Perspective

Microfactories for Colloidal Assemblies

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DOI 10.1002/aic.12187

Keywords: micro-factory, colloidal assembly, colloidal particles

Introduction

Niche markets are often well-served by small producers able to adapt quickly to localized demand. America's brewing industry provides one example through its recent history.[1] Currently about 90% of the domestic market share for beer — roughly 200 million barrels or 6 billion gallons — is in the hands of Anheuser-Busch, Miller, and Coors. However, the number of specialty brewers grew from 10 in 1980 to more than 1,300 by the year 2000.[1] Microbrewers and brewpubs produce less than 15,000 barrels per year, but they focus on high-quality products adapted to particular customers. By having prices 50% higher than usual pale lagers, requiring far less advertising, and even taking advantage of local tax laws, a specialty brewer can produce a gross revenue of a few million dollars per year.

This Perspective explores the development of processes for another category of niche markets: colloidal assemblies. Although colloidal *particles* have been used for millennia, the concept of assembling nanoscale or microscale particles into small "colloidal devices" or "colloidal machines" is a rather recent development.[2] Simple devices, such as colloidal motors[3,4] or colloidal barcodes,[5] have already been fabricated and studied, at least at the research level. Rather than producing one million metric tons per year of commodity vinylacetate or styrene butadiene particles, like BASF or Dow, we explore how companies can develop processes that fabricate specialty colloidal assemblies, perhaps in batches of 10–100 g with a rapid turnaround time, by designing *colloidal microfactories*. Initially such specialty producers of colloidal assemblies might primarily serve research needs for other small or large companies; however, with time, commercial markets might emerge for a greater number of specialized products. The over-arching question in this Perspective is this: Can small, nimble, smart businesses carve out niches in producing specialized colloidal assemblies? In examining this question, we explore four main points:

1. Colloidal assemblies are high-value specialty products.
2. Control of interparticle forces enables "bottom-up" processes for making assemblies.
3. Microfactory processes are adaptable, small, and have low-capital investment.
4. Chemical Engineers are well-positioned to design and operate colloidal microfactories.

As entrepreneurs become willing to engage in these small ventures, the microfactory approach for producing assemblies can add significant value, especially for initial research and development operations, and later in aiding the commercialization of technologies that result from the R&D.

Colloidal assemblies are high-value products

Synthetic rubber demand during World War II caused an enormous scale-up of polymer colloid production.[6] Worldwide there are now more than 500 companies that produce and sell polymer colloids.[7] The three leading suppliers, BASF, Dow, and Rohm and Haas, each has the capacity to produce more than 1 million metric tons (wet) per year, accounting for 20% of polymer colloids produced annually. The particles are typically sold as commodities: a gallon of paint costs roughly \$20, while a bottle of wood glue might cost \$5. Common polymer colloids, such as styrene-butadiene copolymers, polyacrylates and vinyl acetate homopolymers and copolymers, are used in applications from leather finishing to printing inks.[6,7]

In contrast to these bulk markets, small companies such as Polysciences, Interfacial Dynamics (through Invitrogen), Bangs Laboratories, Duke Scientific, and other manufacturers produce particles primarily for research purposes.[8] These particles have tight specifications (e.g., size distribution) and good quality control, and they are high value; our laboratory typically purchases a dozen 15 mL bottles of 8% solid monodisperse polystyrene nano- and microparticles per year, each of them costing more than \$150. By mass, the cost for the polymer particles is three to four times that of gold. Particles with specialized functionalities such as ligands or fluorescent groups cost even more, and the demand for small amounts of the customized particles remains significant.

Colloidal assemblies that function as "colloidal devices" will in general be even more complex than their constituent particles. As a result, they will have even higher value added.

