ISSN : 2249 - 8877 Volume 5 Issue 1

Research & Reviews On Polymer

Full Paper

RRPL, 5(1), 2014 [08-13]

Physical properties and applications of CdS polymer based nanoparticles

M.C.Rao*

Department of Physics, Andhra Loyola College, Vijayawada - 520008, (INDIA)

E-mail : raomc72@yahoo.com

ABSTRACT

The study of semiconductor nanoparticles has been an interesting field of research for more than two decades. This is because it gives an opportunity to understand the physical properties in low dimensions and to explore their vast potential for applications, e.g. in optoelectronics. The latter is particularly based on the large variations of the band gap as a function of particle size, which is a consequence of quantum confinement. Moreover, small nanoparticles allow the study of relevant surface properties due to the high surface to bulk ratio. In semiconductor nanoparticles, strong confinement effects appear when the size of the nanoparticles is comparable to the Bohr radius of the exciton in the bulk material. The active physical and chemical properties of the nanocrystallites make it very important to improve their stability, which has intensive relations with the surface states and environments. Especially, considerable interests have been focused on the organic/inorganic hybrid composite, in which semiconductor nanocrystallites are encapsulated in the organic phase. CdS is an important inorganic semiconductor compound owing to its unique photoelectric properties. The confinement effect is observed for CdS particles when the particle sizes are equal to or less than 50 Å. Bulk CdS is widely used as a commercial photo detector in the visible spectrum. It is also used as a promising material for buffer layers in thin film solar cells. The optical properties of CdS nanoparticles have been extensively studied in recent years as this material exhibits pronounced quantum size effects. A lot of work has been done on the preparation of these nanoparticles and a wet chemical synthesis has come up as a promising technique because of the ability to produce various sizes and large quantities of the nanoparticles.

KEYWORDS

Semiconductor nanoparticles;
CdS;
Preparation methods;
Applications.

INTRODUCTION

Traditionally, polymeric materials have been filled with synthetic or natural inorganic compounds in order to improve their properties, or simply to reduce cost. Conventional fillers are materials in the form of particles, fibers or plate-shaped particles. However, although conventionally filled or reinforced polymeric materials are widely used in various fields, it is often reported that the addition of these fillers imparts drawbacks to the resulting materials, such as weight increase, brittleness and opacity[1]. Nanocomposites, on the other hand, are a new class of composites, for which at least one dimensions of the dispersed particles is in the nanometer range. Depending on how many dimensions are in the nanometer range, one can distinguish iso-dimensional nanoparticles when the three dimensions are on the order of nanometers, nanotubes or whiskers when two dimensions are on the nanometer scale and the third is larger, thus forming an elongated structure and finally, layered crystals or clays, present in the form of sheets of one to a few nanometers thick and hundreds to thousands nanometers in extent[2]. The increasingly demanding applications of polymeric materials require an ever more sophisticated understanding of the relationship between chemical structure, molecular organization and material properties. Defects or local variations in structure are expected to play an important role in limiting macroscopic properties. The impact of structural defects on the optoelectronic and mechanical properties of inorganic materials is fairly well established[3]. Similar ideas have been hypothesized for organic polymers, but a more detailed insight into the role of defects in crystalline polymer and organic molecular solids has only begun to be developed[4]. II-VI semiconductor nano-crystal quantum dots and electro-optic active polymers, which exhibit electro-optic and nonlinear optical properties different from those of corresponding bulk materials, are a new class of materials which hold considerable promise for numerous applications in electronics and photonics[5]. Incorporating such quantum dots into polymer films is of increasing interest because of their application in guided wave nonlinear optics and optical communication devices[6]. In recent years, more and more attentions have been paid to the nanoscaled semiconductor and quantum dots materials[7]. With a lot of novel physical and chemical properties, these materials are of high value in both fundamental researches and practical applications.

