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Evolution of $Au_{25}(SR)_{18}$ Nanoclusters on Ceria Surfaces during in situ Electron Beam Irradiation

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Gold nanoclusters (NCs) containing less than ~200 atoms with sizes smaller than 2nm have demonstrated significantly enhanced catalytic activities compared to their nanoparticle (NP) counterparts [1]. The improved activity is largely attributed to their well-controlled homogenous size and morphology, offering a high density of unsaturated atomic sites. Colloidal sols and surfactants are used during NC synthesis to stabilize the structure and select the preferable surfaces; however, such additives can complicate the catalyst-reactant interactions and often degrade the catalytic performance. The molecules adsorbed on the NC surfaces are typically removed via thermal annealing and oxidative etching and the NCs without surfactant assume a metastable state and become highly active. The nature of the NC atomic configurations upon the removal of ligands, and the NC structural and chemical evolution during specific post-synthesis treatments or reactions remain essentially unknown. Here, we directly observe the atomic structural evolution of $Au_{25}(SR)_{18}$ NCs supported on CeO_2 during the *in situ* removal of surface ligands in a scanning transmission electron microscope (STEM).

$Au_{25}(SR)_{18}$ NCs were synthesized and then loaded onto CeO_2 nanocubes in solution, which were then dispersed on lacey carbon coated Cu grids. *In situ* STEM imaging was performed using an aberration corrected FEI Titan S 80/300 microscope operated at 300kV. A sub-Å electron probe (0.08nm) with controlled beam current (0.65 nA) and dose (220 e/nm^2s) was used as the heating source to remove surface ligands on individual NCs. Sequential high angle annular dark field (HAADF)- and bright field (BF)-STEM images were acquired simultaneously every 3s for each frame.

A HAADF-STEM image of a $Au_{25}(SR)_{18}$ NC supported on a CeO_2 NP is shown in Fig. 1a. The CeO_2 nanocube is orientated along the (100) zone axis. Ce atomic columns are resolved in the HAADF-STEM image while O atoms are not due to its weak scattering of electrons. The structure of the $Au_{25}(SR)_{18}$ NC shown in Fig. 1a has an icosahedron core of 13 Au atoms and the rest of the 12 Au atoms form a disordered exterior shell, with 18 thiolate ligands encapsulating the entire cluster [2], as the inset in Figure 1a. The atoms in Au_{25} are not resolved since the atomic columns are not aligned with respect to the electron beam, and since the NC is surrounded by ligands. Under electron beam irradiation, the atomic structure of the Au_{25} NC changes with time while the CeO_2 remains stable. The structure of the Au_{25} NC evolved through four different stages during the course of ligand removal via electron beam irradiation: (1) increased anchoring of the NC onto the CeO_2 support during partial removal of the surface ligands; (2) the full removal of all surface polymer molecules, which results in an FCC-structured single-crystal Au NC; (3) the atoms on Au nanoparticle gradually, surface-layer by surface-layer, migrate and spread onto the surface of the CeO_2; and (4) finally, a single atomic layer forms on the CeO_2 surface, as shown in Fig. 1b. This *in situ* study revealed a complete reconstruction of a single Au_{25} NC on a CeO_2 (100) surface upon the removal of surface molecular ligands during electron beam irradiation indicating that the NCs do not maintain the same atomic framework as in the as-

processed/untreated $Au_{25}(SR)_{18}$ due to a very strong interaction between the NC and the CeO_2 surface. The true active structural state of such NCs prior to catalytic reaction, after the complete removal of surface ligands, may not be as expected or predicted.

References:

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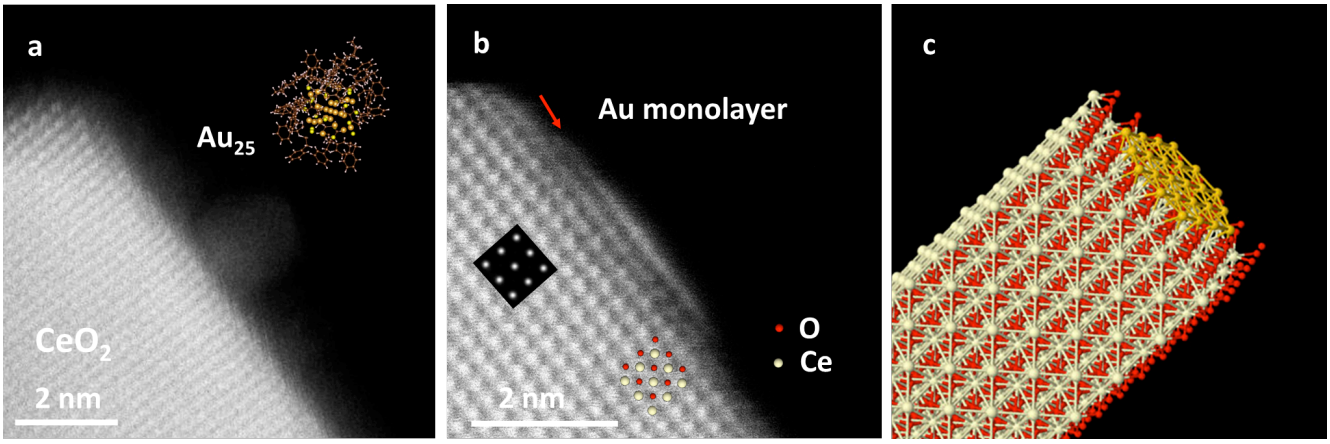

Figure 1. (a) A HAADF STEM image of $Au_{25}(SR)_{18}$ on the (100) surface of CeO_2 nanocube, the inset shows the atomic model of $Au_{25}(SR)_{18}$ cluster. (b) A STEM image of a single layer of Au on CeO_2 surface after electron beam irradiation, with an atomic model and simulated HAADF STEM image of CeO_2 overlay on the image. (c) The atomic model of a single layer of Au on CeO_2 surface.

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