

## The Effect of Substrates / Ligands on Metal Nanocatalysts Investigated By Quantitative Z-Contrast Imaging and High Resolution Electron Microscopy

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### ABSTRACT

Our direct density function-based simulations of Ru-, Pt- and mixed Ru-Pt clusters on carbon-based supports reveal that substrates can mediate the PtRu<sub>5</sub> particles [1]. Oblate structure of PtRu<sub>5</sub> on C has been found [2]. Nevertheless, the cluster-substrate interface interactions are still unknown. In this work, we present the applications of combinations of quantitative z-contrast imaging and high resolution electron microscopy in investigating the effect of different substrates and ligand shells on metal particles. Specifically, we developed a relatively new and powerful method to determine numbers of atoms in a nanoparticle as well as three-dimensional structures of particles including size and shape of particles on the substrates by very high angle (~96mrad) annular dark-field (HAADF) imaging [2-4] techniques. Recently, we successfully synthesize icosahedra Au<sub>13</sub> clusters with mixed ligands and cuboctahedral Au<sub>13</sub> cores with thiol ligands, which have been shown by TEM to be of sub-nanometer size (0.84nm) and highly monodisperse narrow distribution. X-ray absorption and UV-visible spectra indicate many differences between icosahedra and cuboctahedral Au<sub>13</sub> cores. Particles with different ligands show different emissions and higher quantum efficiency has been found in Au<sub>11</sub> (PPH<sub>3</sub>) SC<sub>12</sub>)<sub>2</sub>Cl<sub>2</sub>. We plan to deposit those ligands-protected gold clusters onto different substrates, such as, TiO<sub>2</sub> and graphite, etc. Aforementioned analysis procedure will be performed for those particles on the substrates and results will be correlated with that of our simulations and activity properties. This approach will lead to an understanding of the cluster-substrates relationship for consideration in real applications.

### INTRODUCTION

Nanocatalysts we investigate here are really small (<100atoms). Activity is strongly size dependent of deposited cluster size, for instance, activity is found to peak for Au particles on TiO<sub>2</sub> in a few nanometer range and sub nanometer range [5-6]. Nanosized gold supported on oxides is of great significance in environmental, sensor and chemical technologies [5]. We still don't know the process underlying the catalytic activity of gold in reduced dimensions and reaction mechanisms. What we need know is how the metal oxides substrates affect the presence of Au<sup>0</sup> and Au<sup>1</sup>. We choose ligand protected Au<sub>13</sub> as a model material deposited on anatase TiO<sub>2</sub>, and explore the optimum treatment to remove ligands and control particle size in a certain range.

Scanning transmission electron microscope (STEM)-based z-contrast imaging combined with high resolution electron microscopy (HREM) is robust to determine and predict 3-D structures of subnano-catalysts and confirm extended x-ray absorption fine spectrum (EXAFS) data, because cluster size and substrate interaction directly contribute to the static term of the mean-square deviation.

Nanomaterials prepared via controlled chemical syntheses are characterized using a variety of analytical techniques, highlighted by the complementary use of the advanced Z-contrast imaging, combined with lattice imaging in HREM. Z-contrast imaging or high angle annular dark-field (HAADF) is a novel and emerging technology in determining the number of atoms in a cluster. We have previously determined the number of atoms in very small clusters, such as  $\text{Re}_6$  [4] and  $\text{PtRu}_5$  nanoclusters [2], through quantification of absolute image intensity from HAADF microscopy and our newly developed robust interactive computer program [3]. A similar procedure is currently being performed for ligand-protected  $\text{Au}_{13}$  nanoclusters.

The phosphine-to-thiol exchange technique was adapted to produce the monodisperse and compositionally well-defined *icosahedral* gold clusters,  $\text{Au}_{13}[\text{PPh}_3]_4[\text{S}(\text{CH}_2)_{11}\text{CH}_3]_2\text{Cl}_2$  and  $\text{Au}_{13}[\text{PPh}_3]_4[\text{S}(\text{CH}_2)_{11}\text{CH}_3]_4$ . These clusters were studied and compared to larger, fully-thiolated monolayer-protected clusters (MPCs) that were determined to have *cuboctahedral* structure. In this paper, we report the synthesis of dodecanethiol-stabilized gold nanoparticles with different Au/thiol ratios and a new method of determining their number of atoms by measurement of absolute intensity of particles in HAADF images as well as the exploration of different treatments for ligand removal from gold clusters on the support of the  $\text{TiO}_2$  (anatase). The correlation with EXAFS has been discussed.

