

Dynamic and Extent of both ligand and metal exchange reactions depend on the electronic charges of gold monolayer protected clusters

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The consequences of nanoparticle charging on the ligand/core-metal exchange reactions were investigated. Gold monolayer protected clusters were electrochemically charged to various positive charge states. The rate and extent of ligand place exchange reactions between the hexanethiolate monolayer of Au₁₄₀ monolayer protected clusters (C6 MPCs) and dissolved 6-mercapto-1-hexanol thiol (HOC6SH) both increased with increasingly positive electronic charge on the Au cluster core. Core-metal-exchange reactions occurred between C6 Au₁₄₀ MPCs and silver tiopronin Au₁₄₀ MPCs, the rate of which was also found to increase with the number of positive charges on the gold core. Both ligand and core-metal exchange reactions were remarkably inhibited or even stopped at the presence of N₂. Moreover, acid-base studies showed that thiolate is more reactive in place exchange reactions than the corresponding thiol. Evidences strongly suggest that some gold oxidization form (i.e., Au(I) thiolate (Au(I)-SR)) was generated in the process of this gold nanoparticle charging. Au(I) thiolate was later experimentally proven to participate in exchange reactions. In the end, a general, possible mechanism on ligand/core-metal exchange reactions of gold MPCs was proposed.