

# Kinetics of the plasmon optical response of Au nanoparticles/TiO<sub>2</sub> catalyst under O<sub>2</sub> and H<sub>2</sub> followed by differential diffuse reflectance spectroscopy

Y. Borensztein<sup>1,a</sup>, L. Delannoy<sup>2</sup>, R.G. Barrera<sup>3</sup>, and C. Louis<sup>3</sup>

<sup>1</sup> Institut des NanoSciences de Paris, CNRS and UPMC Univ. Paris 6, UMR 7588, 4 place Jussieu, case courrier 840, 75252 Paris Cedex 05, France

<sup>2</sup> Laboratoire de Réactivité des Surfaces, CNRS and UPMC Univ. Paris 6, UMR 7197, 4 place Jussieu, 75252 Paris Cedex 05, France

<sup>3</sup> Instituto de Física, Universidad Nacional Autónoma de México, México D.F., México

Received 19 September 2010 / Received in final form 24 January 2011

Published online 17 May 2011 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2011

**Abstract.** The changes in the optical properties of Au/TiO<sub>2</sub> powder catalyst, prepared by the deposition-precipitation method, are measured in the visible range by use of a home-made diffuse differential reflectance spectrometer, when the ambient atmosphere is switched between H<sub>2</sub> and O<sub>2</sub>. Two main features are observed: (i) a short wavelength one, located between 400 and 600 nm, is shown to be related to the modifications of the plasmon resonance of the 3-dimensional metallic gold particles with mean size around 4 nm, induced by the exposure to oxygen or by its removal; (ii) a second feature, observed at long wavelengths between 600 and 1100 nm, is extremely sensitive to the exposure to oxygen. This optical feature could be due to the presence in the catalyst, either of Au<sup>0</sup> clusters of several tens atoms, which are expected to display molecular-like transitions in this optical range, or to specific sites of the Au particles (edge atoms or peripheral atoms at the interface with the TiO<sub>2</sub> support), which could be highly reactive to oxygen.

## 1 Introduction

After the discovery by Haruta in the 80's that Au nanoparticles (NPs) smaller than 5 nm and supported on reducible oxide substrates can be very active catalysts for the oxidation of carbon monoxide, there has been a tremendous increase of research in this field [1, 2]. In spite of the huge number of experimental and theoretical works, several issues are still poorly understood or are at least very controversial, such as the interaction of O<sub>2</sub> with gold [3–5], the activation of O<sub>2</sub> and the nature and location of the active sites [6–8], the oxidation state of gold during the reaction [9–12], the size and shape of the most reactive Au particles [13, 14]. Numerous studies were performed on model catalysts, like gold particles deposited on single-crystal-oxide surfaces and studied under vacuum [15]. On the other hand, only few techniques allow us to investigate “real” samples, usually formed by Au particles adsorbed on a powder of oxide, and exposed to “real” conditions, that is, under atmospheric pressure. Among them, optical techniques in the UV-visible range allow such “operando” experiments.

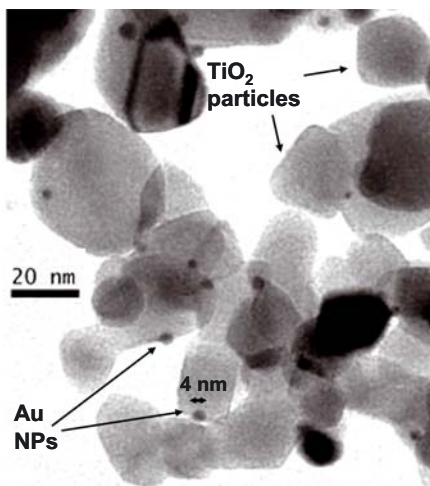
It is known that plasmon resonances can be excited by visible light in nanoparticles of metals like Cu, Au or Ag,

and that their spectral peak location and line-shape are very much dependent on the size and shape of the particles, as well as on their interaction with the substrate and the overall environment [16–21]. The aim of the present work is consequently to investigate the optical properties of real gold-based catalysts, and especially on how their optical properties change when they are exposed to gases. We present and analyze results of optical spectra obtained at room temperature when exposing an Au/TiO<sub>2</sub> catalyst sequentially to dihydrogen, which is a reducing gas, then to dioxygen (and vice-versa) which is an oxidant gas and for which the question of adsorption on the Au particles is still controversial. Since the TiO<sub>2</sub> powder scatters light very efficiently, we used a time-resolved diffuse-reflectance spectrometer that turned out to be very sensitive to the presence of small amounts of absorbing nanoparticles, and enabled us to follow, in real time the spectral changes due to the gas exposure.

