Ag₅-induced stabilization of multiple surface polarons on perfect and reduced TiO₂ rutile (110)

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The recent advent of cutting-edge experimental techniques allows for a precise synthesis of subnanometer metal clusters composed by just a few atoms, opening new possibilities for subnanometer science. In this work, via first principles modeling, we show how the decoration of perfect and reduced TiO_2 surfaces with Ag_5 atomic clusters enables the stabilization of multiple surface polarons. Moreover, we predict that Ag_5 clusters are capable to promote defect-induced polarons transfer from subsurface to surface sites of reduced TiO_2 samples. For both planar and pyramidal Ag_5 clusters, and considering four different positions of bridging oxygen vacancies, we model up to fourteen polaronic structures, leading to one hundred and thirty four polaronic states. About 71% of these configurations encompasses coexisting surface polarons. The most stable states are associated with large inter-polarons distances ($> 7.5 \text{ \AA}$ on average), not only due to the repulsive interaction between trapped $\text{Ti}^{3+} 3d^1$ electrons, but also to the interference between their corresponding electronic polarizations clouds [López-Caballero *et al.*, J. Mat. Chem. A **8** (2020) 6842–6853]. As a result, the most stable ferromagnetic and anti-ferromagnetic arrangements are energetically quasi-degenerate. However, as the average inter-polarons distance decreases, most ($\geq 70\%$) of the polaronic configurations become ferromagnetic. The optical excitation of the midgap polaronic states with photon energy at the end of the visible causes the enlargement of the polaronic wave function over the surface layer. The ability of Ag_5 atomic clusters to stabilize multiple surface polarons and extend the optical response of TiO_2 surfaces towards the visible bears importance in improving their (photo-)catalytic properties, and illustrates the potential of this new generation of subnanometer-sized materials.

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I. INTRODUCTION

The very recent development of highly selective experimental techniques making possible the synthesis of subnanometer metal clusters is pushing our understanding of these, more ‘molecular’ than ‘metallic’, systems far beyond the present knowledge in materials science. Subnanometer metal clusters with sizes below 10–15 Å (i.e., approximately 100–150 atoms) have physical and chemical properties differing significantly from those of nanoparticles and bulk materials, due to quantum confinement effects.^{1,2} When the cluster size is reduced to a very small (less than 10) number of atoms, the *d*-band of the metal splits into a subnanometer-sized network of discrete molecule-like *d* orbitals, with the inter-connections having the length of a chemical bond (1–2 Å). The spatial structures of the molecular orbitals of these clusters make all the metal atoms cooperatively active and accessible, leading to the appearance of their novel properties and air-stability (see, e.g., Refs. 3–6 and references therein). Their possible applications range from visible-light photo-activation of semiconductor surfaces^{7,8} to innovative drugs for cancer therapies.⁹ For instance, new catalytic and optical properties are acquired by titanium dioxide (TiO₂) surfaces when decorated with the Cu₅ atomic cluster:^{8,10} The Cu₅ cluster shifts the absorption of sunlight towards visible light, where the sun emits most of its energy.⁸ The coated titanium dioxide stores the absorbed energy temporarily in the form of charge pairs, i.e., electrons and holes, in the direct vicinity of the surface, which is a perfect prerequisite for follow-up chemistry.¹¹

Seeking for further applications, we have recently modified the TiO₂ surface with a single atomic silver cluster Ag₅.⁶ In this way, we have found that Ag₅-modified TiO₂ surfaces are both visible-light photo-active materials, potential photocatalysts for CO₂ reduction, and capable of hosting surface polarons.⁶ As reported by Selloni and collaborators for various noble metal clusters on anatase TiO₂ surfaces, the charge transfer between the metal cluster and TiO₂ surface is at the very basis of the underlying mechanisms (see, e.g., Refs. 12,13). Moreover, we have also provided new relevant fundamental insights into a general polarization phenomenon accompanying the formation of surface polarons.⁶ This phenomenon has been manifested as a depopulation of titanium 3*d* orbitals in favor of oxygen 2*p* orbitals, as experimentally observed through X-ray absorption spectroscopy at the Ti *K*-edge and theoretically predicted by applying state-of-the-art computational modelling.⁶ In our picture, a surface polaron is visualized as a slow electron projecting a ‘shadow’ on its travelling way, causing not only nuclear motion (i.e., a structural distortion of the crystal lattice) but also electronic rearrangements which are manifested in a carrying ‘polarization cloud’.⁶

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Yet, there is a number of important open questions to be addressed, such as: (1) how Ag₅-induced surface polarons interfere with those formed due to surface defects such as bridging oxygen vacancies (referred to O-vacancy-induced) in reduced samples?; (2) could supported Ag₅ clusters promote O-vacancy-induced polarons transfer from subsurface regions?; (3) are co-adsorbed Ag₅ clusters capable of inducing the formation of multiple (co-existing) surface polarons?; (4) the couplings between Ag₅-induced surface polarons are ferromagnetic or anti-ferromagnetic?; (5) how these couplings and the stability of surface polarons depend on the inter-polarons distance, considering also the possible interference between the corresponding polarization clouds?.

