

Periodic DFT Study of Rutile IrO₂: Surface Reactivity and Catechol Adsorption

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► **To cite this version:**

Olivier Matz, Monica Calatayud. Periodic DFT Study of Rutile IrO₂: Surface Reactivity and Catechol Adsorption. Journal of Physical Chemistry C, American Chemical Society, 2017, <10.1021/acs.jpcc.7b01990>. <hal-01537843>

HAL Id: hal-01537843

<http://hal.upmc.fr/hal-01537843>

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3 **A Periodic DFT Study of Rutile IrO₂: Surface Reactivity and**
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6 **Catechol Adsorption**
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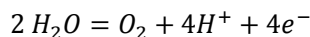
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3 Abstract

4 IrO₂ is a key material for photocatalytic applications as water oxidation catalyst. Despite its
5 increasing interest, little is known about its molecular structure and reactivity. In this study,
6 the surface properties of stoichiometric rutile IrO₂ are investigated by means of periodic
7 density functional theory (DFT), including the structural, energetic, electronic properties and
8 chemical reactivity towards catechol, a probe molecule mimicking photocatalytic linkers. Our
9 results show that the (110)-IrO₂ rutile termination is the most stable, and we discuss the role
10 of the number and type of surface sites in the relative stability compared with (100), (001) and
11 (101) terminations. Regarding the reactivity of the surfaces with catechol, our results show
12 that the molecule dissociates and binds in bidentate, chelate and monodentate modes.
13 Interestingly, we find the chelated mode selectively favored over the (001) termination with
14 the highest adsorption energy -3.93 eV, being unstable on other terminations. The bidentate
15 mode is preferred on (110) -3.83 eV, (100) -3.24 eV, (101) -2.23 eV. The selective
16 stabilization of the chelated mode, suggested in the literature to be responsible for the optical
17 absorption in TiO₂ nanoparticles, could guide in the search of tailored iridia-based interfaces
18 for photocatalytic applications.
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I. Introduction

In a photo-electrochemical cell (PEC), the solar energy is used for splitting the water into hydrogen and oxygen molecules¹. In a time deeply hit by ecological crisis and global warming, the solar hydrogen production seems to be the ideal solution due to the inexhaustible resource of water and the non-emission of pollutant and greenhouse gases²⁻⁴. In this context, iridium oxide is receiving nowadays increasing interest because of its high efficiency in photocatalytic devices, playing a key role as water oxidation catalyst⁵⁻⁷ in the water splitting reaction, in particular for the oxygen evolution reaction (OER):



In PEC, the dyes are used to bridge the different materials and so they must bind strongly to the surface of these materials. In addition, the anchoring groups must ensure an appropriate electron transfer between the different parts. Moreover, dyes must be easily photoexcitable in order to show a wide absorption in the visible spectra.

Despite the promising properties of iridium oxide for PECs, the detailed knowledge of the structure and reactivity of IrO₂ is still very poor. Indeed, although the structural⁸⁻¹⁰, electronic^{7,11-14}, conductivity^{15,16} and optic¹⁶⁻¹⁹ properties are well known for the bulk of iridium oxide, there is an evident lack of knowledge regarding the surface properties and the surface reactivity of this material. In particular, an atomic description of the surfaces is missing, limiting the knowledge and the interpretation of the physico-chemical phenomena taking place. In the present study, we characterize the structural and electronic properties of stoichiometric low index surfaces and investigate their reactivity towards catechol, a test molecule mimicking common linkers used in photocatalytic devices. The aim is to provide fundamental understanding of the interfaces on the molecular level, that can guide in the search of novel systems with tailored properties.

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3 Experimental studies mainly focus on photocatalytic applications, and surface science reports
4 are scarce compared to the abundant literature on isostructural rutile TiO₂. The most stable
5 termination is the (110). This surface was characterized both experimentally^{20,21} and by means
6 of DFT²², and almost all theoretical studies are focused on it. A combination of surface
7 science and Density Functional Theory (DFT) has been used to support the stability of the
8 oxygen rich (100) iridia termination²³. Sen et al.²⁴ have used DFT to parametrize a force field
9 for IrO₂ nanoparticles. Novell-Leruth et al.²² have studied the mixture of different rutile
10 oxides and give a brief description of the structural and energetic properties for IrO₂ surfaces.
11 More recently, the role of hydration and Ir⁴⁺/Ir³⁺ interplay has been suggested as being
12 responsible for the observed optical response of IrO₂ with a combined Raman-DFT
13 approach²⁵. As regards surface reactivity, the oxidation of ammonia²⁶, the dissociation of
14 methane²⁷ and the role of peroxo intermediates in the oxygen evolution reaction mechanism²⁸
15 has been investigated theoretically. Also, the plausibility of hybrid molecular-surface iridium-
16 based materials has been supported by theoretical calculations²⁹ for the same reaction. Finally,
17 the optical spectroscopic response of a dye adsorption system containing TiO₂-IrO₂ has been
18 described ab initio with a realistic model confirming the importance of the surface-molecule
19 interaction in the properties of photo-electrochemical devices³⁰. It appears that to the best to
20 our knowledge, there are no works providing a general picture of the structural, energetic,
21 electronic properties of IrO₂ surfaces, in particular addressing their interaction with dyes from
22 a molecular point of view. The aim of the present paper is to provide valuable information
23 about the structure and reactivity of iridium dioxide surfaces. Special attention will be paid to
24 the interface between the surfaces and the catechol molecule, used as a model for dye
25 adsorption systems. Geometric parameters, energetics and electronic structure will be used in
26 the analysis and characterization of such model adsorption systems.
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II. Methods

