CHAPTER 3

NANOMATERIALS FOR SOLAR CELLS

3.1 INTRODUCTION TO NANOPARTICLES

In nanotechnology, a particle is defined as a small object that behaves as a whole unit in terms of its transport and properties. Particles are further classified according to size: in terms of diameter, fine particles cover a range between 100 and 2500 nanometers. On the other hand, ultrafine particles are sized between 1 and 100 nanometers. Similar to ultrafine particles, nanoparticles are sized between 1 and 100 nanometers. Nanoparticles may or may not exhibit size-related properties that differ significantly from those observed in fine particles or bulk materials. Although the size of most molecules would fit into the above outline, individual molecules are usually not referred to as nanoparticles.

The unique properties of nanomaterials and structures on the nanometer scale have sparked the attention of materials developers. Over the past decade, nanomaterials; materials with structural features (particle size or grain size, for example) of at least one dimension in the range 1-100 nm, have been the subject of enormous interest. Technology in the twenty first century requires the miniaturization of devices into nanometer sizes while their ultimate performance is dramatically enhanced. This raises many issues regarding new materials for achieving specific functionality and selectivity and therefore recently there is tremendous excitement in the study of nanoscale materials with respect to their fundamental properties. Nanomaterials can be metals, ceramics, polymeric materials, or composite materials. The unit of nanometer derives its prefix nano from a Greek word meaning dwarf or extremely small. One nanometer spans 3-5 atoms lined up in a row. By comparison, the diameter of a human hair is about 5 orders of magnitude larger than a nanoscale particle. Nanomaterials are not simply another step in miniaturization, but a different arena entirely; the nanoworld lies midway between the scale of atomic and quantum phenomena, and the scale of bulk materials. At the nanomaterial level, the laws of atomic physics, rather than behaving as in traditional bulk materials, do affect some material properties. The unusual physicochemical and optoelectronic properties of nanoparticles arise primarily due to confinement of electrons within particles of dimension smaller than the bulk electron delocalization length; this process is termed as quantum confinement.

Nanoclusters have at least one dimension between 1 and 10 nanometers and a narrow size distribution. Nanopowders are agglomerates of ultrafine particles, nanoparticles, or nanoclusters. Nanometer-sized single crystals, or single-domain ultrafine particles, are often referred to as nanocrystals.

3.2 NANOMATERIALS IN SOLAR CELLS

Deriving plentiful electricity from sunlight at a modest cost is a challenge with immense implications for energy, technology, and climate policy. Scientists are developing a relatively new approach to solar cells: lacing them with nanoscopic metal particles. This approach has the potential to greatly improve the ability of solar cells to harvest light efficiently.

Like plants, solar cells turn light into energy. Plants do this inside vegetable matter, while solar cells do it in a semiconductor crystal doped with extra atoms. Current solar cells cannot convert all the incoming light into usable energy because some of the light can escape back out of the cell into the air. Additionally, sunlight comes in a variety of colours and the cell might be more efficient at converting bluish light while being less efficient at converting reddish light.

The nanoparticle approach seeks to remedy these problems. The key to this new research is the creation of a tiny electrical disturbance called a "surface plasmon." When light strikes a piece of metal it can set up waves in the surface of the metal. These waves of electrons then move about like ripples on the surface of a pond. If the metal is in the form of a tiny particle, the incoming light can make the particle vibrate, thus effectively scattering the light. If, furthermore, the light is at certain "resonant" colours, the scattering process is particularly strong.

Recent research in this dimension has shown what happens when a thin coating of nanoscopic (a billionth of a meter in size) metal particles are placed onto a solar cell. First of all, the use of nanoparticles causes the incoming sunlight to scatter more fully, keeping more of the light inside the solar cell. Second, varying the size and material of the particles allows improving light capture at otherwise poorly-performing colors.

Recent developments have shown that light capture for long-wavelength (reddish) light can be improved by a factor of more than ten. Previously scientists showed that overall light-gathering efficiency for solar cells using metallic nanoparticles can be improved by 30 percent.