## 2 Experimental methods and transmission electron micrograph

The catalyst was prepared by the deposition-precipitation method with urea as described in references [22, 23], using Degussa P25 TiO<sub>2</sub> as the support and HAuCl<sub>4</sub> as the

<sup>a</sup> e-mail: yves.borensztein@insp.jussieu.fr



**Fig. 1.** Transmission electron microscopy image of the Au/TiO<sub>2</sub> catalyst.

gold precursor, and was calcined in air at 500 °C during 2 h. This results in a powder of TiO<sub>2</sub> crystallites with three-dimensional (3-D) Au nanoparticles (NPs) (Au loading 1 wt%) supported on them. Transmission electron microscopy (TEM) was performed on the sample using a JEOL 100 CX II microscope. The size limit for the detection of gold particles on this support was about 1–1.5 nm. In Figure 1 we show a TEM image of the powder catalyst where the large gray particles are the TiO<sub>2</sub> crystallites, while the darker small spots correspond to the Au nanoparticles. Their distribution of sizes ranges from 1–1.5 nm to 6 nm with an average size of about 4 nm. This is in agreement with previous results where the same preparation procedure was used [8, 23]. Note that the presence in the sample of gold particles smaller than 1–1.5 nm and/or 2-dimensional particles, that are not actually seen, cannot be excluded. For example, clusters containing about ten gold atoms were recently observed on Au/Fe<sub>2</sub>O<sub>3</sub> by use of aberration-corrected scanning TEM [13].

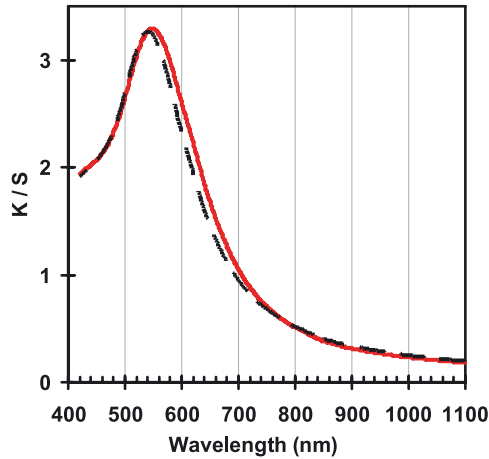
The optical studies were performed by using two different equipments. The absolute diffuse reflectance of the powder catalyst, either in H<sub>2</sub> or in O<sub>2</sub>, was measured with a commercial spectrophotometer with an integrating sphere (Cary5). From the measured reflectance, following the Kubelka-Munk model [24], the ratio  $K/S$  was calculated by using the relation  $\frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty}$ , where  $K$  represents the total absorption of the powder,  $S$  the total scattering intensity and  $R_\infty$  the diffuse reflection of the sample at total hiding. In our measurements on the powder catalyst, the reflectance was normalized by the diffuse reflectance of pure TiO<sub>2</sub>, which is close to 1 in the visible range. The absorption coefficient  $K$  is mainly due to the absorption of the Au NPs, while the scattering coefficient  $S$  is dominated by the scattering of the TiO<sub>2</sub> crystallites [21]. Consequently,  $K/S$  is proportional to the absorption  $K$  of the Au NPs divided by the scattering coefficient  $S$  of the TiO<sub>2</sub> crystallites;  $S$  has been considered

proportional to  $1/\lambda^4$  assuming independent Rayleigh scattering.

In order to measure slight changes in the reflectance when switching from one gas to another, and in order to follow the kinetics of the reaction related to these changes, we used a second equipment, based on a home-made cell with a time-resolved spectrometer, which enabled us to record full spectra every two seconds. The measured quantity is the relative change of diffuse reflectance when switching from gas A to gas B, defined by:  $\text{DDR}_{A \rightarrow B} = \frac{R_B - R_A}{R_A}$  and called diffuse differential reflectance. This technique is very sensitive and allows one to observe very small changes in the optical response of the catalyst. More details of the experimental set-up can be found in [21]. All the measurements were performed at room temperature and at atmospheric pressure, with ultrapure H<sub>2</sub> and O<sub>2</sub> gases (99.999%) in carrying He (99.999%) gas, with flow rates equal to 5 mL/min of H<sub>2</sub> and 20 mL/min of He, and 2.5 mL/min of O<sub>2</sub> and 22.5 mL/min of He, respectively. Before optical measurements, the Au/TiO<sub>2</sub> sample was activated in situ in the cell under H<sub>2</sub>/He at 150 °C for 30 min.

