Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary information for the manuscript "Exploring the properties of Ag_5–TiO_2 interfaces: stable surface polarons formation, UV-Vis optical response, and CO_2 photoactivation"

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S1 Polaronic States in Reduced TiO_2(110) Surfaces

Table S1: Net population (number of electrons) of d(Ti) orbitals in the defect-free rutile TiO_2(110) surface (2nd column), and a reduced TiO_2(110) surface bearing an oxygen vacancy and two polaronic Ti^{3+} $3d^1$ states. The difference between the occupation of orbitals with majority and minority spin component is also indicated as values between parenthesis. The population of $3d$ orbitals of surface titanium atoms (referred to as Ti_{S_0}) is also presented.

	defect-free TiO_2(110) (non polaronic)	reduced TiO_2(110) (polaronic)
d(Ti)	173 (0)	172 (2)
$d(Ti_{S_0})$	42 (0)	41 (2)

As reported in very detailed studies (see, e.g., Ref. 1), the excess charge from oxygen vacancies in reduced TiO_2 surfaces enable polarons formation. This feature is illustrated in Figure S1 (bottom panel), showing the onset of two polaronic Ti^{3+} $3d^1$ states when an bridging oxygen atom is removed. It should be stressed that subsurface locations of the Ti^{3+} $3d^1$ states have been found to be more stable.[1]

As can be observed from the values presented in Table S1, the polarization effect described in the main text (Section 2.2) is not intrinsic of the surface polarons induced by the Ag_5 cluster. In fact, a net depopulation of $3d$(Ti) orbitals is also observed for the case of surface polarons formed in the reduced (rutile) TiO_2 surfaces.

We have also calculated the UV-Vis optical response of the polaronic states hosted by the reduced TiO_2(110) surface. The corresponding photo-absorption spectrum is shown in Figure S2. Similarly to the case of the Ag_5–induced polaronic state, the irradiation with sunlight leads to the distribution of the charge initially located in the Ti^{3+} $3d^1$ site all along the surface plane. However, it should be pointed out that the final distribution of electronic charge is more homogeneous when coming from the photoexcitation of the surface polaron formed at the Ag_5-modified TiO_2 surface. In fact, it is clearly apparent from Figure S2 that the overlap between orbitals of surface Ti atoms is favored in the latter case. This outcome can be partially attributed to the repulsion with the second polaronic Ti^{3+} $3d^1$ state at the surface plane. We notice that the intensity of the absorption signal is much higher when arising from the Ag_5–induced polaron.