To address these questions, we conduct an extended ab initio investigation considering perfect and reduced TiO₂ rutile (110) decorated with Ag₅ atomic clusters. For this purpose, we apply density functional theory (DFT) and an approach combining DFT with reduced density matrix theory. We have chosen a DFT-D3 *ansatz*^{14,15} on the basis of its excellent performance in describing the adsorption of subnanometer silver clusters on rutile TiO₂.⁷ For an appropriate determination of the electronic structure associated with polarons formation in TiO₂ surfaces,^{6,8,16} we employ the HSE06 hybrid functional of Heyd, Scuseria and Ernzerhof^{17,18} on top of the structures optimized via the DFT-D3 approach. We have also calculated the UV-Vis absorption response of the multiple polarons states by employing the reduced density matrix (RDM) theory within the Redfield approximation,¹⁹ combined with DFT calculations using the HSE06 functional. This combination of RDM and DFT, proposed by Micha and collaborators,^{20–22} has been successfully applied to silver^{6,7,23–25} and copper^{8,10} clusters on semiconductor TiO₂ and silicon surfaces.^{6–8,10,23–26}

This article is organized as follows. In Section II, we provide further details of the computational and theoretical approaches developed and applied in this work. Then, the results from our calculations are presented and discussed in Section III. This section is split into several subsections. The first subsection outlines the polaron concept and proves the performance of our approach by applying it to reduced TiO₂ rutile (110), in comparison with reported results. Next, we investigate the Ag₅-induced formation of multiple surface polarons, either by interacting with O-vacancy-induced polarons or by co-adsorption of Ag₅ clusters. Finally, section IV summarizes our main findings, presenting a practical perspective of their implications.

II. COMPUTATIONAL METHODS

A. Periodic calculations

Periodic electronic structure calculations are performed with the Vienna Ab initio Simulation Package (VASP 5.4.4),^{27,28} following a similar computational approach to that reported in previous works on Ag₅- and Cu₅-TiO₂(110) interactions.^{6,8,10} Specifically, structural optimizations and the calculation of interaction energies are carried out with the Perdew-Burke-Ernzerhof (PBE) density functional²⁹ and the Becke-Johnson (BJ) damping¹⁴ for the D3 dispersion correction. This combination is referred to as the PBE-D3(BJ) scheme. These calculations are carried out including spin polarization without imposing restrictions on the overall magnetic moment. The magnetic moments in converged calculations differed by less than 0.015 μ_B on average from the 'nominal' values (e.g., 2 μ_B for two polarons in ferromagnetic configurations).

In order to describe localized 3d-electrons on specific Ti cations, the corresponding Ti–O distances are initially elongated to mimic polaronic structures.³⁰ Next, the resulting structures are optimized with the Hubbard DFT+U term³¹ added and including spin-polarization. The value of U (4.2 eV) reported in previous studies on Cu₅-TiO₂(110) interactions is adopted.^{8,32} The optimized geometries obtained at the PBE+U/D3 level are used in final HSE06 calculations of the electronic structures. The HSE06 approach is applied using a HF/GGA mixing ratio of 25:75 with the screening parameter of 0.11 bohr,⁻¹ as recommended in Ref. 18. It provides a value of the direct band gap for rutile TiO₂(110) (ca. 3.3 eV), which is in a good agreement with the experimental observations. The HSE06 *ansatz* employed in final calculations of the orbitals (but not the adsorption energies or the optimized structures) did not include D3 corrections. It is clear that the inclusion of such dispersion contribution would modify the absolute values of the total energies but not the energy differences between the orbital levels neither the orbital shapes, which are the relevant magnitudes in both the electronic density of states (EDOS) and the UV-Vis spectra calculations.

Electron-ion interactions are described by the projector augmented-wave method,^{28,33} using PAW-PBE pseudo-potentials as implemented in the program. The electrons of the O(2s, 2p), C(2s, 2p), Ti(3s, 4s, 3p, 3d) and Ag(4d, 5s) orbitals are treated explicitly as valence electrons. A plane wave basis set with a kinetic energy cutoff of 700 eV is used. A Gaussian smearing of 0.05 eV is employed to account for partial orbital occupations. The Brillouin zone is sampled at the Γ

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point.³⁴ The convergence criterion is fixed to a value of 10^{-4} eV for the self-consistent electronic minimizations. All the atoms from the supercells are relaxed with a force threshold of 0.02 eV/Å.

Stoichiometric (perfect) TiO₂ rutile (110) is modeled via periodic slabs, using a 4×2 supercell (four TiO₂ trilayers giving ca. 13 Å slab width). The reduced surface is modeled by removing a single bridging oxygen anion from the slab. The adsorption of the Ag₅ clusters are assumed on one side of the slab, with 38 Å of vacuum above it. This large vacuum region ensures that the supercell is not interacting with its periodic images in the direction perpendicular to the surface. Using a larger 8×2 supercell model in structural optimizations, we have tested that the increase of the supercell size does not modify the polarons positions. The influence of the number of layers was analyzed in a previous study by Deskins et al.³⁵ using also a 4×2 supercell model but varying the corresponding slab thickness. It was shown that the decrease of the number of trilayers from nine to five leads to an underestimation of the stabilization energy of configurations bearing surface polarons by ca. 0.1 eV.³⁵ Hence, we can expect that the relative energies of surface polarons are underestimated, at least, by the same value (0.1 eV).

The adsorption energy of n Ag₅ clusters ($n = 1, 2$) on TiO₂ (perfect and reduced) surfaces is obtained as

$$E_{\text{ads}} = \{n E_{\text{Ag}_5/\text{TiO}_2(110)}\}_{(\text{min})} - \{n E_{\text{Ag}_5/\text{TiO}_2(110)}\}_{(\text{long-range})}$$

where $\{n E_{\text{Ag}_5/\text{TiO}_2(110)}\}$ denotes the total energy of the system, with n Ag₅ clusters at the minimum energy position (referred to us as ‘min’) or at a distant position from the surface so that the cluster-surface interaction becomes negligible (referred to us as “long-range”).

