Indian Journal of Pure & Applied Physics
Vol. 63, May 2025, pp. 416-426
DOI: 10.56042/ijpap.v63i5.18117

Bench Top Process and Their Scalability for Industrial Production of Nanoparticles Insights

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Received: 21 March 2025; accepted: 21 April 2025

Production of nanoparticles at industrial scale is certainly required in near future as they are getting successfully executed in different emerging technological areas. Therefore, the scalability will be the one of the most important criteria with respect to the market demands of the nanoparticles. Some of the bench top models experiments are very expensive and may not be approved for the industrial production. The two most important nanocrystals fabrications process in the colloidal phase can be divided to two categories are heat-up and hot-injection method which is successfully used to produce the nanocrystals at the laboratory scale in very economical way. Additionally, both the process is capable of producing nanoparticles with good control on their shape and size. However, these methods have some limitations with respect to the precursor. This review will focus on nucleation and growth process in heat-up and hot-injection method and their pros and cons in scalability at industrial scale with emphasis on quantum dot, iron oxide nanoparticles and sodium lanthanum fluoride.

Keywords: Colloid, Nanostructure, Crystalline, Hydrothermal, Nucleation & Growth, Hot-injection method, Heat-up method

1 Introduction

Nanomaterials term is used for the material's when their at least one or more dimension into nanometer scale. One nanometer approximately billionth of meter or 10^{-9} m[1-12]. This measuring unit can be further simplified as the arrangement of ten hydrogen atom in the straight line. Figure 1 presents the comparisons of the nanomaterials sizes that suggest that the size of the Deoxyribonucleic acid (DNA) molecule ~2.5 nm, water molecule ~ 0.27 nm, and most of the atomic lattice spacing below 0.3 nm[13,14]. It is one of the fastest growing areas across all branches of sciences and engineering due to the huge investment in this field globally. The main reason in growth in nanotechnology is wide application of the nanomaterials in medical science and engineering technologies. Unambiguously the nanotechnology was idea of the noble laureate Dr. Richard Feynman in his influential lecture at California Institute of Technology having the title "There is Plenty of Room at the Bottom" on December 1959 [14]. Though the noble metal in the colloidal (1-1000 nm) state were in the use since the Greek and the Roman era.[2] The tunable shape and size of the nanoparticles makes them highly applicable in various field such as optics, optoelectronics, and photonic displays[4,5,15].

Moreover, there is huge demand of nanomaterials in the printing industries, chemical industries, and space industries[16]. To fulfill the requirement of the technology with respect to good control on the size and shape various new synthesis methods and techniques have been developed in the past as reported in the recent literature[17,18]. In recent years, the synthesis is carefully getting tuned to find a balance between the nucleation and growth process to achieve the monodispersity. Monodispersity of the nanoparticles refers the state when the nanoparticles have nearly same size that is they have approximately zero polydispersity indexes during the observation under the transmission electron microscope[19,20]. To achieve the monodispersed nanoparticles greater extent of control over the nucleation process is certainly be required. The factors on which the nucleation process depends are, the type of reactant precursor, reactant concentration, temperature, partial pressure, and types of the ligands involve in the reaction process. Nucleation is a phenomenon that occurs usually in random way and it may differ between two batches that have been synthesized in nearly same condition.

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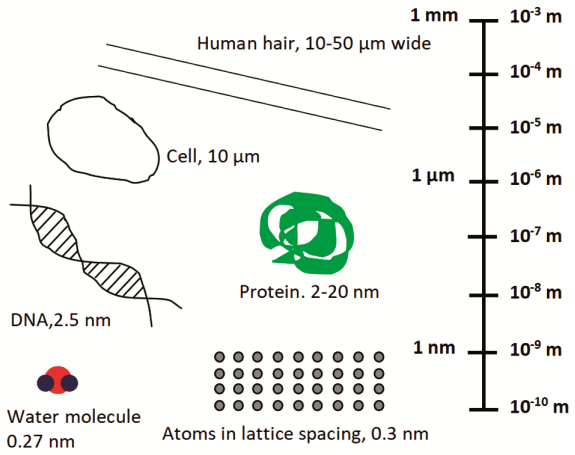

Fig. 1 — Scale representing dimension of nanomaterials

Usually, in the wet chemical and colloidal synthesis process the burst nucleation and diffusion control growth rate are two essential and effective factors to control the uniformity of the nanoparticles[21,22]. The burst nucleation is a transient process appears just after the super-saturation of the monomers but even that cannot assure the uniformity of nanoparticles[7]. The diffusion control suffers the additional challenges in colloidal solution because; the nucleation can start from the wall of a container (scratch position)/the stirrer/ the foreign particles in the solvent. Controlling these parameters is very much difficult than it appears because it is possible that nucleation starts at different time scale in similar reaction process which cause distinct variation in the sizes between the two batches.

Basically the solution based colloidal synthesis can be divided in two categories at the laboratory scale the first can be a low temperate synthesis and high temperature (less than 350 °C). The high temperate synthesis can be further divided into hot-injection and non-injection methods (non-injection is also known as Heat-up method). Hot-injection process is relatively newer method, was reported by Bawendi and his co-worker in 1993 specifically for the synthesis of the quantum dots (QD) of cadmium chalcogenides in colloidal system[23]. However, later this process was used for the synthesis of the variety of the nanoparticles. This synthesis process undergoes a rapid formation of the colloids in presence of more than two reactants at high temperature after injecting a given seeds/reactant. Currently, the hot-injection method is the most effective strategy and common approach to prepare the nanocrystals in the colloidal state. Aforementioned, these processes show batch to batch inconsistency at laboratory scale therefore, they would add more error during their production at the industrial scale. Some of the key challenge at industrial scale would be segregation of the intermediate, product and waste product, they might have lower yield, more sophisticated design of machine, and analysis of the safety risk assessment at industrial scale.

