Controlled-Evaporation Dip Coating for Convective Assembly of Thin Particulate Coatings

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In pursuit of colloidally crystalline monolayers comprising orientable (non-spherical) particles, we have been exploring the potential of dip coating and its variations for producing, by way of convective assembly, particulate coatings on the order of a few hundred nanometers thick. Our main findings are that dip coatings from dilute suspension exhibit multi-layer banding instead of full monolayer coverage, and that the banding structure is critically sensitive to the environmental conditions near the convective assembly front–an apparent contact line. An important encouraging result is that at the onset of every deposited band, the particles are mostly close-packed and well ordered in a monolayer over a narrow strip.

Colloidally crystalline particulate coatings have attracted growing interest in fields as diverse as photonic crystals, chemical sensors, and zeolite-based separations. Our efforts are motivated by zeolite separations. Because zeolites can be prepared as anisometrically shaped nanocrystals, one route to fabricating a functional zeolite separation membrane is to start with a thin but well-packed layer of seed crystallites and to grow them together into a continuous membrane. Thus of paramount interest is how to prepare such a layer of seed crystallites. As a model system, we chose a zeolite that could be prepared as hexagonal plates and therefore has potential to hexagonally close-pack in a monolayer.

Our method is based on past work in coating monolayers of spherical latex particles by dip coating (Dimitrov and Nagayama, 1996), and assembling photonic crystals of spherical silica particles by a "vertical deposition" process resembling dip coating (Jiang et al., 1999). In neither case does dip coating refer to the traditional process whereby particles that are entrained in the fully developed

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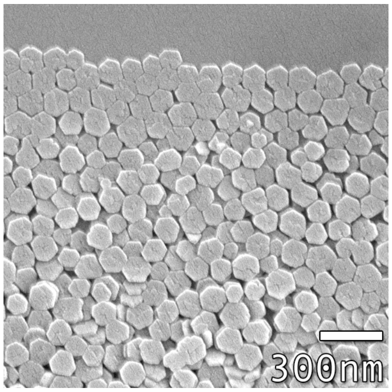

Figure 1: At the onset of each particle deposit band, there is a strip of crystalline monolayer.

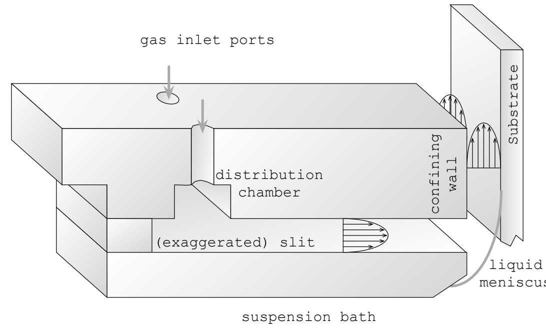

Figure 2: Cross section of our apparatus for controlled evaporation dip coating.

film region dry and consolidate into a solid layer. Rather, the role of dip coating in convective assembly is merely to advance the convective assembly front (at the substrate-suspension-air "contact line") down the coating direction. The convective assembly is driven by capillary pressure gradients in the growing deposit coupled with evaporation of the solvent there. In this respect, the process can be best compared with the famous drying suspension drop, exemplified by the common ring-stains in the coffee mug. The suspension, instead of receding inwards as in the drying drop, is made to recede down a desired coating direction by the controllable action of dipping, which can actually be deferred to the evaporation of the suspension bath (passive dipping) as in the case of vertical deposition.

The coatings we produce by both active and passive dipping, under conditions of controlled evaporation near the meniscus and contact line region, consistently show a banded pattern of particle multilayers followed by voids, affirming the comparison to the ring stains. Though neither techniques produce the desired continuous colloidally crystalline monolayers, every band observed by SEM starts with a strip of crystalline monolayer three to four particle diameters wide (Figure 1).