The active physical and chemical properties of the nanocrystallites make it very important to improve their stability, which has intensive relations with the surface states and environments. Passivation or capsulation is one of the most useful ways to achieve this goal. Especially, considerable interests have been focused on the organic/inorganic hybrid composite[8], in which semiconductor nanocrystallites are encapsulated in the organic phase. Cadmium sulfide (CdS) is an important inorganic semiconductor compound owing to its unique photoelectric properties. CdS holds particle-size-dependent electronic spectrum, which could show the influence of size quantization effects. Its potential applications have been exhibited in many fields such as the nonlinear optics, the photo electrochemical cells and heterogeneous photocatalysis[9]. During the past decade, many reports have been presented on the synthesis of CdS nanocrystallites[10], among which the methods related to organic or polymeric matrices have attracted many attentions[11]. Polymers as matrices have several advantages for encapsulated semiconductor nanocrystallites. On the one hand, polymers with a kind of spatial conformation can be used as a template to make nanoscaled crystallites in solution, polymers are able to achieve surface passivation, prevent particles from agglomeration and maintain the particle dispersion degree, which are in favor of controlling the crystallite size and size distribution effectively[12].

As a direct wide bandgap (2.42 eV) semiconductor, CdS nanocrystals may be potentially used in optoelectronics of nonlinear optics and light emitting diodes. The Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is often not the case. Size-dependent properties are observed such as quantum confinement in semiconductor nanoparticles, surface plasmon resonance in some metal particles and super paramagnetism in magnetic materials[13]. The properties of materials change as their size approaches the nanoscale and the percentage of atoms at the surface of a material becomes significant. Modification in the electronic levels occurred very strongly due to the limited number of atoms in the particles. Such materials in these regime exhibit novel physical and chemical properties due to the large surface to volume ratio as well as size quantization effect in semiconductor nanoparticles[14]. Due to finite size of the nanoparticles the continuous energy band of the bulk crystal transforms into a series of discrete states resulting in widening of the effective band gap. The nanoparticles frequently display photoluminescence and sometimes display electroluminescence. Additionally, some nanoparticles can form self-assembled arrays. Because of these favorable properties, nanoparticles are being extensively displays studied for use in optoelectronics[15].

PROPERTIES OF POLYMER BASED NANOCOMPOSITES

Polymer-based nanoparticle nanocomposites were prepared via various processes and showed improved mechanical, thermal and electrical properties. However, the aforementioned properties of resultant nanocomposites were not always improved. For example, if one property changed for the better, another property changed for the worse. When nanocomposites are designed, one needs to take this tendency into account and find the optimum properties for specific applications.

Mechanical properties

Generally, the reason for adding inorganic particles into polymers is to improve its mechanical properties such as the tensile strength, modulus or stiffness via reinforcement mechanisms described by theories for nanocomposites[16]. However, poor compatibility between the polymer matrices and the inorganic particles in nanocomposites prepared by simple physical mixing will create inherent defects which, consequently, result in a deleterious effect on the mechanical properties of the nanocomposites. The mechanical properties of nanocomposites, prepared from various polymers and inorganic particles, did not always increase. In some cases, the properties of nanocomposites were decreased by the addition of inorganic particles because of aggregation in polymer matrices. To solve this problem, the load amounts of inorganic particles were optimized or were functionalized with organic material[17].

Thermal properties

For structural applications at elevated temperatures, the dimensional stability of low thermal expansion coefficient of these nanocomposites is also very important. The high thermal expansion coefficient of neat polymers causes dimensional changes during the molding process. The changes are either undesirable or, in some cases, unacceptable for certain applications.

Optical properties

The optical properties of discontinuous metallic or granular composite films, consisting of metal nanoparticles embedded in a dielectric, have long been of interest. Moreover, as the market of materials for optical applications expands, the need for novel materials with functionality and transparency increases. Polymer-based inorganic nanoparticle nanocomposites show great promise as they can provide the necessary stability and easy processability with interesting optical properties. As described earlier, metal nanoparticles show characteristic plasmon resonance modes during interaction with electromagnetic waves as a result of collective oscillations of free electrons and local enhancement of the electromagnetic field. This phenomenon largely depends on the particle size, shape, and the surrounding dielectric matrix. Particle plasmon resonances occur through absorption energies in the intraband transitions and can be either dipolar excitation, in the case of spherical particles, or multipolar excitation of particles nonspherical in geometry[18].

