

Structured nanoparticle arrays: coatings by continuous convective assembly with controlled evaporation

J. Alex Lee and Michael Tsapatsis

Department of Chemical Engineering
University of Minnesota, Minneapolis, MN 55455

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Particulate coatings are proving to be very important or at least interesting for the development of many novel technologies and applications including chemical sensing, photonics, optical and display technologies, zeolite-based isomeric separations and catalysis, as well as biologically relevant surfaces. For many of these applications, microstructural order, i.e. order on the particle-particle length scale are the defining characteristic for the film performance. For example photonic applications require a crystalline arrangement of particles in a periodic lattice structure. In nano-particle seeded film growth for zeolite-based membrane separations, the nanoparticles are often anisometric and must be appropriately oriented to provide separation functionality (Lee et al., 2006). Moreover, they should be close-packed to ensure the growth of a void-free film while achieving minimum thickness. Especially in particle systems where the sizes are on the nanometer scale, high degrees of order have not been commonly observed, and in general, rational engineering strategies for the fabrication of ordered particulate films with well-controlled properties has been lacking, though recent years have seen many exciting reports in the lab concerning their characterization and efforts to elucidate the processes.

Of the several methods for particle coating, we are studying the convective assembly of nanoparticles at the three-phase contact line of a substrate immersed in dilute suspension. Convective assembly is comparatively simple in practice, and its essential features lend it to straightforward scale-up in a configuration, for example, resembling continuous dip coating. In convective assembly, the substrate is immersed in a suspension and withdrawn and very low speeds ($Ca \sim 10^{-4}$) such that solvent evaporation prevents the formation of a fully developed wet film. Consequently, the three-phase contact line is

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preserved and provides a wedge region in which particles can assemble, driven by the convective currents in the liquid meniscus set up by solvent evaporation (Figure 1). Thus, substrate withdrawal determines the coating thickness not by setting the wet coated film thickness, but rather by affecting the position of the meniscus and thus limiting the film growth rate at a given particle flux to the assembly front (determined by solvent evaporation and particle concentration in suspension).

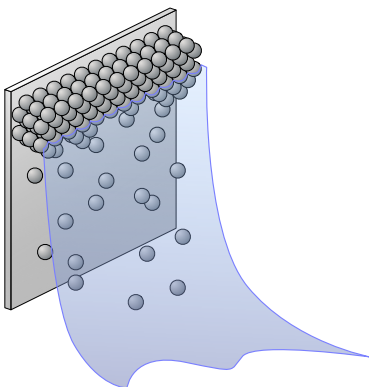


Figure 1. Illustration of the convective assembly process. Particle assemble into a coated film at the contact line.

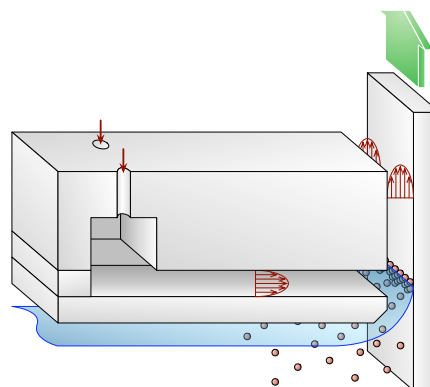


Figure 2. Schematic of the controlled evaporation continuous convective assembly coating device.

Early works have described experiments in which substrates are withdrawn from a pool at stagnant gas phase conditions (Dimitrov and Nagayama, 1996), immersed in an evaporating bath without withdrawal (Jiang et al., 1999), or immersed in an evaporating bath with controlled gas flow to provide controlled solvent evaporation characteristics near the growth front and thus uniform and steady particle flux (Meng et al., 2006). Last year we reported a coating technique that combines both withdrawal for continuous coating and controlled gas flow for nominally uniform and steady film assembly (Figure 2); in principle, this technique allows control of final coating thickness by appropriately matching particle flux with substrate withdrawal (Snyder et al., 2007). In this work, we discussed the application of convective assembly to novel silica nanoparticle system with unprecedented monodispersity at very small diameters ($\sim 15\text{nm}$), and their assembly into near-monolayer coatings (Figure 3). The inset Fast Fourier Transform (FFT) of the SEM micrograph in Figure 3a indicates hexagonal ordering of the nanoparticles while the inset in Figure 3b shows the actual microstructure. The lack of higher order reflections in the FFT

indicates the disruption of order in the particle coating caused by the “cracks” in the high magnification inset (Figures 3a,b).