The average inter-polarons distance (referred to as $\langle d_{pp} \rangle$) is calculated as follows:

$$\langle d_{pp} \rangle = \sum_{ij}^{N_{pol}} \frac{d_{i-j}}{N_{pol}} \quad (1)$$

where N_{pol} is the number of polarons, and d_{i-j} stands from the distance between the i -th and j -th polarons. The periodic images are considered in this definition as well. The average distance between the polarons and either the vacancy or the central atoms of two adsorbed silver clusters is estimated in a similar way.

B. Reduced density matrix treatment

UV-Vis absorption spectra are calculated using the computational approach previously applied to the Cu₅- and Ag₅-TiO₂(110) systems in Refs. 8 and 6. The relaxation processes involved are

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described by the reduced density matrix (RDM) approach in the Redfield approximation,¹⁹ based on orbitals taken from calculations employing the HSE06 hybrid functional. This combined RDM-DFT treatment developed by Micha and Kilin^{20,21} is already a well-established tool in describing the optical spectra of subnanometer-sized metal clusters adsorbed on semiconductor surfaces³⁶ (see, e.g., Refs. 7,23–25,37).

Very briefly, in the presence of a monochromatic electromagnetic field $\mathcal{E}$ of frequency Ω , the evolution equation for the reduced density ρ in the Schrödinger picture takes the form

$$\begin{aligned}\dot{\rho}_{jk} &= -\frac{i}{\hbar} \sum_l (F_{jl} \rho_{lk} - \rho_{jl} F_{lk}) + \sum_{l,m} R_{jklm} \rho_{lm} \\ \hat{F} &= \hat{F}^{KS} - \hat{\mathbf{D}} \cdot \mathcal{E}(t) \\ \mathcal{E}(t) &= \mathcal{E}_0 (e^{i\Omega t} + e^{-i\Omega t})\end{aligned}$$

where $\hat{F}^{KS}$ denotes the effective Kohn-Sham Hamiltonian (the indices refer to its representation in the Kohn-Sham basis set), with $\hat{\mathbf{D}}$ as the electric dipole moment operator, and R_{jklm} as the Redfield coefficients, i.e., the Kohn-Sham components of the relaxation tensor. The latter are defined in Ref. 19, and are implemented as described in Ref. 20.

Within the Redfield approximation, the relaxation tensor embodies not only fast electronic dissipation due to electronic fluctuations in the medium, but also the relatively slow relaxation due to vibrations of the atomic lattice. It is convenient to perform a coordinate transformation into a rotating frame accounting for the electromagnetic field oscillation. This is described via the equations

$$\begin{aligned}\tilde{\rho}_{ij}(t) &= \rho_{ij}(t) \exp(i\Omega t), \varepsilon_i > \varepsilon_j \\ \tilde{\rho}_{ij}(t) &= \rho_{ij}(t) \exp(-i\Omega t), \varepsilon_i < \varepsilon_j \\ \tilde{\rho}_{ii}(t) &= \rho_{ii}(t)\end{aligned}$$

where ε_i is the energy of the i -th Kohn-Sham orbital. Time averaging over the fast terms in the equation of motion for the RDM yields

$$\begin{aligned}\tilde{\rho}_{jj}^{SS} &= \Gamma_j^{-1} \sum_{k=0}^{\text{HOMO}} g_{jk}(\Omega), \quad j \geq \text{LUMO} \\ \tilde{\rho}_{jj}^{SS} &= 1 - \Gamma_j^{-1} \sum_{k=\text{LUMO}}^{\infty} g_{jk}(\Omega), \quad j \leq \text{HOMO}\end{aligned}$$

as stationary-state solutions for the diagonal elements.²⁰ In it, HOMO and LUMO denote the lowest-energy unoccupied and the highest-energy occupied molecular orbital, respectively. Γ_j is a

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depopulation rate, and the sum terms g_{jk} are given by

$$g_{jk}(\Omega) = \frac{\gamma \Omega_{jk}}{\gamma^2 + \Delta_{jk}(\Omega)^2},$$

where γ denotes the decoherence rate, Ω_{jk} is the Rabi frequencies given by $\Omega_{jk} = -\mathbf{D}_{jk} \cdot \mathcal{E}_0 / \hbar$, with $\Delta_{jk}(\Omega) = \Omega - (\epsilon_j - \epsilon_k)$ as detunings. The diagonal elements provide the populations of the KS orbitals. The population relaxation rate $\hbar\Gamma$ and the decoherence rate $\hbar\gamma$ are kept fixed to values of 0.15 meV and 150 meV (27 ps and 27 fs). These values have been chosen according to known rates for phonon decay and electronic density excitations in semiconductors (see, e.g., Ref. 38).

