

Self Assembled Nanostructures using Ice Moulds

**A.S. Karakoti^{1#}, Satyanarayana VNT Kuchibhatla^{1,2#}, D.R. Baer², S. Thevuthasan²,
Dean C. Sayle³, S. Seal^{1*\$}**

¹ Surface Engineering and Nanotechnology Facility, Advanced Materials Processing and Analysis Center, Department of Mechanical Materials and Aerospace Engineering,

^{\$} Nanoscience and Technology Center, Univ. of Central Florida, Orlando-32816

² Pacific Northwest National Laboratory, 3335 Q Avenue, Richland, WA-99352,

³ Department of Materials and Applied Science, Defence College of Management and Technology, Defence Academy of the United Kingdom, Swindon, UK SN6 8LA

[#] Authors have equal contribution

^{*} Corresponding Author: sseal@mail.ucf.edu

Abstract

The formation of nanorods, driven by the physico-chemical phenomena during the freezing of ceria nanoparticle suspension is reported. During freezing a dilute solution of CeO₂ nanocrystals, some nuclei remain in solution while others are trapped inside the voids formed within the growing ice front. Over time the particles trapped within the constrained geometries combined by an oriented attachment process to form ceria nanorods. The experimental observations are further supported through Molecular Dynamics (MD) simulations. These observations suggest a new possible strategy for the templated formation of nanostructures through self assembly by exploiting natural phenomena such as freezing of water.

Nature epitomizes ‘self assembly’ –living cells arranged in a myriad of complex forms and structures act as one particularly complex example. The challenge of synthesizing hierarchically ordered and complex structures with molecular level recognition is another example of a natural process that cannot yet be duplicated in the laboratory. Fundamental

research in understanding such self assembly of molecules has led to new strategies for synthesizing functional nanomaterials(1, 2) Several nanomaterials structures, facilitated via self assembled nanoparticles, have already been demonstrated by various researchers (3-13). Similarities between self assembly of nanoparticles and simple forms of life may lead to additional efforts to unravel and mimic nature(1). Among multitudes of morphologies and configurations, one dimensional nanostructures (ODNS) have received a significant attention from the researchers owing to their potential use in new generation electronics, photo catalysis, sensors and biomedical applications (7).

Here, we demonstrate the self assembly and time dependant evolution of ceria nanoparticles into ultra-long polycrystalline ceria nanorods (length *ca.* 3 – 3.5 micron, diameter *ca.* 30nm) using a simple water based synthesis, freezing and subsequent aging in ice. The mechanism we propose is effectively a natural form of templated self assembly. Over time in the frozen condition particles gradually evolve into polycrystalline nanorods. Our understanding of the process involves structure templating associated with voids known to form in ice(14-16) and localised oriented attachment process. Oriented attachment and anisotropic growth of nanoparticles in solution(17, 18) are vital to the self assembly of polycrystalline nanoparticles in solution. Advances in molecular dynamics (MD) based simulation have enabled interesting and exciting observations in self assembly(3, 19-21) and we use MD calculations to understand the observed aggregation process. We have recently reported the synthesis of polycrystalline ceria octahedral superstructures by self-assembly through oriented agglomeration in both water and Poly (ethylene glycol)(22). These contrast with the spherical (high index planes stabilized), single crystal ceria nanoparticles synthesized by Feng et al(23) in a

high temperature gas phase reaction. Clearly, agglomeration kinetics and behaviour of ceria nanoparticles change with ambient conditions. Motivated by this, we have studied their aging characteristics under different conditions including altering the solution environment and temperature. We have observed the evolution of ceria nanorods supported by the ice templates under freezing conditions. In addition to the formation of nanorods we also observe the formation of polyhedral superstructures which appear during the freezing process and are unaffected by templating effect of ice.

In present work a seeding solution of ceria nanoparticles was synthesized using a simple water based method by oxidizing the Ce(III) precursor salt to Ce(IV) (SI-1). Several 3-5nm crystallites nucleate and start to agglomerate within a short time frame (Figure 1a). The solution containing ceria crystallites was subjected to sub-zero temperatures (-18°C) and aged for different time scales. Crystalline ceria nanoparticles agglomerate in an oriented fashion within 1 day of aging and result in rod type structures together with large faceted agglomerates (octahedral super structures) (Figure 1b, SI 2). Both the superstructures and the nanorods were constituted of truncated octahedral building blocks of ceria nanoparticles(19). The observation of octahedral superstructure within one day of aging in ice directly contrasts the time dependent agglomeration of nanoparticles into polycrystalline superstructures(22). Subsequent aging for one week, facilitated long polycrystalline nanorods (Figure 1c, 1d, SI 3). Retention of the initial 3-5 nm particle size, with predominant (111) surfaces, is observed even in the highly dense and polycrystalline ceria nanorods about 40nm in diameter (SI 3). Further aging of the nanoparticles in ice (2 weeks) resulted in the formation of ultra long ceria nanorods (Figure 1e, 1f, SI 4a,).

