Interplay between Adsorbates and Polarons: CO on Rutile TiO$_2$(110)

Michele Reticcioli, Igor Sokolovic, Michael Schmid, Ulrike Diebold, Martin Setvin, and Cesare Franchini

University of Vienna, Faculty of Physics and Center for Computational Materials Science, Vienna 1090, Austria
Institute of Applied Physics, Technische Universität Wien, Vienna 1090, Austria
Dipartimento di Fisica e Astronomia, Università di Bologna, 40127 Bologna, Italy

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Polaron formation plays a major role in determining the structural, electrical, and chemical properties of ionic crystals. Using a combination of first-principles calculations, scanning tunneling microscopy, and atomic force microscopy, we analyze the interaction of polarons with CO molecules adsorbed on the reduced rutile TiO$_2$(110) surface. Adsorbed CO shows attractive coupling with polarons in the surface layer, and repulsive interaction with polarons in the subsurface layer. As a result, CO adsorption depends on the reduction state of the sample. For slightly reduced surfaces, many adsorption configurations with comparable adsorption energies exist and polarons reside in the subsurface layer. At strongly reduced surfaces, two adsorption configurations dominate: either inside an oxygen vacancy, or at surface Ti$_{5c}$ sites, coupled with a surface polaron. Similar conclusions are predicted for TiO$_2$(110) surfaces containing near-surface Ti interstitials. These results show that polarons are of primary importance for understanding the performance of polar semiconductors and transition metal oxides in catalysis and energy-related applications.

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A wide range of materials form polaronic in-gap states upon injection of extra charge, as the excess electrons or holes couple to the lattice phonon field. The charge carriers generated by defects [1–6], doping [7–9], adsorbates [10–12], or irradiation [13–16], interact with the lattice field to different extents depending on the electron-phonon coupling, which is strongly material dependent [4,17,18]. The formation of polarons prevents a doping-driven insulator-to-metal transition and substantially alters the properties of the system and its functionalities [17,19,20]. In the strong short-range coupling limit, localized (so called small) polarons form; they locally distort the lattice and lead to the formation of in-gap states [21,22]. At low temperature, the ground state is determined by the polaronic configuration that minimizes the energy of the system [23,24], but even small thermal energies can activate polaron hopping to different hosting sites, thereby changing the nature and properties of the polaronic state [9,25–27].

The formation of polarons is particularly favorable in transition-metal oxides, owing to the strength of the electron-electron and electron-phonon interactions, and it is further promoted in the vicinity of the surface, where the crystal lattice is more flexible [27–30]. Therefore, polarons play a decisive role in physical and chemical phenomena taking place on oxide surfaces [27]. Here, we address the interactions between electron polarons and adsorbates. We show that adsorbates are able to alter the stability of polarons and, in turn, the polarons affect the energetics and configuration of the adsorbates. This interplay between adsorbates and polarons has direct impact on catalytic and energy conversion properties.

We considered CO molecules adsorbed on rutile titanium dioxide, an archetype polaronic material [31]. In clean (i.e., without CO molecules) TiO$_2$(110) samples, the formation of polarons is promoted primarily by oxygen vacancies ($V_O$) and Ti interstitials (Ti$_{int}$) [11,32,33]. Oxygen vacancies are easily created at twofold-coordinated surface oxygen sites and each $V_O$ donates two excess electrons that form polarons [34]; the polarons tend to reside at sixfold-coordinated Ti$_{5c}$ atoms of the subsurface layer (S1) in the proximity of the $V_O$, due to the attractive polaron-$V_O$ interaction [23,24,35–38]. Polaron hopping from S1 to the surface layer (S0) is unfavorable but may occur at elevated temperatures [4,8,24,26]. Interstitial Ti atoms, on the other hand, may occupy different lattice sites (difficult to detect in the experiments) and the four excess electrons associated to each Ti$_{int}$ form more complicated polaron patterns, which have not been fully rationalized yet [39,40]. Our combined theoretical and (low temperature) experimental study is conducted on reduced samples containing $V_O$, in which the role of Ti$_{int}$ is considered to be marginal, since the surface oxygen vacancies repel the positively charged Ti$_{int}$ atoms, which are pushed deeper in the bulk [29].

The effect of polarons is usually not considered in adsorption studies. CO adsorption on the rutile (110) surface is a well-studied phenomenon, in particular for reduced surfaces containing $V_O$ [39,41–47], yet controversies appear even in elementary issues. Beyond a general consensus on the local geometric properties (CO molecules adsorb vertically at fivefold-coordinated Ti$_{5c}$ sites at low coverage) [41,42], conflicting outcomes have been reported, which
either suggest [43] or exclude [44–46] the possibility of CO adsorption at $V_O$ sites. We show that the apparent disagreements in the literature can be resolved by a proper treatment of polarons and their interaction with adsorbates by combining density functional theory (DFT) simulations [48,49] with scanning tunneling microscopy (STM) and noncontact atomic force microscopy (nc-AFM). The strong-CO-polaron interaction substantially affects the adsorption energy and also the polaronic ground state.