In terms of the stationary populations, the absorbance is given by^{7,24,25,39,40}

$$\begin{aligned} \bar{\alpha}(\Omega) = & \sum_{j=0}^{\text{HOMO}} \sum_{k=\text{LUMO}}^{\infty} \bar{f}_{jk} (\tilde{\rho}_{jj}^{SS} - \tilde{\rho}_{kk}^{SS}) \\ & \times \frac{1}{\pi} \frac{\hbar\gamma/2}{(\hbar\Delta_{jk})^2 + (\hbar\gamma/2)^2} \end{aligned}$$

where $\bar{f}_{jk}$ is an oscillator strength per active electron.⁴¹ The solar flux absorption spectrum is then expressed as

$$F(\hbar\Omega) = \bar{\alpha}(\Omega) F_{\text{solar}}(\hbar\Omega) \hbar\Omega,$$

where the solar flux is approximated by the black body flux distribution, normalized to an incident photon flux of 1 kW/m²,

$$F_{\text{solar}}(\hbar\Omega) = \frac{(\hbar\Omega)^3}{\pi^3 \hbar^3 c^3} \frac{C_T}{\exp(\hbar\Omega/k_B T) - 1},$$

with C_T the flux normalization constant and the temperature T set to 5800 K.

III. RESULTS AND DISCUSSION

A. Polaron concept: small polarons formation on reduced TiO₂ rutile (110)

The polaron concept characterizes an electron moving in a dielectric crystal.⁴² Its formation is a well-known and fundamental phenomenon in transition metal oxides. In particular, Selloni and collaborators have contributed very significantly to the fundamental understanding of polarons formation in TiO₂ (both rutile and anatase) surfaces (see, e.g., Refs. 43–45). Typical defects of rutile TiO₂ surfaces such as bridging oxygen vacancies⁴⁶ lead to two excess electrons. The latter becomes self-trapped in Ti³⁺ $3d^1$ states and couple to lattice distortions forming small polarons,⁴⁷ as illustrated in panel (a) of Figure 1. The existence of intrinsic small polarons as self-trapped electrons in rutile TiO₂ (i.e., forming stable Ti³⁺ $3d^1$ states) has been both

FIG. 1. Polarons hosted on reduced TiO_2 rutile (110). (a) Polaronic $\text{Ti}^{3+} 3d^1$ states induced by the presence of a bridging oxygen vacancy on TiO_2 rutile (110). The left-hand structure is the most stable, holding two subsurface polarons. (b) Picture illustrating the lattice distortions accompanying the polarons formation. The positions of the Ti atoms where the polarons are localized (referred to us as Ti^{3+}) are represented with yellow spheres. Red and blue spheres indicate the positions of oxygen anions and titanium cations, respectively.

theoretically predicted^{44,45,48–53} and experimentally confirmed.^{54–56} Agreeing well with previous studies,^{53,56,57} we find that subsurface positions of polarons are favored on the rutile surface. For instance, notice that the energies of the left- and right-hand structures shown in panel (a) of Figure 1 differ by ca. 0.36 eV. Consistently, a previous work⁵⁷ reported that the energies of configurations bearing two surface polarons were 0.28–0.44 eV higher in energy than the most stable one with two subsurface polarons. Actually, as predicted from first principles molecular dynamics calculations at experimental conditions, the polarons stay most of the time (ca. 75%) at the subsurface layer but also hop to the top-most layer.⁵⁶ Accordingly, as shown in panel (a) of Supplementary Figure 1, the energy of the configuration featuring polarons at both subsurface and surface layers differs very little (0.02 eV) from that of the most stable state. The two structures featuring surface polarons were also reported in a previous study by Deskins et al. (labelled as 3-1' and 1-3 in Ref. 35), but higher relative energies were estimated (0.02 vs. 0.33 eV and 0.36 vs. 0.87 eV). We attribute such differences to the dispersion forces as they are expected to reduce the so-name ‘structural cost’ (as defined in Ref. 53) in surface polarons formation.

In order to screen the self-trapped $\text{Ti}^{3+} 3d^1$ electrons, the O^{2-} anions depart from their equilibrium positions, as indicated with red arrows in panel (b) of Figure 1. Notice that the Ti–O bond lengths are larger (by about 0.1 Å) when the oxygen anions are bonded to the Ti cation hosting

TABLE I. Adsorption energies (in eV) of one Ag₅ cluster on reduced and perfect TiO₂ rutile (110), with the latter including co-adsorption of a second Ag₅ cluster. For comparison purposes, the adsorption energy for a single cluster is -4.53 eV (-3.03 eV) for the pyramidal-shaped (trapezoidal-shaped) isomer.⁶

Ag ₅ /reduced TiO ₂ (pyramidal)	-4.51
Ag ₅ /reduced TiO ₂ (trapezoidal)	-3.21
Ag ₅ (coadsorption)/perfect TiO ₂ (pyramidal)	-4.34
Ag ₅ (coadsorption)/perfect TiO ₂ (trapezoidal)	-3.00

the polaron (shown with a yellow sphere). Similar values of Ti–O bond elongations have been reported for both anatase⁵⁸ and rutile.⁵⁹ This lattice distortion (known as the phonon cloud) always accompanies the polaron formation wherever it settles down.⁶ The presence of multiple polarons is also revealed at the electronic density of states (EDOS) (see Supplementary Figure 2) through the appearance of a single midgap peak arising from almost degenerate energy levels of the two polarons. In accord with previous determinations (see, e.g., Ref. 60), it is located at about 1 eV below the conduction band. Hence, the overall agreement with previous studies of the polarons formed on rutile TiO₂(110) allows us to further confirm the validity of our theoretical approach to characterize Ag₅-induced surface polarons in the next subsections.