## EXPERIMENTAL DETAILS

### I. Controlled synthesis of Au clusters with mixed-ligand and fully thiolated shells [7-12]

The partial exchange of dodecanethiol ( $\text{C}_{12}\text{SH}$ ) onto phosphine-halide gold clusters was used to produce the monodisperse and compositionally well-defined icosahedral gold clusters,  $\text{Au}_{13}(\text{PPh}_3)_4(\text{SC}_{12})_2\text{Cl}_2$  and  $\text{Au}_{13}(\text{PPh}_3)_4(\text{SC}_{12})_4$ . These clusters exhibit enhanced stability relative to the phosphine-halide parent clusters and are isolated in 100 mg quantities from a single synthesis. It was possible to isolate a fraction of nanoparticles from these preparations that were larger, fully thiol-protected nanoparticles with a distribution of sizes between 0.8 and 3.2 nm. This fully-thiolated sample was studied for a comparison to the monodisperse icosahedral  $\text{Au}_{13}$  clusters. It additionally served as a test of the capability of EXAFS and TEM to provide complementary information on particles with a significant size distribution – a situation more representative of nanoparticle catalysts.

The clusters were characterized by  $^1\text{H}$  and  $^{31}\text{P}\{\text{H}\}$  NMR, UV-visible spectroscopy, XPS, electrochemical measurements, near-IR luminescence, and liquid chromatography. Properties distinctly different from bulk metals were observed in all nanoclusters. The following sections describe the characterization of these clusters by advanced methods of TEM.

### II. Deposition of $\text{Au}_{13}$ onto anatase $\text{TiO}_2$ and exploration of different ligand removal methods

The Au<sub>13</sub> on TiO<sub>2</sub> samples were prepared by dissolving 25 mg of Au<sub>13</sub>(PPh<sub>3</sub>)<sub>4</sub>(SC<sub>12</sub>)<sub>4</sub> in 50 mL n-pentane in a round bottom flask. To this was added 1.4 g of TiO<sub>2</sub> (anatase). The mixture was sonicated briefly (30 s) and then stirred for 30 min. The n-pentane was removed with rotary evaporation. 50 mL n-pentane was again added and the process was repeated to disperse the Au<sub>13</sub> clusters on the support. The Au loading was 1% by weight (calculated from FW of cluster = 4511 g/mol and FW of Au<sub>13</sub> core = 2561 g/mol). Heating was done on a pressed pellet of the supported gold particles in an EXAFS in situ catalysis cell. The sample was heated to 375°C for 1 hour under an inert (He) atmosphere. The sample was then cooled back to RT and EXAFS collected on the sample. The UV-ozone treatment was performed in a UV-ozone cleaning chamber (~15 mW/cm<sup>2</sup> at 254 nm) on finely divided Au<sub>13</sub> on TiO<sub>2</sub> for 20 min. The samples above were then pressed into a pellet for EXAFS measurements. High spatial-resolution TEM, HREM, Z-contrast imaging, electron diffraction and energy-dispersed spectroscopy (EDS) techniques has been used to determine cluster size, structure and shape. The experiments were performed in a Jeol 2010 FEG TEM and HB 501 VG-STEM operated at 200kv and 100Kv, respectively. Samples were prepared by suspending the colloids in ethanol under ultrasonic vibration. Some drops of the thus-produced suspension were brought onto ultrathin carbon coated on a holey carbon Cu grid.

