# Nanoparticle assembly: a perspective and some unanswered questions

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*In early 2016, the Royal Society of Chemistry arranged a meeting on the topic 'Nanoparticle Assemblies: from Fundamentals to Applications' which was hosted at IIT-Bombay, Mumbai. The meeting brought several leading nanoscience and nanotechnology researchers to India and is only the second Faraday Discussions meeting to have been held in the country. The papers presented at the meeting and the resulting active discussions have been summarized in a Faraday Discussion issue[1]. The broad range of topics discussed at the meeting led to an understanding on where we stand in the field of nanoparticle assembly, and also enunciated some of the outstanding fundamental and practical issues that remain to be resolved before these ideas can be applied to practical situations. Driven by these ideas, here we focus on four topics/questions: (i) Can we achieve function-driven design of nanoparticle assemblies? (ii) What is the minimal information needed to build a desired assembly? (iii) How complex a structure can one build? How can one make it responsive? What are the relative roles of equilibrium versus dynamics in the assembly process, and are we at a point where we can now pursue active assembly as a viable mode for creating complex assemblies? (iv) What are the applications that are being targeted and what are the barriers to implementation? In this perspective, we do not present an exhaustive survey of the vast literature in this area, but indicate overarching themes/questions that require immediate attention, largely based on the discussions at the Mumbai meeting.*

**Keywords:** Function-driven design, fundamental issues, nanoparticle assembly, practical applications.

NANOPARTICLE assemblies are encountered in a wide variety of practical applications. For example, over 70% of the approximately 12 million metric tonnes of carbon black nanoparticles (NPs) produced annually goes into rubber compounds used in automotive tyres[2,3]. Controlling carbon NP assembly in the nanocomposite is critical to the performance of the tyre and remains an active area of research. Spontaneous organization of the nanoscale platelets of clay into stacks and higher order structures is the key for balancing their mechanical performance and scalability[4]. Last but not the least, self-organization represent a quintessential biomimetic characteristic of inorganic NPs that leads to numerous implementations in drug delivery, biosensing, biotechnology and even agriculture. The use of colorimetric biosensors based on gold NP assembly is widespread (and growing), thanks to advances in the chemistry of coupling molecules to gold surfaces. Controlling the process of NP assembly and the resultant structure is critical to not only these uses, but also for applications in catalysis, in conversion of solar energy, and for creating materials with unique optical and optoelectronic properties. The assembly of NPs into chains followed by oriented attachment leads to lattice connectivity between initially separated inorganic grains[5,6]. This effect is essential for the energy storage devices[7,8]. What does 'control over NP assembly' entail

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and how does one achieve it? There are several aspects to this underpinning question. To begin with, it is important to be able to synthesize NPs with control over their size, shape, composition and surface chemistry. This topic has received significant attention from the materials chemistry community[9–19], and it is now possible to routinely synthesize large quantities of NPs with desired size distribution, chirality and surface functionalization. NP attributes that result from synthesis, along with any imposed stimuli or external fields, then dictate the nature of assembly. Finally, 'functional' assemblies of the kind that find applications in nanocomposites, thin film NP photovoltaics, pregnancy test kits, batteries, and optoelectronic devices for example, must result from this combination of defined NP synthesis and control over the assembly process. In this article, we focus on aspects downstream of particle synthesis that relate to controlling how NPs assemble, how it relates to biological analogos[20,21] and how this can be used to create functional assemblies.