A. Computational details

The properties and reactivity of rutile IrO₂ surfaces were studied theoretically by means of *ab initio* principles. All the calculations were performed using Density Functional Theory (DFT) and based on the Projector Augmented Wave^{31,32} (PAW) method as implemented in the Vienna Ab initio Simulation Package^{33–36} (VASP) – version 5.4.1. Generalized Gradient Approximation (GGA) was used for the exchange and correlation potential and all the calculations were carried out with the PBEsol³⁷ functional. According to the PAW method, core electrons were kept frozen and replaced by pseudopotentials (Ir, O, C, H) and valence electrons (Ir: 6s² 5d⁷; O: 2s² 2p⁴; C: 2s² 2p²; H: 1s¹) were expanded in a plane wave basis set with kinetic energy cutoff of 400 eV. With the PAW pseudopotentials used, scalar relativistic effects were taken into account the calculations. Spin orbit coupling effects were not included in our calculations because it has been shown that spin orbit did not affect significantly neither structural nor energetic properties of IrO₂^{13,24}. The Brillouin zone was sampled using Monkhorst-Pack³⁸ scheme with a distance between k-points of 0.033 Å⁻¹ for structural optimizations and 0.020 Å⁻¹ for density of states (DOS) calculations. The choice of these parameters was justified by the high coherence between IrO₂ bulk experimental data^{8,9,39,40} and computational one's. More details of the several tests performed are given in Supporting Information.

B. Slab model

In this study, (001), (100), (101) and (110) terminations of rutile IrO₂ were investigated. These four stoichiometric surfaces were modeled as a two-dimensional slab in a three-dimensional periodic cell. All our slabs were built with the MAPS suite⁴¹, with four IrO₂ layers in thickness and a vacuum thickness of 20 Å was introduced with the aim of avoid

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3 interactions between slabs. Energy convergence tests were performed on slab thickness, i.e.
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5 number of atomic layers, and on vacuum thickness in order to find the best compromise
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7 between accuracy and computational cost. The results of these tests, as well as the coordinates
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9 of the slabs for the four terminations, are given in Supporting Information.

10
11 First, the stoichiometric surfaces were optimized by relaxing positions of all the ions with the
12
13 conjugate-gradient algorithm. Then, to compare the stability between the different
14
15 terminations, surface energy was calculated following Eq. (1):

$$\gamma_{hkl} = \frac{E_{slab\ hkl} - N E_{bulk}}{2A_{hkl}} \quad (1)$$

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18 Where $E_{slab\ hkl}$ is the total energy of (hkl) slab, E_{bulk} the total energy of bulk, N is the
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20 number of bulk unit in the slab, and A_{hkl} is the (hkl) surface area. Finally, the DOS was
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22 calculated for all the terminations studied in the bare and adsorption systems.

23 24 25 26 27 28 29 30 31 C. Adsorption

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33 The reactivity of the selected slabs was investigated by adsorption of the catechol molecule.
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35 Catechol has two anchoring points, it could bind with IrO₂ surfaces according to three
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37 dissociative adsorption modes: bidentate (molecule bonded to two Ir sites via its two oxygen
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39 sites), chelated (molecule bonded to one Ir site via its two oxygen sites) and monodentate
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41 (molecule bonded to one Ir site via one oxygen site). Supercells were built from the fully
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43 relaxed slab model for each of the four surfaces in order to avoid interactions between
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45 catechol molecules and have approximately the same surface adsorption coverage for the
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47 different surfaces: (001)-1x3, (100)-2x2, (101)-1x2 and (110)-1x3 that is 1.7, 1.8, 2.1 and 1.7
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49 catechol · nm⁻², respectively. Otherwise, for this part of the study, the bottom-half of the slab
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51 was kept frozen during ionic relaxation to reduce computational cost. The top-half of the slab
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53 and the catechol molecule were optimized using the conjugate-gradient algorithm. The
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3 stability of the adsorption systems was determined by calculating adsorption energy as
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5 defined in Eq. (2).
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$$E_{ads}^{cat} = E_{slab,cat} - (E_{slab} + E_{cat}) \quad (2)$$

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10 Where $E_{slab,cat}$ and E_{slab} are the total energies of a slab with and without catechol molecule
11 adsorbed, respectively, and E_{cat} is the total energy of catechol in gas phase (calculated in a
12 box). Then the DOS of the most stable systems was calculated. Finally, charge transfers
13 between surface and catechol molecule were investigated using Bader charge analysis^{42,43}.
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24 III. Results & Discussion

