Computational Laboratory for Hybrid/Organic Photovoltaics (CLHYO),
Istituto CNR di Scienze e Tecnologie Molecolari (ISTM-CNR)
Perugia, Italy

Perugia, Italy, December 15th 2016

RELAZIONE SCIENTIFICA
BANDO STM 2016

Host Applicant: Dr. Filippo De Angelis (ISTM-CNR Perugia, Italy)
Guest Scientist: Dr. Ivan Rivalta (École Normale Supérieure de Lyon, France)

MODELING WATER SPLITTING REACTION IN PHOTOELECTROCHEMICAL CELLS

Introduction

The aim of the collaborative project between ENS-Lyon and the ISTM-CNR teams is to develop reliable computational models for the study of the water splitting reaction in dye-sensitized photoelectrochemical cells (DSPEC). In particular, we focused on a DSPEC consisting of a bifunctional heteroleptic Ru(II) sensitizer anchored to TiO_2 by phosphonate groups and covalently bound to hydrated iridium dioxide ($IrO_2 \cdot nH_2O$) nanoparticles, i.e. the water oxidation catalyst, by a malonate group (Figure 1).[1] The structural model and the hole/electron transfer reactions occurring at the dye-sensitized TiO_2/IrO_2 photoanode (Fig. 1) have been recently characterized by extensive computational (DFT) studies carried out by the Host-Applicant group.[2] Considering previous Dr. Rivalta's experience in investigating the oxygen evolution catalysis in biological and biomimetic systems[3-5] and in the characterization of Iridium water oxidation catalysts[6], the collaborative project aims at the elucidation of the water splitting mechanism catalyzed by the

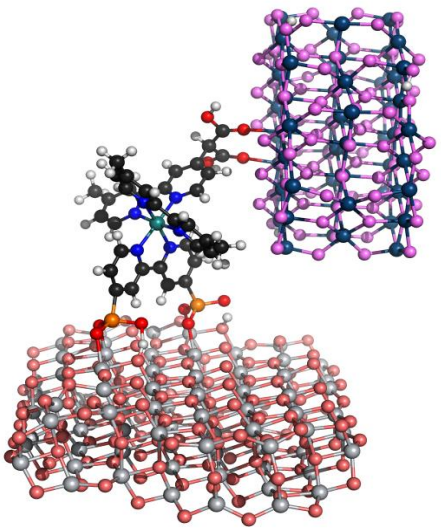

Figure 1. Previously reported[2] model of the dye-sensitized TiO_2/IrO_2 photoanode.

$IrO_2 \cdot nH_2O$ nanoparticles (NP) under oxidative conditions. Given the large computational cost of a first-principles characterization of the potential energy surfaces (PES) involved in the water oxidation mechanism, an accurate and computationally affordable model has to be developed.

Preliminary Data and Project Workplan

Preliminary DFT calculations based on the full IrO_2 NP model, formally $(IrO_2)_{56} \cdot 2H_2O$, were performed with the B3LYP functional and the LANL2DZ basis set, to obtain the relative stability of the adsorbed substrate species (H_2O, OH, O). These computations have been initially performed considering a neutral and closed-shell system, i.e. the NP and the adsorbates are in a singlet state (spin multiplicity, M, equal to 1). During geometry optimizations we observed that water spontaneously dissociates into hydroxyl group on the oxide surface, transferring a proton to the vicinal surface oxo-bridge. The resulting energetics indicate that OH is the favoured adsorbed species with respect to O, with (second) deprotonation being endothermic by ca. 11 kcal/mol. Oxidation of the NPs suggest two things: *i*) the deprotonation of the adsorbed OH is not largely influenced by the creation of a hole (decreasing only to 8.0 kcal/mol) and *ii*) the hole is not strongly localized in the NP, as showed in Figure 1, and a tiny accumulation spin density on the adsorbate is observed only in the O-NP system.

