A SUBNANOMETRIC MATERIAL REVEALS NEW QUANTUM-CHEMICAL INSIGHTS INTO SURFACE POLARONS

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The recent advent of cutting-edge experimental techniques allows for a precise synthesis of monodisperse subnanometric metal clusters composed by just a few atoms, and opens new possibilities for subnanometer science. The decoration of titanium dioxide surfaces with Ag_5 atomic clusters has enabled the stabilization of surface polarons and provided new quantum-chemical insights into an electron polarization phenomenon revealed by their formation.

The very recent development of highly selective experimental techniques enabling the synthesis of subnanometer metal clusters with high monodispersity is pushing our understanding of these, more "molecular" than "metallic", systems far beyond the present knowledge in materials science. When the cluster size is reduced to a very small number of atoms (less than 10), the *d*-band of the metal splits into a subnanometric network of discrete molecule-like *d* orbitals, with the inter-connections having the length of a chemical bond (1–2 Å). The spatial structures of these molecular orbitals make all of the metal atoms cooperatively active, leading to novel properties particularly interesting in nanotechnology including luminescence, sensing, bioimaging, theranostics, energy conversion, catalysis, and photocatalysis. For instance, new catalytic and optical properties are acquired by titanium dioxide (TiO_2) surfaces when decorated with Cu_5 atomic clusters: [1–3]. The Cu_5 clusters shift the material's absorption profile towards visible light, where the sun emits most of its energy [1]. The coated titanium dioxide stores the absorbed energy temporarily in the form of charge pairs, *i.e.*, electrons and holes, in the direct vicinity of the surface. This is a perfect setting for surface chemistry.

Seeking further applications, the TiO_2 surface was decorated with atomic silver clusters, Ag_5 [4,5]. In fact, the coupling with light is expected to be more effective in the silver-modified material. By doing this we uncovered new relevant fundamental insights into a polarization phenomenon accompanying the formation of surface polarons [4].The results from this work are summarized in this contribution.

Surface polaron formation and Ag_5–induced stabilization

The polaron concept, first proposed by Landau and Pekar (see Refs. 6, 7), characterizes an electron moving in a dielectric crystal such as titanium dioxide (TiO_2). Defects on TiO_2 surfaces such as oxygen vacancies lead to excess electrons that become localized in Ti^{3+} $3d^1$ states, as illustrated in panel A of Figure 1. In order to screen the localized Ti^{3+} $3d^1$ electron, the O^{2-} anions depart from their equilibrium positions, as indicated with red arrows in the enlarged view of panel A of Figure 1. This lattice distortion is known as the phonon cloud, and the entity formed by the Ti^{3+} $3d^1$ electron and its associated phonon cloud is the polaron. Furthermore, the electron also carries a polarization cloud which modifies the electronic structure in its vicinity, characterizing a polarization phenomenon associated with the formation of a surface polaron [4,5].

Surface Ti^{3+} cations hosting polarons are easily oxidized, so their formation is more favourable at ●●●

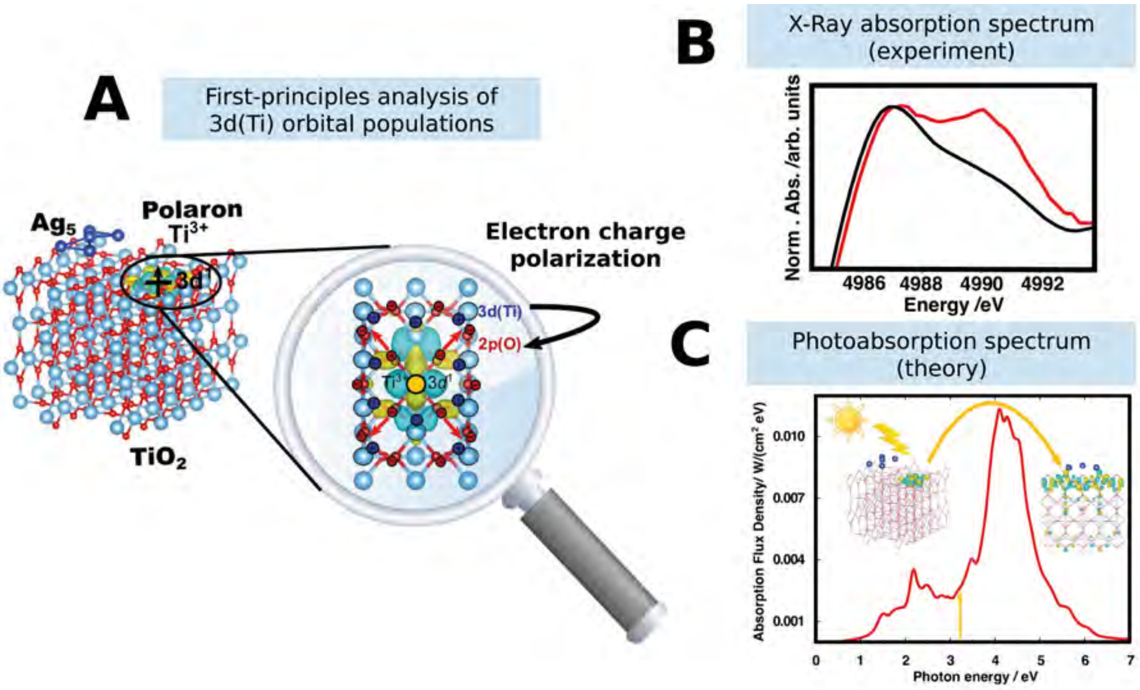
subsurface TiO_2 layers [4,5]. A way to stabilize surface polarons is via the deposition of subnanometric silver (Ag_5) clusters [4]. The first step of the Ag_5–induced surface polaron formation is the donation of an unpaired electron from Ag_5 to the TiO_2 surface. As shown in panel A of Figure 1, the donated electron becomes localized in one specific $3d$ orbital lying at the surface, centered at the Ti atom right below the Ag_5 cluster. After receiving this extra electron, the Ti^{4+} cation becomes a Ti^{3+} cation. As indicated with red arrows in the enlarged view of panel A of Figure 1, the formation of this Ti^{3+} $3d^1$ polaronic state is correlated with the outward movement of the neighboring oxygen anions. The attractive electrostatic interaction between the localized Ti^{3+} $3d^1$ electron and the positively charged Ag_5 cluster favours the stabilization of the Ag_5–induced surface polaron. The pair formed by the polaronic charge and the positively charged silver cluster could ease surface redox chemistry.