Nanomaterials for Solar Energy Conversion

There is an urgent need for cheap and efficient solar cell technology in order for solar energy to become more economically viable. Research employing nanomaterials for solar energy conversion either focuses on improving the energy conversion through better energy/photon management and/or reducing the processing cost through high-defect tolerance conversion approaches, but a deeper understanding of the photon-to-carrier conversion mechanisms and charge transport in nanoscale morphologies is needed. This session will examine recent developments and new approaches in the use of nanomaterials for solar cell devices and will discuss our current understanding of factors affecting conversion efficiencies. Papers representing high quality original research are requested in the following areas:

- Nanostructures for solar energy conversion (nanocrystals, nanowires, quantum dots);
- Carbon nanotubes in solar cell devices;
- Organic solar cells and bulk heterostructure devices;
- Dye-sensitized nanomaterials, Grätzel cells;
- Optical and electronic processes in nanomaterials for solar energy conversion;
- Advanced concepts for solar energy conversion; multiple exciton generation, up and down conversion, intermediate band, etc.;
- Exciton and charge-transfer dynamics in nanomaterials;
- Charge transport in nanoscale architectures;
- Modeling and optimizing solar cell efficiency

How can nanotechnology improve solar cells

Using nanoparticles in the manufacture of solar cells has the following benefits:

- Reduced manufacturing costs as a result of using a low temperature process similar to printing instead of the high temperature vacuum deposition process typically used to produce conventional cells made with crystalline semiconductor material.
- Reduced installation costs achieved by producing flexible rolls instead of rigid crystalline panels. Cells made from semiconductor thin films will also have this characteristic.
- Currently available nanotechnology solar cells are not as efficient as traditional ones; however their lower cost offsets this. In the long term nanotechnology versions should both be lower cost and, using quantum dots, should be able to reach higher efficiency levels than conventional ones.

3.3 SEMICONDUCTOR NANOPARTICLES

The ideal material used in the cell must have a high surface area for light absorption and charge separation. Nanoparticles, having a comparable surface area to volume ratio, provides for just that. Titanium dioxide nanoparticles are used to make nanoporous thin film supported upon a glass substrate. The material obtained has optical transparency, excellent stability and good electrical conductivity. The benefit of these novel photoelectrical solar cells is that they can be fabricated from cheap, low purity materials by simple and low cost procedures. Contrary to expectation, some of the new devices also have strikingly high conversion efficiency. The size-tunable bandgap of the semiconductor nanoparticles, due to size quantization, also means more efficient solar cells can be produced for photovoltaics (electricity production) and water splitting (hydrogen production) processes.

Today’s lifestyle requires a steady supply of energy. However, this high energy consumption associated with high environmental degradation. Environmental problems as global warming or degradation of the ozone layer, along with concern for the long-term constraints that have fossil fuel reserves make every day become more important calls renewable energy.

Among the most important primary sources of clean energy, mainly due to its low environmental impact, is the so-called solar energy. The basis of it is called the photovoltaic effect, whereby the energy of sunlight is converted directly into electrical energy due to the interaction of photons and electrons in a semiconductor material. To produce a high yield it is important that electricity becomes much light on the incident radiation as possible. This is not easy due to energy losses that occur in the process, so try to develop new technologies to improve the performance of existing solar cells and increase their performance. So far, the conversion of sunlight into electricity has been conducted almost exclusively with photovoltaic devices, solid-state union, but the situation could change with the use of nanotechnology. The use of nanomaterials in solar cells to create more efficient solar cells, smaller and with reduced production costs.

This would have gotten plastic photovoltaic devices using conducting polymers, extremely thin and cheap, while scientists has developed new solar cells from nanoscale crystals of (CdSe and CdTe) in the form of nanorods. However, current research, lead us to think about the development of three-dimensional solar cells, which produce high performance with a significant reduction in size. 3D solar cell is based on the deposition of a semiconductor material on a three-dimensional nanostructure. The first 3D solar cells of low cost were based on a heterojunction based on the deposition of CuInSe2 (p-type semiconductor) on TiO2 (n-type semiconductor). But these are not the only materials that can be used. One type of these cells is made and works as follows. Here we have a structure in the form of towers of size 40 × 40 microns, consisting of millions of aligned carbon nanotubes.

This provision allows the solar cells absorb light received from many different positions, so it is not necessary that the cell receives light directly. In addition, once the cell has absorbed the radiation, it is trapped inside the structure, can be absorbed by different parts of it. As a result of absorbing more photons the cell coating may be thinner, so that the electrons spend less time in the semiconductor, reducing the possibility of recombination of them. The electron-hole recombination is the main cause of poor performance of solar cells, so that if we reduce it by increasing the quantum efficiency. In addition to reducing the amount of material we are reducing the weight.