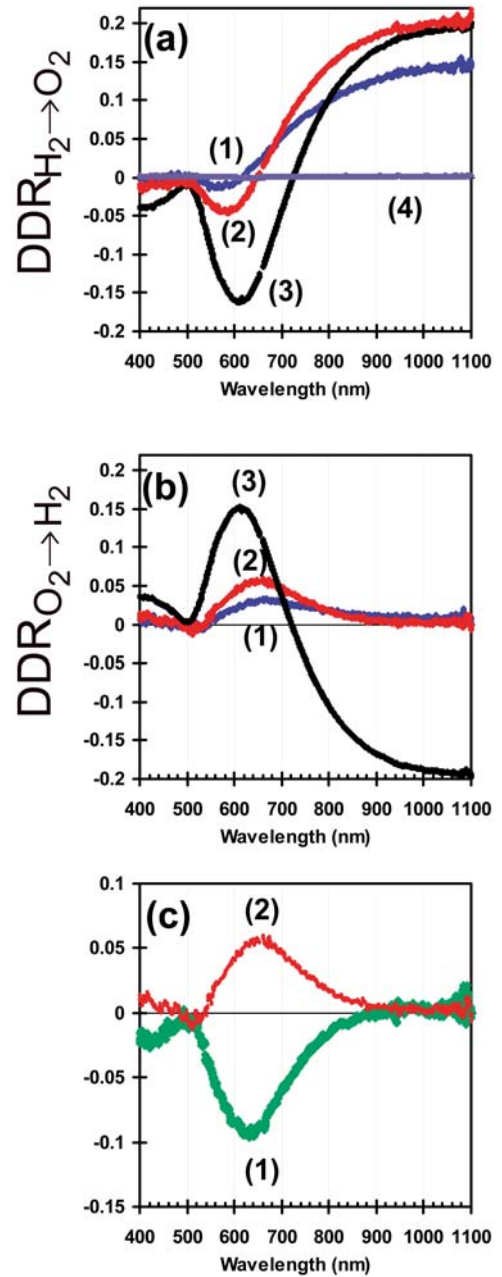
### 3 Optical results and discussion

Figure 2 shows the  $K/S$  spectra of the catalyst under H<sub>2</sub> atmosphere (black dashed line) and under O<sub>2</sub> one (red continuous line). The  $K/S$  spectra, directly related to the absorption of the Au NPs, are dominated by a sharp resonance lying between 450 and 650 nm, centered at 541 nm under H<sub>2</sub>, and slightly shifted to 547 nm under O<sub>2</sub>. As shown previously [21], this absorption is due to the plasmon resonance of the 3-D metallic gold NPs, and the position of the resonance corresponds to slightly flattened particles supported on the TiO<sub>2</sub> substrate, with an aspect ratio close to 0.5. Such flat shape is in agreement with truncated octahedral particles observed by High-Resolution TEM [23]. An absorption tail is present above 700 nm (Fig. 2). The difference between the two spectra is very small. Moreover, since several minutes were needed to record each spectrum, it did not allow us to follow possible fast changes in the spectrum. Thus, in order to better show the differences between the spectra when switching from one gas to the other, and to monitor the changes as a function of time, we used the home-made differential-diffuse-reflectance spectrometer described above. Figure 3 shows the evolution of the  $\text{DDR}_{\text{H}_2 \rightarrow \text{O}_2}$  spectra obtained after switching from H<sub>2</sub> to O<sub>2</sub> (a), and  $\text{DDR}_{\text{O}_2 \rightarrow \text{H}_2}$  spectra during the reverse process (b). In order to ensure that the observed effects are due to the interaction of the supported Au NPs with O<sub>2</sub> or H<sub>2</sub>, the same kind of DDR measurements have been performed with a sample of pure TiO<sub>2</sub>, without Au NPs. The corresponding spectrum is drawn for comparison in Figure 3a, and does not display any optical response upon exposure to O<sub>2</sub>. Consequently, the features of the DDR spectra measured on the Au/TiO<sub>2</sub> sample can be unambiguously assigned to the presence of Au NPs. The kinetics can also be followed by monitoring the signal at different wavelengths as a function of



