

Materials Fabricated by Micro- and Nanoparticle Assembly – The Challenging Path from Science to Engineering

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We classify the strategies for colloidal assembly and review the diverse potential applications of micro- and nanoparticle structures in materials and device prototypes. The useful properties of the particle assemblies, such as high surface-to-volume ratio, periodicity at mesoscale, large packing density, and long-range ordering, can be harnessed in optical, electronic, and bio-sensing devices. We discuss the present and future trends in the colloidal-assembly field, focusing on the challenges of developing fabrication procedures that are rapid and efficiently controlled. We speculate on how the issues of scalability, control, and precision could be addressed, and how the functionality of the assemblies can be increased to better match the needs of technology.

1. Introduction and Classification of Colloidal-Assembly Strategies

The organization of matter in nanomaterials and nanodevices can be accomplished by top-down miniaturization techniques or bottom-up methods typically based on self-assembly or directed assembly. The most widely used classes of objects in bottom-up assembly are colloid micro- and nanoparticles. A large research effort is directed to the fabrication of functional materials from organized particles. These advanced assemblies can find applications in areas such as photonics, electronics, sensing, and drug delivery.^[1] Here, we present an overview of the methods and strategies for the assembly of particle structures classified on the basis of their dimensionality. We survey the potential areas of application of the structures assembled from particles, and discuss why the technological potential of these structures is at present largely unrealized. Many of the challenges in the area of nanocolloidal assembly relate to the development of assembly processes that are scalable, controllable, rapid, and inexpensive.

The power and versatility of colloidal-particle assemblies are best illustrated by the vast number of structures and strategies for their fabrication reported in the literature. A convenient way to classify the majority of the colloidal assemblies could be

based on their dimensionality and degree of ordering – three, two, one-dimensional, or independent clusters. In order to evaluate the ease and precision of the controlled fabrication of such materials, we also need to analyze in each case the physical principles by which a certain structure is assembled. The assembly can be accomplished by an extensive array of techniques based on numerous physical mechanisms. A survey of a few major groups of methods that have found use in the controlled assembly of particles into materials with well-organized and defined microstructures is presented in Table 1. The goal of these techniques is to collect the particles,

organize them, and bind the structure formed into a permanent material. The collection can be achieved by methods as simple as sedimentation,^[2] but can also be directed by convection and capillarity,^[3] or driven by external fields.^[5] The organization can be a result of confining the particles to initiate crystallization,^[9] or templating them on surfaces and objects.^[7] The binding can be achieved with methods as simple as adding (poly)electrolytes of opposite charge,^[4] or as complex as directed key-and-lock recognition of proteins or DNA molecules.^[6] The biological assembly is presently the most precise, albeit also the most expensive one, unless simple inexpensive biomimetic linkers are developed. We present below a few examples of the major classes of particle structures based on their dimensionality, and discuss some of the potential applications of such particle assemblies.

1.1. Three-Dimensional Materials

The simplest and fastest way to obtain such materials is aggregation of suspended particles resulting in a gel or solid phase.^[10] Materials formed by such processes usually have disordered, fractal-like microstructures. This “assembly” process is very simple, inexpensive, and scalable, and works with many classes of particles without need for uniformity in size or shape. It is routinely used in the fabrication of ceramics, catalysts, and a large variety of sol–gel materials.^[11] While the focus of this review are materials with much better-defined structures and more complex properties, it should be noted that the disorganized 3D particle aggregates are possibly the only type of “assembly” that is presently produced on an industrial scale.

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A class of particle-derived materials with much higher degree of organization is that of 3D colloidal crystals. Interest in the physical mechanisms of the particle crystallization in bulk suspensions predates the present day thrust in advanced-materials fabrication. The original methods of crystallization by deep deionization and long-range electrostatic repulsion^[12] are not very practical for materials fabrication. 3D crystals, however, can be easily fabricated by concentration of monodisperse spherical particles through sedimentation.^[2] The process can be speeded up by centrifugation, electrophoretic collection, filtration, and other methods.^[13] The resulting materials possess uniform porosity, higher mechanical stability, well-defined internal-transport characteristics, and extraordinary optical properties. These materials could find applications in catalysis, separations, substrates for biomaterials, and templates for the formation of “inverse opal” structures.^[1a,b,13a]

Two of the major challenges in the formation of 3D crystals are shaping them into a desired shape and controlling the symmetry

and orientation of the particle lattice. The overall shape can be templated by the assembly vessel or, in more straightforward implementations of the technique, by filtering the suspension inside specially designed thin cells.^[13c] The control of the symmetry of the particle crystals is much more difficult, as the particles in confined geometries typically self-assemble into trivial arrays of randomly stacked hexagonal planes (rhcp).^[14] The symmetry and the orientation of 3D crystals from particles can be controlled by the application of external electrical fields,^[15] but facile processes for the extraction of the obtained body-centered tetragonal crystals have yet to be developed.

