Distinct behaviour of localised and delocalised carriers in anatase TiO$_2$ (001) during reaction with O$_2$

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INTRODUCTION

Many functional properties of anatase TiO$_2$ of relevance, e.g., in photocatalysis, solar cells and sensors are critically affected by the presence of excess electrons induced by intrinsic defects, dopants or photoexcitation [1–7]. Understanding and controlling the behaviour of excess electrons is thus essential for improving TiO$_2$’s performance in existing applications and for developing new applications as well. In particular, the chemical doping arising from oxygen vacancies (V$_{O_S}$) induces important changes in the electronic structure, such as the creation of in-gap defect states, the formation of depletion regions, and band bending [3, 8]. Another noteworthy feature connected with V$_{O_S}$ is the presence, under photoirradiation of electronic states with metallic d-character (Ti 3d) at the anatase (010) and (001) surfaces, generally termed two-dimensional electron gas (2DEG) states [9–13]. First observed at the LaAlO$_3$/SrTiO$_3$ (LAO/STO) interface [14], 2DEGs have been reported both in transition metal oxides (TMOs) parent compounds (e.g. bare surfaces of SrTiO$_3$ and KTaO$_3$) and in engineered heterostructures [15, 16]. Nevertheless, a number of important aspects are not yet settled, such as the depth distribution of the oxygen vacancies acting as electron donors. Another critical issue is the behaviour of 2DEG and localised in-gap (IG) defect states under reducing vs. oxidising conditions, notably to what extent and in what conditions it is possible to control the excess of V$_{O_S}$ created by photoirradiation [9, 10, 17].

Here we combine ultraviolet (UV) and X-ray based electron spectroscopies and first principles DFT calculations to clarify the role, the formation mechanism and the possible control of defect states formed at the (001) surface of anatase TiO$_2$ [18–20]. In-situ UHV growth of high quality epitaxial thin films obtained by Pulsed Laser Deposition (PLD) allowed us to identify the types of defect states that either appear under photoirradiation or can be induced and tailored by means of controlled post-growth treatment (UHV annealing). ARPES measurements confirm the existence of both localised and delocalised electronic states, while Resonant-PES in the soft X-ray range identifies their character as Ti$^{3+}$ and Ti$^{4+}$, respectively. Spectral changes were monitored while molecular O$_2$ was steadily fluxed on the sample surface through a metallic capillary [21–23]. Remarkably, the results reveal that 2DEG delocalized features are robust against oxygen exposure, whilst the localised IG states are suppressed. Comparison with DFT calculations provides evidence of a distinct depth-dependence of defect states. The 2DEG originates from subsurface V$_{O_S}$ and resides in sub-surface layers due to the attrac-
tive potential resulting from these $V_{OS}$. In contrast, the deeper lying IG states that are suppressed by $O_2$ originate from the surface $V_{OS}$. Our results also provide a consistent explanation of previous contrasting findings and suggest possible strategies for controlling the carriers’ concentration and transport at the surface of anatase.

**EXPERIMENTAL AND COMPUTATIONAL METHODS**

**Growth**

Anatase TiO$_2$ thin films were grown by Pulsed Laser Deposition (PLD) at a dedicated chamber located at the APE-IOM laboratory (NFFA facility, Trieste, Italy) [24]. Rutile TiO$_2$ single-crystal was ablated using a KrF excimer pulsed laser source kept at about 2 J/cm$^2$ energy density, with a typical laser repetition rate of 3 Hz. The substrate was kept at 700°C growth temperature, while oxygen background pressure was set to $10^{-4}$ mbar. Annealed samples have been kept at the growth temperature for 10 minutes in UHV (PLD chamber base pressure is the range of $10^{-7}$ mbar). Anatase TiO$_2$ thin films were grown on (001)-oriented LaAlO$_3$ (LAO) substrates. Epitaxial strain-less condition was verified for these films. All the samples presented in this work are $\sim 20$ nm thick.

