

A Study on Nano Semiconductors and Its Use

Kavita Rani*

M.Sc. Physical Chemistry, Group- 1, Department of Chemistry, University of Delhi

Abstract – The aim of the study is to know about the nano semiconductors and its use. Semiconductors are characterized by a composition-dependent band gap energy (E_g), which is the minimum energy required to excite an electron from the ground state valence energy band into the vacant conduction energy band. With the absorption of a photon of energy greater than E_g , the excitation of an electron leaves an orbital hole in the valence band. The negatively charged electron and positively charged hole may be mobilized in the presence of an electric field to yield a current, but their lowest energy state is an electro statically bound electron-hole pair, known as the exciton. Relaxation of the excited electron back to the valence band annihilates the exciton and may be accompanied by the emission of a photon, a process known as radiative recombination.

Keywords: semiconductors, Nano, photo catalytic etc.

-----X-----

INTRODUCTION TO SEMICONDUCTOR

A semiconductor is a material that has an electrical conductivity between a conductor and an insulator. In semiconductors, the highest occupied energy band, the valence band is completely filled with electrons and the empty next one is the conduction band. The resistivities of the semiconductor can be altered by up to 10 orders of magnitude, by doping or external biases. In the case of conductors, that have very low resistivities, the resistance is difficult to alter, and the highest occupied energy band is partially filled with electrons and the insulator has extremely high resistivities. It is difficult to alter the resistivity through doping or external fields and the band gap between the valence band and the conduction band is large. In a metallic conductor, the current is carried by the flow of electrons. In semiconductors, current can be carried either by the flow of electrons or by the flow of positively-charged holes in the electron structure of the material.

WHEN SEMICONDUCTORS GO NANO

Recently there has been substantial interest in the preparation, characterization and application of semiconductor nanoparticles that play a major role in several new technologies. When the size of semiconductor materials is reduced to nanoscale, their physical and chemical properties change drastically, resulting in unique properties due to their large surface area or quantum size effect. The conductivity of the semiconductor and its optical properties (absorption coefficient and refractive index) can be altered.

OBJECTIVES OF THE STUDY

The main objectives the study is to know about the nano semiconductors and their uses.

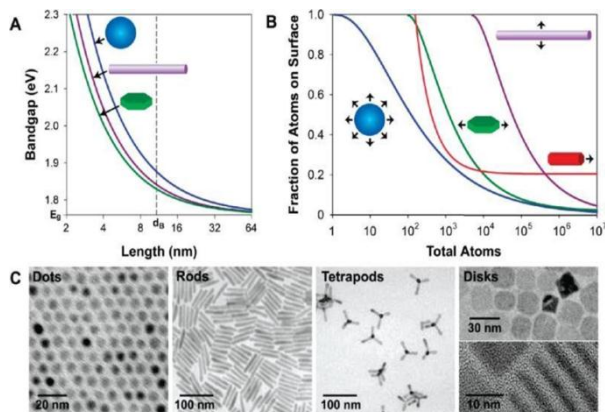
NANO SEMICONDUCTORS

Semiconductor nanocrystals are tiny crystalline particles that exhibit size-dependent optical and electronic properties.¹⁻³With typical dimensions in the range of 1-100 nm, these nanocrystals bridge the gap between small molecules and large crystals, displaying discrete electronic transitions reminiscent of isolated atoms and molecules, as well as enabling the exploitation of the useful properties of crystalline materials. Semiconductor nanocrystals (NCs) are made from a variety of different compounds. They are referred to as II-VI, III-V or IV-VI semiconductor nanocrystals, based on the periodic table groups into which these elements are formed. For example, silicon and germanium are group IV, GaN, GaP, GaAs, InP and InAs are III-V, while those of ZnO, ZnS, CdS, CdSe and CdTe are II-VI semiconductors.

STRUCTURES OF NANO SEMICONDUCTORS

The most important consequence of the quantum confinement effect is the size dependence of the band gap for nanocrystalline semiconductors. By confining the exciton of a semiconductor, the band gap may be tuned to a precise energy depending on the dimensionality and degree of confinement. Figure 2A depicts the shift of the band gap of CdSe nanocrystals confined in three dimensions (quantum dots), two dimensions (quantum wires or rods), or one dimension (quantum wells or disks). An increase

in the number of confined dimensions yields a stronger degree of electronic confinement and thus a wider range of tunability in the band gap, although exceptions to this trend have been reported for CdTe nanocrystals.