## State of the field and outstanding questions

### *Can we achieve function-driven design of NP assemblies?*

The preparation of exquisitely controlled NP assemblies has been enabled by a combination of new methods for particle preparation and surface modification. Enormous strides have been made in precisely controlling the assembly of NPs. Two points are noted here. In the case of popular systems involving DNA-grafted NPs, the size of the ordered domains that can be formed by self-assembly is small, typically micrometres in size[22–24]. Thus, grain boundaries dominate the macroscopic structure, and presumably the properties of these assemblies. Our ability to controllably design these assemblies is at present restricted to the 100–1000 building block size range[25]. However, there is currently no clear pathway to extend these schemes to get a larger number of NPs to assemble into an ordered array in a robust, reproducible manner (either due to defects or due to complexity). Therefore, the preparation of functional materials based on DNA-bridged NP assemblies for use in practical applications does not currently leverage the advances in understanding from these model studies. In a different vein, the spontaneous assemblies of many thousands of anisotropic NPs modified driven by often subtle differences in their interaction reached a level of sophistication comparable to biological systems in respect to geometrical complexities and functions[26,27]. These strides can be made when we partially relax the requirements for structural determinism and rely on dynamic collective interactions of NPs that we have only begun to understand[28]. One could also note that in all cases the development of models that elucidate the rules for NP structure formation is happening largely independent of experiment.

We see two paths to make progress in this topical area: (i) The development of empirical 'morphology' diagrams that can, in the short term, guide researchers in identifying regions of the parameter space where certain (complex) structures form[22,29]. In line with the work on the periodic table of protein complexes[30] and the biomimetic nature of NPs, is it possible to enumerate all possible aggregate motifs? It will be valuable to list the minimum number of parameters required to capture all possible motifs, e.g. particle size, and inter-particle interaction parameters – this will essentially fix the dimension of such a morphology diagram. This will also hint at the existence of a finite number of topological measures, akin to a basis-set of parameters, which can potentially capture all motifs and categorize them systematically in a morphology diagram. Another particularly important point is experimental design to properly enunciate such empirical diagrams – robust combinatorial methods coupled to factorial design concepts, for example, are necessary to optimize such experimental efforts. The development of such combinatorial schemes could have a transformative effect on this field. On a related note, it would be interesting to know if these NP assemblies occur differently on a curved surface, as against the geometrically simpler, flat surface. This is not just an exercise in scientific curiosity, but has the potential dividend in furthering understanding in practical situations, where devices or meso- and macro-scale structures can be of any arbitrary curvature. (ii) Perhaps the more ambitious means of such a priori design is to use reverse modeling tools, e.g. using genetic algorithm[31–34], to design the building blocks that can assemble into a structure with desired function. The current implementation of such ideas has been largely limited to the prediction of colloidal building blocks that assemble into desired ordered structures – in particular, this has been applied to the assembly of colloids grafted with DNA strands, where two colloidal sub-populations have complementary single strands. Multiple developments are necessary to make this approach useful in the present context: While we have a reasonable means of going from crystal structures to building blocks, the corresponding connection to function (or properties) is currently undeveloped. What is central here is that we need simple, but accurate 'forward' models that can relate building blocks to structure and then to properties. Such forward models, which are implemented multiple times in an inverse design protocol, remain to be developed in contexts beyond DNA-driven assembly. For NP assemblies driven by the colloid interactions, much better understanding of the non-addivity of the van der Waals, electrostatic, and other forces is needed[28]. In the majority of the realistic assemblies in solution, the system energetics largely drive the assembly. The inclusion of entropic factors remains an open challenge although a great deal of understanding was achieved of entropy driven assemblies in the Glotzer group[35]. The ability to extend these

ideas to amorphous assemblies is again critical. Most work to date has focused on crystalline assemblies of NPs, but much of the current interest, especially in the context of applications, is in assemblies with dominant organizational motifs rather than with fully deterministic architecture. How do we represent such assemblies and how do we then design the building blocks and processing conditions so that desired properties can be realized?

