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Coalescence dynamics of size-selected gold clusters studied by time-resolved transmission electron microscopy

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Abstract. Coalescence dynamics of size-selected gold (Au) clusters (each with nominal 923 atoms), on amorphous Si_3N_4 substrate at room temperature, has been studied via time-resolved transmission electron microscopy (TEM). We found that the clusters approached each other in two stages. In the first stage, the drift velocity was independent of the particle separation and could be attributed to beam-induced random motion. In the second stage, the clusters were found to jump into contact with a much higher final averaged speed. This is independent of beam dose rates and is attributed to the van der Waal attraction.

1. Introduction

Coalescence of supported metal nanoparticles/clusters is a common phenomenon in the field of catalysis, whose process is known to relate to many factors, such as size, structure, orientation, temperature, support and environment [1, 2]. It is critical to quantify these factors for understanding the physical mechanism of the coalescence if one wants to rationally design a catalyst system. Previous experimental studies of nanoparticle coalescence are mainly on particles of different sizes [1, 3], thus it is difficult to differentiate the effect of size as to other factors such as temperature, structure, etc. Here we utilised the unique capability of an atomically size-controlled cluster source in our group, together with a fast acquisition feature of a microscope camera, to study the coalescence phenomena between gold (Au) clusters. Specifically, we reported the effects of the cluster size and electron dose on the coalescence of Au clusters.

2. Experimental details

The size-selected Au clusters were produced in a magnetron-sputtering gas condensation cluster source equipped with a lateral time-of-flight mass filter [4,5]. In this study, the clusters with atom number of 923±23 (the resolution of the mass filter was ±2.5%) were deposited at 1 eV/atom onto an amorphous Si_3N_4 substrate at room temperature. The dynamics of cluster coalescence at room temperature was captured using a Gatan OneView camera in a 200 kV JEOL 2100F transmission electron microscope (TEM) and at an imaging rate of 302 frame/sec. The videos were recorded under electron dose rate of 2.9×10^5, 5.1×10^5 and 6.5×10^5 $e^-/nm^2/s$, respectively, while keeping the other imaging conditions, such as magnification, frame rate, etc. the same.

3. Results and discussions

Figure 1(a) shows a TEM image example of the deposited Au clusters on an amorphous Si_3N_4 substrate. The diameter distribution histogram, Figure 1(b), shows three discrete peaks at 2.73 ± 0.13 nm, 3.66 ± 0.12 nm and 4.26 ± 0.41 nm, respectively. This size distribution is different from evaporated Au nanoparticles, which had a single broad distribution peak [6]. The Au-Au nearest neighbour distance is 0.288 nm [7] and the theoretical diameter of a spherical Au_{923} cluster (full-shell geometry) is 3.45 nm, which is close to the value of 3.36 ± 0.16 nm measured by an aberration-corrected scanning transmission electron microscope (AC-STEM) [8]. These values are over 0.6 nm bigger than the value measured here by TEM. This is most likely due to the difficulty of visualisation of the outermost layer of the Au cluster in the aberration un-corrected TEM image because of the Fresnel effect. Therefore, the clusters with an average diameter of 2.73 ± 0.13 nm are assigned as single Au_{923} clusters. The diameter (D in nm) for a 2× or 3× Au_{923} cluster (assuming a spherical shape) is calculated with the following formula,

$$D = 3.36 * \left(V/V_{Au_{923}}\right)^{1/3} - 0.576$$

where 3.36 nm is the average diameter of Au_{923} clusters measured by an AC-STEM, V is the volume of a cluster, $V_{Au_{923}}$ is the volume of a Au_{923} cluster, and 0.576 nm is twice of the Au-Au nearest neighbour distance. Here, the volume ratio is either 2 or 3, then the calculated diameter of a 2× and 3× Au_{923} cluster is 3.66 nm and 4.27 nm, respectively. Thus, we attribute the next two peaks in Figure 1(b) to the clusters merged with two and three Au_{923} clusters, respectively, with the merged clusters are approximated spherical as well. We notice that a slightly larger proportion of clusters has size bigger than Au_{923} on the current amorphous Si_3N_4 than that found on amorphous carbon, suggesting a weaker interfacial adhesion of Au_{923} to the current Si_3N_4 substrate.

