

Quality of crystallization of colloidal nanoparticles

Amani Alruwaili
RMIT University, Australia
Email: hhhhhh11@windowslive.com

Abstract: *This paper undertook a systematic review on the methodological studies on the processes and quality of crystallisation of colloidal nanoparticles. Google Scholar database search using the topic itself as the search term yielded 25 usable papers. The review revealed the existence of innumerable methods for the production of equally varied types of colloidal nanoparticles and the effects of these on the outcomes in terms of quality of crystallisation was evident. Many options appear to be available for anyone to mass produce these particles for any of the numerous commercial uses. However, the selection of the most suitable method has been rendered difficult by the multiplicity of methods and outcomes. The implication of this study is that there is a need for research to identify optimal methods for production of colloidal nanoparticles for targeted commercial uses.*

Keywords: *Quality of crystallization, colloidal nanoparticles, review*

1. Introduction

In the early days of finding methods of crystallisation for colloidal nanoparticles, three processes for continuous synthesis of nanoparticles were described by Okuyama and Lenggoro (2003). The first was a salt-assisted aerosol decomposition (SAD) (spray pyrolysis) process. The process allowed adjustment of sizes, narrow range of size distribution, high crystallinity and good stoichiometry. The process was used to produce spherical-shaped porous particles with nanoscale ordering porosity. The second process was a spray drying method to produce zinc oxide quantum dots in silica nanoparticles matrix using a colloidal mixture as the precursor was also developed. The third process was a combined sol–gel and spray drying method was also reported. Another common system used for crystallisation for colloidal nanoparticles in the early days was zeolite crystallization. In a review, Tosheva and Valtchev (2005) described the results on zeolite crystallization mechanisms obtained by using colloidal zeolites as model systems. Also reviewed were the methods for deposition of zeolite nanocrystals from suspensions onto supports of different shapes and compositions, which are used for the fabrication of zeolite films and membranes.

The impact of methodology of crystallisation on the quality of crystallisation of different types of colloidal nanoparticles has been a rich research area due to the multifarious uses of colloidal nanoparticles in many fields. This paper reviews some of the recent works done on this issue in detail.

2. Methodology

This is a simple qualitative preliminary review intended to be a systematic review. The review was aimed at developing an understanding of the interaction between methods of crystallisation of colloidal nanoparticles and the quality of crystallisation.

Google Scholar was used as the search engine for selecting the papers using the review topic itself as the search term. Any paper dealing with crystallisation of nanoparticles of colloidal nature at least in part, was selected. When full texts were not available, abstracts were

included if they contained the relevant information. The above methodology yielded 25 usable papers. The papers are discussed in the following section.

3. Results

Quantum dots and their crystallisation

Colloidal semiconductor quantum dots (QDs) have immense applications in optoelectronics and photonics. Many attempts have been made to improve their characteristics and quality, efficiencies and extension of spectral range and environment-friendliness using less toxic materials. The QDs developed by QD Vision Inc are being used by Samsung, Sony and other firms producing lighting equipment. Among the many techniques devised to improve QDs long term stability over a wide range of temperature and illumination intensities, packing QDs with inorganic matrices is one way. Otto, et al. (2012) identified a new method of doing this by growing them as mixed crystals at ambient temperatures from a saturated salt solution. The authors demonstrated the incorporation of QDs into ionic crystals of salts like NaCl, KCl and KBr. The crystallizations were done at ambient temperatures from saturated aqueous solutions of the respective salts, which contained colloidally prepared, strongly photoluminescing QDs. The optical performance of these mixed crystals was extremely robust. The type, size and size distribution of the nanocrystals used in them determined their photoluminescence and absorption properties. It is possible to increase the range of utility of these crystals by mixing them with epoxy resin, silicone, poly(methyl methacrylate) (PMMA) or other typical matrices. Such mixing will not have any effect on their optical properties. This advantage extends their utility in optoelectronics and photonics like colour convertors, optical gain media, and as elements of optical circuits. The colour range obtained for NaCl-based crystals shown by the authors is presented in Fig 1.

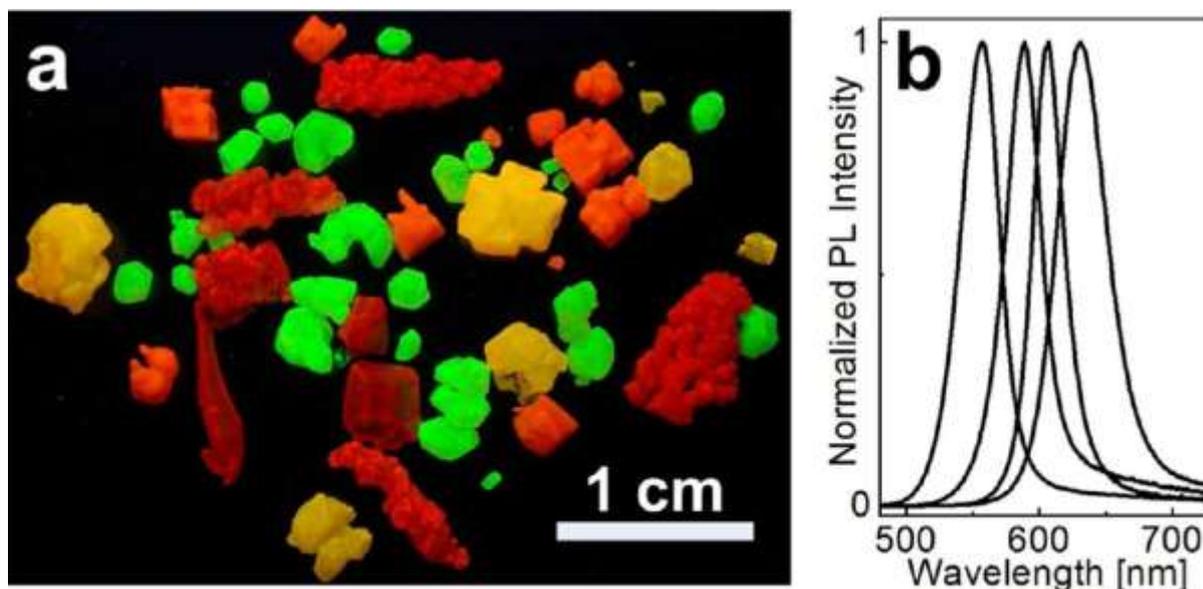


Figure 1 A true colour image of NaCl-based mixed crystal containing CdTe QDs of different sizes and colours and their PL spectra (Otto, et al., 2012).