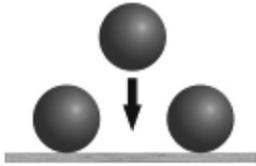
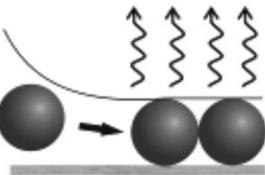
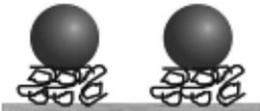
The assembly of colloid crystals from nanoparticles has been another active area of colloid and materials research. The forces operating between the nanoparticles in a suspension are more complex, because the size of the particles is comparable to the range of the intermolecular and surface forces. It has been recognized that nanoparticles can be crystallized by slow concentration similarly to larger microspheres.^[16] Binary mixtures of nanoparticles of different sizes form a variety of crystalline phases.^[17] Well-organized nanoparticle lattices could have very interesting electronic and optical properties.^[18]

The crystallization of particles by restriction of the free volume requires repulsive electrostatic interactions to allow for their rearrangement and organization with minimal friction. Strongly attractive interactions in particulate suspensions lead to aggregation without long-range ordering. It has been realized recently that weak, precisely balanced attractions between oppositely charged spheres can lead to crystallization broadly similar to the formation of ionic crystals by cations and anions. The concept of “ionic colloidal crystals” has now been proven both for oppositely charged particles in the micrometer^[19] and nanometer size ranges.^[20] It is expected that electrostatic binary-crystal assembly could lead to crystals of new symmetry and composition that might find applications in photonics and electronics. In more elaborate experiments, the nanoparticles can be crystallized by inducing attractive dipolar forces photochemically.^[21] Theoretical modeling of the assembly of particles of permanently embedded dipolar moments suggests a rich variety of phases and eventual formation or crystals of very high quality.^[22]

1.2. Two-Dimensional Films and Crystals

The organization of particles in films with controlled structure and thickness opens many possibilities for making products and devices, and is presently an intensively investigated research topic. The simplest way to deposit nanoparticle films on surfaces is adsorption from suspension onto oppositely charged or otherwise “sticky” surfaces (Fig. 1A).^[23] The process of Random Sequential Adsorption (RSA) can result in coverage of up to ~55% of the surface with monodisperse spherical particles in a relatively dense structure without long-range ordering.^[27] The adsorption can be made strong and irreversible by covering the surface with a layer of polyelectrolyte of charge opposite to the one of the particles.^[28] The process of adsorption of a molecular layer of polyelectrolyte over the particles can be repeated to bind them from the top and restore the surface to its original sign of charge. The subsequent “layer-by-layer” (LBL) particle and polyelectrolyte

Table 1. Examples of common techniques for the assembly of structures from colloidal particles and their limitations.

Method of Assembly	Schematics	Types of Assembly	Scalability	Complexity/Cost	Examples
Sedimentation		3D	Yes	Small	Ref. [2]
Evaporation		2D, 3D	Yes	Small	Ref. [3]
Adsorption/LBL		2D, 3D	Yes	Small	Ref. [4]
External force field		1D, 2D, 3D	Limited	Medium	Ref. [5]
Bio-specific		1D, 2D, 3D	Limited	High	Ref. [6]
Templated on surfaces		1D, 2D, 3D	Limited	Very High	Ref. [7]
Templated on droplets		Supra	Yes	Medium	Ref. [8]

adsorption can be repeated as many times as necessary, resulting in polyelectrolyte–particle films with well-controlled thickness and number of layers.^[29] These LBL films can be conveniently used to impart to the surfaces desired properties, such as high wettability^[30] and suppressed reflectance.^[31] LBL techniques have been used in the fabrication of devices such as diodes and solar cells.^[32] Formation of free-standing elastic films containing nanoparticles and polyelectrolytes by similar LBL methods has also been reported.^[33]