25 A. Slab: structural, energetic and DOS

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28 The (001), (100), (101) and (110) stoichiometric terminations are represented in Figure 1.
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30 From a structural point of view, terminations differ from: (i) the coordination number of
31 surface atoms: O-2c, O-3c, Ir-4c, Ir-5c, and Ir-6c where xc denotes the coordination of the
32 atom to x neighbors; (ii) the accessibility of atomic sites at the surface: (001) and (110) are
33 “smooth” while (100) and (101) are uneven; and (iii) the nature of breaking bonds during bulk
34 truncation: the bulk is formed of IrO₆ octahedra with inequivalent Ir-O axial and equatorial
35 bonds. The slabs involving the least number of Ir-O bonds compared to the bulk are axial for
36 (100) and (110), equatorial for (001) and (101). All these criteria can affect the properties and
37 the reactivity of surfaces⁴⁴, in particular in adsorption phenomena. For example, smooth
38 surfaces have adsorption sites which are more accessible, and atoms with low coordination
39 number are expected to be more reactive.
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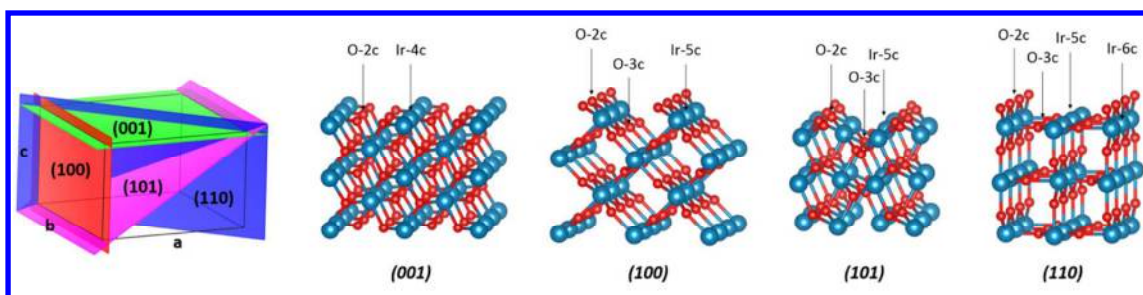


Figure 1. Representation in perspective of the (001), (100), (101) and (110) surfaces with coordination number of atoms at the surface where Ir-nc and O-nc are iridium and oxygen of coordination number n. Iridium cations are represented in blue and oxygen anions in red. The bulk Ir-O bonds broken to create each termination are displayed in Figure S5.

	(001)	(100)	(101)	(110)
γ_{hkl}	2.76	2.24	1.94	1.68
Ir-4c/Ir-5c/Ir-6c	5/-/-	-/7/-	-/8/-	-/5/5
O-2c/O-3c	10/-	7/7	8/8	5/10

Table 1. Surface energy ($J \cdot m^{-2}$) and atom surface density (ions $\cdot nm^{-2}$) in function of coordination number.

The surface energy was calculated for each slab as defined in Eq.1 and is reported in Table 1 and Figure 2. Surface energy ranges between $1.7 - 2.8 J \cdot m^{-2}$ and increases along the series: $(110) < (101) < (100) < (001)$. In this way, (110) corresponds to the most stable surface and (001) to the least one. It can be explained by the fact that the number of total bonds broken per surface unit is the lowest for (110) and the highest for (001) terminations: 10 and 20 broken bonds per squared nanometer, respectively. Due to the relaxation phenomena, the O_{surface} bond distances are smaller compared to the bulk ones, and this for the four terminations studied. This phenomenon is very common and it is explained by the fact that the interactions between oxygen and metal are stronger compared to the bulk due to the low

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3 coordination number of atoms at the surface. However, depending on the termination, surface
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5 oxygens could be in axial or equatorial positions or both, and no relationship between the
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7 changes of bond distances after relaxation and the positions of the atoms (axial or equatorial)
8
9 and the surface energy was observed. Indeed, surface relaxation increases along the series
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11 $(110) > (100) > (001) > (101)$, and so the relaxation trend did not follow the surface stability
12
13 one. More details, including bond distance changes, are given in Supporting Information.
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15 Moreover, the equilibrium shape of IrO_2 rutile crystal was estimated by means of the Wulff
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17 construction⁴⁵ and is depicted in Figure 2. Wulff construction allows depicting the equilibrium
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19 shape of a crystal from the surface energies of the more stable terminations. Indeed, a crystal
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21 reorganizes itself in such a way as to minimize its surface Gibbs free energy. According to the
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23 Wulff theorem, the distance from a surface to the center of mass is proportional to the surface
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25 energy and the envelope formed by these plans is the equilibrium shape of the crystal. Our
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27 Wulff structure is in perfect agreement with previous works^{22,24}.
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32 Figure 2 represents the values of surface energies calculated with different methods. It can be
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34 observed that the absolute values vary about $0.9 \text{ J} \cdot \text{nm}^{-2}$, the PBEsol values being the highest.
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36 This is explained by the fact that PBEsol overstabilizes the bulk compared to the surfaces
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38 rendering then a higher value for the surface energy. Nevertheless, the relative stability of the
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40 different terminations is the same whatever the functional used and the order of stability is
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42 unchanged.
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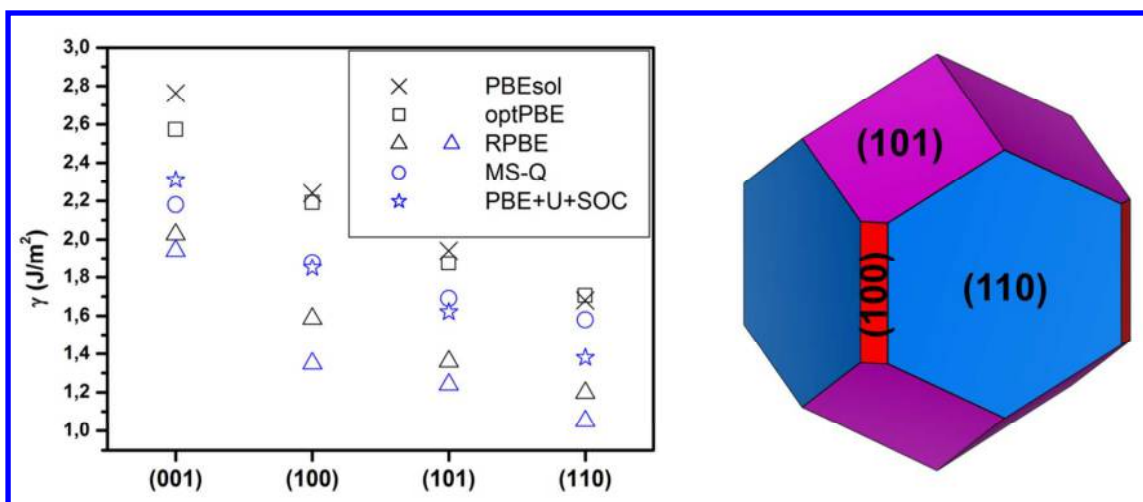