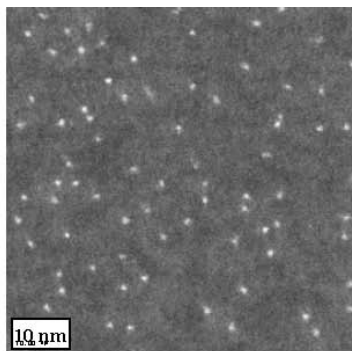
## RESULTS AND DISCUSSIONS

### *I. TEM characterization of mixed-ligand and fully thiolated clusters*

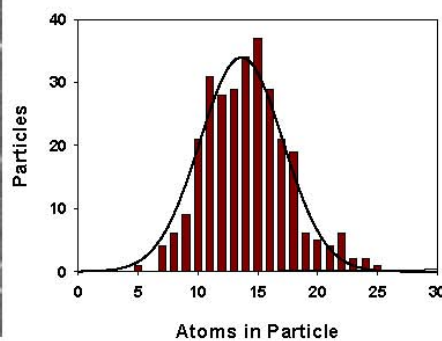
Transmission electron microscopy of the mixed-ligand clusters identified them as sub-nanometer, highly monodisperse nanoparticles with an average core of 13 atoms. STEM measurements were quantitatively analyzed to obtain the number of gold atoms in individual clusters. This was achieved by collecting the scattered electrons only at high angles (> 100 mrad) where the contribution of Bragg electrons is minimized and the electrons collected are predominantly those that are incoherently scattered. This is referred to as high angle annular dark field (HAADF)-STEM or “Z-contrast” microscopy. With careful calibration of the detector efficiency, inner and outer scattering angles of collection, and microscope magnification, the scattering cross-sections of an individual cluster, which is proportional to the absolute scattered intensity, can be calculated. Since the scattering cross-section of a cluster core is simply the sum of the cross-sections of the atoms in the core, the number of atoms in the cluster can be determined using an atomic cross-section calculated from theory. Figure 1 is a representative HAADF-STEM image of Au<sub>13</sub>(PPh<sub>3</sub>)<sub>4</sub>(SC<sub>12</sub>)<sub>2</sub>Cl<sub>2</sub> clusters on an ultrathin carbon (~3 nm) coated TEM grid. Figure 2 is a histogram showing the distribution of the number of atoms in individual nanoparticles. The average measured cross-section for the nanoparticles was  $0.25 \pm 0.06 \text{ \AA}^2$ . The atomic electron scattering cross-section for Au over the collection angles was calculated using partial-wave methods and found to be  $0.019 \text{ \AA}^2$ . Thus, the average cluster core was determined to contain 13 gold atoms with a narrow standard deviation of  $\pm 3$  atoms for the ~300 particles analyzed.

The structures of both mixed-ligand and fully-thiolated nanoparticles were further investigated using HREM. The mixed-ligand Au<sub>13</sub> clusters (Figure 3) and larger, fully-thiolated MPCs were identified as having icosahedral and cuboctahedral geometries, respectively, by analysis of lattice images of HREM performed on a Jeol 2010 field emission gun transmission

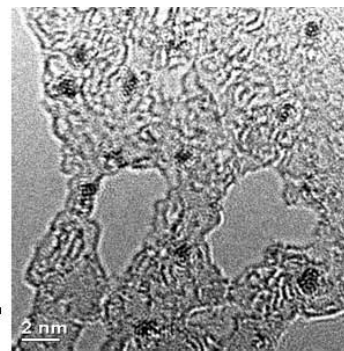
electron microscope (FEG TEM) operating at 200kv. Determination of the icosahedral shape of the  $\text{Au}_{13}$  clusters was achieved by the trace analysis of the particle edges in Figure 3. A d-spacing value of  $2.39 \pm 0.07 \text{ \AA}$  was obtained that corresponds to a cubic 111 net plane (d-spacing of  $2.36 \text{ \AA}$  for bulk gold). Similarly, the cuboctahedral shape of gold particles with fully-thiolated shells can be determined from microdiffraction of single particles. The angle between 1-11 or -111 and 002 and d-spacing can be measured to be about  $56^\circ$  and  $2.32 \pm 0.05 \text{ \AA}$ , respectively, which agrees closely with those calculated for face centered cubic (FCC) Au (where  $a=4.07 \text{ \AA}$ ,  $c/a=1.155$ ,  $\theta = 54.74^\circ$ ). The Au-Au bond length can be obtained as  $2.82 \text{ \AA}$ , which is in excellent agreement with the Au-Au bond distance ( $2.81 \pm 0.01 \text{ \AA}$ ) obtained by our EXAFS analysis.