It is these characteristics that make the 3D cells could have important applications especially in the space field by eliminating the need for systems that maintain a specific orientation as satellite systems, while reducing the weight and complexity and increasing reliability and performance. However, before selling this type of solar cells, to demonstrate they are capable of withstanding the loads that support launch and operation of spacecraft, and to ensure a minimum of life in the harsh vacuum and thermal cycles have to bear.

3.4 ZnS NANOPARTICLES

Fig 3.1 Zinc Sulfide

Zinc sulfide is a chemical compound with the formula ZnS. Zinc sulfide is a white to yellow-colored powder or crystal. The powder is widely used as an additive into numerous materials and products including plastics, ceramics, glass, cement, rubber (e.g., car tires), lubricants, paints, ointments, adhesives, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, fire retardants, first aid tapes, etc. It is typically encountered in the more stable cubic form, known also as zinc blende or sphalerite. The hexagonal form is also known both as a synthetic material and as the mineral wurtzite. A tetragonal form is also known as very rare mineral polhemusite (Zn,Hg)S. Both sphalerite and wurtzite are intrinsic, wide-bandgap semiconductors. The cubic form has a band gap of 3.54 eV at 300 K whereas the hexagonal form has a band gap of 3.91 eV. The transition from the sphalerite form to the wurtzite form occurs at around 1020 °C.

3.4.1 Crystal Structure

Table 3.1 shows some vital statistics of Zinc blende structure.

Zinc blende Vital Statistics	
Formula	ZnS
Cystal System	Cubic
Lattice Type	Face-Centered
Cell Parameters	a = 5.41 Å, Z=4
Atomic Positions	S: 0, 0, 0 Zn: 0.25, 0.25, 0.25 (can interchange if desired)
Density	4.102
Melting Point	phase transition at 1020 degrees C
Alternate Names	Zinc blende, sphalerite
Isostructural Compounds	$AgInS_2$, BN, BC, XY (X = Al, Ga, In; Y = P, As, Sb)

Table 3.1

ZnS occurs in two common polytypes, zinc blende (also called sphalerite) and wurtzite. The two types have these features in common:

- a 1:1 stoichiometry of Zn:S
- a coordination of 4 for each ion (4:4 coordination)
- tetrahedral coordination

Wurtzite and sphalerite polymorphs have no inversion symmetry (reflection of a crystal relatively any given point does not transform it into itself). This and other lattice symmetry properties result in piezoelectricity of the hexagonal and zincblende ZnS, and in pyroelectricity of hexagonal ZnS.

Zinc blende/sphalerite is based on FCC lattice of anions whereas wurtzite is derived from an HCP array of anions. In both structures, the cations occupy one of the two types of tetrahedral holes present. In either structure, the nearest neighbor connections are similar, but the distances and angles to further neighbors differ. Zinc blende has 4 asymmetric units in its unit cell whereas wurtzite has 2.

Zinc blende is best thought of as a face-centered cubic array of anions cations occupying one half of the tetrahedral holes. Each ion is 4-coordinate and has local tetrahedral geometry. Unlike wurtzite, zinc blende is its own antitype, that is we can switch the anion and cation positions in the cell and it doesn't matter (as in NaCl). In fact, replacement of both the Zn and S with C gives the diamond structure.

Fig 3.2 ZnS Nanoparticle

3.5 PROPERTIES OF ZNS NANOPARTICLES

In materials science, ZnS is a wide-bandgap semiconductor of the II-VI semiconductor group (since zinc and sulphur belong to the 2nd and 6th groups of the periodic table, respectively). It can be doped as both n-type semiconductor and p-type semiconductor, which is unusual for the II-VI semiconductors. This semiconductor has several favourable properties: good transparency, high electron mobility, wide bandgap, strong room-temperature luminescence, etc. Those properties are already used in emerging applications for transparent electrodes in liquid crystal displays and in energy-saving or heat-protecting windows, and electronic applications of ZnS as thin-film transistors and light-emitting diodes are forthcoming. ZnS is a covalently bonded solid.

3.5.1 Mechanical Properties

ZnS is a relatively soft material with approximate hardness of 4.5 on the Mohs scale. Its elastic constants are smaller than those of relevant III-V semiconductors, such as GaN. The high heat capacity and heat conductivity, low thermal expansion and high melting temperature of ZnS are beneficial for ceramics.