Figure 2. Left: surface energy ($J \cdot m^{-2}$) after relaxation. In black, the ones calculated in this study, and in blue Ref.^{22,24}. Right: Wulff structure for PBEsol functional.

The DOS is shown in Figure 3. Because of the absence of band gap near the Fermi level on all DOS, both bulk and surfaces exhibit metallic properties. It means that IrO₂ surfaces keep the metallic properties of the bulk. DOS is consistent with most of *ab initio* works^{11,12,17,22} on the electronic properties of bulk IrO₂ rutile. The bulk and surface DOS were very similar, with oxygen states (narrow band centered at -20 eV, and a wider band centered at -6 eV, corresponding with O-2s and O-2p states, respectively; which are in good agreement with experimental results⁴⁶⁻⁴⁸: -22 and -8 eV, respectively) and iridium states (wide band spread between -2.5 eV and 2 eV, thus containing the Fermi level, and a second band ranging from 2 to 5 eV). However, some differences between bulk and surface are observed: the states of surface sites are higher in energy compared to the bulk ones and lead to the appearance of peaks that were absent in the bulk DOS, like the peak at -18 eV (corresponding to surface oxygen 2s states, detached from the bulk O-2s band centered at -20 eV). Moreover, the local environment of the surface iridium states (see Figure S5) also has an impact in the DOS: the terminations where an axial Ir-O bond is missing, (100) and (110), show a sharp peak around -3.5 eV associated with the O-2p states and a small peak at -8 eV associated to iridium d

states. The terminations where an equatorial Ir-O bond is missing, (101) and (001), show a more homogeneous DOS in the valence band region between -2.5 and -7.5 eV.

