Au particles supported on (110) anatase-TiO₂

S. Giorgio a,*, C.R. Henry a, B. Pauwels b, G. Van Tendeloo b

a CRMC2-CNRS, Laboratoire Associé aux Universités d’Aix-Marseille 2 et 3, Campus de Luminy, Case 913, 13288 Marseille Cedex 9, France
b RUCA-EMAT, Groenenborgerlaan 171, 2020 Antwerp, Belgium

Received 15 March 2000; received in revised form 26 May 2000

Abstract

Au particles were prepared by evaporation in ultra high vacuum at high temperature, on the surfaces of TiO₂ micro-spheres with the anatase structure. The morphology and the structural deformation in Au deposits were studied by high resolution transmission electron microscopy and image simulations by the multislice technique. The particles were polyhedral, limited by (100) and (111) faces. Patches with a hexagonal lattice were found around the particles, which was interpreted as thin Au islands on the surface. In these islands the Au lattice was deformed and perfectly accommodated to the (110) surface of TiO₂. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Au particles; Catalyst; Structural deformation; High resolution electron microscopy

1. Introduction

Au particles in the size range 1–5 nm, supported on TiO₂ were reported to be active for CO oxidation at low temperature [1,2]. This surprising activity of gold strongly depends on the structure, the morphology, the deposition method and on the interface with the substrate.

Most of the experimental results found in the literature on this system are obtained with 2 nm sized Au particles prepared by the reduction of a gold precursor, chloroauric acid, stabilized with P(CH₂OH)₄Cl [3], thiols molecules [4,5], or Mg citrates [6], on TiO₂ with the anatase structure.

It has been shown by LEIS at room temperature (RT) that Au grows on TiO₂ (110) with the rutile structure, first as 2D islands, while 3D growth is observed near 1 ML coverage [7]. The transition between quasi- 2D and 3D growth occurs at about 0.15 ML. However, at 475 K, 3D growth appears from the beginning. Qualitatively the same behavior was observed and modeled recently [8].

A high resolution scanning electron microscopy (HRSEM) study has shown that at RT and for total thickness of deposited gold in the range 0.2–12 nm, 3D growth occurs in a (111) epitaxial orientation, with a [111]Au/ [110]TiO₂ (rutile structure) [9,10]. Due to the resolution limit of the HRSEM, the particle morphology was not determined for particles smaller than 5 nm.

Large particles grown at 500 K, or higher temperatures, exhibit an hexagonal faceted shape. An average contact angle of 122° was estimated [10]. The growth of Au on TiO₂ (100) thin films grown on Mo (100) [11] and on TiO₂ (110) single crystals [12] has also been studied at RT by scanning tunneling microscopy (STM). 3D growth is observed in both cases. However, clusters smaller than 2 nm appear two-dimensional. By scanning tunneling spectroscopy (STS) the opening of a gap appears near 3 nm, which was related to the particular catalytic activity of small gold clusters on TiO₂.

To the best of our knowledge there are no surface science studies on the crystalline surfaces of TiO₂ with the anatase or brookite structures. Indeed, single crystals with the anatase structure have not been commercialized.

Here, Au particles in the size range 1–5 nm have been prepared by deposition under ultra high vacuum (UHV) conditions on TiO₂ micro-spheres at high tem-
temperature. The particles shape, their orientation on the substrate and the growth mechanism were determined by high resolution transmission electron microscopy (HRTEM) in top view and profile imaging associated with image simulation by the multislice technique, as in the case of others systems previously studied such as Pd/MgO, Pd/ZnO and PdCu/MgO [13–15].

2. Sample preparation

Au particles were obtained by UHV condensation on TiO$_2$ (anatase) micro-spheres (from Cerac, with an average diameter of 32 nm), previously deposited on a microscope grid covered with a carbon film and cleaned at 800°C in UHV then in O$_2$ at $10^{-4}$ Pa. The metal was evaporated from a Knudsen cell, at a calibrated flux of $10^{13}$ atoms cm$^{-2}$ s$^{-1}$. The temperature of the substrate was chosen between 400 and 550°C in order to favor the growth of larger particle sizes. An overview of the sample is shown in Fig. 1.

