Exploring the properties of Ag₅–TiO₂ interfaces: stable surface polaron formation, UV-Vis optical response, and CO₂ photoactivation†

Patricia López-Caballero, José M. Ramallo-López, Lisandro J. Giovanetti, David Buceta, Salvador Miret-Artés, M. Arturo López-Quintela and Marí Salvador Miret-Artés

Using a combination of first-principles modelling, X-ray absorption spectroscopy, and diffuse reflectance spectroscopy measurements, we explore the properties of Ag₅-modified TiO₂ surfaces. A general electron polarization phenomenon associated with surface polarons on TiO₂ has been revealed theoretically and confirmed experimentally. First, the Ag₅ cluster donates an electron to TiO₂, leading to the formation of polaronic Ti³⁺ 3d¹ states on the rutile TiO₂(110) surface. The analysis of polarization effects in the nearby electronic structure accompanying the polaron formation is confirmed with X-ray absorption spectroscopy measurements at the Ti K-edge of TiO₂ nanoparticles. Next, the UV-Vis optical absorption spectrum of the polaronic state is also computationally modelled and an enlargement of the polaron wavefunction is predicted. Moreover, we find an overall improvement of the UV-Vis optical response of the material through diffuse reflectance spectroscopy measurements. Finally, we predict that charge-transfer processes at the Ag₅–TiO₂ interface triggered by solar photons might allow for a photoinduced activation of CO₂ by sunlight.

1 Introduction

Highly stable metal clusters of subnanometer size, as required in industrial applications, have recently emerged as a new generation of catalysts and photocatalysts with fascinating properties arising from their molecule-like electronic structures. As opposed to metal nanoparticles in the visible region, these ‘atomic’ or sub-nanometer-sized clusters neither sustain their metallicity, nor show their plasmonic behaviour. Instead, the presence of a molecule-like HOMO–LUMO gap drastically transforms their chemical and physical properties, thus creating innovative materials for applications including luminescence, sensing, therapeutics, energy conversion, catalysis, and electrochemistry. Nowadays, these so-called atomic quantum clusters (AQCs) can be synthesized by kinetic control using electrochemical methods, showing an exceptional chemical and thermo-dynamical stability in solution over the whole pH range. As discussed in ref. 9, high monodispersity of synthesized AQCs (e.g., Cu₅) has been achieved since the method of cluster synthesis is extremely size-selective. Moreover, the air stability of AQCs (e.g., Cu₅) with respect to oxidation up to a temperature of 150 °C has been experimentally observed. The resistance of Cu₅ clusters against an irreversible oxidation by a single O₂ molecule has been explained in theoretical studies.

It is well known that new catalytic and optical properties with technological projections are acquired by certain materials when modified with AQCs. The TiO₂ surface has been previously selected as the AQC support due to its abundance, non-toxicity, biological inertness, and chemical stability, being one of the most popular materials for (photo-)catalytic applications and solar energy conversion. However, its large band-gap (3.2 eV) makes ultraviolet irradiation necessary to trigger photocatalytic reactions. The UV part is less than 8% of the solar radiation so that the reaction rate divided by the photon flux is typically less than 10% for TiO₂-based photocatalysts. Several techniques have been developed to extend the photoactivity of TiO₂ to the visible region, most of which involve the direct modification of the electronic structure of the bulk. Very recently, in a joint theoretical–experimental study, we have proposed an alternative technique relying on the deposition of a single monolayer of Cu₅ clusters. It takes advantage of the slightly different electronic structure at the phase boundary and the ability to create electron–hole pairs close to the surface. As
a result, much more energy can be harvested from sunlight, and the coated titanium dioxide stores this energy temporarily in the form of charge pairs, electrons and holes, which is a perfect prerequisite to follow-up chemistry. Moreover, a very recent theoretical study\(^{19}\) has indicated that TiO\(_2\)-supported Cu\(_5\) clusters might allow CO\(_2\) activation through sunlight, as well as a spontaneous decomposition, leading to CO desorption.

AQCs made of a few silver atoms seem to display better chemical and physical properties. The stability of Ag\(_n\) clusters \((n \leq 5)\) on the rutile surface has also been theoretically analysed,\(^{28}\) predicting an enhanced light absorbance intensity of the material upon their deposition, as well as the appearance of secondary broad peaks with positions depending on the size and shape of the supported clusters. In particular, intense peaks have been identified in the visible region of the spectrum for the specific case of the Ag\(_5\) AQCs.\(^{28}\) In this work, for completeness, the visible spectrum of Ag\(_5\)-modified TiO\(_2\) surfaces is experimentally determined using diffuse reflectance spectroscopy. Theoretically, the following relevant aspects are addressed: (1) the existence of surface polarons on TiO\(_2\) through surface activation with Ag\(_5\) AQCs; (2) the stability of the resulting polaronic states as compared to non-polaronic ones as previously reported;\(^{20-22}\) and (3) the UV-Vis optical absorption spectrum of the polaronic states.

Polaron formation is a fundamental and well-known phenomenon in transition metal oxides, for example, reduced titanium dioxide surfaces \(\text{(e.g., for a comprehensive overview see ref. 23).}\) Excess electrons from surface defects such as oxygen vacancies and Ti interstitials locally couple to lattice distortions forming small polarons,\(^{24}\) typically hosted at Ti sites close to the defects. The existence of intrinsic small polarons as self-trapped electrons at Ti\(^{4+}\) ions in rutile TiO\(_2\) \(\text{(i.e., forming stable Ti}\(^{3+}\) 3d\(^1\) states)\) has been both theoretically predicted\(^{21,25-31}\) and experimentally confirmed.\(^{22-24}\) Gono et al.\(^{35}\) have theoretically shown that the presence of surface polarons reduces overpotentials in the oxygen evolution reaction \((\text{OER}).\) This reaction is the major problem to solve in water splitting.

