# Structural and Electronic Properties of Metal/Oxide Nanostructures from first-principles: Ru<sub>13</sub> supported on (TiO<sub>2</sub>)<sub>84</sub> as a case study

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#### Abstract

All electron density functional theory based calculations are carried out to investigate the properties of metal/oxide nanostructures taking the case of a  $Ru_{13}$  cluster supported on an octahedral anatase (TiO<sub>2</sub>)<sub>84</sub> nanoparticle, as a representative systems. The interaction between both system is exothermic showing binding energies below -4 eV. In spite of the large interaction, the structure of the  $(TiO_2)_{84}$  nanoparticle remains unaltered. However, the metal-support interaction promotes the deformation of the Ru<sub>13</sub> cluster atomic structure. This deformation is more accentuated when the Ru13 nanocluster is situated in the facet region of the (TiO<sub>2</sub>)<sub>84</sub> nanoparticle than when the interaction involves the edge regions. The formation of the  $Ru_{13}/(TiO_2)_{84}$  heterostructure leads to a decrease of the energy gap inherent to the bare  $(TiO_2)_{84}$  nanoparticle, becoming almost negligible. This is due to the contribution of the partially filled Ru 4d orbitals with Kohn-Sham energies spanning in the energy range of those of the O 2p occupied and Ti 3d empty manifolds. This feature systematically observed no matter the interaction involves the oxide nanoparticle facet or edge regions. This study constitutes a first step in designing a strategy to investigate metal-semiconductor nanostructures using realistic models that go beyond the use of extended surfaces.

#### **1. Introduction**

Since 1972, when Fujishima and Honda first reported water splitting with TiO<sub>2</sub> photoelectrodes under UV illumination,<sup>[1]</sup> this simple oxide has become the workhorse in the field of photocatalysis. Together with its photocatalytic activity,<sup>[2,3]</sup> low toxicity and cost, high chemical stability are other important features of this semiconductor. However, its restrictive light absorption, requiring UV radiation, and fast recombination limit somehow its use as photocatalyst under sunlight. Therefore, different strategies are being currently investigated with the goal of reducing energy gap and prolonging the lifetime of the photogenerated species. Strategies such as crystal facet engineering, surface modification by supporting metal nanoclusters and metal/non-metal doping, to name a few, emerge as plausible procedures to improve the performance of TiO<sub>2</sub> and related semiconducting photocatalysts.<sup>[4-8]</sup> Among these, the incorporation of metals, typically Pt, Au, or Ru, to semiconducting nanostructures is one of the approaches followed nowadays to enhance the photocatalytic activity of the latter in processes such as water splitting to produce H<sub>2</sub>.<sup>[9,10]</sup> The photocatalytic improvement resides both, the charge separation of the photogenerateed electrons and holes and adsorption of visible light. It has been suggested that the charge transfer between semiconductor and metal cluster is important in separating electron-hole pairs.<sup>[11,12]</sup> This constitutes a great advantage specially for photocatalyst such as titania (TiO<sub>2</sub>) where the fast electron-hole recombination is one of the main drawbacks.

Previous experimental studies have reported that the synergy metal cluster and TiO<sub>2</sub> nanocrystals improve the photocatalytic performance respect to the isolated TiO<sub>2</sub> configuration. Zhang et al.<sup>[13]</sup> synthetized nanocatalysts of Ag nanoparticles (NPs) coating TiO<sub>2</sub> nanocrystals exposing {101} and {001} facets simultaneously. This Ag/TiO<sub>2</sub> system improves the activation of O<sub>2</sub>. Further combined experimental and computational studies confirmed that the adsorption of Pd nanoclusters (NCs) on the TiO<sub>2</sub> NPs reduced the energy activation for the hydrogenation of phenyl acetylene.<sup>[14]</sup> On the other hand, the photoactivity of TiO<sub>2</sub> has been computationally investigated considering the effect of surface deposited Pt on the O<sub>2</sub> adsorption.<sup>[15]</sup> It has been suggested that Pt clusters act as an electron-hole separation center and therefore inhibit the recombination, but that at high loadings Pt acts as an electron-hole recombination center.<sup>[16,17]</sup> These studies manifest the importance of depositing metal clusters on TiO<sub>2</sub> but in a controlled way. It is worth noting that, from a theoretical and computational viewpoints, these studies, and others <sup>[18-20]</sup> use periodic models of extended surfaces to analyze the

fundamental aspects of the interaction between  $TiO_2$  and metal clusters. These extended surface models represent properly the facets of  $TiO_2$  nanostructures but cannot provide information regarding other region such as edges, apical or equatorial region that, involving undercoordinated atoms, are likely to be more reactive. To properly investigate the chemistry involved in these regions, realistic  $TiO_2$  NPs are better suited. Thus, computational studies combining metal clusters and realistic  $TiO_2$  NPs are required to provide a more complete picture of the fundamental structural and electronic aspects of these complex heterostructures.

