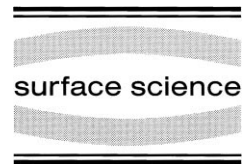




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CO-induced changes of Ir nanoparticles supported on $\text{TiO}_2(110)-(1 \times 2)$ surface

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Abstract

Ir nanoparticles of different sizes are produced on $\text{TiO}_2(110)-(1 \times 2)$ surface and characterized by scanning tunneling microscopy (STM). It was found that at very low coverage Ir is formed in round shape nanoparticles on titania which are mainly centered on the oxygen deficient rows of the (1×2) terraces. The annealing of the iridium covered surface caused an perceivable increase of the particle size only above 700 K. The supported iridium nanoparticles of 1–3 nm exhibit a very high reactivity towards CO. As a result of the CO adsorption at 300 K, crystallites disrupt into smaller particles, and finally into atomically dispersed Ir. This feature was not experienced for larger clusters of 8–10 nm size. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: CO-induced agglomeration of Ir particles; CO-induced disruption of Ir crystallites; Evaporation of Ir; Preparation of Ir nanoparticles; Reactivity of Ir nanoparticles; Scanning tunneling microscopy; $\text{TiO}_2(110)$ support

Materials in the nanometer scale exhibit special properties not observed for larger particles [1,2]. A new, but not fully explored feature of the chemistry of some nanostructural substances is that their size and morphology can be strongly influenced by an interaction with reacting gases, not only during the high temperature reactions, but even during the moderate temperature (150–400 K) adsorption [3,4]. A convenient way of preparing particles of different sizes and morphologies is the evaporation of metals on well-defined oxides of a larger area [5]. For the characterization of metal crystallites scanning tunnelling microscopy (STM) provides the most powerful tool.

In a study of the interaction of CO with supported Ir clusters of small size by means of infrared spectroscopy (IR), significant spectral changes were observed [6]. At the beginning of the adsorption of CO only one IR band at 2060 cm^{-1} appeared which was attributed to the vibration of CO bonded to metallic Ir_x crystallites. After an extended adsorption time, however, this band had been transformed into a pair of bands at 2010–2037 and $2090\text{--}2107 \text{ cm}^{-1}$. Interestingly, such spectral changes were not experienced for larger ($> 5 \text{ nm}$) Ir particles [6]. The position of the new bands agrees well with those established for Ir dicarbonyl species, $\text{Ir}(\text{CO})_2$, in which the atomically dispersed Ir atoms bind two CO molecules. If this surface compound is formed, it means that the adsorption of CO caused a dramatic change in the structure of Ir nanoparticles, namely the

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disruption of Ir crystallites into smaller units, and finally to atomically dispersed Ir. In the present paper an attempt is made to obtain direct evidence for CO-induced structural changes of Ir nanoparticles deposited on a well conducting $\text{TiO}_2(110)$ single crystal surface by scanning tunneling microscopy.

The experiments were carried out in an UHV chamber equipped with a three-grid AES-LEED analyzer and a commercial STM-head purchased from WA-Technology [7]. The home-made evaporator was a liquid nitrogen cooled and thermally heated construction. During the Ir-dosing the distance between the evaporator surface and the sample was approximately 20 mm. The rate of the deposition was controlled by adjusting the current flowing through the Ir-filament spotwelded to a thicker Ta rod. The amount and the purity of the epitaxial Ir layer on the titania was checked by AES spectroscopy. The surface concentration of the deposited metal is given in monolayer equivalent (ML), which corresponds to 1.5×10^{15} Ir atoms cm^{-2} . The calculation of this value was based on the appearing volume of 3D iridium crystallites observed on STM images at around 1 ML of admetal. This method has been applied and described earlier for rhodium deposited on titania surface [8,9]. The polished $\text{TiO}_2(110)$ single crystal sample was purchased from Crystal-Tec. Without any further treatment in air it was clipped with a Ta plate on a transferable sample holder and moved into the chamber. The sample was heated by a W filament positioned just below the Ta plate carrying the probe. By this arrangement it was possible to achieve a surface temperature of 1100 K, which was measured by a thin chromelalumel thermocouple forced to the edge of the sample. The cleaning procedure of the TiO_2 has been described in our previous paper [7]. In this work we also observed that annealing of the cleaned sample at 800–900 K resulted in mainly bulk terminated 1×1 surface, but that good quality 1×2 reconstructed terraces covering 80–90% of the total area could be obtained only after annealing at 1100 K.

