging from 1.6% to 25%. The isolated vacancy was modeled using a unit cell of $\text{Ce}_{32}\text{O}_{64}$ composition. We computed the total energy for structures with Ce^{3+} ions at nearest neighbor (NN), next-nearest neighbor (NNN), third- and fourth- nearest neighbor cation sites to the vacancy. We found that the energies of all structures with either NN-NN, NN-NNN or NNN-NNN localizations lie within a narrow range of 0.1 eV, whereas those of structures with Ce^{3+} ions further away from the defect, have energies that are at least 0.3 eV above the lowest energy structure which is of the NNN-NNN type.

To analyze the interaction between oxygen vacancies, as well as the ordering of defects and Ce^{3+} ions, we used a smaller unit cell with Ce_8O_{16} composition and considered one and two first, second, third and fourth neighboring defects in the oxygen sublattice with all possible configurations for the two and four Ce^{3+} ions, respectively. We found correlations between vacancy–vacancy as well as vacancy– Ce^{3+} relative positions and total energies, providing clear indication of the proneness of both vacancy and Ce^{3+} for particular relative positions. Specifically, we found that: (i) The energy is a decreasing function of the average coordination number of the Ce^{3+} ions, which varies between 6 (all Ce^{3+} NN) and 8 (all Ce^{3+} NNN), (ii) The vacancies prefer to be second neighbors, and (iii) Two oxygen vacancies tend to avoid having common first neighboring Ce ions. For this particular cell at a high vacancy concentration (12.5%), we modeled the total energy as a sum of independent contributions related to the above preferences and fitted the ab initio energies in order to quantify the various terms. This simple model though sound for the specific vacancy concentration and distribution fitted to, its predictive power for more dilute cases is fairly limited.

In addition, we computed the averaged defect formation energy leading to the experimentally stable structures corresponding to Ce_7O_{12} (14%), $\text{Ce}_{11}\text{O}_{20}$ (9.1%) and Ce_2O_3 (25%) compounds and calculated the thermodynamically most stable Ce_xO_y phases as a function of oxygen pressure and temperature. Defect-induced lattice relaxation effects are found to play a crucial role in stabilizing the stable reduced structures.

DFT+U Investigations of Surface Modified Ceria

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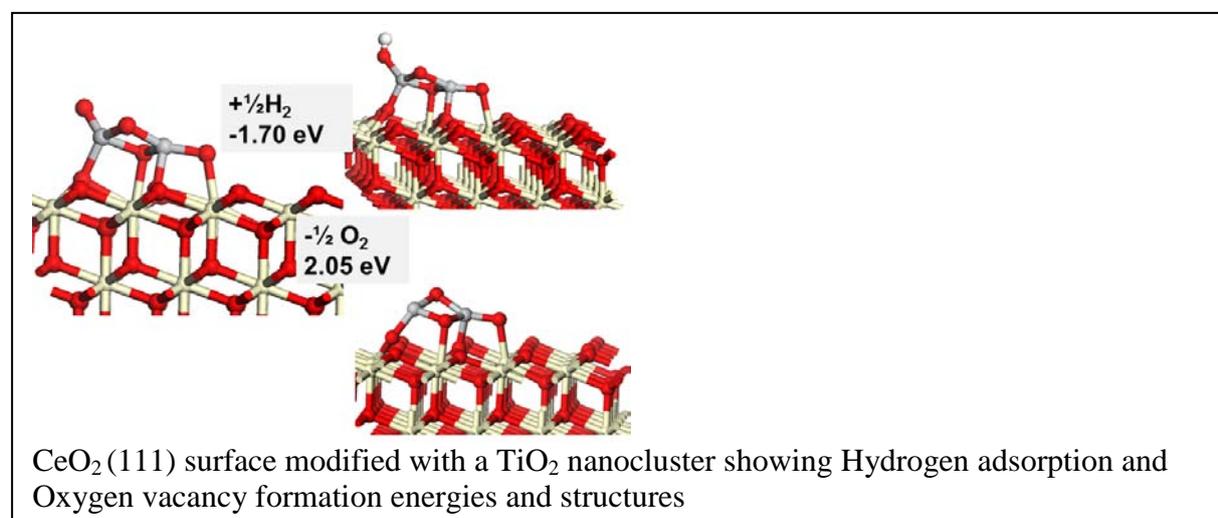
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Cerium dioxide modified with, e.g. metal nanoparticles or small oxide nanoclusters, such as vanadia, is of great interest in catalysis, including reactions such as CO oxidation or oxidative dehydrogenation of alcohols. A key property of ceria is the ability of Ce to undergo a change in oxidation state from Ce⁴⁺ in CeO₂ to Ce³⁺, which endows ceria with great flexibility in accommodating defects such as oxygen vacancies or hydrogen adsorption. The oxygen vacancy formation energy has emerged as a useful descriptor for the reactivity of ceria [1,2]. In the VO_x-CeO₂ system, the O vacancy formation and hydrogen adsorption energies have been used as descriptors in ODH [3], since the rate limiting step is abstraction of H from a C-H bond in the alcohol.