Implementation of nanoparticles is more important now a day than their synthesis. Indeed, it is getting executed very well in the various fields irrespective to the quality (homogeneity) of nanoparticles leading to the technological advancement. However, the shape controlled nanoparticles will be more applicable in the field of biomedical engineering such as for the control drug release[24]. In the hot-injection process, at a certain stage of a reaction when the monomers injected are (M), subsequently they lead to super-saturation and exceed the equilibrium concentration (M_0), which causes usually formation of the smaller nanocrystal faster than the larger nanoparticles. It is designated as a focused down nucleation process that increases the chances to obtain nearly monodispersed particles[7,21].

In other word, we can say we are controlling the Oswald ripening by injecting the nanoparticles seed that maintaining the monomer concentration above the critical threshold. However, this method can have inherent limitation in the scaling up process, when the injection volume is large, usually 20 % of the overall solution, which can lead to the inhomogeneities. Additionally, in the hot-injection process the variation in batch to batch possible due to variation time taken by different users. Consequently, the process can be effective for the small batches of synthesis of nanocrystals but that may not be true for the bigger batches of synthesis of the nanocrystals.

Alternatively, in the heat-up process the precursor materials are steadily heated at high temperature in the presence of ligands and suitable solvent. Suitable solvent means the solvent must have the high boiling point otherwise; the solvent will be evaporated at high reaction temperature. Heat-up process is also reliable and efficient method to achieve good quality nanoparticles. Because it allows the preparation of nanoparticles in single pot and can be salable to industrial scale from bench top laboratory process. The reliable means during the synthesis process the variation in the quality nanoparticles in terms of size and shape can be minimized from one batch to other bath of nanoparticles [7,22]. The heating method can be further classified according to the heating sources

used to heat the reaction mixture such as heating mantle method, electromagnetic induction heating method, microwave heating method etc. The heating mantle utilizes alternating current after plugged in the circuit while the induction heating utilizes the eddy current, which loops current induced within the conductor by the variation in the magnetic field in the conductors.

Microwave is other technique that utilizes the microwave to heat the reaction mixture. Though all the method is user dependent but it more user friendly process compared to hot-injection process. Unlike a hot-injection process it does not dependent on the time of the injection which is really crucial in the hot injunction process. Therefore, this method can circumvent some of the drawback of the hot-injection process. Figure 2 represents a common step involves in the heat-up and hot-injection methods. In heat-up process all the reactants are added in a reacting vessel in the beginning therefore, the reaction mixture and the temperature have the liner relation and it proceeds in control manner. This process is scalable compared to a hot-injection process by carefully selection of legends and precursor that enable the nucleation rapidly and produces greater number of the nuclei in shorter span.

2 Variation in Surface Atoms at Nano-Scale

Relation between the surface atom and size of nanoparticles are inversely proportional. Therefore, as a size particle decrease the surface atoms increases. For instance, as shown with a bar diagram in Fig. 3, the palladium metal nanoparticles surface atoms has increased significantly with the decreasing palladium cluster size. It was shown by Nutzenadel et al.[25] with the varying palladium cluster dimentaion between 1 to 4 nm based on theoretical modeling, which is later on fond to be in agreement other metal nanoparticles. They found the when the palladium cluster were nearly 4 nm the surface atoms where 30 % of the total atoms present in the cluster. Subsequently, on narrow down the size of cluster to 1 nm the surface atom increased to nearly 75 %. These observations have been also seen in chemical reactions if their variation surface atoms between samples. For instance, the powder materials are far more reactive then their crystalline forms because in the case of powder sample (smaller dimension) more surface atoms available to take part in the chemical reaction. As an example the reaction between zinc dust and concentrated sulphuric acid is takes palace rapidly compared to the reaction between zinc crystal and

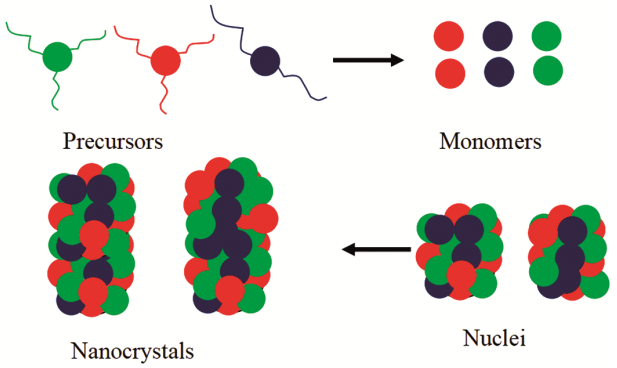

Fig. 2 — Common approach in the heat-up and hot-injection methods where the precursor reacts to form monomer that converted to nuclei subsequently produced nanocrystals at high temperature