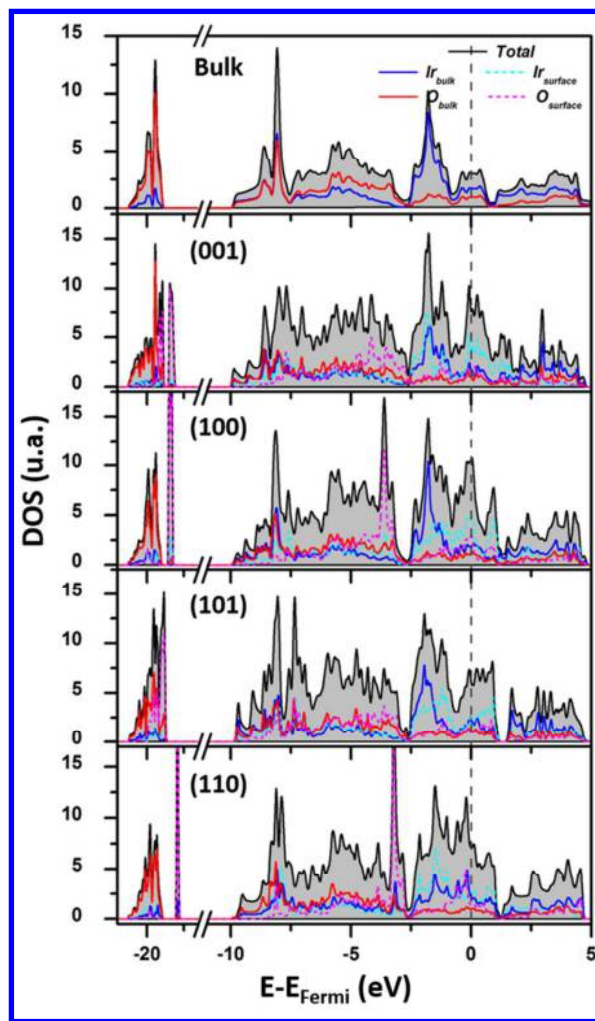


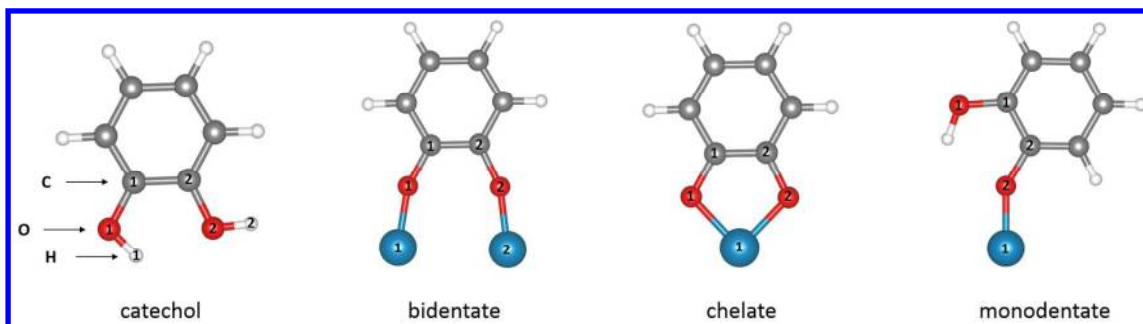
Figure 3. DOS and normalized Projected Density Of States (PDOS) for bulk and surfaces. DOS are given in arbitrary unit and the Fermi level (dashed line) is set to 0 eV.

B. Catechol adsorption

Combined with a dye, IrO_2 are widely used like photocatalysts^{30,49-52}. Because of its chromophore properties and its small size, catechol is a molecule of choice to study interactions and bindings between dyes and IrO_2 surfaces involved in photocatalytic process. Moreover, catechol has received a great attention with surfaces of TiO_2 rutile and anatase⁵³⁻⁵⁸ due to its structural and electronic properties.

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3 Catechol has two hydroxyl groups (Figure 4), that could deprotonate giving rise to catecholate
4 species with one or two protons. In the case of dissociative adsorption modes, catecholate
5 oxygen(s) is bind to a low coordinated surface iridium site and the proton move to a low
6 coordinated surface oxygen site. The deprotonation of catechol on TiO₂ surfaces and nanoparticles
7 has been reported in the literature from experimental and theoretical studies^{53,59-67} and we assume
8 that the same behavior occur in IrO₂. It can be explained by an acid-base adsorption mechanism⁵⁹
9 where the protons of the molecule bind to the basic surface sites (oxygen) and the oxygens of the
10 molecule bind to the surface acidic sites (iridium).
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22 Catechol could bind to the surface according to three dissociative modes, displayed in Figure
23 4: monodentate (partial dissociation where catechol binds to one metallic site via its
24 deprotonated oxygen), bidentate (full dissociation where molecule binds to two metallic sites
25 with two deprotonated oxygens) and chelated (full dissociation where molecule is bind to one
26 metallic site via its two deprotonated oxygens). The dissociative modes are accompanied of a
27 deprotonation of the hydroxyl group, the proton is put on top of a low coordinated oxygen site
28 in the slab model. But catechol can also adsorb according molecular mode, i.e. without
29 deprotonation of hydroxyl group. Dissociative adsorption being significantly more stable than
30 molecular adsorption, only monodentate, bidentate and chelate modes are presented in this
31 study.
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Figure 4. Representation of catechol molecule in gas phase (left) and the three dissociative adsorption modes.