Thus, the quest for experimental systems forming stable surface polarons (clusters on TiO\(_2\) melt at temperatures greater than 700 \(^\circ\text{C}\)) opens new ways to the experimental work on new catalysts. Very recently, a direct observation of magnetic polarons in a doped Fermi-Hubbard system has been reported by Koepsell and co-workers.\(^{36}\)

A theoretical analysis of polaronic states has been provided in studies of Cu\(_{x}\)-TiO\(_2\) \((n \leq 5)\) interfaces.\(^{15-17}\) X-ray absorption spectroscopy measurements at the Cu K-edge have confirmed the theoretical prediction that the 3d levels of the Cu\(_5\) clusters become depopulated upon adsorption on TiO\(_2\) for both polaronic and non-polaronic states.\(^{15}\) However, no conclusive experimental evidence of the modifications of the electronic structure of the Ti atoms upon deposition of Cu\(_5\) AQCs on TiO\(_2\) nanoparticles has been found \(\text{(see the ESI of ref. 15).}\) In this work, X-ray absorption spectroscopy measurements at the Ti K-edge provide unambiguous evidence that these modifications occur at the Ag\(_5\)/TiO\(_2\) interface. Moreover, the experimentally determined modifications are related to electronic polarization effects due to the formation of polarons \(\text{(Ti}\(^{3+}\) 3d\(^1\) states).\) In this way, we extend previous experimental studies proving the existence of Ti\(^{3+}\) 3d\(^1\) states in reduced TiO\(_2\) samples,\(^{12-34}\) including their direct views through scanning tunneling microscopy.\(^{44}\) Furthermore, photoexcitation spectra of the polaronic state with light in the UV-Vis region of the solar radiation are also presented. Clearly, the photoexcitation of polarons is still an unexplored area, for which the first ground-breaking experimental studies have been very recently reported.\(^{38}\)

Finally, the possibility of using TiO\(_2\)-supported Ag\(_5\) AQCs for photocatalysis applications is also studied. Due to its importance in the context of climate change and global warming \(\text{(see ref. 39 for a very recent and comprehensive review on heterogeneous CO}_2\text{ reduction), the photoca}\)

tiviation of CO\(_2\) over Ag\(_5\) has been addressed. A deterrent in the CO\(_2\) elimination is the high stability of the C=O bond, which necessitates an energy as high as 7.8 eV \(\text{(ref. 40) in order to be broken in the gas phase). The radical CO}_2^\cdot \text{ is a clear precursor state for CO}_2\text{ dissociation due to its weakened C} = \text{O bond. The question analysed in this work is twofold: (1) whether CO}_2\text{ can be trapped in a dispersion-dominated physisorption state and (2) if it is irradiated with visible light, whether this molecule can be transformed into the radical CO}_2^\cdot \text{ over TiO}_2\text{-supported Ag}_5\text{ clusters, as already found for copper clusters.}\(^{19}\)

The different topics covered in this work are addressed by applying density functional theory \((\text{DFT}),\) time-dependent DFT, and an approach combining DFT with reduced density matrix theory. We chose a DFT-D3 ansatz\(^{12,14}\) on the basis of its excellent performance in describing the adsorption of the Ag\(_5\) cluster on the rutile TiO\(_2\)(110) surface.\(^{29}\) For an appropriate determination of the electronic structure, we employed the HSE06 hybrid functional of Heyd, Scuseria and Ernzerhof\(^{43,44}\) on top of the structures optimized via the DFT-D3 approach instead. It has been previously shown that the HSE06 functional allows description of localized midgap states below the conduction band which are associated with polarons in reduced TiO\(_2\) \(\text{(ref. 45)}\) and Cu\(_2\)-modified TiO\(_2\) surfaces.\(^{15}\) In order to calculate the UV-Vis absorption spectra, we employed reduced density matrix \((\text{RDM})\) theory within the Redfield approximation,\(^{46}\) combined with DFT calculations using the HSE06 functional. This combination of RDM and DFT, proposed by Micha and collaborators,\(^{47-49}\) has been successfully applied to silver\(^{50,51}\) and copper\(^{54}\) clusters on semiconductor TiO\(_2\) and silicon surfaces.\(^{15,19,20,50-51}\)

The results from our computational calculations and spectroscopy \((\text{diffuse reflectance and X-ray absorption})\) measurements are presented and discussed in Section 2. This section is split in several subsections in order to emphasize at each step the importance of the presence of polarons and, in the last subsection, the prediction of CO\(_2\) photo-activation is briefly described. Section 3 summarizes the main findings. Finally, in Section 4, further details about the materials used as well as the experimental and computational methods developed are provided.

2 Results and discussion

2.1 Surface polaron formation at the Ag\(_5\)/TiO\(_2\) interface

We carried out structural optimizations and interaction energy calculations with the Perdew-Burke-Ernzerhof (PBE) density
functional and the Becke–Johnson (BJ) damping\textsuperscript{44} for the D3 dispersion correction, including spin-polarization. We refer to this combination as the PBE-D3(BJ) scheme. The Hubbard DFT+U term\textsuperscript{44} was added in PBE-D3(BJ) minimizations to describe localized 3d-electrons on Ti cations.