**Figure 1.** Representative HAADF-STEM image of  $\text{Au}_{13}$  clusters.



**Figure 2.** Histogram of quantitative STEM results of  $\text{Au}_{13}$  clusters.  $N=295$ .



**Figure 3.** High-resolution electron micrograph of icosahedral  $\text{Au}_{13}$  clusters.

## II. TEM characterization of post-treated $\text{Au}_{13}$ on anatase $\text{TiO}_2$

In order to realize high activity for CO oxidation, we explore the deposition of ligand-protected  $\text{Au}_{13}$  clusters onto anatase  $\text{TiO}_2$  followed by treatments to remove the ligands while maintaining small particle size. In addition to this, it is still not clear how the metal oxides substrates affect the presence of  $\text{Au}^0$  and  $\text{Au}^1$ . A comparison of EXAFS data for ligand protected  $\text{Au}_{13}(\text{PPh}_3)_4(\text{SC}_{12})_4$  with and without  $\text{TiO}_2$  support indicates little change in either the Au-Au coordination or the Au-S/Au-P coordination. The EXAFS spectrum for  $\text{Au}_{13}$  on  $\text{TiO}_2$  after thermal adsorption of the ligands at  $375^\circ\text{C}$  for 1 hr under He inert atmosphere is qualitatively indistinguishable from that of the gold foil standard, indicating full removal of ligands but also cluster annealing to large particles. Finally, the UV-ozone treated sample shows that the treatment is successful in removing some ligand (evident by a loss of Au-P and Au-S scattering contributions at low R) but does not result in a large increase in Au-Au coordination - either due to the retention of small particle size or to the development of larger gold islands that are raft-like in nature. In order to confirm the EXAFS results above, further TEM examination is needed. Figure 4 shows representative dark field STEM micrographs of heat (Figure 4a) and UV-ozone (Figure 4b) treated  $\text{Au}/\text{TiO}_2$  and next to each micrograph is the representative particle size distribution for each sample. As Figure 4 indicates, average particle size for the UV-ozone treated sample is smaller on average and has a narrower range of sizes centered on an average particle dimension of  $3.7 \pm 1.5 \text{ nm}$ , while the average particle size for heat treated  $\text{Au}/\text{TiO}_2$  is  $6.2 \pm 3.6 \text{ nm}$ . Furthermore, HREM lattice images of UV-ozone treated Au particles on  $\text{TiO}_2$  were analyzed. The Fourier transformed images can be uniquely indexed to a simple close-packed

FCC structure with the zone axis of 110 and 100, consisting of twins, although ligand-protected  $\text{Au}_{13}$  before deposition and post-treatment exhibits icosahedral shape.

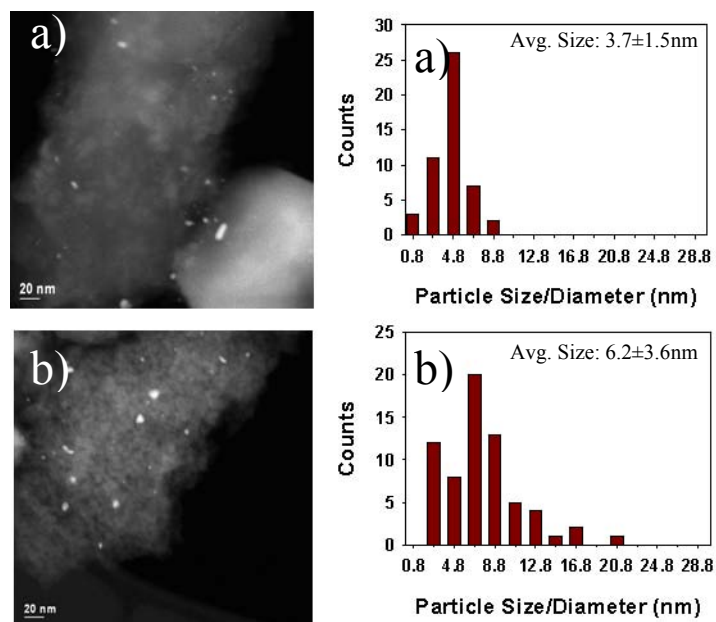


Figure 4. Representative annual dark field (ADF)-STEM images of (a) UV-ozone treated and (b) heat treated ligand-protected  $\text{Au}_{13}$  clusters on  $\text{TiO}_2$ .