Based on our experience in the analysis of the atomic and electronic structure of realistic TiO<sub>2</sub> NPs including not only the design of particular morphologies but also the study of excited states, hydroxylation, and analysis of doping effects,<sup>[21-24]</sup> we move a step further to explore here the formation of nanostructures combining Ru<sub>13</sub> NC with  $(TiO_2)_{84}$  NP. The aim of this study is to investigate in detail the interaction of Ru<sub>13</sub> NC considering the different regions of  $(TiO_2)_{84}$  NP and observe the influence on the electronic properties compared with the isolated  $(TiO_2)_{84}$  configuration. The paper starts with a brief description of the computational strategy and models. Next, we discuss the binding properties of Ru<sub>13</sub> NC on the  $(TiO_2)_{84}$  NP. Finally, we describe the results of the electronic properties of Ru<sub>13</sub>/(TiO<sub>2</sub>)<sub>84</sub> systems and outline the main conclusions.

# 2. Computational Strategy and Models

The formation of metal-oxide heterostructure at the nanoscale is investigated considering realistic models of titania and ruthenium systems. Specifically, we selected the  $(TiO_2)_{84}$  nanoparticle (NP) because of its realistic size and bipyramidal morphology exhibiting the most stable surface of anatase crystals, and the Ru<sub>13</sub> nanocluster (NC) with icosahedral symmetry, likely to be one the most stable isomer. Note that this type of metal cluster composed by 13 atoms has been systematically investigated in previous studies.<sup>[25]</sup> The stability of these, often called magic, transition metal clusters atom is due to their closed shell configuration in the spherical well potential.<sup>[26]</sup> Both  $(TiO_2)_{84}$  and Ru<sub>13</sub> systems are shown in Figure 1.

Attending to the symmetry of the  $(TiO_2)_{84}$  NP, different regions are selected to anchor the Ru<sub>13</sub> NC. We distinguish apical, edge, facet and equatorial regions as reported earlier by some of us.<sup>22</sup> All these sites have been explicitly considered in the present study. To differentiate the sites of interaction we have adopted the following notation: Ap, Fac, Ed and Equat stand for apical, facet, edge, and equatorial regions, respectively. In addition, we use the digit 1 and 2 to distinguish two different sites in the same region (i.e., Fac\_1 and Fac\_2). Finally, the sites simultaneously having two of these terms correspond to models in which the Ru<sub>13</sub> NC simultaneously interacts with these two regions. For instance, the Ed-Fac site denotes that the Ru<sub>13</sub> NC is connected in the edge and facet regions. Figure 2 shows the different configurations for the Ru<sub>13</sub>/(TiO<sub>2</sub>)<sub>84</sub> system.

The stability and the electronic structure of the  $Ru_{13}/(TiO_2)_{84}$  nanostructures are inspected using relativistic density functional theory (DFT) based calculations including all electrons with the electron density described through a numerical atom-centered (NAO) orbital basis set as implemented in the Fritz Haber Institute *ab initio* molecular simulation (FHI-aims) package.<sup>[27]</sup> To describe the properties of the  $Ru_{13}/(TiO_2)_{84}$ nanostructures the generalized gradient approximation (GGA) was selected. In particular, the PBE exchange-correlation density functional.<sup>[28]</sup> A tight grid and tier-1 basis set was appropriately selected. The convergence threshold for atomic forces in relaxation of  $Ru_{13}/(TiO_2)_{84}$ , and isolated  $Ru_{13}$  and  $(TiO_2)_{84}$  systems is set to  $10^{-3}$  eV Å<sup>-1</sup>. Relativistic effects were included through the zero-order regular approach (ZORA) due to the presence of Ti and Ru, relatively heavy transition elements.<sup>[29,30]</sup>

