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# Earle K. Plyler Prize: Probing the Structural Evolution and Size-Dependent Reactivity of Gold Clusters by Photoelectron Spectroscopy

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Gold has attracted much interest in nanoscience because of its emerging catalytical and optical properties at the nanometer scale. A prerequisite to elucidate the molecular mechanisms of the catalytic effects of nanogold is a detailed understanding of the structural and electronic properties of gold clusters as a function of size. Negatively charged gold clusters ($Au_n^-$) up to $n = 12$ were known to be planar. Using photoelectron spectroscopy and computational chemistry, we found that $Au_{16}^-$ to $Au_{18}^-$ possess hollow cage structures, while $Au_{20}^-$ was found to have a high symmetry tetrahedral structure. Beyond $Au_{20}^-$, we have found that low symmetry core-shell type structures started to emerge at $Au_{25}^-$. The size-dependent reactivity of $O_2$ with gold clusters was further studied using photoelectron spectroscopy. Previous works showed that only even-sized $Au_n^-$ clusters react with $O_2$, whereas odd-sized $Au_n^-$ clusters are nonreactive. Superoxo-type $Au_n(O_2^-)$ complexes were proposed for even-sized clusters. We observed van der Waals complexes of odd-sized $Au_n^-$ clusters with $O_2$, confirming the inertness of the odd-sized $Au_n^-$ toward $O_2$. This observation led to new insight into how neutral even-sized $Au_n$ clusters interact with $O_2$. Further studies revealed that there is a superoxo to peroxo chemisorption transition for the $O_2$ interaction with even-sized $Au_n^-$ clusters. The $O_2$ in the peroxo $O_2Au_n^-$ complexes is much more activated (with a longer O–O bond length), suggesting that this mode of chemisorption may play a more important role in the $O_2$ activation by gold nanoparticles.