**Transmission and Scanning Transmission Electron Microscopy**

Cs probe-corrected Jeol ARM 200 CF scanning transmission electron microscope with cold-FEG electron source, operated at 200 kV was used for high-resolution imaging of the samples. Electron Energy Loss Spectroscopy (EELS) was performed using Gatan dual-EELS Quantum ER system and elemental chemical analyses were performed with Centurio Jeol Energy Dispersive X-ray Spectroscopy (EDXS) system with 100 mm$^2$ SDD detector. Cross-sectional samples in the [010] zone axis suitable for TEM/STEM analyses have been obtained by a conventional polishing technique followed by dimpling and ion milling.

**Ultraviolet ARPES, Soft X-ray ARPES, RESPES**

The as-grown samples were directly transferred in-situ to the Angle-Resolved Photoemission (ARPES) end-station installed on the Low-Energy branch of APE beamline (APE-LE) at Elettra synchrotron (Trieste, Italy). Such a chamber is equipped with a Scienta DA30 hemispherical electron energy and momentum analyser ($30^\circ$ angular acceptance), which allows to map the electronic bands over the extended areas of the Brillouin zone without rotating the sample. ARPES experiments were performed at a base pressure $\sim 10^{-10}$ mbar and with the samples kept at liquid Nitrogen. Photon energy of 46 eV was used with the light incidence angle of 45°. All the light polarisation available at the beamline have been exploited (linear vertical, linear horizontal, circular right and circular left). When not otherwise specified, the overall energy resolution was set to $\sim 40$ meV, and the angular resolution was set to $0.2^\circ$ (corresponding to $\sim 0.01$ Å$^{-1}$ at 46 eV photon energy).

Soft x-ray ARPES, Resonant Photoemission (RESPES) and oxygen dosing were performed at 109 beamline at Diamond light source (Didcot, UK). The samples fabricated at the APE-IOM laboratory were transferred to the Soft X-Ray branch of 109 beamline 120 by means of a UHV suitcase. The surface’s contamination was thus prevented throughout the whole experiment. Sample temperature was 90 K. In order to reduce the effects of higher order components coming from the beamline optics in the resonant photoemission measurements, the monochromator has been tuned to obtain the best compromise between flux, resolution and higher order rejection. Furthermore, the residual second-order contribution was subtracted in all spectra. The energy position of the Fermi energy ($E_F$) and the energy resolution have been estimated by measuring the Fermi edge of poly-Au foil in thermal and electric contacts with the sample. The overall energy resolution (analysers + beamline) was kept below 250 meV for the entire photon energy range. Molecular oxygen was injected through a metallic capillary placed close to the sample surface (i.e. $\sim 1-2$ cm). The amount of oxygen has been monitored by means of a Residual Gas Analyser (RGA) available in the experimental chamber. Base pressure in the experimental chamber was $1-10^{-10}$ mbar, up to a maximum $O_2$ partial pressure of $4-10^{-9}$ mbar.

**Computational Details**

DFT calculations for pristine and reduced anatase (001) were performed using the Vienna Ab Initio Simulation Package (VASP)[25, 26]. We used the projector augmented-wave (PAW) pseudopotentials to describe the electron-ion interactions and the PBE functional[27] within the generalized gradient approximation (GGA) to treat the exchange-correlation interaction between electrons. The energy cut-off for the expansion of the wave-functions was set to 500 eV. Since GGA is affected by the self-interaction error that favours delocalized electronic states, selected calculations using the PBE+$U$ method with $U = 3.9$ eV [28] were also carried out in order to check the robustness of the PBE solutions (note that $U$ values in the range 2.5-4 eV are typically used to describe defect states in TiO$_2$ [29, 30]). While predicting a more structured electronic charge distribution in comparison to pure PBE, these PBE+$U$ calculations confirmed the delocalized character of the subsurface excess electron states at the anatase (001) surface [31], which was re-
FIG. 1. (a) Representative high-resolution Z-contrast image of the TiO$_2$/LAO interfacial region. (b) LEED pattern (~110 eV) showing the $(1 \times 4) - (4 \times 1)$ surface reconstruction of the anatase thin films. (c) Sketch of the first BZ of anatase. (d) Fermi surface contour, measured at 46 eV photon energy, covering the first BZ, obtained by superimposing the Fermi surfaces measured with different light polarisations. (e), (f) ARPES spectra of the metallic state acquired at $h\nu=46$ eV photon energy around the $\Gamma$ point of the second Brillouin zone ($\Gamma'$): (e) 2DEG of anatase film with high amount of oxygen vacancies after the annealing treatment; (f) 2DEG of as-grown film. (g) MDCs at the Fermi level, in correspondence of the straight lines in panels (e) and (f)) for the annealed (red) and as-grown (blue) samples respectively; the dashed lines highlight the position of the Fermi momenta $k_F$. (h) EDCs extracted at the $k_F$ of the outer band for the annealed (red) and the as-grown (blue) samples.

