

# Charge State of Gold Nanoparticles Supported on Titania under Oxygen Pressure\*\*

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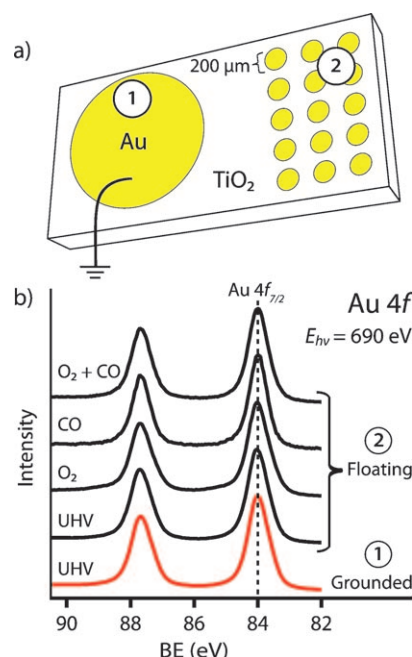
Gold nanoparticles supported on  $\text{TiO}_2$  ( $\text{Au}/\text{TiO}_2$ ) are active catalysts for a variety of reactions even below room temperature.<sup>[1]</sup> This finding has initiated intensive research during the last two decades aimed at explaining the mechanisms responsible for this surprisingly high catalytic activity.<sup>[2]</sup>

Among the proposed explanations are quantum size effects,<sup>[3]</sup> reactive low-coordinate Au atoms,<sup>[4]</sup> oxygen spill-over effects to and from the support,<sup>[5]</sup> support-induced strain,<sup>[4]</sup> and charge transfer between the support and the Au nanoparticles.<sup>[6]</sup> Even though it is accepted that several of these effects play a role,<sup>[7]</sup> there is still no general agreement on the influence of these different mechanisms, particularly the importance of the oxide support, activation of oxygen, and the charge state<sup>[8]</sup> of the Au nanoparticles.

To study the changes in charge state of Au nanoparticles on a  $\text{TiO}_2$  substrate under elevated-pressure reaction conditions, ambient-pressure X-ray photoelectron spectroscopy (APXPS)<sup>[9]</sup> is the technique of choice. By means of XPS, the charge transfer can be revealed as a shift in the apparent binding energy (BE), since a peak shift to a higher apparent BE indicates donation of electrons, whereas a peak shift to a lower apparent BE indicates acceptance of electrons.<sup>[10]</sup> However, to correctly assign the origin of peak shifts, it is necessary to use a proper reference that is unaltered during the experiment. A particular challenge is the band-bending effect, which has been observed in the case of  $\text{TiO}_2$ .<sup>[11]</sup> For example, Kurtz et al.<sup>[11b]</sup> reported an irreversible band-bending effect on reduced  $\text{TiO}_2$  samples on  $\text{O}_2$  exposure caused by oxidation of the reduced  $\text{TiO}_2$  surface, and band-bending effects have also been observed for  $\text{SnO}_2$  by APXPS.<sup>[12]</sup>

Here we report on a reversible band-bending effect in the  $\text{Au}/\text{TiO}_2$  system and discuss its importance for the detection of charge-transfer phenomena in general. Our results reveal that reversible adsorption of  $\text{O}_2$  molecules on  $\text{TiO}_2(110)$  occurs through charge transfer from the oxide support to the adsorbates, a finding which is important with regard to the high catalytic activity observed on  $\text{Au}/\text{TiO}_2$  for numerous reactions, including CO oxidation.

To establish a proper binding energy reference system in our APXPS measurements, we designed a sample (sample 1) with two separate Au areas on a rutile  $\text{TiO}_2(110)$  single-crystal surface: 1) an area 4 mm in diameter covered by Au and connected to ground, and 2) an array of 200  $\mu\text{m}$ -diameter electrically floating Au islands (Figure 1a). This sample was initially cleaned by sputtering/annealing cycles and subsequently oxidized by air, since the lithography process was performed in a separate chamber (see Experimental Section). A set of Au 4f spectra recorded in different gas atmospheres



**Figure 1.** a) Sketch of the fabricated sample of gold evaporated on top of a rutile  $\text{TiO}_2(110)$  single crystal (sample 1). This sample had two distinct areas: 1) An area 4 mm in diameter covered by Au and connected to ground, and 2) An array of 200  $\mu\text{m}$ -diameter electrically floating Au islands. b) XPS spectra of Au in the two sample areas for different gas exposures. The total chamber pressure of  $\text{O}_2$ , CO, and the mixture ( $\text{O}_2 + \text{CO}$ ) was 1 Torr. The spectra are shown offset for clarity.