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3 Table 2 summarizes the energetic and geometric results obtained in the present work.
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5 Catechol adsorption is exothermic for all the systems studied with adsorption energy ranged
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7 between -3.93 and -1.51 eV · catechol⁻¹. Bidentate adsorption is systematically more stable
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9 than monodentate one for each termination. (001) surface with chelated mode and (110)
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11 surface with bidentate mode are the most reactive with adsorption energy of -3.93 and -3.83
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13 eV · catechol⁻¹, respectively. Due to their similar adsorption energies, the chelated adsorption
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15 on (001) is competing with bidentate adsorption on (110). The (101) surface is the least
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17 reactive with catechol with the highest adsorption energy for bidentate mode of -2.23 eV ·
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19 catechol⁻¹. Besides, only (001) surface allows chelate adsorption which can be explained by
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21 the fact that this is the only one to have iridium with coordination number of four at the
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23 surface. This result highlights the fact that the chelated mode can only be stabilized over (001)
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25 terminations, or alternatively surfaces containing undercoordinated Ir-4c sites, such as in
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27 nanoparticles or defective surfaces. Recently, some of us have shown that the adsorption
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29 mode of catechol in TiO₂ clusters is intimately related to the optical properties: the chelated
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31 mode results in a significantly lower absorption threshold compared to the bidentate mode¹⁷,
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33 despite the fact that the bidentate mode is thermodynamically more stable. Our results
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35 indicate that the chelate mode could be selectively stabilized on (001) IrO₂ terminations.
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39 The bond lengths of Ir – O_{cat} range between 2.046 Å for (101) monodentate adsorption and
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41 1.948 Å for (100) bidentate adsorption. Although no correlation between bond lengths and
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43 adsorption energy are observed, the bonds are longer for monodentate than bidentate mode,
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45 except for the (001) surface where the opposite is observed. Moreover, (001) and (101) have
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47 longer Ir – O_{cat} than (100) and (110) surfaces. It can be explained by the fact that (001) and
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49 (101) have equatorial broken bonds at the surface unlike (100) and (110) exhibiting axial
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51 broken bonds. And it should be reminded that in the bulk, the distance Ir – O_{eq} is longer than
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53 Ir – O_{ax}: 1.993 and 1.958 Å, respectively.
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3 Furthermore, adsorption leads to structural modifications of catechol: on the one hand C – O_{cat}
4 shortening, on the other hand C₁ – C₂ elongation, and this for all modes and surfaces. More
5 precisely, bidentate mode is characterized by a significant elongation of O_{1,cat} – O_{2,cat}: from
6 +0.142 Å for (001) to +0.523 Å for (110). Indeed, this deformation of catechol can be
7 understood by the fact that iridium sites at the surface try to find their octahedral geometry,
8 and thus force catechol oxygens to occupy vacant sites. For the bidentate and chelate
9 adsorptions, it is observed that the surface iridium atoms involved in the catechol adsorption
10 restore their 6-fold coordination, this is accompanied by more exothermic adsorption energies.
11 Indeed, in the case of (100) and (110) terminations where oxygens from catechol take an axial
12 position, the O_{1,cat} – O_{2,cat} distance increases significantly in such way that the Ir-Ir and the
13 O_{1,cat} – O_{2,cat} distances match very well: $d_{Ir-Ir} - d_{O_{1,cat}-O_{2,cat}}$ for (100) and (110) are 0.049
14 and -0.053 Å, respectively. This means that the bulk-like configuration of the iridium sites
15 involved is restored upon adsorption, and explain why the bidentate adsorption of catechol are
16 very strong on these two surfaces. In the case of (001) and (101) surfaces, oxygens of catechol
17 take the equatorial positions. For both of these surfaces, the comparison of the O_{1,cat} – O_{2,cat}
18 distance with the distance between the two respective surface oxygens at the same positions
19 do not match: $d_{O_{1,eq}-O_{2,eq}} - d_{O_{1,cat}-O_{2,cat}}$ for (001) and (101) are 0.322 and -0.270 Å,
20 respectively. And so, the bulk-like configuration is not restored, explaining the fact that
21 bidentate catechol adsorption on (001) and (101) surfaces is less stable than on (100) and
22 (110). Figure 5 illustrates this point.
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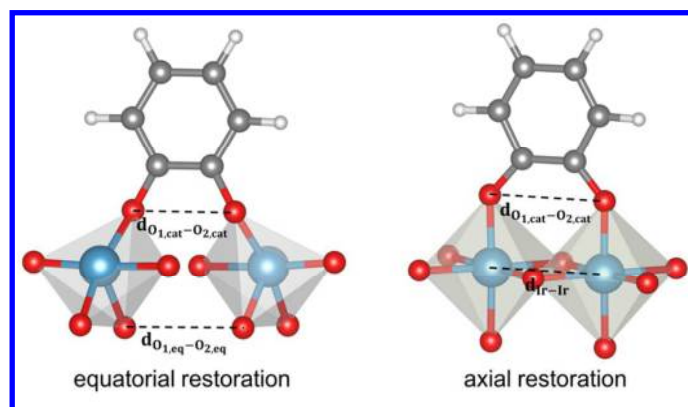


Figure 5. Schema illustrating the bulk-like configuration upon bidentate catechol adsorption.

Bader charge analysis was performed in order to study the charge transfer induced by catechol adsorption. For that purpose, Bader populations after adsorption of all catechol atoms were summed then subtracted to the total population of the molecule in gas phase. Bader charge analysis shows that catechol adsorption is systematically accompanied with a charge transfer from catechol to surface, and this for all the adsorption systems. This phenomenon was also observed in the case of adsorption on TiO_2 ⁵⁷. However, although charge transfers are more important for bidentate compared to monodentate mode, the quantity of transferred charge is not additive.

	(001)			(100)		(101)		(110)	
	mono	bi	chel	mono	bi	mono	bi	mono	bi
E_{ads}	-2.16	-3.04	-3.93	-1.99	-3.24	-1.51	-2.23	-2.26	-3.83
q	+0.65	+1.05	+1.22	+0.86	+1.27	+0.63	+1.19	+0.75	+1.28
$d_{Ir_1O_{1,cat}}$	/	2.042	2.003	/	1.949	/	1.997	/	1.954
$d_{Ir_1O_{2,cat}}$	1.975	/	1.989	1.971	/	2.047	/	1.976	/
$d_{Ir_2O_{2,cat}}$	/	2.029	/	/	1.957	/	1.989	/	1.951
$\Delta d_{O_{1,cat}O_{2,cat}}$	-0.041	+0.141	-0.057	+0.021	+0.464	+0.036	+0.381	+0.093	+0.523

$\Delta d_{C_1O_{1,cat}}$	-0.010	+0.004	-0.018	-0.028	-0.034	-0.010	-0.020	-0.014	-0.031
$\Delta d_{C_2O_{2,cat}}$	-0.025	-0.011	-0.033	-0.045	-0.042	-0.008	-0.035	-0.038	-0.047
$\Delta d_{C_1C_2}$	+0.013	+0.019	+0.012	+0.031	+0.049	+0.006	+0.037	+0.028	+0.048

Table 2. Adsorption energy (E_{ads} in $eV \cdot catechol^{-1}$), Bader charge of catechol (q in $|e|$), distance iridium-catechol oxygen (d in \AA) and distance difference between adsorbed (ads) and gas phase (GP) catechol ($\Delta d = d_{ads-cat} - d_{GP-cat}$, in \AA).