ported also in a previous PBE+U study [32].

We modeled the anatase TiO$_2$ (001)-(1 x 4) surface using a repeated slab geometry. We considered slabs of 8 TiO$_2$ layers with a (3 x 4) surface supercell for calculations of defect formation energies, in order to minimize interactions between defects in periodic replicas, and slabs of 12 TiO$_2$ layers with a (2 x 4) surface supercell for calculations of the electronic structure and charge densities. The vacuum region between consecutive slabs was larger than 12 Å and dipole corrections were added to remove the electric field in this region [33]. A 3 x 2 x 1 Monkhorst-Pack mesh was used to sample the Brillouin zone (BZ). All atoms of the slab were relaxed except those in the two bottom layers, which were kept fixed at their bulk positions. Geometry optimizations were carried out with convergence thresholds of $10^{-4}$ eV and $10^{-2}$ eV/Å for the total energy and the forces on the ions, respectively. Reaction pathways were determined using the climbing image nudged elastic band method[34].

Oxygen vacancies were created by removing a neutral oxygen atom. The resulting neutral V$_{O}$s consist of a vacant site, effectively bearing a 2+ positive charge, and two compensating excess electrons. Their formation energies were calculated as $E_{\text{form}}(V_O) = E_{\text{def}} - E_{\text{stoich}} + 1/2E_{\text{tot}}(O_2)$, where $E_{\text{def}}$ and $E_{\text{stoich}}$ are the total energies of the reduced (defective) and stoichiometric (defect-free) slabs, respectively, and $E_{\text{tot}}(O_2)$ is the total energy of the O$_2$ molecule.

EXPERIMENTAL RESULTS

Structural and Ultraviolet ARPES results

Epitaxial strainless anatase TiO$_2$ thin films were grown by PLD on LAO substrates. Details of the growth protocol and structural characterization by X-ray diffraction are given elsewhere [24]. The results of our cross-sectional high-resolution Transmission Electron Microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) measurements are shown in Fig. 1. In panel a), a representative high-resolution Z-contrast image shows an atomically sharp interface region. The typical dumbbell structure of Ti ions in TiO$_2$ anatase is clearly distinguishable in the film and occurs in the entire film region with no sign of presence of secondary phases. The crystal quality of the films extends up to the surface, as confirmed by the Low Energy Electron Diffraction (LEED) $(1 \times 4) - (4 \times 1)$ surface reconstruction pattern in panel b)[9, 10, 24].