The method of Otto et al (2012) described above was followed by Adam, et al. (2015) to incorporate QDs into ionic matrices using a new, fast, and versatile method through liquid-liquid diffusion. The liquid-liquid diffusion-assisted crystallization (LLDC), resulted in faster ionic crystallization of the QDs. This reduced the crystallization time by half. The accelerated crystallisation helps to incorporate even the less stable colloids such as initially oil-based

ligand-exchanged QDs into salt matrices. Thus, LLDC offers a robust, adaptable and rapid technique for obtaining high quality QD-salts. The authors reported their results on MeOH-NaCl solution rather than NaCl in water. The schematic drawing and the colour images of the NaCl-based mixed crystals obtained by the process were presented by the authors as given in Fig 2.

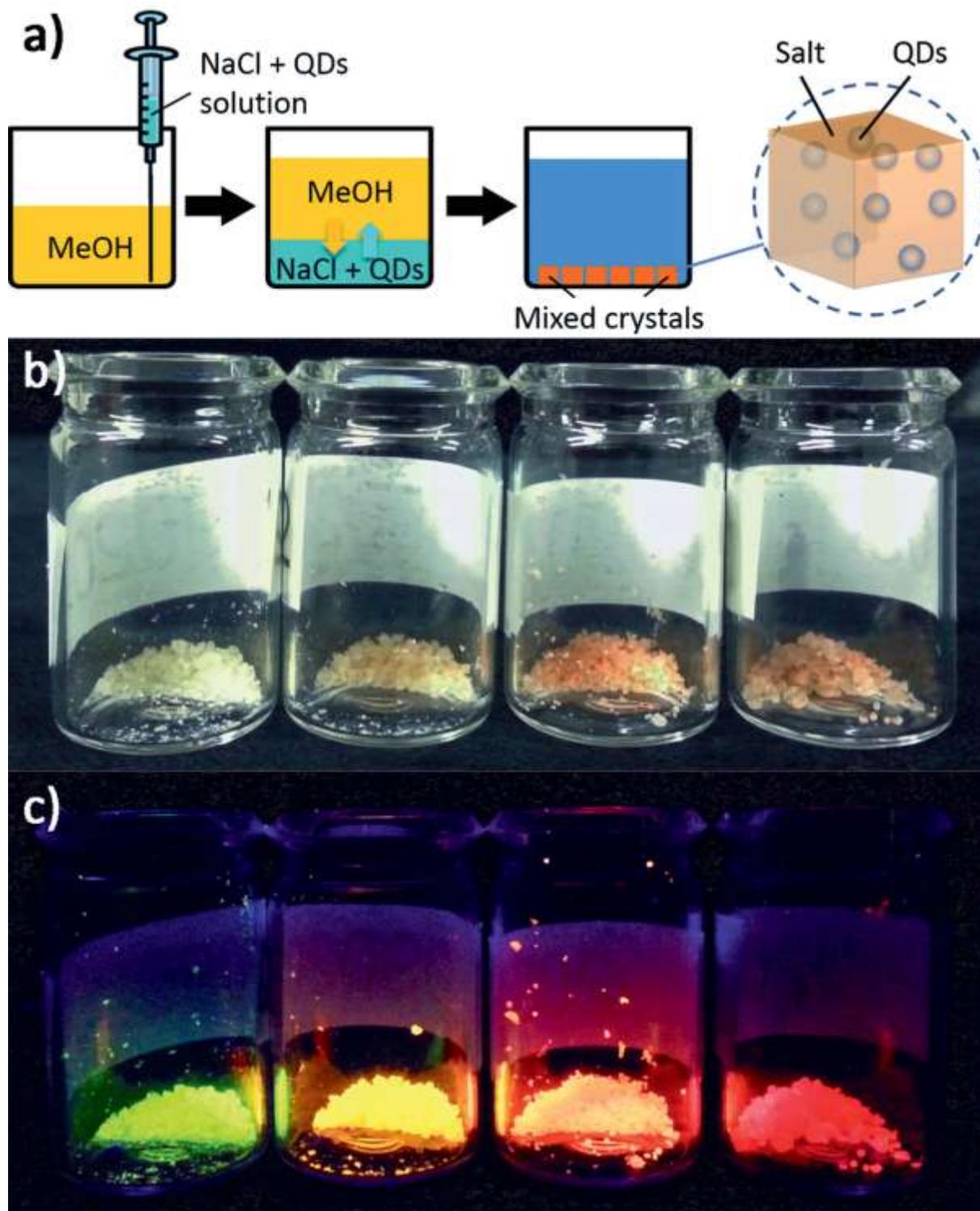


Figure 2 The LLDC crystallisation process (a), colour of crystals in daylight (b) and under 365 nm UV light (c) (Adam, et al., 2015).

A method of preparation of mixed-crystals using oil-based QDS without a prior ligand exchange mechanism has also been described, as given in Fig 3.

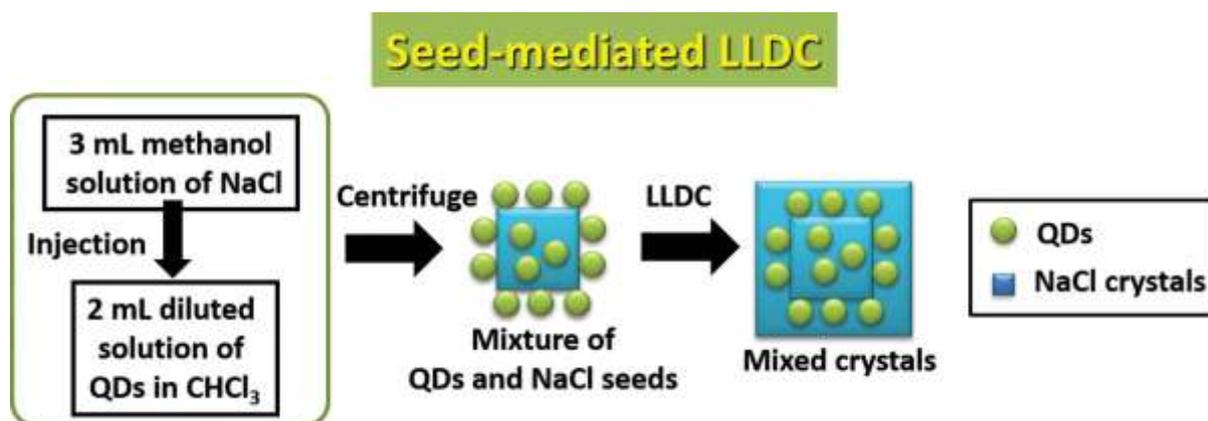


Figure 3 A seed mediated LLDC for direct use of oil-based QDs for crystallization without prior ligand exchange (Adam, et al., 2015).

Here, in the first step, QDs are adsorbed at the surface of the NaCl seeds formed from the MeOH-NaCl solution. In the second step, the LLDC facilitates a complete encapsulation of the QDs by growing the seeds to larger mixed crystals.