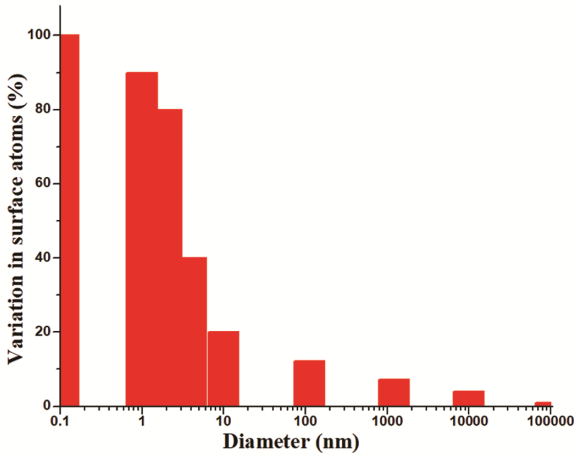

Fig. 3 — Bar plots shows the variation of the surface atoms of nanoparticles with the size of nanoparticle

sulphuric acid. It is basically due to the higher surface atom at low dimension that increases the surface-to-volume ratio at nanoscale. For a spherical particle, it can be justified by dividing the surface of the particle by its volume such as, i.e., $4\pi r^2/4\pi r^3/3 = 3/r$ where r is radius of a particle. For the particles having radius 1 nm the surface is volume ratio is 3 but as the particles radius increase to 2 nm the surface atom drop to half of the total surface atom. Large number of surface atoms compare to their bulk counterpart could have lower symmetry, lower number of neighboring atoms compared to bulk structure which enhance their interaction with the surrounding that eventually modified their photophysical, photochemical, magnetic properties, etc. at nanoscale.

3 Basic Concept of Nucleation

Nucleation process triggers with a small molecules ion, atoms that act as seeds act as templates for the

nucleation to start usually in liquid or vapor phase. Subsequently, the atoms are produced that arrange themselves in a specific pattern of the nanocrystals that is the final crystal structure of a compound. This is known as bottom up process to produce the nanocrystals structure with smaller building block of atoms. The seeds can also be added extrinsically sometimes to enhance the nucleation process in a control manner. Usually, extrinsic addition process is adopted at industrial scale to produce the nanocrystals. Mostly, a nucleation takes places in two ways that is homogeneous and heterogeneous. Usually, the heterogeneous nucleation is easier to proceed the nucleation with respect to homogeneous nucleation due to the lower favorable energy. If a reaction is taking place in a liquid phase then it would be proceed mostly by a heterogeneous process, from the inhomogeneous part of the system such as container surface, stirrer bar or any impurity present in the system and grain boundaries while the homogeneous nucleation believed to start from bulk of the solution where the nuclei are evenly distributed throughout the system. Homogeneous nucleation occurs in solution phase under an extremely high level super-saturation of the monomers that produce more nuclei but it promotes the crystal growth (the one formed earlier will keep growing) and leads to broader size distribution. Generally, the homogeneous nucleation process the total change in Gibbs free energy can be sum of the surface energy and the volume energy of a particle that can be described as Eq. 1 given below[2,26]:

$$\Delta G = 4\pi r^2 \sigma + \frac{4}{3}\pi r^3 \Delta G_v \quad \ldots (1)$$

where, r is radius of a particle , σ is surface energy per unit area and ΔG_v energy per unit volume.

The ΔG_v eventually is the energy difference between crystalline phase and solution phase of the monomer as given by Eq. 2 as below, where R Gas constant and T is temperature of the reaction. S, and V_m represent super-saturation and molar volume of the monomer.

$$\Delta G_v = -RT\ln S/V_m \quad \ldots (2)$$

On differentiation, ΔG with respect to r and keeping d(ΔG)/dr = 0, the energy maxima between the reactant and product can be obtained[26].

$$\frac{d(\Delta G)}{dr} = 8\pi r\sigma + 4\pi r^2 \Delta G_v \quad \ldots (3)$$

Now, $8\pi r\sigma = -4\pi r^2 \Delta G_v$ and $r^* = -\frac{2\sigma}{\Delta G_v}$ or $r^* = \frac{2\sigma V_m}{RT\,(lnS)}$ … (4)

In the above equation r replaced by r^* that is critical radius. On putting the value of r^* in Eq. 3 produces the critical free energy term ΔG*. The ΔG* is minimum free energy required for particle to grow in solution. Figure 4 shows the diagram of changes taking place in nucleation and growth process.

$$\Delta G^* = \frac{16\pi\sigma^3}{3\Delta G_v^2} \quad \ldots (5)$$

On substituting the ΔG_v from Eq. (2) in Eq. (5), the final equation is given by Eq. (6)

$$\Delta G^* = \frac{16\pi\sigma^3 V_m^2}{3R^2T^2\,(\ln S)^2} \quad \ldots (6)$$

The rate of formation of nuclei at a particular time can be described by theArrhenius type Eq. 7. If at that point of the energy required for the formation of nuclei is ΔG_N then it must be equal to ΔG^* that is critical free energy need to sustain the nuclei in solution. If we substitute the value of ΔG^* (as ΔG^* equal to ΔG_N) in Eq. 7 then Eq. 8 will be obtained[26].

$$\frac{dN}{dt} = A\exp\left[\frac{-\Delta G_N}{RT}\right] \quad \ldots (7)$$

$$= A\exp\left[\frac{-16\pi\sigma^3 V_m^2}{3R^3T^3(\ln S)^2}\right] \quad \ldots (8)$$

