1. PROPERTIES OF NANOMATERIALS

Introduction – Optical properties – Mechanical properties – Magnetic properties – Catalytic properties – Electrical properties – Thermodynamic properties – Electronic properties – Transport properties – Chemical properties – Electrochemical properties

Introduction

Nanostructures and Nanomaterials displays of a self-purification process in that the impurities and intrinsic material defects will move to near the surface upon thermal annealing. This increased materials perfection affects the properties of nanomaterials. For example, the chemical stability for certain nanomaterials may be enhanced, structural, mechanical, electrical, dielectric, transport and magnetic properties, of nanomaterials will be better than the bulk materials. The type of properties displayed by nanostructured materials includes electrical, structural, chemical, magnetic and catalytic properties as well as, in the case of metals and semiconductor, their electronic and optical properties. These interesting properties allow the nanostructured materials to be utilized in novel applications in the field of optoelectronic devices, photocatalysis, gas sensing, medical fields, information storage, and magnetic refrigeration etc.

The structural, mechanical, electrical, chemical, magnetic, catalytic, electrochemical and optical properties of nanophase materials change with the reduction in the particle size of the material. The physical and chemical properties of the nanomaterials tend to be exceptionally closely dependent on their size and shape or morphology. Nanomaterials have the structural features in between atoms and the bulk materials. While most micro-structured materials have similar properties to the corresponding bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulks materials.

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In the past decades, studies on metal based nanomaterials are focused largely on their unique chemical or physical properties for diverse technological applications. When the size of the semiconductor materials is reduced to nanoscale, their physical and chemical properties change dramatically, resulting in unique properties due to their large surface area or quantum size effect. Further development of nanotechnology will certainly lead to a significant breakthrough in the semiconductor industry. In search of new semiconducting materials for efficient solar energy conversion through photo electrochemical solar cells, metal oxides, and chalcogenides are increasingly studied.

The properties of materials can be different on a nanoscale for two main reasons. First, nanomaterials have relatively, large surface area than the same mass of material produced in larger form. This can make materials more chemically reactive (in some cases materials that are insert in their larger form are reactive when produced in their nanoscale form) and affect their strength or electrical properties. Second, below 50 nm, the laws of classical physics give way to quantum effects, provoking optical, electrical and magnetic behaviors different from those of the material at a larger scale.

Nanomaterials, having thickness less than 100 nm, have received increasing interest owing not only to their fundamental scientific significance but also to the potential applications that derive their fascinating optical, electrical, electrochemical, magnetic and catalytic properties. For nanoscale material, its physical and chemical properties depend on its surface area. Properties like catalytic reactivity, electrical resistivity, adhesiveness, gas sensing depends on the nature of the interface.

3.1 Optical properties

One of the most fascinating and useful aspects of nanomaterials are their optical properties. Applications based on the optical properties of the nanomaterials, include optical detector, laser, sensor, imaging, phosphor, display, solar cell, photocatalysis and biomedicine.

The optical properties of nanomaterials depend on parameters, such as the feature size, shape, surface characteristics, and other variables including doping and interaction with the surrounding environment or other nanostructures.

In small nano clusters the effect of reduced dimensionality on electronic structure has the most profound effect on the energies of highest occupied molecular orbital (HOMO) which is valence band and the lowest unoccupied molecular orbital (LUMO), essentially the conduction band. The optical emission and adsorption occurs when the transition of the electrons occur between these two states. Semiconductors and many metals show large changes in optical properties such as color, as a function of particle size. Colloidal suspense’s of gold nano particles have a deep red color which becomes progressively more yellow as the particle size increases.

- Gold spheres of 10-20nm exhibit red color
- Gold spheres of 2-5nm exhibit yellow color.
- Gold spheres of >20nm exhibit purple color

Similarly,

- Silver particles of 40nm exhibit blue color
- Silver particles of 100nm exhibit yellow color
- Prism shaped Silver particles red color.

Other properties which may be affected by reduced dimensionality include photocatalysis, photoconductivity, photoemission and electroluminescence.