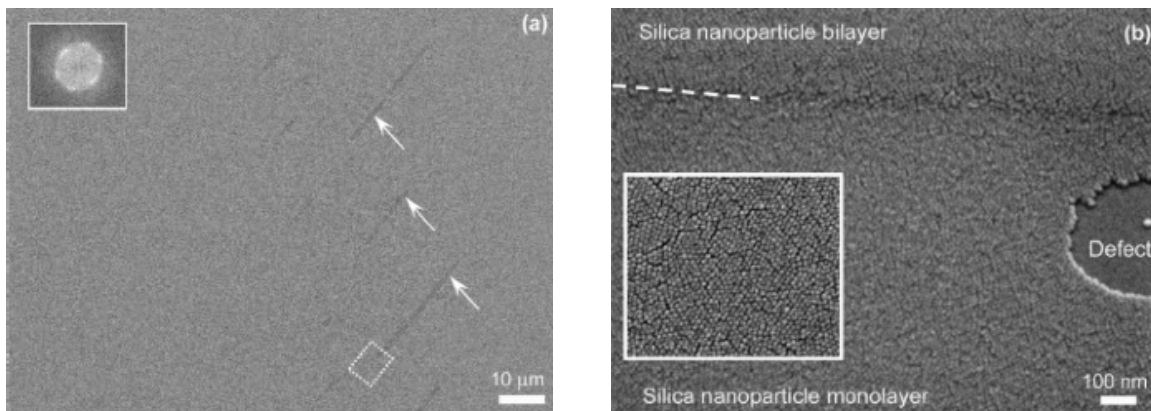


Figure 3. a) Near monolayer coating with narrow void defects visible (dark areas). Inset FFT indicates mild hexagonal order. b) Close up of region indicated by white box in Figure 3a shows part of void defect and a bilayer defect. Inset close up shows actual coating microstructure (Snyder et al., 2006).

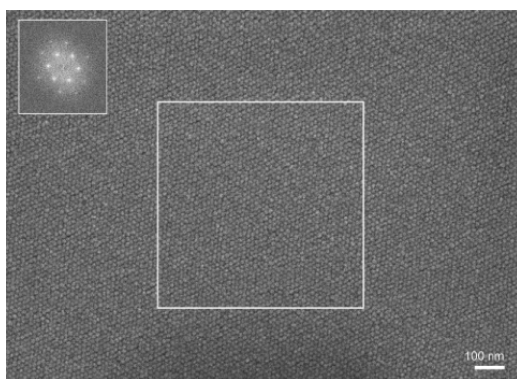


Figure 4. Silica nanoparticles assembled from rapid drying of a horizontal droplet. Inset shows FFT with multiple reflections indicating high degree of order over a large area (white square).

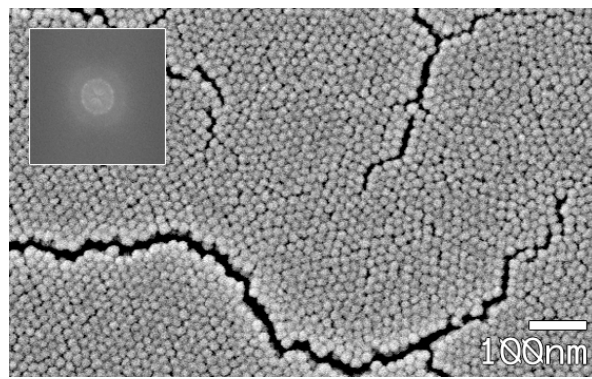


Figure 5. Coatings carried out from suspension with added electrolyte (0.1M NaCl) displays random packing, according to the nearly circular ring pattern in the FFT.

Observation of similarly prepared nanoparticles that have crystallized into an ordered superstructure by rapid drying from a horizontal droplet suggests that the silica nanoparticles are monodisperse enough in both size and shape to achieve a high degree of order (Figure 4). Thus, it is of interest whether or not coatings resulting from convective assembly can produce high quality nanoparticle crystals under the right conditions. We are considering several factors, namely particle speed (gas flow rate), electric double layer (EDL) repulsion strength (particle surface charge) and range (electrolyte concentration), final dry coating thickness, and particle size. Results to date indicate that particle speed is not very relevant in the

range of conditions tested, and reducing the range of EDL repulsions seems to disrupt order in the coating (Figure 5), as illustrated by the smeared rings of the inset FFT taken over a very selective area on the image. Under the hypothesis of Koh et al. (2008), it is expected that as the constituent particles become larger relative to the EDL repulsion range (the Debye length), the final dry coating will suffer less cracking (disorder) due to drying stresses induced by the lattice mismatch between the dry crystal (close-packed) and the wet crystal (loosely packed, stabilized by mutual repulsion) states. This poses an interesting question about the possibility of highly crystalline order in nanoparticle coatings.

References

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