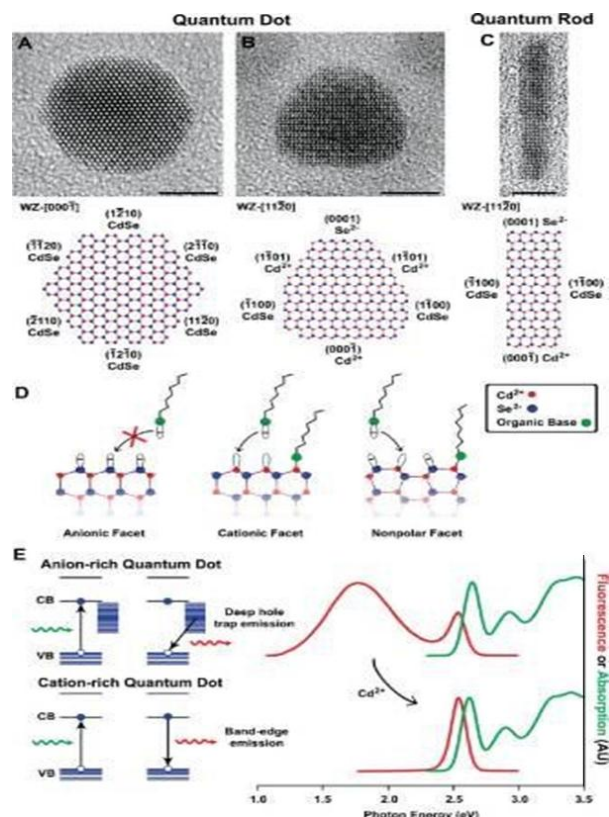


SURFACE PROPERTIES OF NANO SEMICONDUCTORS

The dependence of optical properties on particle size is largely a result of the internal structure of the nanocrystal. However, as the crystal becomes smaller, the number of atoms on the surface increases, which can also impact the optical properties. The atoms on the surface of a crystal facet are incompletely bonded within the crystal lattice, thus disrupting the crystalline periodicity and leaving one or more “dangling orbital” on each atom pointed outward from the crystal.

Most nanocrystals are highly faceted and each surface contains a periodic array of *unpassivated* orbitals with two-dimensional translational symmetry, which may form a band structure similar to that of the three-dimensional crystal itself. If these surface energy states are within the semiconductor band gap, they can trap charge carriers at the surface, thereby reducing the overlap between the electron and hole, increasing the probability of nonradiative decay events. In practice, however, most semiconductor nanocrystals are not used in vacuum, but instead are either embedded within a solid matrix such as another crystal or a glass, or suspended in solution and coated with organic ligands such as trioctylphosphine oxide (TOPO) or hexadecylamine (HDA).

Thereby, the dangling bonds on the exposed facets are *passivated* by bonding with atoms or molecules, minimizing intraband gap surface states and reducing surface atomic reconstruction. For colloidal particle suspensions, molecules such as TOPO and HDA adsorb to the nanocrystal surface through dative ligand-metal bonds between the basic moiety on the ligand and metal atoms on the nanocrystal surface, solubilizing the crystal in nonpolar solvents through hydrophobic interactions with the alkyl chains on the ligands.



APPLICATIONS OF NANO SEMICONDUCTORS

Semiconductor nanomaterials have interesting physical and chemical properties and useful functionalities, when compared with their conventional bulk counterparts and molecular materials. Narrow and intensive emission spectra, continuous absorption bands, high chemical and photobleaching stability, processability, and surface functionality are among the most attractive properties of these materials. The development of “nanochemistry” is reflected in an immense number of publications on the synthesis of semiconductor nanoparticles. For instance, the spatial quantum confinement effect results in significant change in optical properties of semiconductor nanomaterials. The very high dispersity (high surface-to-volume ratio), with both physical and chemical properties of the semiconductor has a major influence on their optical and surface properties. As a result, semiconductor nanomaterials have been the focus of research for about 20 years and have attracted significant interest in research and applications in diverse disciplines such as solid-state physics, inorganic chemistry, physical chemistry, colloid chemistry, materials science, and recently biological sciences, medical sciences, engineering, and interdisciplinary fields. Among the unique properties of nanomaterials, the movement of electrons and holes in semiconductor nanomaterials is primarily governed by the well-known quantum confinement, and the transport properties related to phonons and photons are largely affected by the size and geometry of the materials. The specific surface area and surface-to-volume ratio increase drastically as

the size of the material decreases. Parameters such as size, shape, and surface characteristics can be varied to control their properties for different applications of interest. These novel properties of semiconductor nanomaterials have attracted significant attention in research and applications in emerging technologies such as nanoelectronics, nanophotonics, energy conversion, non-linear optics, miniaturized sensors and imaging devices, solar cells, catalysis, detectors, photography, biomedicine etc.