An additional level of functionality of the films of particles can be achieved by arranging them into large-scale arrays, or 2D crystals. This can not be accomplished by random sequential adsorption. One of the commonly used processes is the convective assembly.^[3a,34] The 2D crystals in this method are assembled in the moving meniscus of the drying particle suspension. The crystallization occurs when the particles carried by the flux of liquid towards the drying front are concentrated and incorporated in the transition region between the meniscus and the drying crystal (the process can be compared to filtering of the suspension on the moving crystal front). While it is often claimed that the process is driven by “capillary forces”, these forces

associated with particles protruding through free liquid interfaces^[3b] are involved mostly in films with two fluid surfaces.^[35]

Various implementations of the convective assembly aimed at making the process simple and inexpensive^[3c] or highly controlled^[24] have been reported. The deposition can be speeded up using suspensions of particles of high volume fraction or volatile organic solvents (Fig. 1B–E),^[24] yet the relative slowness of the process remains a problem. Alternative techniques for the assembly and deposition of 2D particle crystals have been based on the ability of the particles adsorbed onto free liquid interfaces to form 2D crystals, either by compression^[36] (akin to Langmuir–Blodgett molecular self-assembly) or due to capillary forces. The organized films of adsorbed particles are then transferred and immobilized onto solid surfaces.

The above techniques for direct particle assembly onto plain surfaces currently lack the ability to deposit single-domain crystals of specific orientation, due to multiple nucleation sites in the drying contact line.^[37] One of the promising strategies for organizing particles into large crystals and arrays with specific orientation is the application of external electric fields across the suspension. The particles can be assembled into closely packed

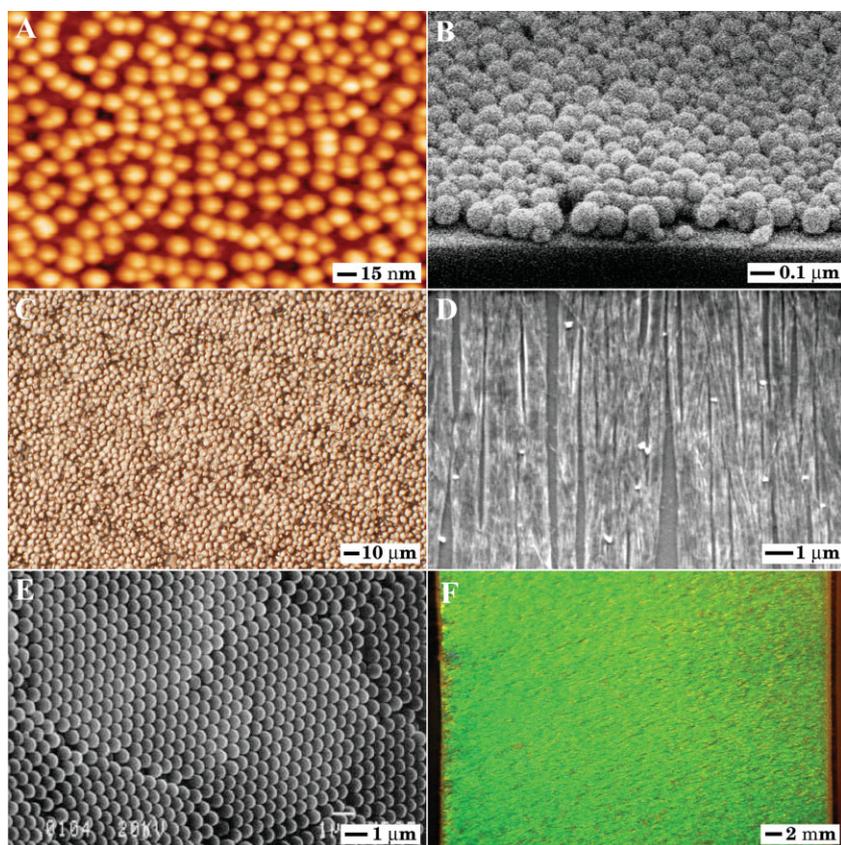


Figure 1. Examples of 2D particle assemblies. A) Electrostatic deposition of gold nanoparticles on a self-assembled monolayer of 3-aminopropyltriethoxysilane (e.g., [23b]). B–E) Structures fabricated via convective assembly: B) Unordered assembly from a binary mixture of particles in antireflective coatings. Reprinted with permission from [24b]. Copyright 2005 American Chemical Society. C) Organization of live yeast cells into surface arrays (e.g., [24c]). D) Assembly of Tobacco Mosaic Virus (TMV) into directed bundles (e.g., [24d]). E) Colloidal-crystal surface. Reprinted with permission from [25d]. Copyright 2000 American Association for the Advancement of Science Chemical Society. F) 2D crystallization of latex microspheres using AC electric field (e.g., [26]).

