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HRTEM and HAADF Analysis of Au Nanoparticles Supported on TiO_2 Thin Films

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Recently growing attention has been put to the novel properties of supported gold catalyst on semiconductor metal oxides [1-3]. It was found that dispersed ultrafine Au particles supported on metal oxides such as TiO_2 exhibits an extraordinary high activity for low-temperature catalytic combustion, partial oxidation of hydrocarbons, hydrogenation of unsaturated hydrocarbons, and reduction of nitrogen oxides [3]. The oxidation has been found to be a structure-sensitive reaction, this means that the activity depends upon the size and the shape of gold particles. The structure sensitivity of the CO oxidation reaction on Au clusters supported on TiO_2 is related to a quantum size effect with respect to the thickness of the Au clusters [1]. In this work, the morphology, size and crystalline structure of gold nanoparticles deposited onto TiO_2 thin films were analyzed by electron microscopy, using high resolution transmission electron microscopy (HRTEM) and high angle annular dark field (HAADF) techniques.

Titanium dioxide thin films were deposited onto glass substrates by spray pyrolysis, as reported elsewhere [4]. Film thickness was determined by fiber optic reflectance spectrometry in contact mode. Before the deposition of Au nanoparticles; films of around 100 to 200 nm of thickness were peeled off from the glass substrate by immersion in diluted HF (5 % vol.). Then films were immediately floated and rinsed in deionized water. Finally, they were mounted on 1000 mesh copper grids. Gold clusters ranging in diameter from 1 to 6 nanometers have been deposited on TiO_2 film by magnetron sputtering. Relatively high Ar pressure was used, in the interval between 200 to 500 mTorr to minimize the energy of Ar ions and sputtered Au atoms. HRTEM was employed to analyze the microstructure of the film and particles. HAADF technique was applied for obtaining Z-contrast images of the gold particle profiles. In addition, an x-ray energy dispersive spectroscopy (EDS) system was utilized for micro-analysis and elemental mapping.

Figure 1 shows typical microstructure of the TiO_2 films used in this work. It can be seen, that the surface grains are either irregular or round shaped, with characteristic length between 100 to 300 nm. The grains are composed of many 5 to 10 nm crystallites. The films were polycrystalline, and their structure corresponds to the tetragonal Anatase phase. Any contamination was detected by EDS analysis. HRTEM and HAADF images of the gold nanoparticles supported on the TiO_2 film are shown in Figure 2. In the HRTEM images, the particles seem to be embedded in the TiO_2 film, suggesting a very strong interfacial interaction has occurred. The average size of the particles was around 3.5 nm. The use of HAADF technique was very useful to detect very small nanoparticles.

References

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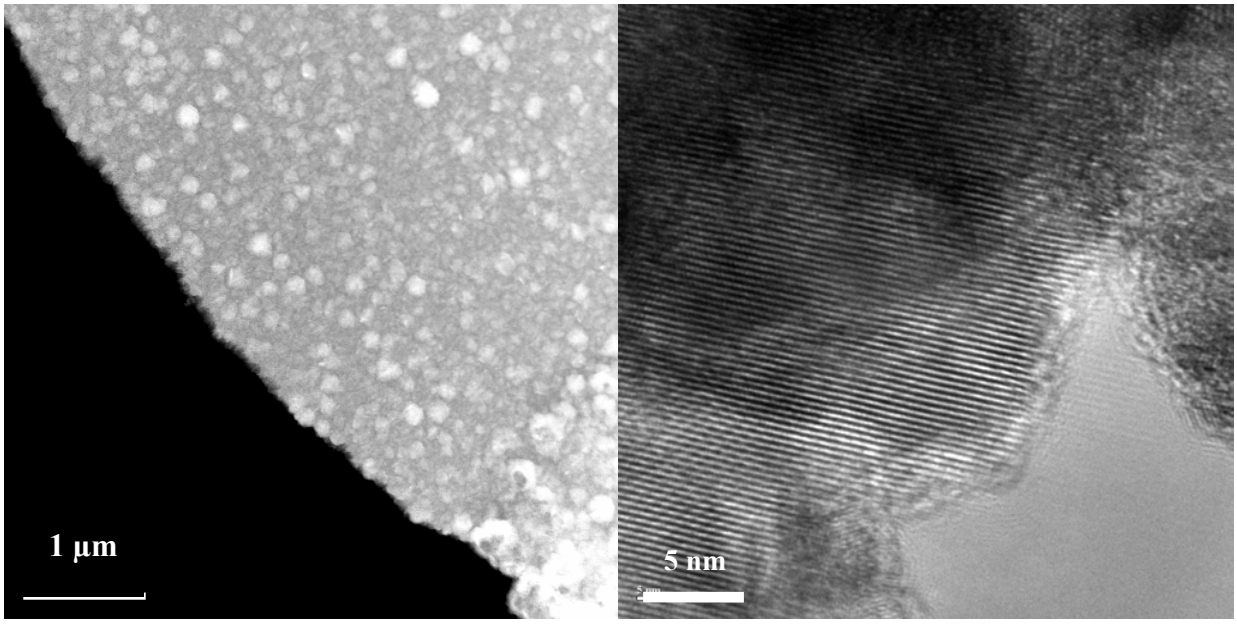