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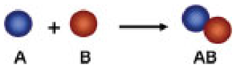
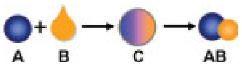
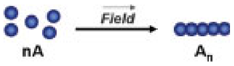
Table 1. Model “Reactions” for Creating Colloidal Assemblies

1	Controlled Aggregation		Hiddessen, et al. *Langmuir* 2000, 16 [ref 22] Johnson et al. *Langmuir* 2005, 21 [23] Yake et al. *Langmuir* 2006, 22 [15] Zhao et al. *Phys. Rev. Lett.* 2007, 99 [24] Snyder et al. *Soft Matter* 2009, 5 [17]
2	Template-Driven Assembly		Manoharan et al. *Science* 2003, 301 [ref 18] Xia et al. *Adv. Funct. Mater.* 2003, 13 [25] Pantina et al. *Langmuir* 2004, 20 [26] Hernandez et al. *J. Phys. Chem. C* 2007,111 [27] Shi et al. *Lab Chip* 2008, 8 [28]
3	Coalescence and Dewetting		Fujimoto et al. *Langmuir* 1999, 15 [ref 29] Lu et al. *J. Am. Chem. Soc.* 2003, 125 [30] Kim et al. *J. Am. Chem. Soc.* 2006, 128 [31] Kim et al. *Macromol. Res.* 2007, 15 [32] Studart et al. *J. Phys. Chem. B* 2009,_113 [33]
4	Field-Driven Assembly		Yeh et al. *Nature* 1997, 386 [ref 34] Furst et al. *Langmuir* 1998, 14 [35] Hermanson et al. *Science* 2001, 294 [36] Doyle et al. *Science* 2002, 295 [37] Roh et al. *Nat. Mater.* 2005, 4 [38]

[a](1) Controlled aggregation, similar to second-order chemical reactions. Aggregation is controlled through particle functionalization or manipulation of system thermodynamics.[15,17,22–24] (2) Template-driven assembly, similar to catalysis. Specific assemblies can be made by varying template geometry and order of particle addition.[18,25–28] The wells of the template can be physical wells that use gravitational force, but also force wells created through optical or acoustic trapping. (3) Coalescence and dewetting requires the addition of a functionalizing solvent or monomer. Solution conditions are then changed to induce phase separation into two distinct regions, similar to a decomposition reaction.[29–33] (4) Field-driven assembly works as particles begin to assemble under the influence of an externally applied field, forming chains or cross-linked structures.[34–38] Magnetic, electric, shear, and other fields may be used to produce chains or sheets of particles, a process with similarities to polymerization.

In 1998 Jacobson and coworkers published their work concerning a capsule, in which tiny dark or light particles could be moved electrically.[9] This research has now turned into E Ink, the Cambridge, Massachusetts-based company that produces the display technology for the Amazon Kindle and the Barnes and Noble Nook. There are many more types of smart particles on the way, including the mobile microscale and nanoscale motors mentioned earlier,[3,4] which are environmentally responsive, and can perform chemotaxis in the manner of motile bacteria.[10,11]

Control of interparticle forces enables “bottom-up” processes

In recent years the concept of colloidal molecules[12] has emerged, in which colloidal particles are treated analogously to atoms and molecules in molecular chemistry. Glotzer and Solomon established a “periodic table” concept,[13] in which the constituents are not atoms, but nanoscale or microscale particles with various morphologies, size, material composition, and other defining characteristics. Many unique assemblies have already been fabricated, including doublets,[14,15,16] “colloidal water”,[14,17] and grape-like clusters.[18] Most of these have been produced using bottom-up assembly, at least in some steps, which usually corresponds to less expensive processes. In bottom-up assembly, a chemistry is patterned onto the particle surfaces so that the particles are “chemically programmed” thermodynamically to favor specific assembly. The potential combinations for assembly are immense in number, and many of these particles have in fact been comprehensively reviewed in a previous *AIChE Journal* Perspective.[19]

Two key barriers remain in using bottom-up techniques to fabricate colloidal assemblies. First, most techniques allow only a limited number of particle materials to be used, for instance certain polymer types or certain metal types. The challenge here is that sophisticated colloidal assemblies or devices might often require *combinations* of various polymers, oxides, metals, semiconductors, or hydrogels. Additionally, specific applications sometimes require that various materials be compared for performance in a given application. In contrast to molecular chemistry, in which covalent bonds dominate, colloidal assembly is usually governed by physical interactions,[20,21] and these forces are readily manipulated. Van der Waals forces, hydrophobic forces, electrostatic forces, and similar physical phenomena — many of which are readily controlled by changing the solution or ambient conditions, provide an enormous toolset by which to assemble a broad range of particles.

