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Towards Real Time Quantitative Analysis of Supported Nanoparticle Ensemble Evolution Investigated by Environmental TEM

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Metallic nano-particles and nano-precipitates find a wide range of applications ranging from heterogeneous catalysis to structural reinforcement [1-2]. Once exposed to harsh working environments and conditions these nano-structured systems tend to undergo structural and morphological evolution resulting in increased size distribution of particles or precipitates over time, which can degrade their original properties. The primary reason for this is that, when compared to bulk, such highly dispersed systems have larger number of atoms located at the surface with respect to their volume, resulting in a higher thermodynamic free energy. Once substantial atomic mobility exists the system will evolve towards reduction of the free energy via Ostwald ripening or coarsening [3-4], both resulting in larger average particle size. Both processes are well studied theoretically and experimentally. At the same time an accurate kinetic model of nanoparticles evolution towards an equilibrium does not exist. Recent developments in environmental aberration-corrected transmission electron microscopy, heating holders that utilize MEMS-based heating elements and direct electron detectors allow investigation of nano-structured systems with high spatial and temporal resolutions in gaseous environments at elevated temperatures. Once collected together these game-changing technologies represent a perfect setup to study the evolution of supported nanoparticles with the possibility to extract quantitative data that can be fitted into a theoretical model. Here we report on evolution study of an Au particles ensemble supported on SiN thin film during annealing at 950°C for over 120 minutes. The study is done in column of Environmental FEI Titan 80-300 (S)TEM operated at 300kV, equipped with DENS Solutions heating holder and Gatan direct electron detectors capable of acquiring streams of 1920 x 1792 pixels images at 400 frames per second, which results in a tremendous data rate of approximately 3GB/s. This data rate compels the development of automatic image analysis algorithms to handle the torrent of data in order to extract quantitative information. We developed an algorithm that allows automated particle tracking and indexing. Once indexing is done and threshold images are created, information such as particle size distribution and particle diameter versus annealing time can be extracted (Figure 1). The latter points to significance of gold atoms sublimations at 950°C. Ostwald ripening and coarsening processes (Figure 2) also can be captured with great detail, allowing us to study the preference of one process over the other based on gold atom diffusion rate on a support, particle sizes, distance between a particle and its closest neighbors. In addition, the current setup can be applied to a variety of particle and substrates materials in the presence of different environments. Furthermore, the ability to extract quantitative data in real time will greatly reduce the time required for acquiring a complete data set [5].

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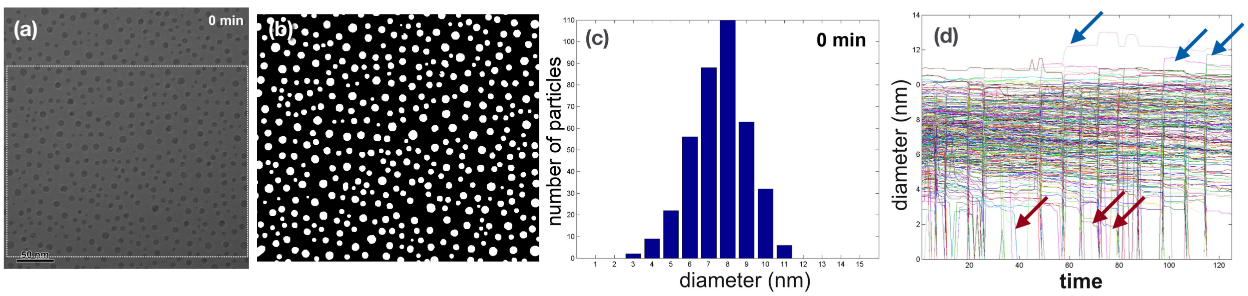

Figure 1. Quantitative analysis of Au nanoparticle ensemble supported on amorphous SiN film during over 120 minutes annealing in microscope column at 10^{-7} Torr and 950°C. (a) Original TEM image frame extracted from data stream acquired during the experiment. (b) Threshold image from automatic particle indexing procedure ran on rectangular area in (a). (c) Particle size histogram generated from (b). (d) Plotted diameter of each particle over time shows gradual loss of mass, as well as rapid changes of particular particle diameter due to Ostwald ripening and coarsening (red and blue arrows).

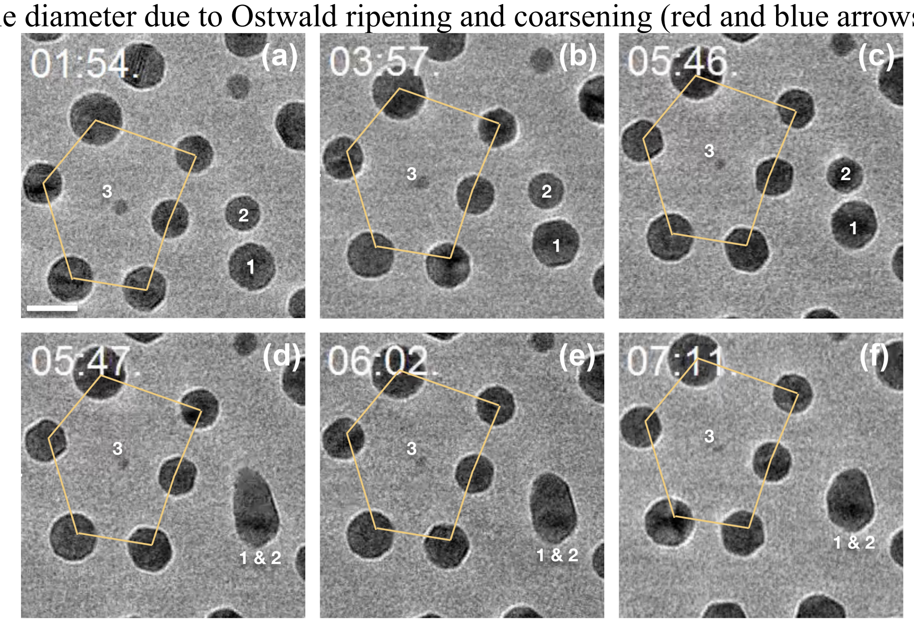

Figure 2. Selected frames from annealing experiment are tracking coarsening and ripening of individual Au nanoparticles on a SiN substrate. In case of particles marked 1 & 2 large-scale mass transfer occurs between frames (c) and (d) that involves center of mass of each particle move towards each other called coarsening. The resulting particle re-shape process is captured in frames (e) and (f). Particle marked "3" has the center of mass fixed. Yet it reveals gradually decreasing diameter and, thus, mass, due to Ostwald ripening. Note, that surrounding particles do not exhibit any noticeable movement of center of masses (yellow outline) with respect to each other or particle "3". Time stamp is noted in top left corner of each TEM image frame. Scale bar in lower left corner of image (a) is 10 nm.