The cluster size and their number density on the surface of TiO$_2$ are given in Fig. 2, according to the deposition time. For long deposition times (17 min), the density decreases as the particle size increases due to coalescence.

3. HRTEM imaging

The samples were examined with the Jeol 4000EX microscope at the University of Antwerp.

Fig. 3 shows a 4 nm large particle on a (110) surface of TiO$_2$, with nearly the Bragg (110) orientation. On the (110) face of TiO$_2$ all the particles are oriented according to the epitaxial relations: (110)Au//(110)TiO$_2$ and [11 1]Au//[001]TiO$_2$.

According to the profile views of the particles, the ratio between the height and the diameter is about 0.4, i.e. in Fig. 3, the large particle thickness has about six layers.

By taking into account the diameter of the observed TiO$_2$ sphere, the thickness below the particle (Fig. 3) can be evaluated to about 39 nm. The simulated image of anatase observed in the [110] direction at the Scherzer focus is given in Fig. 4. The fringes are parallel to the (004) lattice planes of anatase.

The superimposition of six layers of Au (110) on 39 nm of anatase was simulated (Fig. 5a). The dimensions
of the supercells of Au and TiO$_2$ are: $1.63 \times 1.05$ nm$^2$, with a sampling of $256 \times 164$ points per nm, which gives a precision of $0.64 \times 10^{-2}$ nm in the image. The misfit between the lattice distances (111) of Au and (004) of anatase is high (12.5%). No lattice deformation was introduced in this simulation. However, the representation of Au (on a quasi hexagonal array) is deformed compared to the simulation of unsupported gold in the same (110) orientation. The image shows a good contrast in Au in the areas were Au and TiO$_2$ lattices are in coincidence, while the contrast is blurred in the other areas. For lower thickness of Au the quasi hexagonal lattice is no longer visible on the simulations.

As in the experimental images, the contrast in gold is strong in all the particles, other simulations have been performed with a dilatation in gold along the [001]Au axis, by 12.5% and a contraction along the [100]Au and [010]Au axes by 5.3%. Then the lattice distances $d(111)_{\text{Au}}$ and $d(004)_{\text{TiO}_2}$ are equal and $d(002)_{\text{Au}} = d(112)_{\text{TiO}_2}$.

The simulation of the superimposition of six layers of stretched Au (110) on 39 nm of TiO$_2$ is given in Fig. 5b. The parameters of the supercell are: $2.52 \times 1.48$ nm with a resolution of 1 point per $0.987 \times 10^{-2}$ nm in the calculation. The simulated image is in good agreement with the experimental image in Fig. 3.

However, the lattice deformation in the particle is not necessarily homogeneous in all the volume. Indeed, the superimposition of two Au layers with the bulk parameter on four Au stretched layers, gives an image (Fig. 5c) with the same quasi hexagonal array as in the experimental one. In previous studies [13], in the system: Pd/MgO, the first three layers of metal at the interface were progressively accommodated to the substrate, then after the 4th layer, the lattice parameter was equal to the bulk parameter.

In the experimental images (see Fig. 3) around the particles, on the TiO$_2$ surface, some areas present a weak contrast with the quasi hexagonal array instead of lines as in the simulation of pure TiO$_2$. This contrast can be due to thin Au islands on the substrate, around the 3D particles. The simulation of two layers of Au, with the same deformations as in the simulations of Fig. 5b, superimposed on 39 nm of TiO$_2$ gives a very weak contribution of Au in the image. However, as soon as the gold thickness reaches four layers the contribution of Au is visible on the simulated image (Fig. 5d). This contribution from Au is enhanced when the sample is slightly tilted from the Bragg orientation.

In Fig. 5d the supercells are constructed with the Au atoms on top of the Ti atoms at the surface (the dense rows of Au atoms are aligned with the Ti rows in the [110]Au direction). The location of the Au atoms on the surface of TiO$_2$ is drawn in Fig. 5e. If the Au atoms are translated along [111]TiO$_2$ from the Ti atoms at the surface to the position between the Ti atoms, then the simulated image does not correspond to the experimental one (Fig. 5f).