crystals by the electrohydrodynamic flows pulling them together,^[38] or into a long-ranged lattice by the repulsion of the parallel induced dipoles.^[39] The particles in a thin cell in-between two planar electrodes can also be organized into very long-ranged 2D crystals by alternating (AC) fields applied in the direction of the crystal plane (Fig. 1F).^[40] The forces involved include induced dipole chaining and dielectrophoresis, the mobility of particles along the direction of the gradient of the field.^[26] The application of AC fields can also lead to lateral motion of anisotropic particles due to induced-charge electrophoresis.^[41] The use of dielectrophoresis facilitated the assembly of single-domain 2D crystals with centimeter size and excellent, “clean” diffraction patterns. This can be used for the formation of new types of materials with strong anisotropy.^[42] It is still necessary, however, to develop processes for the immobilization and extraction of such crystals assembled in liquid-filled chambers.

1.3. One-Dimensional Structures

These assemblies are restricted in size and structure in two directions, while extending in one direction. The simplest

prototype of such a material is an aggregated chain of particles.^[43] The dipolar attraction induced by magnetic or electric fields is one of the most efficient ways to align the particles in chains (Fig. 2A–C). The chains of particles aligned in the directions of the field can be conveniently rotated,^[41,44] and if the interactions induced by strong fields are large enough, the chains can also assemble into 2- and 3D crystals by lateral attraction and alignment.^[26] AC electric fields can be used to assemble 1D structures from metallic nanoparticles as well (Fig. 2B).^[45] The nanoparticles in suspension are drawn into “microwires” growing in the direction of the field. The main effect driving the particle collection during the microwire growth is the dielectrophoresis.^[46] These microwire assemblies are many particles thick and permanently bound because of the strong irreversible aggregation of the particles collected by the field.^[47]

An alternative method for assembling particles in chains of strictly defined structure is the use of templates, where the particles are deposited inside precisely etched grooves and pits on the surface of micropatterned wafers (Fig. 2D).^[7b,d,48] The particles collected in the grooves can be bound together, resulting in chains of varying “bond angles” between the particles. The chain-like assemblies can also be produced in microfluidic devices.^[49] On a larger size scale, particles and particle-based materials can be assembled in the form of uniform cylinders by crystallization inside capillaries.^[50]

2D and 1D assemblies are common precursors and components in the fabrication of photonic and electronic devices, sensors, and biologically active structures.^[51] For example, semiconductor particles can be layered with polyelectrolytes to form electronic components, such as rectifying and light-emitting diodes and solar cells.^[52] Quantum confinement in arrays of metallic particles could be used in memories and nanoelectronic circuits.^[48a] Thin films of colloidal crystals have been studied as potential precursors to photonic devices.^[7a] Methods for patterning of the crystals in 3D have been developed,^[53] even though no true photonic circuits have been demonstrated to date.

Many of the potential uses of the assemblies are targeted to some biological or medical application in order to meet the growing needs of health care, drug and gene delivery, diagnostics, and tissue regeneration.^[51d] Particle assemblies have formed the basis of many types of biosensors, including those for protein, bacteria, and DNA detection.^[1i,51c,54] The biological functionality of these assemblies, however, is often limited by the relatively simple chemistry and properties of the particles involved. One way to increase the functionality of the assemblies that we have explored recently is to use live cells as “particles” that can be assembled by electric fields on chips^[44b] and in responsive coatings.^[24c]