Other types of nano colloids and processes

In a different perspective, Wu, Derks, van Blaaderen, and Imhof (2009) studied on shear-induced melting and crystallization in concentrated colloidal suspensions of hard-sphere-like particles. Confocal microscopy was used for measurements. Silica and PMMA suspensions were sheared using a counter-translating parallel plate shear cell or a counterrotating cone-plate shear cell at constant rate. The shearing methods facilitated tracking of particles being sheared for longer time in a zero velocity plane. With large scale shearing, the flow profile ceased to be linear. However, the flow of the crystals was in an aligned sliding layer structure when the shearing rates were low. The crystals melted slowly at higher shear rates. Initially disordered suspensions crystallized at low shear rates. It was observed that shear-induced crystallisation of hard spheres did not follow the nucleation-growth path.

Self-assembly of man-made nano-scale units into functional superstructures in the case of colloidal inorganic nanocrystals is not progressing beyond the elementary level. The reasons are the simplistic shapes of and interactions among these nanocrystal units and poor understanding of the variables which determine the mechanism of their building up into complex structures. In this respect, the work of Miszta, et al. (2011) significant. They showed that monodisperse octapods of colloidal nanocrystals can self-assemble when placed in a suitable solution environment. The assembling process occurs at two sequential levels. In the first step, linear chains of interlocked octapods are formed. In the second step, these chains self-assemble into three-dimensional superstructures in a spontaneous manner. It was also noted that all the instructions for these steps of self-assembly were encoded in the octapod shape. The constituent nanocrystals can be welded together to increase their mechanical strength. In this work, eight CdS ‘pods’ were grown from a central region made of CdSe. The octapods were synthesised using the method of Deka, et al. (2010). Briefly, this method consisted of “synthesis of branched nanocrystals, preformed monodisperse Cu_{2-x}Se nanocrystals synthesized as per a previously published procedure having cuboctahedral habit and 10-15 nm diameter and mixing it with a solution of trioctylphosphine (TOP) chalcogenide (either S, Se, or Te), prepared by dissolving the chalcogenide powder in TOP. The resulting solution was then injected into a flask containing a cadmium alkylphosphonate

(a mixture of hexylphosphonate and octadecylphosphonate) in trioctylphosphine oxide (TOPO) heated at a temperature ranging from 280 to 380 °C, under nitrogen. The synthesis was allowed to run for 7 min at that temperature. During that time, the Cu_{2-x}Se nanocrystals underwent first a rapid cation exchange with Cd²⁺ ions and were transformed into sphalerite cadmium selenide nanocrystals. These nanocrystals acted as seeds for the growth of wurtzite arms, so that ion exchange and growth of the cadmium chalcogenide on top of the cation-exchanged seeds occurred sequentially, in the same reaction flask (i.e., in “one-pot”).” (p 3771). The synthesised octapods were processed for formation of assemblies. For this purpose, a stock solution of octapods in toluene was stored in a nitrogen-filled glove box. Due to the unstable nature of the octapod suspension in toluene, a precipitate was formed at the bottom of the vial, visible after 24 hours. Then, the vial was shaken for a couple of minutes to re-disperse the aggregates. From this solution, 100 µl was transferred into another empty vial and diluted with an additional of 150 µl of toluene. Then the vial was left undisturbed for 12/24 h and then 1 ml acetonitrile was added and left untouched for 2–5 h more. Now the precipitate at the bottom of the vial with almost transparent solution was seen. The wet precipitate was collected and transferred onto the conductive substrate for scanning electron microscopy (SEM) or transmission electron microscopy (TEM) analysis. Aggregation in solution was monitored by DLS. The concentration of octapods in the solution was about 10⁻⁸ molar. For cation exchange reactions, the CdSe/CdS octapod superstructures, which was deposited on the conductive substrate, were dipped in a solution of 37 mg Cu(CH₃CN)₄PF₆ in 5 ml of methanol for at least 15 min. The substrate, which now has the cation-exchanged superstructures, was dipped into 5 ml of pure methanol for 15 min twice to wash away excess Cu(CH₃CN)₄PF₆ and Cd-containing species, released by the cation exchange reaction. This sample was dried and used for oxygen plasma treatment of cation exchanged octapod assemblies. The cation-exchanged octapod superstructures in the substrate was placed in a Gatan Advanced Plasma System. The oxygen plasma was applied for 3 min at 40 s.c.c.m. O₂ flow rate and 25 W power and 13.56 MHz frequency. In summary, these sequential procedures consist of synthesis of complex building blocks and their hierarchical assembly and welding is an innovative approach towards the realization of ordered meso-structures using a simple bottom-up approach.

In a review on studies on methods of particle manipulation and assembly based on electric fields, Velev and Bhatt (2006) pointed out that assembly of cells and nanoparticles can be driven by electric field to produce new types of biosensors, micro-bioassays and bioelectronic circuits. Particles suspended in water can easily respond to AC or DC electric fields. Electrophoresis can be used to move charged particles towards oppositely charged electrodes. Dielectrophoresis allows particles to move in electric fields and precise manipulation of particles is possible using field strength, frequency and electrode geometry. Electrokinetics may drive flow of liquids inside the experimental cells resulting in transport and assembly of nanoparticles. In a specific example of crystallisation of colloids, the authors used alternating electric fields applied to the gap between planar electrodes for a rapid and switchable assembly of colloidal crystals from polymer and silica microspheres. These two-dimensional crystals are specifically oriented by the field without the need for prior templating by microlithography or micromolds. Schematics of the DEP cell and images of the stages of particle assembly observed in these experiments obtained by the authors have been presented in Fig 4.