The optical conductivity is one of the fundamental properties of metal oxides and can be experimentally obtained from reflectivity and absorption measurements. While reflectivity is clearly size-dependent as scattering can display drastic changes when the oxide characteristic size is in/out the range of photon wavelength, absorption features typically command main absorption behavior of solids. Due to quantum-size confinement, absorption of light becomes both discrete-like and size-dependent. For nano-crystalline semiconductors, both linear (one exciton per particle) and non-linear optical (multiple excitons) properties arise as a result of transitions between electron and hole discrete or quantized electronic levels. In the first case, depending on the relationship between the radius of the nanoparticles (R) and the Bohr radius of the bulk exciton ($R_B = \varepsilon\ \hbar^2/\mu e^2$; μ exciton reduced mass and ε dielectric constant of the semiconductor), the quantum confinement effect can be divided into three regimes; weak, intermediate and strong confinement regimes, which correspond to $R >> R_B$, $R \approx R_B$, and $R << R_B$, respectively. The effective mass theory (EMA) is the most elegant and general theory to explain the size dependence of the optical properties of nano-meter semiconductors, although other theories as the free-exciton collision model (FECM) or those based in the bond length -strength correlation have been developed to account for several deficiencies of the EMA theory. For the onset of light absorption, e.g. the optical band gap, as well as for all other electronic transitions present in the optical absorption spectrum, the EMA theory predicts a r^{-2} dependence, with a main r^{-1} correction term in the strong confinement regime, while FECM gives a exp (1/r) behavior. It can be thus concluded that metal oxide semiconductors would present, as a first rough approximation, optical band gap energy with an inverse squared dependence of the primary particle size if quantum confinement dominates the energy behavior of the band gap.

Vacancy defects introduce gap states in proportion to the defect number; in fact, a random distribution of (equal) vacancy defects introduce a Gaussian-like density of states which may produce mid-gap states and/or be localized near the valence and conduction bands depending on the electronic nature (donor/acceptor) of the defect and giving characteristic “localized” features in the UV-visible spectrum. Such point defects mainly contribute to the Raman spectra by producing a broadening of the peaks. Strain effects (including parameter variations measured in optical phonons with the help of the Gruneisen parameter) are inherent to nanostructured materials and may be comprised in the general, ambiguous term of “surface” effects usually claimed to account for significant deviations the confinement theories. Surface effects and, particularly, nonstoichiometry related to the preparation method are critically important for very low particle size and produce characteristic features in the UV-visible spectrum for certain metal oxides.

3.2 Mechanical Properties

An important mechanical properties concerned that the low (yield stress and hardness) and high temperature observables. Information on oxide nanomaterials is scarce and mainly devoted to analyze sinterability, ductibility, and superplasticity. In particular, an important number of works have showed significant improvement in sintering with up to 600 K lower temperatures with respect to bulk counterparts. In conventional/bulk materials the yield stress (σ) and harness (H) follow the Hall-Petch (H-P) equation:

$$\sigma/H = \sigma_0 / H_0 + k\, d^{-1/2}$$

where the initial constants describe friction stress and hardness, d is the primary particle/grain size and k the corresponding slope. The H-P effect in bulk materials is attributed to the particle/grain boundaries acting as efficient obstacles for slip transfer (stress) or dislocations (hardness). Typically by decrease the particle/grain size down to the order of a few tens nanometers the H-P slope, which is positive, gets smaller values. However, below such critical point it appears that conventional dislocation mechanism ceases to operate and a d^{-n} ($|n| > \frac{1}{2}$) behavior or a “reversal” H-P mechanism would become progressively dominant. It is clear that oxide materials (like Al_2O_3, ZrO_2, CeO_2, and TiO_2) sintered under vacuum or using the spark plasma technique display enhanced yield strength and hardness with respect to conventional/bulk ceramic materials and have the additional properties of being transparent (films), being potential materials for the aerospatial industry. Superplasticity refers to the capacity of oxide materials to undergo extensive tensile deformation without necking or fracture. The phenomenological relationship for superplasticity is defined as:

$$\varepsilon = A\,\frac{DGb}{kT}\left(\frac{b}{d}\right)p\left(\frac{\sigma}{G}\right)n$$

where ε is the strain rate, D is the adequate diffusion coefficient, G is the shear modulus, b is the Burger´s vector, σ is the applied yield strength, and p/n the particle size and yield strength exponents. Equation implies that reduction of the particle size leads to an where ε is the strain rate, D is the adequate diffusion coefficient, G is the shear modulus, b is the Burger´s vector, σ is the applied yield strength, and p/n the particle size and yield strength exponents. It implies that reduction of the particle size leads to a compressive ductility and strain rate sensitivities that are indicate of superplasticiy.