The optimization of the bare cluster Ag\textsubscript{5} gives rise to a planar trapezoidal structure as in experimental observations.\textsuperscript{55} We then inserted the Ag\textsubscript{5} cluster into our slab model and optimized the whole Ag\textsubscript{5}-slab geometries. The pyramidal- and trapezoidal-shaped Ag\textsubscript{5} structures shown in Fig. 1 are thus predicted. Both structures are highly stable, with adsorption energies (-4.53 eV for the pyramidal-shaped geometry at the PBE-D3BJ/U level) being of the same order of magnitude as in previous studies.\textsuperscript{20,21}

Next, we used the wavefunctions calculated at the PBE-D3(BJ)/U level in a follow-up HSE06 calculation at the relaxed geometries. It was thus found that the Ag\textsubscript{5} cluster donates its unpaired electron to the TiO\textsubscript{2} surface and loses its magnetic moment in either pyramidal- and trapezoidal-shaped geometries. Using a Bader decomposition scheme,\textsuperscript{56} we estimated charge donations of about -1 and -0.8|e| from the Ag\textsubscript{5} cluster for pyramidal- and trapezoidal-shaped geometries, respectively. As can be observed in Fig. 1, the donated electron becomes localized in one specific 3d orbital lying at the surface plane and centered at the Ti(5f) atom right below the Ag\textsubscript{5} cluster.

The charge trapping via the localization of one electron on the Ti(5f) atom is correlated with the typical lattice distortion accompanying the formation of a small polaron in reduced TiO\textsubscript{2} surfaces (see, e.g., ref. 23). Thus, as we can see in Fig. 1, the oxygen ions depart from the Ti atom hosting the polaron by 0.08 Å in average. For the pyramidal-shaped Ag\textsubscript{5} structure, the polaronic solution is -0.9 eV more stable than the non-polaronic counterpart. For the latter, the “extra” electronic charge donated by the Ag\textsubscript{5} cluster becomes delocalized over several neighboring Ti atoms. As reported in ref. 20 for non-polaronic Ag\textsubscript{5}-TiO\textsubscript{2} states, the pyramidal-like structure is preferred over the trapezoidal-shaped arrangement also in polaronic solutions. The adsorption energy differences are ca. 0.3 and 1.5 eV at the HSE06 level and PBE-D3(BJ)/U levels, respectively. This is consistent with previous studies, reporting the hollow site as the most favored position for single Ag atoms adsorbed on both rutile\textsuperscript{26,57} and anatase\textsuperscript{22} TiO\textsubscript{2} surfaces. Accordingly, as shown in Fig. 1, four Ag atoms locate at hollow sites in the pyramidal-shaped structure. The central Ag atom is localized on top of one fivefold (5f) Ti atom instead.

Besides the Ti(5f) ion, alternative locations of the polarons exist with similar energies in hydroxylated and reduced TiO\textsubscript{2}(110) surfaces.\textsuperscript{26,27} Very recent molecular dynamics simulations under experimental conditions\textsuperscript{22} indicate that a subsurface Ti atom is the most stable polaron site on reduced TiO\textsubscript{2}(110) surfaces. The stabilization of the surface polaron induced by the Ag\textsubscript{5} cluster is favored by an attractive electrostatic interaction between the localized Ti\textsuperscript{3+} 3d\textsuperscript{1} electron and the positively charged Ag\textsubscript{5} cluster. As pointed out in a theoretical-experimental study,\textsuperscript{23} an adsorbate (a CO molecule) is capable of promoting polaron transfer from the subsurface to surface sites also in reduced TiO\textsubscript{2} samples. Similar to the case of the Ag\textsubscript{5}/TiO\textsubscript{2} interface, the favored surface location is caused by an attractive (repulsive) interaction of the CO molecule with the surface (subsurface) polaron.

2.2 Polarization effects induced by surface polarons

In order to analyze the polarization effects induced by the polaronic charge, we calculated the net population (number of electrons) of d-type orbitals centered at Ti atoms for Ag\textsubscript{5}-modified and unmodified TiO\textsubscript{2} surfaces. We considered the two different (trapezoidal and pyramidal) Ag\textsubscript{5} isomers and both polaronic and non-polaronic states. We found the main modifications in the population of 3d(Ti) orbitals upon Ag\textsubscript{5} adsorption while those of s(Ti) and p(Ti) orbitals (not shown) were kept almost unperturbed. As can be deduced from Table 1, a net depopulation of 3d(Ti) orbitals can be observed upon the polaron formation (see Table 1). This is clearly seen when comparing the 3d(Ti) orbital populations in the unmodified (2nd column) and Ag\textsubscript{5}-modified (3rd and 4th columns) TiO\textsubscript{2} surfaces hosting the polaron. Note that this is also clearly apparent in the population difference between polaronic (3rd and 4th columns) and non-polaronic (last column) states.