The characteristic morphology of $\text{TiO}_2(110)$ -(1×2) annealed at 1100 K is presented in Fig. 1A–C. The STM picture shows characteristic

step lines in the direction of $[001]$, $[\bar{1}13]$ and $[1\bar{1}1]$ and well ordered terraces with an average size of 200 nm^2 and (Fig. 1C). This arrangement is easily perceptible even if the terrace inner structure is strongly disturbed by the different treatments. The magnified images of $50 \times 50 \text{ nm}$ (Fig. 1B) and $20 \times 20 \text{ nm}$ (Fig. 1A) make the terrace morphology better seen: the distance of the parallel rows running in the orientation of $[001]$ is 1.35 nm. The total area of the terraces shows a complete reconstruction into 1×2 arrangement. The average corrugation in the direction perpendicular to the rows is 0.08 nm. The fine details and the interpretation of the structure of the rows were recently discussed in several papers [7,10–12]. In the subsequent measurements we selected tendentially the regions where the $[001]$ oriented steps are the dominant features.

Deposition of a very small amount of Ir, 0.02 monolayer (ML), produced Ir adparticles of approximately 1 nm, which contain about 10 Ir atoms (Fig. 1D). The round shape nanoparticles are mainly centered on the outlying rows of the (1×2) terraces, but some of the Ir clusters are located at the step sites, too. With the increase in the amount of Ir deposited, the size of the Ir nanoparticles is gradually increased and a value of 5.0 nm at 2.0 ML is obtained (Fig. 1E and F). Annealing of the Ir/ $\text{TiO}_2(110)$ system at low Ir coverages resulted in an appreciable increase in the size of Ir above 500 K: from 1 nm (300 K) to 3 nm (1100 K) at 0.02 ML (Fig. 1G), and from 2 nm (300 K) to 5 nm (1100 K) at 0.2 ML (Fig. 1H). At 2.0 ML no change in the size of crystallites was observed in the temperature range of 300–700 K, it did occur, however, above 900 K. Annealing the sample at 1100 K resulted in hexagonal coin shape crystallites (average diameter of 8 nm) oriented in parallel with one side to the crystallographic orientation of $[001]$ of the substrate (Fig. 1I). This behaviour clearly refers to crystallization coordinated by the row structure of the support and suggests that the top facet of the crystallites is (111) oriented plane. From the height of the crystallites it was calculated that they consisted of approximately 4–5 layers.

For the study of the effect of CO on the morphology of Ir crystallites a sample was chosen first,

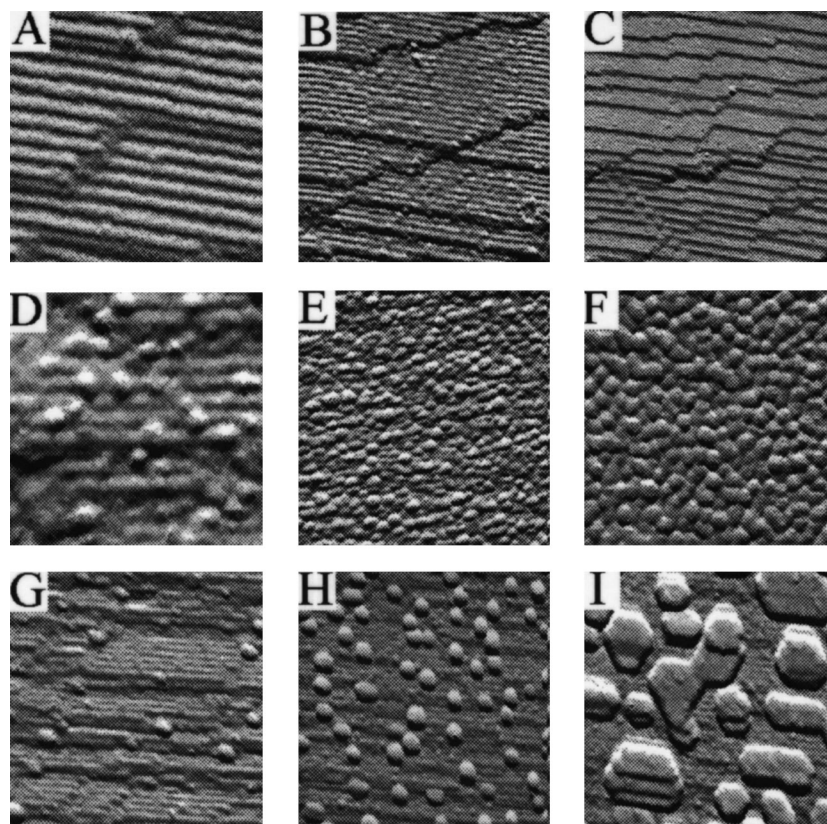


Fig. 1. STM images of clean and Ir-covered $\text{TiO}_2(110)-(1 \times 2)$ surfaces. Terrace structure of the clean $\text{TiO}_2(110)-(1 \times 2)$ surface on the scale of: (A) 20×20 nm; (B) 50×50 nm; and (C) 100×100 nm. The typical morphology of the $\text{TiO}_2(110)-(1 \times 2)$ covered by Ir of: (D) 0.02 ML; (E) 0.2 ML; and (F) 2 ML at room temperature and after annealing at 1100 K in UHV (G–I). The size of image D, is 20×20 nm and that of images E–I is 50×50 nm.