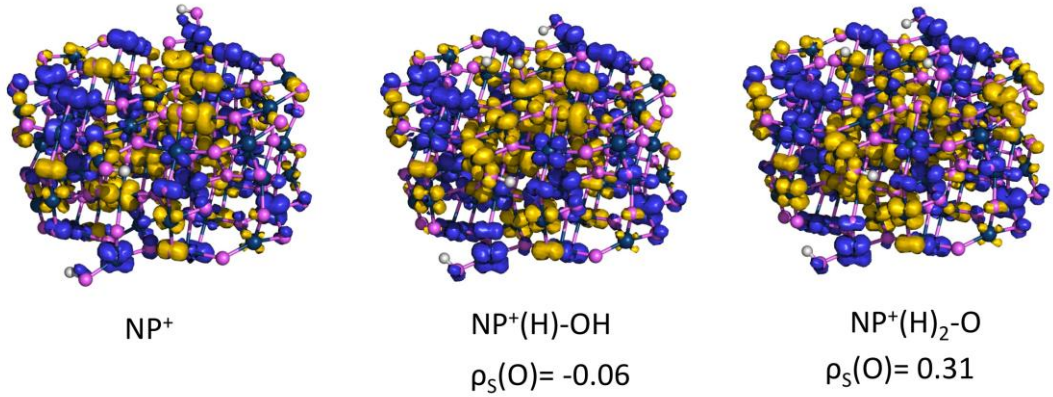

Figure 1. Spin densities of oxidized NPs and atomic spin densities of O atoms of the adsorbed species.

The calculations of the full $(IrO_2)_{56} \cdot 2H_2O$ NP model are computationally very expensive, with geometry optimizations requiring several weeks to complete even using minimal convergence thresholds. Thus, it results necessary to develop smaller NP model to investigate more deeply the electronic structure properties of the NP. We have thus developed three cluster models with a minimum amount of

Ir atoms that guarantee a good description of the absorption of the substrate species, see Figure 2. The models have been constructed considering a central Ir atom, where the adsorbate binds, and adding the neighbouring atoms in the first and second shells and fulfilling the coordination spheres of the peripheral Ir atoms. This yields a cluster with 9 Ir atoms that after capping the dangling O atoms at the cluster periphery with H atoms, in order to make a stoichiometric neural model, leads to a $(IrO_2)_9 \cdot 16H_2O$ model. Since the saturation of the dangling O atoms with H is not unique (with hydroxyl or water ligands) we have considered two possible capping schemes (namely c1 and c2). Starting from one of the capping scheme (c2) we have, however, enlarged the model to include an even number of Ir atoms, i.e. $(IrO_2)_{10} \cdot 19H_2O$, so that the cluster model maintains the same total spin of the large NP model. In fact, each Ir(IV) center has a single unpaired electron in the occupied d orbitals, and an even number of Ir atoms gives as low-spin configuration a closed-shell system. In general, the three cluster models provided very similar results and reduce significantly the cost of the computations with respect to the large $(IrO_2)_{56} \cdot 2H_2O$ model.

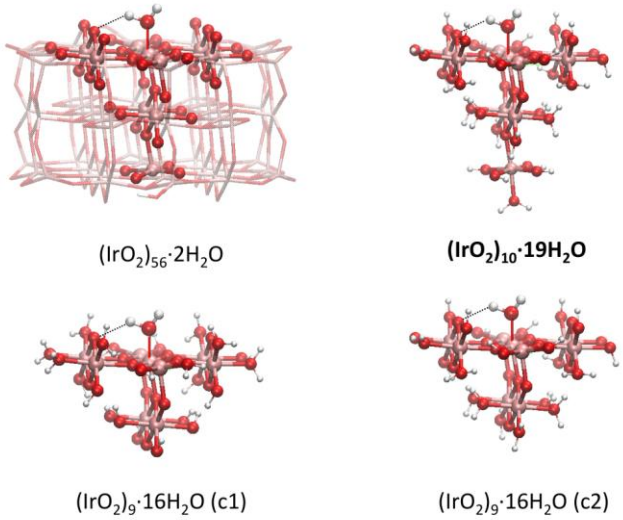

Figure 2. Cluster models extracted from the $(IrO_2)_{56} \cdot 2H_2O$ NP.

During the 10 days of Dr. Rivalta's visit we plan to study the influence of the spin state on the energetics of the adsorption of the different species on the $(IrO_2)_{10} \cdot 19H_2O$ cluster model. Restricted closed-shell DFT calculations will be compared with unrestricted closed-shell and with higher spin multiplicities (M), accounting for the high-spin configuration with all (ten) unpaired Ir atoms (M=3,5,7,9,11), and an even higher-spin configuration (M=13) for comparison. After determining the trend for the total energies of the clean clusters, the relative stability of each adsorbed species (H_2O, OH, O) will be evaluated as function of

the cluster spin state. Analogous study will be performed for the oxidized clusters. The outcome of these calculations will allow selecting the active surface species (and the correct spin multiplicity of the cluster models) for the study of the O-O bond formation. The research program will continue after the period of the proposed mobility mission in order to complete the study with various DFT exchange-correlation functional and including elucidation of the water splitting reaction mechanism on the large NP model.

Results

Following the workplan previously reported, here we describe the results obtained.