In this poster, we present results from DFT+U studies where we examine ceria (111) modified with (a) 1 nm diameter metal nanoclusters and (b) clusters of the transition metal oxides CrO_x and TiO₂ [4] with respect to oxygen vacancy formation and hydrogen adsorption. We show that modifying ceria (111) with CrO_x and TiO₂ enhances the oxygen vacancy formation and hydrogen adsorption compared to the individual oxides and we discuss the details of the activity of these structures. We show that 1 nm diameter Au, Ag and Cu nanoclusters adsorb on the (111) surface and can also reduce the formation energy of oxygen vacancies over the unmodified (111) surface.



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Structure, morphology and reducibility of mass-selected CeO_{2-x} nanoparticles

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CeO_{2-x} nanoparticles were deposited using an inert gas aggregation cluster source, composed of a magnetron target, a variable-length aggregation region filled with Ar and a quadrupole mass filter. We used a metallic Ce target and oxidized the nanoparticles either by introducing oxygen in the aggregation region or in the deposition chamber. In the latter case a post-deposition oxidizing treatment was necessary to fully oxidize the nanoparticles. By changing the length of the aggregation region we obtained nanoparticles with lateral size varying from 6 to 12 nm. The morphology of the nanoparticles was investigated using SEM, HR-TEM and HAADF imaging. The nanoparticles produced by oxidation in the aggregation chamber show a polycrystalline structure (Fig.1 b), while using deposition in oxygen and post-growth oxidation we obtained a single crystal structure (Fig.1 a). Spatially resolved EELS was employed to study the spatial distribution of Ce^{3+} and Ce^{4+} atoms inside individual particles, following [1]. The Ce^{3+} ions are preferentially located at the surface of the particles and their concentration is higher for smaller nanoparticles and for particles grown by oxidation in the aggregation region.

Space averaged information on the stoichiometry of the nanoparticles was also obtained from the deconvolution of Ce 3d XPS spectra. The nanoparticles were reduced and re-oxidized by thermal treatments in ultra-high vacuum and in oxygen partial pressure, respectively. The Ce^{3+} concentrations obtained at different temperatures was compared to the one of epitaxial cerium oxide films of comparable surface to volume ratio. The nanoparticles showed a significantly higher degree of reduction than films.

