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Three-dimensional structure of Au nanoparticles supported on amorphous silica and carbon substrates

A Bruma, Z Y Li

Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, B15 2TT, UK

Abstract. Scanning Transmission Electron Microscope (STEM) has been employed to study the three-dimensional structure of gold (Au) nanoparticles deposited by means of thermal evaporation in high vacuum on amorphous silica (a-SiO$_2$) and amorphous carbon (a-C) supports. By performing quantitative analysis on the evolution of the high angle annular dark field (HAADF) images, we studied the influence of the nature and the temperature of support on the growth mode of gold nanoparticles.

1. Introduction

Gold nanoparticles in the size regime of a few nanometers, supported on insulating oxides, have attracted much research efforts recently due to a variety of applications such as nanoelectronics and catalysis [1,2]. Silica (SiO$_2$) is one of such supports [3]. Transmission Electron Microscopy (TEM) have been employed to establish the influence of the environment on the size and structure of Au nanoparticles on/in SiO$_2$ [4, 5], yet the information about the growth modes of the nanoparticles has been lacking. In this study, we address this issue by application of scanning transmission electron microscopy (STEM).

Recently, we have demonstrated that quantitative analysis of high angle annular dark field (HAADF) imaging in a STEM can be employed to explore the three-dimensional shapes of nanoparticles when combined with simple geometric models [6]. Using this approach, we can gain insights into growth modes of nanoparticles and the interaction of nanoparticles with substrate. The growth of Au on amorphous carbon (a-C) via physical vapor deposition has been well documented [6, 7]. It is generally accepted that the bonding of Au nanoparticles with a-C substrate is weak [8] and the 3D shape of the Au nanoparticles can be approximated as hemispherical-like. However, this is not the case when using silica as supports for Au nanoparticles. The shape and thermal stability seems to vary, depending on how the supports are prepared [9]. In the present study, we conduct a comparative investigation on Au nanoparticles grown on amorphous SiO$_2$ substrate (Au/a-SiO$_2$) with Au grown on amorphous carbon (Au/a-C) to emphasize the influence of the substrate on the size and shape of nanoparticle formation. On addition, we investigated effects of substrate temperature on the growth mode of the Au nanoparticles.

2. Experimental details

The Au nanoparticles are produced via thermal vapour deposition on amorphous carbon and SiO$_2$ thin film-covered TEM grids (Agar Inc.), under high vacuum conditions (~10$^{-7}$ mbar). During the deposition of Au, the substrate temperature was maintained at either 300 K or 473 K. A JEM 2100F STEM, with an acceleration voltage of 200 kV and fitted with a CEOS probe corrector, was employed.

1 To whom any correspondence should be addressed. E-mail address: Z.Li@bham.ac.uk
to image supported nanoparticles. The typical number of nanoparticles examined in each experimental series was 100-150. All the HAADF-STEM images within the series are recorded using the same brightness and contrast setting. A camera length of 10 cm was used, which corresponds to the inner-angle of the HAADF detector of 62 mrad. The emission current was noted stable throughout the investigation.

3. Results and discussions

Figure 1 shows four representative HAADF-STEM images of Au nanoparticles deposited on SiO$_2$ (a, b) and carbon (c, d) maintained at 300 and 473 K, respectively, during the deposition process. It is clear that the deposited Au forms separated nano-islands on both substrates. Most nanoparticles are circular in projection, except for a few closely spaced clusters that tend to be touching. The histograms of diameters of the nanoparticles are presented in Figure 1 (e-h).

Figure 1. Representative HAADF-STEM images and corresponding size distribution of evaporated Au nanoparticles on a-SiO$_2$ at 300K (a) and 473K (b) respectively; Deposition on a-C at 300K (c) and 473K (d) respectively. Histograms of the corresponding diameter distribution are shown in (e)-(h), placed directly besides the representative figures.
As the substrate temperature increases from 300 K to 475 K, the mean value of the diameters increases from 3.45 nm to 4.39 nm for Au/a-SiO$_2$, and from 2.22 nm to 3.18 nm for Au/a-C. It can be seen that the higher the temperature is, the larger the particles are, indicating that the nano-islands are formed as a result of kinetic limited aggregation. The larger particles formed on a-SiO$_2$ may be associated with the longer diffusion length of Au on a-SiO$_2$ than that on a-C. It is also interesting to note that the standard deviation of the size distribution is independent on the substrate temperature. The larger standard deviation for nanoparticles on SiO$_2$ support suggests a more random distribution of defects on the SiO$_2$ substrate, which act as nuclear center for Au.