The depopulation of 3d(Ti) orbitals might be an outcome challenging common intuition. As a localized Ti\textsuperscript{3+} 3d\textsuperscript{1} electron state, the polaron is in fact characterized by excess charge (i.e., one “extra” electron) trapped at the Ti site hosting it. Accordingly, the unpaired electron of the Ag\textsubscript{5} cluster becomes trapped at the 3d orbital of one specific Ti(5f) atom. As a result, the difference in the population of 3d(Ti) orbitals with majority and minority spin components is unity (3rd and 4th columns of Table 1). However, we must consider that the polaron becomes effectively screened by the polarization of the surrounding electronic cloud and it is not only manifested in structural lattice distortions. This polarization is also manifested in the formation of a delocalized hole accompanying the trapped Ti\textsuperscript{3+} 3d\textsuperscript{1} electron in the 3d-network of occupied orbitals centered at neighboring (mostly surface) Ti atoms. Actually, this
polarization effect extends to subsurface layers. As a result, the net population of 3d(Ti) orbitals decreases in the Ag5-modified polaronic state with respect to that existing in the unmodified TiO2 surface. In a slightly simplified picture, the localized Ti3+ 3d1 electron attracts positively charged Ti4+ centers, which become even more positively charged upon polaron formation in order to favour the attractive electrostatic electron–Ti3+ attraction. The electronic charge is transferred to the p orbitals of neighboring O2– ions which, being repelled by the localized Ti3+ 3d1 electron, move away from it (see Fig. 1). Note that this polarization effect holds for both trapezoidal- and pyramidal-shaped structures of the Ag5 cluster.

The finding that the polaron formation (as a localized Ti3+ 3d1 electron state) is accompanied by a polarization of the crystal electronic cloud becomes even more clear, when the analysis of orbital populations is restricted to 3d(Ti) and 2p(O) orbitals of titanium and oxygen atoms located at the polaron plane. Thus, as can be observed when comparing these populations in polaronic and non-polaronic states (values indicated in the 2nd and 4th columns and 2nd and 3rd rows, of Table 1), the electron, having left an effective hole delocalized over the 3d-network of surface Ti atoms, is transferred to 2p orbitals of oxygen atoms lying at the polaron plane. It can be noted from Table 1 that one electron located at 3d orbitals of titanium atoms in the non-polaronic state becomes localized at 2p orbitals of oxygen atoms in the polaronic counterpart. The Bader charge of surface oxygen atoms is also larger (by ca. 0.6|e|) in the polaronic state, as opposed to the surface titanium atoms.

| Table 1 | Net population (number of electrons) of d(Ti) orbitals in the unmodified TiO2 surface (2nd column) and the modified TiO2 surface bearing supported Ag5 clusters in both pyramidal- and trapezoidal-shaped structures (3rd and 4th columns). For the most stable pyramidal-shaped isomer, the d(Ti) orbital population is also presented for the non-polaronic state (last column). The population of d and p orbitals of surface titanium and oxygen atoms (referred to as TiS0 and O2S0) is presented for the pyramidal-shaped isomer in polaronic and non-polaronic states. The difference between the occupation of orbitals with majority and minority spin components is also indicated as values between parenthesis. |
|---|---|---|---|
| Unmodified TiO2 | Ag5/TiO2 (pyramidal polaronic) | Ag5/TiO2 (trapezoidal polaronic) | Ag5/TiO2 (pyramidal non-polaronic) |
| d(Ti) | 173 (0) | 172 (1) | 172 (1) | 175 (1) |
| d(TiS0) | 41 (1) | | | |
| p(O2S0) | 93 (0) | | | |

2.3 Experimental evidence of polarization effects induced by surface polarons

We found experimental evidence of the described modifications in the electronic structure of Ti atoms through X-ray absorption near edge structure (XANES) spectroscopy. This technique is characterized by a high chemical selectivity. Fig. 2 shows the XANES spectra at the Ti K-edge of bare TiO2 nanoparticles (NPs) and TiO2 NPs bearing supported Ag5 AQCcs. We observed a shift of the edge position (ca. 0.1 eV) when adding Ag5 AQCcs to the TiO2 NPs. An additional peak at 4990 eV was also found. As previously shown,29 the multiple structure appearing immediately after the main 1s → 4p transition emerges from a two-electron transition. It consists in the simultaneous excitation of one core electron, associated with 1s → n4p transitions, and one valence electron.30 In particular, resonances appearing at ca. 4990 eV are attributed to 2p(O) → 3d(Ti) transitions.31 The increase of the XANES area in this region indicates charge transfer from Ti atoms to the ligands (i.e., oxygen ions), resulting in a decrease of the Ti electron density at the 3d levels in average. Thus, the experimental measurements confirm our finding that there is an effective depopulation of 3d(Ti) orbitals favouring 2p(O) orbitals as a result of the polaron formed. As will be next discussed, our interpretation is further supported by the theoretical modelling of the polaron photo-excitation.

As mentioned in the introduction, no modification of the XANES spectra at the K-edge of Ti atoms was found in the case of the Cu5 cluster15 as the adsorbate so that no unambiguous proof of the polaron formation could be provided. On the other hand, one key difference between Ag5 and Cu5 as adsorbates is that the 3d orbitals of the latter present a very pronounced hybridization with 2p orbitals of oxygen atoms from the TiO2 surface. Hence, from our analysis above, the polarization process, which involves the transfer of electronic charge from 3d(Ti) to 2p(O) orbitals, might be somehow constraint at the Cu5/TiO2 interface. On the other hand, the employment of smaller TiO2 nanoparticles has allowed for a larger Ag5–TiO2 contact region than in our previous work.15

![Fig. 2 XANES spectra at the Ti K-edge of TiO2 NPs (black line) and the Ag5 atomic quantum cluster (AQC) supported on TiO2 NPs (red line).](image)
We note that the depopulation of 3d(Ti) orbitals is the same for Ag5 and Cu5 clusters. Also, we obtained similar values for the surface polaron formed from oxygen vacancies in the reduced TiO2(110) rutile surface (see Section S1 of the ESI†). Hence, we have provided general microscopic details of polarons: the mechanism leading to their internal structure through the polarization effects in the electronic structure of the environment. This important aspect of the polaron formation is deduced theoretically not from a model Hamiltonian but from our extended ab initio calculations. The strategy followed has been obviously motivated by the presence of Ag5 clusters which seem to be determinant.