Figure 6 shows the calculated DOS for catechol adsorption systems. Compared to clean surfaces, DOS after catechol adsorption are similar: peak positions and band widths are almost the same, meaning that catechol adsorption did not affect the electronic properties of the surface. However, strong hybridization between catechol and surface states is observed, corresponding to a large mixing of catechol and iridium states, especially in the upmost valence band (-15 to +2 eV). This hybridization results mainly in the disappearance of well-defined pics for catechol (compared to the gas phase depicted in grey in Figure 6). Hybridization can explain the large adsorption energies observed (between -1.51 and -3.93 $eV \cdot catechol^{-1}$), and more precisely, the larger the extent of hybridization, the larger the adsorption energy.

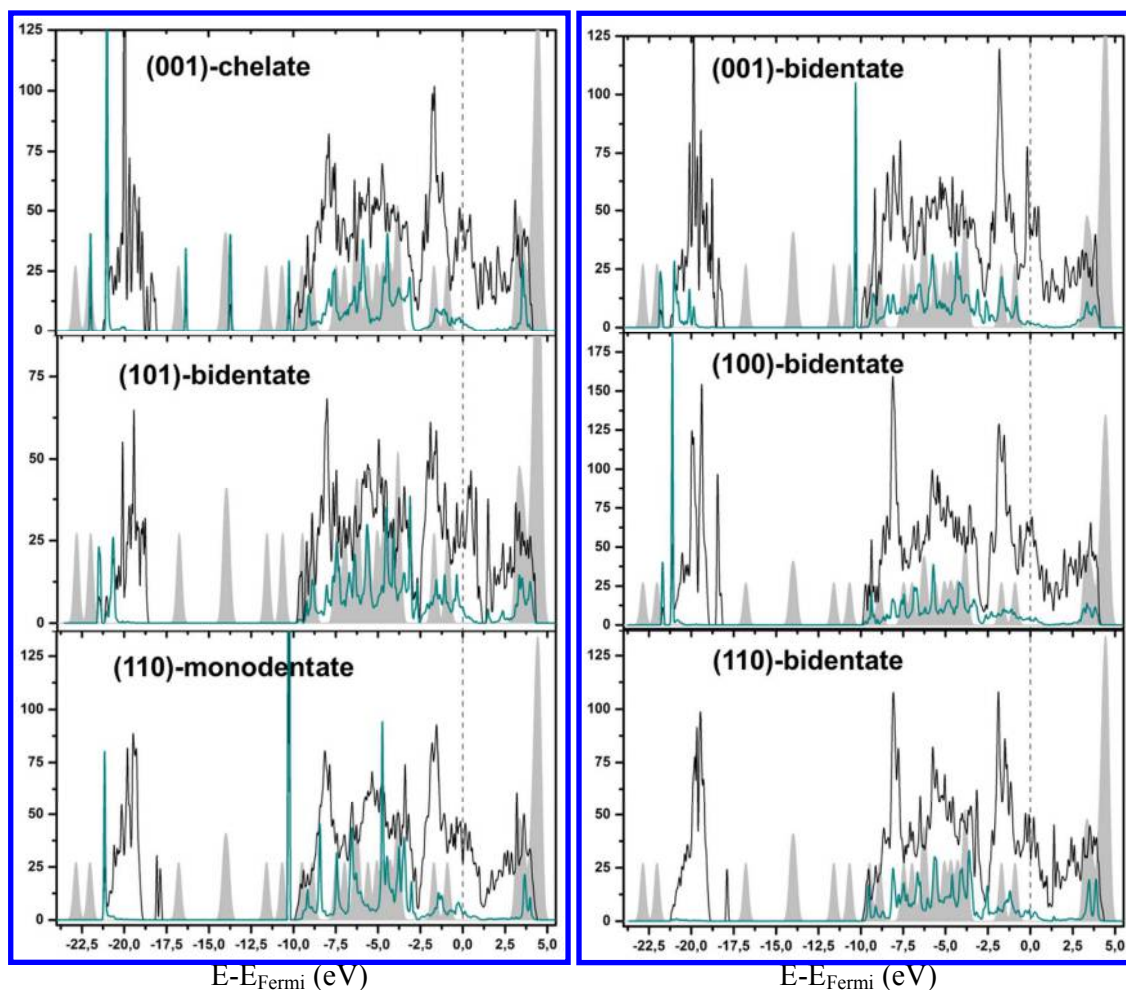


Figure 6. DOS total (black) and catechol PDOS $\times 5$ (green) for chelate, monodentate and bidentate adsorption modes. Fermi level is set to 0 eV and DOS of catechol in gas phase is depicted in grey.