In Fig. 5a, b, c and f the particular contrast seen on the right side is only due to the edge effects of the supercells.

At the edge of the TiO$_2$ spheres, some particles are seen in a [1 − 10] direction, (111) oriented on a (1 − 11) face of TiO$_2$ parallel to the electron beam, with [001]Au/[001]TiO$_2$. Such a particle is seen in profile view on Fig. 6a and b, with a slight tilt angle and at the Bragg orientation. The interface line is better seen in Fig. 6a. Here the (111) lattice distances of Au are equal to the (004) lattice distances of the substrate, which corresponds to a weak dilatation of +0.9% of the (111) distances of bulk Au.

As we assume that in this size range, the equilibrium shape is obtained after annealing at 500°C, its shape has been drawn in Fig. 7. In this drawing the particle center is close to the interface and the anisotropy ratio between the surface energies is $\sigma_{100}/\sigma_{111} = 1.16$ which is in agreement with our previous study on Pd/MgO [16]. Then, the adhesion energy between the particles and the substrate is deduced from the observed shape. From the Wulff–Kaishev construction [16], using the surface energy of the (111) face of Au, which is about $0.80–1.28$ J m$^{-2}$, [17,18], we get an adhesion energy between 0.75 and 1.21 J m$^{-2}$. This value of the adhesion energy of gold on TiO$_2$ is larger than the value previously deduced for gold particles on TiO$_2$ (110) with the rutile structure [10]. These measurements gave an estimated average contact angle of 122° (close to the value determined on a macroscopic liquid droplet on TiO$_2$) [19], corresponding to an adhesion energy between 0.38 and 0.60 J m$^{-2}$. The high adhesion energy measured on the (111) face of TiO$_2$ anatase may also be due to the fact that this face is not the most stable one compared to the (110) face.

4. Summary

We have studied the growth under UHV conditions at high temperature, of Au particles on TiO$_2$ micro-
Fig. 5. (a) Simulated image of the superimposition of Au (110) (six layers), with the bulk lattice parameter, on TiO$_2$ (110), (thickness: 39 nm). (b) Simulated image of the superimposition of Au (110) (six layers) with the [100] and [010] axis contracted by 5.3% and the [001] axis dilated by 12.5%, on TiO$_2$ (110) (thickness: 39 nm). (c) Simulated image of the superimposition of stretched Au (110) (four layers), with two layers of bulk Au (110), without substrate. (d) Simulated image of the superimposition of stretched Au(110) (four layers), on TiO$_2$ (thickness: 39 nm). Au atoms located on the Ti atoms of the substrate. (e) Drawing of the location of Au atoms on the surface of TiO$_2$ (110). Au atoms are on the Ti atoms of the substrate. (f) Simulated image of the superimposition of stretched Au (110) (four layers), on TiO$_2$ (thickness: 39 nm). Au atoms between the Ti atoms of the substrate.
of TiO$_2$ the particles are completely accommodated to the substrate at least in the first four layers from the interface with deformations of the lattice parameter by +12.5% along [001] and by −5.3% along [100] and [010]. These deformations may be due to the preferential growth of Au atoms on top of the Ti atoms of the (110) TiO$_2$ surface. Indeed, on the (110) surface of TiO$_2$, the distance between two neighboring Ti atoms is 0.27 nm. If the Au atoms grow first on these Ti atoms, they form a rectangular lattice with a side of 0.27 nm in this direction and a length of 0.459 nm in the perpendicular direction. This lattice at the interface corresponds to a (110) plane of gold. With this deformed (110)Au lattice plane, the Au–Au distances are contracted by 5.3% along the Ti rows (Au [110] directions) and dilated by 12.5% between the Ti rows (Au [001] directions). The preferential growth of gold atoms on top of Ti atoms can be explained by the interaction with Ti atoms but more likely to the high coordination of the Au atoms with more oxygen atoms in a position of highest symmetry. The same behavior has already been observed for Pd [20] and Pt [21] on rutile–TiO$_2$ [110].

The strong deformation of the gold lattice could be at the origin of the surprising catalytic properties of gold nanoparticles as recently suggested by Norskov group [22].

References