2.4 UV-Vis optical response of surface polarons

Fig. 4 (bottom panel) shows the photo-absorption spectra of the Ag5-modified TiO2 surface, with the Ag5 cluster in the most stable (i.e., pyramidal-shaped) structure. The photo-absorption spectrum for the trapezoidal-shaped structure is very similar (see Section S2.2 of the ESI†). For the sake of clarity, the density of states is presented in the upper panel of Fig. 4 while the most relevant frontier orbitals are shown in Fig. 3, with the Ti3 3d1 electron characterizing the highest-energy single-occupied (referred to as SOMO) orbital of the system (see also Fig. 3 and Section S2 of the ESI†). As can be observed in the projected electronic density of states, the localized Ti3 3d1 state (marked with a yellow arrow in the upper panel of Fig. 5) appears about 1.2 eV below the bottom conduction band. The same value was reported by Di Valentin et al. for a Ti(5f) 3d1 state in hydroxylated and reduced rutile TiO2(110) surfaces.25

Moving to the photo-excitation processes, the first thing to note from Fig. 4 is that the excitation of the Ti3 3d1 electron with a photon energy at the end of the visible region (marked with a yellow arrow at about 3.1 eV) leads to its transfer to 3d orbitals of Ti atoms spread all over the TiO2 surface. Essentially, the delocalized hole accompanying the formation of the polaronic Ti3 3d1 state becomes filled, indicating the existence of the delocalized hole itself. This is further confirmed by an analysis of the acceptor orbital, being mainly composed of 3d states of surface Ti atoms (ca. 64%). Alternatively, our finding could also be viewed as the photo-induced conversion of a small polaron into a large polaron. Previous experimental measurements68 have shown that visible light excitation of Ti3 centers on reduced TiO2 nanoparticles leads to the transfer of the localized 3d1 electrons into the conduction TiO2 band.

2.5 Improvement of the UV-Vis optical response of TiO2: experimental confirmation

As found for non-polaronic states28 and the Cu5/TiO2 interface,15 it can be noted from Fig. 4 (bottom panel) that the Ag5 cluster increases the UV and extends into the visible the optical response of TiO2. Fig. 5 shows the comparison of the theoretical and experimental absorbance in the visible region going from 1.65 to about 3.08 eV. All the DRS spectra show the typical behavior expected in TiO2-based semiconductors consisting of a nearly flat region, at small photon energies, that is dominated by reflection and scattering due to the high refractive index of the investigated material. The milling process decreases the nanoparticle size increasing the surface area. In this way, the amount on deposited clusters increases and the light absorption is higher (by about a factor of three) than for nanoparticles without milling. The abrupt increase when radiation becomes more intensively absorbed with increasing photon energy corresponds to an onset of transmission near the optical absorption. The experiment corroborates the theoretical prediction that Ag5 clusters are capable of extending the optical response of TiO2 into the visible.

As can be seen in the bottom panel of Fig. 4, the main absorption peaks in the visible (pink and forest-green arrows) involve the electron transfer from ‘isolated’ midgap states (the HOMO−1 and HOMO orbitals) to acceptor Ti(3d) states in the TiO2 conduction band (the LUMO+26 and LUMO+76 orbitals). In contrast with the case of the Cu5/TiO2 interface,25 the frontier HOMO−1 orbital bears a dominant Ag5s atomic contribution (see Section S2 of the ESI†) and not chemical mixing of Cu(3d) orbitals with O(2p) and Ti(3d) states. For the Ag5–TiO2 system, there is also photo-induced electron transfer from frontier Ag(4d) orbitals having chemical mixing with O(2p) and Ti(3d) states such as the HOMO−2 orbital (see Section S2 of the ESI†). However, the associated absorbance contribution (dotted blue arrow in Fig. 4) is located in the UV and not the visible region.

Our results are consistent with previous studies15,20 indicating that the main mechanism driving photoabsorption is a single electron ‘jumping’ from 5s (Ag5) or 3d (Cu5) orbitals to the conduction band, leaving behind a long-lived ‘hole’ at the subnanometer clusters. Similar to the case of the Cu5–TiO2 interface,25 the Ag5 cluster induces a spatial separation of photogenerated holes and electrons. It can be noted from the orbital pictures of Fig. 4 that the acceptor state bears a depleted region of charge (empty region) at the Ag5–TiO2 layer, hindering
electron–hole recombination and then, improving the photocatalyst efficiency of TiO$_2$.\textsuperscript{61}