We propose simultaneous occurrence of two different processes during the freezing of ice lead to the formation of nanorods along with observed octahedral superstructures. While the formation of octahedral superstructures is inherent to the process of freezing, the formation of nanorods occurs due to ice templating effect. To explain it further, it is proven through both experimental and modeling studies that the “ice structure can not accommodate foreign molecules other than water”, this results in the well known “solute rejection” phenomenon(24). This process is very well acknowledged by the metallurgical engineering literature for alloy solidification and zone refining kind of phenomenon, where the progress of solidification front results in the rejection of impurity particles into the liquid phase. In case, of dilute ceria suspensions, as the freezing front proceeds from top to bottom, the ceria nanoparticles will be expelled into the water phase. This leads to a significant increase in concentration of nanoparticles in unfrozen sol, followed by aggregation and kinetically driven octahedral morphology evolution. The higher concentration of solute ceria particles and the increasing pressure exerted by the ice front on the water phase results in the chemico-physical process (physical process driving assisting chemical bonding) mentioned above. It is well known, the ice front will be porous with some capillaries present at the ice – water interface. The nanoparticle suspension will end up absorbed into these channels due to pressure differences, however, significantly higher concentration of nanoparticles results in their entrapment in these channels as the solidification continues. It was earlier shown that there will be high concentration, unfrozen brine sols left out with in channels formed in ice(25).

The formation of nanorods is assisted by the physical templating of ice. At -18°C under atmospheric pressure, ice conforms to the “Ice I” structural polymorph(26) and

microstructural features, including nano and micro channels, evolve to accommodate the stress and expansion during solidification(27). These channels, with nanometer diameters and a few microns in length, serve as nano-capillaries (hard templates) and the water, supersaturated with ceria nanoparticles, is forced into the capillary, driven by capillary forces emanating from the freezing front(28, 29). The initially oriented particles are locked in the capillary under the ice pressure and undergo uni-dimensional oriented agglomeration to form ceria nanorods(30). It should be noted from this study that a very dilute solution and nanometer size of the particles are central to the formation of channels or capillaries. The perturbation, caused by nanoparticles at the ice-supercooled liquid interface causes channel formation as depicted in figure 2 (and SI-5). Ceria nanoparticles trapped in such nanochannels transform into nanorods with predominant $\{111\}$ terminated surfaces. Specifically, particles trapped in long nanochannels form the nanorods while those trapped in voids or wide capillaries or in the last portion of the frozen water will retain the octahedral superstructures. A schematic, depicting such morphological evolution, is presented in figure 3a and 3b.

Once trapped inside the channels and surrounded by ice, the mobility of ceria nanoparticles is restricted to one dimension. However, the very high surface energy of the nanoparticles drives the intra – agglomerate rotation to achieve partial oriented attachment at two, three particle interfaces. Such orientation proceeds by incorporation of defects such as dislocations along the interfaces of nanoparticles as shown in figure 3c. The white circles indicate the interfacial dislocations formed during the oriented agglomeration. Both, the formation of octahedral morphologies and nanorods involve rotation and orientation of the nanoparticles to facilitate low energy configurations and

coherent/semi-coherent interfaces. This can be visualized as an imperfect attachment as described in an earlier observation with titania nanoparticles(17, 18). Higher activation energies and brownian motion etc. are required for a full crystal rotation or recrystallisation to facilitate complete coherence and formation of single crystals. However, in a time limited aggregation under freezing conditions, complete rotation is not achieved and screw/edge dislocations form at the interface between three or more orienting particles (SI-6). As three or more particles align, elastic deformation results in partial coherence together with the evolution of screw dislocations(18). The formation of screw dislocations is also predicted by the theoretical investigation and is discussed below and shown in SI-7. Upon aging, the misorientation and associated dislocations are finally annihilated resulting in energetically stable interfaces.

A comparison of oriented attachment was made using the particle encounter complex (K_{os})(31) model, following equation 1.

$$K_{os} = \frac{4000 \Pi N_{av} h^3}{3} \exp(-V_T(h)/kT), \quad (1)$$

where N_{av} is the Avogadro number, V_T is the total interaction energy between two spherical particles, h is the separation distance between the particles, k is the Boltzmann constant and T is the temperature. The K_{os} value for ceria nanoparticles indicates a tendency to agglomerate at ambient temperatures even in a low concentration solution(32).