ARPES measurements were performed along the $\Gamma$-$X$ direction of the surface projected Brillouin zone (Fig. 1c), obtained by superimposing the Fermi surfaces measured with different light polarisations (i.e. linear horizontal and vertical, circular right and left). With such a procedure we could compensate the lack of intensity due to symmetry-related selection rules typically occurring for bands of $d_{xy}$ orbital character. The surface structural reconstruction is reflected in the Fermi surface measured in the first Brillouin zone, shown in Fig. 1d and the Supplemental Material [31]: The bright circle centred at the $\Gamma$ point corresponds to a 2DEG, characterised by a parabolic dispersion
findings agree with previous results\cite{10, 13}, and are after about 25-30 minutes of beam irradiation. These metallic 2DEG intensity also increases and saturates in-gap region increases and stabilises after roughly 1 der beam irradiation, the intensity of the DOS in the curve, t=0) displays IG states at \(\sim\) density vs. time. The DOS of the pristine surface (red Fig. 2a reports the evolution of the spectral intensity reaches a saturation value (see be- appears also upon beam irradiation and its spectroscopic intensity reaches a saturation value (see be-). A further significant spectral change in the two EDCs of Fig. 1h is present at the Fermi energy: a shoulder on the 2DEG peak of the as-grown sample (i.e. \(\sim\) 1 eV BE). This may indicate that the localised states are related to two inequivalent oxygen vacancy sites and that the formation of the latter is more favourable under the beam.

Soft-X ray ARPES, Resonant Photoemission (RESPES) and dosing experiment

While some reports suggest that the metallic state has a 3D character\cite{9} a model linking the metallic state to the specific anatase surface arrangement has recently been shown to provide excellent agreement with the experimental data\cite{11}. The 2D nature of the metallic state is also supported by experiments studying both the effect of electron doping through alkaline adsorption and the influence of beam irradiation at the anatase surface\cite{10, 12}. To gain further insight, we have performed soft X-ray ARPES and Resonant PES (RESPES) experiments, while simultaneously compensating the production of oxygen vacancies arising from photoirradiation. This has been achieved during the measurements by \textit{in-operando} fluxing molecular oxygen through a metal capillary positioned in the proximity of the sample surface\cite{21–23}. Fig. 3 shows the ARPES spectra acquired in the second BZ for the pristine sample in UHV (i.e. base pressure \(10^{-10}\)
2DEG has not been reported before in anatase TiO$_2$.

Effects of O$_2$ dosing on the absorption spectrum (total yield) edges of anatase TiO$_2$ film were measured at 90 K. Pristine sample refers to base pressure in the chamber of 1·10$^{-10}$ mbar, while the dark blue curve corresponds to the highest oxygen partial pressure of the present work (4·10$^{-9}$ mbar). Upon oxygen dosing, the spectral intensity is lowered in the pre-edge as well as in the valleys at $\sim$459 eV and $\sim$462.5 eV, which correspond to spectral lines of Ti$^{3+}$[43]. As found in similar systems, e.g. rutile TiO$_2$[45] and SrTiO$_3$[46], the observed changes can be directly linked to the number of oxygen vacancies.

ResPES in the second BZ were acquired upon oxygen dosing (red line corresponds to partial pressure $P = 1 \times 10^{-9}$ mbar, light blue $P = 1 \times 10^{-9}$ mbar and dark blue $P = 4 \times 10^{-10}$ mbar).

The four main peaks (located at approximate excitation energies of 458.3 eV, 460.5 eV, 463.5 eV, and 465.5 eV excitation energies) can be ascribed to the combination of spin-orbit splitting of the initial states (L$_2$-L$_3$) and crystal field splitting of the d orbitals in the final state ($t_{2g}$-e$_g$) for Ti atoms in +4 oxidation state. The additional splitting of the L$_3$-e$_g$ peak ($\sim$460.5 eV) is the fingerprint of the anatase phase arising from distortion of the ideal octahedron around Ti atom and long-range effects[42-44].

In contrast to our results, studies on SrTiO$_3$ have shown that both the IG and the 2DEG are completely suppressed under O$_2$ dosing, with the spectral weights of the two states reducing at the same pace [15, 17, 22, 38-40]. While incomplete compensation of the 2DEG was observed at the buried interface between a 4 u.c. epitaxial LaAIO$_3$ deposited on SrTiO$_3$ [22], in our study we are not sensitive to the film-substrate interface due to the short probing depth typical of photoemission spectroscopies. Therefore, our results should be compared to the bare SrTiO$_3$ rather than the LAO/STO buried interface.