CRYSTALLINE LATTICE OF SMALL NANOPARTICLES

Physics of semiconductor theory use macroscopic charge carrier statistic parameters of bulk crystals for all structures types including microns and sub- microns elements in microchips. It is correct approximation now as the sizes of microchips elements more than 100 nm are more time larger in comparison to interatomic distances. In contrary, typical nanoparticles, for example CdS or ZnS with the size of 1 - 3 nm include a few atomic layers and its interatomic distance can differ essentially from same of bulk crystals. Now are a few of works where these effects are investigated. Indeed, if to shrink elements down to the nanometer scale, creating nanodots, nanoparticles, nanorods and nanotubes a few tens of atoms across, they've found weird and puzzling behaviors unexpected for bulk and micron sized material[19]. Certainly at decreasing of nanoparticles sized up to few nanometers that correspond to some tens atoms its crystalline lattice change essentially from same of bulk crystal and it is appear instability of crystalline lattice. Large surface of small particle will result on augmentation of influence of surface states on crystalline lattice of nanoparticles. There is a lot of work that show size and surface effects of crystalline lattice change in nanometers size nanoparticles[20].

STRUCTURE OF CdS NANOPARTICLES

CdS has two crystal forms; the more stable hexagonal wurtzite structure and the cubic zinc-blende structure. In both of these forms the cadmium and sulfur atoms are four coordinate. Figure 1 shows the crystal structure of CdS in (a) Wurtzite and (b) Zinc-blende symmetries. There is also a high pressure form with the NaCl rock salt structure. Cadmium sulfide is a direct band gap semiconductor. The magnitude of its band gap means that it appears coloured[21].

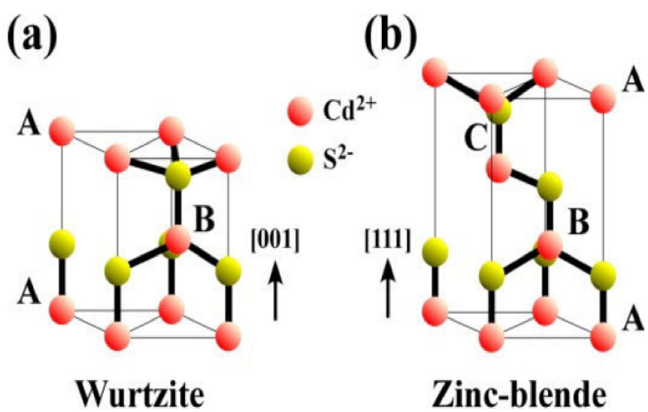

Figure 1 : Crystal structure of CdS in (a) Wurtzite and (b) Zinc-blende symmetries

OVERVIEW OF VARIOUS SYNTHESIS TECHNIQUES FOR CdS NANOPARTICLES

There exists a large number of methods to obtain clusters with different properties. These were developed over many years. The cluster preparation methods can be classified in two general classes as gas phase methods and condensed phase methods. Often gas phase clusters are produced and studied in the gas phase only, or they are deposited on a solid surface. These methods are used for small quantities of clusters. The second class of synthesis is that in which the clusters are obtained in the condensed phase. These methods are mainly divided into two classes as chemical and physical methods. Chemical methods are promising in terms of cost reduction and ability to produce large amounts of particles. Usually the nanoparticles are being capped by different organic molecules since this is an easy way of stabilizing them to avoid agglomeration. CdS nanoparticles are of the great interest since many years. The reason may be that this small band gap material shows interesting size quantization effects and the nanoparticles can be obtained in macroscopic amounts for various characterizations, which is difficult for many other II-VI semiconductor particles excluding CdSe and to some extend CdTe. An important aspect of research on nanoparticles has been to prepare size selected particles in order to study various size dependent features[22].