SEMICONDUCTOR NANOMATERIALS FOR HYDROGEN PRODUCTION

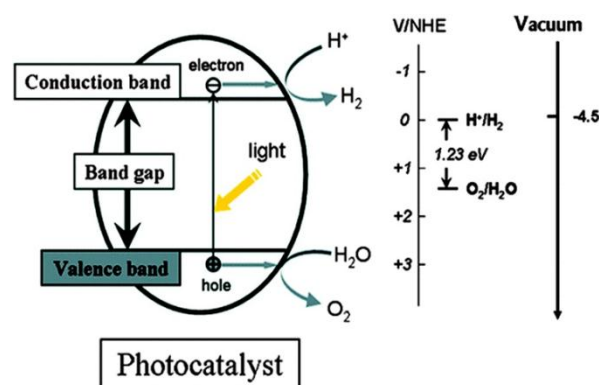
Growing environmental concerns are related to the extensive use of non-sustainable fossil fuels (oil, natural gas and coal) and a constantly increasing energy demand for clean and sustainable sources of energy. Hydrogen is a promising alternative fuel, since it is completely pollution-free and can readily be produced from renewable energy resources, thus eliminating the net production of greenhouse gases. Recent studies have indicated that hydrogen fuel costs are reasonable and hydrogen is therefore an ideal candidate to replace fossil fuels as an energy carrier. There is increasing environmental pollution, caused by combustion engines, and additional problems associated with large-scale mining, transportation, processing and usage of fossil fuel. Photocatalysis is expected to make a great contribution to both environmental treatment (emission cleaning and water purification) and renewable energy. Hydrogen (H₂) is widely considered to be the future clean energy carrier in many applications, such as environmentally friendly vehicles, domestic heating, and stationary power generation. Photocatalytic hydrogen production from water is one of the promising techniques due to following advantages:

- It is based on photon (or solar) energy, which is a clean, perpetual source of energy, and mainly water, which is a renewable resource.
- It is an environmentally safe technology without undesirable by-products and pollutants.
- The photochemical conversion of solar energy into a storable form of energy, i.e.

Hydrogen, allows one to deal with the intermittent character and seasonal variation of the solar influx.

The structural and electronic properties of semiconductor photo catalysts largely determine the process of photocatalytic H₂ production, including basic steps such as the absorption of photons, charge separation and migration, and surface reactions. The photo generated electrons and holes may recombine in the bulk or on the surface of the semiconductor on a time scale, which is slower than the time required for their formation. Electrons and holes that travel to the

surface of the semiconductor before they recombine can cause reduction (H₂ formation) and oxidation (O₂ formation) reactions, respectively. For H₂ production to occur, the CB bottom-edge must be more negative than the reduction potential of H⁺ to H₂ (E_{H⁺/H₂}=0 V vs NHE at pH=0), while the VB top-edge should be more positive than the oxidation potential of H₂O to O₂ (E_{O₂/H₂O}=1.23 V vs NHE at pH=0) for O₂ formation from water to occur.



Semiconductors such as TiO₂, ZnO, ZrO₂, V₂O₅, WO₃, Fe₂O₃, SnO₂, CdSe, GaAs, GaP and metal sulphides (CdS and ZnS) are employed as photocatalysts. Among the semiconductors, titanium dioxide (TiO₂) is one of the most important and widely used photocatalysts, because of its suitable flat band potential, high chemical stability, nontoxicity, corrosion resistance, abundance, cheapness, and high photocatalytic activity. TiO₂ is used not only for the photocatalytic degradation of environmental pollutants; it also applied to produce and storage of hydrogen gas. The use of semiconductor other than TiO₂ such as ZnO, ZrO₂, V₂O₅, WO₃, Fe₂O₃, SnO₂, CdSe, GaAs, GaP, CdS and ZnS have the drawback of instability and/or corrode easily, either dissolving or forming a thin film, which prevents the electrons from transferring across the semiconductor/liquid interface.