It is expected that with the onset of ice nucleation and crystallisation, the pH increases to a high (acidic) indeterminate value(33). According to subsequent experiments using the particle encounter complex model, oriented agglomeration at high particle concentrations was possible only at high acidity(11). These conditions are satisfied when the ceria

nanoparticles reach a stage of supersaturation while migrating into the aqueous region during freezing process which also increases the acidity in the remaining unfrozen solution. As the freezing front traverses through the system, the supersaturation in the liquid region forces the nanoparticles to agglomerate quickly into octahedral superstructures, driven primarily by the kinetics of the system rather than the thermodynamics. It is evident from our analysis that the formation of such super structures is complete as soon as the freezing is complete. Conversely, several days of aging are required to facilitate superstructures at room temperature. Nanoparticles trapped in ice channels agglomerate in a similar fashion via localised oriented assembly to form nanorods as the solution from the capillary drives out.

The observation of polycrystalline nanorods under freezing conditions enlightens another side of oriented agglomeration in which anisotropic self assembly does not progress through a stage of amorphisation and complete reorientation to form single crystalline structure. The very low thermal energy during freezing and aging at -18°C is responsible for maintaining polycrystalline nature while the one dimensional confinement caused by channels in ice results in attachment of different polycrystalline particles.

The role of ice as a physical template along with the importance of freezing rate was further investigated by subjecting the initial ceria seed solution to direct quenching in liquid nitrogen. During quenching under liquid nitrogen environment (SI-1b) the total solution was frozen in 50 seconds while the solution which comes in contact with the liquid nitrogen was frozen instantaneously. This extreme freezing rate does not allow the phenomena of freeze fractionation (solute rejection etc). It is also important to note that there is a fundamental difference in the freezing process while the vials are left in a

“freezer” at -18°C and while they are gradually immersed into the liquid nitrogen. While the freezing front proceeds from top to bottom and the capillary phenomena occur in the former case, the same are not feasible in the latter. Hence, the nanoparticles are trapped (frost) as is at random positions and thus we have not observed significant differences between as synthesized particles and those frozen in liquid N_2 (i.e. octahedral superstructures were also not observed SI-8). On the other hand aging of ceria nanoparticles solution at 4°C for 2 weeks, resulted in formation of faceted agglomerated nanoparticles [SI-8]. The absence of nanorods from the unfrozen solution suggests that templating effect of ice is required for synthesis of nanorods.

Whitesides et al (1) have proposed the ‘ground rules’ for the self assembly of basic building blocks as the ease to attain equilibrium between aggregated and non aggregated states or to adjust their position relative to one another once in an aggregate. While the latter seems to happen in the formation of nanorods under the influence of capillary pressure, morphological evolution within the time frame of freezing reflects the tendency of $\{111\}$ terminated ceria nanoparticles to assemble even under fast kinetic conditions. This kind of process has very important and broad implications in establishing the self assembly mechanism in ceria nanoparticles as the morphology appears within a very short time frame. This also suggests that the total time to achieve morphologically stable equilibrium conditions is very short in case of ceria nanoparticles or the morphology can be achieved despite quenching the equilibrium conditions. This phenomenon could be unique to the fluorite structure of ceria nanoparticles. The most interesting part of the present nanorod formation is the evolution of longer nanorods how long with time (aging under ice) which proves the dynamic nature of self assembly in static ice templates. It can

be observed directly from SI-9 that the zig-zag attachment of ceria nanoparticles through (111) planes occur within 1 day of aging at -18°C . A strong evidence of oriented attachment is observed from the FFT pattern of SI-9 which indicates preferential attachment of planes instead of random aggregation of nanoparticles.

Synthesis of fibrous and layered sheets of composites exploiting the ‘physics of ice formation’ was demonstrated recently (27). In this present study, we have successfully exploited the physico-chemical processes happening during and after the freezing of ceria nanoparticle sols to mould one-dimensional nanorods (30nm diameter) and three-dimensional superstructures. This is a first step in using ice moulds to direct the self-assembly of nanoparticles into different shapes, sizes and assemblages. Aforementioned observations are also validated with the help of MD simulations as discussed below.

We have used molecular dynamics (MD) to simulate nanoparticle self assembly. Specifically, we explored agglomeration constrained in one and three dimensions, which led to models of chains/nanorods and octahedral superstructures, respectively. The simulation code and potential models have been described previously in reference 3.

To facilitate one-dimensional agglomeration, amorphous/molten CeO_2 nanoparticles, each comprising 6144 atoms and about 5nm in diameter, were positioned equally spaced, within a simulation cell box, $13 \times 13 \times 13 \text{ nm}$ in size, fig. 4(a). Each simulation cell comprised four nanoparticles. Constant *volume* Molecular Dynamics (MD) simulation was applied to the system for 6800ps at 3200K. The high temperature accelerates the dynamical simulation such that the crystallisation and aggregation is complete within the (small) timescale of the simulation. The simulations revealed attractive forces acting between neighboring amorphous/molten nanoparticles. Accordingly, under the MD

simulation, the nanoparticles started to move closer to one another and started to crystallize. Specifically, nucleating seeds spontaneously evolved within the nanoparticles facilitating their crystallisation. The resulting nanocrystal morphologies comprised $\{111\}$ octahedra with the sharp corners truncated by $\{100\}$ in accord with the experiment. Once crystalline, the nanoparticles continued to be attractive towards one another.