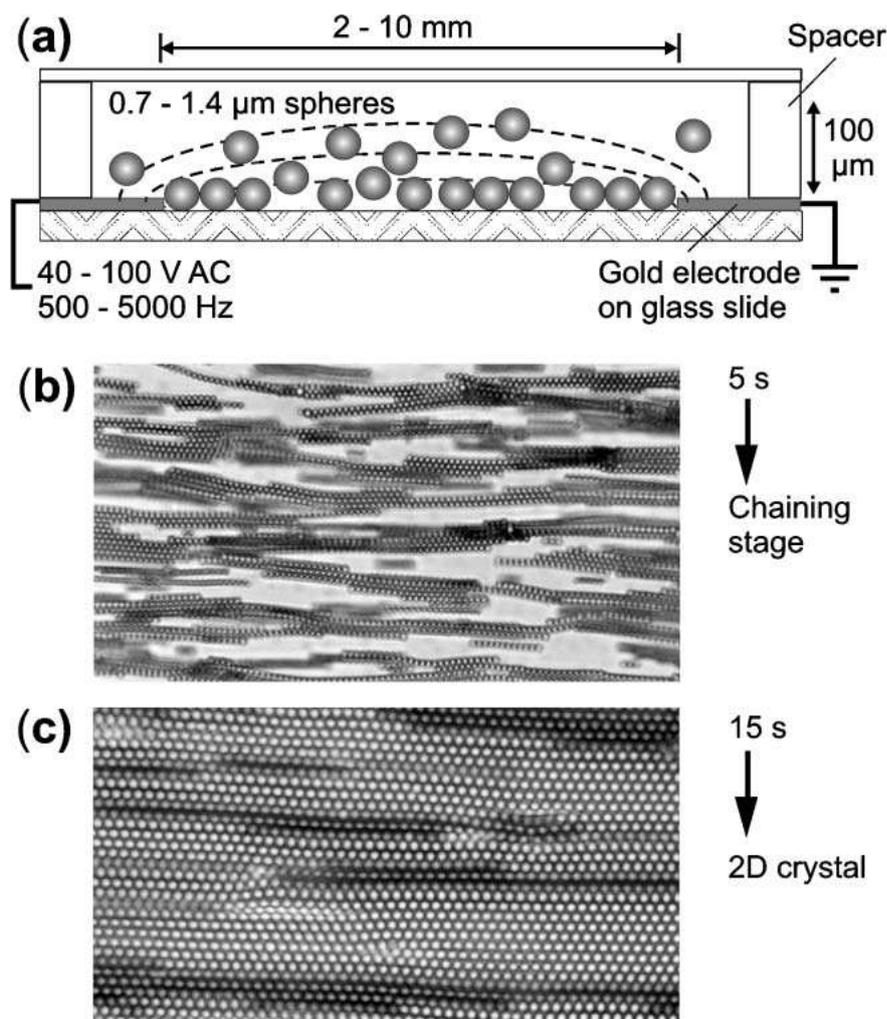


Figure 4 Crystallisation process in an electric field (Velev & Bhatt, 2006).

A rapid stage of the crystallization consisted of particles being assembled in chains along the direction of the field by dipolar attraction. Dielectrophoresis was used to attract the particle chains to the surface of the glass plate between the electrodes. The chains were collected to the surface in the form of hexagonal particle crystals. One axis of this was always aligned in the field direction, which was at right angle to the electrode gap. This was the second slower crystallization stage driven by lateral attraction between the particle chains. The threshold field intensity for crystallization E_{th}^i of particles of different radii r was a constant group even at varying frequencies, which could be expressed as $E_{th}^2 r^2 = \text{a constant}$. However, the crystallised arrays diffuse out when the electric field is switched off. Hence, this method of crystallisation cannot be applied to make permanent nanocrystals.

In a study, Compton and Osterloh (2007) found that nanoparticles could be aggregated to form colloid gold crystals by the addition of dodecanethiol to a solution of oleylamine-stabilized gold nanoparticles in chloroform. Three different growth mechanisms were seen in this respect: direct nanoparticle aggregation, cluster aggregation, and heterogeneous aggregation, leading to the production of amorphous, single-crystalline, polycrystalline, and core-shell type clusters. In the core-shell type clusters, encapsulation of an impure nucleus by gold nanoparticles was noted. All crystalline structures exhibited face centred cubic (FCC) or icosahedral packing and were terminated at different planes, which resulted in truncated tetrahedral, octahedral and icosahedral shapes. Most clusters in this system grew by aggregation of 60–80 nm structurally nonrigid clusters that formed in the first minute of the

experiment. The shapes of the gold nanocrystals obtained in the experiment given by the authors is presented in Fig 5.

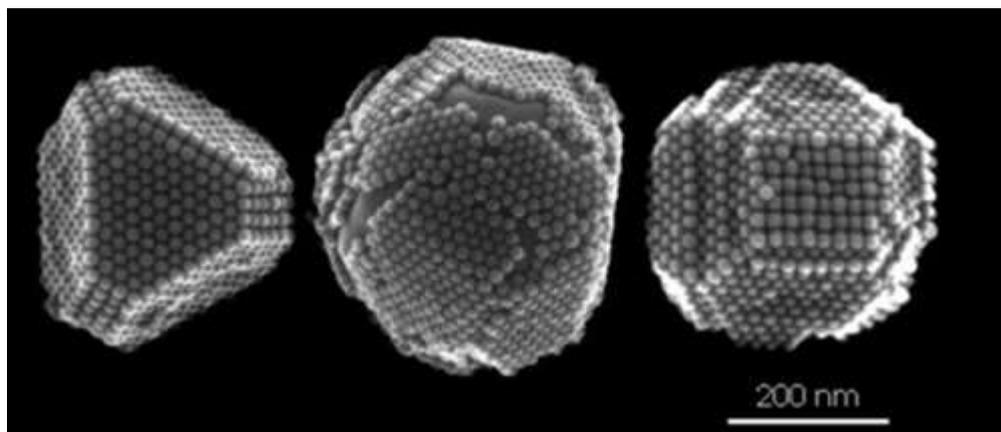


Figure 5 Shapes of gold nanocrystals obtained in the experiment by (Compton & Osterloh, 2007).

There has been rapid growth in research in the area of colloidal assembly and it is likely to continue. In a review, some methods of assembling structures from colloidal particles and their limitations were tabulated by Velev and Gupta (2009). The methods listed were: evaporation, sedimentation, adsorption, external force field, bio-specific, templated on surfaces and templated on droplets. Many figures explaining these methods leading to the different structures have been provided in the paper. When transforming science into engineering to mass produce these materials for innovative uses factors like precision, control, scalability, costs and value are important. The importance of the last two points was highlighted by the authors using a graph, presented in Fig 6. Interestingly, as the cost increases, value is also increasing almost linearly. Thus, it is more beneficial to fabricate 1D chains and wires, bioelectronic materials and micro-electronic chips than supra-particles, 2D and 3D crystals. Of course, the method of costing and estimating value are important.

