Lecture 3. Metal Nanoparticles. Paramagnetic Metal Nanoparticles. Porous and Hollow Metal Nanoparticles.

The purpose of the lecture: to familiarize students with paramagnetic, porous and hollow metal nanoparticles.

Expected results: students getting information about paramagnetic, porous and hollow metal nanoparticles.

Metals are located on the left side and the middle of the periodic table. Group IA and Group IIA metals are alkali metals, while group IB-VIIIB metals are transition metals (less reactive than alkali metals). The elements to the right of the transition metals are basic metals. One of the common properties of metals is their ability to donate electrons; thus, they are good electrical and heat conductors. They are also generally malleable and ductile. The valence electrons of transition metals are present in multiple orbitals, and they exhibit several common oxidation states. Iron (Fe), cobalt (Co), and nickel (Ni) generate a magnetic field. Most metal nanoparticles are colloids suspended in a continuous dispersion phase. Because of the perpetual motion, nanoparticles in dispersion medium constantly collide with other nanoparticles and/or particles of the dispersion media. This improves dispersion of metal nanoparticles in a solution. When the light passes through a colloidal solution, its path becomes visible because of light scattering. The intensity of the scattered light depends on the difference between the refractive indices of the dispersed phase and the dispersion medium. Structurally, the unique thermodynamic properties confer amorphous characteristics to the metal nanoparticles. Martin et al. (1991) and Martin (1996) have demonstrated the existence of anomalous stable conformations of metal nanoparticles called "magic number" nanoparticles (where the so-called magic number is defined as the discrete number of atoms that correspond to the formation of the energetically most favorable clusters). The ambient stability of Ag magic number clusters may be a function of size, where the smaller magic number clusters could be the most stable.

SYNTHESIS OF METAL NANOPARTICLES

Metal nanoparticles are synthesized using topdown or bottom-up approaches. The bottom-up approach uses molecular components that are built-up into complex assemblies. The top-down approach uses microfabrication techniques where externally controlled tools cut, mill, and shape materials into the desired shape and size.

BOTTOM-UP METHODS

Faraday et al. (1857) pioneered chemical synthesis of metal nanoparticles by reducing metal salts using a phosphorus and carbon disulfide mixture. At present, many reagents (e.g., citrate, hydrazine, NaBH4, boranes, polyols, tetraoctylammonium bromide) are available for reduction of metal salts into colloids. A number of green biosynthesis approaches using plant reducing agents have been developed for synthesis of magnetic nanoparticles. The hydroxyl and carbonyl groups present in plant extracts act as reducing as well as stabilizing agents.

In traditional reductive synthesis, the newly synthesized metal nanoparticles are highly reactive and aggregate rapidly into larger particles as well as undergo oxidation during synthesis. To prevent this, the newly synthesized metal nanoparticles must be stabilized during or immediately following their synthesis. The BrusteSchiffrin method provides simultaneous synthesis and stabilization of metal nanoparticles. The method yields relatively high monodispersity and size control using a molar ratio of thiolated functional groups and metal salts. The first step of the BrusteSchiffrin method is conversion of Au(III) into a [TOA][Au(III)X4] complex by the surfactant tetraoctylammonium bromide (TOAB). The [TOA][Au(III)X4] complex, being water insoluble, undergoes phase transfer from the aqueous solution to the toluene phase.

Thereafter, the toluene phase is collected and used for one-phase synthesis, while the toluene-water mixture is used for two-phase synthesis of metal nanoparticles. Addition of the thiol ligand (dialkyl disulfide or dialkyl diselenide) partially reduces Au(III) and forms nanoparticle precursors. A single precursor is formed when the toluene phase is reduced (hence the term one-phase synthesis), while two precursors were formed when the toluene-water mixture was reduced (hence the term two-phase synthesis) with thiol ligands. The next step is complete reduction of Au cations to AuO using NaBH4 aqueous solution, resulting in the formation of metal nanoparticles.