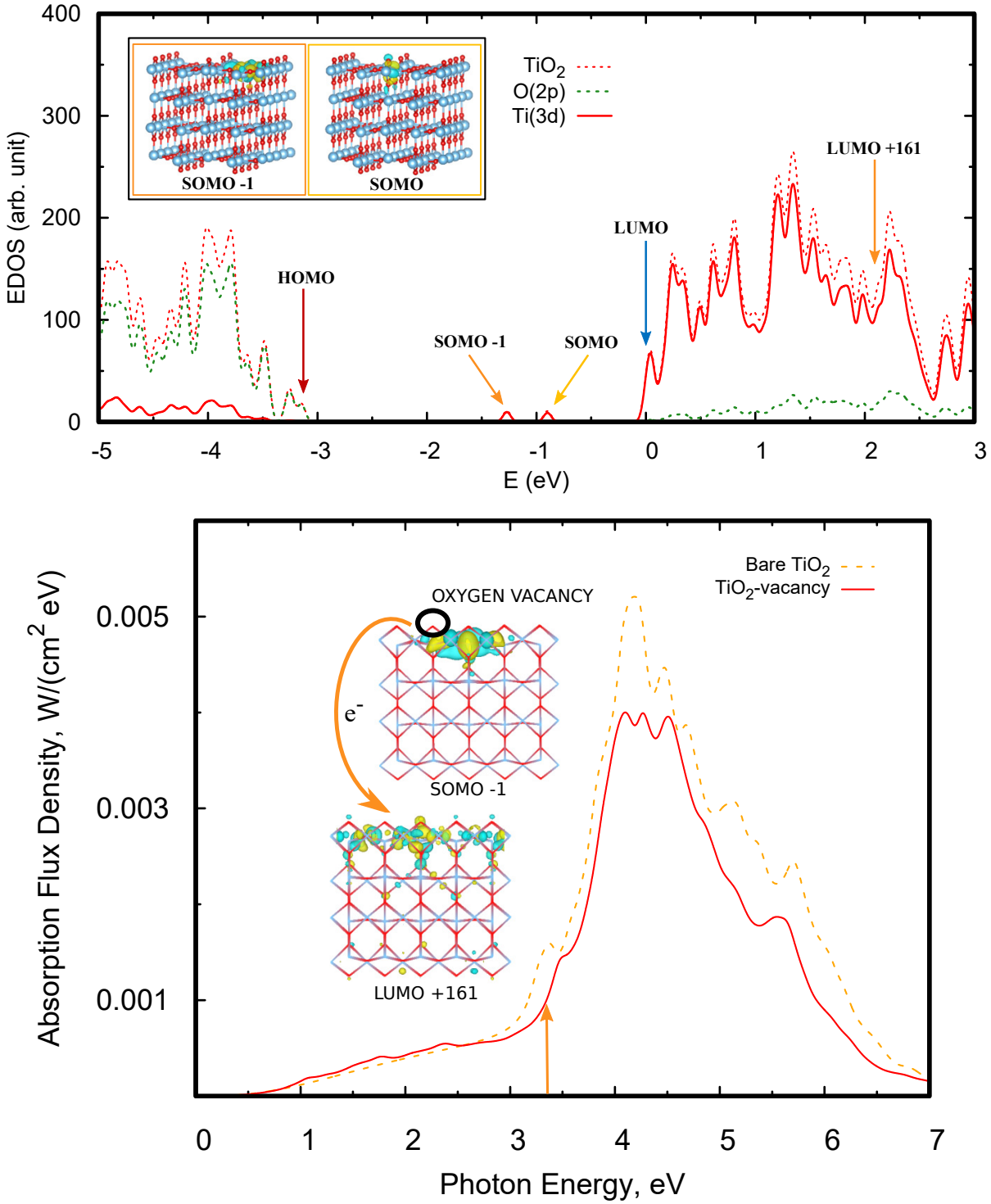

Figure S1: Upper panel: Electronic density of states (EDOS) of the reduced TiO_2(110) surface when bearing an oxygen vacancy. The SOMO and SOMO-1 orbitals are associated with the polaronic Ti^{3+} $3d^1$ states. Bottom panel: photo-adsoption spectra of the same system. The insets present iso-density surfaces of the orbitals involved in the photo-induced transition from the surface polaronic states.