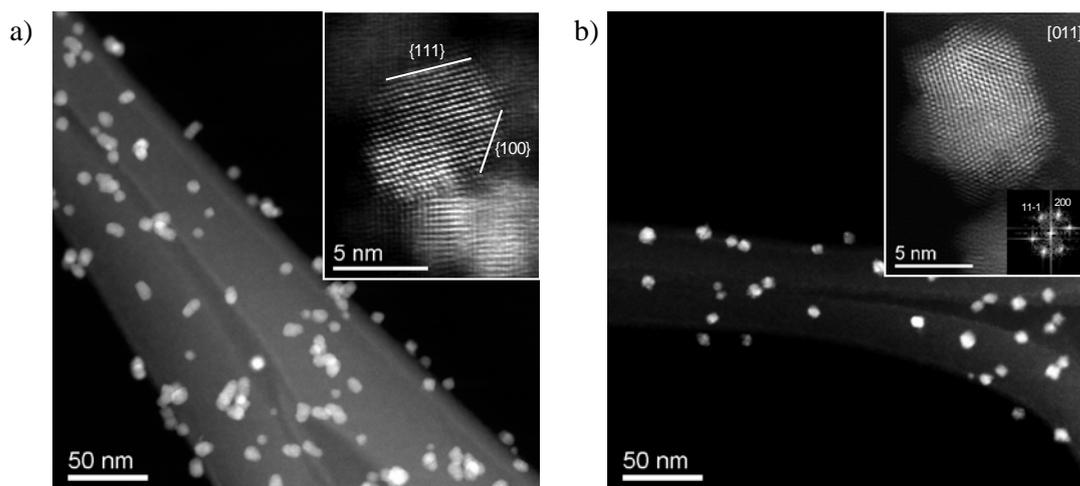


Fig. 1: CeO_{2-x} nanoparticles of comparable size obtained by a) post oxidation in the deposition chamber ($d = 8.9 \pm 1.8$ nm) and b) direct oxidation in the aggregation chamber ($d = 8.5 \pm 1.3$ nm). The insets show high-resolution HAADF images

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Growth and morphological analysis of Ag nanoclusters on ultrathin ZrO₂ films

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Zirconium oxide (ZrO₂) in pure and doped form is a very interesting material, with applications in a wide range of fields. It is both an electronic insulator and ionic conductor, which makes it a suitable material for Solid Oxide Fuel Cells, where it acts as electrolyte and catalyst support. It has also been shown that noble metal nanoparticles can be enhanced in their catalytic properties by the interaction with a catalytically active substrate, such as a reducible oxide like ZrO₂, and can introduce plasmonic properties into the system, opening possible applications also in the field of photocatalysis [1]. To this purpose, growth and self-assembly of Ag nanoparticles on a ZrO₂ trilayer obtained by oxidation of Pt₃Zr(0001) [2] have been studied. Ag clusters have been deposited by MBE and analyzed by scanning tunneling microscopy in a UHV chamber and the dependence of morphological and structural properties of the samples on preparation protocols have been investigated. The evolution of the morphology of Ag nanoparticles with post-deposition treatments (temperature and time) has also been studied. For low coverage (0.1 ML), the morphology of Ag nanoclusters depends on nucleation site (terraces center, terraces borders and domain boundaries), while with 2 ML no preferential site are noticeable. Most clusters show a (111) FCC surface orientation. Desorption of Ag from the surface was observed at 400°C.

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[2] M. Antlanger et al., Phys. Rev. B 86, 035451 (2012)

Nanostructurization of Iron and Manganese Oxides by Alkali Ions – Redox Properties, Activity and Stability

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The nanostructuration of Fe and Mn oxides by alkali insertion into tunneled and layered forms led to substantial changes in their redox properties and catalytic activity. The guiding hypothesis consists in exploration how the catalytic reactivity can be associated with the work function and surface status of alkali promoters. The methodology combining the experimental investigations and molecular modeling allows for establishing the rational principles for designing the optimal soot oxidation catalyst based on iron (layered $\text{K}_2\text{Fe}_{22}\text{O}_{34}$, tunneled KFeO_2) and manganese (layered birnessite KMn_4O_8 and cryptomelane $\text{KMn}_8\text{O}_{16}$) oxides.

Series of potassium nanostructured iron and manganese oxides were prepared by the reaction of stoichiometric amounts of K_2CO_3 with $\alpha\text{-Fe}_2\text{O}_3$ or KMnO_4 and $\text{Mn}(\text{CH}_3\text{COO})_2$ (for cryptomelane) or glucose (for birnessite). The samples were thoroughly characterized by several methods including XRD, SEM-EDX, HR-TEM/FIB, XPS, RS, BET. Electronic properties expressed as the surface work function (Kelvin Probe) and conductivity measurements. The stability and surface state of potassium was investigated by the Species Resolved Thermal Alkali Desorption. Soot combustion catalytic activity (loose and tight contact) was determined by TPRS and isothermal oxidation (TG/DTA - QMS) for various catalyst/soot ratios. It was found by SR-TAD studies that such structures are beneficial for high mobility of potassium promoter (bulk diffusion, surface segregation and desorption). The comparison of the soot combustion activity of the investigated catalysts shows a strong effect of potassium additions and correlation with the materials work function.