B. Ag₅-induced stabilization of surface polarons on reduced TiO₂ rutile (110)

When supporting a single Ag₅ atomic cluster onto the reduced TiO₂(110) surface, the planar trapezoidal- and pyramidal-shaped structures shown in Figure 2 are both predicted to be highly stable (see Table I). As for the case of Ag₅ adsorption on stoichiometric TiO₂,⁶ the pyramidal-shaped isomer, lying flat over the surface, is found to be the most stable structure with an adsorption energy of -4.51 eV, differing by ca. 1.3 eV by that of the trapezoidal isomer (see also Section 2 of Supplementary Material). As can be observed in Table I, the adsorption energies are only slightly affected by the presence of an oxygen vacancy. As mentioned above, an oxygen vacancy of reduced TiO₂ rutile (110) induces the formation of two small polarons mostly located at a subsurface layer.⁵⁶ The further modification of the surface via decoration with the open-shell Ag₅ cluster leads to the appearance of a third polaron through the donation of its unpaired electron to the TiO₂ surface. The donated electron becomes localized in one specific 3d orbital lying at the surface, centered at one Ti atom in the nearby of both trapezoidal and pyramidal-shaped Ag₅

FIG. 2. Panels a, b, and c (d, e, and f) correspond to the trapezoidal-shaped (pyramidal-shaped) Ag_5 isomer. Upper panels (a and d): Structures for trapezoidal- and pyramidal-shaped Ag_5 clusters adsorbed on reduced TiO_2 rutile (110), bearing an oxygen vacancy. The different positions considered for the oxygen vacancy are also indicated. Red, blue, and gray spheres stand for oxygen, titanium, and silver atoms, respectively. Middle panels (b and e): energy difference between a given polaronic structure and the most stable configuration (ΔE) versus the average inter-polarons distance (see also Tables 1–8 of the Supplementary Material). The oxygen vacancy positions of the polaronic configurations are indicated with different colors. Bottom panels (c and f): an enlarged view of the graphics shown at the middle panels. The two most stable structures are also shown, with the Ti^{3+} atoms hosting the polarons marked in yellow color. The labels 's0', 's1' and 's2' stand for the surface and subsurface (first and second layer) locations of the polarons. The values of the adsorption energies are also indicated.

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isomers, as illustrated in panels (c) and (f) of Figure 1. The most relevant frontier orbitals are shown in Figure 3, with the $\text{Ti}^{3+} 3d^1$ electrons characterizing the single occupied (referred to as SOMOs) orbitals.

Considering the four different positions of the bridging oxygen vacancies shown in the upper panels of Figure 2, we have sampled over seventy polaronic configurations. The initial structures were created by enlarging $\text{Ti}^*\text{-O}$ bond distances, with Ti^* denoting the specific sites where the polarons are assumed to be hosted. These calculations were performed by applying the PBE+U/D3(BJ) approach. Panels (b) and (e) of Figure 2 show the relative stability of a given configuration (with the most stable structure as the reference) as a function of the average inter-polarons distance. For both trapezoidal- and pyramidal-shaped isomers, we find that the stability of a given structure is higher when the polarons are located further away from each other. This is due to both the repulsion between the trapped $\text{Ti}^{3+} 3d^1$ electrons and the interference between the associated polarization clouds.⁶ As reported in Ref. 6, the polarization phenomenon accompanies the formation of surface polarons, modifying the electronic structure in their neighborhood: self-trapped $\text{Ti}^{3+} 3d^1$ electrons repel near oxygen anions and attracts near titanium cations which, in turn, affects their electronic structure, causing the transfer of electronic charge from Ti^{4+} cations to O^{2-} anions. This surface polarons property favors large inter-polarons distances as the interference between the polarization clouds associated with different polarons is better avoided. Yet, there are a number of exceptions to this ‘rule of thumb’ when the polarons are located on titanium atoms next to the bridging oxygen vacancies (see Supplementary Section II). In fact, the interaction between the vacancy and the polaron is attractive. As comprehensively reported by Reticcioli et al.,⁵³ the O-vacancy-polaron distance between a polaron is another important factor determining the stability of a given polaronic structure over the bare $\text{TiO}_2(110)$ surface. In order to better visualize its influence for the Ag_5 -decorated reduced surface, Supplementary Figure 5 presents the relative energies vs. the average polaron-vacancy distance. It clearly illustrates an enhanced stability as the polaron-vacancy distance decreases in a quasi-linear dependence for the lowest-energy states.

It is worth stressing that structures with two surface polarons are more stable than those featuring just one surface polaron despite of the larger inter-polarons distance for the former. This finding points out that Ag_5 clusters are capable not only of inducing their ‘own’ surface polarons via transfer of their unpaired electrons but also of promoting polarons transfer from subsurface to surface sites (see also Supplementary Section 2). As previously reported for CO as the adsorbate,⁶¹

the favored surface location is caused by the attractive interaction of Ag_5 clusters with surface polarons.

From our extended sampling of polaronic configurations, the repulsion that each polaron exerts on each other is clearly apparent and especially noticeable at short distances. For this reason, when examining the ferromagnetism featured by the different configurations, the associated inter-polarons distances should be accounted for. The quasi-degeneration of polaronic configurations is clearly apparent when the average inter-polarons distance is large (more than $3.5 \text{ \AA}$): 45% (55%) of the polaronic configurations are anti-ferromagnetic (ferromagnetic). However, at short distances, below $3.5 \text{ \AA}$, the ferromagnetic couplings dominate the whole scenario so that 70% of the polaronic configurations become ferromagnetic. Assuming a Maxwell-Boltzmann distribution, the polaronic states encompassing short inter-polarons distances become accessible upon increasing the temperature above 490 K.

