Journal of Advances in Science and Technology

Vol. IV, Issue No. VII, November-2012, ISSN 2230-9659

AN ANALYSIS UPON VARIOUS STRATEGIES FOR NANOSTRUCTURE FORMATION BY UTILIZATION OF DIPOLE-DIPOLE INTERACTIONS

AN INTERNATIONALLY INDEXED PEER REVIEWED & REFEREED JOURNAL

www.ignited.in

Journal of Advances in Science and Technology
Vol. IV, Issue No. VII, November-2012, ISSN 2230-9659

An Analysis upon Various Strategies for Nanostructure Formation by Utilization of Dipole-Dipole Interactions

Sakarwala Hiteshkumar Prakashkumar[1]* Dr. Gopal Chandra Bag[2]

[1]Research Scholar

[2]Assistant Professor

Abstract – Chalcogenide nanocrystals, synthesized in solution, can shape bigger nanostructures through the association of the nanocrystals. There are an assortment of structures that shape which range from basic chains to more unpredictable tripod, tetrapod furthermore, star morphologies. The association of the nanocrystals has been hypothesized to be the result of dipole-dipole associations between nanocrystals.

An expansive range of size proportions are analyzed, mirroring the size distribution of nanocrystals present in synthesis. There are various basic models that can portray the development of basic chain or ring nanostructures. A huge stride forward in the comprehension of nanoparticle self-assembly is to model the development of the more intricate tetrapod structures. In this setting an altered Stockmayer fluid model is created in which a single nanocrystal is represented by four off kilter Stockmayer fluid particles.

----------♦----------

INTRODUCTION

There has been significant interest in the world of nanotechnology over the past decade. This is due to the potentially unique properties of a nanomaterial: materials which are made up of building blocks in the order of 1-10 nm in size, relative to their bulk counterparts. This difference in properties is largely attributed to the greater surface to volume ratio in nanomaterials relative to the bulk material. This essentially means there are more surface atoms as opposed to core atoms, atoms not directly exposed to external stimuli, in nanomaterials relative to bulk materials where the situation is reversed with more core atoms than surface atoms1. There are many changes to the physical and chemical properties of materials as a result of quantum confinement in the nano regime. One of these is a lowering of the melting/boiling temperature; there tends to be an exponential decrease in the melting temperature of nanocrystals as the volume of nanocrystals decreases due to the rapidly increasing crystal surface to volume ratio2. Important changes for many semiconductor materials include the increasing size of the band gap, the separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), with decreasing nanocrystal size or nanostructure size.

There are a number of potential uses of nanomaterials. For instance, nanoparticles that luminesce are being exploited for bio-sensing and magnetic nanoparticles are used for targeted drug delivery. Nanoparticles also have other potentially useful applications in the production of nanodevices for use as single-electron transistors (SET), nonvolatile memories and as photovoltaic materials (solar cells) due to their inherent higher quantum yields. There is also the possibility of using these nanomaterials in performing redox reactions with higher efficiency. Many other fields of science are also expected to benefit from the continued development of nanomaterials such as biomedicine, optoelectronics, and many more applications are expected as new nanomaterials are developed.

There are also changes in the chemical activity of materials on reaching the nanometer scale. For instance, gold is normally thought of as an inert metal in the bulk phase. Nanoparticles of gold display catalytic activity, for example the epoxidation of alkenes, and there is also a change in the colour of gold nanoparticles ranging from red to blue depending on size and shape of the nanoparticles. These chemical and physical changes observed in nanomaterials are not simply abrupt transitions from bulk to nano properties, but rather continuous changes in chemical and physical properties as the

size of the nanocrystals decreases. This is an important feature of nanomaterials and the ability of chemistry to exploit this, as subtle changes in both shape and size of nanomaterials allows fine tuning of the crystals properties for its desired purpose.

The process of crystallization, the formation of a solid from a liquid, vapour or amorphous solid phase is in essence what gives rise to formation of nanostructures.

There are two fundamental steps that lead to the formation of nanostructures through crystallization; the first is nucleation where the precursor material aggregates to form small clusters called nuclei. These aggregates serve as seeds for the second step of growth into the larger nanostructures via the Ostwald ripening process, where larger nuclei grow at the expense of smaller nuclei (Figure 1).