We start by showing how the presence of CO alters the stability and orbital topology of polarons. We consider one CO molecule adsorbed at the Ti$_{5c}$ site next nearest neighbor to the $V_O$ (NNN-Ti$_{5c}$) for a $V_O$ concentration of 5.6% (see Methods [50] for details). The spatial extension of the S1 and the S0 polaron electronic charge is shown in Figs. 1(a) and 1(b), respectively. The S1 polaron retains the same characteristic spatial distribution as in the absence of CO [24,63], with a $d_{z^2}$-$d_{x^2-y^2}$-like orbital character at the hosting Ti$_{5c}$ site and about 1/3 of the charge distributed on the surrounding atoms. Only very little (0.1%) polaronic charge is transferred to the CO molecule. This can be observed in filled-state STM images when the CO molecule is adsorbed above or in the proximity of an S1 polaron [see the weak circular spots in the inset of Fig. 1(a) and Fig. SF3 in the Supplemental Materials [50]].

Conversely, a polaron in the S0 layer strongly interacts with the CO molecule [Fig. 1(b)]. The S0 polaron acquires a stronger $d_{z^2}$ (54%) character as compared to the case with no adsorbates (43%) [24], and a non-negligible portion of the polaronic charge (1%) is transferred to the $2\pi^*$ antibonding orbital of the adsorbed CO [64,65]. This causes the formation of a double-lobed polaronic cloud above the CO molecule [see the filled-state STM images in the inset of Fig. 1(b)], which has a distinctly different shape from the one shown in Fig. 1(a) for a CO in the vicinity of an S1 polaron. The CO-polaron interaction affects strongly the polaron formation energies ($E_{POL}$), as shown in Fig. 1(c). While in the S1 case the polaron formation energy is marginally destabilized by the CO ($\Delta E_{POL}^{S1} = +23$ meV), the formation of an S0 polaron becomes much more favorable ($\Delta E_{POL}^{S0} = -161$ meV): The adsorbate changes the polaronic ground state of the system, an effect that was overlooked in previous studies [39,66]. By inspecting the contributions to the polaron formation energy (determined by the balance between the electronic energy gain due to the electron-phonon coupling and the energy cost to locally distort the lattice [8]) we find that the presence of the CO reduces significantly the structural energy cost in the S0 polaron case. Moreover, we verified that CO adsorbed at a NNN-Ti$_{5c}$ site with an S0 polaron below is more favorable than any other configuration (see Fig. SF5 [50]).

Next we focus on the CO adsorption as a function of the $V_O$ concentration ($c_{V_O}$) and CO coverage ($\theta_{CO}$), see Fig. 2. For locating the adsorbed CO we use nc-AFM imaging with a CO-terminated tip (blue-white images). The light (yellow)-black image show the polaron states mapped by filled-states STM images.

Figures 2(a) and 2(b) shows data obtained on a slightly reduced ($c_{V_O} = 5.8\%$) surface with a low CO coverage ($\theta_{CO} = 0.09$ ML). The CO molecules are predominantly adsorbed on Ti$_{5c}$ sites [brighter spots in the AFM image in Fig. 2(a)], and less frequently at $V_O$ sites ($CO + V_O$, solid circles). The filled-state STM image of the same region [Fig. 2(b)] shows mostly weak circular spots at the CO molecules on Ti$_{5c}$ sites (two marked by down pointing triangles), which we attribute to the electronic cloud of S1 polarons in the vicinity of the CO, similar to those predicted in the inset of Fig. 1(a). There is only one intense double-lobed feature in the STM image [up pointing triangle in Fig. 2(b)], sandwiched by two oxygen vacancies (see also Fig. SF6 [50]). We attribute this to a CO at the NNN-Ti$_{5c}$ site, coupled to an S0 polaron ($CO + S0$-polaron complex), as predicted in Fig. 1(b). The CO adsorbed at $V_O$ sites (solid circles in Fig. 2) observed by nc-AFM is invisible in filled-state STM images, since the polaronic clouds do not extend to these sites and these molecules have no in-gap states.