TOP-DOWN NANOFABRICATION

The top-down methods include nanoimprint, soft and step and flash lithography, thermal embossing, particle replication in nonwetting templates, solvent molding-based fabrication, ultraviolet (UV) embossing, and focused ion beam and nanodispension methods. All of the listed methods exhibit nanometer resolution. Currently, nanoimprint lithography, including step flashimprint lithography (S-FIL), particle replication in nonwetting templates, and solvent moldingbased fabrication, are the most powerful methods for fabricating polymer nanocarriers of specific shape, size, and aspect ratios.

Paramagnetic Metal Nanoparticles
STRUCTURE OF PARAMAGNETIC NANOPARTICLES

Paramagnetic metal nanoparticles have an iron oxide core coated by inorganic materials (silica, gold), organic materials such as phospholipids, fatty acids, polysaccharides, peptides or other surfactants, and polymers. The unpaired electrons in paramagnetic nanoparticles, in the absence of a magnetic field, remain disorganized and do not exhibit magnetism. In applied magnetic fields, the electrons align in the direction of the field lines; thus, the nanoparticles gain magnetic moments. A repulsive force exists perpendicular to the aligned magnetized particles. The attractive force depends on the number of particles in the chain. The inducible magnetization allows them to be used for many applications, including as contrast-enhancing agents for magnetic resonance imaging (MRI), drug delivery systems, magnetic hyperthermia for local heat sources in the case of tumor therapy, and magnetically assisted transfection of cells.

SYNTHESIS OF PARAMAGNETIC NANOPARTICLES

Hyeon (2003) and Murray et al. (1993) have described a simple procedure for synthesis of nanostructured T1 MRI contrast. Particle growth is controlled by Oswalt ripening in which smaller nanoparticles dissolve and deposit on the bigger nanoparticles. Decreasing reaction temperature stopped the nanoparticle growth. Further size selection processes can narrow down the particle size distribution below 5%. The iron oxide core provides excellent image contrast properties for MRI monitoring as well as for thermal ablation, providing a valuable tool for locating and destroying tumors.

Porous and Hollow Metal Nanoparticles
STRUCTURE OF POROUS AND HOLLOW METAL NANOPARTICLES

Metal nanoparticles with pores (micropores_2 nm, mesopores 2 to _50 nm, macropores >50 nm), or hollow metal nanoparticles (metal nanocapsules) have generated considerable interest over the past few years. These nanoparticles exhibit high loading capacity, functionalization for both inner and outer walls, high chemical and thermal stabilities, large surface area, permeability, and good biocompatibilities. Porous nanoparticles have potential applications in catalysis, drug carriers, biosensors, prosthetic materials, gas adsorbents, and heavy metal ion adsorbents. Mesoporous silica nanoparticles are comprised of a honeycomb-like mesoporous structure that is able to encapsulate relatively large amounts of bioactive molecules. Unlike porous nanoparticles, hollow particles contain empty space that can be filled with active ingredients.
SYNTHESIS OF POROUS AND HOLLOW METAL NANOPARTICLES

POROUS SILICA In 1971, Chiola et al. (1971) filed a patent for preparation of low-density porous silica nanoparticles. Unfortunately, the method remained unnoticed for almost 20 years, until Beck et al. (1991) developed and patented an ordered mesoporous silica nanoparticle (MCM-41, an acronym for Mobil's Composition of Matter). The nanoparticle developed by Chiola et al. (1971) met all the criteria established for MCM-41. In 1992, Kresge et al. (1992) published a surfactant template based synthesis of mesoporous silica materials. Thereafter, the synthesis and functionalization of nanoparticles for various applications, such as catalysis, medicine, and sensors, have been described. In general, porous nanoparticles are synthesized either (1) directly by condensation of oppositely charged metal and surfactant moieties or (2) indirectly by similarly charged metal and surfactant moieties and an oppositely charged halide ion Cl_ or Br_.

HOLLOW SILICA NANOCAPSULES

Specific templates, such as latex particles, emulsion droplets, and block copolymer micelles, are commonly used for synthesis of hollow silica nanoparticles. Hu et al. (2013) devised a one-step method using water/oil inverse immersion and templates consisting of ammonia water stabilized in alkyl phenol polyoxyethyleneether, tetraethoxysilane, and cyclohexane.