There were many efforts to synthesize size selected CdS with a very narrow size distribution, however only a few were successful[23]. Most of the techniques follow an organic capping route and a wet chemical synthesis with solvents like ethanol, methanol, acetonitrile, dimethylformamide (DMF), etc. The particles are obtained as free standing powders and can be re dissolved to form a nanoparticle solution. Polyphosphate and thiols are the most commonly used capping agents. Use of monochromatic light to irradiate a colloidal solution of CdS particles was adopted in order to produce various sizes[24]. Monodispersed CdS particles can be found in the literature in a few cases, who report a very sharp absorption peak for a 10 Å size CdS cluster obtained by fusion of two $[Cd_{10}S_4(Sphen)_{16}]_4$ molecular clusters. A very good example for a size quantization effect can be seen in the absorption spectra of highly monodisperse CdSe nanoparticles[25].

APPLICATIONS OF CdS NANOCOMPOSITES

The advantages of nanoscale inorganic particle incorporation into polymer matrices can lead to a number of applications that the incorporation of the analogous larger scale particles do not allow due to an insufficient property profile for utilization. These areas include barrier properties, membrane separation, UV screening, flame retardation, polymer blend compatibilization, electrical conductivity, impact modification, biomedical applications, etc. Hence, polymer-based inorganic nanoparticle nanocomposites emerging as new materials provide opportunities and rewards creating a new world of interest[26]. CdS is predominantly used as a pigment. CdS and CdSe are used in manufacturing of photo resistors sensitive to visible and near infrared light. In thin-film form, CdS can be combined with other layers for use in certain types of solar cells. CdS was also one of the first semiconductor materials to be used for thin film a transistor which is shown in Figure 2. Thin films of CdS can be piezoelectric and have been used as transducers which can operate at frequencies in the GHz region.

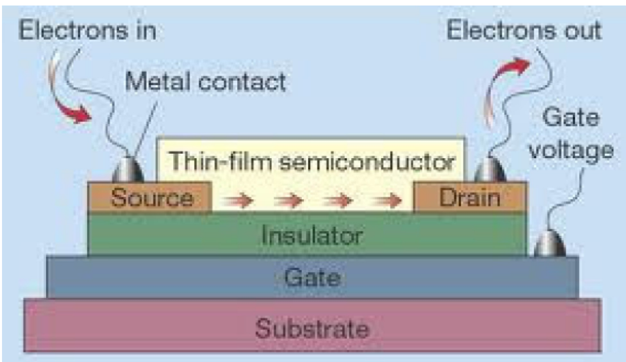

Figure 2 : Thin film transistor

CONCLUSIONS

Nanocomposites on base of semiconductor nanoparticles and polymer matrix are prospective materials for application in optoelectronics, for creation of luminescent materials and sensor electronics.. Introducing semiconductor nanoparticles into polymer matrix volume changes physicochemical properties of the system. The properties of the obtained structures depend on a semiconductor particle type, dimensions of particles. II-VI semiconductor nano-crystal quantum dots and electro-optic active polymers, which exhibit electro-optic and nonlinear optical properties different from those of corresponding bulk materials, are a new class of materials which hold considerable promise for numerous applications in electronics and photonics. Incorporating such quantum dots into polymer films is of increasing interest because of their application in guided wave nonlinear optics and optical communication devices. Beside zinc oxide and zinc sulphide the cadmium chalcogenides are the prototypical systems of the II–VI semiconductor compounds. Already for some hundred years, CdS has been used as a pigment because of its colour. Solid CdS is a yellow material, due to its band gap of 2.42 eV. It provides useful properties for optoelectronic devices, such as photosensitive and photovoltaic devices or as photo resistors.