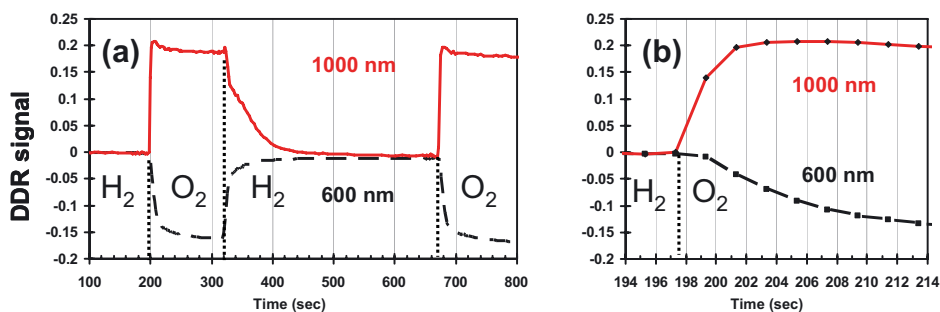
**Fig. 2.** (Color online) Optical absorption ( $K/S$ ) of the powder catalyst in H<sub>2</sub> (black dashed line) and in O<sub>2</sub> (red continuous line). The diffuse reflectance spectra were normalized to the pure TiO<sub>2</sub> one.

time. This is reported in Figure 4, where the DDR signals measured at 600 nm and 1000 nm are plotted as a function of time during which H<sub>2</sub> and O<sub>2</sub> are switched several times. Let us first discuss the spectra of Figure 3a. The blue spectrum (1), recorded just after O<sub>2</sub> has been introduced in the cell (about 1 s), is dominated by a signal at long wavelengths, starting above 600 nm. Two seconds later, this signal has increased, and a small feature appears at short wavelengths, between 400 nm and 700 nm (red spectrum 2). The spectrum continues developing with time and progressively stabilizes to reach the black spectrum (curve 3). This spectrum that gives the difference between the catalyst in steady states under O<sub>2</sub> and under H<sub>2</sub>, clearly displays two features: the increase at long wavelength that does not change significantly after 3 s, and the short wavelength one, which appears as a derivative-like curve with a maximum at 500 nm and a minimum at 600 nm. The changes at short wavelengths can be highlighted by taking the difference between the black spectrum 3 (O<sub>2</sub>/60 s) and the red spectrum 2 (O<sub>2</sub>/3 s), which is drawn in Figure 3c (curve 1). The short wavelength feature is clearly related to the main plasmon resonance of the metallic gold NPs centered at 550 nm (Fig. 2), and can be understood as the shift of this resonance due to the exposure to O<sub>2</sub>. Previously, we showed with similarly-prepared catalysts that the modification of the plasmon resonance due to exposure to O<sub>2</sub> could be attributed to a slight charge transfer from gold to oxygen species (0.05 electron per gold surface atom), together with a slight flattening of the 3-D gold NPs [21]. In other words, exposure to oxygen leads to a loss of electrons by gold, that is, to some kind of “oxidation” of gold atoms, probably due to adsorption of oxygen species on the Au NPs. It cannot be deduced from our results whether these oxygen species are adsorbed under molecular or atomic form or where they adsorb: on sites located on the Au particles or at the perimeter of the contact area between the Au particles and the oxide



**Fig. 3.** (Color online) DDR spectra when switching from H<sub>2</sub> to O<sub>2</sub> (a) and from O<sub>2</sub> to H<sub>2</sub> (b); 1 s after switching to O<sub>2</sub> (H<sub>2</sub>) (blue curve (1)); 3 s after switching to O<sub>2</sub> (H<sub>2</sub>) (red curve (2)); 60 (100) s after switching to O<sub>2</sub> (H<sub>2</sub>) (black curve (3)); (c) thick green curve (1): difference between curves 3 and 2 of (a); red curve (2): same as curve (2) in (b). Curve (4) in (a) is the DDR spectrum obtained on pure TiO<sub>2</sub>, without Au NPs.

substrate, as it has been also proposed [6–8]. The second effect, that is a modification of the shape of the Au NPs, is consistent with recent Environmental TEM experiments performed by Giorgio et al., who showed that gold NPs on TiO<sub>2</sub> displayed facets under 2 mbar of H<sub>2</sub>, and were reversibly rounded under 2 mbar of O<sub>2</sub> [4].



**Fig. 4.** (Color online) (a) Evolution of the intensity of the DDR signals at 600 nm (dashed black line) and at 1000 nm (continuous red line) as a function of time during several H<sub>2</sub> – O<sub>2</sub> switches (b) enlargement at the first introduction of O<sub>2</sub>.

