Lecture 12. Optical Properties of nanoparticles. Mechanical Properties of nanoparticles

The purpose of the lecture: to familiarize students with optical and mechanical properties of nanoparticles.

Expected results: students getting information about optical and mechanical properties of nanoparticles.

Nanoparticles, along with exhibiting a sizedependent increase in electronic band gap, also exhibit a size-dependent increase in the optical band gap (Og)da level of energy that activates the electron-hole complex but is not able to free the electron for conduction. The electron then returns to its original state by emitting photons in the process. The energy of the emission photon is equal to the Og energy.

In 1968, Tauc developed a model that related the Og values with optical energy. In this equation, a is the absorption coefficient given by a j 2.303 log (T/d), where d is the thickness of the sample, T is the transmission, and hn is the photon energy. A graph between (ahn)2 versus hn is used to determine the optical band gap. The values of Og have been estimated by the extrapolation to the linear part of the curve to the Hv axis: (ahn)2/0.

A decrease in semiconductor particle size from the bulk level (>500 nm) to the nano level (<0 nm) resulted in a 200e450 nm absorption drop. Thus, as the particle size decreases, a shift in the absorption toward lower wavelengths occurs possibly because of a size-dependent increase in the Og.

Absorption occurs at higher energies, resulting in a shift toward shorter wavelengths. Because of size-dependent optical properties, semiconductor nanoparticles can be applied for development of imaging and screening devices, where the free and bound particles may emit different light spectra.

Mechanical Properties

When the size of a nanoparticle approaches or become smaller than 0 nm, it acquires physical properties (fraction, hardness, elastic modulus, fracture toughness, scratch resistance, fatigue strength, etc.) that are different from its bulk counterpart. Mechanical properties have made important contributions to the fields of nanomedicine and nanobiology because they modulate the molecular forces that drive the molecular interaction, thermodynamic properties, and interface of the nanoparticle with the liquid, etc. Biological systems such as proteins and DNA create interfaces with the surrounding fluids that may govern their interactions with nanoparticles. The interaction of cell membranes with nanoparticles is governed by the mechanical properties, such as friction, adhesion, or elasticity, of both the cells and the materials because the cells dynamically react to the mechanical cues.

Therefore, an understanding of the mechanical properties of nanoparticles is essential to bring modern nanomedicine from the bench to clinical applications. The objective of this section is to discuss the basic principles of the nanoparticles' mechanical properties, especially surface friction and tensile strength.

Surface Friction

BULK PARTICLES

The surface topology of bulk particles exhibits considerable roughness, depressions, and projections due to their molecular arrangements. An interlocking of the irregularities of two surfaces in contact causes friction (defined as the force resisting the relative motion of solid surfaces sliding against each other). If the two contacting surfaces possess interlocking structures or spacing, then they can lock with each other periodically; this must be overcome to commence

motion. If they have different atomic spacing, then the atoms of the top surface will not fit into the valleys; thus, they will experience less friction.

Friction force (Ff) for bulk particles is defined by the equation Ff j mFn, where Ff is the repulsive force linearly proportional in the opposite direction of the force applied (Fapplied), m is the ratio of the frictions of two surfaces, and Fn is the normal force (usually the force of gravity) on the particle mass. If the force applied is less than Ff, then the particle will remain static. If the force applied is greater than Ff, the particle will move. In 1699, Guillaume Amontons proposed the two laws of friction:

1. Friction is directly proportional to the applied load, which is described by the equation Fmax j mFn. As an example, for a particle with 0.1 kg mass and 0.6 mm, Ff can be calculated as follows: Ff j ((0.1 kg _ 9.8 m/s/s)) _ 0.6 j 0.59 N. This suggests that a force >0.59 N must be applied to commence motion.

2. Friction is independent of the area of contact. Thus, a force greater than 0.59 N will be needed irrespective of the area of contact.

NANOPARTICLES

Earlier studies have shown that many metal oxide nanoparticles or nanotubes, when mixed with lubricants, provided surface repair by reducing friction.

A commercial firm Nanoprofix (http://www.nanoprofix.com/) has developed nanomaterial lubricant additives that, when mixed with oil and grease formulations, deliver a range of performance enhancements, including significant friction reduction, reduced wear of contacting surfaces, reconditioning of existing wear damage, enhanced energy and fuel efficiency, reduced operating temperature, etc. (www.digitaljournal.com/pr/1185283#ixzz30zs3z4K6).

This superlubrication performance is attributed to the nanoparticles' nanometer size as well as replenishment of nanoparticles onto the contact, thus forming a transfer layer. However, there is one basic flaw in this explanation.

As described previously, for bulk particles, Ff is linearly proportional to the Fapplied and the area of contact is not a determinant of Ff. For nanoparticles, the relationship between Ff and Fapplied appears to be extremely nonlinear. In addition, unlike for bulk particles, the area of contact (Ac) plays a critical role in the development of Ff. The adhesion of small nanoparticles may depend not only on the Ac but also on the structure of the nanoparticles, particularly in the direction of Fnormal to the surface. Desanguliers proposed that the contact between two surfaces is not whole-surface contact but a finite number of small asperities; although the surface may appear flat and smooth in bulk particles, it may be rough with structural deformations when viewed under a microscope. Bulk particles may not interact with another bulk surface's nanoasperities. Nanoparticles may interact with the bulk surface's nanoasperities in an area-dependent manner, with smaller nanoparticles exhibiting greater friction than larger ones, via the following possible mechanisms:

1. Absorption, in which nanoparticles may form noncovalent bonds (van der Waals and hydrogen bonds) with the surface

2. Mechanical, in which nanoparticles may form electrical double layers due to noncovalent electron sharing

3. Topological indices, in which nanoparticles may fit into the grooves; thus, more energy may be needed to push them out.

In addition to metal oxide nanoparticles, carbon-based and inorganic nanotubes, either as pure solid lubricants or as additives to various fluid lubricants, may reduce friction and wear. Recently, Tevet et al. (2011) showed that an inorganic 2D nanotube combined with hollow polyhedral fullerenelike nanoparticles (called IF-WS2) provided excellent lubricating properties. They explained this mechanism by superposition of rolling, sliding, and exfoliation-material transfer (third body).

Rolling is an important lubrication mechanism for IF-WS2 in the relatively low range of normal stress (0.96 _ 0.38 GPa), sliding is relevant under slightly higher normal stress, and

exfoliation of the nanoparticles is the dominant mechanism at the high end of normal stress (>1.2 GPa). The rolling mechanism, which leads to low friction and wear, requires spherical and dispersed nanoparticles and smooth contact surfaces.