Fig. 4(b) shows the configurational energy of the system, calculated as a function of time. The first 300ps of time is associated with a steep gradient and reflects, in part, the crystallisation of the nanoparticles. The energy difference between the start of the simulation, where all the nanoparticles are amorphous, and fully crystalline nanoparticles, is loosely associated with the heat of crystallisation. After 300ps, the nanoparticles have already aggregated together forming part of a chain, fig. 4(c). During the next 1200ps, fig. 4(b), point A to point B, two nanoparticles (green and blue, fig 4(c)) attach themselves to one another via $\{111\}$ surfaces; a plan view of the epitaxy between the two nanoparticles is shown in fig. 4(d). The attachment energy can be determined as the energy difference between point A and point B, fig 4(b). A movie showing the attachment is available as supporting information SI 9. As the MD continues, the energy continues to reduce reflecting annealing conditions. This may include, for example, surface relaxation, rotation of the nanoparticles to facilitate a better fit, annealing out of dislocations etc. An illustration is shown in supporting information SI 7 in which a screw dislocation anneals out and facilitates coherent matching between the atomic planes of two attached CeO_2 nanoparticles. We also modeled a three dimensional aggregation of

$\{111\}$ terminated ceria nanoparticles (34) which form a closed packed octahedral structure as shown in figure 4e.

Our simulations, where we simulate the self-assembly *directly*, predict that when the system is constrained in one-dimension (modeling the reduced dimensionality of the ice cavities), then the Ceria nanoparticles attach via $\{111\}$ faces resulting in a ‘zig-zag’ structure of the nanorod, fig. 4(c); rather than, for example, a parallel chain via attachment of $\{110\}$. Clearly, random ‘zig-zag’ attachment would not facilitate a linear chain. However, the constraining influence of the straight ice mould forces nanorod evolution. By simulating self-assembly dynamically, similar to experiment, the models derived are metastable and do not represent thermodynamically the lowest energy structures. Accordingly, after attachment, the nanoparticles (attempt to) rotate to improve the epitaxy and area of coherence (animations of the behaviour are available, SI 10). We also observe from the simulations that once attached, the translational and rotational degrees of freedom for the individual nanocrystals are reduced and therefore optimum attachment (thermodynamic) is difficult to attain. We note that the atomistic model of the nanorod/chain, figure 4(c), can be used to help describe and understand the observed structure, figure 1b, which is the 1-day old sample. During prolonged aging, the ice becomes harder and denser and will impose high localized pressure upon the chain within the ice-mould. Accordingly, we performed MD simulations on the chain under 0.1 - 0.5 GPa pressure. The animations of the simulation revealed that the nanocrystals reorient and pack tighter together.

In contrast, when we do not constrain the nanocrystals to one-dimension (unconstrained) the resulting (kinetically driven) models are three-dimensional, fig. 4(e). A more detailed

description of the three dimensional geometry of the superstructures is provided in reference (35) and was found to retain their nanocrystal identity upon rearrangement giving rise to polycrystalline superstructures.

In the present communication, we mimic natural self-assembly by using crystallizing ice cavities to architecturally sculpt 1-D ceria nanostructures. While much has been learnt from various resources of nature, harnessing the use of ice as tools to self assemble nanomaterials should be explored further. By altering freezing rates, initial particle concentrations and aging temperature, it should be possible to use these processes and changes in ice structures to sculpt desirable nanostructures comprising nanoparticle building blocks. Clearly, water/ice environments are pivotal to the natural world and its evolution and therefore understanding and controlling the behaviour of ceria nanoparticles in such environments, as we have done here, is a first step to facilitate future advances spanning, for example, nanofluidics to nano-bio applications(36).

References and Notes

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30. An important factor in freezing is the ice-water interfacial effects, especially surface tension arising from interface curvature. The smaller size of particle produces larger curvature effect, which is essential to create nano perturbations and nanochannels during the progression of freezing front. We have noted particle size and dilute concentration of solute as two important parameters for such nanochannel formation giving rise to capillary effect and solute trapping in channels.
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32. K_{os} was calculated using the supporting equations for the total interaction energy VT

$$V_T(h) = \pi R \left(\frac{-H_{121}}{12\pi h} + \frac{64c_{io}^* kT \Gamma_o^2 e^{-\kappa h}}{\kappa^2} \right)$$

For a non symmetrical electrolyte the κ was calculated using

$$\frac{1}{\kappa} = \sqrt{\frac{\epsilon_r \epsilon_o kT}{2000e^2 N_{Av} I}}$$

Where ϵ_r is the unitless dielectric constant of the medium, ϵ_o is the vacuum permittivity, κ is the reciprocal of Debye length, T is the temperature, I is the ionic strength and N_{Av} is the Avogadro's number.