The kinetics of spectrum changes at 600 and 1000 nm upon exposure to O<sub>2</sub> or to H<sub>2</sub> is presented in Figure 4. An enlargement corresponding to the first introduction of O<sub>2</sub> (Fig. 4b) shows clearly that the two features, at long and short wavelengths, display different kinetics, the one at 1000 nm develops within a very short time, of the order of one second, while the second one at 600 nm appears with a delay of one or two seconds and stabilizes after about 15 s. This indicates that these two resonances may have a different physical origin as it will be discussed below.

Similar effects are obtained when O<sub>2</sub> is replaced back by H<sub>2</sub>, and the corresponding DDR<sub>O<sub>2</sub>→H<sub>2</sub></sub> spectra are drawn in Figure 3b. The spectra after one and three seconds under H<sub>2</sub> (blue (1) and red (2) curves, respectively) are dominated by the short wavelength feature between 400 and 700 nm. Curve 2 redrawn in Figure 3c has the same shape with opposite sign, as the difference spectrum (1) obtained from Figure 3a. This shows that the introduction of H<sub>2</sub> first cancels the shift of the plasmon resonance in the 3-D NPs induced by the previous exposure to O<sub>2</sub>. On the contrary, black curve 3 in Figure 3b shows that it takes longer time before the long wavelength feature starts to develop, and stabilization is obtained after about 80 s. The final spectrum is exactly the opposite in sign of the steady-state spectrum shown in Figure 3a (curve 3), which demonstrates the reversibility of the phenomena.

A phenomenological conclusion can be drawn from these results. The Au/TiO<sub>2</sub> catalyst displays two changes in its optical diffuse reflectance, a band shift at short wavelength related to the plasmon of 3-D metallic gold NPs, which occurs in the presence of O<sub>2</sub> and disappears with H<sub>2</sub> in a time scale of about 10–20 s under our experimental conditions. It was checked that the kinetics depends on the O<sub>2</sub> and H<sub>2</sub> flow rates, and that these changes are slower or faster with lower or higher flow rates. The second resonance-like feature at long wavelength, above 600–700 nm, is extremely sensitive to O<sub>2</sub> and is modified almost immediately after the introduction of O<sub>2</sub> into the cell. However, when switching back to H<sub>2</sub>, the initial state takes longer time to be restored, which could be related to the very reactive character of the sites and/or particles towards O<sub>2</sub>, giving rise to the long wavelength resonance.

The origin of this long wavelength resonance-like feature, which is shown to be the most reactive towards O<sub>2</sub>, is an important issue, as the origin of the high catalytic activity of Au/TiO<sub>2</sub> catalyst in the CO oxidation reaction is still under debate. A first explanation which comes to mind is the possible coupling of Au NPs. It is known that pairs of Au particles display long wavelength plasmon resonance because of their electromagnetic coupling. However, the TEM measurements performed on our samples did not show any coupled or agglomerated particles. Moreover, the intensity of the long wavelength resonance is the same for a 1% Au-loaded sample and for a 4% one, while it would be expected to be larger in the 4% sample if it were due to the coupling of the particles. Consequently, this explanation can be ruled out. In our previous paper [21], we modeled this feature as due to the change of the plasmon resonance of very flat metallic Au particles interacting with O<sub>2</sub>; the plasmon resonance of very flat metallic Au particles is indeed known to be red-shifted compared to that of 3-D Au NPs. However, such very flat particles (with an aspect ratio below 0.12 in order to have a resonance around 1000 nm) with a lateral size of 2 to 4 nm, would have a thickness of 1 or 2 monolayers, and might not be expected to display any plasmon resonance [25]. Consequently, we explore in the following other possible explanations for the long wavelength resonance.

The nature of the most active gold particles and the location of the active sites in gold/oxide catalyst is a hot topic and very controversial. Most authors agree that the gold NPs should have sizes below 2 or 3 nm to display high activity. Moreover, it has been claimed by Herzing et al. [13], by use of aberration-corrected scanning TEM performed on Au/Fe<sub>2</sub>O<sub>3</sub> catalysts prepared by co-precipitation, that the “high catalytic activity for carbon monoxide oxidation is correlated with the presence of bilayer clusters that are ~0.5 nanometer in diameter and contain only ~10 gold atoms”. This result is in agreement with previous prediction that Au clusters with a few atoms supported on MgO would be very active towards the oxidation of CO [26, 27]. However, very recently, using the same technique for Au/Fe<sub>2</sub>O<sub>3</sub> prepared via a colloidal path, Liu et al. [14] reached the opposite conclusion: “for the current catalyst, gold nanoclusters have diameters larger than 1 nm and bilayer structures

