PR 0558

Size-dependent electric charge transport in carboxylate modified water-soluble gold clusters

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Investigation of mechanism of electric charge transport in monolayer-protected clusters (MPCs) assumes great scientific and technological importance owing to them being tipped as possible building blocks for future nanoelectronic devices, given their tunable solid-state conductivity. The electronic properties of the MPCs could be tuned by varying the size and shape of the cluster cores as well as the separation between them. According to the current understanding, MPCs which behave as weakly coupled molecular solids consisting of small metallic grains dispersed in an insulating ligand matrix, follow thermally activated stochastic multiple site hopping processes at low temperatures and nearest neighbor electron hopping at high temperatures.

We have investigated the charge transport processes in mercaptosuccinic acid (MSA) and mercapto N-(2-propionyl glycine, MPG)-protected gold (Au) clusters (Au-MSA and Au-

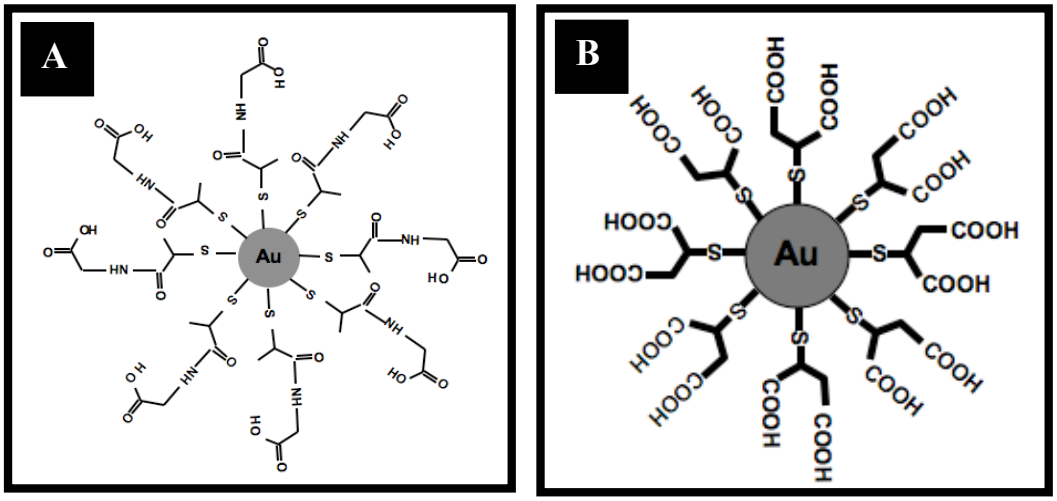

Figure 1. Schematic of the Au-MSA (A) and Au-MPG (B) MPCs showing terminal carboxylic acid groups of the monolayers.

MPG respectively, in further discussion below) having different cluster core sizes as a function of temperature by a four-probe methodology. Au-MSA and Au-MPG represent two novel networked MPCs due to intra and/or inter molecular hydrogen bonding between the terminal carboxylic groups of the monolayers. Schematics of the MPCs are shown in Figure 1. Figure 2 shows variation of the resistivity (ρ) of the Au-MSA and Au-MPG MPCs with different cluster core sizes as a function of temperature. Au-MSA MPCs with cluster core sizes of ~ 2, ~ 4 and ~ 7 nm (traces a, b and c in Figure 2A) show a metallic-like behavior at low temperatures (20-60 K), which crosses over to that of semiconductors at high temperatures. At low temperatures, the transport behavior of a small fraction of conductive alignment of particles is dominant (metallic-like nature) and that of the non-metallic majority is absent due to thermal activation. At high temperatures, the behavior of thermally activated free carriers in the majority channel dominate the charge transport process due to nearest neighbor electron hopping and semiconductor nature sets in. For Au-MPG MPCs, the resistivity was nearly independent of temperature (temperature-independent tunneling) for smaller clusters (~ 1.6 nm, trace a) and larger clusters (~ 3 and ~ 4 nm) show metallic-like to semiconductor crossover with temperature.

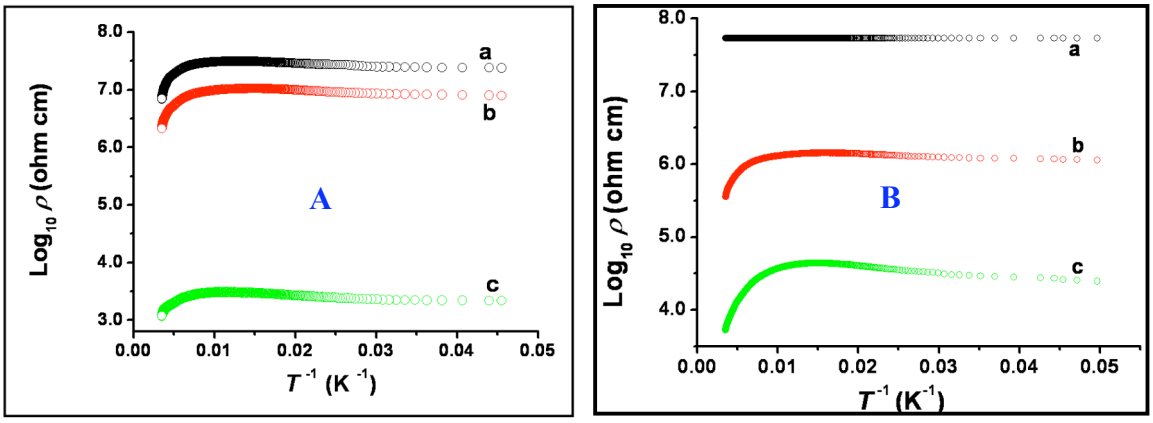

Figure 2. Variation of resistivity of Au-MSA (traces a, b and c in Figure A represent MPCs with ~ 2, ~ 4 and ~ 7 nm cores) and Au-MPG (traces a, b and c in Figure B are for cluster cores of ~ 1.6, ~3 and ~ 4 nm sizes) MPCs with temperature.