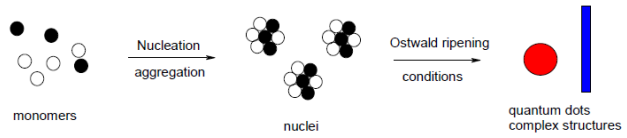

Figure 1 - The process of crystallization in forming nanostructures. The figure shows monomers aggregating together to form nuclei seeds.

The nuclei are affected by the condition of the synthesis, for example the temperature, Ostwald ripening occurs where larger nuclei grow at the expense of smaller nuclei. The final result is the formation of nanocrystals (quantum dots) and possibly more complex nanostructures such as nanorods.

There are a number of methods for synthesising nanomaterials which allow for a degree of control in the size and shape of nanocrystals. These methods can be broadly split into two types with those involving gas phase syntheses such as vapour-liquidsolid (vls) and thermal evaporation21,22 and those methods which involve liquidphase synthesis. The liquid phase synthesis is of great interest as it allows for greater fine tuning of the nanocrystals size and shape due to the large number of parameters that can potentially be exploited to allow for absolute control over the nanocrystals. These parameters include the monomer concentration, temperature, pH, surfactants in solution, whether synthesis occurs in aqueous and non-aqueous media, use of templates, presence of catalysts and the presence of external fields.

The ability to alter these various conditions gives rise to many different nanostructres, which can be classified in terms of their dimensionality. The nanoparticles that are initially formed in solution can be considered as essentially spherical entities, though in many cases the nanoparticles can adopt a multitude of structures from spherical to cubic resulting in faceted crystals; these structures are hence defined as zerodimensional nanostructures. One-dimensional nanostructures are composed of nanowires and nanorods, defined as one-dimensional simply because these structures elongate in one direction. The same analogy is applied to two-dimensional nanostructures which are growing or elongating in two directions and these include structures such as discs and prisms. Three-dimensional nanostructures do not strictly exist as spherical nanocrystals, defined as zero-dimensional if the crystal has stopped growing, but can be considered as three dimensional only if the crystal continues to grow in all directions. In addition to these defined nanostructures other complex nanostructures exist which do not quite fulfil the requisite requirement of being either formed in one phase of synthesis or structures being composed of different polymorphs of the same precursor material. The most commonly adopted crystal morphologies are either tetrahedral (four coordinate) or octahedral (six coordinate) structures. The tetrahedral crystals adopt either zinc blende or wurtzite morphologies. These differ only in the stacking of atoms between layers. Typical examples of complex nanostructures include stars, bipods, tripods and tetrapods. These pod structures have a zinc blende nanocrystals core with additional wurtzite arms or rods attached to form tetrahedral like structures.

HYBRID NANOCRYSTAL STRUCTURES

In addition to forming homogenous nanocrystals and nanostructures these chalcogenide nanoparticles are also used prevalently in the design of hybrid nanocrystals structures. This normally involves the formation of one set of homogenous nanocrystals initially. Once formed these nanocrystals are then exposed to a second stage of synthesis whereby a new precursor material is added to the solution so that a second layer of nanocrystals form around the first set of nanocrystals. The first set of nanocrystals formed in solution hence form the core, whilst the latter introduced precursor material grown on the core nanocrystals form the shell (Figure 2). This results in the so called hybrid core-shell nanocrystals

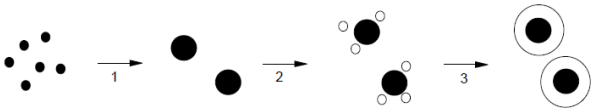

Figure 2 - The formation of core-shell hybrid nanocrystals.