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is shown in Figure 1 b. To calibrate the energy scale, we also recorded spectra from the grounded Au area of sample 1 (Area 1). In ultrahigh vacuum (UHV) we did not observe any shift in the Au 4f peak positions for the electrically floating Au (Area 2) relative to grounded Au. This indicates that the Au islands in Area 2 do not accumulate charge during XPS measurements, because the conductivity of the TiO<sub>2</sub> substrate is high enough to compensate the emission of photoelectrons. In O<sub>2</sub> or CO atmospheres at 1 Torr, the Au 4f<sub>7/2</sub> peak position in the floating Au also remained unchanged at  $84.00 \pm 0.05$  eV, that is, the Au 4f peak of the macroscopic Au island is not altered on exposure to reducing and oxidizing gases up to 1 Torr. These results show that calibration of the binding-energy scale by using the Au 4f<sub>7/2</sub> peak position of grounded Au is reliable. Care was taken in these in situ experiments to ensure that the reference material did not undergo a chemical reaction that could produce chemical shifts. As we have shown earlier,<sup>[13]</sup> gold can be oxidized by prolonged exposure to X-ray photons at elevated oxygen pressures.

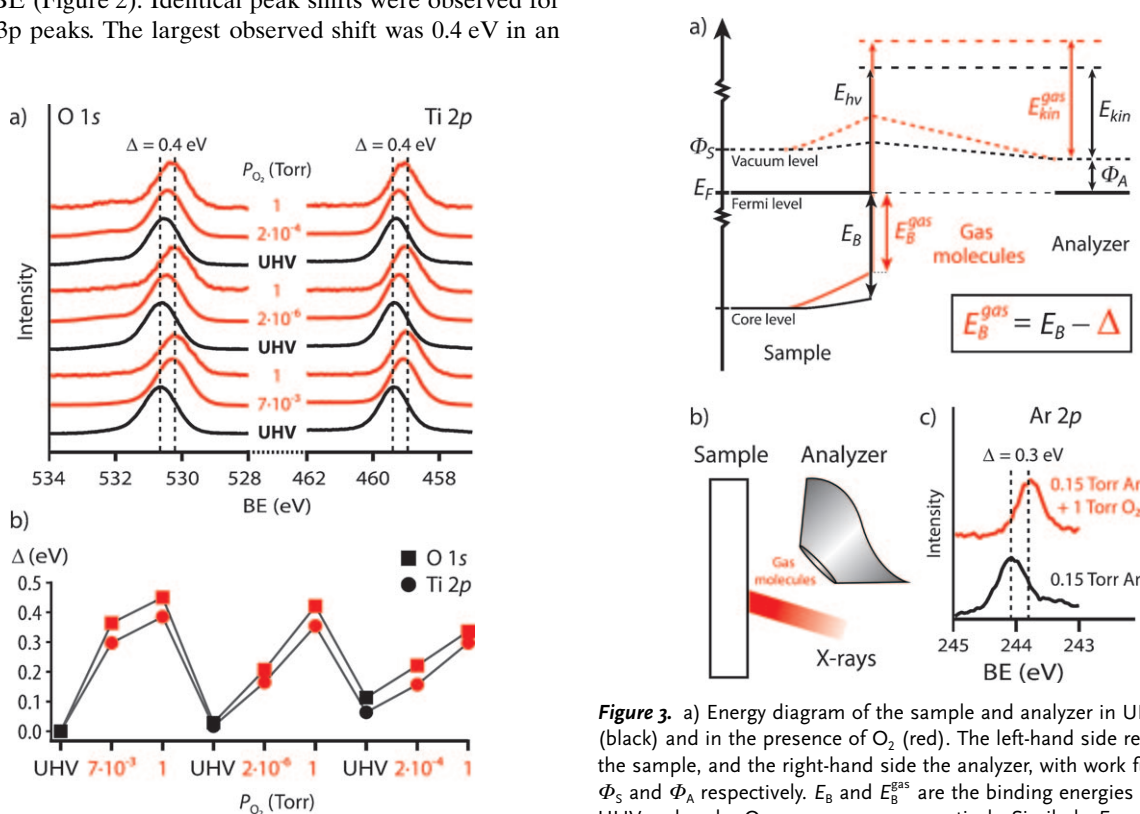
We are now in a position to properly measure chemical shifts of the core levels of the Ti and O atoms, adsorbates, gas molecules, and Au in nanoparticles grown by thermal evaporation. On a clean TiO<sub>2</sub> sample (sample 2), the O 1s and Ti 2p XPS spectra were found to be unchanged by exposure to CO up to 1 Torr. However, exposure to O<sub>2</sub> induces a shift of both the Ti 2p and the O 1s peaks towards lower BE (Figure 2). Identical peak shifts were observed for the Ti 3p peaks. The largest observed shift was 0.4 eV in an

atmosphere of 1 Torr O<sub>2</sub>. However, the absolute values of the peak shifts may depend on the initial oxidation state of the TiO<sub>2</sub>(110) crystal. After pumping the O<sub>2</sub> gas out of the vacuum chamber, all core-level peaks shifted back close to their original position, that is, the peak-shift effect is reversible. Figure 2b shows the peak shifts obtained from the APXPS spectra by Gaussian fits to the peaks. A detailed analysis reveals that the peaks do not shift completely back to their original positions, and this suggests that two different mechanisms are at play.