and/or diameters of about 0.5 nm are not mandatory to achieve the high activity". From grazing-incidence small angle X-ray scattering experiments, Saint-Lager et al. also proposed that the active particles are actually 3-dimensional [28, 29]. Bond proposed recently that the transition between catalytic and non-catalytic particles is related to their size, and that the transition occurring around 2 nm corresponds to the transition between the metallic and non-metallic characters of the particles, the smallest ones being the catalytic ones [30]. As stressed by him, the discrepancy between the results reported by the different authors could be due to differences in the distribution of sizes and shapes, and only the lower tail of the size distribution (the smallest particles) could be the primary source of activity. A 2 nm gold hemisphere contains around 120 atoms. Small clusters with a number of atoms of the order of one hundred are not expected to have a well-defined metallic character and can rather be considered as giant Au molecules with discrete atomic levels [31, 32]. Whetten and coll. proposed that for Au clusters, there is a "critical size around 2 nm for which the electronic structure changes dramatically" [32, 33]. Such very small clusters display optical absorptions due to molecular-like transitions between filled and empty electronic states. For instance, it has been shown experimentally and theoretically that thiol-protected Au<sub>25</sub> clusters display a transition around 680 nm with a shoulder around 800 nm [34–36]. HOMO-LUMO gaps equal to 0.85 eV (1460 nm) has been calculated for protected Au<sub>39</sub> clusters [37], while optical experiments for Au<sub>38</sub> showed a gap of 0.9 eV, with a maximum of absorption at 1030 nm [38]. It has been shown also that bare Au hollow clusters with 3-D shape ranging between 23 and 42 atoms, which are stable on MgO, display small gaps [39]. In the case of the most stable 32-atom cages with icosahedral or truncated-octahedral shape on MgO, the HOMO-LUMO gaps have been found equal to 1.19 eV (1040 nm) and 1.23 eV (1008 nm) [39], respectively. The case of intermediate size (around 100 to 200 atoms) is not as clear [32]. Consequently, an explanation for the optical absorption observed in our experiments between 700 and 1100 nm, could be the presence in our Au/TiO<sub>2</sub> sample of such type of small Au clusters with molecular-like transitions.

Another alternative explanation for the long-wavelength resonance can be proposed. It is known that 3-D Au NPs, with a size around 2 nm or above, have a pyramidal shape, like for instance truncated octahedral shape observed by TEM [23]. When such kinds of particles with well-defined facets and edges have a metallic character, both experiments and calculations have shown that they can sustain several multipolar plasmon resonances at different wavelengths, and that slight changes of the edges (as the removal of some edge atoms) can strongly modify the optical response of the NPs [18]. In our case, it is possible that the long wavelength resonance could be related to multipolar resonances in the supported Au NPs with specific pyramidal shape. As the shape of the Au NPs, especially their edges, appears to be modified by exposure to oxygen as shown by environmental

TEM [4], such multipolar resonance could be modified upon oxygen adsorption. From calculations, it has been proposed that the reactive sites towards O<sub>2</sub> in the CO oxidation reaction could be the Au peripheral atoms located at the interface edges of the Au NPs, i.e. the edges of the NPs lying at the interface between the Au NPs and the TiO<sub>2</sub> substrate [6, 8, 40–42]. Therefore, the adsorption of oxygen on these atoms could modify the local electronic structure of the interface edges of the Au NP, and therefore the corresponding resonances.

Whatever the origin of the long wavelength resonance is, molecular-like clusters or specific edge sites of metallic NPs, the concerned species are very reactive towards O<sub>2</sub>, as shown by the rapid change of the long wavelength resonance when the sample is exposed to O<sub>2</sub>. This effect can be understood as an "oxidation" of these clusters or sites, in agreement to a recent theoretical prediction of a reversible formation of Au-O "oxide" phase at boundaries of MgO-supported Au clusters [43]. In spite of our observation, a direct correlation between the species responsible for the long wavelength resonance and the high catalytic activity of the samples cannot be drawn so far from our results. It is worthwhile mentioning that it has been proposed, either by model calculations or experimentally, that unsupported small Au clusters with 10 to 38 atoms [5, 44], TiO<sub>2</sub>-supported Au<sub>10</sub> clusters [45], ligand-protected Au clusters [37], or Au<sub>55</sub> clusters supported on inert substrates [46], could dissociate efficiently O<sub>2</sub> and therefore could play a main role in the oxidation of CO. On the other hand, considering the large number of articles revealing the influence of the nature of the oxide support on the activity in CO oxidation for gold supported catalysts, the assumption based on the existence of specific gold sites at the gold nanoparticles-TiO<sub>2</sub> support interface has also to be considered.