1. Frontier orbitals, electronic density of states, and UV-Vis spectra

FIG. 3. Picture showing iso-surfaces of the frontier ‘singly occupied’ molecular orbitals (SOMO, SOMO–1 and SOMO–2) and the highest-energy and second ‘doubly occupied’ molecular orbitals (HOMO and HOMO–1) for the most stable structures of Ag_5 -modified reduced TiO_2 rutile (110). Upper panel: planar trapezoidal-shaped isomer. Bottom panel: pyramidal-shaped isomer.

Having analyzed the Ag_5 -modified reduced $\text{TiO}_2(110)$ surface in the ground electronic state, we focus now on its optical excitations. Figure 4 (bottom panel) shows the photo-absorption spectra of the Ag_5 -modified reduced TiO_2 surface, with the Ag_5 cluster located at the most stable

FIG. 4. Ag_5 -lying down- TiO_2 + oxygen vacancy system. Upper panel: Electronic Density Of States (EDOS). The zero of energy corresponds to the Fermi level, defined here as the lowest unoccupied level. The energy positions of the HOMO, HOMO–1, SOMOs and LUMO orbitals are indicated with arrows of different colors. The projected density of states onto $\text{O}(2p)$, $\text{Ti}(3d)$, and orbitals centered at the Ag_5 cluster is also shown. Bottom panel: photo-adsorption spectra. The insets present iso-density surfaces of the orbitals involved in the photo-excitation processes marked in the photo-absorption spectrum.

(i.e., pyramidal-shaped) arrangement. For the sake of clarity, the corresponding electronic density of states (EDOS) is shown in the upper panel of Figure 4 (see also Figure 3 for a picture of the most relevant frontier orbitals). As can be observed in the EDOS, the localized Ti^{3+} states (characterizing the SOMOs orbitals) appear 1 – 1.5 eV below the bottom conduction band. Similar values have been reported by Di Valentin et al. for $\text{Ti}(5f) 3d^1$ states in hydroxylated and reduced rutile $\text{TiO}_2(110)$ surfaces.⁴⁵ A more detailed description of the frontier orbitals and EDOS spectra is presented in Supplementary Section 2, extending the analysis to the trapezoidal-shaped isomer.

Moving to the photo-absorption process, the first thing to notice from Figure 4 is that the excitation of the $\text{Ti}^{3+} 3d^1$ electrons (located at the SOMOs orbitals) with a photon energy at the end

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of the visible region (marked with yellow, orange, and green arrows) leads to their spreading over the top-most layer of the the TiO_2 surface. This behavior can be explained as follows: the hole generated due to the depopulation of the titanium $3d$ orbitals when a surface polaron is created becomes filled with the polaron becomes photo-excited. The same phenomenon has been reported for the case when the Ag_5 atomic cluster is supported on stoichiometric TiO_2 rutile (110).⁶ However, notice that the polaron charge spreads less efficiently on reduced TiO_2 rutile and that oxygen vacancies hinder somewhat the hole filling process itself. The transfer of localized $3d^1$ electrons to the conduction band via visible light excitation has been also experimentally observed in reduced TiO_2 nanoparticles.⁶²

In contrast to the bare TiO_2 surface, Figure 4 (bottom panel) shows that the Ag_5 -modified reduced surface absorbs at the visible region with the most intense peak located at about 2.3 eV. This feature has been both theoretically predicted^{6,7} and experimentally confirmed.⁶ The Ag_5 modification is also responsible for the increase of the absorption in the UV region. The most intense peak (marked with a red arrow) involves a single electron ‘jumping’ from $5s$ orbitals centered at the Ag_5 cluster (the HOMO orbital), to the conduction band, leaving a long-lived (localized) ‘hole’ at the cluster. The density of the acceptor state (i.e., the LUMO+223 orbital) extends all along the subsurface layers of the TiO_2 slab, bearing a depleted (empty) region at the cluster-surface interface, and thus hindering the electron-hole recombination. Since the latter process is a key factor limiting the photo-catalytic activity of the unmodified TiO_2 surface, the Ag_5 -induced ability to separate charge-carriers is expected to improve the visible photocatalytic properties of the modified material (see also Refs. 6,8).

C. Interaction of Ag_5 -induced surface polarons on perfect TiO_2 rutile (110)

New polaronic structures have been determined when supporting two Ag_5 clusters over stoichiometric TiO_2 rutile (110). Each Ag_5 atomic cluster induces the formation of one surface polaron, allowing us to analyze the inter-polarons interaction. Considering both planar trapezoidal and pyramidal-shaped Ag_5 structures, the relative positions of the two Ag_5 clusters have been varied to create a total of six different structures. For each structure, we modeled up to thirteen polaronic configurations, with the follow-up PBE+U/D3(BJ) calculations leading to a total of fifty-nine polaronic states. Panels (b) and (e) of Figure 5 show the relative stability of a given configuration (with the most stable structure as the reference energy) as a function of the inter-polarons distance.