In metal oxide nanomaterials, the elastic strength is low however; its plastic behavior is high. In some nanophase materials, it is noted that there is decrease in hardness when the grain size is less than10nm. However, for many nanocrystalline, pure metals (10nm), the hardness is about 2 to 7 times greater than that of large-grained (> μm) metals. They have higher hardness and mechanical strength (2-7 times) when grain size reduces from 1μm to 10μm. It has very high ductility and superplastic behavior at low temperatures.

3.3 Magnetic properties

Magnetism is one of the basic properties of materials. When a material is placed in a magnetic field (H), it acquires a dipole moment. The magnitude of this dipole moment depends upon the nature of the material, the applied magnetic field strength, and is proportional to its volume. Therefore, we define the total dipole moment per unit volume induced in the material as magnetization (M), which is the sum of all the atomic/nuclear magnetic moments of the material. The response of the material to the applied magnetic field can be expressed, for H → 0, as:

$$M = \chi H$$

where χ is defined as the magnetic susceptibility, the most important magnetic material property.

When the volume of a particle is reduced below a certain value, called critical domain size D_c, the proximity of many domain walls in a small volume is not energetically favored, so that a single-domain configuration is adopted. For spherical crystals, Kittel et al proposed the following expression for the critical diameter:

$$D_c = 36\, E_\sigma / \mu_o M_s^2$$

Where $E_\sigma = 2\,(A.K)^{1/2}$ is the surface energy of a Bloch wall in an infinite material with low anisotropy, K is the anisotropy constant, A is the exchange energy, μ_o is the vacuum permeability, and M_s is the saturation magnetization.

When a magnetic field is applied, for non-interacting nanoparticles, the magnetization reversal for single domain nanoparticles is realized by coherent rotation, meaning that all spins of the ions in nanoparticles are parallel to each other. One of the most recognized models describing the coherent rotation of magnetization for an assembly of non-interacting single domain magnetic nanoparticles with uniaxial anisotropy is the Stoner-Wohlfarth theory.

The magnetic properties of the nanoparticles are generally anisotropic. There are some low energy directions in the crystal, called easy directions, which are separated by an anisotropy energy barrier. Several different sources can give rise to the total anisotropy of the magnetization:

Magneto-crystalline Anisotropy: This property is intrinsic to the material and it is related to the crystal symmetry and to the arrangement of atoms in the crystal lattice. The origin of this contribution lies in the spin-orbit coupling. In fact, the orbital wave function will reflect the symmetry of the lattice and the spins are made aware of this anisotropy via the spin-orbit coupling.

Shape Anisotropy: The source of this kind of anisotropy is the presence of free magnetic poles on the surface of a magnetized body. These poles create a magnetic field inside the system, called demagnetizing field. Variation from spherical form can induce competing shape anisotropy with respect to the magneto-crystalline contribution.

Surface Anisotropy: When the surface atoms are present in a number comparable to that of atoms within the particle, another form of anisotropy is observable. This kind of anisotropy is very sensitive to the chemical environment of surface spins and may be different depending also on the chemical species bounded to the surface. The magnitude of this contribution increases on decreasing the size of the particle due to the increasing of surface to volume ratio. Néel has shown that the surface contribution becomes relevant only for particles smaller than 10 nm.

Stress Anisotropy: It is well known that when a specimen is magnetized in a given direction, there is a change of length in that direction. This phenomenon was first observed by Joule in 1842 and is called magneto-striction. Its existence indicates that there is an interaction between magnetization and strain, which is again due to spin-orbit coupling. Since the strain is related to any stress that may be acting on the considered system, this implies that the anisotropy energy depends on the stress state of the system.