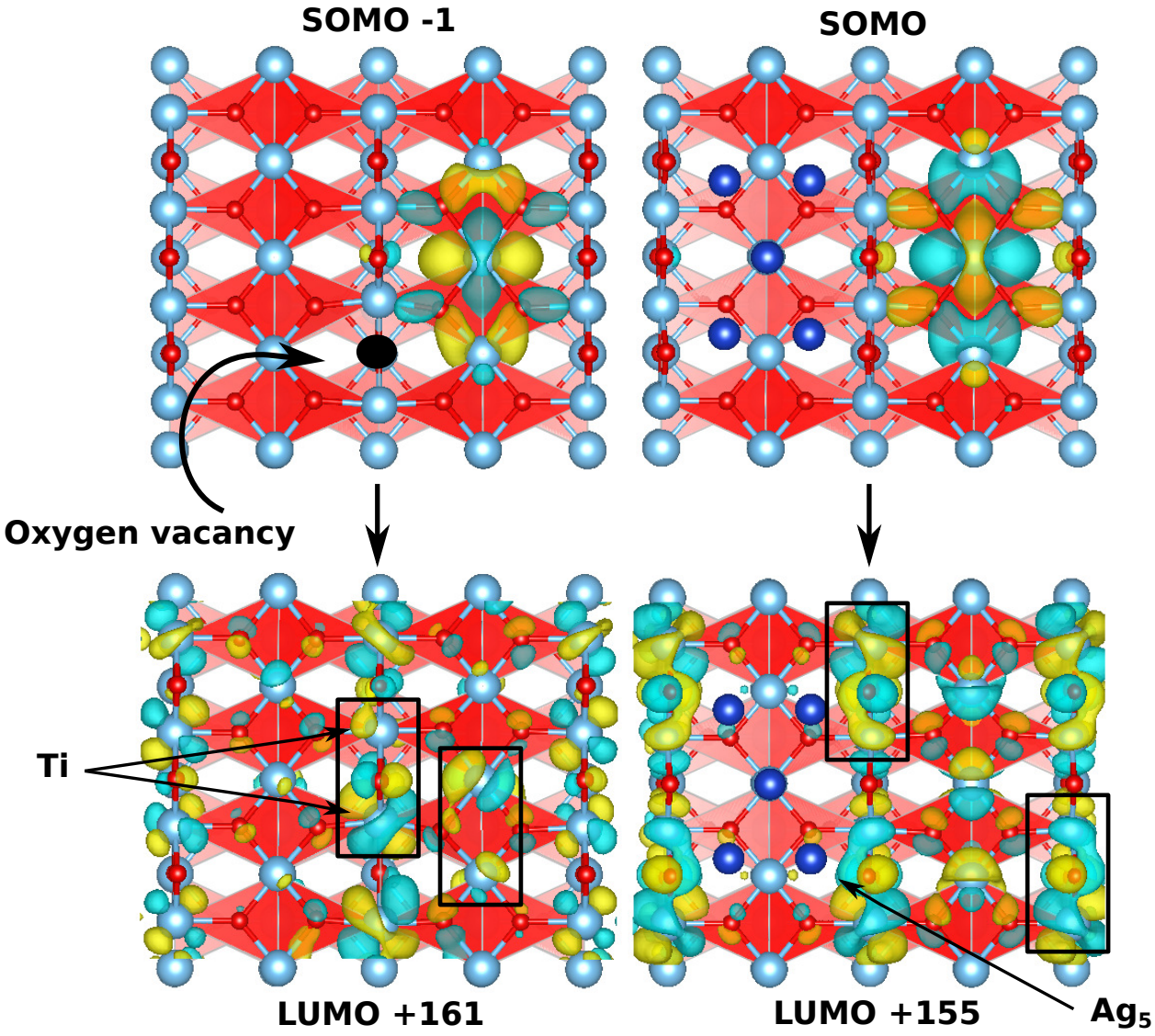

Figure S2: Top view of TiO_2 surfaces bearing an oxygen vacancy (left-hand panels) and the Ag_5 cluster (right-hand panels). The panels show the initial and final orbitals involved in the photo-excitation of the polaronic Ti^{3+} $3d^1$ states with sunlight. Notice that the electron-acceptor orbital shows a larger overlapping between atomic Ti($3d$) orbitals when the surface polaron is induced through the Ag_5 cluster deposition.

S2 Characterization of the Most Relevant Orbitals in the Photoexitation

S2.1 Ag_5 (Pyramidal-Shaped Isomer)/TiO_2(110)

In this subsection, we compare the composition of the orbitals involved in the most intense absorption peaks in the infrared, visible, and UV regions of the photoabsorption spectra of the Ag_5–modified rutile TiO_2(110) surface. Color coding refers to Figure 4 of the main manuscript, which shows the absorption spectra with peak contributions highlighted by arrows of the same color. The majority spin components are presented.

Table S2: Characterization of the orbitals involved in the electronic excitation providing the yellow transition in Figure 4 of the main manuscript.

	SOMO			LUMO +155		
	s	**p**	**d**	**s**	**p**	**d**
O	0	0.1	0	0	0.1	0
Ti	0	0	0.9	0	0	0.9
Ag_5	0	0	0	0	0	0

Table S3: Characterization of the orbitals involved in the electronic excitation providing the dark-red transition in Figure 4 of the main manuscript.