The different reactivities of the IG and 2DEG in anatase suggest that these states may arise from different oxygen vacancy sites inside the material. Moreover, since the O$_2$ exposure in our setup occurs at the surface, the healing of the oxygen defects strongly depends on the $V_O$ capability to migrate inside the material. The suppression of the IG suggests that the relative oxygen vacancies are located either at the surface or at buried sites that can easily move to the surface and recombine with the adsorbed molecules, as observed in anatase (101) [41]. Conversely, the 2DEG insensitivity against O$_2$ dosing indicates that the migration of the corresponding vacancies to the surface is unlikely, at least in the examined pressure and temperature range.

The electronic character of the 2DEG and the localized IG states was investigated by means of resonant photoemission (RESPES) measurements at the Ti L$_2$-L$_3$ edges. As both IG and 2DEG arise from Ti 3d states[11, 12], RESPES provides additional information by exploiting the energy shift between the core levels of titanium atoms with different oxidation states. Fig. 4a shows the X-ray absorption spectra (XAS) measured in TEY across the Ti L$_3$ edge from an as-grown sample (red curve) and under oxygen dosing (dark blue curve).

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The value of $k_F$ is reduced from 0.19 Å$^{-1}$ to 0.15 Å$^{-1}$ (~20%) under oxygen dosing, i.e. it shows the opposite trend compared to that observed upon annealing in Fig. 1e and 1f, giving direct evidence of (partial) healing of the 2DEG maximum healing was ascribed to the changes in the background signal. We also stress that the 2DEG maximum healing was complete suppression of the IG states is observed as soon as oxygen is dosed; the residual IG intensity is little affected by further increase of the oxygen partial pressure up to four times the initial dose (i.e. from $10^{-9}$ mbar to $4\times10^{-9}$ mbar recorded on RGA) did not further affect the 2DEG state. Such a distinct behaviour of IG and 2DEG has not been reported before in anatase TiO$_2$. The electronic character of the 2DEG and the localized IG states was investigated by means of resonant photoemission (RESPES) measurements at the Ti L$_2$-L$_3$ edges. As both IG and 2DEG arise from Ti 3d states[11, 12], RESPES provides additional information by exploiting the energy shift between the core levels of titanium atoms with different oxidation states. Fig. 4a shows the X-ray absorption spectra (XAS) measured in TEY across the Ti L$_3$ edge from an as-grown sample (red curve) and under oxygen dosing (dark blue curve).
the Ti L₃ show the intensities of the IG and 2DEG states across of the photon energy scan (459.7 eV). Figs. 5d and 5e localized in the BZ centre, more intense in the middle 458.5 eV), whereas the electron pocket at Fermi is lo-

cated around the L₃-edge) the IG and 2DEG states resonate with the L₃-e_g doublet, whereas the in-gap state has Ti character, as it resonates on the rising edge of the L₃-t₂₂g peak, out of the Ti⁴⁺ resonance.

Altogether, these findings provide evidence that: i) the 2DEG and the IG states could be related to distinct Vₐ sites and the former is robust against oxygen dosing ii) the IGs are strongly localised on Ti atoms close to vacancy sites (Ti⁴⁺) while the 2DEG wavefunction is delocalised over many Ti sites that largely maintain the Ti⁴⁺ oxidation state found in pristine TiO₂.

THEORETICAL RESULTS

The observed different dependence of IG and 2DEG states to oxygen dosing suggests that they could be linked to different vacancy sites. To confirm this hypothesis, we performed DFT calculations of surface and subsurface V₀ sites at the anatase (001)-(1 × 4) surface, with the underlying assumption that photoirradiation creates oxygen vacancies at the top few layers and vacancy diffusion to the bulk is negligible at the low temperature of our experiment [35]. We described the reconstructed surface using the widely accepted model of Ref. [20], where ridges exposing twofold co-
nected oxygen (O₂c) and four-fold Ti atoms (Ti₄c) are separated by terraces exposing O₂x, three-fold O (O₃c) and five-fold Ti (Ti₅c) atoms with a (1 × 4) peri-

odicity (Fig.6a). We used slabs of 8 TiO₂ layers with a (3 × 4) surface supercell to calculate V₀ formation energies at the different surface and subsurface sites shown in Fig.6a.