FIG. 5. Panels a, b, and c (d, e, and f) correspond to the trapezoidal-shaped (pyramidal-shaped) Ag_5 isomer. Upper panels (a and d): Structures for two trapezoidal- and pyramidal-shaped Ag_5 clusters supported on TiO_2 rutile (110). Blue, red, and gray spheres stand for oxygen, titanium, and silver atoms, respectively. Middle panels (b and e): difference between the adsorption energy of a given polaronic structure and that of the most stable configuration (ΔE) versus the inter-polarons distance (see also Tables 9–14 of the Supplementary Material). Energy differences of configurations featuring different relative positions are indicated with different colors (see Supplementary Section 3 for the details). Bottom panels (c and f): an enlarged view of the graphics presented at the middle panels. The two most stable structures are also shown, with the Ti^{3+} atoms hosting the polarons marked in yellow color. The labels 's0' stand for surface locations of the polarons. The values of the adsorption energies are also indicated.

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As for a single cluster,⁶ the pyramidal-shaped structure is more stable also when two clusters are supported on TiO₂ rutile (110) (see Table I and Supplementary Section 3 for details). As can be observed in Table I, coadsorption effects make the adsorption energies smaller (ca. 0.2 eV for the most stable isomer).

Similarly to the case of Ag₅ supported over reduced TiO₂ rutile (110), the analysis of the results presented in Figure 5 for the trapezoidal isomer shows that the stability of a given configuration is higher as the inter-polarons distance increases. Still, despite of having associated smaller inter-polarons distances in some cases, configurations featuring two surface polarons are more stable than those bearing just one surface polaron, making evident the capability of the Ag₅ clusters to promote surface polarons formation. Interestingly, polaronic structures having one Ti atom in between two surface polarons are more stable than those with an oxygen atom instead, indicating that Ti atoms better screen the polaronic charges from each other. Similarly, when Ag₅ clusters are lying flat on the TiO₂ surface, the further the polarons locate, the higher the stability of the corresponding structure. Yet, as for the trapezoidal-shaped Ag₅ isomer, the exceptions make even more evident the ability of Ag₅ clusters to stabilize surface polarons (see Supplementary Section 3 for details).

Altogether, our results for two Ag₅ clusters supported on TiO₂ highlight the role of the repulsion between trapped as Ti³⁺ 3d¹ electrons in favoring rather large inter-polarons distances for the most stable structures. However, as for a single Ag₅ cluster adsorbed on reduced TiO₂ rutile (110), the polarization phenomenon accompanying polarons formation is also partly responsible: The Ti³⁺ 3d¹ electrons attract Ti⁴⁺ cations and repels O²⁻ anions located at their nearby. As a result, there is transfer of electronic charge from Ti⁴⁺ 3d orbitals to O²⁻ 2p orbitals and an average depopulation of 3d orbitals has been found. Consequently, as illustrated in Supplementary Figure 12, oxygen anions thus hold excess of electronic charge, which increase when two polarons are located in adjacent positions and destabilizes the corresponding polaronic configuration. For the case of free-Ag₅ TiO₂ surfaces, it has been reported that the polaronic charge itself is located not only on the 'nominal' Ti³⁺ site, but also shared with surrounding atoms.^{53,63,64} This would explain the increase of excess charge on the oxygen anions when the polarons are settled in adjacent positions over the bare TiO₂(110) surface.

Another factor influencing the stability of a given structure is the average distance between the polarons and the central atoms of the silver clusters. Thus, a 'central position' allows for a more attractive cluster-polaron interaction than the polaron location at one end side of the clusters (see

Supplementary Section 3). In order to illustrate it, Supplementary Figure 11 presents the average distance between the polarons and the central atoms for the trapezoidal-shaped Ag_5 isomer: it can be observed that shorter distances favour the stability of the polaronic structures, which tend to be less stable as the polaron- Ag_5 distance increases.

Large inter-polarons distances on the average result in the weight of anti-ferromagnetic and ferromagnetic polaronic configurations being almost the same. However, considering surface polarons located at distances shorter than 3.5 Å from each other, 75% of the configurations are ferromagnetic (70% for the case of the reduced sample). Hence, we can conclude that the dominant coupling is ferromagnetic. Accurate estimations of these couplings from the energy splittings between ferromagnetic and antiferromagnetic states will involve future research, considering larger supercell models and both constrained and unconstrained magnetic moment calculations.

1. Frontier orbitals, electronic density of states, and UV-Vis photoabsorption spectra

FIG. 6. Isosurfaces of the frontier ‘singly occupied’ molecular orbitals (SOMO and SOMO–1) and the highest-energy and second “doubly occupied” molecular orbitals (HOMO and HOMO–1) for the most stable structures of the $2\text{Ag}_5\text{-TiO}_2$ system, considering both trapezoidal-shaped (upper panel) and pyramidal-like (bottom panel) structures.

As mentioned above, the modification of TiO_2 rutile (110) with two Ag_5 clusters leads to the formation of two polarons, holding surface positions. The polaronic $\text{Ti}^{3+} 3d^1$ states characterize the SOMO–1 and SOMO orbitals shown in Figure 6. For the trapezoidal-shaped Ag_5 isomer, one polaron is located just in front of one Ag_5 cluster. The second polaron is also at the surface, but

hosted in a different row (see also Supplementary Figure 10). For the case of two Ag_5 clusters lying flat over the surface, both polarons are located below the clusters, but shifted from the position of their central Ag atoms.

FIG. 7. Electronic Density Of States (EDOS) and UV-Vis photo-absorption spectrum of the 2Ag_5 -lying down- TiO_2 system (corresponding to the most stable polaronic state). Upper panel: Electronic Density Of States. The zero of energy corresponds to the Fermi level, defined here as the lowest unoccupied level. The projected density of states onto $\text{O}(2p)$, $\text{Ti}(3d)$, and orbitals centered at the Ag_5 clusters is also shown. The energy positions of the HOMO, HOMO-1, SOMOs and LUMO orbitals are indicated with arrows of different colors. Bottom panel: photo-adsorption UV-Vis spectra. The insets show iso-density surfaces of the orbitals involved in the photo-excitation processes that have been indicated with arrows.

