

## Deposition of Au Nanocrystals on TiO<sub>2</sub> Crystallites

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Preformed dodecanethiol-passivated Au nanocrystals of controlled size distribution were deposited onto TiO<sub>2</sub> crystallites in an attempt to produce a Au nanocrystal catalyst with superior catalytic properties. The procedure for preparing and processing the dodecanethiol-passivated Au nanocrystals has been described previously [1]. Solutions of the dodecanethiol-passivated Au nanocrystals in toluene at concentrations of 0.38 mg/ml, 0.19 mg/ml, 0.09 mg/ml and 0.04 mg/ml were prepared. The Au nanocrystals were deposited by suspending 500 mg of TiO<sub>2</sub> (Strem, Cambridge) crystallites (avg. diameter of 200 nm, predominately anatase) in 100 ml of the solution and stirring vigorously. The Au-decorated TiO<sub>2</sub> crystallites were filtered and then rinsed twice with ethanol.

Scanning transmission electron micrographs of the co-precipitated Au/TiO<sub>2</sub> nanocrystal assemblies were acquired on an Hitachi HD-2000 scanning transmission electron microscope (STEM). The HD-2000 is a 200 kV, cold field emission STEM equipped with a secondary electron detector, an on-axis bright-field detector for traditional transmitted-electron imaging and a high-angle annular dark-field (HA-ADF) detector for Z-contrast imaging. The HD-2000 is also equipped with an energy dispersive X-ray spectrometer (EDS) which subtends the largest solid angle (0.3 steradians) of any commercially available detector system. The dark-field STEM image in Fig. 1 is from the 0.39mg/ml solution. The STEM Z-contrast permits easy differentiation of Au nanocrystal compounds (small bright areas) and TiO<sub>2</sub> crystallites. EDS from areas containing bright spots confirmed the presence of Au and S, along with Ti, O and other expected elements. At this concentration the Au nanocrystal compounds are dispersed both on exposed surfaces (facets) of the TiO<sub>2</sub> crystallites and in the interfacial regions between adjacent TiO<sub>2</sub> crystallites. At the interface between two TiO<sub>2</sub> crystallites, the Au nanocrystals align along the boundary to form a single line of nanocrystals.

At the lowest concentrations (0.09 and 0.04 mg/ml) the Au nanocrystals are deposited predominantly on the boundaries between the TiO<sub>2</sub> grains. Figure 2 shows the typical distribution of the Au nanocrystals on TiO<sub>2</sub> for the 0.09 mg/ml solution. In contrast to Fig. 1, no Au nanocrystals are observed on the faces of the TiO<sub>2</sub> grains. Brust and coworkers have reported on the ordered deposition of passivated Au nanocrystals on lithographically patterned silicon [2]. In contrast to that work, the gold concentration was much lower for our samples, and no specific patterning step was required to produce the aligned Au nanocrystals. The novel result is the production of single lines of Au nanocrystals through the relatively simple control of the nanocrystal solution concentration[3].

### References

- [1] T. G. Schaaff et al., *J. Phys. Chem. B*, 105 (2001), 8785.
- [2] A. J. Parker et al., *Appl. Phys. Lett.*, 74 (1999), 2833.
- [3] Research sponsored by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, and the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of the High

Temperature Materials Laboratory User Program, under contract DE-AC05-00OR22725 with UT-Batelle, LLC.



FIG. 1. Z-contrast image of Au nanocrystals deposited on a TiO<sub>2</sub> support from a 0.39 mg/ml Au toluene suspension. The Au deposits both on the facets of the TiO<sub>2</sub> and in the boundaries between crystals.

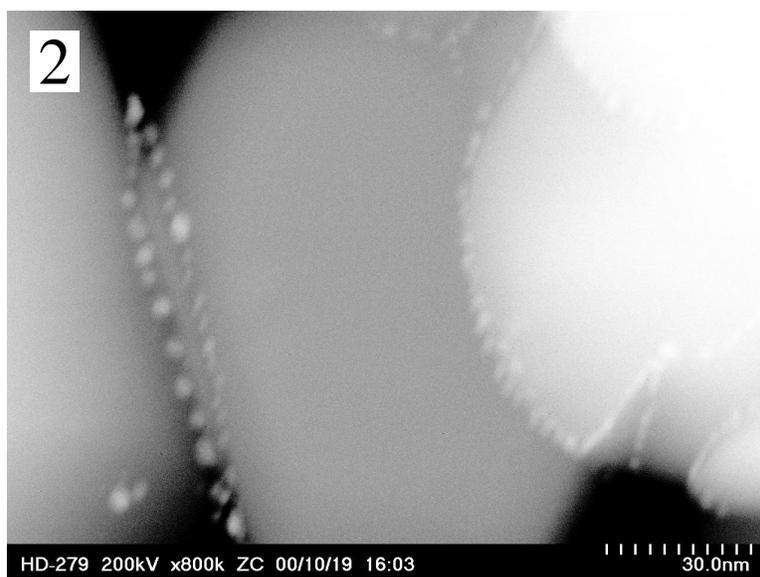


FIG. 2. Z-contrast image of Au nanocrystals deposited from 0.09 mg/ml toluene solution onto titania support. Note the lack of Au nanocrystals on the titania facets.