ACKNOWLEDGEMENTS

The corresponding author (M. C. Rao) is thankful to UGC for providing the financial assistance through Major Research Project (Link No. F.No. 40-24/2011(SR))

REFERENCES

[1] H.Fischer; Mater.Sci.Eng.C, **23**, 763 **(2003)**.
[2] G.Gorrasi, M.Tortora, V.Vittoria, G.Galli, E.Chiellini; J.Polym.Sci.Polym.Phys., **40**, 1118 **(2002)**.
[3] A.Hellemans; Science, **281**, 943 **(1998)**.
[4] K.Christian, G.R.Lebzylisbeth, F.D.Lawrence, C.M.David; J.Phys.Org.Chem., **13**, 816 **(2000)**.
[5] M.V.Artemyev, U.Woggon; Appl.Phys.Lett., **76**, 1353 **(2000)**.
[6] Y.Shi, C.Zhang, H.Zhang, J.H.Bechtel, L.R.Dalton, B.H.Robinson, W.H.Steier; Science, **288**, 119 **(2000)**.
[7] R.M.Penner; Acc.Chem.Res., **33**, 78 **(2000)**.
[8] A.K.Boal, F.Ilhan, J.E.Derouchey, T.Thurn-Albrecht, T.P.Russell, V.M.Rotello; Nature, **404**, 746 **(2000)**.
[9] A.P.Alivisatos; J.Phys.Chem., **100**, 13226 **(1996)**.
[10] M.Chen, Y.Xie, Z.P.Qiao, Y.J.Zhu, Y.T.Qian; J.Mater.Chem., **10**, 329 **(2000)**.
[11] M.Moffitt, H.Vali, A.Eisenberg; Chem.Mater., **10**, 1021 **(1998)**.
[12] Y.Yanga, Hn.Chena, X.Bao; J.Crys.Grow, **252**, 251 **(2003)**.
[13] Y.T.Nien, B.Zaman, J.Ouyang, I.G.Chen, C.S.Hwang, K.Yu; Mater.Lett., **62**, 4522 **(2008)**.
[14] M.Sun, H.Yu, W.Yang, L.Qi, F.Yang, X.Yang; Physicochem.Engg.Aspects, **350**, 91 **(2009)**.
[15] Z.Wu, Y.Zhao, F.Qiu, Y.Li, S.Wang, B.Zhang, B.Yang, Y.Zhang, R.Gao, J.Wang; J.Lumin, **129**, 1125 **(2009)**.
[16] K.Wang, L.Chen, J.Wu, M.L.Toh, C.He, A.F.Yee; Macromolecules, **38**, 788 **(2005)**.
[17] K.Han, M.Yu; J.Appl.Polym.Sci., **100**, 1588 **(2006)**.
[18] A.Biswas, O.C.Aktas, J.Kanzow, U.Saeed,

T.Strunskus, V.Zaporojtchenko, F.Faupel; Mater. Lett.. **58**, 1530 **(2004)**.
[19] P.A.Buffat; Mater.Chem.Phys., **81**, 368 **(2003)**.
[20] Y.W.Jun, J.S.Choi, J.Cheon; Angew.Chem., **118**, 3492 **(2006)**.
[21] R.Viswanatha, D.D.Sarma; Chem.Asian J., **4**, 904 **(2009)**.
[22] N.Gaponik, D.V.Talapin, A.L.Rogach, K.Hoppe, E.V.Shevchenko, A.Kornowski, A.Eychmüller, H.Weller; J.Phys.Chem.B, **106**, 7177 **(2002)**.
[23] L.Manna, E.Scher, A.P.Alivisatos; J.Am.Chem. Soc., **122**, 12700 **(2000)**.
[24] L.P.Jiang, S.Xu, J.M.Zhu, J.R.Zhang, J.J.Zhu, H.Y.Chen; Inorg.Chem., **43**, 5877 **(2004)**.
[25] S.Maksimuk, X.Teng, H.Yang; Phys.Chem. Chem. Phys., **8**, 4660 **(2006)**.
[26] K.M.Bratlie, H.Lee, K.Komvopoulos, P.Yang, G.A.Somorjai; Nano Lett., **7**, 3097 **(2007)**.