The integrated HAADF-STEM intensities over each particle are analyzed and plotted as a function of diameter in Figure 2. Here, the intensities are determined for each particle after local background subtraction and the diameters are estimated by taking the average of the long and short axis of the projection of each particle. HAADF-STEM is an incoherent imaging technique and, as a consequence, the integrated intensity of small Au nanoparticles has been shown to be proportional to their volume [6, 10]. If we take a simple geometrical consideration by assuming that the particles can be modeled by either a 3D sphere or hemisphere or a 2D circular raft-like disk, then the HAADF-STEM intensities would be proportional to $d^3$ or $d^2$ in each cases, where $d$ is the diameter of the nanoparticles.

![Figure 2](image_url)

**Figure 2.** Double logarithmic plot of the evolution of integrated intensity as a function of nanoparticle diameters: (a) Deposition on a-SiO$_2$ at 300K (●) and 473K (○). (b) Deposition on a-C at 300K (●) and 473K (○). The solid lines are the best fit for the data for SiO$_2$ (R=0.93) and carbon (R=0.87) (R is the fitting residual). The 3D spherical and hemispherical model are shown in dashed lines together with the 2D model in dashed dotted line.

In Figure 2, a double logarithmic plot is shown for a-SiO$_2$ (a) and a-C (b) together with 2D disk and 3D spherical and hemi-spherical models. The solid lines show the least square fitting of the data, which give the slope 2.09 in the case of SiO$_2$ and 2.14 in the case of carbon. Both are clearly shown to be away from the 3D spherical model, which has been described well for colloidal nanoparticles as well as for soft-landing nanoclusters formed in the gas phase [6]. The plots suggest that the particle shape is more close to the hemispherical or other 2D models than to the spherical growth model, meaning Au particles are wetting on both substrates. What is the most interesting observation from the Figure 2 is that the scaling exponents are unchanged, i.e. the growth mode kept the same, irrespective of the substrate temperature change from 300 to 473 K. This phenomenon again confirms the conclusion drawn from Figure 1 above that the nucleation of Au nanoparticles is controlled by kinetics within the temperature range. The almost identical scaling exponent for Au on amorphous SiO$_2$ and carbon may be interpreted as the similar size-dependent 3D shape of Au nanoparticles on these two supports, which indicates the similar binding energy for Au/a-SiO$_2$ and Au/a-C. It is interesting to compare our results to that reported by Veith et al. on Au/SiO$_2$, where the high thermal stability of Au nanoparticles of size ~2.5 nm was shown, up to at least 773 K in an oxygen containing environment.
environment [11]. The authors attributed the stability of Au to the substrate surface defects where protons or surface hydroxyl groups have been removed during the Au deposition process using the magnetron sputtering technique. The mechanism of Au nanoparticles growth and the role of the supports on the shape of Au nanoparticles is clearly a topic of further investigation.

4. Conclusions
In summary, we have shown in this study that quantitative analysis of HAADF-STEM intensity is invaluable to nanoparticle characterization. We have established a correlation between integrated HAADF-STEM intensity over each Au nanoparticle with the diameter of nanoparticles. A quantitative analysis of the scaling exponent together with the simple geometrical models allows us to obtain characteristics of the nanoparticles’ three-dimensional morphology. The growth via thermal vapor deposition is intermediate between 3D and 2D mode. It is shown that the scaling exponent is not influenced by the temperature of the substrates. The broad-brush approach described in this paper may be applied to similar systems to gain a quick and efficient assessment of nanoparticle’s shape. The method would be particularly useful for industrial catalysts, where performance is dependent on particles having complex shapes with large surface areas. Combined with aberration-corrected STEM imaging, one may gain such information at atomic-details.

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