### 2.6 Prediction of CO$_2$ photo-activation

A previous theoretical study\textsuperscript{19} has indicated that subnanometer Cu$_5$ clusters could enable the photo-activation of the CO$_2$ molecule and we analyse here if similar conclusions hold for unsupported and TiO$_2$-supported Ag$_5$ clusters. By relaxing the whole CO$_2$/Ag$_5$ geometry (see the inset of Fig. 6), we estimated a physisorption energy of $-0.10 \ (-0.12)$ eV for the CO$_2$ molecule over the Ag$_5$ cluster at the MP2 (DFT-D3) level. We also estimated the Helmholtz free energy of formation,\textsuperscript{60} finding that the CO$_2$/Ag$_5$ complex is still stable at room temperature but by $-0.03$ eV only. Follow-up TDDFT calculations of the UV-Vis spectrum (see Fig. 6) show that the bare Ag$_5$ clusters induce CO$_2$ activation with photon energies in the UV region (from about 3.4 eV).
When considering TiO$_2$-supported Ag$_5$ clusters as the photocatalysts, we find that the physisorption state and energy (0.11 eV) are very similar to the case of the unsupported cluster. However, it can be noted from Fig. 7 that a photon energy in the visible region is already capable of inducing CO$_2$ activation. The transition responsible for the peak in the visible involves an electron “jump” from the HOMO orbital and the final state is the CO$_2$ radical attached to the Ag$_5$-supported cluster. It is well-known that the radical CO$_2$ is a clear precursor-state for dissociation of the CO$_2$ molecule due to its weakened C=O bond.

Also, we found that both the physisorption and the photoactivation of CO$_2$ are possible over the pyramidal-shaped Ag$_5$ isomer shown in Fig. 1, with an almost identical physisorption energy (~0.12 eV). The order of magnitude of our estimated physisorption energies are the same as in previous studies on CO$_2$ capture through TiO$_2$ nanoparticles (between ~0.16 and ~0.28 eV in ref. 63). In view of the similar properties of Ag$_n$ clusters ($n < 5$) when adsorbed on rutile and anatase phases, we expect that the photoinduced activation of CO$_2$ occurs also on anatase-supported Ag$_5$ clusters. We also calculated the UV-Vis spectra of CO$_2$ adsorbed on the bare TiO$_2$ for one specific configuration (over the Ti(5f) site). However, no transition with a significant oscillator strength has been found for a photoexcited electron from the bare TiO$_2$ surface to the CO$_2$ molecule. This outcome also indicates that the Ag$_5$ cluster is responsible for the predicted CO$_2$ photoactivation.

3 Conclusions

The very recent development of cutting-edge experimental techniques making the synthesis of subnanometer metal clusters possible is pushing our understanding of molecule-like catalysts and photocatalysts far beyond the theory developed for metal nanoparticles and bulk materials. As an example, it has been previously shown how new photocatalytic and optical properties with technological projections are acquired by TiO$_2$ surfaces upon deposition of Cu$_5$ clusters. In this work, we computationally and experimentally explored the properties of Ag$_5$-modified TiO$_2$ surfaces instead, taking advantage of the high monodispersity of the method for Ag$_5$ cluster synthesis.

On the one hand, we have clearly shown that these Ag$_5$ clusters are capable of inducing the formation of stable surface
polarons, as localized Ti$^{3+}$ 3d$^1$ states, as well as photogenerated large polarons at the Ag$_5$/TiO$_2$ interface of the material. Moreover, new fundamental insights have been gained on general electronic polarization effects accompanying the formation of surface polarons (along with the well-known structural distortion of the crystal lattice). This phenomenon has been manifested as a depopulation of titanium 3d orbitals favouring oxygen 2p orbitals, as experimentally observed through X-ray absorption spectroscopy at the Ti K-edge and theoretically predicted by applying state-of-the-art computational modellings. The self-trapped Ti$^{3+}$ 3d$^1$ electron repels nearby oxygen ions and attracts nearby titanium cations, which, in turn, affects their electronic structure, causing the transfer of electronic charge from Ti$^{4+}$ cations to O$^{2-}$ ions. On the other hand, our results point out that TiO$_2$-supported Ag$_5$ clusters are not only visible-light photo-active materials but are also potential photocatalysts for CO$_2$ reduction.

From a practical perspective, the modification of TiO$_2$ surfaces with subnanometer Ag$_5$ clusters has revealed a new way of stabilizing surface polarons and producing at the surface a kind of polaronic 2D material, which could be used for further experimental and theoretical studies of polaron interactions, currently a matter of high relevance. From a broader perspective, the main novelty of our present work is that we revealed theoretically and confirmed experimentally an electron polarization phenomenon associated with a surface polaron formation for the first time. At present, the experimental observation along with the theoretical interpretation suggests an important step for the fundamental understanding of surface polarons and photocexcitation.

4 Materials and methods

4.1 Materials

Ag$_5$ clusters were synthesized and characterized according to a previously developed electrochemical method,$^{18,31}$ using a Ag electrode.$^{18}$ The experimental method for Ag$_5$ cluster synthesis and full characterization has been described in ref. 65. TiO$_2$ titanium dioxide nanoparticles were purchased from GetNanoMaterials,$^{84}$ in the form of nanopowders, which according to the supplier are composed of particles with a primary particle size (99.9%) of 5 nm.