Although there are differences between molecular synthesis and colloidal fabrication, numerous analogies may also be made. For example, template-based assembly may be considered a type of heterogeneous catalysis which combines some aspects of bottom-up and top-down assembly. Controlled assembly, occurring either when “patchy particles” bond at specific sites or when bare particles bond during a certain time period, may be considered a type of homogeneous reaction. Examples of a few colloidal assembly strategies and their corresponding “chemical reactions” are shown in Table 1. The caption lists other analogies between molecular synthesis and colloidal assembly.

The second key challenge is that most assembly techniques produce only small quantities of particles, say milligrams at present. While this is sufficient to publish a high-impact image in a journal, it is considerably less than the 10 to 100 g or more required even at a niche commercial level. As assemblies used for research lead entrepreneurs to assemblies with potential application in broader commercial uses, even larger quantities will need to be produced. This requires that we consider colloidal assembly in a manner beyond the methods shown in Table 1. We will need to start considering entire processes for producing the assemblies.

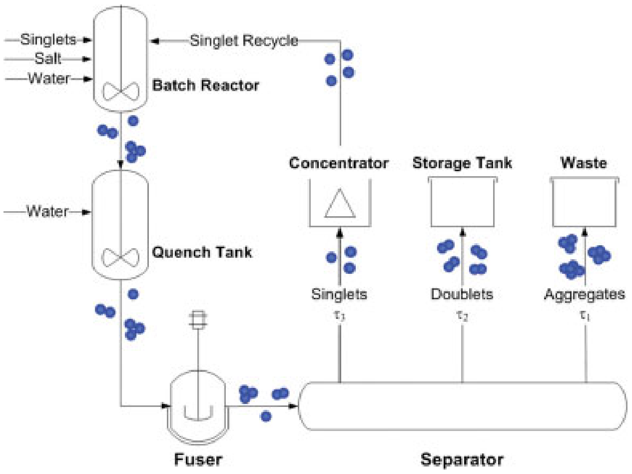


Figure 1. Process flow diagram for batch process to assemble doublets.

Just as molecules are fed as inputs into a process, here colloidal particles are fed into a batch reactor. After the designed colloidal aggregation occurs, we have "unreacted" single particles, doublets (the desired product), and a small quantity of triplets and other undesired higher-order aggregates (side products). The assemblies go through an autoclave to fuse at 118°C, and then they go through a separator (e.g., a field-flow fractionator), after which singlets are returned to the reactor, doublets are stored, and other products are treated as waste.

Microfactories have quickly-adaptable, batch unit operations.

In scaling laboratory methods to commercial processes, training in Chemical Engineering is especially useful. The principles used to design reactors of various volumes, ranging from a 10,000 L continuous stirred-tank reactor to a 100 mL batch reactor, are similar, and the conceptual integration of mass balances, rate equations and other defining equations to account for relevant phenomena such as diffusion is critical regardless of scale.

Continuous processes have little merit for the small-scale fabrication of assemblies. The primary costs will be in rapid engineering and prototyping, rather than in equipment capital investment or sometimes even raw materials. Small batch or semibatch unit operations will likely prevail, many of which are already used in laboratories around the world. As a result, capital expenses for the equipment will be low, and the operations will require minimal commissioning time. Moreover, the small-batch process enables users to morph a process quickly, in order to produce custom particles and assemblies. Thus, sophisticated process control schemes can often be avoided, and if product quality is insufficient, the next batch can be optimized and processed.

As an example of a microfactory design, consider the "stimulus-quenching-fusion" method for producing doublets.[15] A process flow diagram (PFD) of the process is shown in Figure 1. Spherical particles with diameters ($2a$) from several micrometers down to less than 100 nm are fed into a batch reactor. The particles might be negatively-charged in aqueous solution, with a surface potential (ψ_0). Ordinarily, we seek colloidal suspensions in which the particles do *not* aggregate (i.e., they are "stable"), with a large magnitude of ψ_0 (corresponding to highly negatively charged particles due to dissociating carboxyl, sulfate or other groups on the particle surface). Such particles have significant repulsive electrostatic forces, which maintain a gap (δ) between the particles. The electrostatic forces work against the attractive van der Waals forces, which are stronger for material systems with a higher Hamaker constant (A). A simplified version of the interaction potential between two particles, commonly known as the Derjaguin-Landau-Verwey-Overbeek (DLVO) potential energy, is

