Metal-Chalcogenide Superatomic Clusters with Closed Electronic Shells as Super Donors for Novel Doped Semiconductors

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Due to quantum confinement, the electronic states in compact clusters are bunched into shells much in the same way as in atoms. Clusters with filled electronic shells and a large gap between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) are generally energetically and chemically stable. Enabling clusters to become electron donors with low ionization energies or electron acceptors with high electron affinities usually requires changing the valence electron count. I will show that a metal cluster may be transformed into a donor with low ionization energy or an acceptor with high electron affinity by attaching ligands. During the transformation, the clusters maintains its closed electronic shell and a high HOMO-LUMO gap and this transformation is related to ligands creating a crystal field that shifts the electronic spectrum. I will further show that a cluster may be transformed from an electron donor to an acceptor by exchanging ligands. I will present our studies on $Co_6Te_8(PEt_3)_m(CO)_n$ (m+n=6) clusters which show that $Co_6Te_8(PEt_3)_6$ has a closed electronic shell and a low ionization energy of 4.74 eV, and the successive replacement of PEt_3 by CO ligands ends with $Co_6Te_8(CO)_6$ exhibiting halogen-like behavior. Both the low ionization energy $Co_6Te_8(PEt_3)_6$ and high electron affinity $Co_6Te_8(CO)_6$ have closed electronic shells marked by high HOMO-LUMO gaps of 1.24 eV and 1.39 eV respectively.

The new donor and acceptor superatoms can be used to create doped semiconductors by using superatoms, as effective super-dopants for two-dimensional semiconducting films. Unlike conventional dopants that are embedded in the semiconductor, the superatom dopants act by using the two dimensional semiconductor as a solid state ligand. I will demonstrate this intriguing possibility by considering WSe_2 films that are transformed from a p-type to an n-type semiconductor when $Co_6Se_8(PEt_3)_6$ (PEt_3-tri-ethylphosphene) superatoms are supported on the surface. The theoretical findings complement recent experiments by Yu et. al. where WSe_2 films doped with $Co_6Se_8(PEt_3)_6$ indeed showed a change in behavior from p- to n-type. We further show that by continually replacing the PEt_3 ligands by CO ligands, one can control the chemical potential of the semiconductor and even introduce magnetic carriers by controlling the number of ligands, opening a pathway to superatomic doped magnetic semiconductors.

Finally, I will present our recent work on the magnetic response of an assembly of magnetic nanoparticles. These developments follow our work on mixed Fe-Co systems where we collaborated with experimental groups to provide experimental evidence substantiating the synthesis of a novel cobalt iron carbide phase ($CoFe_2C$) of nanoparticles that revealed a blocking temperature, T_B, of 790 K for particles with a domain size as small as 5 ± 1 nm. The particles have magnetocrystalline anisotropy of $4.6 \pm 2 \times 10^6$ J/m^3, which is 10 times larger than that of Co nanoparticles. I will present our results on the magnetic behavior of an assembly of such nanoparticles as a first step towards developing hard and soft magnetic materials.