Lecture 11. Electronic Properties of nanoparticles

The purpose of the lecture: to familiarize students with electronic properties of nanoparticles.

Expected results: students getting information about electronic properties of nanoparticles.

Classic Theory of Atomic Structure

Atoms consist of negatively charged electrons orbiting the nucleus, which contains protons (positively charged) and neutrons. According to Bohr's model, electrons are distributed in discrete energy bands called occupied orbitals. The outermost occupied orbital is the valence orbital or the highest occupied molecular orbital (HOMO). The number of electrons in valence orbital determines the chemical and electrical properties of an atom.

In the occupied band, electrons (e_) exist bound with a positively charged electrone hole, the mathematical opposite of electrons. When an electron in HOMO is excited by absorbing energy (light or heat), it separates from the "hole" and jumps into the conduction band, resulting in the creation of a positively charged hole in the HOMO. The newly formed hole attracts neighboring electrons, resulting in propagation of a positively charged hole-current in the HOMO, moving opposite to the direction of the electron current in the conduction bands. In metals, because the HOMO and LUMO overlap, electrons from both HOMO and LUMO can bind the hole.

Quantum Mechanical Theory

In simple terms, the basic rules of quantum theory of atomic structure are the following:

1. Electrons can be found in certain energy states called the density of states (DOS) in a occupied molecular orbital. Electrons cannot jump from the HOMO (valence band) to the lowest occupied molecular orbital (LOMO) unless a DOS is available in the conduction band.

2. Only one particle can occupy a particular state at any one time. This is the called the Pauli Exclusion Principle.

3. Electrons exhibit both wave-like and particle like behaviors (the wave-particle duality).

4. Classic physics describes light as a wave (electromagnetic radiation) with a set of frequency and amplitude. Einstein proposed that light travels in small quantized packets of energy called photons instead of a classic wave. For an electron to occupy a DOS, the photon's wavelength must match the wavelength of the atom's orbital.

5. The classic atomic structure is deterministic - that is, one can calculate both its location in the orbit and its velocity as it revolves around the orbit. The electron will always be there until some energy is absorbed or given off to change the orbit, all of which are totally certain. The quantum atomic structure is probabilistic - that is, it is not possible to predict where in its orbit an electron will be found. One can only determine the probability of finding an electron at certain points. The electron is therefore described in terms of its probability distribution, which is also known as probability density (Shrodinger's wave equation for matter: Hj j Ej).

In 1925, de Broglie proposed particle-wave theory for electrons in which electrons, in addition to being particles, could also be thought of as a wave with a characteristic wavelength (de Broglie was awarded the Nobel Prize with Paul Dirac in 1929). Davison and Germer (1927) experimentally confirmed the particle-wave nature of electrons.

Because electrons can exist as either a wave or a particle at a given instant of time, there is a fundamental limitation to finding an electron at a particular point in space. The quantum mechanical model, therefore, shows that electrons are in random motion confined within the areas of electron probability distribution. In 1926, Erwin Schrodinger mathematically described the likelihood of finding an electron at a certain position and proposed an atom consisting of a nucleus surrounded by an electron cloud. The probability of finding the electron is greatest where the cloud is most dense and, conversely, the electron is less likely to be in a less dense area of the cloud.

If the electron's wavelength is longer or shorter, then they will not fit in that orbit (wavelength exclusion). Thus, electrons may not exist at one single spot in its orbit, bringing up the idea of the DOS. The DOS of a system describes the number of states at each energy level that are available for occupation by electrons. In metals, the LUMO, HOMO, and the Fermi level (Eg) overlap; thus, electrons nearest to the Fermi level cross to the conduction band. In semiconductors, there is an energy gap between the HOMO and the LUMO, with the Fermi level situated in between (at 0 K, Eg j E gap/2). The electrons in the HOMO must be energized to the Eg for its translocation from the HOMO to LUMO. In insulators, a large band gap prevents electron transfer. For bulk particles, the band structure is an intrinsic property of an atom that is independent of the particles' size or shape. For nanoparticles, the band structure is influenced by the particles' size and shape.

Unique Electronic Properties of Nanoparticles

JELLIUM MODEL OF ELECTRONIC STRUCTURE

The Jellium model allows evaluation of the valence and conduction electronic orbitals in nanoparticles. The HOMO and LUMO overlap in metals, while they are separated by an energy gap (band gap), characterized by a Fermi energy barrier in semiconductors and insulators. However, in semiconductors but not in insulators, electrons in the HOMO can absorb sufficient optical or heat energy to cross the Fermi energy barrier and jump into the conduction band, thus becoming free of its nucleus and moving freely within the atomic lattice (delocalized electron). Electron delocalization in the conduction band is crucial to the conduction process.

ELECTRON CONFINEMENT AND THE DENSITY-OF-STATE

Unlike the bulk particles, the band structure in the nanoparticles is strongly influenced by their size and shape. Smaller nanoparticles (less than 10 nm or smaller than the electron wavelength. As the nanoparticles become smaller, a decrease in confining dimensions makes the energy levels discrete, resulting in an increase or widening up of the band-gap energy. Because the band-gap energy and wavelength are inversely related to each other, the wavelength decreases, resulting in the emission of blue radiation by the nanoparticles as opposed to red radiation emitted by the bulk particles.

In the process, the valence orbital acquires a positive charge (the electron hole) that is mathematically opposed to the electronic charge. However, if the electron is not extracted from the conduction band, it may release photons and revert to the valence band.

Although the size dependence of the band gap is well established (the band gap increases as the nanostructure size decreases), the shape dependence of band gap is not fully known.

In earlier studies, Yu et al. (2003) have shown that the band gaps in one-dimensional (1D)-confined wells, two-dimensional (2D)-confined wires, and three-dimensional (3D)-confined dots evolved differently than the size effects. The Deg (the increase in the effective band gap above the bulk value) depends linearly on 1/diameter2 for wire and dots or 1/thickness2 for wells. The DEg values for well, wire, and dot were 1.00, 1.17, 2.00, respectively. The sizedependent changes showed the following relationship: dots (3D) > wire (2D) > wells (1D). Thus, losing dimension also reduced the effects of size on opening of the band gap. More research is needed to establish the effects of shape on band-gap energy.