### *What is the minimal information needed to build a desired assembly?*

Recent computational work has shown that structures of arbitrary complexity can be assembled[36] – assemblies comprising about 1000 building blocks can be formed in 'high yield' – so long as the building blocks and their interactions are properly defined (Figure 1)[25]. In practice, the desired equilibrium assemblies have been observed when solutions of DNA-tethered NPs are carefully cooled to within a narrow temperature range (below which undesired aggregates that represent glassy minima are accessed)[37,38]. The equilibrium assemblies are also formed in case of supraparticles – the terminal virus-like assemblies of a few hundred of NPs[39,40]. Unlike DNA-bridged systems these structures form under a variety of temperatures and other media conditions. While a wide variety of theoretical models and simulation schemes are being used to model the equilibrium assemblies of NPs, we do not have guidance as to where the experimental systems actually attain their equilibrium states[22,31,41–45]. Even in case of supraparticles that represent the case of equilibrated superstructures, the assembly pathway may not go through the valley of the minimal energy. There is a significant opportunity to use models and simulations to design increasingly robust pathways that can help achieve this goal. Two important points that have been learned from such studies are: (i) As one considers these more complex structures, the kinetics of assembly become increasingly important. Thus, it is necessary that 'misassembled' particles can go on and off so that the ultimate complex, desired structure can preferentially assemble in an experimentally meaningful timescale. These results place stringent demands on the barriers and activation mechanisms that underpin each step. In particular, it suggests that nucleation and subsequent growth processes have to be slow (or at least reversible) as one synthesizes progressively more complex assemblies. (ii) We must have an intimate knowledge of the interactions between the building blocks, and the ability to control these interactions. While the dispersion interactions between colloidal particles have been enunciated[46], the relevance of these ideas on interactions between much smaller NPs remains unclear. Additionally, the effects of charge, of solvation forces, any interactions emerging from the nonsphericity (e.g. arising from the faceting of the NPs, or of any asymmetry in the grafting of chains or ligands to the NP), and the interactions between any bound ligands play a large role but the methods for their proper account remain unclear at this time[28]. Many of our current constructs to model these different elements use conventional macroscopic ideas – for example, the polymer-induced inter-NP interaction in the presence of unbound polymer chains is assumed to be modelled by the venerable ideas of Asakura and Oosawa[47,48]. How do these colloidal ideas get modified when we consider situations where the constituent NPs and polymers are comparable in size? Similarly, while we acknowledge the limitations of the DLVO formalism[28], we continue to employ it to calculate inter-particle interactions in the absence of alternate methods. It is clear that development of more reliable methods to estimate inter-particle interactions in the presence of solvents and other matrices will be critical for theory/simulations to provide predictive inputs.



**Figure 1.** An assembly formed from 86 DNA building block bricks (from Jacobs and Frenkel[25]).

### *What are the limits to the complexity of structures formed by NP assemblies?*

Preparation of DNA-tethered gold NPs has been an enabling technology for researchers investigating this question[23,24]. The ease of design and synthesis of specific DNA sequences and their coupling to gold NP surfaces affords model NP systems with precisely tunable inter-particle interactions. These have allowed the realization of ordered superlattices of gold NPs directed by linking through DNA tethers, including a recent demonstration of diamond-like open lattices[49]. Recent simulations have demonstrated that structures as complicated as 'Big Ben' (rectangular parallelopiped with a pyramidal top) may be realized with 69 particles[50,51], and experiments have demonstrated that gold NPs can be directed to form a human stick figure.

Recently, NP assembly has been used to prepare aggregates comprised of a small number of colloidal

particles, organized into motifs that mimic the complex geometries associated with molecular bonding. In all these examples, particle assemblies are organized at equilibrium out of dilute dispersions, using DNA-functionalized particles with precisely tailored interactions. Practical limitations in the large-scale preparation of such functionalized particles, and kinetic limitations (described earlier in the text) suggest that such assemblies are likely to be limited to less than $10^3$ particles. This constraint is removed when the assemblies are made driven by the balance of the colloidal forces. They lead to the formation of large-scale superlattices that can comprise billions of constitutive units and results in both simple hexagonal[52], open Kagome lattices[53], intricate crystalline patterns[54] and complex quasicrystalline motifs.

When NPs are polymer-grafted (rather than simply capped with small molecule ligands), a much richer particle assembly emerges[29,55]. Interactions between surface-grafted polymer chains can drive the NPs to assemble anisotropically, at specific graft densities and size ratios of grafted to matrix polymer chains. The polymer-grafted NPs dispersed in a polymer matrix represent a convenient model system. Such systems are sufficiently simple to yield insights into the process of NP assembly and have implications for the design of practical functional composites.