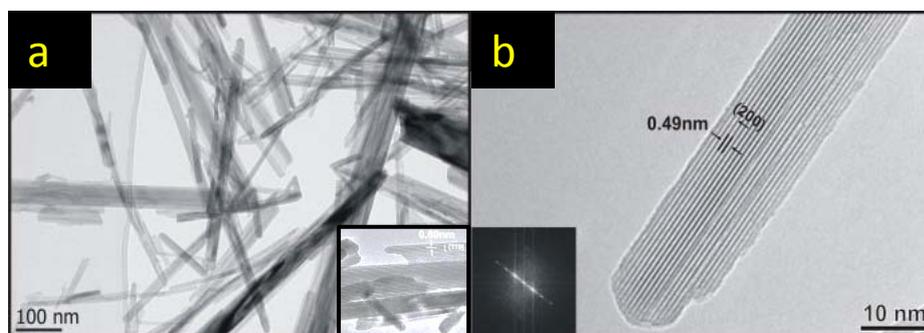


Figure 1. TEM and HR-TEM imaging of the cryptomelane nanorods.

The transformation of iron oxide into ferrites by potassium addition lowers the light off temperature by about 100°C , whereas for transformation from manganese spinel to layered mixed potassium oxides by 150°C .

Acknowledgements

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ZnO nanopowders: identification of bulk and surface defects

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With its outstanding chemical and physical properties, ZnO encompasses an amazing spectrum of applications competing, thus, to be one of the most promising compounds among other functional materials. The presence of very rich defect chemistry – with Zn interstitials and oxygen vacancies known to be the predominant ionic defect types – complicates, however, the advances necessary for ZnO to become a front-runner in the context of new applications. Only to precise which defect dominates in native, undoped ZnO is still a matter of great controversy.

Our goal was to establish the relationship between, synthesis, processing, and defects' chemistry of ZnO nanoparticles. For this purpose ZnO nanopowders – different in terms of defects – were fabricated via metal combustion technique and characterized under various ambient conditions by combining Raman, Photoluminescence and Electron Paramagnetic Resonance spectroscopies. Here we will show that the nature of defects in ZnO (both, in the bulk and at the surface) can be: (i) controlled by the judicious choice of synthesis and processing parameters and (ii) can be identified on the basis of their interaction with hydrogen through a combination of complementary spectroscopic techniques.

First-principles study of Na insertion/extraction in the $\text{FePO}_4\text{-NaFePO}_4$ system for cathode material in Na-ion batteries

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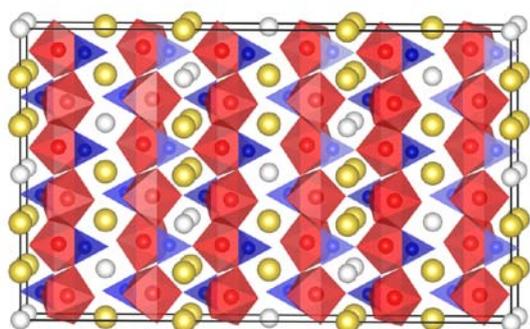
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Na-ion batteries are promising candidates for allowing stationary storage of large amounts of energy, an essential requirement for implementing most of future energy infrastructures based on renewable energy sources. Similarly to broadly used Li-ion cells, in Na-ion batteries Na ions are shuttled between the positive and negative electrodes during charging and discharging, with an electrolyte acting as the transportation medium for those ions. Promising new electrodes are often based on nanostructured interfaces and improved organic and inorganic electrode materials are being sought, in particular those showing high energy densities. The development and deployment of useful future technologies depends greatly on being successful in this quest for which a fundamental understanding of atomic structures and properties of electrode materials is a prerequisite.