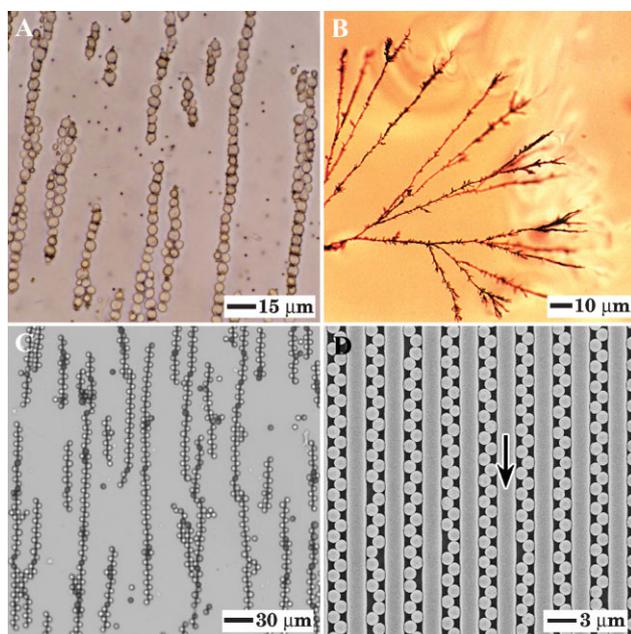


Figure 2. Examples of 1D particle structures. A–C) Colloidal assembly in external AC electric fields: A) Permanent chains from live yeast cells and lectin-functionalized microparticles (e.g., [44b]). B) Self-repairing micro-wires from gold nanoparticles (e.g., [45b]). C) Zigzag chains from anisotropic microspheres in AC electrical field (e.g., [42]). D) Zigzag chains formed via templated assembly. Reprinted with permission from [7b]. Copyright 2001 American Chemical Society.

1.4. Supraparticles, Colloidosomes, and Colloidal Molecules

The particles in these systems are assembled into small self-contained clusters with well defined structure and size. A simple, large-scale process to fabricate assemblies of large and small particles is the adsorption of small particles around larger particles of opposite charge. This process results in raspberry-type assemblies.^[6] A more elaborate method for assembling clusters from a single type of particle components is to use liquid emulsion droplets as templates that can be dissolved after the assembly and immobilization of the particles. This method has first been demonstrated with assemblies of particles both around and inside droplets (Fig. 3A, E, F).^[25] Subsequently, the empty ordered shells of particles assembled around droplets have been named “colloidosomes” (Fig. 3B and D).^[55] The assemblies of small clusters of particles compressed inside droplets have been called “colloidal molecules”, due to their resemblance to the ball-and-stick molecular models (Fig. 3C).^[4b,25c,56] The colloidosomes can find applications as semipermeable capsules for drug delivery and biotechnology as well as in pharmaceutical, cosmetic, and food products with advanced structure. The colloidal molecules have potential as precursors for producing colloidal and photonic crystals of unusual symmetry, however, the fabrication of large quantities of monosized clusters still appears to be a challenge.

The recent advances in the microfluidic dispensing and manipulation of fluid streams and suspended droplets have created another field of opportunities for fabrication of special particles and particle assemblies. The droplets in which the

particles are assembled can be floated up on the surface of perfluorinated oil.^[25d] These individual droplets acting as assembly sites can be moved and manipulated using electric fields generated by arrays of electrodes submerged below the oil.^[25e,57] Microfluidic devices with channels offer an efficient way to generate droplets of single size distribution and anisotropic properties. These droplets can be used as templates for fabricating special anisotropic particles and assemblies.^[58] It is likely that complex particle assemblies could soon be fabricated by more complex devices combining microfluidic delivery and external fields. While the “factory-on-a-chip” devices can produce extremely uniform assemblies, the small throughput of such methods is a major problem that can be addressed partially by massive parallelization of the microchannel lines. One simple and efficient way to assemble larger number of particles inside shrinking droplets is to deposit and dry the droplets on top of superhydrophobic surfaces.^[59] The droplets above these substrates remain in a nearly suspended state, and the “supraparticles” formed are easily removed from the surfaces, which can be readily reused.

2. Perspectives and Challenges

The colloidal-assembly research is thriving and attracting significant public attention and funding. Inasmuch, many of the structures assembled either include nanoparticles, nanowires, and nanotubes, or possess interesting properties derived from their nanoscale structural features, the colloidal assembly is considered to be one of the major fabrication tools in nanoscience and nanotechnology. A few examples of highly functional materials fabricated by colloidal assembly are presented in Figure 4.^[1h,51a,60] As this research area nears maturity, however, new problems and challenges are facing the community of scientists. The immense array of exciting achievements in research has not yet been matched by a commensurate progress in applications and manufacturing. To a large extent, this is because the area is still in infancy, and the academic rewards in creatively developing new materials and methods outweigh the need to consider the more mundane tasks of reducing the discoveries to practice. However, there also appears to be a number of serious challenges that the materials and nanoscience researchers today need to face and solve on the road to manufacturing and commercialization of technologies based on particle assembly. We define and discuss some of the challenges here as viewed from the perspective of the authors.

The first major challenge facing the investigators is the transition from synthesis and demonstration to engineering and process design. Many of the materials reported to date have been obtained in small domains or small volumes. While it may be relatively easy to assemble a structure of certain type on the scale of micrometers to centimeters, controlling and repeating the process over and on large scales might be problematic. The small sizes and large specific areas of the particles mean that the assembly processes in liquids are governed by colloid and surface interactions, including van der Waals, electrostatic, steric, and hydrophobic.^[61] These interactions are usually difficult to adjust precisely, and thus the control of the assembly process can be difficult and unreliable.