Finally, complexity in organization can also be driven by templating effects of various interfaces. For example, macroscopic ice-templated assemblies formed by freezing aqueous particle dispersions[56], recover elastically from large deformations due to the unusual inter-particle bonding resulting from the assembly process[56]. The ice-templating process is versatile and can be used to assemble NPs into one-, two- and three-dimensional assemblies (Figure 2)[56–59]. External fields, such as flow, can be used to drive the formation of particle assemblies for photonic applications. In contrast to these examples, in nature, energy is generated and propagated through a system to drive the assembly. Synthetic systems that mimic such biological processes are termed 'active'. Interesting new work has demonstrated the potential of this approach to generate complex assemblies in Janus particles in external rotating magnetic fields.

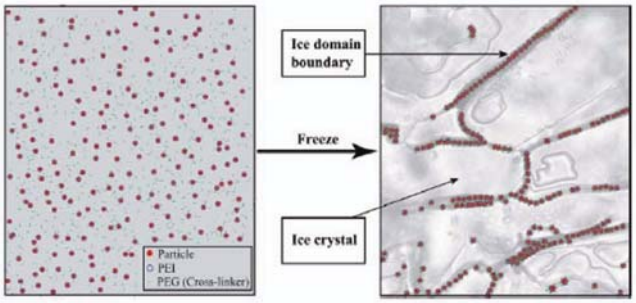



**Figure 2.** Organization of nanoparticles by the freezing of water (from Kumaraswamy *et al.*[57]).

Thus, we are continually pushing the limits of experimentally achievable complexity in NP assemblies. For practical applications, we will need to realize the precision achieved for NP assembly over macroscopic scales. Macroscopic assemblies result from techniques that employ external fields or from active assembly, but without the same level of local precision.

### *What are the applications that are being targeted and what are the barriers to these implementations?*

The applications of materials with self-assembled NP structures have relevance to a variety of contexts. They act as a source for mechanical reinforcement, in packings as enhancers of barrier properties, as flame retardants in airline applications, as additives to polymer membranes to enhance ionic conductivity and selectivity, and most recently, in organic photovoltaics and in the creation of photonic materials (especially in the context of plasmonics). We consider (largely based on the discussions we had) two such applications: one a mature application, namely rubber tyres, and other on plasmonic applications of NP assemblies. In both of these areas, the barrier to the use of these assemblies is the ability to reproducibly achieve the same sets of structures in an industrial context.

The situation with rubber tyres is particularly insightful – while much progress has been made over the last seven decades in effecting rational improvement, researchers at Michelin[60,61], for example, continue to probe how the NP dispersion state can be further improved, while using essentially unchanged processing conditions. The ultimate goal is to improve the desirable mechanical properties of the resulting tyres, e.g. reduce wear resistance and minimize rolling resistance. In particular, Michelin researchers used *in situ* reactive functionalization of NP surfaces with polymer chains (these chains have an appropriate functionality that can react with moieties on the surface) to improve the NP dispersion state. While this approach is useful, it remains unclear as to the optimal degree of functionalization that can be achieved under a desired processing condition, namely what level of chain functionalization is necessary to optimize the properties of the materials in question? Going further, can we achieve even better results through (minor) modifications of the processing conditions? This relationship between materials structure, processing and the resulting properties, and how we can continually improve the desired properties of rubber networks are the focus areas that continue to be of interest. In particular, we highlight that predictive relationships between these variables need to be developed if rational improvements are to be achieved.