Among the tetrahedrally bonded semiconductors, it has been stated that after ZnO, ZnS has the highest piezoelectric tensor or at least one comparable to that of GaN and AlN. This property makes it a technologically important material for many piezoelectrical applications, which require a large electromechanical coupling.

3.5.2 Electronic Properties

ZnS has a relatively large direct band gap of ~3.68 eV at room temperature. Advantages associated with a large band gap include higher breakdown voltages, ability to sustain large electric fields, lower electronic noise, and high-temperature and high-power operation. The bandgap of ZnS can further be tuned to ~3–4 eV by its alloying with magnesium oxide or cadmium oxide.

The unusual property of ZnS of being doped as both n-type semiconductor and p-type semiconductor shows peculiar electronic properties. Controllable n-type doping is easily achieved by substituting Zn with group-III elements such as Al, Ga, In or by substituting oxygen with group-VII elements chlorine or iodine.

Electron mobility of ZnS strongly varies with temperature and has a maximum of ~2000 $cm^2/(V\cdot s)$ at 80 K. Data on hole mobility are scarce with values in the range 5–30 $cm^2/(V\cdot s)$.

Fig 3.3 (a) Sphalerite, more common polymorph of ZnS (b) Wurtzite, less common polymorph of ZnS

In Figure 3.4 below, only 1/2 of the tetrahedral sites (i.e. four of the eight octants of the cube) are occupied by Zn^{2+} (red).

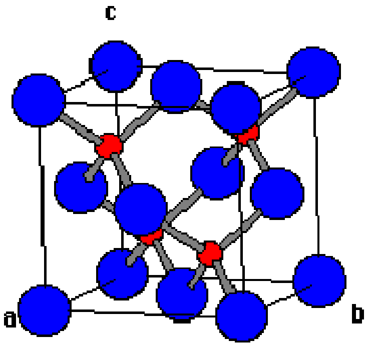

Fig 3.4 A single unit cell of zinc blende

3.5.3 Chemical Properties

Zinc sulfide is an amphoteric oxide. It is insoluble in water and alcohol and solutions containing Zn^{2+} readily precipitate ZnS in the presence of sulfide ions (e.g., from H_2S)., but it is soluble in (degraded by) most acids, such as hydrochloric acid:

$$ZnS + 2\ HCl \rightarrow ZnCl_2 + H_2S$$

ZnO reacts slowly with fatty acids in oils to produce the corresponding carboxylates, such as oleate or stearate. ZnO forms cement-like products when mixed with a strong aqueous solution of zinc chloride and these are best described as zinc hydroxy chlorides. This cement was used in dentistry.

ZnO also forms cement-like products when treated with phosphoric acid; related materials are used in dentistry. It is easily produced by mixing an amount of zinc and sulfur and then igniting it. The result (after cooling) is zinc sulfide.

$$Zn^{2+} + S^{2-} \rightarrow ZnS$$

This has formed the basis of a gravimetric analysis for zinc. It is produced in quantity from zinc oxide as a by-product of the synthesis of ammonia from methane.

Zinc oxide can react violently with aluminium and magnesium powders, with chlorinated rubber and linseed oil on heating causing fire and explosion hazard.

Zinc oxide reacts with hydrogen sulfide to give Zinc Sulfide: this reaction is used commercially in removing H_2S using ZnO powder (e.g., as deodorant).

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

When ointments containing ZnS and water are melted and exposed to ultraviolet light, hydrogen peroxide is produced. Table 3.2 below shows some basic properties of ZnS along with other zinc metalloids and compounds.

Table 3.2 Properties of ZnS

Property \ Material	ZnO	ZnS	ZnSe	ZnTe
Zinc Blende Lattice Parameter a_0 at 300K	. . .	0.541 nm	0.567 nm	0.610 nm
Zinc Blende Nearest-Neighbour Dist. at 300K	. . .	0.234 nm	0.246 nm	0.264 nm
Zinc Blende Density at 300K	. . .	4.11 g.cm^{-3}	5.26 g.cm^{-3}	5.65 g.cm^{-3}
Melting Point	1975 ^{o}C	1850 ^{o}C (wurzite, 150 atm.)	1100 ^{o}C	1240 ^{o}C
Dielectric Const, low frequency	. . .	8.9	9.1	7.4
Refractive Index		2.368	2.5	2.72
Energy Gap E_g at 300 K zinc blende structure: wurzite structure:	. 3.4 eV, Direct	3.54 eV, Direct 3.911 eV, Direct	2.8215 eV, Direct .	2.394 eV, Direct .