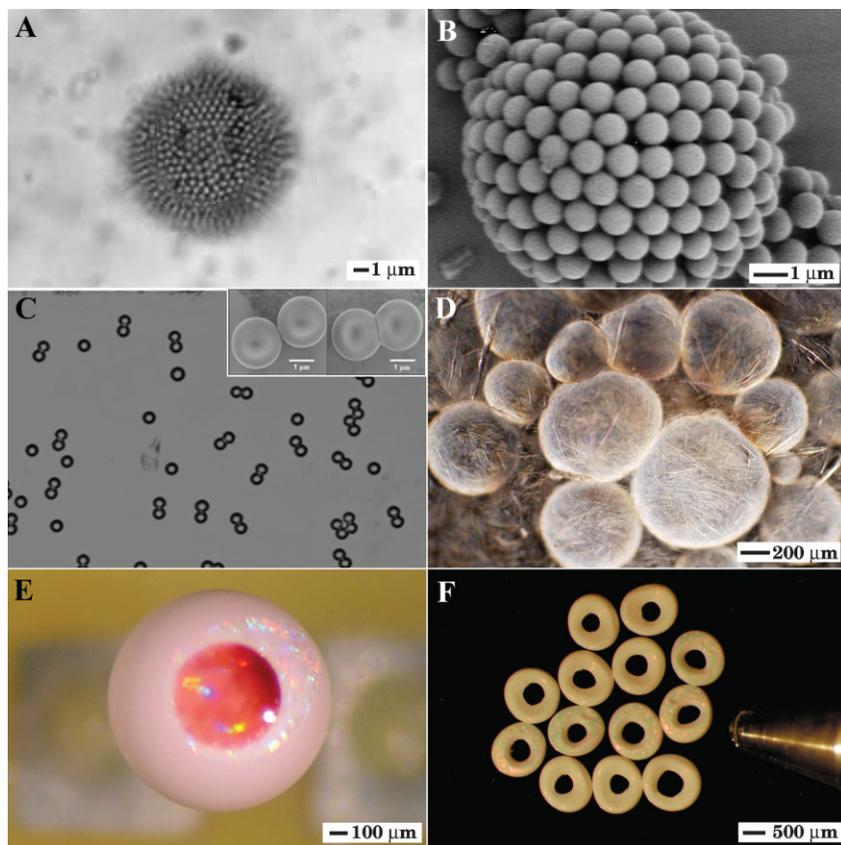


Figure 3. Examples of self-contained clusters and supraparticles. A) Particle collection around emulsion droplets (e.g., [25a]). B) Semipermeable colloidosomes. Reprinted with permission from [55a]. Copyright 2002 American Association for the Advancement of Science Chemical Society. C) Colloidal doublets. Reprinted with permission from [4b]. Copyright 2005 American Chemical Society. D) Microrod-stabilized “hairy” colloidosomes (e.g., [55b]). E) Anisotropic “eyeball” supraparticles. Reprinted with permission from [25e]. Copyright 2005 Nature Publishing Group. F) Doughnut-like assemblies. Reprinted with permission from [25d]. Copyright 2000 American Association for the Advancement of Science.

A few other major problems with the synthesis methods become evident when considering the related issues of fabrication time, scalability, and cost. A common problem with many particle-assembly processes is the relatively large time (minutes to hours) required for the assembly. Processes that take a long period to complete are not suitable for industrial fabrication. In some cases, long times are needed when the particles have to come together slowly, rearrange, and form an ordered structure, such as a highly organized crystal. Such processes typically cannot be speeded up easily, as they are kinetically restricted by the small diffusion rates of the particles. In other processes, such as convective assembly, the deposition requires the evaporation of relatively large fractions of a liquid, leaving behind the particle structure. The evaporation of water at room temperature is too slow for producing large-scale coatings. The removal of the liquid can be speeded up using high-temperature environments or volatile organic media, both of which pose problems in a manufacturing process.