Recent experimental studies proved the reversible electrochemical insertion/extraction of Na into FePO_4 to give NaFePO_4 olivine [1]. It was suggested that the insertion process occurs via an intermediate phase which buffers the internal stresses due to the large dimensional mismatches between FePO_4 and NaFePO_4 . In addition, chemical preparation of this intermediate phase revealed that a range of compositions might exist with very similar Na content but different Na/vacancy arrangements [2]. These findings can strongly affect the cyclability of the system and the performance of these new promising cathode materials. In order to understand the origin of such intermediate phase and related metastable Na compositions, we have carried out a series of systematic computational studies of possible Na/vacancy configurations for different Na composition in Na_xFePO_4 (x ranging from 0.0 to 1.0). Through a combination of density functional theory calculations and a cluster expansion method we have investigated the structure, electronics, and thermodynamics of Na and vacancy ordering in Na_xFePO_4 . The superstructure found at $x=2/3$ (Figure 1) agrees well with the composition of the observed intermediate phase.

Our calculated composition/temperature phase diagram and structural models agree well with the available experimental data. Such results not only help to understand the intrinsic mechanism of the phenomenon observed in the Na-ion battery experiments, but also suggest



that the insertion/extraction chemistry of Na ions in FePO_4 is in contrast with that of its isostructural Li-ion counterpart, LiFePO_4 , where the transformation into FePO_4 occurs without intermediate phases.

Figure 1. $\text{Na}_{2/3}\text{FePO}_4$ intermediate phase. Yellow, red and blue spheres stand for Na, Fe, and P atoms, respectively. White spheres are Na vacancies. For the sake of clarity, O atoms at the vertex of each polyhedra are not shown.

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Modification of ultrathin films of TiO₂(110) supported on W(100)-O(2×1)

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We have grown ultrathin films of rutile TiO₂(110) on W(100)-O(2×1). Low energy electron diffraction (LEED) shows the presence of two orthogonal rotational domains of rutile TiO₂(110). In line with this, scanning tunneling microscopy (STM) reveals that the rutile TiO₂ grows as discrete islands with high resolution images showing the presence of atomic-scale rows as well as point defects characteristic of the native rutile TiO₂(110)-(1×1).

Native TiO₂(110)-(1×1) surfaces are initially decorated with bridging oxygen vacancies (O_b-vac) which, over time, react with water in the residual vacuum to form surface hydroxyl (OH_b). Although the appearance of O_b-vac and OH_b are similar in STM, they can be distinguished from their relative brightness when both are present and also from their response to electrical pulses from the STM tip [1]. Pulses at positive sample bias remove OH_b from the surface and cause SOV to move parallel to the [001] direction [1,2].

When the ultrathin film is left for several hours in the vacuum chamber, one would expect the surface to hydroxylate. However, applying positive electrical pulses to the point defects has had no effect in our preliminary experiments. In order to investigate the reason for this and to ensure we can distinguish O_b-vac from OH_b, we electron bombard the film in order to obtain a surface with a high density of O_b-vac [3]. We can then follow the reaction of these O_b-vac with water [1].

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Dissecting formaldehyde reduction to ethylene on rutile TiO₂

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Rutile TiO₂ is considered to be a model oxide in reductive reactions of organic species. It has previously been shown that it can be used to reduce formaldehyde to ethylene using temperature-programmed desorption (TPD). In this case, oxygen vacancies caused by annealing was key in order for this reduction to occur [1]. Recently, it has been shown that oxygen vacancies on step edges can contribute significantly to the reduction of ethanol[2]. Using density functional theory implemented by GPAW the adsorption modes of formaldehyde on a flat TiO₂(110)-(1×1) edge and on the terrace with and without the most favourable oxygen vacancy[3] will be explored. Simulated TPD results will be discussed.

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Lattice dynamics and its impact on HR TEM images of the Co_3O_4 nanocrystals.

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Shape and structural defects of nanocrystalline oxides determines their electronic structure and redox properties. Being able to provide local information, Cs-corrected high resolution transmission electron microscopy becomes important tool for retrieving comprehensive morphological and structural information needed for complete characterization of oxide nanomaterials. Increasing interest in subtle differences in structure (eg. atomic vacancies, location of oxygen, bonding effect in electron correlated spinels) creates need for tools providing not only qualitative but also quantitative comparison of experimental and simulated images. HR TEM pictures are extremely sensitive to changes in imaging parameters (both sample properties and microscope settings). It makes images simulations indispensable for correct data interpretation. Due to the combination of many factors (such as: electron scattering mechanism, aberration effects, point spread function of detector), contrast in experimental HR images is also inevitably much weaker, typically by about a factor of three, than that predicted by image simulations.

