Hydride-doped gold superatoms: formation, structure, and reactivity

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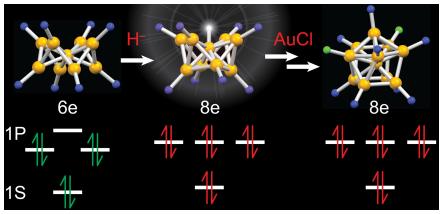
Atomically size-selected gold clusters protected by organic ligands or stabilized by polymers provide an ideal platform to test fundamental concepts and size-specific phenomena, such as the superatomic concept and metal-to-nonmetal transition. Recent studies revealed that these stabilized Au clusters take atom-like quantized electronic structures and can be viewed as chemically-modified Au superatoms. An analogy between Au and H is an interesting proposal made for bare Au clusters: an Au atom at a low-coordination site of an Au cluster can be replaced with H while retaining the structural motif and electronic structure. However, this proposal has not been experimentally proved in chemically-modified Au superatoms while a recent theoretical study predicted the formation of $[HAu_{25}(SR)_{18}]^-$ (RS = thiolate). Investigation of the interaction between H and Au superatoms will deepen our understanding on the role of H in the formation processes of Au superatoms, the effect of adsorbed H on the electronic structure of Au superatoms, and the activity of adsorbed H for hydrogenation catalysis.

This talk introduces our recent studies on the interaction of hydride with two types of chemically-modified Au-based superatoms.

(1) $(Au_9)^{3+}$ and $(PdAu_8)^{2+}$ superatoms protected by phosphine ligands[1,2)]

A single hydride was selectively doped to $(Au_9)^{3+}$ and $(PdAu_8)^{2+}$ upon reaction with BH_4^- to form hydride-doped superatoms $(HAu_9)^{2+}$ and $(HPdAu_8)^+$. The structures and growth processes of these hydride-doped Au superatoms were studied experimentally and theoretically.



(2) Au_{34} superatoms stabilized by polymers[3–6)]

The Au_{34} superatom exhibited the localized surface plasmon resonance (LSPR) band by reacting with BH_4^- due to the electron donation by multiply-adsorbed hydrides. The LSPR band disappeared by exposing hydride-doped Au_{34} to dissolved O_2, but reappeared by reaction with BH_4^-. Catalysis for hydrogenation of C=C bonds was generated by doping a single Pd or Rh atom to Au_{34}.

The results demonstrate that the hydride in chemically-modified Au superatoms mimics the Au atom in terms of electron count. The hydride-mediated growth processes observed will contribute to the development of an atomically-precise, bottom-up method of synthesizing new artificial elements in a periodic table for nanoscale materials. The interaction of hydride with Au superatoms will find application in hydrogenation catalysis and hydrogen sensing.

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