Individual Nanometer-Sized Platinum Clusters Supported on Titanium Dioxide under Electrochemical Investigation

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Electrochemistry plays a major role in the quest for the preparation and the study of submicrometer and nanometer scale structures. Electrochemical deposition of small metallic clusters (1) and nanowires (2) is an attracting possibility to obtain modified surfaces for heterogeneous catalysis and especially electrocatalysis. Studies concerning the chemical reactivity at nanometer-scale structures takes an increasing interest in electrochemical science. Specifically, the case of metal electrodeposition on semiconducting surfaces has been studied on H-terminated Si(100) (3).

PREPARATION OF NANOSTRUCTURED Ti/TiO$_2$/Pt EDIFICES

In this work, electrodeposited patterns of platinum clusters have been prepared by electrodeposition (4). The substrate is a thin layer, 35 nm, of anodized titanium which has been previously characterized (5,6).The effect of different parameters has been studied on the deposition of platinum nanoparticles, e.g. the nature of the platinum complex in solution and the surface preparation of electropolished titanium surfaces.

Specifically, the nature of the platinum complex in sulfuric acid has been studied by visible spectrometry and by time-resolved XPS experiments. An electrochemical study of the platinum complex in solution has been also carried out. The complex which is electrochemically active during the electrodeposition is identified as a binuclear complex involving two Pt(III) centers with sulfato, amino and aqua ligands in the coordination environment.

SCANNING TUNNELING SPECTROSCOPY ON INDIVIDUAL SUBMICROMETER Ti/TiO$_2$/Pt EDIFICES

Scanning tunneling spectroscopy experiments consist in recording i=f(E) curves between the sharp platinum tip of a STM and the surface under investigation. The result of the complete scanning of the surface is a map of the local tunneling current on the surface. Three different behaviors were identified:

- Region (1) = Schottky junction between the Pt nanoelectrode and the n-type TiO$_2$ surface.
- Region (2) = Enhancement of the electron transfer rate on the oxide surface directly adjacent to the Pt cluster.
- Region (3) = Ohmic junction between the tip and the Pt cluster. *See figures 1 and 2.*

PROPOSED THEORETICAL MODEL FOR Ti/TiO$_2$/Pt EDIFICES

Such characterized structures are related to the fundamental notion of “active sites” in heterogeneous reactivity. Tunneling spectroscopy shows the experimental evidence of the non-uniform activity of surfaces and clearly demonstrates the great importance of the structuring of the reactivity around “active sites”. The special arrangement of platinum on the semiconducting titanium oxide film create a modulation of electronic paths through the oxide layer. The oxide part of the surface which is covered by platinum acts as the “heart” of the electrochemical activity due to the band overlap between the oxide and the platinum cluster. The oxide part of the exposed surface toward the solution has a pure n-type behavior which has been previously described (5). The most interesting phenomena occur where those two ideal comportments are adjacent at the boundary of the platinum cluster. The model takes into account the space charge region in the semiconducting film which is modified by the presence of the platinum nucleus. Thus, the electron transfer reaction is less inhibited at the platinum adjacent oxide ring.

Those results exhibit the local behavior of electrocatalytic centers which may be useful in a wide field of the heterogeneous chemical reactivity.

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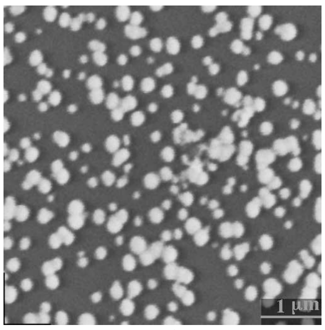

Fig. 1 - Titanium oxide surface covered by randomly electrodeposited platinum clusters.

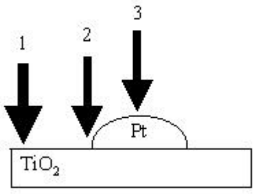

Fig. 2 - Schematic view of the three different regions for electron transfer.