

## Nanostructured Gold and Alloy Catalysts

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The high population of surface atoms for nanometer-sized metal or oxide particles and their unique electronic and interfacial properties are of increasing interest to catalytic explorations. The propensity of nanoparticle aggregation is however a major challenging issue. Core-shell nanoparticles and network assemblies provide a new pathway to enhance the stability of nanosized catalysts against the propensity of aggregation, while imparting abilities to manipulate core size, shape, interfacial composition and surface structure for catalytic fine-tuning. This presentation describes findings of an investigation of core-shell assembled gold and alloy nanoparticles as catalysts for electrocatalytic oxidation of C1 molecules (e.g., CO, methanol, etc.). The aim is to probe the structural and morphological evolution and reconstitution upon catalytic activation. Gold nanoparticles of 2-nm core size are linked by alkyl dithiolates into a network thin film assembly on planar substrate as a model system of the nanostructured catalyst. In addition to the detection of the potential-driven catalytic activation and the formation of surface oxygenated species, infrared reflection spectroscopy and atomic force microscopy provided important insights into the structural and morphological reconstitution of the nanostructured catalysts. The morphological changes in terms of the particle size and interparticle spatial properties are dependent on the thickness of the nanoparticle assembly. The catalytic activation in alkaline electrolytes is believed to involve a partial or complete desorption of the interparticle shell components accompanied by the formation of surface oxygenated species, a reconstitution process that is important for the delineation of design and preparation parameters of nanoporous and highly active nanoscale catalysts. A polymeric film was also used as a matrix for the assembly of the nanoparticle catalysts. When the polymer was pre-doped with a small amount of Pt, a remarkable catalytic activity was observed upon catalytic activation. The findings demonstrated that the electrocatalytic activity could be activated and controlled by manipulation of the core-shell structures and reactivities. The implication of the results to the general concept of nanostructured catalysis will also be discussed.