The morphology of TiO₂ plays a very important role in the efficiency of photocatalysis for H₂ production. One-dimensional TiO₂ (nanowires, nanorods, nanotubes and nanofibers) has attracted more and more attention. Compared to spherical particles, one-dimensional TiO₂ nanostructures could provide a high surface area and a high interfacial charge transfer rate. In particular, the particle size, chemical composition (including dopants), microstructure, the crystal phase, morphology, surface modification, bandgap and flat-band potential of the nanophotocatalysts have shown a visible effect on photocatalytic H₂.

The biggest disadvantage of TiO₂ is that it is inactive under visible light irradiation, due to its large bandgap, which impedes the use of TiO₂ as a solar energy harvesting photocatalyst. In order to overcome these deficiencies, TiO₂ doped with different metals, nonmetals, and surface

modifications has been used to utilize solar energy as the irradiation source. Nanocomposites have been studied extensively in photocatalytic H_2 production. The intercalation of semiconductor nanoparticles such as

TiO_2 , CdS, $Cd_{0.8}Zn_{0.2}S$ and Fe_2O_3 into layered compounds such as $H_2Ti_4O_9$, $H_4Nb_6O_{17}$, $K_2Ti_{3.9}Nb_{0.1}O_9$, $HNbWO_6$, $HTaWO_6$, $HTiNbO_5$ and $HTiTaO_5$ has been reported for H_2 production. The intercalation suppresses the growth of the nanoparticles. When these intercalated nanoparticles are excited by bandgap irradiation, the photogenerated electrons can be quickly transferred to the matrix layered compounds. For example, in the $LaMnO_3/CdS$ nanocomposite, the holes photogenerated by visible light in the valence band of CdS can move to the valence band of $LaMnO_3$ and react with electron donors (Na_2S and Na_2SO_3), while the photogenerated electrons remain in the conduction band of CdS and react with water to produce H_2 . This charge-carrier separation at the nanoscale is responsible for the improved photocatalytic activity. Nanostructured photocatalysts are expected to be a future trend, since nanosized photocatalysts have shown much better performance than their bulk counterparts. Many of semiconductor nanomaterials have been used to produce H_2 .

SILICON SEMICONDUCTOR NANOMATERIALS AND DEVICE

The development of silicon based materials and devices will influence the future development of current microelectronics and information technology to a certain extent, which has an important strategic significance. Besides the widely used crystalline silicon wafers, silicon nanostructures have been considered as the basic components for future nano/microelectronic devices. The size effect of silicon nanostructures leads to a lot of novel properties. One typical example is the size-tunable highly-luminescent silicon nanostructures due to the quantum effect. Several silicon based novel devices like highly sensitive biological and chemical sensors, high-efficiency solar cells and light-emitting diodes have been developed. Therefore, silicon nanostructures show wide application prospects in many fields.

NANO OPTOELECTRONIC SENSORS AND PHOTOVOLTAIC DEVICES

This area includes surface modification, aligned assembly of nanomaterials, and conjugation of nanomaterials with bio-molecules. Employing the interactions between nanomaterials and analytes, and the trace detection of target samples based on the property change in optics, electronics, magnetics, sound, force, and their combinations, nano chemical sensors will be very useful in the applications of safety, health, hygiene, and anti-terrorism.

CONCLUSIONS

Semiconductor nanomaterials are advanced materials for various applications. The unique physical and chemical properties of semiconductor nanomaterial make it suitable for application in emerging technologies, such as nanoelectronics, nanophotonics, energy conversion, non-linear optics, miniaturized sensors and imaging devices, solar cells, detectors and photography. Nanosized semiconductor optoelectronic sensors and photovoltaic devices have several advantages like energy saving, high efficiency, and high stability, which make them more and more useful in many applications.