There are currently a number of core-shell hybrid nanocrystals that have been realized for many semiconductor nanocrystals; including CdSe/CdS, CdSe/ZnS, and ZnSe/ZnS. The core-shell hybrid nanocrystals are potentially very useful as the addition of shell nanocrystal typically enhances the properties of the core nanocrystals such as photoluminescence and quantum yield. If the two nanocrystals are carefully chosen with overlapping

Sakarwala Hiteshkumar Prakashkumar[1]* Dr. Gopal Chandra Bag[2]

band gaps, classed as type 1, they can also result in highly fluorescent nanocrystals, which could be useful in biological probe processes. The photoluminescence can also be made more efficient by having the two types of nanocrystals with their band gaps staggered, classed as type 2, such that the photon emission from one nanocrystal is in the region of the band gap of the second nanocrystal. This results in an increased quantum efficiency in some hybrid core-shell nanocrystals, such as CdTe/CdSe and CdSe/ZnTe, which have shown near-IR emission typically not observed for high band gap materials. These type 2 core-shell nanocrystals are particularly useful in biomedical imaging. The technique has been extended to forming core-shell hybrid nanocrystals composed of more than two types of nanocrystals. The core shell nanocrystals are not limited to quantum dots as nanostructures ranging from rods to tetrapods composed of CdTe/CdSe, CdS/CdTe and CdS/CdSe have been produced.

ORIENTED ATTACHMENT AND DIPOLES

The oriented attachment mechanism was initially found to be displayed in many metal oxide systems, TiO_2, ZnO and CuO, however later work showed the mechanism to be present in many metal-chalcogenide systems, including CuS, CdTeand ZnS. However recent work suggested that a primary reason for nanocrystals coming together in such a fashion is more fundamentally related to the presence of dipole moments in semiconductor chalcogenide nanocrystals. The mechanistic driving force therefore for the self-assembly of these nanocrystals into higher dimensional nanostructures is the dipole-dipole inter-particle interactions between nanocrystals. In the early 1990's experimental work in which an electric field was applied to a sample of CdSe nanocrystals revealed, through analysis of the absorption spectra and use of the Stark effect, a dipole moment approximately 32 Debyes in magnitude present when the nanocrystals were in the first excited state. Further research into CdSe nanocrystals led to the conclusion that the dipole moment was not only prevalent, but was in essence the result of the wurtzite structure being adopted by the nanocrystals, as in the bulk structure it is known to be polar. Hence this tended to support the origin of the dipole moment as being intrinsic to the wurtzite structure. The evidence for this arises from the fact that the wurtzite nanocrystals of CdSe were assigned to belong to the C3V point group. It is typical of molecules that are assigned to this point group, such as $POCl_3$ which intrinsically have dipole moments. Similar arguments are made by Nann and coworkers in which the dipole moment in wurtzite nanocrystals is attributed to the distortion of the tetrahedral structure, such that essentially bonds in a particular direction are longer than in other directions, also resulting in a dipole moment within the nanocrystals.

Dipole moments in zinc blende and wurtzite crystals - It was similarly proposed by Blanton and co-workers through conductivity measurements of CdSe nanocrystals that the hexagonal wurtzite lattice was responsible for the resulting dipole moment in the nanocrystals. This meant a cubic zinc blende lattice of nanocrystals would be expected to have a zero dipole moment as these zinc blende nanocrystals are assigned to the T_d group, assuming the lattice structure determines this apparent dipole moment.

Dipoles and crystal structure - There are a number of feasible causes for the dipole moment as outlined previously, though the most likely cause is attributed to the lack of inversion symmetry in nanocrystals. This essentially means that the nanocrystals have different terminating atoms at either side of the nanocrystals resulting in the dipole moment. This can be exemplified by imagining a CdSe nanocrystal in two dimensions terminating with cadmium atoms on the top surface of the nanocrystal, whilst the bottom of the nanocrystal surface terminates with selenium atoms.

Metal nanocrystals - Semiconductor nanocrystals are not the only nanocrystals to exhibit the self-assembly by the proposed dipole-dipole interaction between nanocrystals. Metals such as gold nanoparticles, which do not display an intrinsic electric or magnetic dipole, are also thought to self-assemble through a dipole-dipole interaction between nanocrystals.

This is unusual as semiconductor nanocrystals which are composed of metal cations and chalcogen anions can display asymmetry in the distribution of the cations and anions on the surface, leading to the dipole moment. The gold nanoparticles are known to be surrounded by a negative charge which prevents them from aggregating in solution. The negative charge is attributed to arise from partial oxidation of the gold particle surface. However, it is thought an asymmetric distribution of the negative charge on the gold nanoparticle will lead to one side of the surface becoming relatively electron poor resulting in the dipole moment that drives the formation of the characteristic linear pearl necklace structures. There are similar arguments made in the formation of palladium nanoribbons.