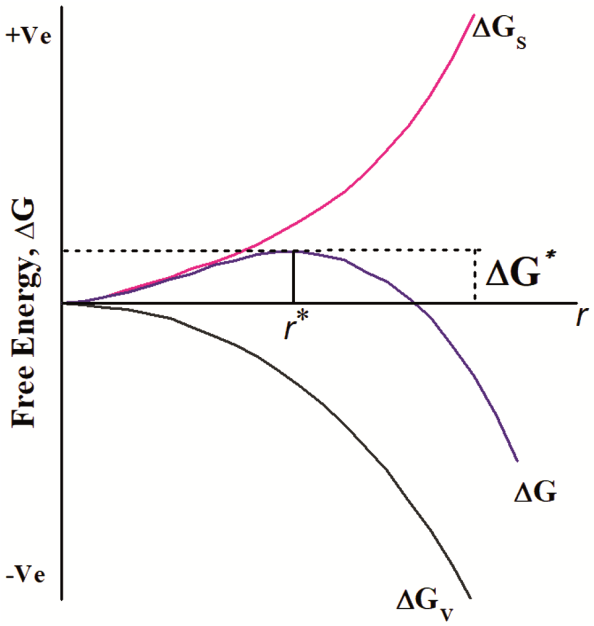

Fig. 4 — Variation of energy in nucleation and growth process

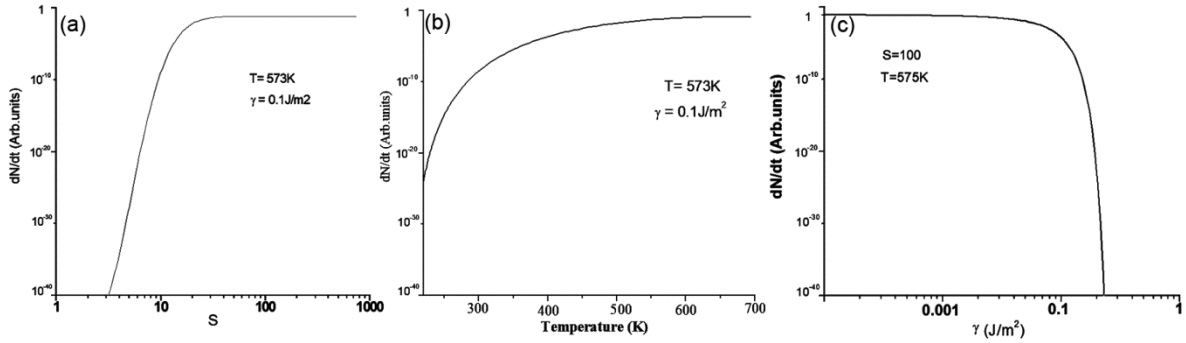

Fig. 5 — Representation of Nucleation rate with (a) super-saturation, (b) temperature, and (c) surface energy[22]

Where, N is one mole of nuclei, Pre exponential factor A, T is temperature, Gas constant R respectively. It is clear from the Eq. 8, the variable parameters are temperature, supersaturating and surface energy for given reaction. The plots of these three variable parameters versus the nucleation rate as shown in Fig. 5. The figure suggests that the nucleation rate extremely sensitive to the level of super-saturation compare to other parameter therefore it is very important parameter for both heat-up and hot-injection process. As super saturation S increases from 2 to 4 the rate of nucleation increased to 10^{70} times[22]. The nucleation rates can be controlled by using different types of surfactant and varying their concentration.

The hot-injection and the heat-up method differ in the nucleation process but both the process produces the uniform nanoparticles that means the mechanism of the controlling their size may be very similar. In both the process are accompanied by the burst nucleation and size focusing after the high super-saturation of the monomer. But they differ in the process of attaining the super-saturation. In the hot-injection process is the pre-synthesized small nano-seeds are rapidly added at high temperature while in heat-up method it is believed that the higher energy barrier of the homogeneous nucleation lengthen the nucleation process and suppress the nanocrystals formation until the nucleation high is enough to accomplish the stage of burst nucleation.

3.1 Two Major Theories Growth Process

LaMer gave the first theory about the nucleation and growth process by studying decomposition of sodium thiosulfate. The process explained in three steps first increase in the concentration of monomer and their number of collision in solution subsequently burst nucleation in second step followed by growth in third step. However the lower concentration of monomer can inhibit the reaction [21]. Additionally, the separation between the nucleation and growth process is important to achieve the narrow size distribution. Three stages of the reaction process are shown in Fig. 6 with the plot of monomer concentration versus time.

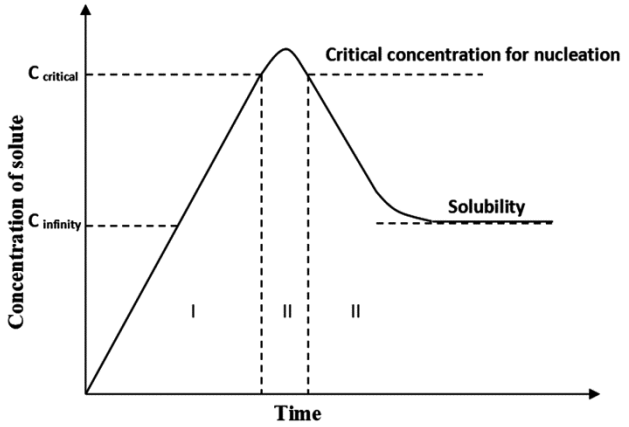

Fig. 6 — Demonstration of nucleation and growth via LaMer diagram[21]

It is clear from the graph burst nucleation occurs when the monomer concentration is above the critical concentration. This is also applicable for heat-up process but the hot-injection process.

3.2 Growth by Ostwald Ripening and Coalescence

It is process in which a system tries to attain the stability by minimize the overall energy. For instance, the nanoparticles with higher surface energy grow to bigger particles that have greater stability. Ostwald ripening is a condition where the smaller particles of high energy therefore they interact with solvent and re-dissolved and absorbed on the bigger particles and the overall energy of the system minimizes and provide greater stability. Coalescence is process in which the smaller nanoparticles two or more combined together to form the bigger nanoparticles.