3.6 APPLICATIONS OF ZnS NANOPARTICLES

ZnS is used as detector because it emits light on excitation by x-rays or electron beam, making it useful for x-ray screens and cathode ray tubes. It also exhibits phosphorescence due to impurities on illumination with blue or ultraviolet light.

Zinc sulfide, with addition of few ppm of suitable activator, is used as phosphor in many applications, from cathode ray tubes through x-ray screens to glow in the dark products. When silver is used as activator, the resulting color is bright blue, with maximum at 450 nm. Manganese yields an orange-red color at around 590 nm. Copper provides long glow time and the familiar glow-in-the-dark greenish color. Copper doped zinc sulfide (ZnS+Cu) is used also in electroluminescent panels.

Zinc sulfide is also used as an infrared optical material, transmitting from visible wavelengths to over 12 micrometres. It can be used planar as an optical window or shaped into a lens. It is made as microcrystalline sheets by the synthesis from hydrogen sulfide gas and zinc vapour and sold as FLIR (Forward Looking IR) grade ZnS a pale milky yellow visibly opaque form.

3.7 SCOPE AND FUTURE SCOPE OF ZnS NANOPARTICLES IN MATERIAL PHYSICS

ZnS has wide direct band gap (3.54 eV). Therefore, it's most common potential applications are in laser diodes and light emitting diodes (LEDs). Some optoelectronic applications of ZnS overlap with that of GaN, which has a similar bandgap (~3.4 eV at room temperature). Compared to GaN, ZnS has a larger exciton binding energy (~60 meV, 2.4 times of the room-temperature thermal energy), which results in bright room-temperature emission from ZnS. Other properties of ZnS favorable for electronic applications include its stability to high-energy radiation and to wet chemical etching. Radiation resistance makes ZnS a suitable candidate for space applications. ZnS is currently the most promising candidate in the field of random lasers to produce an electronically pumped UV laser source.

The pointed tips of ZnS nanorods result in a strong enhancement of an electric field. Therefore, they can be used as field emitters.

Aluminium-doped ZnS layers are used as transparent electrodes. The constituents Zn and Al are much cheaper and less poisonous compared to the generally used indium tin oxide (ITO). One application which has begun to be commercially available is the use of ZnS as the front contact for solar cells or of liquid crystal displays.

Transparent thin-film transistors (TTFT) can be produced with ZnS. As field-effect transistors, they even may not need a p–n junction, thus avoiding the p-type doping problem of ZnS. Some of the field-effect transistors even use ZnS nanorods as conducting channels.

- **Zinc sulfide nanorod sensor**

Zinc sulfide nanorod sensors are devices detecting changes in electrical current passing through zinc sulfide nanowires due to adsorption of gas molecules. Selectivity to hydrogen gas was achieved by sputtering Pd clusters on the nanorod surface. The addition of Pd appears to be effective in the catalytic dissociation of hydrogen molecules into atomic hydrogen, increasing the sensitivity of the sensor device. The sensor detects hydrogen concentrations down to 10 parts per million at room temperature, whereas there is no response to sulphur.

- **Spintronics**

ZnS has also been considered for spintronics applications: if doped with 1-10% of magnetic ions (Mn, Fe, Co, V, etc.), ZnS could become ferromagnetic, even at room temperature. Such room temperature ferromagnetism in ZnS:Mn has been observed, but it is not clear yet whether it originates from the matrix itself or from secondary oxide phases.

- **Piezoelectricity**

The piezoelectricity in textile fibers coated with ZnS has shown capability of fabricating "self-powered nanosystems" with everyday mechanical stress from wind or body movements.

Scientists have reported producing electricity generating device (called flexible charge pump generator) delivering alternating current by stretching and releasing zinc oxide nanowires. This mini-generator creates an oscillating voltage up to 45 millivolts, converting close to seven percent of the applied mechanical energy into electricity. Researchers used wires with lengths of 0.2–0.3 mm and diameters of three to five micrometers, but the device could be scaled down to smaller size.

- **Biosensors**

ZnS has high biocompatibility and fast electron transfer kinetics. Such features advocate the use of this material as a biomimic membrane to immobilize and modify biomolecules.