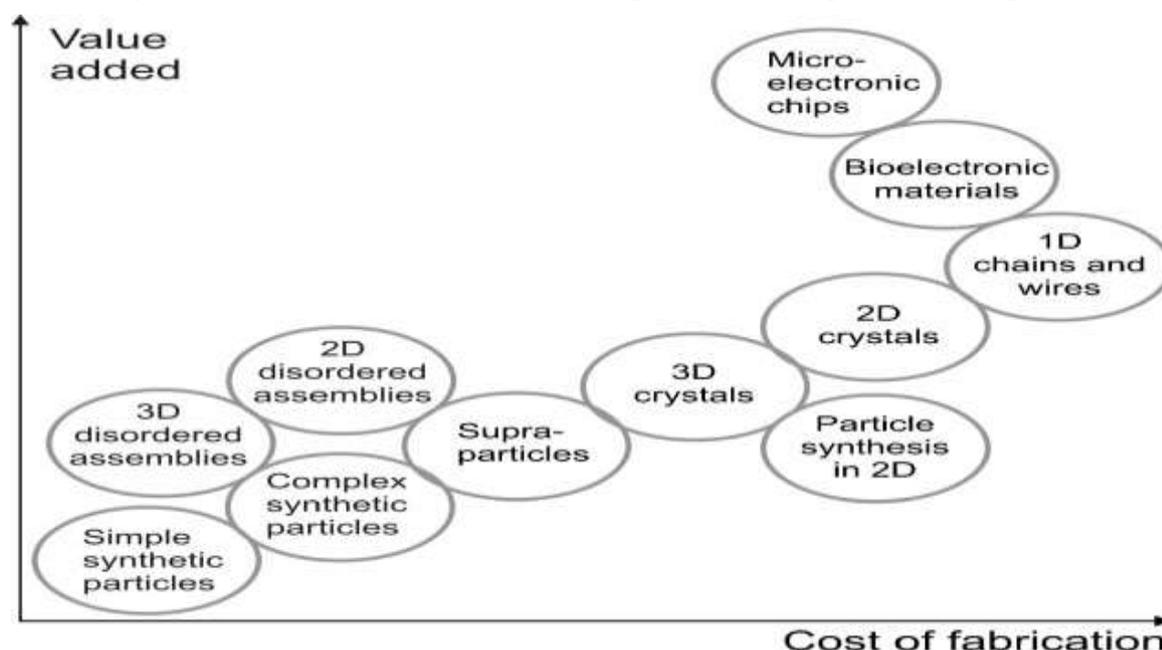


Figure 6 Value-cost relationships of different types of nanocolloids when considered for mass production for commercial use (Velev & Gupta, Materials Fabricated by Micro- and Nanoparticle Assembly—The Challenging Path from Science to Engineering, 2009).

Free-standing nanoparticle superlattices, suspended highly ordered nanoparticle arrays, can be useful for designing metamaterials and nanodevices without substrate-induced electromagnetic interference. The method overcomes the stability problems associated with aqueous solutions. Cheng, et al. (2009) used DNA as a ‘dry ligand’ in a microhole-confined, drying-mediated self-assembly process. The process did not require specific Watson–Crick base-pairing to obtain discrete, free-standing superlattice sheets. The DNA length could be adjusted to control both structure (inter-particle spacings) and functional properties (plasmonic and mechanical) of these lattice sheets. It was also possible to tune up the edge-to-edge inter-particle spacing for monolayered superlattice sheets to 20 nm. This is very wide compared to what can be obtained with alkyl molecular ligands. In a related work, Macfarlane, et al. (2009) described an analysis of the key steps involved in the DNA-directed assembly of nanoparticles into crystallites and polycrystalline aggregates. The rate of crystal growth as a function of increased DNA linker length, solution temperature, and self-complementary versus non-self-complementary DNA linker strands (1- versus 2-component systems) were also researched. The results revealed that the crystals grow in a 3-step process: an initial “random binding” phase resulting in disordered DNA-AuNP aggregates, then a localized reorganization and subsequent growth of crystalline domain size and finally to well-ordered crystals at all subsequent stages of growth. The process was described as given in Fig 7 and described below it.

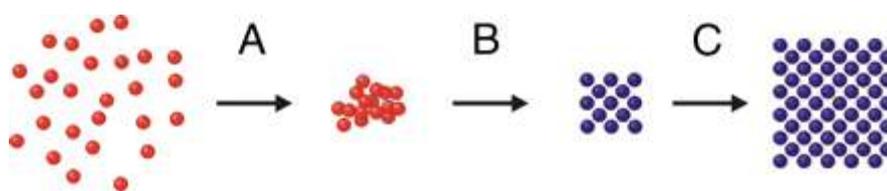


Figure 7 The processes of DNA-AuNP crystal growth

The DNA-AuNPs cool below their melting temperature. As they cool, they quickly form aggregates of a small number of nanoparticles in a disordered packing arrangement. The size of the aggregates increases slowly with time. Then the nanoparticles within the aggregates rearrange to form FCC crystalline domains. The rate of crystalline formation depends on the length of the DNA linker strands. These aggregates remain highly ordered even as their size increases. Three phases of early stages of crystal growth were also described in another figure.

Large scale molecular dynamics simulations of the evaporation-induced assembly of nanoparticles were reported by Cheng and Grest (2013). These nanoparticle assemblies were suspended in a liquid with controlled evaporation. Better quality of the nanoparticle crystals were obtained at slower evaporation rate, which were formed just below the liquid/vapor interface. There were less defects and grain boundaries. This was due to the competition between the accumulation and diffusion times of nanoparticles at the liquid/vapor interface. With smaller rates of accumulation, nanoparticles were deposited very rapidly at the interface. This did not give them sufficient time to arrange through diffusion. Prevalence of defects and grain boundaries were noted when this happened.

A process of colloidal surface additivation of polyamide 12 powders with well-dispersed laser-generated plasmonic silver nanoparticles to increase the crystallization from a low 0.01 vol%, was described by Hupfeld, et al. (2020). There was increased dispersion of the nanoparticles on the micropowder surface and the reproducibility was good. The powders could be successfully processed powders on a PBF-LB machine for plasmonic-functionalized parts generation. Then the authors introduced the surface specific nanoparticle dose (surf%)

as scaling parameter complementary to the commonly used mass specific dose (wt%). There was significant nanoparticle-induced heterogeneous nucleation was obtained with 0.01% of silver load by volume, without affecting thermal properties.

In a study on the coupled dynamics of oleate-passivated PbSe colloidal nanoparticle spreading and self-assembly at a fluid–fluid Interface, Balazs, Dunbar, Smilgies, and Hanrath (2020) observed coupled effects of solvent spreading, nanoparticle assembly, and recession of the vapor–liquid interface on the morphology of the self-assembled thin films. Thenanoparticles dispersed across an ethylene glycol subphase. The solvent parameters such as surface tension, nanoparticle solubility, aromaticity, and polarity influenced the mesoscale morphology of its superlattice. Also, a nanoparticle precursor monolayer film spread in front of the bulk solution and influenced the fluid spreading across the subphase.

According to the results obtained by Chen, Bae, and Granick (2011), it is possible to induce colloidal spheres to self-assemble into a complex predetermined colloidal crystal, such as colloidal kagome lattice. This could be done by decoration of their surfaces with a simple pattern of hydrophobic domains. Simple micrometre-sized spheres are used as the building blocks. These building blocks could then be interacted using simple mechanisms like electrostatic repulsion in the middle, hydrophobic attraction at the poles. However, the self-assembly of the spheres into an open kagome structure is completely different from the previously known close-packed periodic arrangements of spheres. The functionality of the lattice structure is enhanced by it having both hydrophobic (on the rims of pores) and hydrophilic pores it has. This convergent self-assembly method from easily fabricated colloidal building blocks facilitated encoding of the target supracolloidal architecture in in large redundantly attractive regions. This could be extended to form other supracolloidal networks.