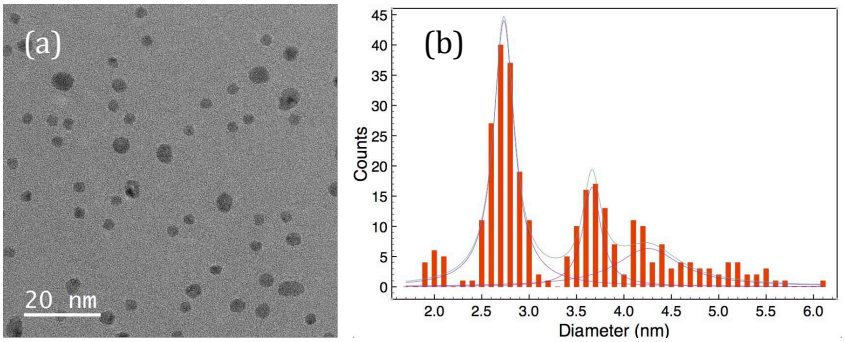

Figure 1 (a) A typical TEM image of the size-selected Au_{923} clusters deposited onto an amorphous Si_3N_4 substrate. (b) Diameter histogram of the Au clusters. The solid line curves are the Gaussian fitting.

Under the electron beam exposure, the clusters initially stayed still at room temperature. As the beam dose rate increased to the order of 10^5 $e^-/nm^2/s$, they started to move in random directions on the surface, indicating that this Brownian-like motion was largely electron beam driven. The e-beam driven phenomena are commonly observed in electron microscopy studies, particularly for nanomaterials, for example, ref. [9], Despite that, a recent work [10] suggests that an electron beam driven stochastic motion can be very useful to study the mechanism of thermal driven stochastic motion underpinning coalescence in catalytic particles. Here, we focus on those clusters that got closer and coalesced. As demonstrated in Figure 2(a) (bottom left), the two Au_{923} clusters approached towards each other when imaged at an electron dose rate of 6.5×10^5 $e^-/nm^2/s$ (the first two images). When they contacted, a "neck" was seen to form and widen at the contacting planes (the third and fourth images), and finally the two clusters merged into one as shown in the last image.

The distance between the geometric centers of the two clusters was measured and the relative speed was calculated from the distance changing between frames, as shown in Figure 2 (b) and (c). It was

noticed that there was a steady fluctuation in the centre-to-centre distance followed by a big change of about 1 nm (indicated by an arrow) at about 0.3 s, just before the two clusters merged. The average approaching speed, before the clusters coalesce, is 48 ± 36 nm/s. This speed is relatively slow compared to the contacting speed in the final approach at about 320 nm/s. It suggests that the approaching process consists a long-range drift superimposed on the stochastic motion of the clusters. It also shows that a fast camera is essential to resolve the details of this final contacting process, since only one or two frames were captured even at the frame rate of 302 frames/s.