In authors views, the most challenging problem that has to be resolved in reducing most colloidal assembly processes to practice is scalability. As most of the materials synthesis processes

yield products in microscopic quantities, scaling up to the usual size scales of materials fabrication might not be straightforward, and in some cases can be a daunting challenge. The increase of the size of an assembly device might be problematic due to the emergence of thermal and chemical gradients in the system, and the difficulty in controlling and maintaining uniform process conditions. The scalability can also be impeded by the slow speed of assembly. In general, the scalability and cost of fabrication appear to limit severely the number of applications of well-organized particulate materials. In light of all above challenges and limitations, it appears that many of the proposed or perceived applications of the nanostructures and materials formed by colloid assembly should be critically evaluated.

The evaluation of the potential of any structure in future technology is a difficult and somewhat arbitrary process. Still, it makes sense to try to assess the technological potential of some typical structures made by colloidal assembly, and to identify a few general trends that may help with bringing these materials closer to practice. We present an attempt to classify and compare some of the more intensively studied materials by colloidal assembly in Figure 5. The *x*-axis position reflects the cost of materials fabrication, which includes the expected expenses and effort for synthesis of particles and/or process of assembly. On the other axis of the graph, we plot the expected value added of the materials after the assembly, based on the projected complexity and the technology where they will be applied. In order to “calibrate” the graph,

we have also included the expected domain positions of three technologies widely used in practice, the synthesis of simple inexpensive particles, such as polymeric spheres, the synthesis of more complex synthetic particles, such as ones with physical or chemical anisotropy,^[8b,58g,62] and the common photolithographic fabrication of electronic microcircuits on a chip.

The position of the domains in Figure 5 is somewhat arbitrary, yet it allows for a speculative evaluation of the potential usability of the technologies. In general, techniques situated more to the left (less expensive fabrication) and higher up (better functionality) will be more competitive. Typically, the cost of assembly of better-ordered structures is higher because of the higher cost of monodisperse suspensions, the longer time required to accomplish the process, and the need to reduce or remove defective structures. Amongst the well-defined colloidal architectures, structures with lower dimensionality have higher fabrication costs, since they require larger effort and longer time for assembly. These materials are, however, of greater potential value, due to the demand for electronic and photonic conductors in high technology applications, like electrical circuits and sensors. Processes taking place in lower dimension, which do

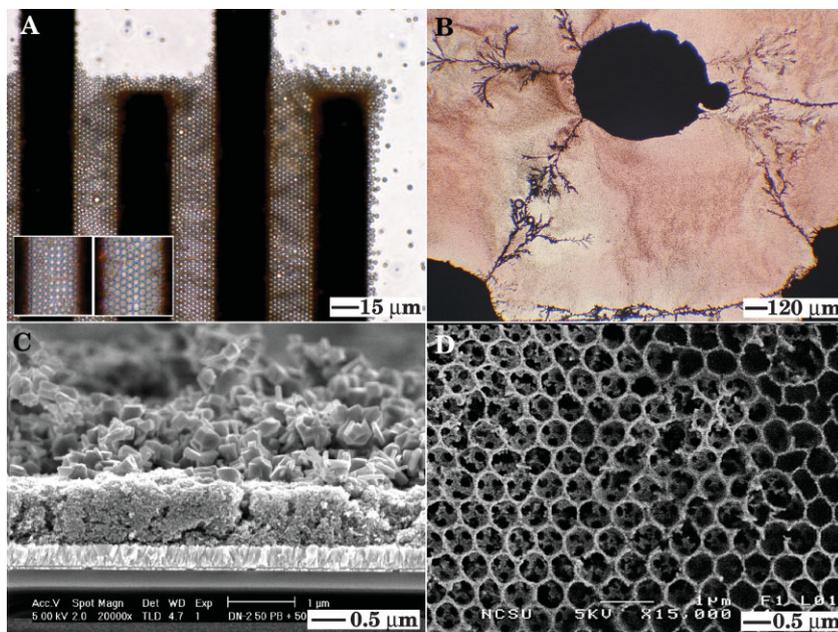


Figure 4. Examples of functional materials fabricated from micro- and nanoparticles. A) Particle collection between electrodes for biosensor applications (e.g., [11]). B) Gold microwires grown in situ for bioelectronic circuits (e.g., [45a]). C) High-resolution scanning electron microscopy image of a cross-section of a nanoparticulate film in a dye-sensitized solar cell. Reprinted with permission from [52b]. Copyright 2006 American Chemical Society. D) Inverted nanoparticle opals for surface-enhanced Raman spectroscopy chemical sensors. Reprinted with permission from [60a]. Copyright 2005 Society for Applied Spectroscopy.

not result in highly functional materials, are of little industrial value, as the ones where anisotropic particles are synthesized after treatment in a thin surface layer and then redispersed in suspension. On the other side of 2D fabrication efficiency is the photolithographic electronic manufacturing, a mature technology that is very hard to beat in terms of fabricating very complex structures by design.

