On the Role of Ni-based Co-catalyst in Inhomogeneous RVO_4 Photocatalyst Systems (R=Y, Gd)

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SUPPORTING INFORMATION

Table S1. Main geometrical parameters of the simulated Ni-doped system.

Bond	Bond length (Å)								Av. (Å)	Av. (left column) /Av. bond length of Ni-O inside Ni doped bulk YVO_4 (%)	Remark
Ni1-O (Y-O)	2.155	2.335	2.352	2.355	2.401 ($O108_{wt}$)	2.451	2.454	2.574	2.384	+1.7	(a) init
Ni2-O (Y-O)	2.191	2.222	2.261	2.337	2.391 ($O130_{wt}$)	2.538	2.557	2.687	2.398	+2.3	
Ni1-O	1.963	1.973	2.079	2.265	2.614 ($O108_{wt}$)	2.691	3.060	3.458	2.515	+7.3	(b) 4.03ps
Ni2-O	1.990	2.000	2.126 ($O130_{wt}$)	2.199	2.319	2.715	3.183	3.199	2.466	+5.2	
Ni1-O	1.887 ($O108_{wt}$)	2.048	2.083	2.162	2.231	2.569	2.792	3.578	2.419	+3.2	(c) 4.13ps
Ni2-O	2.010 ($O130_{wt}$)	2.140	2.202	2.300	2.381	3.061	3.145	3.261	2.563	+9.3	
Ni1-O	2.031	2.047	2.067 ($O97_{wt}$)	2.089	2.122	2.431	3.258	3.396	2.430	+3.7	(d) 1 wt gpt
Ni1-O	2.100	2.155	2.206	2.214	2.259	2.356	2.365	3.090	2.343	-	(e) Inside bulk
Ni2-O	2.135	2.224	2.241	2.245	2.250	2.284	2.294	3.083	2.345	-	

(a) Initial stage. (just after exchanging two Y with two Ni after having optimized cell thickness) Then the initial Ni-O distance is same as Y-O distance. Atomic index: Ni 1-2, Y 3-16, V 17-32, O_{cat} 33-96, O_{wt} 97-131, H 132-201 for (a)-(c). (b) Point C [4.03 ps] in Figure 1 (b). (c) Point D [4.13 ps] in Figure 1 (b). (d) Relaxed Ni1-O distance by geometry optimization (gpt) after removing all but one water molecule close to the surface of $Y_{14}Ni_2V_{16}O_{64}$+35wt. Atomic index: Ni 1-2, Y 3-16, V 17-32, O_{cat} 33-96, O_{wt} 97, H 98-99 for (d). (e) Doped inside the bulk (not on the surface). Atomic index: Ni 1-2, Y 3-16, V 17-32, O_{cat} 33-96 for (e).

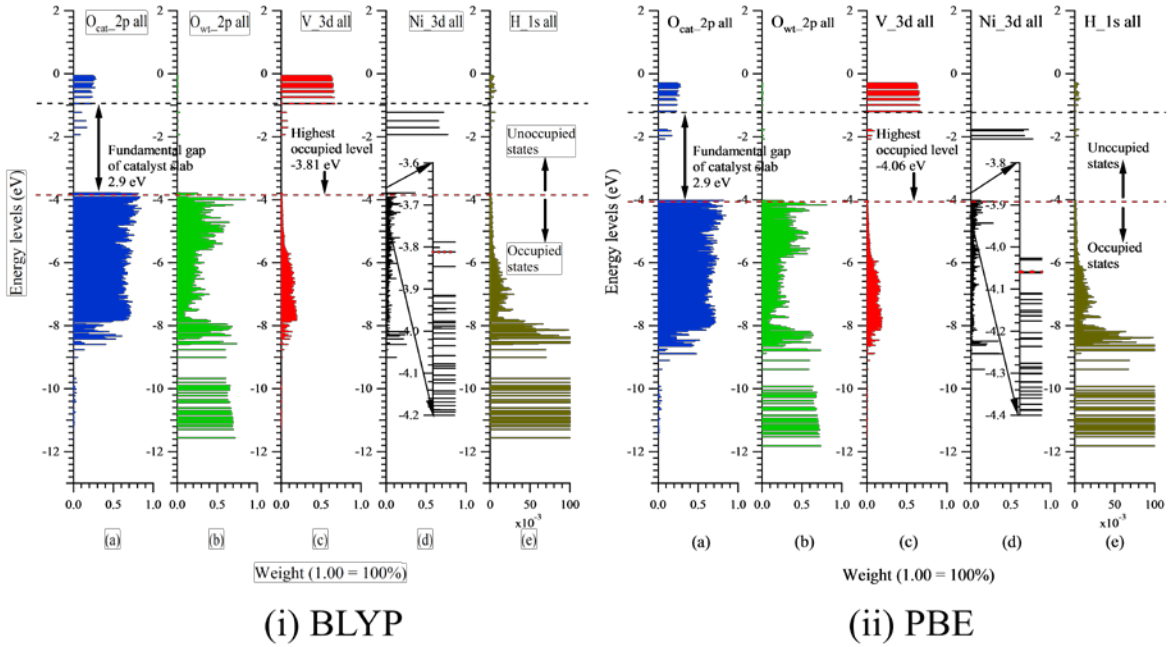

Figure S2. Electronic structure comparison of the Ni doped YVO_4 in contact with water between the BLYP (i) and the PBE (ii) functionals.[1] The various profiles indicate the weights associated with the most relevant atoms, obtained as projections of each eigenfunction of the Kohn-Sham Hamiltonian onto atomic orbitals. Both panels refer to the point C of Figure 1 (b), where the distance between the O atom of adsorbed water molecule and the exposed Ni is relatively large (O108 - Ni1 = ~2.61 Å). This result confirms that both functional have similar performances and give almost identical results, within the allowed numerical accuracy, in terms of electronic structure. This is in full agreement with the results reported in *ChemistryOpen* **2013**, *2*, 115-124 showing that PBE and BLYP are comparable.[1] Moreover, whenever water is involved, the performance of BLYP is preferable, as discussed in *J. Chem. Phys.* **1996**, *105*, 1142-1152.[2]

RREFERENCES

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(2) Sprik, M.; Hutter, J.; Parrinello, M. Ab initio Molecular Dynamics Simulation of Liquid Water: Comparison of Three Gradient-Corrected Density Functionals. *J. Chem. Phys.***1996**, *105*, 1142-1152.