It could be speculated that the small irreversible peak shift may be caused by O<sub>2</sub> molecules, which are known to dissociate on the TiO<sub>2</sub> surface.<sup>[14]</sup> However, dissociation of O<sub>2</sub> molecules cannot account for the observed reversible peak shift, since recombination of O atoms on TiO<sub>2</sub>(110) at room temperature can be ruled out.<sup>[14]</sup> Instead, we propose that the reversible peak shifts are due to band bending induced by charge transfer between adsorbed O<sub>2</sub> molecules and the substrate [Eq. (1)], which changes the surface potential.



Molecularly adsorbed oxygen on TiO<sub>2</sub> surfaces has been previously observed by EPR spectroscopy.<sup>[15]</sup> Figure 3a shows



**Figure 2.** a) Series of O 1s and Ti 2p spectra measured on TiO<sub>2</sub>(110) (sample 2) for different pressures of O<sub>2</sub>. The spectra acquired in UHV (black lines) are the first in the series. The spectra are shown offset for clarity. b) Shifts in the peak position relative to the positions in the first spectrum.

**Figure 3.** a) Energy diagram of the sample and analyzer in UHV (black) and in the presence of O<sub>2</sub> (red). The left-hand side represents the sample, and the right-hand side the analyzer, with work functions Φ<sub>S</sub> and Φ<sub>A</sub> respectively. E<sub>B</sub> and E<sub>B</sub><sup>gas</sup> are the binding energies under UHV and under O<sub>2</sub> gas pressure, respectively. Similarly, E<sub>kin</sub> and E<sub>kin</sub><sup>gas</sup> are the measured kinetic energies, and E<sub>F</sub> is the Fermi level. b) Drawing of the experimental setup, with X-rays incident at an angle of 17° from the surface normal. The take-off angle of the photoelectrons relative to the sample normal is 44°. c) Ar 2p gas-phase XPS spectra for pure Ar and a mixture of Ar and O<sub>2</sub>, respectively.

a schematic energy diagram for the  $\text{TiO}_2$  sample in UHV and in an  $\text{O}_2$  atmosphere. The vacuum level changes gradually between the sample and the nozzle of the analyzer. Since the electronic levels of the gas-phase species are pinned to the vacuum level,<sup>[16]</sup> their XPS peaks will shift following the changes in contact potential (Figure 3b). To prove this we performed a similar experiment as described above, but this time the sample was also exposed to argon (0.15 Torr). Figure 3c shows the gas-phase Ar 2p XPS spectrum at 0.15 Torr of argon. After addition of 1 Torr of  $\text{O}_2$  we observed that the Ar 2p peak shifts by 0.3 eV towards lower BE, that is, the vacuum level indeed shifts. Hence, we conclude that the XPS peak shifts in Figure 2 are caused by a band-bending effect.

The shift of the Ar 2p peak shown in Figure 3 is smaller than that of 0.4 eV of the Ti 2p and O 1s peaks (cf. Figure 2). This smaller peak shift can be attributed to the finite width of the gas volume irradiated by the incident X-ray beam, with gas molecules at different distances from the sample surface and thus at different vacuum levels. Thus, the Ar 2p peak shift represents a minimum value of the vacuum-level shift at the sample surface. No peak shift was observed upon CO exposure (not shown).

We now turn our attention to shifts in the Au 4f peak positions of supported Au nanoparticles. After Au evaporation onto a clean  $\text{TiO}_2(110)$  substrate (sample 3), the 4f core-level peak of Au in the nanoparticles was found at a slightly higher BE than that of 84.0 eV for the Au foil. This is usually explained by a combination of initial- and final-state effects.<sup>[2b,e,17]</sup> It is unclear whether this effect, measured under UHV conditions, is relevant at the higher pressures of real catalysts. To study the influence of the reactants for CO oxidation, we sequentially exposed the  $\text{Au/TiO}_2(110)$  sample to 200 mTorr of  $\text{O}_2$  and 200 mTorr of CO (Figure 4). No shift of the Au 4f peak was observed upon exposure to either  $\text{O}_2$  or CO. However, the O 1s and Ti 3p peaks shift on  $\text{O}_2$  exposure. If the Ti 3p peak were used as a BE reference, however, an apparent shift of Au 4f towards higher BE would be obtained and erroneously interpreted as electron donation from the Au nanoparticles. The use of a grounded piece of Au foil as external reference instead allowed us to reveal that the