In addition to these well-established applications, a new area that is emerging is plasmonics (Figure 3)[62,63]

and especially chiroplasmonic assemblies and composites[64,65]. DNA-bridged NP assemblies can have a particularly essential role in the latter because they afford automatic assembly of such superstructres with exceptionally strong polarization rotation using PCR technique. There is also an increasing drive to assemble NP structures using DNA and proteins as guiding motifs, to develop more complex structures. For example, one design for an negative refractive index material in the visible region requires the three-dimensional organization of splitring resonators. Assemblies of a small number of metal NPs that exhibit Fano resonances have been reported in the literature[66,67]. Larger length scale plasmonic assemblies of mesogen-coated gold NPs have also been reported. However, strategies that combine precise local assembly into plasmonic motifs with precise positional and orientational ordering of these motifs to form macroscopic plasmonic materials are currently unavailable. In analogy to the discussion on tyre compounds, here too, relationships between structure and 'processing' strategies need to be developed to achieve practically useful plasmonic structures.

We end by discussing two aspects which are possible barriers to any new applications. The first concerns the appearance of defects in an ordered structure of NPs. In making a functional device, the aim would be to minimize defect density. Fundamental studies in establishing the role of size, shape and functionality of the individual NPs (the building blocks) on the type and density of defects would provide valuable insights towards this objective. The second impediment in more advanced application scenarios could be along the lines of feedback or feed-forward coupling between the NP assembly and the embedding environment in which it has to be functional. Such coupling can be detrimental to its intended function, in the sense of random, external noise. However, one can expand this aspect to make it intellectually more stimulating. For instance, one might be interested to explore the likelihood of having assembly formation to follow a pre-determined time-line which can be clearly seen in the previously discussed biomimetic assemblies of NPs. This can lead to two apparently opposing demands of functional assemblies, which nevertheless are conceptually alike: (i) The question of whether assemblies can be made to be adaptive to their environment, in a deterministic, pre-programmed manner. (ii) In addition, the opposite question of how to make assemblies robust and immune to unwarranted changes or random noises in the environment, which can possibly be tackled by building-in certain redundancies in the assembled network of NPs. Steps towards addressing the above barriers and questions require setting-up new model problems in both experimentation and modeling, which can open up new avenues in the science of engineered NP assemblies.

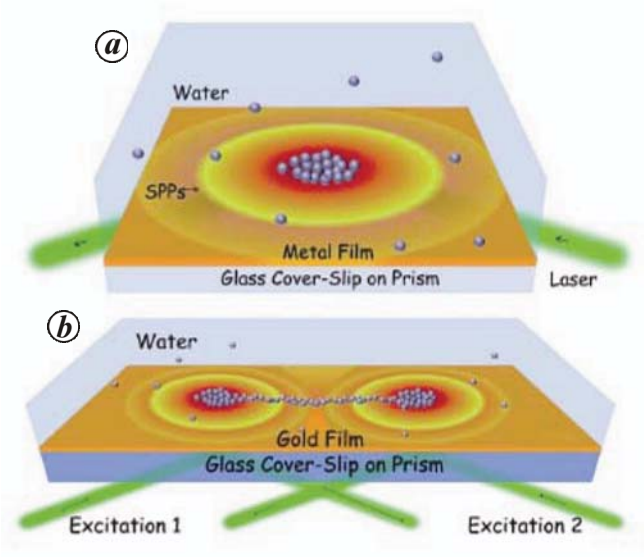



**Figure 3.** Excitation of a metal film by a laser induces a flow field that drives the linear assembly of nanoparticles[62].


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ACKNOWLEDGEMENTS. The meeting ‘Nanoparticle assemblies: from fundamentals to applications’ was sponsored by the Royal Society of Chemistry and co-organized by Charusita Chakravarty (IIT Delhi) and Sanat Kumar (Columbia University, USA). Unfortunately, Prof. Chakravarty passed away soon after the meeting. We would like to acknowledge the guiding spirit of Prof. Chakravarty, both for the conference and for this article, and dedicate both to her memory. S.K.K., B.L.V.P., G.K. and R.B. thank the Indo-US Science and Technology Forum for support through the joint center grant on Nanoparticle Assembly: From Fundamentals to Applications. N.A.K. is grateful to the National Sciences Foundation and Biointerfaces Institute for the support of his participation in the meeting.

Received 13 September 2016; accepted 23 October 2016

doi: 10.18520/cs/v112/i08/1635-1641