In passive dipping, we control evaporation by slit-delivered gas positioned "by eye" aimed somewhat arbitrarily onto the bath surface at an arbitrary acute angle. We can better control the dipping action and gas delivery with a simple controlled evaporation dip coating apparatus (Figure 2) designed to deliver a laminar sheet of gas towards the meniscus at a reproducible distance (as in air knife), and most importantly, to confine the path of the gas in a duct as it flows up the coating direction to provide better controlled and more uniform evaporation where it matters. The coated bands from passive dipping experiments are generally wiggly along their length with widely varying

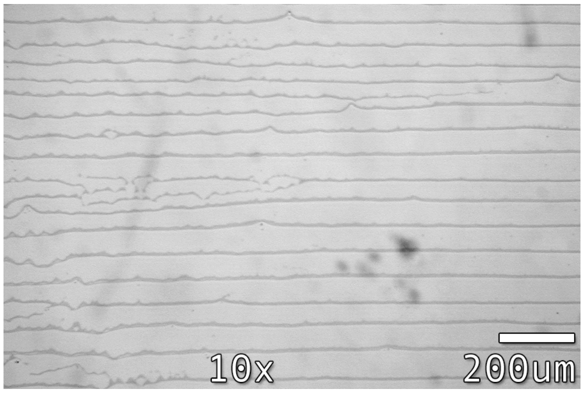

Figure 3: Coatings by passive dipping and loosely controlled evaporation are banded, but with variation in banding straightness, width, and spacing.

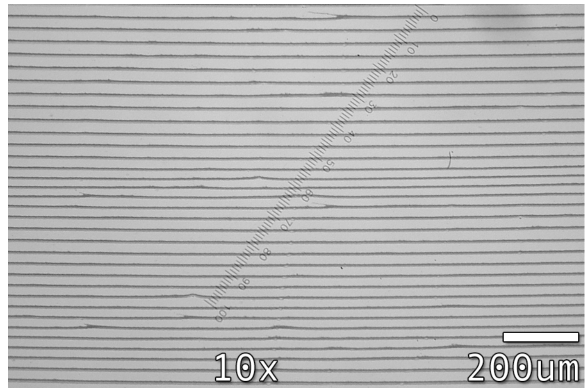

Figure 4: Coatings by active dipping and tightly controlled evaporation are banded with more uniform banding straightness, width, and spacing.

band width and spacing (Figure 3). On the other hand, coatings by the controlled evaporation dip coating apparatus are banded with more straightness and uniformity of width and spacing (Figure 4), and thus better suited for further study.

Of the several explanations of banding that have been put forth, none seem complete and none have been confirmed. Abkarian et al. (2004) called to attention the phenomenon of capillarity, which we have since shown as relevant. Adachi et al. (1996) imagined a periodic "stick-slip" motion of the contact line governed by a balance of liquid-gas surface tension on opposite sides of the contact line with an ill-defined friction force there. A plausible start of an explanation by Ray et al. (2005) described the meniscus configuration trailing from the back end of a particle deposit as being too thin to accommodate additional particles until farther down the substrate, to where particles can be convected and trapped to start the next band of deposited particles.

We have been able to capture the action of banding that occurs during a passive dipping experiment with video microscopy. The first particles to arrive at the assembly front form a line along the contact line to start the band. At some point, the contact line suddenly detaches from the assembly front, either all at once or in a tearing motion from one side to the other, slides down the substrate, and reattaches at a new position where a new band starts to assemble.

When does the contact line detach, and where does the contact line reattach? Our proposed explanation starts with solving the visco-capillary film flow equation for the shape of a meniscus pinned at a corner of the particle deposit versus separation of the pinning corner from the coating bath surface, or pinning height, and flow rate into the deposit. When the pinning height is increased (as in when the substrate is dipped out of the bath) or when the flow rate through the meniscus is increased (as in when the demand for suction provided by the evaporating deposit surface increases as the deposit grows), the meniscus configuration goes through a turning point—a stable meniscus cannot exist at high enough flow rates and/or high enough pinning heights. These results suggest that the meniscus may break (the contact line detaches) under such conditions during the coating process. The contact line should reattach at a position according to a new equilibrium meniscus configuration according to the bath level and deposit thickness. Ignoring viscous terms, a meniscus can be imagined to break when the surface nearly intersects the substrate, and the new equilibrium contact line position would be at the point of intersection. Even with this simplified picture, we can obtain qualitative agreement with the observed band spacing and the deposit thickness in any active dipping experiment. More experiments with widely varying conditions, especially particle size (to vary the deposit thickness), are underway for more complete comparison with the theory.

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