As can be observed from the electronic density of states (EDOS) of the system composed by two Ag_5 clusters lying flat over the TiO_2 surface (upper panel of Figure 7), the formation of two polarons as two $\text{Ti}^{3+} 3d^1$ states with very similar energies (i.e., the SOMOs orbitals), cause the appearance of two close peaks located 1–1.5 eV below the conduction band (see Supplementary Figure 13 for the EDOS of the trapezoidal-shaped Ag_5 isomer). The peaks associated to

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the HOMO and HOMO–1 orbitals, bearing also very close energies, are located in between the SOMOs and the LUMO orbitals at the EDOS spectra. Notice from the photo-absorption UV-Vis spectrum (bottom panel of Figure 7) that the excitation of the polaronic $\text{Ti}^{3+} 3d^1$ states with photon energies at the visible (about 3–3.15 eV) leads to the enlargement of the polaronic wave function over the top-most layer of the TiO_2 surface (see also Supplementary Section 3 for details), as previously discussed for a single Ag_5 cluster on reduced TiO_2 . The improvement of the optical response of the material at the visible region is also very clear: The highest absorption peak is located at ca. 2.4 eV, involving transitions from the highest-energy HOMOs orbitals, centered at the Ag_5 cluster (see Figure 6), to delocalized states in the conduction band formed by $3d(\text{Ti})$ atomic orbitals (the LUMO+99 orbital, see the insets at the bottom panel of Figure 7).

IV. CONCLUSIONS

In this work, we have shown that the TiO_2 surface modification with subnanometer silver clusters⁶ serves to induce the formation of multiple surface polarons via the donation of the clusters unpaired electrons as well as the promotion of polarons transfer from the subsurface to surface sites. From a practical perspective, this capability to stabilize multiple surface polarons has interest in building the so-called *polaronic 2D materials*,⁶⁵ favoring a more efficient charge transfer to adsorbed catalytic species, and thus improving the catalytic properties of the material. For instance, it has been suggested that surface polarons could be employed to solve one of the major problems of water splitting (i.e., the reduction of overpotentials in the oxygen evolution reaction).⁶⁶

Due to both the repulsion between the polarons as trapped $\text{Ti}^{3+} 3d^1$ electrons and the interference between the corresponding polarization clouds,⁶ the average inter-polarons distances are larger for the most stable states. As a result, ferromagnetic and anti-ferromagnetic states are energetically almost degenerate. However, ferromagnetic states become dominant in polaronic structures implying relatively short inter-polarons distances ($< 3.5 \text{ \AA}$) which could be populated, e.g., upon increasing the temperature, combined with the application of (strong) magnetic fields. The possibility of controlling the ferromagnetism of these polaronic 2D materials might become relevant in future studies of new quantum technologies but further research is necessary.

As theoretically predicted^{6,7} and experimentally observed,⁶ we confirm that Ag_5 clusters either in perfect or reduced samples improve the optical response of the material by extending its absorption towards the visible region and augmenting it in the UV. Thus, the photo-excitation of

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Ag₅-induced surface polarons with photon energy at the end of the visible leads to the enlargement of the polaron wave function and formation of large surface polarons. It is also worth stressing that our results are consistent with the polarization phenomenon of surface polarons.⁶ In the experiment, the intensity of the associated X-ray peak was only significant on Ag₅-modified TiO₂ samples.⁶ This can be explained, as shown in this work, due to the fact that Ag₅ clusters favor multiple surface polarons formation. Moreover, the coupling with light is expected to be more effective in the silver-modified material.

This work along with our very recent studies on subnanometer-sized metal (silver and copper) clusters^{5–8,10} confirm the great potential that lies in this new generations of materials, not only from the application perspective but also from a fundamental view, as demonstrated through the theoretical prediction and experimental demonstration of a surface polaron property.⁶ All our findings have been issued from extended state-of-the-art first principles calculations and not from theoretical models, pointing out the key role of first principles tools in shaping the modern field of subnanometer science.

SUPPLEMENTARY MATERIAL

See Supplementary Material for Supplementary Figures, including additional details, as indicated in Section III. Supplementary Tables 1–14 summarize the results found for all polaronic structures.

DEDICATION

This paper is dedicated to the memory of Professor Carmela Valdemoro (1932–2017), who worked at the Spanish Research Council (in the Institute of Materials Science and the Institute of Fundamental Physics) for more than 25 years. Prof. Valdemoro was a pioneer of reduced density matrices-based methodologies for electronic structure studies. She was an enthusiastic, creative, generous, and encouraging researcher, having inspired generations of scientists.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Ag₅-up-TiO₂ + oxygen vacancy

Ag₅-lying down-TiO₂ + oxygen vacancy

Ag₅-up-TiO₂ + oxygen vacancy

Ag₅-lying down-TiO₂ + oxygen vacancy

2Ag₅-up-TiO₂

(a)

(b)

2Ag₅-lying down-TiO₂

(d)

(e)

(c)

(f)

2Ag₅-up-TiO₂

SOMO -1

SOMO

HOMO -1

HOMO

2Ag₅-lying down-TiO₂

SOMO -1

SOMO

HOMO -1

HOMO