![FIG. 1. Effects of a CO molecule adsorbed at NNN-Ti$_{5c}$ site on polaronic states at low reduction level (5.6%, i.e., one $V_O$ in a 9 x 2 two-dimensional unit cell). (a) and (b) electronic charge density of the S1 (a) and S0 (b) polarons in presence of CO. Atoms at the back are depicted by bleached spheres. A top view of the considered configuration is also sketched in each panel. The insets represent the experimental and simulated filled-state STM images. (c) Polaron formation energy of S0 and S1 polarons, in case of a TiO$_2$(110) surface with and without adsorbed CO.](image-url)
changes to their coupling to
reduction level (occupied by CO molecules [Fig. 2(c)]. The filled-states
images of the same region show many double-lobed
dashed circles show the positions of
the rutile (110) surfaces at different surface
states. Down-pointing triangles indicate coupling with
S1 polarons, up-pointing triangles indicate coupling with S0 polarons. (a) and (b) Low CO
coverage and low reduction level (θCO = 0.09 ML and cνO = 5.8%). (c), (d), and (e) moderate CO coverage and high
reduction level (θCO = 0.15 ML and cνO = 14.5%). The STM
images (d) and (e) were measured sequentially, and the arrows
indicate the diffusion of CO along Ti5c sites, accompanied
by polaron hopping. (f) and (g) High CO coverage and high
reduction level (θCO = 0.57 ML and cνO = 14.5%).

At a more reduced surface (cνO = 14.5% and θCO = 0.15 ML), the nc-AFM image shows that all V0 sites are occupied by
CO molecules [Fig. 2(c)]. The filled-states
STM images of the same region show many double-lobed
CO molecules at Ti5c sites, indicating the formation
of CO + S0-polaron complexes [Figs. 2(d) and 2(e)]. The two
consecutive filled-state STM images Figs. 2(d) and 2(e)
show diffusion of several CO molecules. The molecules
become brighter or darker when they move closer or further
away from the V0 sites, respectively. We attribute these
changes to their coupling to S0 and S1 polarons.

Finally, by further increasing the CO concentration up
to θCO = 0.57 ML [67] at the highly reduced surface
(cνO = 14.5%), all oxygen vacancies are occupied by
CO molecules [Fig. 2(f)], again with no in-gap state found
there in the filled-state STM images [Fig. 2(g)]. The nc-
AFM image clearly shows that CO avoids V0-nearest
neighbor sites [Fig. 2(f)], and prefers NNN-Ti5c sites in
combination with the S0 polaron [double-lobed features in
Fig. 2(g)], particularly intense when the CO is adsorbed at a
NNN-Ti5c site sandwiched between two V0s, CO molecules
adsorb also at other Ti5c sites, characterized by
weaker STM signals. These weak filled states originate
from “tails” of electronic charges of S1 polarons and of
CO + S0-polaron complexes spreading over CO molecules
at neighboring Ti5c sites (see Fig. SF4 [50]). We note that
all filled states measured on the CO molecules are deep in-
gap states; i.e., no tunneling current is measured for small
sample biases (VS > -0.6 V): this confirms the polaronic
character of these electronic states.

The interpretation of the experimental data is supported by calculated site-dependent CO adsorption energies (Ead), see
Fig. 3. At low reduction [cνO = 5.6%, Fig. 3(a)], the stability of the CO adsorption at nonpolaronic Ti5c sites
(i.e., CO + S1 configurations, down pointing triangles)
increases with an increasing distance from the V0 in accordance with the experiment [see CO + S1 circular spots in
Fig. 2(b)], CO adsorption at a V0 (CO + V0) or at
polaronic NNN-Ti5c (CO + S0-polaron complex) sites are essentially degenerate in energy, comparable to the most
favorable CO + S1-polaron configurations. In the experiment,
the rare occurrence of the double-lobed CO + S0 spots and CO + V0 features [Figs. 2(a) and 2(b)] originates
from a smaller number of available NNN-Ti5c and V0

FIG. 2. Experimental constant-height nc-AFM (blue-white)
and filled-state STM images (yellow-black) of CO adsorbed on
the rutile (110) surfaces at different surface reduction states.
Dashed circles show the positions of V0s, solid circles show
V0s with an adsorbed CO molecule, triangles show CO
molecules adsorbed on Ti5c atoms. Down-pointing triangles
indicate coupling with S1 polarons, up-pointing triangles indicate coupling with S0 polarons. (a) and (b) Low CO
coverage and low reduction level (θCO = 0.09 ML and cνO = 5.8%). (c), (d), and (e) moderate CO coverage and high
reduction level (θCO = 0.15 ML and cνO = 14.5%). The STM
images (d) and (e) were measured sequentially, and the arrows
indicate the diffusion of CO along Ti5c sites, accompanied
by polaron hopping. (f) and (g) High CO coverage and high
reduction level (θCO = 0.57 ML and cνO = 14.5%).