4 Nanocrystals Formation Via Heat-Up Process And Hot-Injection Process

This section compares the highly uniform nanocrystals prepared by heat-up process and hot-injection process with example of QD, iron oxide and sodium lanthanum tetra-fluoride.

4.1 Quantum Dots

The quantum dot is special class of materials, which is intermediate between the molecular and bulk form of the matter. In these materials the quantum confinement of electron and holes occurs in all three dimensions, therefore on decreasing the particles size the effective band gap (i.e. HOMO-LUMO) increases subsequently, the optical absorption and emission peaks shift toward the higher energy[23,27]. Though they showed many novel properties, such as electronic and physical properties compared but their crystal pattern remains same as of the bulk materials. QD can be prepared at low and high temperature depending on the nature of the quantum dot via heat-up process with fairly good control of the size of the QD and quantum rods[28,29]. Yang *et al.*[30] had synthesized CdSe and CdTe based quantum dot via Heat-up process. The CdSe were synthesized at 240 °C as growth temperature because of suitability of the cadmium precursor that decomposes above 226 °C. Additionally, the selenium powder was chosen as an effective selenium precursor because it decomposes above 221°C and becomes slightly soluble in octadecene at about 190 °C.

Figure 7 shows the florescence intensity their absorption maxima in (7a) and (7b) obtained from the CdSe nanocrystal. The reported quantum yields were around 30-40%. The PbSe QD had shown the standard deviation below 5 % as shown TEM image in figure 7.The QD obtained mostly in the zinc blend (ZB) structure not in the wurtzite (W) structure. Recently Luo *et al.*[31] prepared the CdSe QD with microwave heat-up process for industrial scale production. They have used the effective heating rate in the reaction process that reduces the nucleation process and narrows the nucleation window and provides the greater control on the QD.

Hot-injection method of synthesis is more common process for the production of quantum dots in particular the lead based QD. The lead based QD emits near infrared region between 1 to 3 μm have variety of application in the field of bio-imaging, sensors inorganic solar cells, telecommunications and in fabrication of the light emitting diodes. Usually, the lead precursor is at high temperature is injected with the sources of sulfur or selenium leading to the formation of PbS or PbSe QD[32,33]. The common stabilizer that was used in this process was oleic acid in solvent like octadecene which is non-coordinating in nature. Several groups had produced the uniform QD past literature of size ranging between 3-10 nm[28,29,33].We had also prepare the PbSe QD[34] by using oleylamine as reducing agent at low temperature by hot-injection method as shown in Fig. 8, and studied the photoconductivity behavior. The sizes of the PbSe QD were between 4 to 5 nm with 95 % quantum yield. These PbSe QD were called magic size clusters. The term magic size is used when the PbSe QD has well defined sizes and they undergo only nucleation without further growth process. That means the Ostwald ripening process does not occur in the case of the magic size clusters, because the tiny small particles of uniform size do not re-dissolved to increase the size of the bigger particles.

The hybrid device was fabricated using the PbSe of thickness ~5 nm and 2-5-(2-ethylhexyloxy)-1,4-

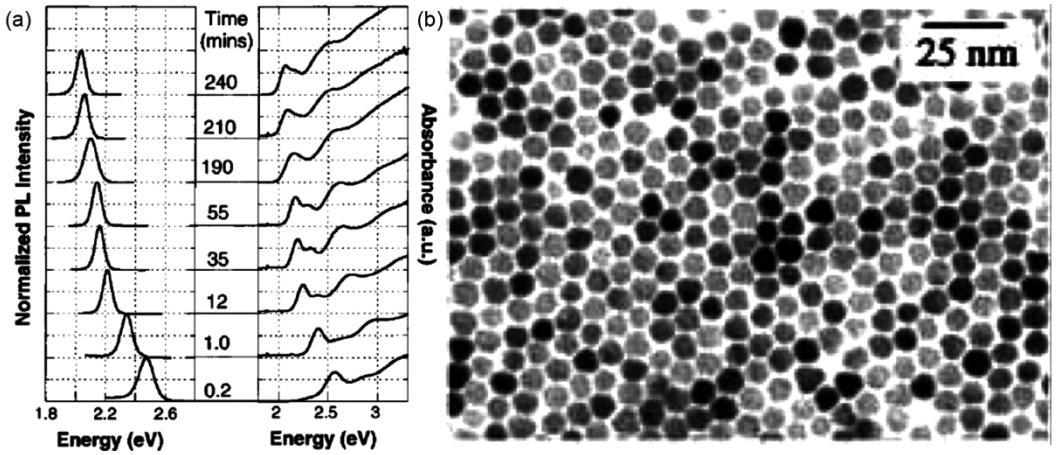

Fig. 7 — Chronological progress of (a) fluorescence, (b) absorption spectrum, and (c) TEM image of CdSe QD[29]