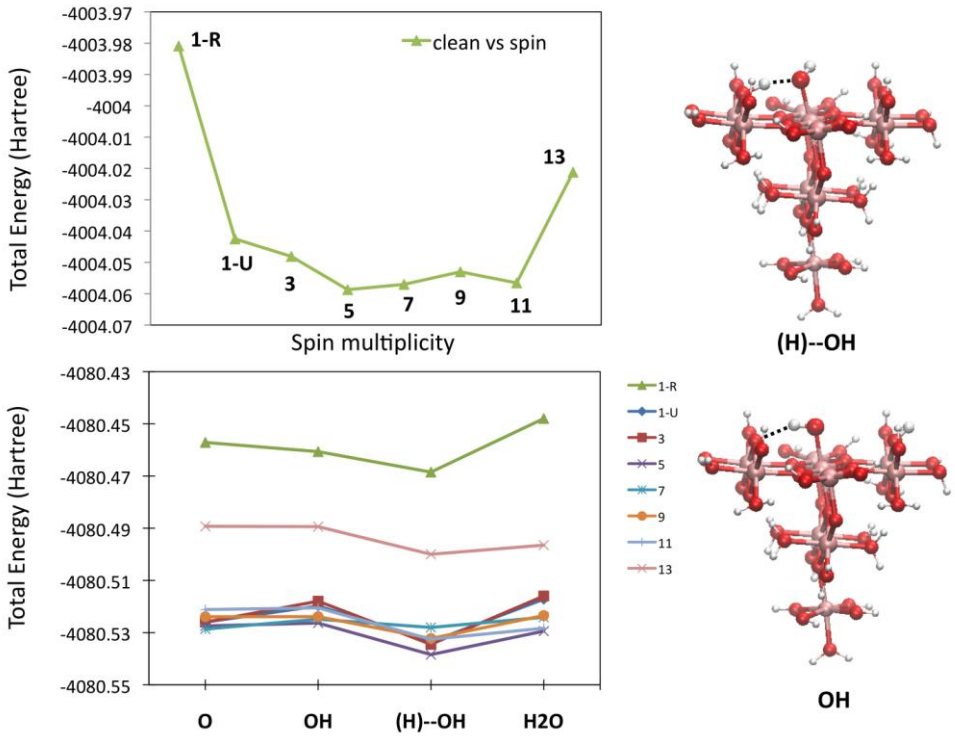

Figure 3. Spin dependent total energies of the (top left) clean $(IrO_2)_{10}\cdot 19H_2O$ cluster model and (bottom left) adsorbed species, with depiction of structures of OH and (H)--OH surface species (right column).

Figure 3 shows that the trend observed for the total energies of the clean cluster with 1R and M=13 calculations having much higher total energies than the M=3-11 high-spin configurations. However, the relative stability of each adsorbed species seems to be affected by the spin state to a small (not negligible) extent. The most stable surface species is, as for the large NP model, the hydroxyl group.

Table 1. Relative energies (in kcal/mol) of the absorbed species on the $(IrO_2)_{10}\cdot 19H_2O$ cluster model as function of the spin multiplicity. Constrained optimizations are indicated with asterisks. The relative energies among the structures with the lowest total energies are reported at the bottom with their corresponding spin multiplicities.

Multiplicity	ΔE (Kcal/mol)			
	H_2O	**OH**	**(H)--OH**	**O**
1-R	12,9*	4,9	**0,0**	7,1
1-U	10,2*	8,6	**0,0**	4,7
3	11,6	10,3	**0,0**	5,3
5	5,6	7,6	**0,0**	6,9
7	2,8	2,4	0,4	**0,0**
9	5,5	5,2	**0,0**	5,2
11	2,7	7,6	**0,0**	7,1
13	2,2	6,7	**0,0**	6,7
Lowest	**5,6**	**7,6**	**0,0**	**6,1**
Multipl.	*5*	*5*	*5*	*7*

A strong H-bond with the surface stabilizes the hydroxyl surface species, with the OH group being a H-bond acceptor from a protonated oxo-bridge, namely (H)--OH in Figure 3. If the OH group is instead H-bond donor to an oxo-bridge and the water proton is transferred to another oxo-bridge (namely OH in Fig. 3) the hydroxyl species has comparable stability with respect to that of the oxo (O) or the water (H_2O) adsorbed species, see Table 1. Overall, we observed that the 1R calculations reproduce nicely the restricted closed-shell calculations of the large NP model, with the OH species being more stable than the oxo by ca. 7 kcal/mol (vs 11 kcal/mol in the $(IrO_2)_{56}\cdot 2H_2O$ model) and the water molecule spontaneously dissociating on the surface (the value of 12.9 kcal/mol reported in Table 1 is referred to a constrained optimization avoiding water deprotonation).