Exchange and Dipolar Anisotropies between Particles: Two particles close enough to each other, will have a magnetic interaction. This interaction can be either due to magnetic dipole interaction or to exchange interaction leads to additional anisotropy energy. In this case the easy direction is determined by the relative orientation of the two interacting magnetic moments. The observed anisotropy energy depends on the relative magnitude of each contribution, which depends on the structure of the material, its shape and size.

Table 3.1 Magnetism in bulk and in nanoparticles

Metal	Bulk	Nanophase
Nickel, Cobalt, Iron, Terbium	Ferromagnetic	Superparamagnetic
Sodium, Potassium	Paramagnetic	Ferromagnetic
Chromium	Anti-ferromagnetic	Frustrated paramagnetic

Bulk gold and platinum are non-magnetic, but at the nano size they are magnetic. Surface atoms are not only different to bulk atoms, but they can also be modified by interaction with other chemical species, that is, by capping the nanoparticles. This phenomenon opens the possibility to modify the physical properties of the nanoparticles by capping them with appropriate molecules. Actually, it should be possible that non-ferromagnetic bulk materials exhibit ferromagnetic-like behavior when prepared in nano range. One can obtain magnetic nanoparticles of Pd, Pt and the surprising case of Au (that is diamagnetic in bulk) from non-magnetic bulk materials. In the case of Pt and Pd, the ferromagnetism arises from the structural changes associated with size effects.

3.4 Catalytic properties

Nanomaterials have gained much attention for their varying physical and chemical properties as a function of their dimension. Significant factors influencing the catalytic activity and selectivity are surface structure, mobility of the active species to restructure as well as the mobility of the adsorbates on these active species. Nanomaterials have various advantages over its bulk counterpart like short range ordering, enhanced interaction with environments due to the large number of dangling bonds, great variety of the valence band electron structure and self structuring for optimum performance in chemisorptions. As a result of the size reduction, large portion of their existing atoms are placed at the surface and higher the surface area, the higher the surface atoms. Normally, increase in the surface area gives more adsorption of reactant molecules on its surface, which results the higher catalytic activity. Internal surface area can be increased by introducing atomic defects such as dislocations to enhance species diffusivity and chemical reactivity.

This enhances their use in the field of oxidation - reduction chemistry with many expected applications in fields like photocatalysis or photodegradation and detoxification of chemical waste and environmental pollutants. Nanoparticles can be employed to remove the contaminations in a medium through chemical reaction to make it harmless. For example, ground water can be purified by removing carbon tetrachloride from it using iron nanoparticles. Gold tipped carbon nanotubes can clean polluted water by trapping oil drops from polluted water. Light activated nanoparticles like titanium dioxide are continued to be studied for their ability to remove contaminants from various media. Photoactive titanium dioxide nanoparticles are used for cleaning polluted waters by removing various toxic metal ions like mercury, cadmium, arsenic, chromium and copper through reduction. Nanoparticles can also be used in treating water and contaminated air with various organic compounds, dyes and pesticides.

3.5 Electrical Properties

The energy band structure and charge carrier density in the materials can be modified from their bulk and in turn leads to changes in the associated electronic properties of the materials. These effects are normally termed as quantum confinement effect and relates to the structure and occupation of outermost electronic energy levels of the material. When the size of the system becomes comparable with the de - Broglie wavelength of electrons, the discrete nature of the energy state becomes observable once again, although a fully discrete energy spectrum is only observed in systems that are confined in all the three dimensions. Discrete energy bands considerably changes the transport properties of the system. In typical cases, the conducting materials become insulators below a critical length scale, as the energy band cease to overlap.

Electrical transport properties for bulk system are determined by phonons scattering, impurities and other carriers or scattering at rough surfaces. The electrical transport is diffusive and the path of each electron represents a random walk. But in the nanostructured systems, electrons can travel through the system without randomization of the phase of their wave functions as the system dimensions are smaller than the electron mean free path for inelastic scattering. This results in additional localization phenomena which are basically related to phase interference. In highly confined structures like quantum dots, conduction is mostly dependent on the presence of other charge carriers and hence the charge state of the quantum dot.