	HOMO			LUMO +26		
	s	**p**	**d**	**s**	**p**	**d**
O	0	0.1	0	0	0	0
Ti	0	0	0.2	0	0	1
Ag_5	0.5	0.2	0	0	0	0

Table S4: Characterization of the orbitals involved in the electronic excitation providing the magenta transition in Figure 4 of the main manuscript.

	HOMO -1			LUMO +26		
	s	**p**	**d**	**s**	**p**	**d**
O	0	0.2	0	0	0	0
Ti	0	0	0.1	0	0	1
Ag_5	0.5	0.1	0.1	0	0	0

Table S5: Characterization of the orbitals involved in the electronic excitation providing the light-blue transition in Figure 4 of the main manuscript.

	HOMO -2			LUMO +69		
	s	**p**	**d**	**s**	**p**	**d**
O	0	0.4	0	0	0	0
Ti	0	0	0.2	0	0	1
Ag_5	0	0	0.4	0	0	0

Table S6: Characterization of the orbitals involved in the electronic excitation providing the green transition in Figure 4 of the main manuscript.

	HOMO			LUMO +76		
	s	**p**	**d**	**s**	**p**	**d**
O	0	0.1	0	0	0	0
Ti	0	0	0.2	0	0	1
Ag_5	0.5	0.2	0	0	0	0

Table S7: Characterization of the orbitals involved in the electronic excitation providing the dark-blue transition in Figure 4 of the main manuscript.

	HOMO -57			LUMO		
	s	**p**	**d**	**s**	**p**	**d**
O	0	0.8	0	0	0	0
Ti	0	0.2	0	0	0	1
Ag_5	0	0	0	0	0	0

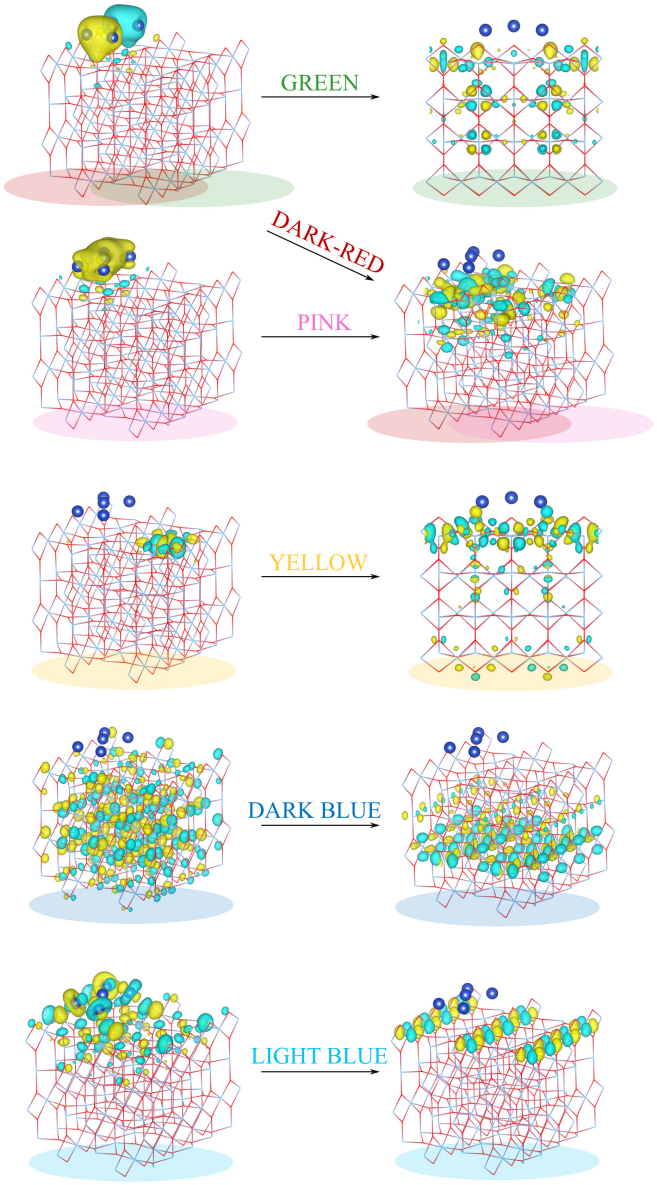

Figure S3: Picture illustrating iso-density surfaces of the orbitals responsible of the absorption spectra with peak contributions highlighted by the same color as the arrows in Figure 4 of the main manuscript.

