Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information for:

Tuning electronic levels in photoactive hydroxylated titania nanosystems: combining the ligand dipole effect and quantum confinement

Miguel Recio-Poo,[a] Ángel Morales-García,*[a] Francesc Illas,[a] Stefan T. Bromley*[ab]

[a] Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, c/Martí i Franquès 1-11, 08028 Barcelona, Spain

[b] Institució Catalana de recerca i Estudis Avançats (ICREA), Passeig Lluis Companys 23, 08010 Barcelona, Spain

*Corresponding authors: angel.morales@ub.edu ; s.bromley@ub.edu

Table S1. Comparison of total energies for hydroxylated anatase slab models with Γ point and 5×5×1 **k**-point sampling.

	Degree of hydroxylation		
	0%	50%	100%
Γ point	-1972829.149	-1985324.399	-1997809.979
5×5×1	-1972828.579	-1985323.859	-1997809.445
ΔE per TiO_2 unit (eV)	-0.00791	-0.00749	-0.00741

Figure S1. Evolution of the LUMO+5, LUMO+4, LUMO+3, LUMO+2, LUMO+1, HOMO-1, HOMO-2, HOMO-3, HOMO-4, HOMO-5 orbital energies corresponding to faceted $(TiO_2)_{35}$ NP.

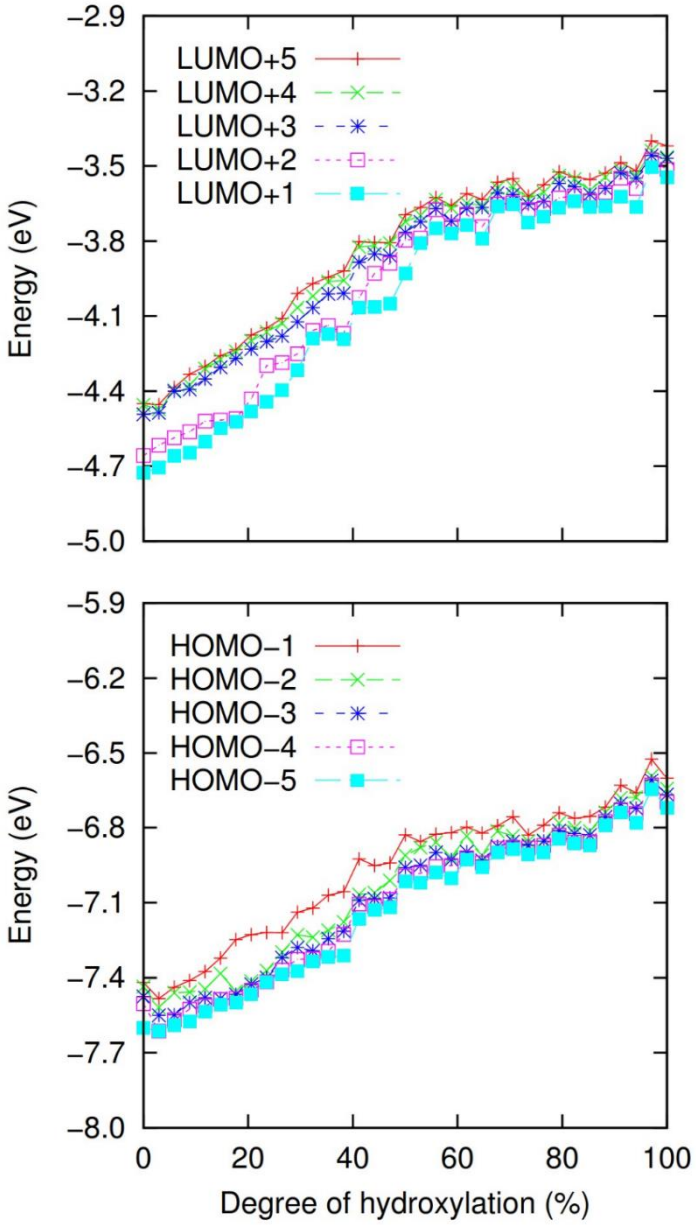

Figure S2 Evolution of HOMO, LUMO and a deeper lying energy level for the faceted $(TiO_2)_{35}$ and $(TiO_2)_{165}$ NPs. Besides of proving again the electrostatic nature of the ligand dipole effect, the considerably slower slopes in the HOMO and LUMO levels with respect to the deeper orbitals (i.e. HOMO-250 for the $(TiO_2)_{35}$ NP and HOMO-500 for the $(TiO_2)_{165}$ NP) shows the stabilization happening due to defects healing effect upon hydroxylation.

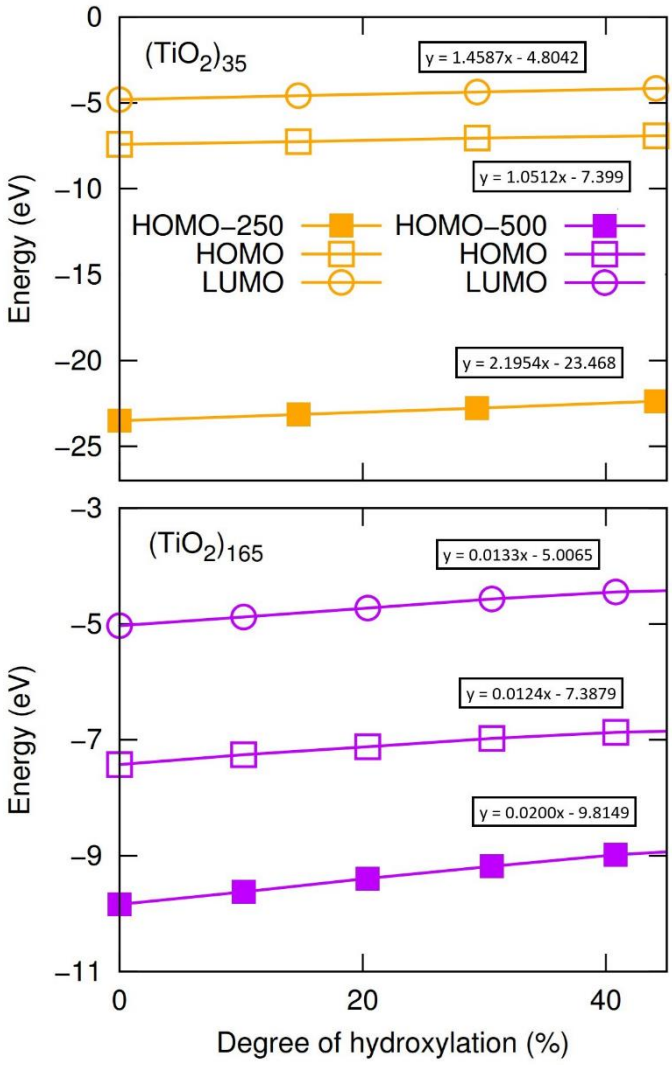

Figure S3 Evolution of both the average value of α and ΔQ_{OH} with respect to the degree of hydroxylation for the n = 35 and n = 165 $(TiO_2)_n$ anatase NPs is provided in the SI.