4.2 Experimental methods

We carried out X-ray absorption spectroscopy measurements (XAS) in the XANES (X-ray absorption near edge structure) regions at the XAFS2 beamline$^{67}$ of the Laboratório Nacional de Luz Sincrotron (LNLS), Campinas, Brazil. These XANES measurements were performed in transmission mode using a Si(111) crystal monochromator around the Ti K-edge (4966 eV) at ambient temperature using three ion chambers as detectors. Harmonics were attenuated by detuning to 50% of the peak intensity. We determined the sample absorption between the first two chambers. For calibration purposes, the third chamber was used to measure a metallic Ti reference. In order to achieve an edge-step close to unity in the XAS measurements, we calculated the optimum amount of material. Powdered samples were dispersed in 10 ml of isopropyl alcohol and then filtered through a 0.45 µm pore size MF-Millipore$^{74}$ membrane filter. We normalized XANES data by standard methods using ATHENA software which is part of the IFEFFIT package.$^{68}$

We obtained the optical absorption spectra through diffuse reflectance spectroscopy (DRS) using a Shimadzu ISR-2600 Plus spectrophotometer. The setup includes an integrating sphere with two detectors, a photomultiplier and an InGaAs detector. The DRS spectra were collected at room temperature in the range between 200 and 700 nm with a step of 1.0 nm using standard BaSO$_4$ (Nacalai Tesque) as a reference. DRS was obtained by determining the ratio of intensities of diffusely reflected radiation from the sample and from the standard.

4.3 Computational methods

4.3.1 Periodic calculations. We carried out the periodic electronic structure calculations with the Vienna Ab initio Simulation Package (VASP 5.4.4),$^{69,70}$ following the same computational approach reported in previous work on the Cu$_5$/TiO$_2$(110) and CO$_2$/Cu$_5$–TiO$_2$(110) interactions.$^{15,19}$

Electron–ion interactions are described by the projector augmented-wave method,$^{76,77}$ using PAW-PBE pseudopotentials 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 occupancies, and the Brillouin zone sampled at the $\Gamma$ point.$^{72}$ The convergence criterion was $10^{-4}$ eV for the self-consistent electronic minimization. Geometries were relaxed with a force threshold of 0.02 eV Å$^{-1}$.

The TiO$_2$ surface is modelled via periodic slabs, using a $4 \times 2$ supercell (four TiO$_2$ trilayers giving ca. 13 Å slab width). Ag$_5$ adsorption and CO$_2$ physisorption are assumed on one side of the slab, with 38 Å of vacuum above it.$^{73}$

Adsorption energies of the Ag$_5$ cluster on the surface are derived via

$$E_{\text{int}} = E_{\text{Ag}_5/\text{TiO}_2(110)} - E_{\text{Ag}_5} - E_{\text{TiO}_2(110)}$$

where $E_{\text{Ag}_5/\text{TiO}_2(110)}$ is the total energy of the system, $E_{\text{TiO}_2(110)}$ is the energy of the substrate, and $E_{\text{Ag}_5}$ denotes the energy of the bare silver cluster. When considering the adsorption of CO$_2$ on TiO$_2$-supported Ag$_5$ clusters, the interaction energies are derived via

$$E_{\text{int}} = E_{\text{CO}_2/\text{Ag}_5/\text{TiO}_2(110)} - E_{\text{CO}_2} - E_{\text{Ag}_5/\text{TiO}_2(110)}$$

with $E_{\text{CO}_2/\text{Ag}_5/\text{TiO}_2(110)}$ as the total energy of the system, $E_{\text{Ag}_5/\text{TiO}_2(110)}$ as the energy of the supported-TiO$_2$–Ag$_5$ cluster, and $E_{\text{CO}_2}$ stands for the energy of the free (gas-phase) CO$_2$ molecule. All these values were calculated in the same supercell slab for the sake of consistency.

The geometries were optimized with the PBE-D3(BJ) scheme with the Hubbard term (DFT+U) added and including spin-polarization. We used the same value of $U$ (4.2 eV) reported in
previous studies of TiO2-modified copper clusters.\textsuperscript{15,37} For the

dispersion-dominated Ag\textsubscript{5}/TiO\textsubscript{2} interaction,\textsuperscript{29} the PBE-D3(BJ)
interaction energies agreed to within 10% with reference values
obtained with the domain-based pair natural orbital correlation
approach DLPNO-CCSD(T)\textsuperscript{74} as well as the symmetry-adapted
perturbation theory [SAPT(DFT)] method.\textsuperscript{75,76} The performance of
the PBE-D3(BJ) approach against higher levels of \textit{ab initio} theory has also
been tested for the estimation of the CO\textsubscript{2} phys-
isorption energy on TiO\textsubscript{2}-supported Cu\textsubscript{5} clusters.\textsuperscript{39} An agreement
to within 10% was found between PBE-D3(BJ) and second-order
Möller–Plesset perturbation theory (MP2) levels.

We used the optimized geometries, obtained at the PBE+U/ D3 level in final HSE06 calculations. The HSE06 exchange–correlation functional uses a screened Coulomb potential for increased efficiency on metallic systems.\textsuperscript{43,44} It has been the preferred approach in previous studies of optical and other
electronic properties of TiO\textsubscript{2}.\textsuperscript{77–79} We applied the HSE06
approach using a HF/GGA mixing ratio of 25 : 75 with a screening parameter of 0.11 bohr\textsuperscript{–1}, as recommended in ref. 44. At a variance with our previous study of TiO\textsubscript{2}-supported Ag\textsubscript{n}
clusters (n < 5),\textsuperscript{38} all calculations are spin-polarized and all
atoms and ions from the supercell models were relaxed.

\subsection*{4.3.2 Reduced density matrix treatment.}

We calculated the UV-Vis absorption spectra using the computational approach
previously applied to TiO\textsubscript{2}-supported Cu\textsubscript{5} clusters.\textsuperscript{29} The relax-
ation processes involved are described by the reduced density
matrix (RDM) approach in the Redfield approximation,\textsuperscript{46} based on
orbitals taken from calculations employing the HSE06 hybrid functional. This combined RDM-DFT treatment developed
by Micha and Kilin\textsuperscript{47,48} is already a well-established tool in
describing the optical spectra of subnano metal clusters
adsorbed on semiconductor surfaces\textsuperscript{49} (see, e.g., ref. 20 and
50–52).