In recent years, many advances are made in the field of molecular and nano electronics. Single molecules are expected to be able to control electron transport in molecular electronics. This offers the promise of exploring the vast variety of molecular functions for electronic devices.

3.6 Thermodynamic properties

The surface atoms play a significant role in determining the thermodynamic properties of nanostructured materials. The reduced coordination number of the surface atoms considerably increases the surface energy resulting in atomic diffusion at comparatively lower temperatures. The melting point of CdS particles falls to as low as ~400ºC with diameters less than 3 nm, much lower than the bulk melting point ~1600 ºC for CdS. Also, the gold nanoparticles with diameter less than 3 nm, experiences a much lower melting point close to ~500ºC as compared to the bulk gold melting point ~1064ºC. This is due to the increasing number of surface atoms with decreasing particle size. Moreover, the density of surface atoms varies considerably for different crystallographic planes, possibly leading to different thermodynamic properties.

3.7 Electronic properties

The changes which occur in electronic properties as the system length scale is reduced are related mainly to the increasing influence of the wave-like property of the electrons (quantum mechanical effects) and the scarcity of scattering centers. As the size of the system becomes comparable with the de Broglie wavelength of the electrons, the discrete nature of the energy states becomes apparent once again, although a fully discrete energy spectrum is only observed in systems that are confined in all three dimensions. In certain cases, conducting materials become insulators below a critical length scale, as the energy bands cease to overlap. Owing to their intrinsic wave-like nature, electrons can tunnel quantum mechanically between two closely adjacent nanostructures, and if a voltage is applied between two nanostructures which aligns the discrete energy levels in the DOS, resonant tunneling occurs, which abruptly increases the tunneling current. Conduction in highly confined structures, such as quantum dots, is very sensitive to the presence of other charge carriers and hence the charge state of the dot. These Coulomb blockade effects result in conduction processes involving single electrons and as a result they require only a small amount of energy to operate a switch, transistor or memory element. All these phenomena can be utilized to produce radically different types of components for electronic, optoelectronic and information processing applications, such as resonant tunneling transistors and single-electron transistors. The main characteristic electronic properties are: (i) The energy bands in nano-phase materials will be very narrow (ii) The ionization potential is found to be higher for nanomaterials (iii) when the nanomaterials are prepared from bulk materials, they have more localized molecular bonds and (iv) Nanophase materials are capable of storing hydrogen atoms.

3.8 Transport properties

Oxide materials can present ionic or mixed ionic/electronic conductivity and it is experimentally well established than both can be influenced by the nanostructure of the solid. The number of electronic charge carriers in a metal oxide is a function of the band gap energy according to the Boltzmann statistics. The electronic conduction is referred to as n- or p-hopping-type depending on whether the principal charge carrier are, respectively, electrons or holes. The number of “free” electron/holes of an oxide can be enhanced by introducing non-stoichiometry and, in such case, are balanced by the much less mobile oxygen/cation vacancies. In an analogous manner to hoping-type conduction, ionic conduction takes place when ions can hop from site to site within a crystal lattice as a result of thermal activation, and is typically interpreted on the basis of a modified Fick´s second law. Four mechanism types have been observed for ionic conduction: direct interstitial, interstitially, vacancy, and growths. As charge species (defects; impurities) in polycrystalline oxides typically segregate to particle boundaries to minimize strain and electrostatic potential contributions to the total energy, there is a contribution to the conductivity parallel to the surface which becomes important at the nanoscale regime. The charge carrier (defect) distribution also suffers strong modification from bulk materials as there is presence of charge carries through the whole material as a consequence of the shielded electrostatic potential depletion at surface layers of nanosized materials.

As a result of these nanoscale derived effects, it is well known that CeO_2 exhibits an improved n-type conductivity which may be four orders of magnitude greater than the corresponding to bulk/micro-crystalline ceria, and is ascribed to a significant enhancement of the electronic contribution. Alteration of the transport properties is also observed in ZrO_2 but the physical ground is still far from being understood. The strong size-dependence observed for the electrical conductance in the context of gas-sensing devices has been recently reviewed for the SnO_2, WO_3, and In_2O_3 oxides. An outstanding enhancement of Li^+ -ion vacancy conductivity has been achieved using Li-infiltrated nanoporous Al_2O_3.