In conclusion, using real-time measurements of the diffuse optical reflectance of a Au/TiO<sub>2</sub> catalyst, we have shown that two different kinds of optical resonances are present. A short wavelength one corresponds to the usual plasmon resonance of slightly flattened 3-D Au particles and is modified by the adsorption of oxygen. A long wavelength resonance which could be due, (i) either to small Au clusters which display molecular-like transitions; or (ii) to resonances related to specific sites located at the edges of the faceted Au nanoparticles, possibly peripheral sites at the Au/TiO<sub>2</sub> interface edges. These specific sites (small clusters, or edge atoms of NPs) are shown to be very swiftly modified by the exposure to O<sub>2</sub>. Calculations of the equilibrium shapes, optical properties and O<sub>2</sub> ability to adsorb/dissociate on Au clusters or on edges of small NPs supported on TiO<sub>2</sub> surfaces would therefore be a relevant issue to determine a possible relation between the observed long-wavelength resonance, the presence of small clusters or specific sites on edges of the NPs, and their possible high activity. Aberration-corrected STEM studies are in progress in order to determine the possible presence of small clusters and the shape of larger NPs for the Au/TiO<sub>2</sub> catalyst.

This work has been partially supported by the French National Agency (ANR) in the frame of its Nanoscience Program (PNano, project Reactgold No. ANR-07-NANO-024-01). One of us (RGB) acknowledges the financial support of Consejo Nacional de Ciencia y Tecnología (Mexico) through project No. 82073 and Dirección General de Asuntos del Personal Académico (UNAM, Mexico) through project PAPIIT 111710. We thank Ignacio Garzon for fruitful discussions.