COMPUTATIONAL STRATEGIES

Monte Carlo Strategy- The simulation of the Stockmayer fluid uses the Monte Carlo method, which makes use of a random number generator to carry out the random movement of particles within the simulation cell. How the Monte Carlo routine works is briefly described.

The system begins with a set of coordinates and dipoles orientations, which are stored in memory. The energy of the system in its initial state is calculated and designated U_{old}. The coordinates and dipoles are both then randomly moved and rotated respectively and the energy of the system is calculated, designated U_{new}. If the energy of the new configuration is more favorable than the old configuration, the move is accepted and the procedure is repeated this time with the new accepted coordinates and dipoles. This means U_{old} is equal to U_{new} before the subsequent move of particles.

However if the move is not accepted because the new configuration is less favourable in energy than the old configuration, then the Boltzmann factor, P, is calculated. This is then compared to a random number, distributed 0-1. If the P value is greater than the random number the move is accepted. However, if the P value is less than the random number, the move is rejected and the loop begins again with the original coordinates and dipoles.

Periodic boundary conditions - The periodic boundary conditions are employed so that the effects of having surface particles in the simulation box are avoided and as such the simulation mimics the bulk behaviour of the fluids. In a simple 2D example of the simulation box it can be imagined the simulation box has four boundaries. If the particles are moved towards the outside of the simulation box they are deposited to the opposing boundary of the simulation box.

Ewald Summation - The modelling of dipolar systems makes it necessary to perform a treatment of long range terms that arise from dipoles. Since the interaction is long range, falling away at 1/r3, the minimum image convention and a short range cutoff cannot be used as interactions with separations greater than half the cell length L/2 offer a significant contribution. The simulations in this work make use of the Ewald summation to calculate the long range dipole interactions. In this method the dipole-dipole energy in the infinitely periodic system comprised of the simulation cell and all its images is written as a sum of three terms for dipole pairs.

Multipole interactions - The dipole-dipole interactions have been discussed previously with regards to the Stockmayer fluid; however other multipole interactions may be important in the selfassembly processes between nanoparticles. The higher order multipole interactions, following the dipole-dipole interactions, are the dipole-quadrupole and quadrupolequadrupole interactions. The energy of interaction between two bodies i and j, with respective magnitude of dipoles μ_i and quadrupole θ_j moments, can be calculated using the dipole-quadrupole interaction tensor. The energy of interactions between two bodies i and j, with respective quadrupole moments θ_i and θ_j, can be calculated using the quadrupole-quadrupole interaction tensor.

Construction of crystal structures - The interactions between nanocrystals are of primary interest. In order to achieve understanding of these interactions between nanocrystals, nanoclusters need to be constructed with the polymorphs commonly found in nanocrystals. The unit cell allows for the construction of different morphologies of crystals structures; this is achieved by alteration of the lengths (a, b and c) and angles (α, β and γ) of the unit cell. The unit cell of the zinc blende polymorph has all three lengths of equal size and all angles are 90 degrees. The unit cell of the wurtzite polymorph has the lengths a and b of the same size, and the length c is $(\sqrt{8/3})a$. The angles α and β are both 90 degrees, and the final angle γ is 120 degrees. The unit cell of zinc blende is considered to be cubic, whilst that of wurtizte is hexagonal.

STOCKMAYER FLUID

In order to understand the evolution of nanostructures a computational model needs to be used that could possibly describe their formation, such as the one-dimensional nanowires observed. A significant motivation is to choose a model which is both relatively simple in terms of its parameterisation, and hence is computationally tractable and well understood. One possible computational model fitting the criteria is the Stockmayer fluid. This model in part contains a more familiar function, the Lennard-Jones 6-12 potential, which describes the interaction between two neutral spherical bodies i and j with diameters σ and well depth ε.

The Lennard-Jones 6-12 potential contains essentially two terms, a long-range attractive term. $(1/r_{ij})^6$, and a short-range repulsive term, $(1/r_{ij})^{12}$, to calculate the energy of interaction between particles. The well depth s simply determines the energy value of the minimum in this potential, whilst the minimum in the Lennard- Jones 6-12 potential always occurs at $2^{1/6}\sigma$ (if λ=1). This is exemplified by using set values for all these parameters. The Lennard-Jones potential graph is clearly shown to have the well depth s and minima at the expected positions.