While the Γ_o is given by

$$\Gamma_o = \frac{\exp(ze\phi_o / 2kT) - 1}{\exp(ze\phi_o / 2kT) + 1}$$

It must be noted that the estimation of K_{os} assumes a spherical shape of the nanoparticles a homogenous distribution of surface charge over the particle surface. For ceria nanoparticles in a

30mM solution using a surface potential value of 30mV, a room temperature value of 298K, particle size of 5nm, and obtaining other values from reference (31) the stability constant was found on the order of 10^{-3} . It must be noted that value of K_{os} obtained is for ceria nanoparticles in solution at room temperature and not for rapidly changing conditions during the freezing of ice.

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34. To facilitate three-dimensional agglomeration, crystalline {111} terminated CeO₂ nanoparticles, 8nm in diameter, (models generated previously, see reference 13) were positioned, equally spaced, within a simulation box 13.5x13.5x13.5nm. Constant pressure MD was then applied to this system at -180C for 350ps. This (constant pressure) enables the size of the simulation cell to change and therefore the nanoparticles can compact close together – driven by their attraction to one another. Here the nanoparticles agglomerated and attached via {111} surfaces to form a close packed structure, fig 4e.
35. When we do not constrain the nanocrystals to one-dimension (unconstrained) the resulting (kinetically driven) models are three-dimensional, fig. 4(e). However, in contrast to the 1D chain, the CeO₂ nanocrystals comprising the 3D superlattice are tightly bound to twelve nearest neighbours. Accordingly, the degrees of freedom are very much reduced and the activation energy associated with any movement of one nanocrystal (to improve, for example, epitaxy or coherence) is so high as to prevent rearrangement. Thus the initial agglomeration (kinetically driven) gets locked into the structure and any extended periods of simulated annealing have little influence upon structural rearrangement. The simulation thus provides model atom positions for the schematics shown in fig. 3b. We note that the CeO₂ nanocrystals in the close-packed structure are not space filling, rather the nanocrystals occupy 73% of the space (calculated using solvent surface of 1.4Å; Ce4+=0.92Å, O2-=1.32Å). We also performed simulations at 20GPa pressure and found that the nanocrystals do not agglomerate into the bulk parent material; rather the nanocrystals retain their individual identity, whilst becoming more space filling.
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List of Figures

Figure 1: TEM images taken from frozen ceria solution (after melting) a) Immediately after the formation of ceria nanoparticles, and after freezing and subsequent aging for b) 1 day c) 1 week d) 1 week aged showing several ceria nanorods and octahedral structures e) 2 weeks f) 2 weeks aged showing polycrystalline nature of ceria nanorods with 3-5nm nanocrystallites. These 3-5nm nanocrystallites are retained and serve as the building blocks for both nanorods and octahedral morphology

Figure 2: Shows the systematic motion of the freezing front producing nano voids and nano capillaries during solidification of ice from water. The perturbations caused by the solute are assumed to be same as during the solidification of a binary alloy. However, the nanoparticles cause nano level perturbations during the cellular growth forming nano channels in which solute particles can be trapped. Such a phenomenon is also observed during freezing of polar ice in which brine channels are formed (the brine channels are microscopic in dimension due to high concentration of salt and large size of secondary particles). The rapid agglomeration in the remaining solution forms octahedral superstructure.

Figure 3: Schematic of the evolution of nanorods and octahedral morphology during freezing and subsequent aging of the ceria nanoparticles. Initial seed of ceria nanoparticles having a truncated octahedral geometry grows in an oriented agglomeration to form truncated octahedrons during the initial stages. Upon further aging the particles trapped in ice capillaries form nanorods while those remaining in solution during progression of freezing front agglomerate as octahedrons. b) building blocks of octahedral superstructure and nanorods. c) Image generated by selected masking and inverse FFT of a high magnification image of ceria nanorods showing dislocations (circles) formed during orientation and self assembly

Figure 4: Results from MD simulation of self assembly of nanorods and octahedral superstructure: Atom positions comprising the CeO₂ nanostructures. (a) Starting configuration comprising CeO₂ nanoparticles placed equally spaced into a simulation box a 2×2×2 supercell is shown; (b) configurational energy, calculated as a function of time; (c) structure of a chain/nanorod comprising CeO₂ nanocrystals. Top: after 300ps of MD simulation. The arrows indicate the trajectory followed by the blue and green nanoparticles as they attach themselves to one another; bottom: after 1500ps showing the attached configuration; (d) view showing the epitaxy between the nanoparticles attached at (111) surfaces; (e) close packed structure comprising CeO₂ nanocrystals (which corresponds to figure 3b). Cerium is coloured to help visualise the individual CeO₂ nanocrystal secondary building units.