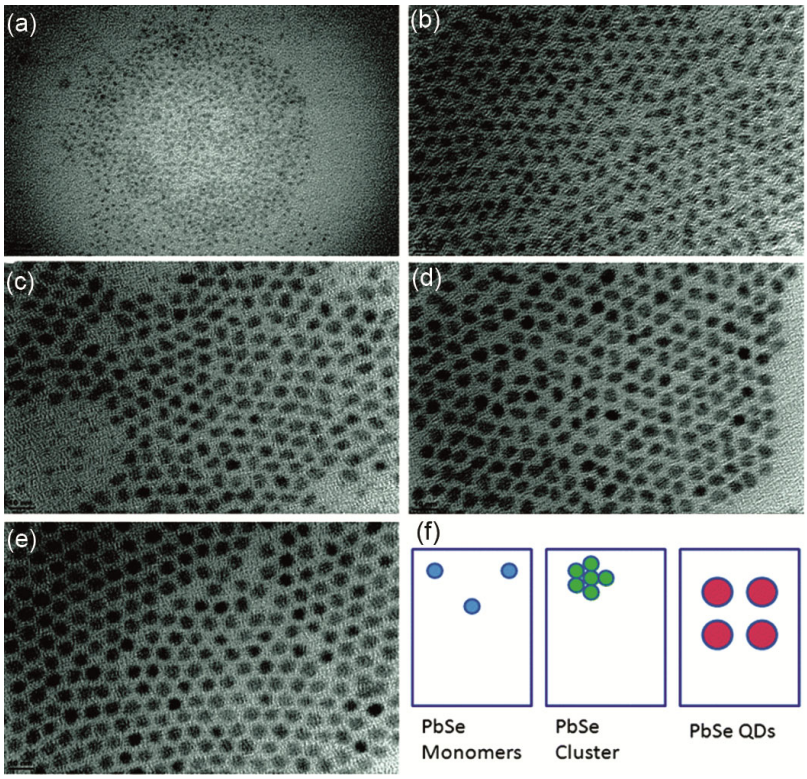

Fig. 8 — TEM images of PbSe QD taken out at different intervals (a) 0.5, (b) 2, (c) 5, (d) 10 (e) 30 min and (f) represent formation of QD from the monomers[34]

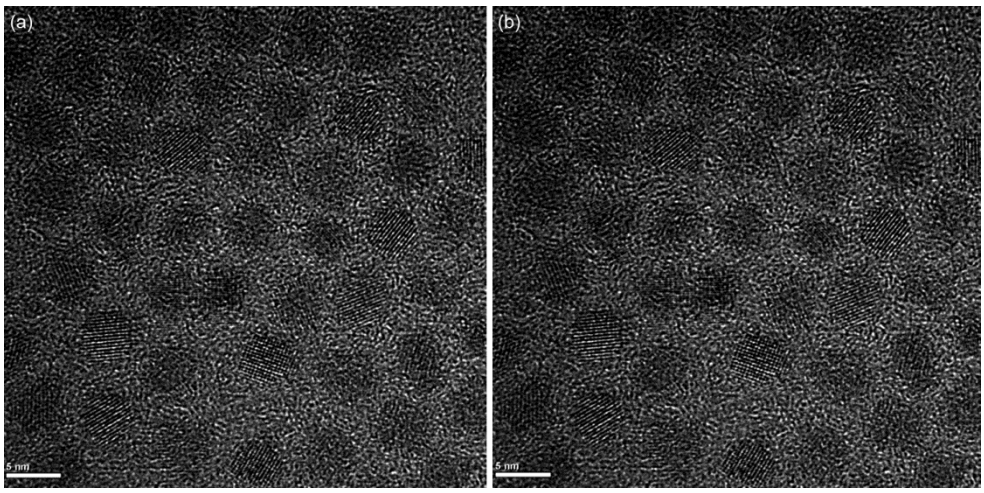

Fig. 9 — TEM images of lead selenide core (left) and cadmiumselenide core/shell (right) QDs[35]

phenylene vinylene for the photoconductivity study, that showed the improved conductivity both in dark and light area owing to the absorption of near IR photon darker region and visible photon in presence of light respectively. Previous report published on QD in core/shell structure [35] also suggested hot-injection process provide the good control on the size of quantum dot in core/shell arrangement as well. For instance, Fig. 9 shows the core shell arrangement of PbSe/CdSe QD with uniform distribution with size ~4 nm. Initially the core was prepared by the hot-injection process the shell was created by applying the cation exchanger process which was developed by Alivisatos and co-workers in 2004[36]. The cation exchange process was well known for the bulk reaction but their studied suggested that the rate of the

cations exchange process was rapid for QD. For instance, the synthesis of PbSe/CdSe core/shell was achieved by controlled exchange of Pb^{2+} for Cd^{2+} at the surface of the PbSe QD. The name cation exchange is appropriate because the exchange is taking place only for cations. This is also categorised as the hot-injection process but cation exchange is carried out at modest temperature nearly 80°C that prevent the optical properties of the QD unlike the epitaxial growth of the shell material at 150°C that suffers with a loss in the optical properties.