S2.2 Ag_5 (Trapezoidal-Shaped Isomer)/TiO_2(110)

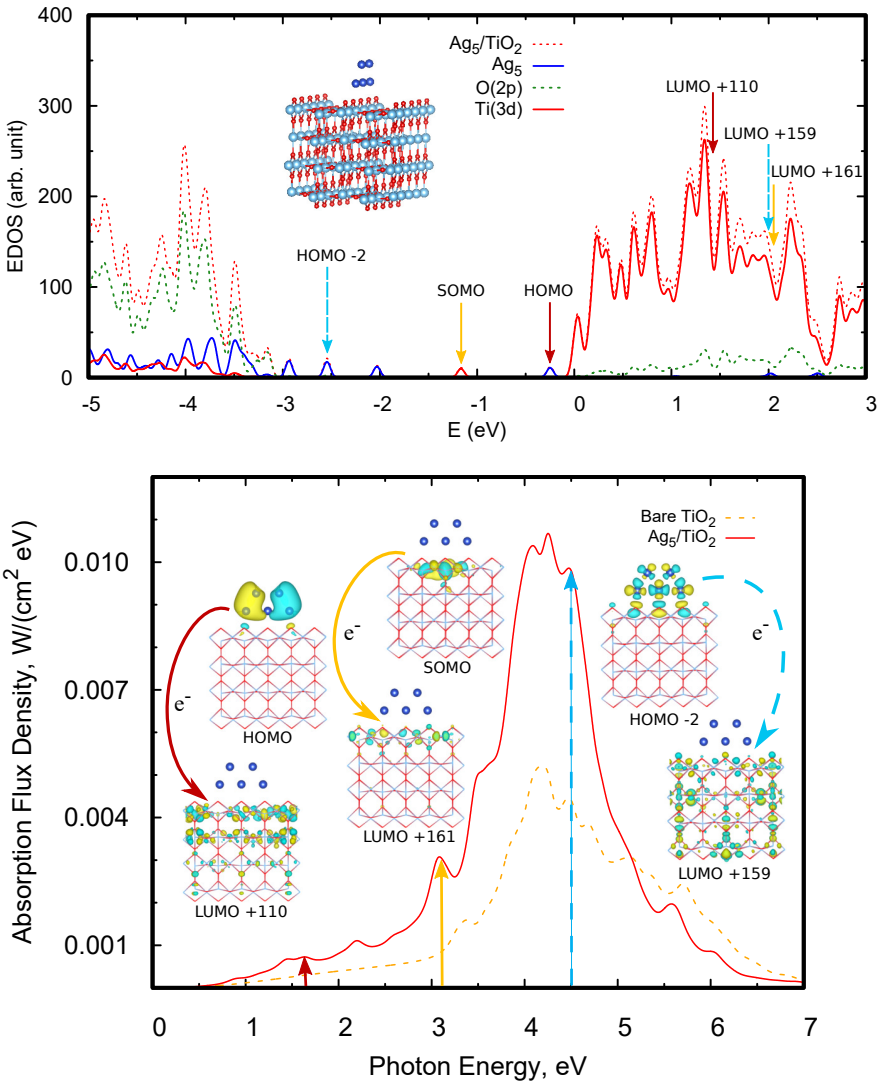

Figure S4: Same representation as in Figure 4 of the main manuscript but considering the Ag_5 trapezoidal-shaped isomer. Upper panel: Electronic density of states (EDOS). Bottom panel: UV-Vis absorption spectra.

References

(1) Reticcioli, M.; Setvin, M.; Schmid, M.; Diebold, U.; Franchini, C. Formation and Dynamics of Small Polarons on the Rutile TiO_2 (110) surface. *Phys. Rev. B* **2018**, *98*.