The comparison of the materials domains and trends outlined in Figure 5 suggests a couple of directions of high growth potential in the colloidal assembly area. First, the fabrication of simple unordered assemblies could find practical uses as long as it is based on inexpensive particles and is scalable and robust. One example of such an application is the use of simple silica particles in antireflective coatings, which may also be superhydrophobic. We have demonstrated how inexpensive polydisperse commercial particles can be deposited directly from aqueous suspension in antireflective coatings over solar cells, leading to a significant improvement of their efficiency at very low materials and fabrication costs.^[63] A large variety of coatings and patches based on commercial particles can largely improve the quality of products for consumer and energy uses.

The colloidal-assembly research in the last couple of decades has been intensely focused on high-technology materials and devices for photonics, electronics, and biomedical applications. The development of active, functional, and manufacturable nanostructures has been a major research target of funding agencies such as the US National Science Foundation.^[64] This requires the fabrication of highly ordered and functionalized structures, effectively increasing the value of the assemblies. Not all advances in this area have paved the way to practical applications yet. Photonic and electronic circuits formed by wet particle assembly have yet to find industrial use, and a more careful consideration of these research thrusts reveals a number of serious obstacles. It might be hard to develop assembly methods that can compete with the mature and highly precise electronic microfabrication techniques, which will soon be able to create sub-50 nm structures and ones extending in 3D. While the idea of self-assembled 3D photonic crystals has been immensely stimulating for the field and has motivated a large number of publications, few studies have resulted in viable technologies.

There is a colloidal-assembly research direction that is clearly promising and of high potential value. Structures that include biomolecules and interface liquid media cannot be created readily by conventional vacuum-based lithographic techniques. Liquid-based assembly allows precise formation of such microscopic structures without losing the activity of the biomolecules around the particles. This can be used in the fabrication of sensors, bioassays, and various biomedical devices. This research direction is naturally combined with the increasing potential of microfluidics. In the longer perspective, one interesting and promising application of wet assembly techniques might be the

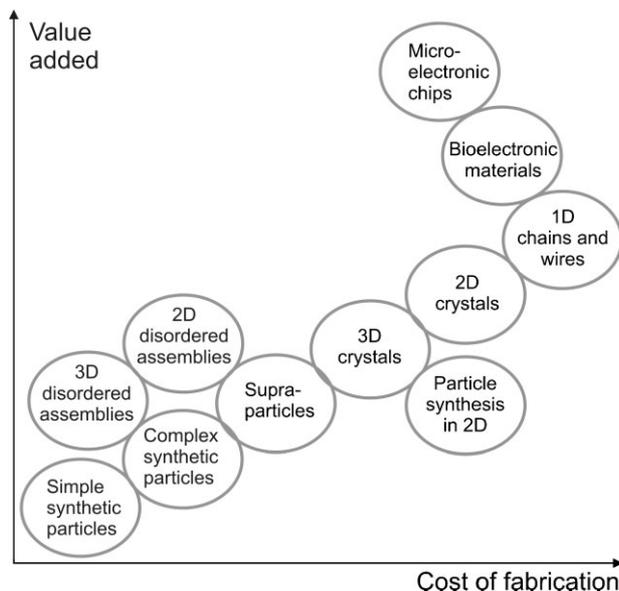


Figure 5. A hypothetical qualitative comparison of the value added for different types of colloidal assemblies versus the cost of their fabrication. Materials positioned to the left and the top side of the graph are more likely to find applications in technology. The likely positions of simple and complex synthetic particles and microelectronic chips are shown for comparison.

application of colloidal assembly into the formation of well-defined and organized structures from live cells.^[44b] Cell-based assemblies can be used in sensors, bioassays, advanced vaccines, or “smart” biomaterials or coatings that respond to changes in the composition of the environment.

3. Conclusions

The area of colloidal assembly has seen impressive growth, and is likely to continue developing extensively given the large number of physical processes used and types of materials than can be formed. A few of these processes are listed in Table 1, and some resulting structures are exemplified in Figures 1–5. A better focus, however, will be required in research aimed at the formation of practical materials. The issues of scalability, control, and precision need to be resolved in many processes, and the functionality of the assemblies has to be increased if the resulting structures were to find applications in technology. The area of particle self-assembly and the types of materials resulting from such processes are far from being depleted in terms of science and ideas, while they move in the direction of engineering and fabrication.

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