From the computed V₀ formation energies (Fig.6b), it appears that oxygen vacancies are most likely to oc-
cur at surface VO1 (ridge O₂c) and VO4 (terrace O₃c) sites as well as at subsurface VO6 and VO7 sites, while the surface VO2 and VO3 sites are energetically un-

favourable. From the charge density plots in Fig.6d-i and the Supplemental Material [31], it also appears that the character of the defect states is very different for surface and subsurface V₀ sites, as these states become increasingly less localized moving from the surface to the subsurface. In particular, the two excess electrons from the vacancy are well localized on the Ti atoms.
FIG. 5. (a), (b) DOS evolution at the Fermi level as a function of the photon energy before and during oxygen dosing; (c) Resonant angle-resolved-photoemission (ResARPES) spectra acquired while dosing oxygen; (d), (e) Intensity of the IG and 2DEG states across the Ti L$_3$-e$_g$ absorption edge respectively.

FIG. 6. (a) Side view of the reconstructed anatase TiO$_2$(001)-1 × 4 slab model; the investigated oxygen vacancy sites are indicated; Ti and O atoms are light blue and red, respectively. (b) V$_O$ formation energies (eV; blue bars) at different surface and subsurface oxygen sites computed using DFT-PBE; (c) Electrostatic potential profile in the surface region, computed from the shift of the Ti 3s peak in the different Ti layers of the pristine and reduced slabs with V$_O$1, V$_O$4 or V$_O$7 defects. Here, layer 0 corresponds to the ridge Ti$_{4c}$ sites, layer 1 to the terrace Ti$_{5c}$ sites, and so forth. The yellow shading highlights the region of negative (attractive) potential; (d,e,f,g,h,i) Charge density contours of the excess electron states induced by V$_O$1, V$_O$3, V$_O$4, V$_O$5, V$_O$6 and V$_O$7, respectively; the vacancy positions are indicated by dashed red circles; dashed black lines show the unit cell used for the calculations. Additional density contours are shown in Supplemental Material [31].

adjacent to the vacant site and form deep energy levels in the band gap in the case of V$_O$1, in agreement with previous calculations by Shi et al.[47]. In contrast, the defect states are partially delocalized in the case of V$_O$4 and V$_O$5 and become fully delocalized over few (001) planes in the case of subsurface V$_O$6 and V$_O$7 (and deeper V$_O$s as well), where they give rise to shallow energy levels at the bottom of the conduction band [31]. The delocalized character of subsurface defect states is confirmed by PBE+U calculations with U=3.9 eV, reported in the Supplemental Material [31].

The electrostatic potential profile in the surface region was computed from the energies of the semi-core Ti 3s levels in different layers of the slab in the absence/presence of V$_O$s [31]. As shown in Fig.6c, the potential becomes repulsive near the surface of a defect-free slab[11, 32], and this effect is further enhanced in the presence of V$_O$1 (green line). In contrast, V$_O$4 (blue) and V$_O$7 (red) induce an attractive potential well of depth ~ 0.2 eV (very similar for VO4...
and VO7) that confines the excess electron states in the subsurface Ti layers. Note that, unlike in previous modelling studies[11], this confining potential emerges naturally in our calculations for the reduced slabs.

To model the effect of oxygen dosing, we considered the adsorption of an O2 molecule on the anatase surface with a surface or subsurface VO (Fig. 7). O2 adsorption on TiO2 is known to involve the transfer of excess electrons from the oxide to the molecule[1, 3, 41, 48]. In the presence of a VO1, O2 undergoes a strongly exothermic and barrier-less adsorption at the vacancy site [31], which results in the formation of a bridging peroxy (O2−) at the ridge, denoted (O2)o in Fig. 7. The two excess electrons of VO1 are both transferred to the adsorbed species, so that no excess electron remains in TiO2, consistent with the strong reduction of the IG signal observed in ARPES when exposing the surface to O2.