Very briefly, in the presence of a monochromatic electromagnetic
field $\varepsilon(t)$ of frequency $\Omega$, the evolution equation for the
reduced density $\rho$ in the Schrödinger picture takes the form

$$
\dot{\rho}_{jk} = -i \hbar \sum_{lm} \left( F_{jm} \rho_{lk} - \rho_{jm} F_{lk} \right) + \sum_{lm} R_{jklm} \rho_{lm},
$$

$$
\dot{F} = \tilde{F}^{KS} - \mathbf{D} \cdot \varepsilon(t)
$$

$$
\varepsilon(t) = \varepsilon_0 \left( e^{i\omega t} + e^{-i\omega t} \right)
$$

where $\tilde{F}^{KS}$ denotes the effective Kohn–Sham Hamiltonian (the
indices refer to its representation in the Kohn–Sham basis set),
$\mathbf{D}$ is the electric dipole moment operator, and $R_{jklm}$ stands for the
Redfield coefficients, i.e. the Kohn–Sham components of the
relaxation tensor. The latter is defined as in ref. 46 and is
implemented as described in ref. 47.

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

$$
\rho_0(t) = \rho_0(t)e^{i\Omega t}, \quad e_i > e_j
$$

$$
\dot{\rho}_0(t) = \rho_0(t)\exp(-i\Omega t), \quad e_i < e_j
$$

where $e_i$ 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

$$
\tilde{\rho}_{jj}^{SS} = \Gamma_j^{-1} \sum_{k=0}^{\infty} g_k(\Omega), \quad j \geq \text{HOMO}
$$

$$
\tilde{\rho}_{jj}^{SS} = 1 - \Gamma_j^{-1} \sum_{k=\text{LUMO}}^{\infty} g_k(\Omega), \quad j \leq \text{HOMO}
$$
as stationary-state solutions for the diagonal elements.\textsuperscript{47} In this
HOMO and LUMO denote the lowest-energy unoccupied and
the highest-energy occupied molecular orbital, respectively. $\Gamma_j$ is a
depopulation rate, and the sum terms $g_k$ are given by

$$
g_k(\Omega) = \frac{\gamma \Omega_k}{\gamma + \Delta_k(\Omega)^2},
$$

where $\gamma$ denotes the decoherence rate, $\Omega_k$ as the Rabi frequen-
cies given by $\Omega_k = -D_{jk} \cdot \varepsilon_0 / \hbar$, and $\Delta_k(\Omega) = \Omega - (e_j - e_k)$ as
detunings. The diagonal elements provide the populations of the
KS orbitals. The population relaxation rate $h\Gamma$ and the
decoherence rate $h\gamma$ 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 exci-
tations in semiconductors (see, e.g., ref. 81).

In terms of the stationary populations, the absorbance is given by\textsuperscript{46,51,52,82,83}

$$
\tilde{A}(\Omega) = \sum_{j=0}^{\text{HOMO}} \sum_{k=\text{LUMO}} \tilde{F}_{jk} (\tilde{\rho}_{jj}^{SS} - \tilde{\rho}_{kk}^{SS}) \times \frac{1}{\pi} \frac{h\gamma/2}{(h\Delta_k)^2 + (h\gamma/2)^2},
$$

where $\tilde{F}_{jk}$ is an oscillator strength per active electron.\textsuperscript{46} The solar
flux absorption spectrum is then expressed as

$$
F(h\Omega) = \tilde{A}(\Omega) F_{\text{solar}}(h\Omega) h\Omega,
$$

where the solar flux is approximated by the black body flux
distribution, normalized to an incident photon flux of 1 kW m\textsuperscript{–2},

$$
F_{\text{solar}}(h\Omega) = \frac{(h\Omega)^3}{\pi^2 \hbar^3 c^3} \exp(h\Omega/k_B T) - 1,
$$

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

\subsection*{4.3.3 Cluster model calculations.}

Cluster model calculations were performed for the interaction between CO\textsubscript{2} and the
bare Ag\textsubscript{5} cluster by applying the PBE-D3(BJ) scheme and the
MP2 method with the ORCA\textsuperscript{85} suite of programs (version
4.0.1.2). For this purpose, we used an atom-centered def2-
TZVPP\textsuperscript{86} basis set for carbon, oxygen, and silver atoms. When
optimizing the geometries in the CO\textsubscript{2}–Ag\textsubscript{5} sub-systems were allowed to relax. We also
calculated Helmholtz free energies of formation\textsuperscript{82,87} using the
thermochemistry output of ORCA.\textsuperscript{85} Next, we carried out time-
dependent DFT (TDDFT) calculations of the UV-Vis spectra
using the PBE-D3(BJ) scheme.
Author contributions
Conceptualization and coordination, M. P. d. L. C.; theoretical work, P. L. C., S. M. A., M. P. d. L. C.; experimental work, J. M. R. L., L. J. G., D. B., M. A. L. Q., F. R.; writing manuscript, M. P. d. L. C.; editing, P. L. C., J. M. R. L., L. J. G., D. B., S. M. A., M. A. L. Q., F. R., M. P. d. L. C.; all authors have read and agreed to the published version of the manuscript.

Conflicts of interest
There are no conflicts to declare.

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