Nanostructured lipid carriers (NLC) consist of liquid-lipid blended with a solid-lipid to form a nanostructured solid particle matrix. NLC possesses controlled release characteristics with some advantages over solid-lipid nanoparticles (SLN). SLN is used as emulsions of solid-lipid. They are widely used in intravenous, oral, dermal and topical applications of drugs due to their low cytotoxicity, long shelf-life without becoming unstable, high reproducibility, cost-effectiveness and included in generally approved materials (GRAS) for healthcare use. There are three types of NLCs: amorphous, imperfect and multiple. Due to their highly dispersed particles, the drug content can be increased. NLCs are produced by high pressure homogenisation, microemulsion, solvent emulsification followed by evaporation or diffusion, water-in-oil-in-water double emulsification and high shear homogenisation with or without ultrasonication. When the emulsified dispersion is produced for use in drug delivery systems, it must be cooled down to lower than the critical crystallization temperature of the lipid. The crystallisation behaviour is influenced by production method, the presence of surfactant, melting point of the lipid, lipid concentration, high dispersity and the small particle size of the resulting systems. These factors also affect the degree of crystallinity and crystal modifications of the matrix constituents compared to the bulk materials. The loading capacity of the drug into SLN or NLC depends on solubility of the drug in the lipid, how well lipid and drug melts are mixable, physical and chemical structure of lipid solid matrix, extent of polymorphism of the lipid. Drugs can be incorporated into the core or shell. Many factors affect the actual drug delivery efficiency achieved and chemical stability of the drug when incorporated into the emulsion (Üner, 2006).

Limitations of low water-solubility, chemical instability, and poor oral bioavailability affect the application of curcumin as a nutraceutical in commercial food and beverage products. Peng, et al. (2018) developed all-natural colloidal delivery systems to solve these

problems. The method was to produce saponin-coated curcumin nanoparticles using a pH-driven loading method. The nanoparticles of the coated product contained curcumin in an amorphous form. A simulated gastrointestinal tract study demonstrated that the In vitro simulations revealed bio-accessibility of about 3.3-times higher for curcumin nanoparticles than for free curcumin. Oral administration of the nanoparticles to Sprague Dawley rats showed an in vivo bioavailability of about 8.9-times higher for curcumin nanoparticles than for free curcumin.

A utilitarian aspect stems from the discussions of Müller-Goymann (2004) on physicochemical characterisation of colloidal drug delivery systems. Such substances include reverse micelles, vesicles, liquid crystals and nanoparticles. The methods used for physicochemical characterisation include X-ray diffraction, laser light scattering, electron microscopy, and differential scanning calorimetry. The focus of the author in describing these methods is on the topical applications of the colloidal drug delivery systems (DDS) which requires sustained drug release and improved stability.

Another method of producing nanoparticles discussed by Colson, Henrist, and Cloots (2013) was nanosphere lithography (NSL), also known as Colloidal lithography or Natural lithography. It is a suitable method for wafer-scale processes to manufacture several homogeneous 1-D, 2-D and 3-D nanostructures. In this method, the advantages of both top-down and bottom-up can be combined. There are two steps here as shown in Fig 8. In the first step, a colloidal crystal mask (CCM) is prepared out of nanospheres. In the second step, the desired material is deposited through the mask. The mask is then removed. The layer maintains the ordered patterning of the mask interstices.

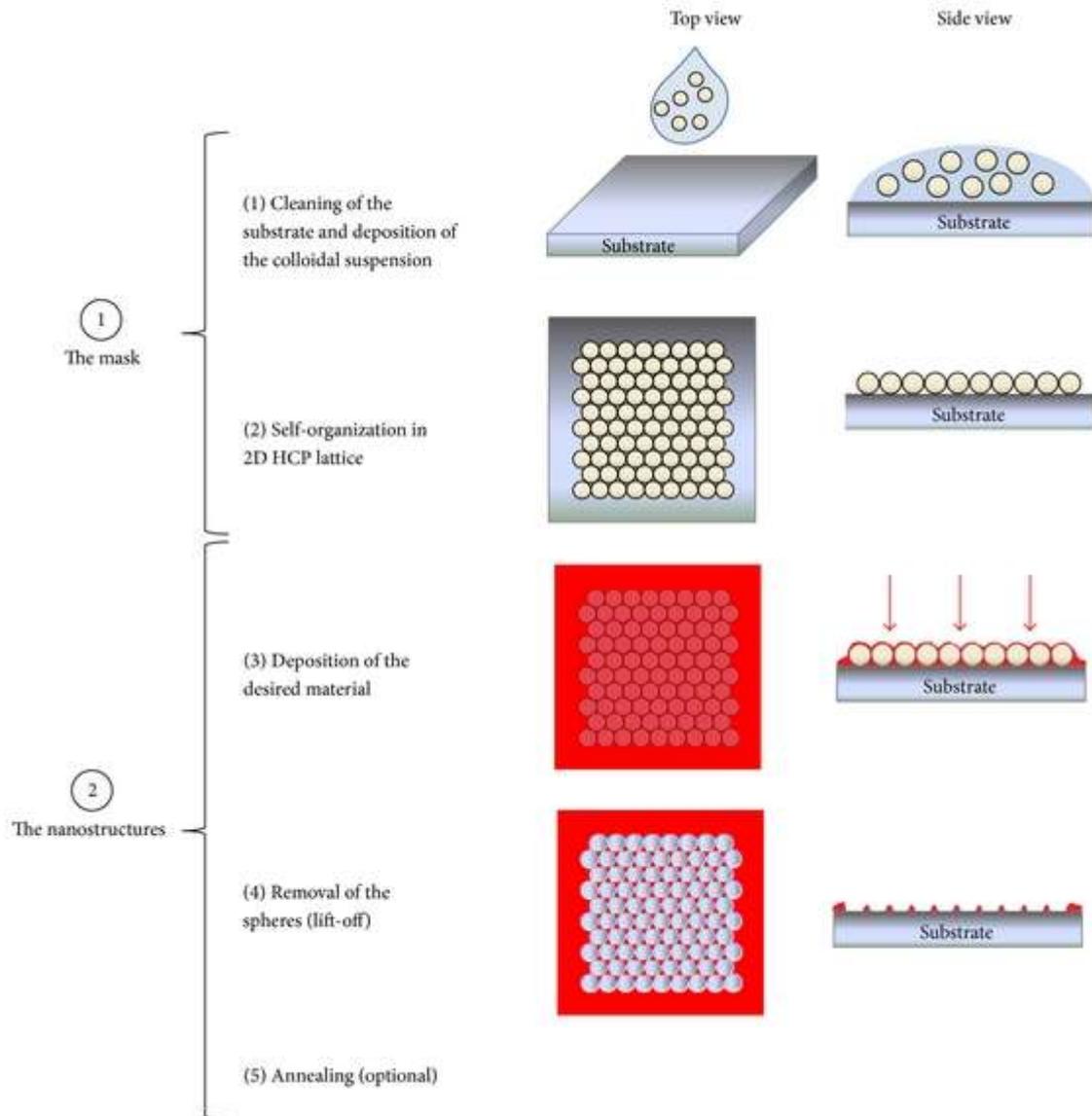


Figure 8 Nanosphere Lithography process (Colson, Henrist, & Cloots, 2013).

