

# The Effect of the Oxide/Au Interface on the Chemical Activity of Au nanostructures on oxides: A DFT study

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## Introduction

Au nano-structures anchored on oxide supports are active in many heterogeneous reactions [4]. Multiple factors including particle size and shape [1-4], charge transfer between Au and the oxide support [6], metal-to-insulator transition [7], the presence of under-coordinated Au atoms [8], and quantum size effects [9] have been correlated with the catalytic activity. While these contributions have shed light on many aspects of the chemistry of Au, there is a lack of agreement regarding the nature of chemically active Au sites. Multiple reports indicate that anionic Au is required to facilitate catalytic reactions [6, 9]. While others have argued that cationic Au is present and active under relevant reaction conditions [10].

We have employed first principles Density Functional Theory (DFT) calculations to study the impact of Au/oxide interface on the chemical and catalytic activity of Au nanostructures anchored on the oxide [11]. Our conclusions are obtained by comparing the chemical activity of Au nano-structures anchored on off-stoichiometric defects on an oxide surface to the identical nano-structures on stoichiometric oxide surfaces. The investigated off-stoichiometric defects were either extra oxygen atoms or oxygen vacancies at the oxide surface. We show that the chemical activity of Au nano-structures on oxide supports can be enhanced significantly by the strong interaction between the Au nano-structure and the oxide support. We show that the defects interact strongly with the Au nano-structure, reducing the Au–Au bonding within the nano-structure, and forming chemically active Au sites. When the oxide surface is defect-free (stoichiometric), the interaction between Au and the oxide is minimal and Au behaves much like bulk Au. Our analysis also shows that there is no clear correlation between the nominal charge on Au and its chemical activity, and that the enhanced activity of supported Au can be related to the existence of strong covalent bonds between the off-stoichiometric defect on the oxide and the Au nano-structure.

The analysis of the formation energy of various model structures showed that the most thermodynamically stable structures are those with extra oxygen atoms between an Au nano-structure and the oxide support, bonded between the coordinatively unsaturated cations of the oxide and the Au nanostructure. We find that the Au/oxide interfaces with oxygen vacancies are significantly less stable and are not expected to be present in significant concentration at relevant reaction conditions.

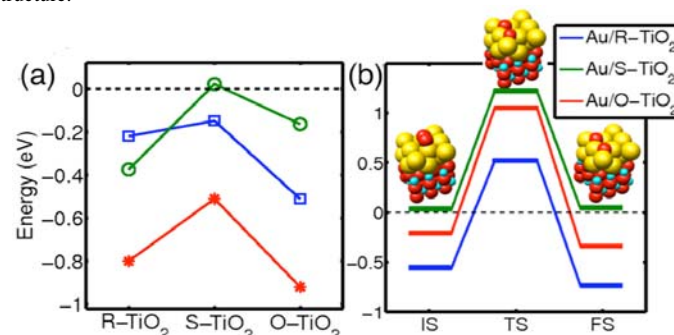
## Materials and Methods

We have employed Density Functional Theory (DFT). The oxide support was modeled using a two tri-layer oxide slab, which was allowed to relax in the presence of the oxide surface defects (oxygen vacancies or extra oxygen atoms). Three oxide terminations were entertained: reduced (R-TiO<sub>2</sub>), stoichiometric (S-TiO<sub>2</sub>), and oxidized (O-TiO<sub>2</sub>). The gold nanostructures were modeled by a continuous double monolayer (2ML Au) and a nanorod (Au-Rod), also two Au layers.

## Results and Discussion

Figure 1(a) shows calculated adsorption energy for oxygen and CO on the two model systems. From the calculated adsorption energies it can be seen that in the presence of oxide surface off-stoichiometric defects (either oxygen vacancies (R-TiO<sub>2</sub>) or extra oxygen

atoms (O-TiO<sub>2</sub>)) there is a general increase in the binding of the adsorbates. From calculated Bader charges we find that Au is electron rich, metallic, and electron poor in Au/R-TiO<sub>2</sub>, Au/S-TiO<sub>2</sub>, and Au/O-TiO<sub>2</sub> respectively, i.e., the charge does not correlate directly with the adsorption energies. Furthermore, the pathway of O<sub>2</sub> dissociation has also been calculated over the 2ML Au model (figure 1(b)), and similar oxide surface defect promotion is present. Through a simple analysis of the Au geometry and electronic structure (not shown) it is found that the presence of the oxide surface defects leads to a reduction of the Au–Au bonding within the Au nano-structure, which leads to more chemically active Au sites on the surface of the nano-structure.



**Figure 1.** (a) Adsorption energy (with respect to gas phase molecular species) of atomic oxygen on 2ML Au (green circles) and Au-Rod (blue squares) and the adsorption of CO on the 2ML Au (red asterisk). (b) O<sub>2</sub> dissociation barriers over 2ML Au.

## Significance

DFT calculations were employed to study the effect of oxide/metal interface on the chemical activity of the nano-structured metal clusters. We find that oxygen atoms at the oxide/metal interface are thermodynamically stable and that these might affect significantly the chemistry of the system. The role of interfacial oxygen atoms has not been explored previously.

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