To explore whether the formation of  $Ru_{13}/(TiO_2)_{84}$  is energetically favorable we define an energetic descriptor as the adsorption energy ( $E_{ads}$ ) as

$$E_{\rm ads} = E_{\rm Ru_{13}/(TiO_2)_{84}} - E_{\rm Ru_{13}} - E_{(TiO_2)_{84}}$$
(1)

where  $E_{\text{Ru}_{13}/(\text{TiO}_2)_{84}}$ ,  $E_{\text{Ru}_{13}}$ , and  $E_{(\text{TiO}_2)_{84}}$  correspond to the DFT energies of the Ru<sub>13</sub>/(TiO<sub>2</sub>)<sub>84</sub> nanostructures and isolated Ru<sub>13</sub> NC, and (TiO<sub>2</sub>)<sub>84</sub> NP respectively. According to the Eq. (1) the formation of  $E_{\text{Ru}_{13}/(\text{TiO}_2)_{84}}$  is exothermic and favorable when  $E_{\text{ads}} < 0$ .

### 3. Results and Discussion

We first focus on the interaction of the  $Ru_{13}$  NC with the  $(TiO_2)_{84}$  NP. Different configurations are analyzed considering the icosahedral symmetry of  $Ru_{13}$  cluster and the well-defined regions of the bipyramidal  $(TiO_2)_{84}$  NP (i.e., apical, edge, facet, and equatorial). Starting with the interaction in the apical region of the  $(TiO_2)_{84}$  NP, we consider two different paths to study the interacting landscape in the potential energy surface moving from the apical to the equatorial regions: (*i*) the facet and (*ii*) the edge routes (see Figure 2). All in all, this analysis includes ten different adsorption sites, which

can be systematically reproduced due to inherent symmetry of the bipyramidal  $(TiO_2)_{84}$ NP and the results derived from  $E_{ads}$  are listed in Table 1.

Clearly, the interaction between both nanostructures is highly exothermic, featuring  $E_{ads}$  values below -4 eV. Thus, this energetic descriptor confirms the thermodynamically favorable formation of these metal-semiconductor heterostructures. We note that this energy is calculated using exclusively the PBE density functional without including dispersion correction. Its consideration would add to a systematic extra energy around 0.2-0.3 eV. Nevertheless, preliminary tests confirm that the dispersion unalters the optimized structure obtained from PBE analysis. This is a clear indication that ionic and/or covalent character governs the interaction, being the dispersion a negligible contribution. Based on our statement, it is reasonable to focus on the PBE results as in Table 1 for further discussion and analysis.

To facilitate the discussion of the results, two different interaction routes are considered. Based on this choice, one can observe interesting results related over Ru13 clusters supported on the (TiO<sub>2</sub>)<sub>84</sub> NP. Moving from apical to equatorial region of the  $(TiO_2)_{84}$  NP thought the exposed (101) facets, one notes that  $E_{ads}$  increases from -5.83 (apical) to -7.09 eV (apical-facet). Interactions slightly below -7.00 eV are systematically observed in the facet region, but its value decreases below -6.5 eV when Ru<sub>13</sub> clusters is close to the equatorial region. The results obtained for the interaction in the facet regions are consistent with those reported by Pacchioni and coauthors using extended supercell models of anatase TiO<sub>2</sub> and a Ru<sub>10</sub> NC.<sup>[18]</sup> On the other hand, the same path but through the edge region reports different results. Here, the interaction of Ru<sub>13</sub> NC with (TiO<sub>2</sub>)<sub>84</sub> NP is less favorable as  $E_{ads}$  decreases from a pure apical region (-5.83 eV) to a pure edge site (-4.43 eV). Then, the interaction increases up to -5.59 eV in the equatorial region. These differences are somehow expected because the interacting surface, and thus number of contacts between the interacting nanoparticles, is larger in facet than in edge regions. From this analysis, we conclude that facet regions are the most suitable sites for supported Ru<sub>13</sub> NCs and edge regions, containing undercoordinated atoms and expected to be reactive, are relatively less favorable. In an intermediate situation, we find the apical region. Interestingly, two sites can be distinguished in the equatorial region, those located at the corners of the (TiO<sub>2</sub>)<sub>84</sub> NP connected with the edges and the equatorial region located in the middle of two of these corners. The interaction in the first type of sites ( $E_{ads}$ = -5.59 eV) is less exothermic than in the equatorial region located in the middle of two of these corners ( $E_{ads} = -6.42$  eV). The latter one is also the equatorial region connected with the facets of the  $(TiO_2)_{84}$  NP. Similar behavior has been recently reported by some of us investigating the hydration of the  $(TiO_2)_{84}$  NP with dissociative water.<sup>[22]</sup>

