Bridging the gap between self-assembly and hybrid materials: from particle dispersions to rational arrangements

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Living organisms combine inorganic particles and biopolymers to hierarchically structured materials. Can we do the same in artificial hybrid materials? Is it possible to create and connect synthetic nanoparticles and polymers into spatially well-defined arrangements and thereby obtain materials with defined properties? In this talk, I will discuss the state of the art and present strategies towards composites with engineered microstructures.

Current routes to particle-polymer composites yield useful materials. The level of control that we have over the distribution of particles is very limited, however:

- Silica nanoparticles increase the strength of polymers, but they are uniformly distributed throughout the volume rather than being arranged to reinforce regions of high stress.
- ZrO_2 nanoparticles uniformly increase the refractive index of polymer lenses, but particle-based index grading or antireflective particle arrangements have not been realized.
- Printable, conductive layers suffer from low electron mobility and roughness caused by voids, agglomerates and imperfect particle packing in the layers.

In the laboratory, monodispersed nanoparticles have already been assembled with exquisite structural control: binary and ternary mixtures of such particles spontaneously arrange into crystalline "superlattices" with structures that remind of ionic crystals, metallic alloys and even quasicrystals.

In this talk, I will discuss how these results can be exploited in the structuring of hybrid materials. The transfer requires understanding the ordering mechanisms and defining prerequisites for order, a task that we have undertaken in the past years. We

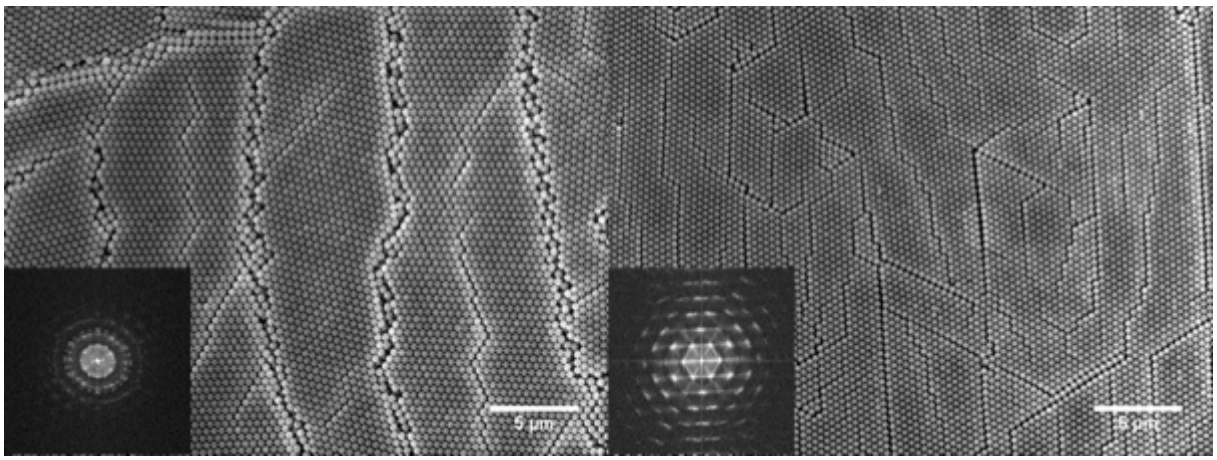

Figure 1: Convectively deposited polystyrene particles (500 nm diameter) assembled into layers. The degree of order as indicated by Fourier transforms in the lower left corner depends on the process conditions. [1]

investigate whether the same principles can be applied in technical formulations, where particles are often less narrowly dispersed and mixtures are complex.

Consider, for example, "convective assembly", a coating process that is similar to classical dip coating but can deposit particles as dense, crystalline monolayers (Figure 1). A liquid meniscus moves over the wetting substrate. Particles move in the wetting film and arrange into dense layers. The process can be used for the deposition of conductive nanoparticle layers, particle films for sensor applications and photovoltaics and provides an alternative to photolithography. We find that predictable particle arrangements only form if

- sufficient particles are transported to the assembly site (transport limit),
- directed forces overcome random thermal agitation (Brownian limit),
- particles are narrowly dispersed (dispersity limit),
- they have enough time to assume regular positions (mobility limit).

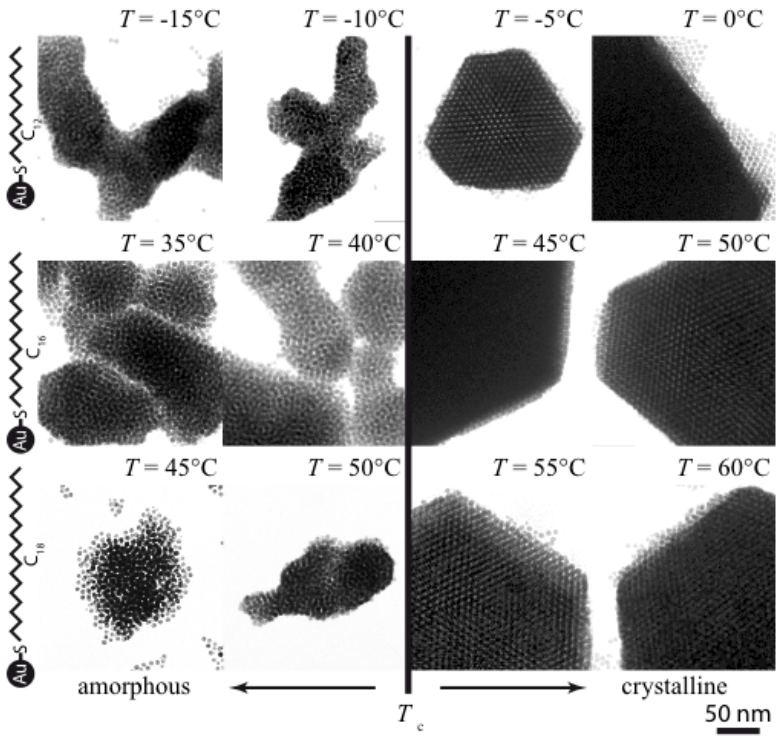

Figure 2: Electron micrographs of gold nanoparticles (6 nm core diameter) assembled at different temperatures. A critical temperature minimum T_c for crystallization exists. [2]

Similar prerequisites exist in the bulk assembly of particles: identical nanoparticles agglomerate either into disordered agglomerates or crystalline superstructures depending on the process parameters (Figure 2). While the interactions that govern the process are different from convective assembly, the prerequisites for order derive from the same principle. I will discuss how the preparation of hybrid materials can be adapted to provide the desired structural control and which applications can profit from it.

References

[1] P. Born, A. Munoz, C. Cavelius, and T. Kraus, *Langmuir* 2012, 28, (22), 8300-8308

[2] T. Geyer, P. Born, and T. Kraus, *Phys. Rev. Lett.* 109 (2012) 128302