3.9 Chemical Properties

Metal oxides are used for both their redox and acid/base properties in the context of Absorption and Catalysis. The three key features essential for their application as absorbents or catalysts are (i) the coordination environment of surface atoms, (ii) the redox properties, and (iii) the oxidation state at surface layers. Both redox and acid/base properties are interrelated and may attempts can be found in the literature to establish correlations of both properties. In a simple classification, oxides having only s or p electrons in their valence orbital tend to be more effective for acid/base catalysis, while those having d or f outer electrons find a wider range of uses. The solid in a given reaction conditions that undergoes reduction and re-oxidation simultaneously by giving out surface lattice oxygen anions and taking oxygen from the gas phase is called a redox catalyst. This process necessarily demands microscopy reversibility and implies dynamic operation. Based on modern isotopic exchange experiments, the redox mechanism of chemical reactions can be more specifically divided in (i) extra-facial oxygen in which adsorbed (oxygen) species react (electrophilic reaction), and (ii) interfacial oxygen where lattice oxygen vacancies are created (nucleophilic reaction). There are enormous evidence that nucleophilic oxygen is capable of carrying out selective oxidations while it seems that electrophilic species seems to exclusively work on non-selective ones. Latter, it was shown that hydrocarbon selective oxidation starts with H-abstraction steps and that the filling of oxygen vacancies require the cooperation of a significant number of cations. The effect of size on these key steps is unknown but can be speculated to be related to the oxidation state of surface cations and their ability to manage electrons and the influence of non-stoichiometry on the gas-phase oxygen species handling and activation. Many oxides also display acid/base properties. Oxide materials can contain Bronsted and Lewis acid/base sites. Bronsted acid (A) and base (B) interactions consist of an exchange of protons as $HA + B = A^{-} + HB^{+}$. In any solid, two independent variables, the acid/base strength and amount (density per surface unit) need to be addressed to give a complete picture of its acid/base characteristics. Essentially, Lewis acidity is characteristic of ionic oxides and practically absent in covalent oxides. The strongest Lewis acid oxides are Al_2O_3 and Ga_2O_3. As a general rule, the stronger the Lewis acid, the few available sites due to the higher level of surface hydroxylation. As mentioned, because Lewis acidity is mostly associated to oxides with ionic character, Lewis basicity is mostly associated with them. On the contrary, most of the ionic metal oxides do not carry sufficiently strong Bronsted acidity to protonate pyridine or ammonia at room temperature although the more acid of them can do it at higher temperatures. In spite of this, the surface OH groups of most ionic oxides have a basic more than acid character. Covalent low-valent nonmetal oxides (SiO_2, GeO_x, BO_x) also show quite weak Bronsted acid properties. Finally, strong Bronsted acidity appears in oxides of elements with formal valence five or higher (WO_3, MoO_3, N_2O_5, V_2O_5, and S-containing oxides).

3.10 Electrochemical properties

Supercapacitors, also known as electrical double layer capacitor, ultra capacitor, or electrochemical capacitor (EC), have attracted much attention because of their high power density, long cycle life (>100 000 cycles), and rapid charging-discharging rates. They can be applied in a large variety of applications, including consumer electronics, memory back-up systems, industrial power, energy management, public transportation, and military devices. More importantly, super capacitors are critical components in the next generation all-electric cars and cars based on fuel cells that use hydrogen or alcohol as clean and renewable energy media.

Various materials have been investigated as the electrodes in ECs, including carboneous materials, conducting polymers and transition-metal oxides. Manganese oxide and cobalt oxide are generally considered to be the most promising transition metal oxides for the next generation of super capacitors because of its high-energy density, low cost, environmental friendliness, and natural abundance. For composites with carbonaceous materials, including

CNTs, the reported enhancement of electrochemical performance is more pronounced when only a small amount of metal oxide is incorporated in the electrode. However, for practical applications, particularly for large capacitor applications, such as power sources for the hybrid electric vehicle or fuel cell electric vehicle, high metal oxide concentration in electrodes and high mass loading of total active materials are needed.

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