To rationalize the trends in  $E_{ads}$ , we select the average coordination number (ACN) of the Ru<sub>13</sub> NC as a structural descriptor. The Ru<sub>13</sub> NC shows ACN = 6.46 in its gas phase conformation with a highly symmetrical icosahedral shape (see Figure 1). In principle, one may assume that those interactions with large  $E_{ads}$  promotes the loss of gas phase symmetry of the Ru<sub>13</sub> NC reflected in the ACN parameter. Consequently, its values should be in principle below 6.46. This prediction is systematically observed as shown in Table 1. However, this descriptor is not accurate enough since no trends are observed on ACN moving from the apical to the equatorial regions of the (TiO<sub>2</sub>)<sub>84</sub> NP. This indicates that other parameters in addition to the structural descriptors govern the interaction between both nanostructures. Besides, one may assume that the deformation of the Ru<sub>13</sub> NC is energetically compensated by highly exothermic interaction energies. Nevertheless, the structure of the (TiO<sub>2</sub>)<sub>84</sub> NP is unaltered by the presence of Ru<sub>13</sub> NC. This indicates that the Ru<sub>13</sub> NC induces a local effect on the titania nanostructure. To confirm this issue, we investigate the electronic properties based on the density of state (DOS) analysis.

Figure 3 shows the partial density of states (PDOS) of the Ru<sub>13</sub>/(TiO<sub>2</sub>)<sub>84</sub> in different situations. The PBE energy gap,  $E_{gap}$ , of the (TiO<sub>2</sub>)<sub>84</sub> NP is 2.51 eV, lower than the experimental value of bulk anatase 3.2 eV. The value is excessively low as for a nanoparticle the energy gap is larger than for the bulk material as evidenced in previous studies.<sup>[31,32]</sup> This discrepancy is well known and due to the limitations to GGA methods in accurately describing the electronic structure of oxides.<sup>[33,34]</sup> Including hybrid density functionals with an appropriate amount of Fock exchange can solve this issue.<sup>33</sup> In the particular case of TiO<sub>2</sub> polymorphs, a PBEx, with 12.5% Fock exchange provides results matching the experiment.<sup>[35,36]</sup> Nevertheless, while hybrids functionals open the energy gap in semiconducting materials with predicted values close to the experiment, the orbital distribution, eventually resulting in bands, is less affected. Thus, to investigate the influence of the Ru<sub>13</sub> NC on the electronic structure of the bare (TiO<sub>2</sub>)<sub>84</sub> NP, the choice of the PBE functional is adequate.

As expected, the one electron levels of the  $(TiO_2)_{84}$  NP that upon growing to the bulk will generate the valence band is dominated mainly by O 2p orbitals with a low contribution from Ti 3d orbitals. This situation is the opposite in the levels that are related to the conduction band dominated by Ti 3d orbitals with a minimum contribution by O 2p orbitals.<sup>[37]</sup> Adding the Ru<sub>13</sub> NC to the  $(TiO_2)_{84}$  NP introduces a large number of Ru states within the energy gap region. The PDOS depicted in Figure 3 shows clearly that the new states coming from Ru 4d orbitals are systematically located in the same energy region between -2 and 0 eV regardless the interaction and orientation of the Ru<sub>13</sub> NC with the  $(TiO_2)_{84}$  NP. In general, there are no significant differences among the investigated cases. One can see that the projection of the PDOS of Ru 4d orbitals is slightly higher in the configuration where the Ru<sub>13</sub> NC is interacting mainly in facet regions than those configurations where the interaction is located in the edges.