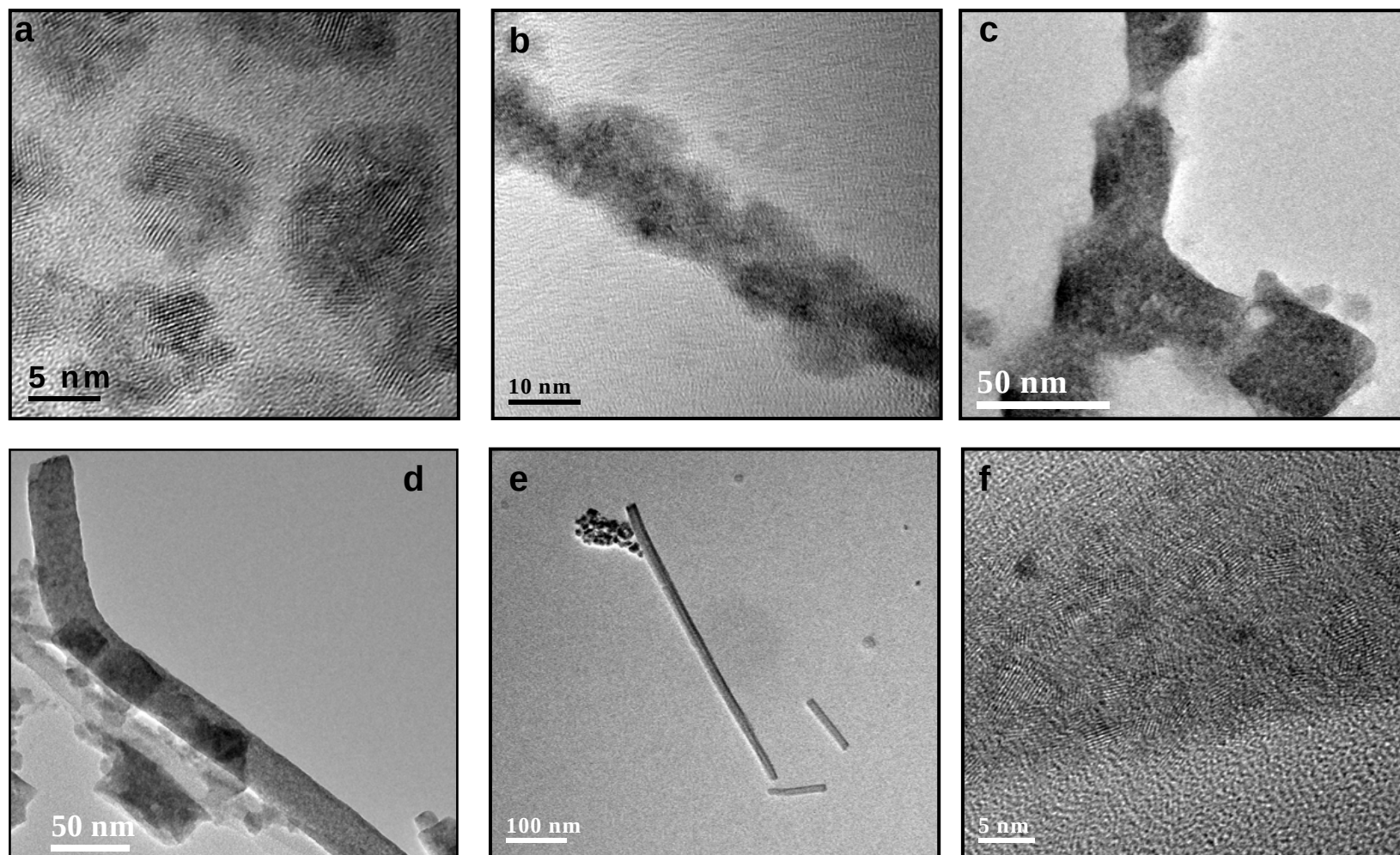


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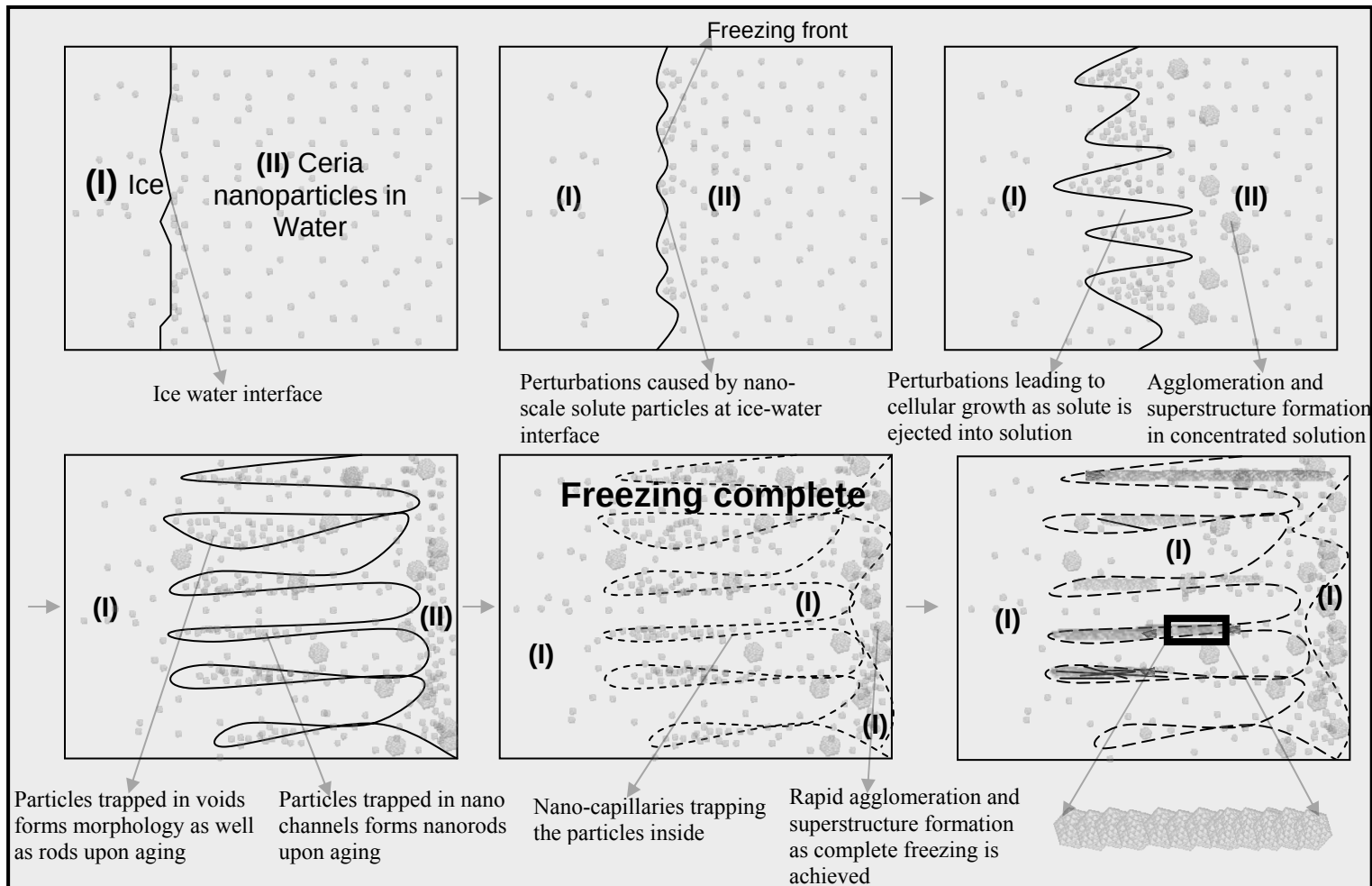