$$\Phi = 2\pi\varepsilon a\psi_0^2 \exp(-\kappa\delta) - \frac{aA}{12\delta} \tag{1}$$

where ε is the permittivity for water, and κ^{-1} is the Debye screening length. The Debye length, which is readily calculated from the solution conditions,[21] serves as the characteristic length scale over which particles interact electrostatically in an ionic solution. A plot of Eq. 1 for $\Phi(\delta)$ reveals a potential energy barrier between particles, analogous to an activation energy barrier in transition state theory.

Using Equation 1 as a guide, we can manipulate the potential energy between particles. By increasing the ionic strength, we can decrease the Debye length and lower the potential barrier, allowing particles to aggregate together.[20] We could solve for the case when the potential energy barrier indicated by Eq 1 (or more complicated and accurate expressions[20,22] for the energy) is small enough to allow aggregation, but in practice, we know that having 1.0 M KCl solution gives a Debye length of 0.3 nm, which is small enough to allow rapid, diffusion-limited aggregation of the particles. The particles do not, however, simply clump-up instantaneously. Their aggregation is diffusion-limited, like many reactions. Singlets form doublets; doublets combine with singlets to form triplets; doublets combine with doublets to form 4-lets, and higher-order aggregates continue to form.

If we have a volume fraction (ϕ) of particles, we could solve the population balances to determine the entire range of aggregates as a function of time. On the other hand, we can treat the aggregation of singlets as a binary reaction given by the usual rate expression $r_1 = dn_1/dt = -kn_1^2$, and then use several equations from colloid science to find that the rate constant is given by $k = 8k_BT/3\eta$, where k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the suspending solution. Using these equations, we can estimate a time constant (τ) for diffusion-limited aggregation as[21]

$$\tau = \frac{\pi\eta a^3}{k_BT\phi} \tag{2}$$

By decreasing the ionic strength or other stimulus, we can increase this time scale many times over this diffusion-limited result, usually in a controllable manner. Thus, a few simple *estimates* from colloid science have given us an equation to relate parameters easily controlled in solution, and this equation is often sufficient as a starting point to predict and reliably scale-up the aggregation step.

In continuing the process, we "quench the reaction" after the rapid aggregation time by diluting with water to decrease the ionic strength. This increases the repulsion between the particles. In some ways the high-ionic strength has served as a catalyst for the reaction. If one of the particle types is polymeric, we can make the doublets very mechanically stable by raising the temperature above the glass transition temperature of the polymer, allowing the particles to fuse. Finally, since the random aggregation step has given unaggregated singlets, the desired doublets, and some side products (triplets and higher-order aggregates), we require a sorting or separation step. Techniques such as hydrodynamic chromatography and field-flow fractionation can sort singlets (which are recycled to aggregate again) from doublets (which are stored for use) from side products (treated as waste). Currently these sorting operations are done at a very small scale.

We have discussed the design of a microfactory for producing a simple type of colloidal assembly (i.e., doublets), using a process flow diagram. Similar process flow diagrams can in principle be designed for the formation of more complex types of assemblies (Table 1), thereby creating microfactories for the fabrication processes.

Colloidal microfactories can fit in a single room, and perhaps even on a tabletop, since the "unit operations" are small. Furthermore, the equipment can be assembled *quickly*, with sufficient design knowledge. For companies wanting rapid prototyping of an idea, these factories will serve an important purpose, as a process can transition from conception of the idea to reception of the assemblies within two months, by contracting a niche company. Currently, many particle assemblies are produced using the beakers and flasks on a laboratory bench, or a small microfluidic network created at a nanofabrication facility. To a chemical engineer, however, that same beaker resting on a bench top serves as a "batch reactor"; a centrifuge or rack of test tubes for settling is an effective separator; a microfluidic network or syringe pump acts as the transport system; while an autoclave or water bath functions as a heat exchanger. Both the materials and methods scale down for microfactories, although in addition to the usual design parameters like viscosity, heat capacity, and diffusivity, colloidal processes involve parameters such as zeta potentials (surface potentials on particles in solution), ionic strengths and double layer thicknesses, surface tension, surface adsorption, and Hamaker constants.[21]