Figure 1 Typical microstructure of the TiO_2 films.

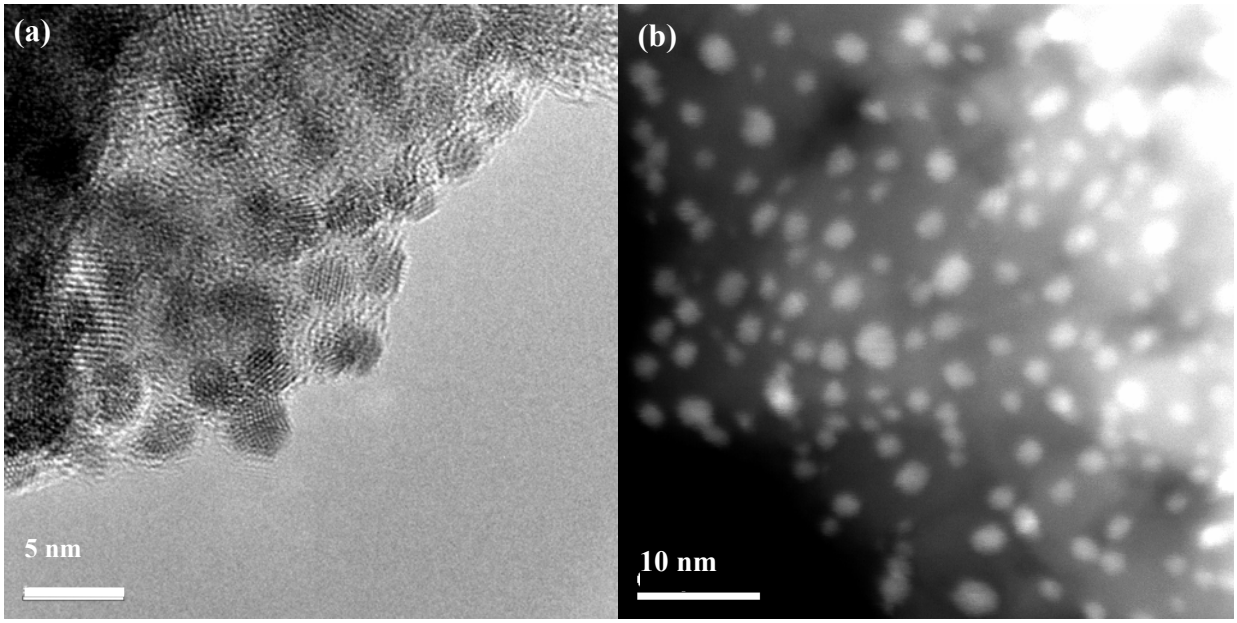

Figure 2. Electron microscopy images of Au nanoparticles onto TiO_2 thin film. a) HRTEM. b) Z-contrast image.

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