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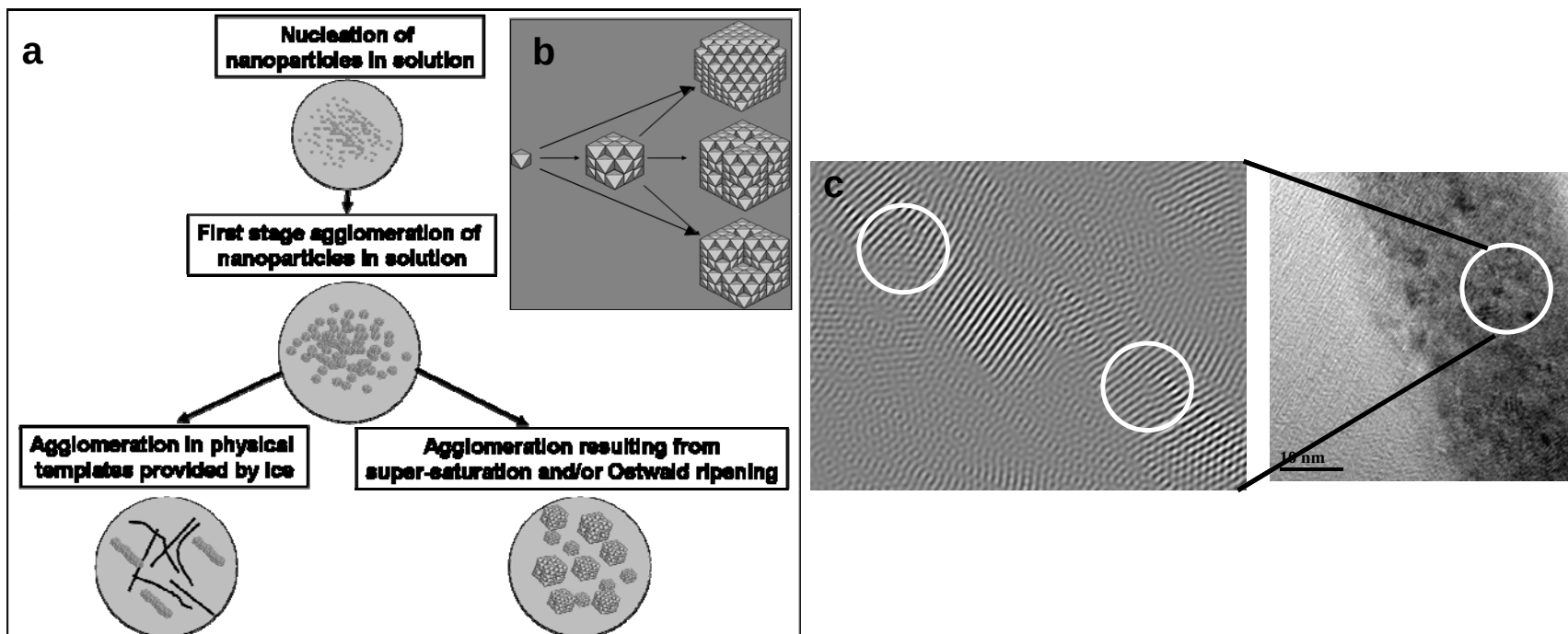


