Impacts of Copper Position on the Electronic Structure of $[Au_{25-x}Cu_x(SH)_{18}]^-$ Nanoclusters

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Recently, atomically precise noble metal nanoclusters have emerged as useful targets to study the electronic structure of nanoparticles due to their well-defined architectures and accessibility to both theory[1] and experiment.[2] Heteroatomic substitution in these systems can be used to tune their electronic properties, however due to synthetic limitations, controlling the position of heteroatomic substitution within a well-defined architecture is not feasible and can therefore not be studied in detail.[3] This work aims to elucidate the impact that single and double heteroatom substitutions to each symmetrically unique position in a gold nanocluster has on the overall electronic structure of the cluster. We do this by utilizing density functional theory (DFT) to model the electronic and optical properties of $[Au_{25}(SH)_{18}]^-$ cluster, and substitute Cu atoms at three geometrically unique positions within the cluster. These clusters have well-defined, atomically precise structures and show an electronic structure that is a function of both composition and heteroatom position. We then model clusters containing Cu substitutions at two positions, and demonstrate an additional and significant impact from heteroatom proximity with respect to one another. For each system, we use electronic descriptors such as formation energies, HOMO-LUMO gap, electron density and orbital energy levels, and suggest how the trends in these parameters as a function of compositional architecture may be explained using atomic descriptors such as electronegativity, analogous to design principles widely used in the field of organic electronics. Further, we use linear response time-dependent DFT to model the optical absorption behavior of these systems, providing a convenient readout of electronic structure that serves as a figure of merit to correlate observed and computed electronic properties.

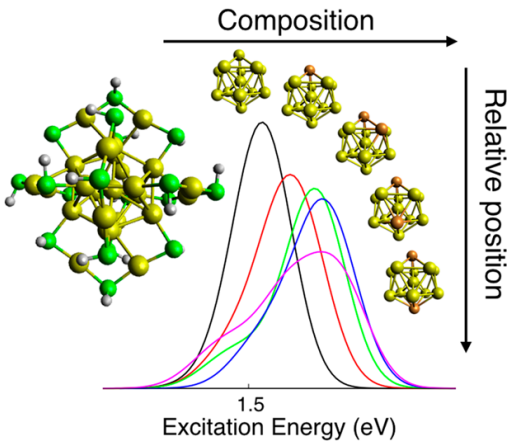

Figure 1. Both composition and relative substitution position play are important in optical absorption behavior of $[Au_{25-x}Cu_x(SH)_{18}]^-$ clusters[4]

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