4.2 Iron Oxide Nanoparticles

The iron oxide nanoparticles have immense uses in magnetic data storage, drug delivery, bio sensing, imaging and in hypothermia application due to the biocompatibility character, chemical stability and substantial accumulation at diseased site[37,38]. At present it is more fascination in the field of magnetic resonance imaging (MRI) as they bring the change in T_1 and T_2 relaxations rate of the water protons present in the body and known as contrast agent. Additionally, these magnetic nanoparticles are very useful as a therapeutic agent because of their heating ability which is dependent of the size of the nanoparticles is effective in killing the cancer cell[39]. Usually, all the polymorphs of the iron oxide can be prepared by the hot-injection process. But the polymorphs such as hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4), have interesting properties such as they high superparamagnetic behavior high coercivity and low Curie temperature. Solodove *et al.* [40] reported the Fe_2O_3 nanoparticles by thermal decomposition of iron-oleate complexes via Heat-up process to understand the mechanism of the formation of Fe_2O_3nanoparticles that was unknown due to the complexity in process. The diameter of Fe_2O_3nanoparticles was tracked by the NMR relaxation method. The NMR analysis was studied with respect to T_1/T_2 ratio and value of $1/T_2$ values. The analysis suggests that nucleation and nucleation growth process can proceed in two ways. In presence of the excess of oleic acid in the reaction mixture the LaMer model is followed and the nucleation and growth process were separated that goes in two steps first is the nucleation followed by the growth process. In case of absence of oleic acid the nucleation and growth were never be separated that would mostly lead to non-uniform nanoparticles. Therefore, addition of the excess of oleic acid in the beginning of the reaction the Heat-up process follows the same path of the hot-injection process as the sufficient amount of oleic acid act as fuse for the burst nucleation to occur. Earlier, Kwon *et al.*[41] also prepared the Fe_2O_3 nanoparticles by the Heat-up process. They studied the decomposition kinetics of the iron-oleate complex via Heat-up process. The aliquot was taken out at different interval of time (Fig. 10) showed uniform distribution of Fe_2O_3nanoparticles.

As can see in TEM image initially there is lower concentration of the nanoparticles subsequently,

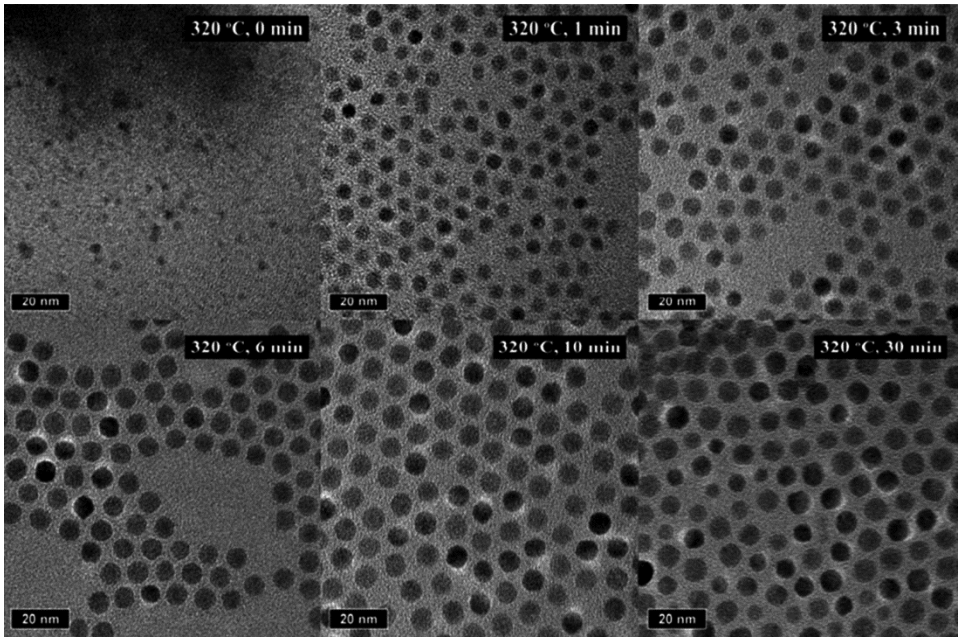

Fig. 10 — TEM images of Fe_2O_3 nanoparticles, the aliquot taken out at different interval of time[41]

sudden increase in the concentration of the nanocrystals due to the burst nucleation followed by the narrowing size distribution. In another report, Lassenberger *et al.*[42] prepared the uniform Fe_2O_3nanoparticles by heat-up process. Therefore, the heat-up method have shown immense potential to have control the shape and size of the nanoparticles and any desired product can be prepared by tuning the reaction condition.

Hyeon *et al.*[43] followed the hot-injection method to synthesize high crystalline mono-dispersed magnetite (Fig. 11) by injecting $Fe(CO)_5$ in to a mixture of lauric acid, octyl ether, and $(CH_3)_3NO$ at 100 °C under argon atmosphere. Recently, Herman *et al.*[44] had synthesized the iron/iron oxide core/shell nanoparticles by injection, bis(η5-1,3,5-exo-6-tetramethylcyclohexadienyl) iron(II), [Fe(η5 - $C6H3Me4)_2$] into the octadecene (ODE) with the presence of oleylamine at 300ºC. However, solid precursor must be avoided as injection source because the rate of mixing of solid precursor with the solvent will be slower compared to liquid phase dispersion of the precursor with the solvent. The small delay in the mixing of solid solute with solvent at high temperature can lead to the non-uniform nanoparticles.

4.3 Synthesis of Sodium Lanthanum Tetra-Fluoride ($NaLaF_4$ La= Y, Gd, Dy) Nanoparticles

Lanthanide ion in trivalent state has attractive properties both in the up-conversion or in down conversion process. However, the up-conversion phenomenon is more useful for the biomedical engineering such as for marking cells and detection of DNA because the NIR light has no damage to cells