Some most popular lithographical techniques are: deep, immersion and extreme UV methods, X-ray, electron beam, soft and scanning probe. Only deep UV, soft and electron beam have been used in industry so far. The time scale related to the development and convergence of bottoms-up and top-down methods given by the authors is presented in Fig 9.

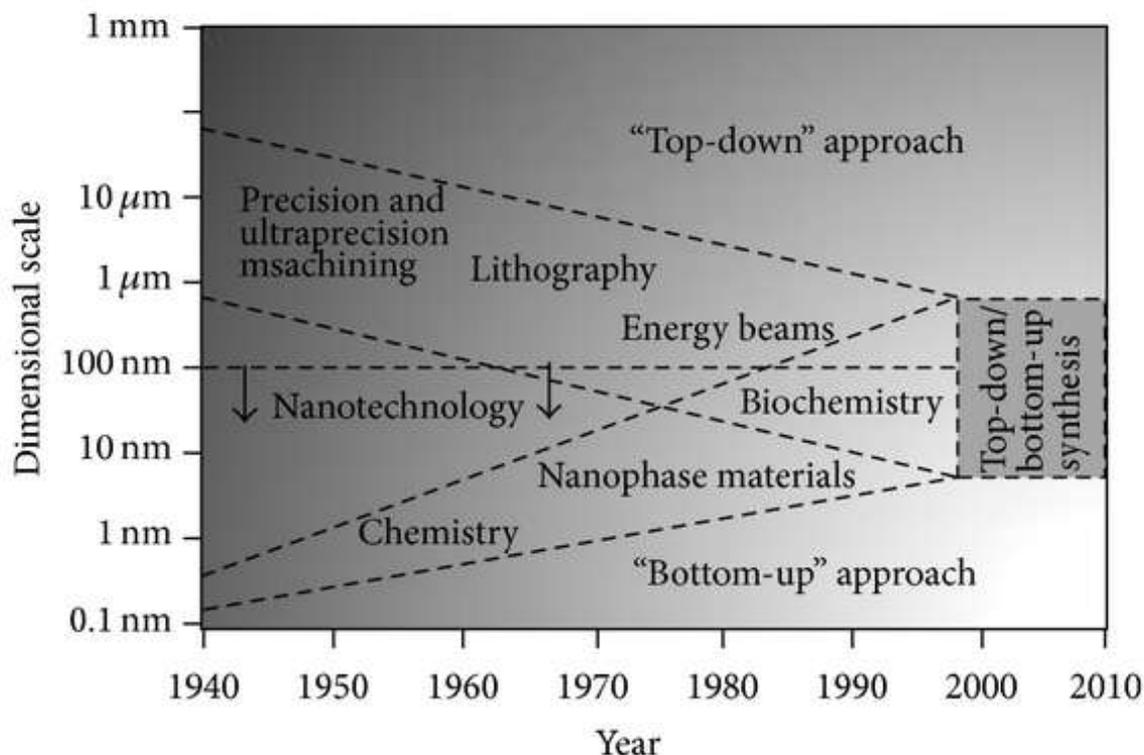


Figure 9 Time course of development of bottoms-up and top-down methods and their convergence in lithography (Colson, Henrist, & Cloots, 2013).

Production of liquid crystals and their types

A liquid crystal is a state of matter, mesophase, between liquid and solid. One of the properties of LCs is existence of two melting points. Together with the molecular alignment characteristics of a solid crystal, it also changes shape like a fluid. Liquid crystals consist of organic, rod-shaped molecules that align in parallel, and the common types used in electronic displays are nematic, cholesteric and smectic. Nematic LCs, when placed in parallel randomly, react quickly to electric fields. Hence, it is used in LCD screens. Cholesteric LCs, also called Chiralnematic LCs, are lined up in separate layers to form a helical spiral. The image displayed is retained even when power is removed and hence is bistable. But it reacts slower to changes in electric fields than nematic screens. Smectic LCs are positioned side by side in layers and are similar in properties to cholesteric LCs. A detailed review of liquid crystals was done by Lagerwall and Scalia (2012). The authors recognise two main classes of LCs. One is the thermotropic LCs built up by individual molecules requiring no further solvent molecular species for the liquid crystal phase formation. The phase is primarily determined by the temperature. There are two key temperature values: one defining the beginning and end of liquid crystalline order, the melting point T_m from the crystalline solid and the other is the clearing point T_c into an isotropic liquid. There are thermotropic mesogen and lyotropic micelle. The authors present many diagrams and pictures of production of LCs and their applications. In a review, Hegmann, Qi, and Marx (2007) observed that LCs naturally are very suitable candidates for matrix-guided synthesis and self-assembly of nanoscale materials. This is because the combination of order and mobility of the liquid crystalline state occurs at the molecular or at the nanoscale levels. In the paper, the authors review synthesis procedures in which LCs are used as templates, the methods used to design LC nanomaterials, use of LC phases for self-assembly of nanomaterials, creation of defects in

LC-nanoparticle suspensions and potential applications. The authors have used various types of diagrams and figures to explain the methods of synthesis of the LCs.