Au 4f peak actually does not shift (within the 0.05 eV accuracy of the experiment) on exposure of the  $\text{Au/TiO}_2$  sample to  $\text{O}_2$ . We estimated the order of magnitude limit on the charging of Au nanoparticles by modeling them as spherical capacitors. For a sphere of 2 nm radius a voltage of 0.05 V would correspond to a charge of roughly 0.07 electrons or approximately  $10^{-5}$  electrons per atom.

In conclusion, our results show that all  $\text{TiO}_2$ -related peaks, that is, Ti 2p, Ti 3p, and O 1s, shift together by the same amount under exposure to  $\text{O}_2$ , while those of supported Au nanoparticles do not. The binding energies from the core levels of the  $\text{TiO}_2$  substrate cannot be used as energy reference for calibration of the XPS spectra. We have shown that the BE shifts of these peaks are due to band-bending effects caused by molecular  $\text{O}_2$ , adsorbed on the  $\text{TiO}_2$  support at an  $\text{O}_2$  pressure of 1 Torr. The band-bending also affects the vacuum level of  $\text{TiO}_2$ , causing the XPS peaks of nearby gas species to shift by similar amounts. The present results clarify the origin of peak shifts of Au nanoparticles and improve our fundamental understanding of catalytic reaction mechanisms, for example, in CO oxidation, because adsorbed  $\text{O}_2$  and  $\text{O}_2^-$  may play a key role in supplying reactive oxygen for surface-catalyzed reactions. Our findings demonstrate that Au nanoparticles supported on  $\text{TiO}_2$  do not donate or accept additional charge when the sample is exposed to either CO or  $\text{O}_2$ , at least at levels that would produce measurable shifts in the XPS peaks.

### Experimental Section

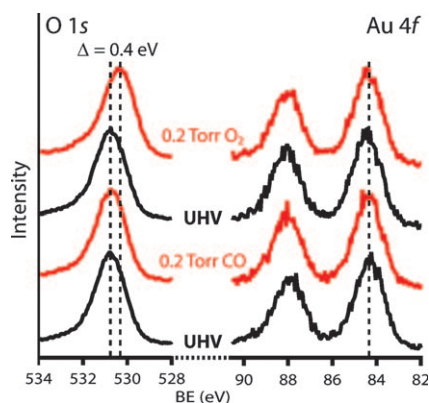
The experiments were carried out at beamline 11.0.2 and beamline 9.3.2 at the Advanced Light Source, Berkeley.<sup>[9]</sup> The samples were fresh  $5 \times 10$  mm rutile  $\text{TiO}_2(110)$  single crystals that were cleaned by sputtering/annealing cycles until no contamination was detected by XPS. The  $\text{Au/TiO}_2$  sample (sample 3) was produced by exposing the  $\text{TiO}_2$  crystal to Au vapor after exposure to  $\text{O}_2$ .

To test the validity of the Au reference we fabricated a sample (sample 1) with a gold pattern consisting of a circular area of 4 mm diameter and an array of 200  $\mu\text{m}$ -diameter islands (Figure 1). This reference sample was fabricated in a separate chamber and transferred through air to the experimental chamber. After air exposure, no contamination was detected. To minimize shifts of the photon energy due to physical movement of the monochromator, all XPS measurements with Au nanoparticles were carried out with a constant photon energy of 830 eV. In all other experiments, the photon energy was 690 eV. For reference purposes XPS spectra were recorded frequently on a grounded Au foil in UHV to obtain a  $\text{Au } 4f_{7/2}$  spectrum, which is calibrated to 84.0 eV. This procedure was followed throughout all the experiments to check for changes in the photon energy. All measurements were done with a typical acquisition time of 1 min per spectrum, and multiple spots were measured to minimize beam-damage effects. This careful procedure excludes effects such as beam-induced oxidation, as observed in previous studies.<sup>[13]</sup> The values for the peak shifts were obtained by subtracting the Shirley background and by Gaussian fitting to the peaks in the APXPS spectra. All experiments were carried out at room temperature, and gases were dosed by backfilling the chamber.

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**Figure 4.** Au 4f and O 1s XPS spectra for different gas and pressure conditions on  $\text{Au/TiO}_2(110)$ . The spectra acquired in UHV are the first in the series. The spectra are shown offset for clarity.

**Keywords:** charge transfer · gold · nanoparticles · photoelectron spectroscopy · supported catalysts

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