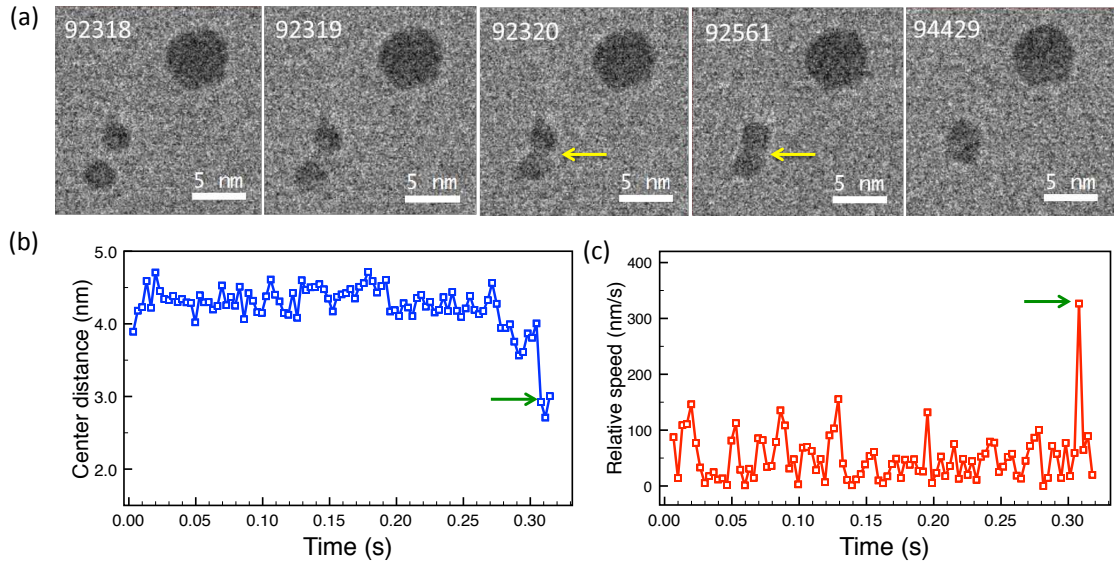

Figure 2 (a) Coalescence between two Au_{923} clusters (bottom left). The frame number is labelled on the top left corner of each image and the time interval between each frame is 3.31 ms. The yellow arrows indicate the "neck" formation. (b) Center-to-center distance versus time, and (c) relative speed changing of the two clusters versus time. The distance and relative speed were measured from frame 92220 to 92320. The contacting points are indicated by the green arrows.

It is interesting to compare our experimental result with available simulations. Wang *et al*. [11] studied the coalescence process of two 8 nm diameter gold nanoparticles on a solid silicon surface by conducting Molecule Dynamic (MD) simulations. They defined the approach as the stage before two particles were in contact and the coalescence as the structure relaxation after the contact. The interactions of these two processes were simulated using Lennard-Jones potential and Embedded Atom Model (EAM), respectively. They found that the coalescence was not obvious when the temperature was lower than 800 K. This is consistent with our observation at room temperature (~300 K) that the clusters were largely immobile at low beam intensity. Focusing on the approaching process, the simulation (which was conducted over 0.2 ns time window) showed that the average speed was 0.7 nm/ns at 300 K. However even within this simulation window, the actual speed increased rapidly as the particle separation decreased because of the van der Waal attraction. Thus, one may be sure that the final jump distance (< 0.14 nm) would be completed within the sub-nanosecond time scale. If the same jumping event was recorded with a 3.31 ms frame interval as in the present experimental study, the corresponding 'frame-average' approach speed would be about 40 nm/s. This is about the same order of magnitude as our experimental results, Figure 3(c). However, we also notice that the simulation was for 8 nm Au nanoparticles on crystalline Si substrate and our present experiments were conducted on 3 nm Au clusters on an amorphous Si_3N_4 substrate. Therefore, more realistic simulations would be useful in order to properly interpret the experimental results. Nevertheless, the order-of-magnitude agreement may not be surprising as gold atoms interact weakly

with both substrates and as the gold particles retained their spherical shapes in both simulation and experiments.

To study the effect of the electron beam irradiation, we analysed the experimental 'frame-averaged' contacting speed under different electron dose rates (Figure 3). We found that the average contacting speed varied from about 100 to 400 nm/s and was almost independent of the electron dose rate employed. This suggests again that the rate of the final approach is not due to the beam-induced effect. In addition to the van der Waal attraction, other factors, such as interaction with the substrate and crystalline structure of nanoclusters [3], may also contribute to the average contacting speed.

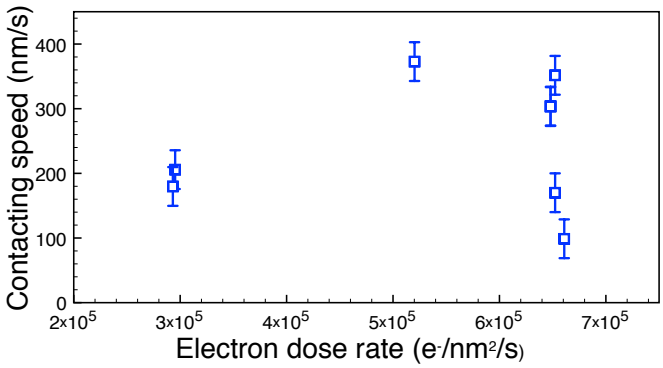

Figure 3 Contacting speed against electron dose rate. The error bar is calculated from the distance measurement error of 0.1 nm.

4. Conclusions

In summary, we have studied the coalescence dynamics of size-selected Au_{923} clusters by using a time-resolved TEM. The ultra fast camera allows us to estimate the timescale for the contact process to be millisecond or less. The final contacting speed of two clusters ranges from about 100 to 400 nm/s and is weakly dependent of the electron doses employed. The variation of contacting speed under the same irradiation condition indicates that other factors, such as orientation and substrate, may also play a role. The work illustrates the usefulness of time-resolved high-resolution TEM in combination of size-selected atomic clusters, in studying the atomistic process underlying the fundamental process of cluster coalescence with implications for future rational design of catalytic nanoparticles. It also highlights the need for joint theoretical and experimental studies over the same system.

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