A different picture holds for the adsorption of O2 on a surface with subsurface VO2. In this case, O2 adsorbs at a terrace Ti5c site and only one of the two excess electrons of the vacancy transfers to the molecule[1, 3, 48], thus resulting in the formation of an adsorbed superoxide (O2−), denoted O2* in Fig. 7. As previously discussed for the reaction of O2 with the reduced anatase (101) surface [41], the negatively charged adsorbate has an attractive interaction with the subsurface vacancy, so that migration of VO toward the surface would be energetically favourable (Fig. 7a). At variance with what found for anatase (101)[41], however, the energy barrier for subsurface → surface migration of the VO is quite high at the anatase (001) surface[49], at least for the O2 concentration considered here, as shown by Fig. 7b for the case of the VO4 → VO3 migration step. It is thus quite likely that the VO2 remains subsurface at the low temperature of our experiment, so that the adsorbed O2 remains a superoxide, i.e. one of the two excess electrons of the vacancy remains in TiO2. This explains the persistence of the 2DEG at the anatase-TiO2(001) as well as the decrease in the number of carriers observed under oxygen dosing without the necessity to include any interface effect with the substrate in the calculation.

CONCLUSIONS

In summary, our results reveal distinct behaviours of localized and delocalized states induced by oxygen vacancies at the surface of anatase TiO2. Due to their different spatial locations and the kinetics of defect diffusion in anatase, the 2D delocalized states are much more robust than the localized in-gap states when exposed to molecular oxygen in a wide range of pressures. This robustness of the delocalized states is an important feature that could be exploited for different applications, e.g. to tune the electronic structure of TiO2 in engineered interfaces and heterostructures, or to precisely control the concentration of charge carriers in photo-sensitive devices.

Our findings unveil a new and relevant aspect of the surface chemistry of TiO2, providing a pathway to tailor the performance of future devices.

ACKNOWLEDGMENTS

This work has been partly performed in the framework of the nanoscience foundry and fine analysis (NFFA-MIUR Italy) facility. We thank Fabio Miletto Granazio (Spin-CNR) and Ralph Claessen (Univ. Wurzburg) for useful discussions. A.S. acknowledges the support of DoE-BES, Division of Chemical Sciences, Geo sciences and Biosciences under Award DESC0007347. Z. T. was supported by the National Natural Science Foundation of China (No. 51602092), the Science and Technology Innovation Project Foundation of Hunan Province (No. 2018RS3103). GD acknowledges the financial support from Slovenian Research Agency (P2-0393). E. Cociancich from CNR-IOM and A. Di Cristo from Universita’ Politecnica delle Marche are gratefully acknowledged for the support in the TEM specimen preparation.

AUTHOR CONTRIBUTIONS


FIG. 7. (a) $O_2$ adsorption energy as a function of the subsurface (VO$_4$–VO$_7$) or surface (VO$_3$) oxygen vacancy location. Relevant structures with a subsurface VO, denoted VOn+O$_2^*$ (n=4-7), are shown in panels (c-f). For VO$_3$, two nearly degenerate structures are present, as shown in panels (g-h), where O* indicates an oxygen adatom and (O$_2$)$_a$ a bridging peroxide replacing an O$_2c$. The energy zero corresponds to the adsorption energy of VO$_7$+O$_2^*$. (b) Energy barrier for the diffusion of an O-vacancy from VO$_4$ to VO$_3$ in the presence of adsorbed oxygen. (c-h) Atomic geometries of adsorbed $O_2$ on reduced anatase (001) with a subsurface (VO$_4$-VO$_7$) or surface (VO$_3$) oxygen vacancy, as described in (a). Ti atoms are blue, O atoms are red, adsorbed $O_2$ is orange; dashed red circles indicate the positions of the vacant sites.


atures of the Fermi surface as a function of light polarization, computed PBE band structure for pristine and reduced anatase (001)-(1×4), computed layer-resolved Ti-3s density of states, DFT+U calculations for reduced anatase, potential energy profile for the adsorption of an O₂ molecules at a VO₁ site.