Evidence of the surface polaron-induced electron polarization phenomenon

As illustrated in Figure 1, the evidence for the electron polarization phenomenon has been found in three different ways as follows [4]:

1) Our first-principles analysis has provided evidence for the Ag_5–induced depopulation of $3d$(Ti) orbitals, typically in favour of $2p$(O) orbitals, despite the fact that polarons are characterized by an excess charge (*i.e.*, "extra" electrons) trapped at the Ti sites hosting them.
2) A second evidence of the depopulation of $3d$(Ti) orbitals in favour of $2p$(O) orbitals has been found through X-ray absorption near edge structure (XANES) spectroscopy. This technique is characterized by a high chemical selectivity. Panel B of Figure 1 shows the XANES spectra at the Ti K-edge of bare TiO_2 nanoparticles (shown in black) and Ag_5–modified TiO_2 nanoparticles (shown in red). The increase of the spectral feature appearing at ca. 4990 eV for Ag_5–modified TiO_2 nanoparticles indicates a charge transfer from Ti cations to O anions, which results in an on average decrease of the $3d$(Ti) orbitals population.
3) Moreover, a first-principles simulation of the UV-Vis optical response of the surface polaron provided further insights into the correlation between the depopulation of the $3d$(Ti) orbitals and the polaron formation as follows: the excitation of the Ag_5–TiO_2 system with a photon energy at the end of the visible region causes the "jump" of the polaron Ti^{3+} $3d^1$ electron to the 3d orbitals of the surface Ti atoms that have suffered depopulation. Hence, the polaron induces a hole (lack of one electron) which is extended over the surface Ti atoms in its vicinity and this hole becomes filled upon photo-excitation of the polaron. The photo-absorption spectrum is calculated by weighting the absorbance of the system with the solar flux [4] (*i.e.*, the absorption of solar energy). It is shown in panel C of Figure 1, together with the jumping of an electron from the polaron Ti^{3+} $3d^1$ state to an acceptor state formed by many surface $3d$(Ti) orbitals.

▾ **FIG. 1:** a) Figure illustrating the formation of a surface polaron as a localized $3d^1$ electron, and an enlarged view illustrating how the Ti^{3+} $3d^1$ electron repels nearby oxygen ions while attracting nearby titanium cations, which, in turn, affects the local electronic structure and causes an electron charge polarization phenomenon. b) X-ray absorption spectrum at the Ti K-edge of bare TiO_2 (black line) and Ag_5–modified TiO_2 nanoparticles (red line). c) Theoretical UV-Vis spectra showing how the polaronic Ti^{3+} $3d^1$ state is modified when exciting it with a photon energy of about 3.1 eV (marked with a yellow arrow) [4].



The mechanism responsible for the average depopulation of $3d$(Ti) orbitals in favour of $2p$(O) orbitals in the presence of a surface polaron can be explained as follows: the localized Ti^{3+} $3d^1$ electron repels nearby oxygen anions and attracts nearby titanium cations which, in turn, affects their electronic structures, causing the transfer of electronic charge from Ti^{4+} cations to O^{2-} anions (see panel A of Figure 1).

Summarizing, the TiO_2 surface modification with the atomic cluster Ag_5 has served to disclose a new way of stabilizing surface polarons, and to reveal a polarization phenomenon associated with surface polaron formation. This polarization phenomenon arises from quantum-chemical effects and, particularly, electron charge transfer processes induced by the unpaired electron of the adsorbed subnanometric Ag_5 cluster. The exploration of the internal structure of the polarons has been achieved by combining state-of-the-art first principles theory with XANES spectroscopic measurements.

Our findings are expected to contribute not only to an improved fundamental understanding of surface polarons but also to the controlled formation of, *e.g.*, two-dimensional polaronic materials [5] and usage in applications. Our very recent studies [1–5] thus confirm the great potential that lies in this new class of materials, which are shaping the modern field of subnanometer science. ■

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