It is worth pointing out that for such a finite systems, the energy levels are discrete but the energy separation becomes almost negligible and appear as a continuum in the PDOS plots in Figure 3. Interestingly, the distribution of the O and Ti states remain in similar locations relative to one another with and without the presence of the  $Ru_{13}$  NC (Figure 3). Indeed, the  $Ru_{13}$  NC interacts with only those Ti and O atoms to which it is directly bonded, leaving most states unperturbed. Thus, the energy gap of the (TiO<sub>2</sub>)<sub>84</sub> NP does not change upon the addition of  $Ru_{13}$  NC. Instead, new states are introduced throughout the energy gap regions so that, in practice, the gap of all investigated  $Ru_{13}/(TiO_2)_{84}$  systems becomes negligible, and we can extrapolate this results to other cluster and nanoparticles sizes, provide the metal NC dimension is significantly smaller than that of the oxide NP. Analogous results have been reported for the Pt<sub>37</sub> NC on the (101) anatase surface.<sup>[15]</sup>

## 4. Conclusion

Relativistic, all electron, density functional theory based calculations have been performed to investigate the structural and electronic properties of  $Ru_{13}/(TiO_2)_{84}$  nanostructures. We conclude that the interaction between the metal cluster and semiconducting nanoparticle is highly favorable according to the calculated adsorption energies that are larger than 4 eV. We found out that the binding is more favorable in the facet regions than in the edge ones which may seem counterintuitive due to the expected larger reactivity of these regions with undercoordinated atoms but that is easily understood from the number of involved atomic contacts. This has a direct consequence on the average coordination number of the  $Ru_{13}$  NC because its deformation is larger when located in facet region. Such deformation is compensated with a highly exothermic binding energy.

The analysis of the electronic properties based on the density of states shows that the interaction is quite local because there no significant change in the structure of  $(TiO_2)_{84}$  NP, nor in the main features of its electronic structure. The contribution of 3d and 2p states of Ti and O slightly modifies once the Ru<sub>13</sub>/(TiO<sub>2</sub>)<sub>84</sub> nanostructure is formed. This situation is systematically observed regardless the interaction region (i.e., apical, facet, edge, or equatorial). Interestingly, the 4d states coming from Ru fill the energy gap observed in isolated (TiO<sub>2</sub>)<sub>84</sub> NP promoting an almost vanishing energy gap. The contribution of such states is higher when more exothermic the interaction is.

The present results, are likely to be valid for other metal clusters supported on different types of  $TiO_2$  NPs, provides the size of the former is significantly smaller thant that of the oxide NP. The presence of the metal states would favor adsorption of photons at energies below the UV which is required for  $TiO_2$  systems. However, the role of the metal cluster in promoting charge separations remains to be investigated and work is in progress to analyze the excited states of these systems and their time evolution.

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# **Conflict of Interest**

The authors declare no conflict of interest

#### Keywords

Density functional theory, metal-semiconductor nanostructures, titania nanoparticle, ruthenium nanocluster, density of states

**Table 1.** Adsorption energies,  $E_{ads}$ , and average coordination number, ACN of the Ru<sub>13</sub>/(TiO<sub>2</sub>)<sub>84</sub> systems. Note that ACN parameter corresponds to the Ru<sub>13</sub> nanocluster. The ACN value of isolated Ru<sub>13</sub> NC is also included for comparison.

Notation	E <sub>ads</sub> , eV	ACN Ru <sub>13</sub>
Isolated	-	6.46
Ар	-5.83	4.69
Ap-Fac	-7.09	5.92
Fac_1	-7.24	5.77
Fac_2	-6.86	5.61
Fac-Equat	-6.42	5.15
Ap-Ed	-5.16	6.15
Ed	-4.43	5.92
Ed-Fac	-6.49	5.61
Ed-Equat	-5.41	5.85
Equat	-5.59	5.54

**Figure 1.**  $(TiO_2)_{84}$  and  $Ru_{13}$  nanostructures employed in this study. The former has a bipyramidal symmetry and the (101) surface is exposed in all facets. The latter has an icosahedral symmetry. Blue, red and light gray spheres correspond to Ti, O and Ru atoms, respectively.



**Figure 2.** Ru<sub>13</sub>/(TiO<sub>2</sub>)<sub>84</sub> nanostructures. The adsorption energies of all these systems are listed in Table 1. Blue, red and light gray spheres correspond to Ti, O and Ru atoms, respectively.



**Figure 3.** Partial density of states (PDOS) of the  $Ru_{13}/(TiO_2)_{84}$  structures depicted in Figure 2. Fermi level is fixed at 0 eV and marked with a pointed line.



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