## References

- G.C. Bond, C. Louis, D. Thompson, *Catalysis by Gold* (Imperial College Press, London, 2006), Vol. 6
- M. Haruta, *Nature* **437**, 1098 (2005)
- M.S. Chen, D.W. Goodman, *Science* **306**, 252 (2004)
- S. Giorgio, M. Cabie, C.R. Henry, *Gold Bull.* **41**, 167 (2008)
- N. Lopez, J.K. Nørskov, *J. Am. Chem. Soc.* **124**, 11262 (2002)
- Z.P. Liu, X.Q. Gong, J. Kohanoff, C. Sanchez, P. Hu, *Phys. Rev. Lett.* **91** (2003)
- S. Aii, F. Mortin, A.J. Renouprez, J.L. Rousset, *J. Am. Chem. Soc.* **126**, 1199 (2004)
- M. Kotobuki, R. Leppelt, D.A. Hansgen, D. Widmann, R.J. Behm, *J. Catal.* **264**, 67 (2009)
- J.T. Miller, A.J. Kropf, Y. Zha, J.R. Regalbuto, L. Delannoy, C. Louis, E. Bus, J.A. van Bokhoven, *J. Catal.* **240**, 222 (2006)
- J.A. van Bokhoven, C. Louis, T.J. Miller, M. Tromp, O.V. Safonova, P. Glatzel, *Angew. Chem. Int. Ed.* **45**, 4651 (2006)
- L.K. Ono, B.R. Cuenya, *J. Phys. Chem. C* **112**, 4676 (2008)
- P. Jiang, S. Porsgaard, F. Borondics, M. Kober, A. Caballero, H. Bluhm, F. Besenbacher, M. Salmeron, *J. Am. Chem. Soc.* **132**, 2858 (2010)
- A.A. Herzing, C.J. Kiely, A.F. Carley, P. Landon, G.J. Hutchings, *Science* **321**, 1331 (2008)
- Y. Liu, C.J. Jia, J. Yamasaki, O. Terasaki, F. Schuth, *Angew. Chem. Int. Ed.* **49**, 5771 (2010)
- R. Meyer, C. Lemire, S.K. Shaikhutdinov, H. Freund, *Gold Bull.* **37**, 72 (2004)
- U. Kreibitz, M. Vollmer, *Optical Properties of Metal Clusters* (Springer, New York, 1994)
- C. Beitia, Y. Borenstein, R. Lazzari, J. Nieto, R.G. Barrera, *Phys. Rev. B* **60**, 6018 (1999)
- C. Noguez, *J. Phys. Chem. C* **111**, 3806 (2007)
- I.O. Sosa, C. Noguez, R.G. Barrera, *J. Phys. Chem. B* **107**, 6269 (2003)
- V. Myroshnychenko, J. Rodriguez-Fernandez, I. Pastoriza-Santos, A.M. Funston, C. Novo, P. Mulvaney, L.M. Liz-Marzan, F.J.G. de Abajo, *Chem. Soc. Rev.* **37**, 1792 (2008)
- Y. Borenstein, L. Delannoy, A. Djedidi, R.G. Barrera, C. Louis, *J. Phys. Chem. C* **114**, 9008 (2010)
- R. Zanella, L. Delannoy, C. Louis, *Appl. Catal. A Gen.* **291**, 62 (2005)
- R. Zanella, S. Giorgio, C.H. Shin, C.R. Henry, C. Louis, *J. Catal.* **222**, 357 (2004)
- P. Kubelka, *J. Opt. Soc. Am.* **38**, 448 (1948)
- Y. Borenstein, M. Roy, R. Alameh, *Europhys. Lett.* **31**, 311 (1995)
- A. Sanchez, S. Abbet, U. Heiz, W.D. Schneider, H. Hakkinen, R.N. Barnett, U. Landman, *J. Phys. Chem. A* **103**, 9573 (1999)
- B. Yoon, H. Hakkinen, U. Landman, A.S. Worz, J.M. Antonietti, S. Abbet, K. Judai, U. Heiz, *Science* **307**, 403 (2005)
- M.C. Saint-Lager, A. Bailly, M. Mantilla, S. Garaudee, R. Lazzari, P. Dolle, O. Robach, J. Jupille, I. Laoufi, P. Taunier, *Gold Bull.* **41**, 159 (2008)
- I. Laoufi, M.-C. Saint-Lager, R. Lazzari, J. Jupille, O. Robach, S. Garaudée, G. Cabailh, P. Dolle, H. Cruguel, A. Bailly, *J. Phys. Chem. C* **115**, 4673 (2011)
- G. Bond, *Gold Bull.* **43**, 88 (2010)
- T.G. Schaaff, M.N. Shafiqullin, J.T. Houry, I. Vezmar, R.L. Whetten, W.G. Cullen, P.N. First, C. Gutierrez-Wing, J. Ascensio, M.J. Jose-Yacamán, *J. Phys. Chem. B* **101**, 7885 (1997)
- M.M. Alvarez, J.T. Houry, T.G. Schaaff, M.N. Shafiqullin, I. Vezmar, R.L. Whetten, *J. Phys. Chem. B* **101**, 3706 (1997)
- T.G. Schaaff, R.L. Whetten, *J. Phys. Chem. B* **104**, 2630 (2000)
- J. Akola, M. Walter, R.L. Whetten, H. Hakkinen, H. Gronbeck, *J. Am. Chem. Soc.* **130**, 3756 (2008)
- Y. Negishi, N.K. Chaki, Y. Shichibu, R.L. Whetten, T. Tsukuda, *J. Am. Chem. Soc.* **129**, 11322 (2007)
- M. Zhu, C.M. Aikens, F.J. Hollander, G.C. Schatz, R. Jin, *J. Am. Chem. Soc.* **130**, 5883 (2008)
- O. Lopez-Acevedo, K.A. Kacprzak, J. Akola, H. Hakkinen, *Nature Chem.* **2**, 329 (2010)
- H.F. Qian, Y. Zhu, R.C. Jin, *ACS Nano* **3**, 3795 (2009)
- R. Ferrando, G. Barcaro, A. Fortunelli, *Phys. Rev. Lett.* **102**, 216102 (2009)
- M.M. Schubert, S. Hackenberg, A.C. van Veen, M. Muhler, V. Plzak, R.J. Behm, *J. Catal.* **197**, 113 (2001)
- L.M. Molina, B. Hammer, *Appl. Catal. A Gen.* **291**, 21 (2005)
- L.M. Molina, M.D. Rasmussen, B. Hammer, *J. Chem. Phys.* **120**, 7673 (2004)
- P. Frondelius, H. Hakkinen, K. Honkala, *Angew. Chem. Int. Ed.* **49**, 7913 (2010)
- A. Roldan, S. Gonzalez, J.M. Ricart, F. Illas, *Chem. Phys. Chem.* **10**, 348 (2009)
- I.N. Remediakis, N. Lopez, J.K. Nørskov, *Angew. Chem. Int. Ed.* **44**, 1824 (2005)
- M. Turner, V.B. Golovko, O.P.H. Vaughan, P. Abdulkin, A. Berenguer-Murcia, M.S. Tikhov, B.F.G. Johnson, R.M. Lambert, *Nature* **454**, 981 (2008)