Compared to catechol in the gas phase, the adsorption systems do not exhibit peaks in the region between -17.5 eV and -10 eV (only one exception: monodentate on (101); see Supporting Information). The peaks corresponding to catechol in the valence band shift toward higher energy, for all the adsorption systems. It can be explained by charge transfer from molecule to the surface destabilizing the catechol molecules. Moreover, it was observed that peaks are better localized for monodentate than bidentate mode. It can be explained by two effects which contribute to create new states for catechol with bidentate adsorption: on

the one hand a larger charge transfer and on the other hand a larger deformation of the molecule ($\Delta d_{O_{1,cat}O_{2,cat}}$).

Catechol adsorption is accompanied by the molecular HOMO-LUMO gap decrease (Table 3), making in principle easier the electronic excitation. In order to evaluate how the adsorption of catechol changes its photoexcitation properties, the molecular HOMO-LUMO gap were calculated by making the difference between the energy of the lowest empty state and the highest occupied state of the molecule: $\Delta E_{HOMO-LUMO} = E_{LUMO} - E_{HOMO}$. A diminution of this molecular gap means that the catechol molecules will be more easily photoexcitable. Particularly in the case of bidentate adsorption on (101) where the HOMO-LUMO gap was reduced by half compared to gas phase: 1.86 and 4.21 eV, respectively. It was observed that gap diminution is larger for bidentate than monodentate mode, except for (001) surface where the HOMO-LUMO gap of bidentate mode is approximately equal to the one of gas phase molecule.

	(001)	(100)	(101)	(110)	Gas phase
monodentate	3.81	3.74	2.69	3.91*	
bidentate	4.17	3.32*	1.86	3.46*	4.21
chelated	3.75		/		

Table 3. HOMO-LUMO gap of catechol: $\Delta E_{cat}^{HOMO-LUMO}$ (eV). * indicates hybridization between HOMO of catechol and Ir-5d states.

IV. Conclusion

The surface structure and reactivity of rutile IrO₂ were studied by means of periodic density functional theory calculations. The stability of the terminations in vacuum was found to be (110) > (101) > (100) > (001), and is related to the number of dangling bonds compared to the

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3 bulk. The electronic structure analyzed with the density of states indicates a metallic character
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5 for the bulk and all the surfaces studied, with iridium level not completely filled. The
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7 adsorption of catechol, used as a dye model, is found to be dissociative by full deprotonation,
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9 and energetically favorable. Interestingly, the most exothermic mode is chelated on the (001)
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11 termination, whereas the preferred mode for the other terminations is bidentate. The chelate
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13 (001) and the bidentate (110) are almost isoenergetic. This indicates a selective adsorption in
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15 a chelated mode over low-coordinated iridium sites such as those probably present in
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17 nanoparticles. The adsorption of catechol is accompanied by a charge transfer from the
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19 molecule to the surface, a hybridization of the surface-molecule bands and a decrease of the
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21 molecule HOMO-LUMO gap.
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25 In the development of novel iridia-based PECs, the following points should be considered.
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27 First, the topology of the surface sites critically influences the adsorption mode of the linker:
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29 whereas 5-fold Ir leads to bidentate adsorption, the presence of 4-fold Ir leads to the
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31 stabilization of the chelated mode. Second, the catechol band gap decreases upon adsorption;
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33 this should have an impact in optical measurements. Third, catechol transfers electrons to the
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35 surface upon adsorption, with effect in both optical and catalytic activity. Our results may
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37 serve as a guide to design experiments aiming at establishing structure-properties
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39 relationships. In this sense, a controlled shape and size of iridia particles, or a specific surface
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41 termination, may ensure the presence of a given adsorption mode, allowing to perform a
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43 series of measurements on a well-defined system with only one adsorption mode. Thus,
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45 according to our results cubic particles exhibiting (001) facets, or a (001)-terminated single
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47 crystal, should adsorb selectively catechol in the chelated mode, while octahedral particles or
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49 other terminations lead to the stabilization of bidentate modes. The observations made on
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51 these systems (nuclear magnetic resonance, photoelectron spectroscopy, cyclic voltammetry,
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3 ...) could thus be assigned to a certain species, enabling the possibility of discriminating the
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5 contribution of each species in a complex system.
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10 11 Supporting Information

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14 The results of the several tests on both bulk and slab, as well as the structure (POSCAR) of
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16 the four terminations studied are given in Supporting Information. Density of states for the
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18 monodentate adsorption systems is also provided in the Supporting Information file.
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25 Acknowledgment

26
27 Authors acknowledge Scienomics for the MAPS program used in the construction of
28
29 the slab models for a courtesy license. Dr. B. Diawara is acknowledged for the Modelview
30
31 program. Dr. L. Gracia for valuable help regarding the Wulff construction. This work was
32
33 performed using HPC resources from GENCI- CINES/IDRIS (Grants 2016- x2016082131,
34
35 2017- x2012082131), the CCRE-DSI of Université P. M. Curie for computational
36
37 resources. This work has been carried out in the frame of the COST action CM1104
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39 *Reducible metal oxides*.
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27 TOC Graphic