Classification of nanoparticles and their crystallisation processes

In this respect, in another review, Stamatoiu, Mirzaei, Feng, and Hegmann (2011) categorised nanomaterials based on shapes as zero-dimensional nanoparticles which are quasi-spherical, one-dimensional, rod or wirelike, nanomaterials like nanorods, nanotubes, or nanowires, and two-dimensional, disc-like, nanomaterials like nanosheets, nanoplatelets, or nanodiscs. Methods of production of these materials have also been reviewed. The authors describe one-phase and two-phase Brust–Schiffrin method, place exchange (thiol for thiol exchange) reaction on the surface of the nanoparticle, post-synthetic modifications, as in the case of using a reactive R group on the nanoparticle corona as in Scheme 1), displacement of weaker ligands or weaker surface protective agents with functional, stronger binding ligands as in the case of a thiol-for-dimethylaminopyridine or a thiol-for-triphenylphosphine exchange, which provides access to gold nanoparticles with low polydispersity indices. In the case of both hydrophilic and hydrophobic quantum dots, either high-temperature thermolysis of a precursor based organometallic synthesis or sol-gel type aqueous synthetic process is possible. Place exchange reaction for efficient synthesis of hydrophilic, thiol-capped CdTe quantum dots can also be used. This can be transformed to lipophilic, alkanethiol-stabilized CdTe quantum dots. The reorientation of nematic liquid crystal molecules by an applied magnetic field to produce magnetic nanoparticles is another process. The methods of preparing magnetic iron oxide nanoparticles are: coprecipitation, non-aqueous and aqueous sol-gel, microemulsion, hydrothermal/solvothermal and sonochemical processes. Coprecipitation is widely used for iron oxide nanoparticles dispersed in aqueous media. Ferroelectric nanoparticles are produced by high-temperature protocols commonly using autoclaves, biosyntheses using template syntheses, sol-gel, molten hydrate salts and grinding. One-dimensional metal nanostructures (gold nanorods mostly) are produced using template-based, electrochemical or seed-mediated wet chemistry methods. The last one is more common. A common approach to grow nanorods from vapour phase is the vapor-liquid-solid (VLS). It requires high operating temperatures of about 500° C and a metal catalyst such as Au, Cu, or Ni. Colloidal synthetic methods are also useful to produce semiconductor nanorods. Carbon nanotubes (CNT) of two types exist: single walled and double walled. Postgrowth directional alignment is a serious problem in the case of both the anisotropic CNTs. A variety of methods have been developed for solving this problem. Two-dimensional, disc-shaped nanomaterials mostly nanoclays. Exceptional cases reported are those of a liquid crystal phase formation and self-assembly of nanomaterials in the form of two-dimensional disc or sheet like the organization of nanodiscs or nanoplatelets into nematic, smectic, or columnar morphologies.

In their work, Lee, Chan, Bevan, Lewis, and Braun (2004) described a process of assembling 3-D colloidal crystals in the following manner, These “were produced from binary mixtures of colloidal microspheres and highly charged nanoparticles on flat and epitaxially patterned substrates created by focused ion beam milling. The microspheres were settled onto these substrates from dilute binary mixtures. Laser scanning confocal microscopy was used to directly observe microsphere structural evolution during sedimentation, nanoparticle gelation, and subsequent drying. After microsphere settling, the nanoparticle solution surrounding the colloidal crystal was gelled in situ by introducing ammonia vapor, which increased the pH and enabled drying with minimal microsphere rearrangement. By infilling the dried colloidal crystals with an index-matched fluorescent dye solution, we generated full 3-D reconstructions of their structure including defects as a function of initial suspension composition and pitch of the patterned features. Through proper control over these important

parameters, 3-D colloidal crystals were created with low defect densities suitable for use as templates for photonic crystals and photonic band gap materials.” A schematic representation of the colloidal assembly process given by the authors is presented in Fig

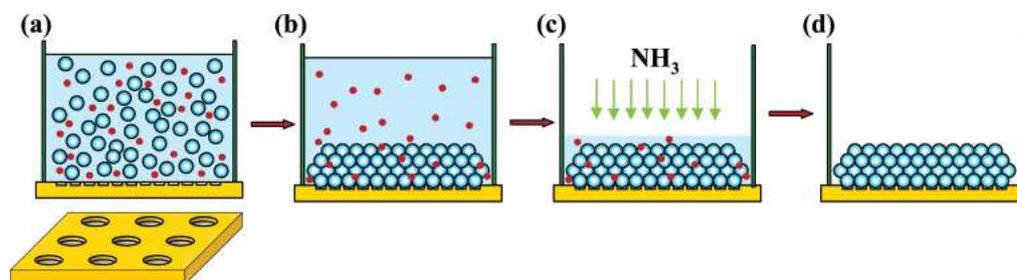


Figure 10 Schematic representation of the colloidal assembly process (Lee, Chan, Bevan, Lewis, & Braun, 2004). (a) microspheres settling from a dilute binary mixture onto an epitaxially patterned substrate, (b) formation of a 3-D colloidal crystal, (c) removal of excess supernatant solution followed by in situ gelation of the remaining nanoparticle solution through exposure to ammonia vapor and (d) dried colloidal crystal. Another colloidal assembly process on epitaxially patterned substrates has also been described by the authors. Defect density was found to be affected by composition and substrate factors.

The pathways towards crystallization at nanoscale has not been researched adequately due the difficulty of determining the motion of individual building blocks in a liquid medium. To solve the problem, Ou, Wang, Luo, Luijten, and Chen (2020) directly imaged the full transition of dispersed gold nanoprisms to a superlattice at the single-particle level. Low-dose liquid-phase TEM was used to achieve the in situ imaging of nanoscale entities ordering into crystals without disturbing their motions. This approach was different from the non-periodic nanoparticle aggregates observed in many other liquid-phase TEM studies. The emphasis was on a system of triangular gold nanoprisms to represent nonspherical, anisotropic nanoscale building blocks. The large aspect ratio renders the nanoparticle interactions highly directional. The prisms were coated with negatively charged thiolated ligands to disperse them well through electrostatic repulsion in the initial suspension. A surprising observation was that dispersed prisms transitioned from standing columns of stacked, misaligned prisms into a hexagonal lattice, which was then constructed hierarchically in 3D forms. The hierarchical construction happened as follows. Through radiolysis of water, the ionic strength in the illuminated region was increased monotonically by the imaging beam within seconds. This made counterion screening of the electrostatic repulsions possible. The prisms in a column were misaligned in an angular orientation, rather than in perfect registry. The final structure was formed by the interactions of these columns. The final structure had the appearance of a hexagonal lattice of evenly spaced, dark, circular discs under TEM. The columns vibrate rapidly, eventually annealing. All imperfectly bonded 5- and 7-fold clusters were eventually annealed into hexagonal sublattice units by the rapid vibration of columns. At the low electron dose rates used in the study, the ligands on the prism surface remained intact. Only through variations of ionic strength, the nanoparticle interactions were affected. It was found possible to trigger and capture the complete crystallisation process starting from the dispersed prisms through quantification of the relationship between dose rate and ionic strength. Monte Carlo simulations were combined with this particle tracking to show that positional ordering of the superlattice emerged from orientational disorder. Using this method, line tension and phase coordinates were measured. The charting of the nonclassical nucleation pathway involving a dense, amorphous intermediate was also observed. The

approach was found to be versatile permitting its application for crystallization of different nanoparticles.

4. Conclusions

The varieties and types of colloidal nanoparticles and equally varied production and crystallisation methods and their effects on the quality of crystallisation are very clear from the above review. Although seemingly, there are many options available for anyone to mass produce these particles for any of the numerous commercial uses, selection of the most suitable method has been rendered difficult by the multiplicity of methods and outcomes. The implication of this study is that there is a need for research to identify optimal methods for production of colloidal nanoparticles for targeted commercial uses.

5. References

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