REFERENCES

1. Astruc, D. (2008). Nanoparticles and Catalysis (ed. D. Astruc), Wiley-VCH Verlag GmbH, Weinheim, Germany, p. 1.
2. Cuenya, B.R. (2010). Synthesis and catalytic properties of metal nanoparticles: size, shape, support, composition, and oxidation state effects. *Thin Solid Films*, 518, pp. 3127–3150.
3. Cole-Hamilton, D. (2003). Homogeneous catalysis – new approaches to catalyst separation, recovery, and recycling. *Science*, 299 (5613), pp. 1702–1706.
4. Dunworth, W.P. and Nord, F.F. (1954) Noble metal-synthetic polymer catalysts and studies on the mechanism of their action, in *Advances in Catalysis and Related Subjects* (ed. W.G. Frankenburg), Academic Press Inc., New York, pp. 125–143.
5. Dubosc M, Casimirius S, Besland M-P, Cardinaud C, Granier A, Duvail J-L, et. al. (2007). Impact of the Cu-based substrates and catalyst deposition techniques on carbon nanotube growth at low temperature by PECVD. *Microelectronic Engineering*; 84: pp. 2501e5.
6. Duy DQ, Kim HS, Yoon DM, Lee KJ, Ha JW, Hwang YG, et. al. (2009). Growth of carbon nanotubes on stainless steel substrates by DC-PECVD. *Applied Surface Science*; 256: pp. 1065e8.
7. Feldheim, D.L. (2007). The new face of catalysis. *Science*, 316 (5825), 699–700.
8. Klabunde, K.J. (2001). Introduction to nanotechnology, in *Nanoscale Materials in Chemistry* (ed. K.J. Klabunde), John Wiley & Sons, Inc., Hoboken, USA, pp. 1–13.
9. Joo SH, Pak C, You DJ, Lee SA, Lee HI, Kim JM, et. al. (2006). Ordered mesoporous

- carbons (OMC) as supports of electrocatalysts for direct methanol fuel cells (DMFC): effect of carbon precursors of OMC on DMFC performances. *Electrochimica Acta*; 52:1618e26.
10. Jhaa N, Reddy ALM, Shaijumona MM, Rajalakshmi N, Ramaprabhu S. (2008). PtRu/multi-walled carbon nanotubes as electrocatalysts for direct methanol fuel cell. *International Journal of Hydrogen Energy*; 33:427e33.
 11. Mohlala MS, Coville NJ (2007). Floating catalyst CVD synthesis of carbon nanotubes from CpFe(CO)₂X (X = ¼ Me, I): poisoning effects of I. *Journal of Organometallic Chemistry*; 692:2965e70.
 12. McKee GSB, Decker CP, Vecchio KS (2009). Dimensional control of multi-walled carbon nanotubes in floating catalyst CVD synthesis. *Carbon*; 47:2085e94.
 13. Pannopard P, Khongpracha P, Probst M, Limtrakul J. (2009). Gas sensing properties of platinum derivatives of single-walled carbon nanotubes: a DFT analysis. *Journal of Molecular Graphics and Modelling*; pp. 28:62e9.
 14. Shao Y, Yin G, Gao Y. (2007). Understanding and approaches for the durability issues of Pt-based catalysts for PEM fuel cell. *Journal of Power Sources*; 171: pp. 558e66.
 15. Sebastián D, Suelves I, Lázaro MJ, Moliner R. (2009). Carbon nanofibers as electrocatalyst support for fuel cells: effect of hydrogen on their properties in CH₄ decomposition. *Journal of Power Sources*; pp. 192:51e6.
 16. Thomas, J.M. (1988). Colloidal metals: past, present and future. *Pure & Appl. Chem.*, 60 (10), pp. 1517–1528.
 17. Tao, A.R., Habas, S., and Yang, P.D. (2008) Shape control of colloidal metal nanocrystals. *Small*, 4 (3), pp. 310–325
 18. Van Santen, R.A. (2009) Complementary structure sensitive and insensitive catalytic relationships. *Acc. Chem. Res.*, 42 (1), pp. 57–66.
 19. Wong YM, Wei S, Kanga WP, Davidson JL, Hofmeister W, Huang JH, et. al. (2004). Carbon nanotubes field emission devices grown by thermal CVD with palladium as catalysts. *Diamond & Related Materials*; 13:2105e12.
 20. Zhang J. (2008). PEM fuel cell electrocatalysts and catalyst layers: fundamentals and applications. , London: Springer-Verlag London Limited.

Corresponding Author

Kavita Rani*

M.Sc. Physical Chemistry, Group- 1, Department of Chemistry, University of Delhi