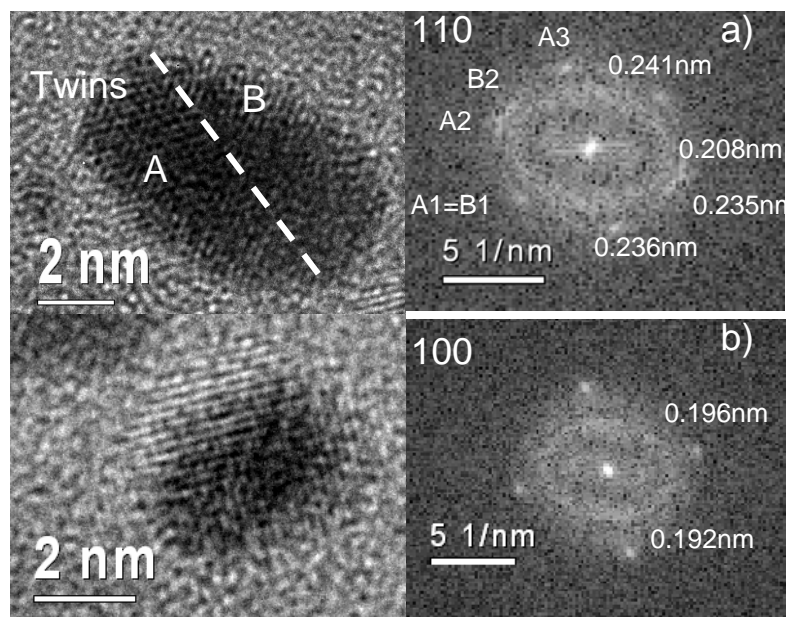


Figure 5. Representative HREM images and corresponding Fourier transformed images taken from individual particles in UV-ozone treated ligand-protected  $\text{Au}_{13}$  clusters on  $\text{TiO}_2$ . The particles are of zone axis of 110 (Figure 5a) and 100 (Figure 5b), respectively, showing twinned face centered cubic (FCC) structure.

## CONCLUSIONS

1. Successful synthesis of monodisperse, subnanometer Au<sub>13</sub> clusters with mixed-ligand shells (Au<sub>13</sub>(PPh<sub>3</sub>)<sub>4</sub>(SC<sub>12</sub>)<sub>4</sub>) and majority of which consists of 13 atoms per cluster determined accurately by STEM-based atom counting.
2. No significant change in the Au-Au coordination after deposition of Au<sub>13</sub>(PPh<sub>3</sub>)<sub>4</sub>(SC<sub>12</sub>)<sub>4</sub> upon the support. Some interaction of Au<sub>13</sub>(PPh<sub>3</sub>)<sub>4</sub>(SC<sub>12</sub>)<sub>4</sub> with the TiO<sub>2</sub> surface upon deposition on the support.
3. Heat treatment at 375°C for Au<sub>13</sub>(PPh<sub>3</sub>)<sub>4</sub>(SC<sub>12</sub>)<sub>4</sub> on anatase TiO<sub>2</sub> results in complete loss of ligands and a significant increase in particle size, which is measured by STEM to be 6.2 ± 3.6(nm).
4. The UV-ozone treated Au<sub>13</sub>(PPh<sub>3</sub>)<sub>4</sub>(SC<sub>12</sub>)<sub>4</sub> on anatase TiO<sub>2</sub> shows that the treatment is successful in removing some ligand, but results in a limited increase in particle size, which is determined by STEM to be 3.7 ± 1.5 (nm).

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