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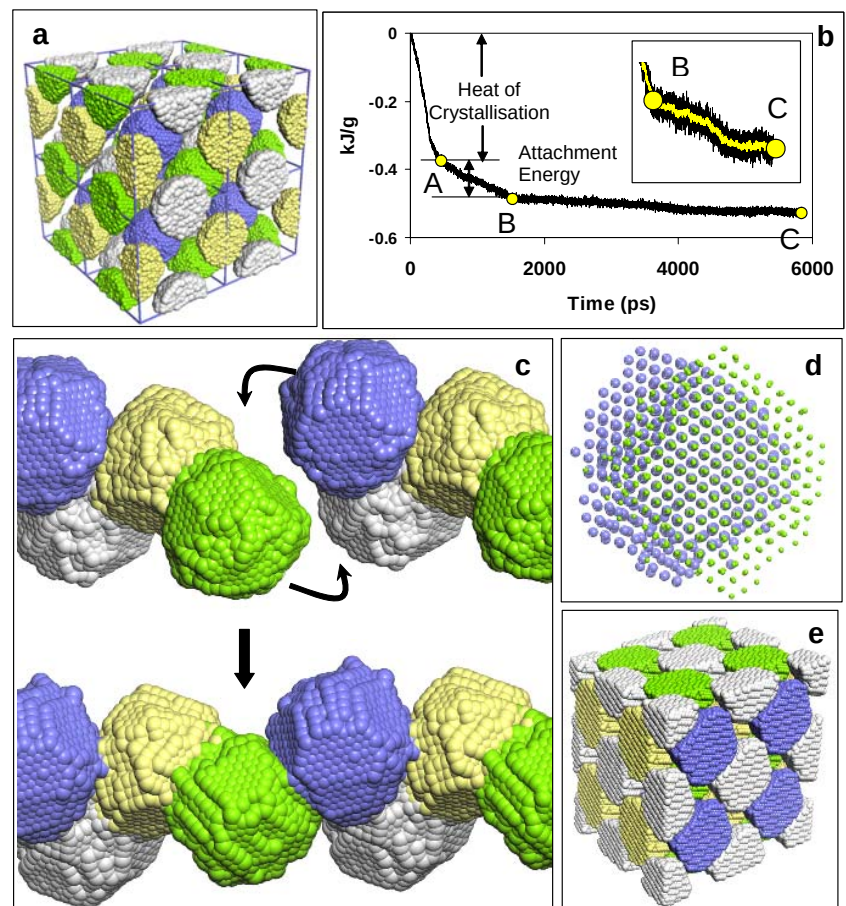


Fig. 4 Results from MD simulation of self assembly of nanorods and octahedral superstructure : Atom positions comprising the CeO_2 nanostructures. (a) Starting configuration comprising CeO_2 nanoparticles placed equally spaced into a simulation box a $2 \times 2 \times 2$ supercell is shown; (b) configurational energy, calculated as a function of time; (c) structure of a chain/nanorod comprising CeO_2 nanocrystals. Top: after 300ps of MD simulation. The arrows indicate the trajectory followed by the blue and green nanoparticles as they attach themselves to one another; bottom: after 1500ps showing the attached configuration; (d) view showing the epitaxy between the nanoparticles attached at (111) surfaces; (e) close packed structure comprising CeO_2 nanocrystals (which corresponds to figure 3b). Cerium is coloured to help visualise the individual CeO_2 nanocrystal secondary building units.



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Symmetry-driven spontaneous self-assembly of nanoscale ceria building blocks to fractal superoctahedra

Kuchibhatla, Satyanarayana V. N. T.; Karakoti, A. S.; Sayle, Dean C.; Heinrich, H.; Seal, S.

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