When optimizing yields of the colloidal assemblies, one of the most critical yet daunting unit operations is sorting or separations. There is no equivalent of a distillation column for micron-size particles. Although small scale, analytical sorting techniques such as field-flow fractionation and hydrodynamic chromatography exist, the ability to sort 1 to 100 kg per year of material is a significant challenge — one that the authors of this article have been studying for more than five years.[23,24] Processes such as field-flow fractionation, hydrodynamic chromatography, or density gradient centrifugation can be used to sort assemblies, but they are limited in throughput. Sorting is an important research need for colloidal assemblies.

Due to the size of the equipment and its availability, a great advantage of colloidal microfactories is the need for lower capital investment relative to larger factories. Designing processes at the nanoscale or microscale opens up possibilities for integrating unit operations in new ways, for instance, using some surface techniques for both assembly and sorting. Moreover, the small size of the microfactories translates to a greater potential for safer processes, as many assembly techniques are performed in aqueous solution at ambient temperature and pressure. Still, it is imperative that a thorough safety analysis be performed, and HAZOPs and operability guidelines be generated regardless of the size of the microfactory. Although waste product volume is minimal, that material must be handled responsibly.

Chemical engineers can design colloidal microfactories

The enabling factor in using bottom-up processes for colloidal assemblies is the design of the colloidal microfactories. Detailed physical and chemical intuition about colloidal processes is helpful; however, the engineer must also have a proper feel for systems thinking, as well as for the design of unit operations. Chemical engineers understand process design.[25,26,27] The familiar unit operations mentioned previously can be drawn and designed quickly, often with only semiquantitative accuracy being sufficient. Numerous parallels exist between colloidal microfactories and the plants that chemical engineers have designed, optimized, and maintained safely for decades. Furthermore, design equations for reactors, separators and pumps at the macroscale are readily adapted to the microscale, and chemical engineers are well-suited to scaling-up lab-scale techniques to processes that produce 1 to 100 kg/year. The ability to think from the molecular level to the systems level — even though the system now fits on a tabletop — is critical to designing the factories quickly.

There are several additional factors that will enable chemical engineers to thrive in advancing colloidal microfactories. One important change in technical design, compared with some industries, is that the speed in designing new processes will be critical. In addition to the usual technical skills that chemical engineers use, they must continue to develop skills in recognizing consumer needs, practicing entrepreneurship, and managing intellectual property. They will need to quickly develop knowledge of local *context* — needs and culture — to better capture niche markets. Markets to create particles for research will gain ground only as engineers and other entrepreneurs begin to see possibilities for end use. It is also critical to quickly establish trust-based relationships and forge partnerships to jointly develop the particle assemblies, while remaining an expert in the processes and analyses required for generating high-quality materials.

Conclusion and Outlook

An irony of colloidal microfactories is that while the materials being synthesized — colloidal particles instead of molecules — are individually larger than molecules, the factories used to produce them will be much smaller than for most molecular processes. Some of the organizations mentioned earlier that produce specialty particles might well be interested in incorporating new sections into their factories, and also in rooms in an already existing facility. That is, already-small factory buildings can house even smaller colloidal microfactories.

Several critical barriers have been addressed in this article, concerning the advancement of colloidal microfactories. Technical issues in colloidal fabrication and sorting are currently being addressed in research labs around the world. Important engineering challenges exist in rapid design and scale-up of not just fabrication techniques, but entire processes for producing assemblies. Building teams who understand outside technical issues, including molecular biology, medical applications, or polymeric applications, is crucial. Addressing local, niche markets requires a detailed knowledge of local contexts, as well as specialized science and technology and implementation with integrity. In educating future chemical engineers for the traditional skills, as well as the newly-needed skills, universities will continue to play an important role.

Acknowledgments

We thank many colleagues for stimulating discussions, including Bob Nedwick, Ayusman Sen, Tom Mallouk, Milton Cole, Jim Adair, Jack Matson, Ted Alter, Orlin Velev, and Ilona Kretzschmar. We also thank those who have funded our research in colloidal assembly and interparticle forces, especially the National Science Foundation and the Dept. of Energy.

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