where the Ir particles are well separated. This configuration was attained at 0.05 ML of Ir following an annealing of the Ir– $\text{TiO}_2(110)$ system at 1100 K. Fig. 2A shows that the lateral distribution of the metal adparticles is rather homogeneous, and the size distribution is quite narrow: it fell in the range of 2.5–3.0 nm. Most of the crystallites are bonded at the steps running in the [001] direction, or at the crosspoints of different steps. Some Ir particles are in the middle of the (1×2) reconstructed terraces. Exposing this sample to 1×10^{-1} mbar CO at 300 K causes a dramatic change, which consists of a corrosion of Ir particles, and their disintegration into smaller units and very likely even to Ir atoms, which forms Ir dicarbonyl detected by IR spectroscopy (Fig. 2B–D) [6]. After 1 min exposure of CO new

round like features of approximately 1 nm clearly appear around the larger (probably original) particles (Fig. 2B). On increasing CO exposure, the extra protrusions of 1 run on average are distributed more homogeneously on the surface, and the size and number of the original particles clearly decrease (Fig. 2C and D). Raising the temperature to 450 K further strengthens this change. The same features were observed for the non-annealed system, where the Ir particles are not so well separated and distinguished.

These features clearly indicate that the adsorption of CO basically alters the morphology of Ir crystallites: it induces the disruption of particles into smaller units and finally to isolated Ir atoms. The possible driving force of this process is the formation of a strong bond between CO and Ir

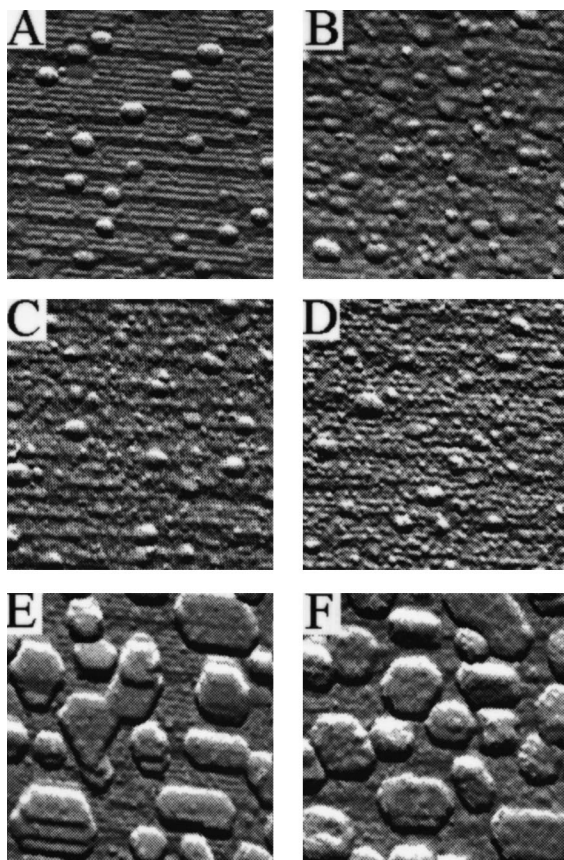


Fig. 2. Effect of CO on the morphology of well separated Ir crystallites of (A–D) 3 nm and (E and F) 6–8 nm size produced by deposition of Ir on $\text{TiO}_2(110)-(1 \times 2)$ at room temperature and subsequent annealing at 1100 K: (A) before CO adsorption and after exposure to 10^{-1} mbar CO at room temperature for (B) 1 min, (C) 5 min, and (D) 20 min. (E) before CO adsorption, and (F) after exposure of 10^{-1} mbar CO for 10 min. The size of the images is 50×50 nm. In the case of Ir particles of 3.0 nm, 0.05 ML of Ir, while for particles of 6–8 nm 2.0 ML of Ir was used.

which leads to the weakening of Ir–Ir bonds. This process also results in the reduced barrier of the surface diffusion of “–Ir–CO” moieties. This high reactivity is, however, exhibited only by the very

small Ir particles of 1–3 nm, as when using much larger Ir clusters, 8–10 nm, we observed only the corrosion, mainly at the edges of the crystals without any detectable disintegration of the Ir crystallites (Fig. 2E and F).

When the disrupted Ir nanoparticles had been heated in the presence of CO to 600 K, the Ir nanoparticles reappeared with larger sizes (3–4 nm) compared with that measured before CO adsorption. The size of Ir clusters corresponded to that obtained after sintering at a much higher temperature, 1000 K. This clearly suggests that at high temperature, CO adsorption induces the agglomeration of isolated Ir atoms and very small nanoparticles into larger metal clusters.

Acknowledgements

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