FIG. 3. Site-dependent adsorption energy. A CO molecule
explores Ti5c sites at various distances from the oxygen vacancy
down pointing triangles), and the V0 site (circle), in the presence
of polarons localized at the S1 layer in a reduced slab with cνO = 5.6% (a) and cνO = 16.7% (b). The inset sketches the considered
configurations. In addition, we report the case of adsorption at the
NNN-Ti5c hosting an S0 polaron (up pointing triangle).
adsorption sites, as compared to the nonpolaronic Ti_{5c} sites [43].

For a strongly reduced surface \( [c_{V_O} = 16.7\%] \), Fig. 3(b)], adsorption at Ti_{5c} sites in combination with S1 polarons becomes less favorable, mainly due to the absence of Ti_{5c} sites at large distances from the V_{O}s, whereas the CO + S0-polaron and CO + V_{O} configurations retain their high stability and represent the most stable solutions. This is in excellent agreement with the filled-state STM measurements showing an increase of double-lobed spots arising from CO + S0-polaron complexes with increasing \( c_{V_O} \) [see Figs. 2(c)–2(g)] combined with a large density of CO + V_{O} features [see Figs. 2(c) and 2(d)]. The formation of the CO + S0-polaron complexes on the strongly reduced sample is in line with the previously reported polaron dynamics on clean surfaces [27]: In strongly reduced TiO_{2}, the S1-to-S0 polaron hopping is promoted by the repulsive polaron-polaron interactions in the S1 layer and by the attraction of polarons to the V_{O}s (see Fig. SF1) [24].

The interaction between polarons and adsorbed CO molecules significantly affects the adsorption energies (Fig. SF7 [50]), the bonding distances from the surface as well as the CO bond length (Fig. SF2 [50]). The various polaron-CO coupling schemes reported here are consistent with reported experimental data on CO adsorption: Temperature-programmed desorption shows multiple desorption peaks on the rutile (110) surface [47]. In contrast, the same experiment performed on the anatase TiO_{2}(101) surface [68] shows a single peak only. This can be associated with the absence of small polarons at the anatase (101) surface [4], which simplifies the adsorption in comparison to the polaronic rutile. Similarly, infrared absorption spectra of CO on the anatase (101) surface always exhibit a single C–O vibrational peak [68], while the rutile (110) surface shows either one or two peaks, depending on the reduction level of the crystal [45]. We identify the additional vibrational frequency as CO coupled with the S0 surface polaron and to CO adsorbed at oxygen vacancies (see Fig. SF8 [50]).

For the sake of completeness and to underline the generality of our conclusions, we inspected by DFT also the CO adsorption under the influence of polarons caused by Ti_{int}S (see Fig. SF9 [50]). In the absence of nearby V_{O}, the Ti_{int}-induced excess electrons lead to the formation of robust CO + S0-polaron complexes, which exhibit the characteristic double-lobed feature in the simulated STM images, in analogy with the V_{O} case (see Fig. SF10 [50]). Our experiments on V_{O}-reduced samples detect the double-lobed STM signal only in correlation with the V_{O} (precisely, on NNN-Ti_{5c} sites). This is an additional indication that near-surface Ti_{int}S are not present in samples with V_{O}S.

In summary, by combining first-principles calculations and surface-sensitive techniques we have elucidated the key role of the interaction between polarons and CO adsorbates on V_{O}-reduced rutile TiO_{2}(110). We have shown that CO adsorption promotes polaron transfer from subsurface to surface sites, in particular at highly reduced TiO_{2} samples, enhancing the activity of surface Ti_{5c} sites. We have identified three distinct adsorption configurations: CO at V_{O} sites, CO at Ti_{5c} sites weakly coupled with polarons in the subsurface (manifested by weak circular features in filled-state STM), and strongly coupled CO + S0-polaron complexes at NNN-Ti_{5c} sites (appearing as double-lobes in filled-state STM). The coupling between CO and polarons and its interaction with V_{O}S strongly influences CO adsorption and causes breaking and recombination of the CO + S0/S1 complexes. Similar conclusions are valid for the Ti_{int}-reduced surfaces, since shallow Ti_{int} atoms promote the formation of S0 polarons and, consequently, of CO + S0-polaron complexes on V_{O}-free surfaces. Our study delivers a consistent and comprehensive picture of CO adsorption on an archetypical polaronic material, solves long-standing ambiguities and conflicting interpretations of experimental results, and sets the path for revisiting the interpretation of adsorption processes in polar semiconductors and transition metal oxides.

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\[ \text{cesare.franchini@univie.ac.at} \]

\[ \text{setvin@iap.tuwien.ac.at} \]

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