Within this work we apply DFT geometry optimization and lattice dynamics analysis of Co_3O_4 to reduce discrepancies between the simulated and experimental HR TEM images. Using Birch–Murnaghan equation of state, fully relaxed structure of unit cell was obtained. To include thermal diffuse scattering effect into the simulations, phonon density of states for Co_3O_4 lattice was calculated to obtain temperature – dependent Debey-Waller factors for symmetrically independent atomic sites using PHONON software [1]. Calculated DW factors, in comparison with those obtained from X-Ray diffraction, are more accurate, and can be calculated for particular atoms localized at or near to the structural defects such as: surface, vacancies or dislocations. Simulated images are based on electrons elastically scattered by the sample up to a few degrees. In order to include bonding charge density as well as to determine optimized conditions for imaging of such subtle effects, modified version of the multislice algorithm was applied. Using molecular dynamics modelling, a number of different structures for each slice were calculated. Then, for each structure, full charge density was obtained using all-electrons code Wien2K[2] and transformed into the corresponding projected potential using FFT and further to ASF using Mott - Bethe formula. This procedure replaces the problem of using DW factors for projected potential, retrieved from full charge density, and is computationally less demanding. Finally, using the so called ab initio ASF within traditional multislice algorithm HR TEM images of Co_3O_4 were obtained and compared with classic multislice calculations.

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Understanding the SERS effect of dopamine adsorbed on TiO₂ nanoparticles.

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Recently it has been observed an important increase of the emitted Raman signal upon adsorption of dopamine on titania nanoparticles with respect to the bare molecule [1]. This phenomenon known as Surface Enhanced Raman Scattering (SERS) is quite common for metallic supports, but is by far less characterized for semiconducting materials. The mechanism explaining the enhancement of the Raman signal in the dopamine-TiO₂ system has been postulated as a charge transfer one, involving an electron charge transfer from the molecule to the nanoparticle. The goal of the present work is to investigate the interface dopamine-TiO₂ on an atomic level by means of Density Functional Theory (DFT) periodic calculations in order to elucidate the features connecting geometrical and electronic structures.

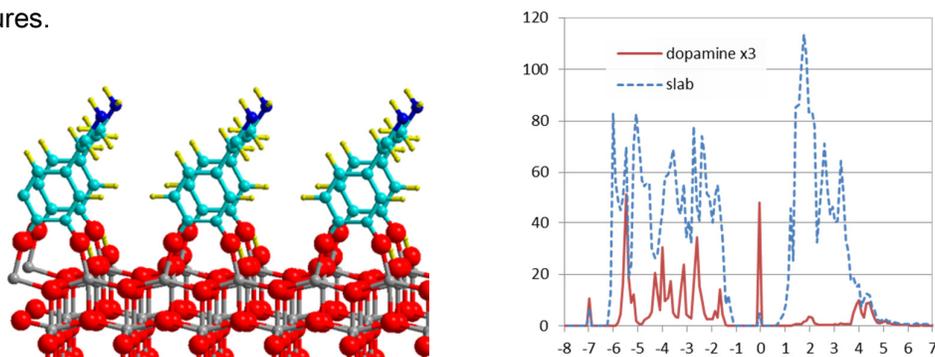


Fig. 1: left, periodic model for dopamine adsorbed on a (001) TiO₂ anatase slab; right, density of states projected on the molecule and on the slab (arbitrary units vs eV) $E_F=0$ eV.

Dopamine adsorbs by an acid/base mechanism with the surface, transferring the two H⁺ to surface oxygen sites, and forming two Ti-O bonds. The calculated adsorption energy is exothermic by more than 1 eV and depends on the anatase surface exposed. The corresponding electronic structure presents the HOMO states located at the dopamine and the LUMO states at the surface Ti sites. This picture is coherent with a charge transfer from the molecule to the nanoparticle and would support the CT transfer mechanism proposed in the literature to explain the SERS effect.

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