The Lennard-Jones potential described contains an adjustable parameter λ, which can be changed from any value from zero to one. When this parameter is set to one then the typical Lennard-Jones 6-12 potential is achieved, however when set to zero the attractive component of the Lemiard-Jones potential is removed and only the repulsive components remains. This results in a transition from the Lennard-Jones potential to the soft sphere potential as the value of λ decreases from 1 to zero.

The Stockmayer fluid potential in addition to the Lennard-Jones potential contains a dipole-dipole energy interaction term between two bodies i and j.

Sakarwala Hiteshkumar Prakashkumar[1]* Dr. Gopal Chandra Bag[2]

the magnitude of the dipole moments on each body are represented as μ_i and μ_j respectively.

The Stockmayer fluid, for which $\lambda = 1$, encompasses the $U_{ij}(LJ) + U_{ij}(DD)$ term to give the total energy of the system, $U_{ij} = U_{ij}(LJ) + U_{ij}(dd)$. The dipole-dipole interaction energy can be derived by considering the fact that dipole moments in a neutral body arise from an imbalance of charges, the interaction energy of two charges vary according to $1/r_{ij}$ and are represented in terms of a tensor.

CONCLUSION

In this paper the formation of potentially complex nanostructures from seemingly simple nanoparticles has been investigated. The Monte Carlo simulation method has been employed throughout. The resultant structures range from simple nanowires to more complex pod structures. The nanoparticles have been modelled as soft spheres with additional dipole moments, also known as the Stockmayer fluid potential. In addition the Stockmayer fluid model was modified to represent more complex nanoparticles in order to model the formation of tetrapod structures observed experimentally.

REFERENCES

Cheng, C. T.; Chen, C. Y.; Lai, C. W.; Liu, W. H.; Pu, S. C.; Chou, P. T.; Chou, Y. H.; Chiu, H. T. Journal of Materials Chemistry 2005, 15, 3409.

Cozzoli, P. D.; Manna, L.; Curri, M. L.; Kudera, S.; Giannini, C.; Striccoli, M.; Agostiano, A. Chemistry of Materials 2005, 17, 1296.

Cui, Y.; Banin, U.; Bjork, M. T.; Alivisatos, A. P. Nano Letters 2005, 5, 1519.

Jun, Y. W.; Seo, J. W.; Oh, S. J.; Cheon, J. (2005). Coordination Chemistry Reviews, 249, 1766.

Kan, S. H.; Aharoni, A.; Mokari, T.; Banin, U. (2003). "Shape control of III-V semiconductor nanocrystals: Synthesis and properties of InAs quantum rods"; Nanoparticle Assemblies Meeting, Liverpool, England.

Kudera, S.; Carbone, L.; Zanella, M.; Cingolani, R.; Parak, W. J.; Manna, L. (2005). "Synthesis and perspectives of complex crystalline nano structures"; International Conference on Trends in Nanotechnology, Oviedo, SPAIN.

Laurent, S.; Forge, D.; Port, M.; Roch, A.; Robic, C.; Elst, L. V.; Muller, R. N. (2008). Chemical Reviews, 108, 2064.

Lee, H.; Yoon, S. W.; Ahn, J. P.; Suh, Y. D.; Lee, J. S.; Lim, H.; Kim, D. (2007). "Synthesis of type II CdTe/CdSe heterostructure tetrapod nanocrystals for PV applications"; 17th International Photovoltaic Science and Engineering Conference, Fukuoka, JAPAN.

Sinha, A. K.; Seelan, S.; Tsubota, S.; Haruta, M. (2003). "Catalysis by gold nanoparticles: epoxidation of propene"; 16th National Meeting of the Catalysis- Society-of-India/1st Indo-German Conference on Catalysis, Hyderabad, INDIA.

Sonvico, F.; Dubernet, C.; Colombo, P.; Couvreur, P. (2005). Current Pharmaceutical Design, 11, 2091.

Corresponding Author

Sakarwala Hiteshkumar Prakashkumar*

Author Designation

E-Mail – hiteshpsakarwala@gmail.com