In general we observed fluctuations of the relative energies of the adsorbed species as function of the spin multiplicity of the cluster. However, taking into account the lowest energy structures of each adsorbate among the various spin multiplicities, we observed that the hydroxyl is overall the most favourable surface species, with the oxo and the adsorbed water having similar relative energies. Notably, this outcome does not differs from that obtained with the preliminary restricted closed-shell calculation of the large $(IrO_2)_{56}\cdot 2H_2O$ model.

Table 2. Relative energies (in kcal/mol) of the absorbed species on the oxidized $(IrO_2)_{10}\cdot 19H_2O$ cluster model as function of the spin multiplicity. Constrained optimizations are indicated with the asterisks. The relative energies among the structures with the lowest total energies are reported at the bottom with their corresponding spin multiplicities.

Multiplicity	ΔE (Kcal/mol)			
	H_2O	**OH**	**(H)--OH**	**O**
2	8,9*	6,2	**0,0**	8,4
4	5,4	7,6	**0,0**	5,9
6	2,0	2,7	**0,0**	2,2
8	5,4	4,6	**0,0**	3,1
Lowest	**5,5**	**6,2**	**0,0**	**6,0**
Multipl.	*4*	*2*	*2=4*	*4*

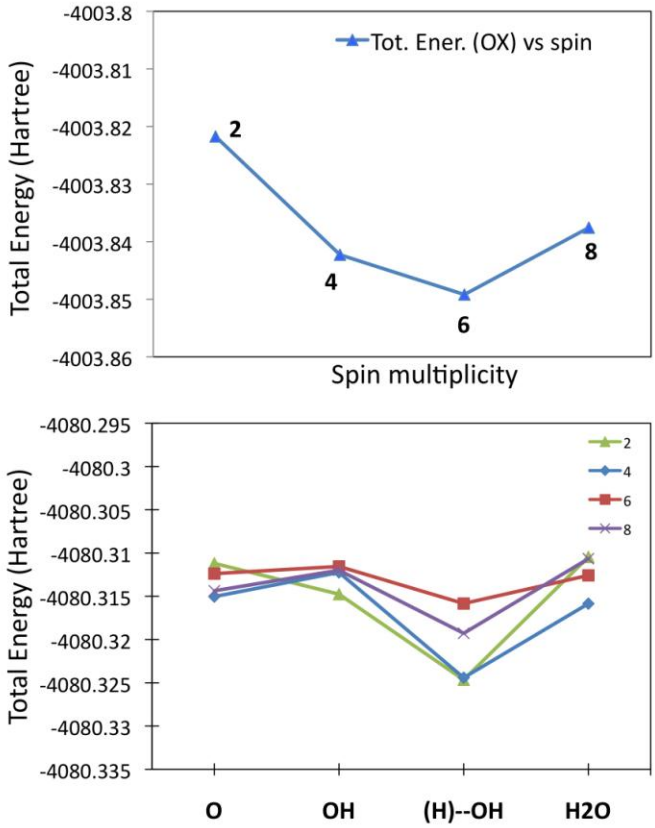

Figure 4. Spin dependent total energies of the (top) clean oxidized $(IrO_2)_{10}\cdot 19H_2O$ cluster model and (bottom) adsorbed species.

We have also investigated the effect of the oxidation of the cluster model on the relative stabilities of the adsorbed species. Figure 4 and Table 2 show that the doublet spin state, directly derived from oxidation of the closed-shell neutral system, is not always the lowest energy state for the oxidized cluster model. However, the overall picture of the NP oxidation is not different from that determined with the large $(IrO_2)_{56}\cdot 2H_2O$ model: the oxidation only slightly affect (reducing) the relative stability of the OH with respect to the O surface species. This information is crucial while pursuing further studies on the oxidation of the large NP model.

Further studies accounting for the influence of the DFT exchange-correlation functional on the above analysis are in progress, along with computations of high-spin configurations of the large NP model. Preliminary calculations on the O-O bond formation reaction on the $(IrO_2)_{10}\cdot 19H_2O$ cluster model are also in progress.

References

1 Youngblood, W. J., Lee, S.-H. A., et al. *J. Am. Chem. Soc.* **131**, 926-927, 2009.
2 Pastore, M., De Angelis, F. *J. Am. Chem. Soc.* **137**, 5798-5809, 2015.
3 Luber, S., Rivalta, I., et al. *Biochemstry*. **50**, 6308-6311, 2011.
4 Rivalta, I., Brudvig, G. W., et al. *Curr. Opin. Chem. Biol.* **16**, 11-18, 2012.
5 Rivalta, I., Yang, K. R., et al. *Acs Catalysis*. **5**, 2384-2390, 2015.
6 Blakemore, J. D., Mara, M. W., et al. *Inorg. Chem.* **52**, 1860-1871, 2013.