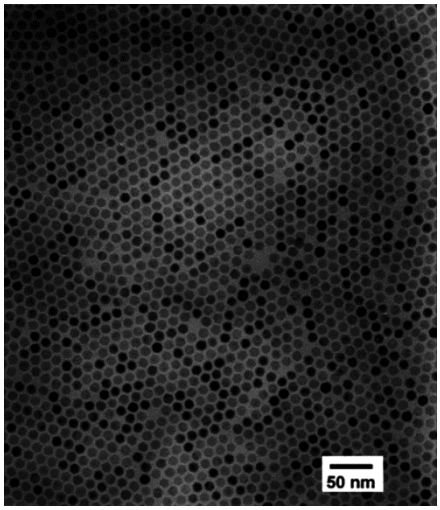

Fig. 11 — TEM image of maghemite nanoparticles[43]

and tissues[45–49]. In the particular the $NaYF_4$ (low phonon energy ~360 cm^{-1}~ 45 meV) and frequently used as up-conversion host materials. The $NaYF_4$exist in two phases, hexagonal and cubic but the hexagonal crystal structure is more efficient for the up-conversion than the cubic crystal structure $NaYF_4$ owing to the higher degree of Crystallinity[50]. TheHeat-upprocess is used to prepare the sodium yttrium fluoride doped with ytterbium and erbium ($NaYF_4$:18%Yb, 2%Er) nanocrystals in spherical shape or plate like structure with good control on the particles size and shape with the help of time and temperature[51]. It is more common method for preparation of sodium lanthanum tetra-fluoride. Initially, the entire constituent was mixed in appropriate required proportion with oleic acid as surfactant in high boiling solvent octadecene at 150 °C that produces their oleates. Subsequently, the solution was cooled down to room temperature and precipitated with the addition of methanol solution containing NaOH and NH_4F in the required and pre-calculated amount. Afterward the methanol form the solution was evaporated at 70°C, the temperature of mixture was quickly raise to the 300 °C for 1 h under a argon atmosphere that produce the uniform hexagonal phase of the$NaYF_4$:18%Yb, 2%Er nanoparticles which is green emitter on exciting with 980 diode laser. Variation in the dopants[53] ratio and nature of the dopants can modify the emission.For example, doping in $NaYF_4$(20%Yb^{3+}, 2%Er^{3+}), 70%Yb^{3+}, 2%Er^{3+}) or (20%Yb^{3+}, 0.5%Tm^{3+}) can modify the emission as shown in Fig. 12.

The hot-injection process were also used to prepare the sodium lanthanum tetra-fluoride but in limited extent[47,52]. For instant Tian *et al.*[47] prepared the hexagonal $NaYF_4$:Yb, Er nanocrystals by hot-injection process by injecting the rare-earth trifluoroacetate solution (in oleic acid, trioctylphosphine and octadecene) in the solvent (in oleic acid, rioctylphosphine and octadecene) heat at 300 °C under nitrogen atmosphere and the reaction was continued for 1h to accomplished the product. They also prepared the hexagonal NaYF4:Yb, Er via Heat-up process and the results of the both process were compared. The size of nanoparticles prepared by the Heat-up process were in the range of 6-18 nm with the average nanoparticles diameter 12.4 nm while the size of the nanoparticles prepared by the hot-injection process were also in the similar rage but small change observed at different stage of the reaction.

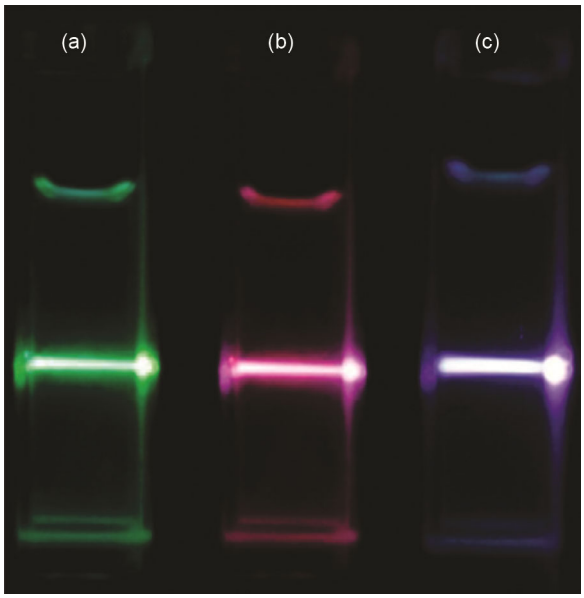

Fig. 12 — Optical emission form sodium yttrium tetra-fluoride nanocrystals in hexagonal phase on exciting with 980 nm diode laser dispersed distilled water (A)sodium yttrium tetra-fluoride doped with 20%Yb^{3+},2%Er^{3+}; (B) sodium yttrium tetra-fluoride doped with 70%Yb^{3+},2%Er^{3+}; (C) sodium yttrium tetra-fluoridedoped with 20%Yb^{3+}, 0.5%Tm^{3+} samples[53].

5 Conclusion

We have compared and discussed the two well-known methods heat-up process and hot-injection process for the colloidal synthesis. The comparison is done with respect to the quantum dot, iron oxide nanoparticles and sodium lanthanum tetrafluoride. Undoubtedly, the both process have taken the research and development activity to high level in economical approach at the laboratory scale. But taking it from the table top model at laboratory scale to industrial scale for production of nanoparticles can be challenging with respect to the yield of nanoparticles, segregation of intermediate and final product and risk management due the larger scale production. In our view heat-up process can be scalable because all the precursors are added at the begging of the reaction unlike the hot-injection process where the injection is done at different stages of the reaction with respect to time and required product. For the production of the bigger batches the too large injection volume would be required which is impractical and unrealistic. Both the methods provide the good controls on the shape and size of the nanoparticles but both are limited with respect to the precursors. In our view the scalability is more important factor because with the increased industrial demand it certainly needs to scale up the synthesis to fulfill the requirement. There are potent literatures that suggest that small variation in the standard deviation with respect to the size of the nanoparticles will not change the properties drastically. Therefore, we expect the field to grow in future with respect to their production, so that these nanoparticles can be available to the laboratory and industry just like any other chemicals.

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