Synchrotron studies of solvent mediated nanocrystal thin film self-assembly.

Diego Pontoni[1], *K. Alvine*[1], *A. Checco*[2], *O. Gang*[2], *B. Ocko*[2], *P.S. Pershan*[1], *F. Stellacci*[3]

[1] Physics Department and DEAS, Harvard University, Cambridge, MA, 02138
[2] Brookhaven National Laboratory, Upton, NY, 11973
[3] Massachusetts Institute of Technology, Cambridge, MA, 02129

diego@xray.harvard.edu

Since the discovery of super-crystal formation [1] and opal nucleation from solutions of highly polydisperse gold nanocrystals [2], a growing set of experimental and theoretical studies have investigated self-assembly and ordering phenomena that occur as a consequence of solvent evaporation from metal and semiconductor nanocrystal solutions (see for example [3-6]). Initially, the experiments consisted in real-space (microscopy) characterization of the end products obtained after rapid and complete solvent evaporation [2]. Subsequent studies recognized and exploited the importance of control over the evaporation rate [5,7,8], while recent x-ray experimental developments allowed kinetic scattering studies of the micro-structural evolution during partially controlled evaporation [9]. However even in the latter case the self-assembly evolved in conditions that are far from thermodynamic equilibrium.

We have initiated a research effort aimed at the detailed investigation of the nanocrystal microstructure in states of thermodynamic equilibrium that are intermediate between those of the disordered bulk nanocrystal suspension and the completely dry, self-assembled nanocrystal thin film.

Extended monolayers of bimodal/polydisperse thiol-stabilized gold nanocrystals were prepared on a water surface using a Langmuir trough and were transferred to flat silicon substrates at a controlled surface pressure. The substrates were subsequently wet by solvent adsorption from vapours having a precisely controlled chemical potential. Solvents of different quality were probed. The method allowed in practice to stop and restart at will the solvent adsorption (or evaporation) and to control the thickness of the adsorbed solvent film with angstrom resolution over the range 1-100 Å. The corresponding equilibrium nanocrystal microstructure was probed in-situ by surface x-ray scattering and diffraction techniques. Complementary microscopy data (TEM, SEM, AFM) were acquired prior and after the x-ray/wetting experiments.

Results include: (a) hints of core size dependent effects not only in the plane of the monolayer but also in the vertical structure characterized by the nanocrystal-substrate separation; (b) monolayer expansion followed by dissolution upon adsorption of increasing amounts of a good solvent; (c) reversibility of the monolayer dissolution/assembly process upon film thickness cycling with a good solvent; (d) expansion of the monoloayer in the thin film regime regardless of the solvent quality; (e) self-assembly of oriented 3D nanocrystal aggregates in the thick film regime with a poor solvent; (f) compaction and fixation of the 3D aggregates upon poor solvent thinning and final drying. All the different structures can be reversibly obtained from the same starting sample upon choice of the correct solvent and amount of liquid adsorbed (Fig. 1).

In view of the fact that there are subtle problems associated with analysis of the measurements involving the bimodal/polydisperse size distribution there is a clear need for other investigations. On the other hand, we believe that the approach presented here can contribute to one of the main objectives of modern nanoscience, namely understanding the fundamental mechanisms of nanocrystal self-assembly and exploiting its technological potentialities.

References:

[1] M.D. Bentzon, J.v. Wonterghem, S. Morup, A. Thoelen, and C.J.W. Koch, *Phyl. Mag. B.*, **60** (1989) 169.

[2] P.C. Ohara, D.V. Leff, J.R. Heath, and W.M. Gelbart, *Phys. Rev. Lett.*, **75** (1995) 3466.

[3] C. B. Murray, C. R. Kagan, and M. G. Bawendi, *Science*, **270** (1995) 1335.

[4] B.A. Korgel, S. Fullam, S. Connolly, and D. Fitzmaurice, *J. Chem. Phys. B*, **102** (1998) 8379.

[5] J. Tang, G.L. Ge, and L.E. Brus, *J. Phys. Chem. B*, **106** (2002) 5653.

[6] E. Rabani, D.R. Reichman, P.L. Geissler, and L.E. Brus, *Nature*, **426** (2003) 271.

[7] X.M. Lin, H.M. Jaeger, C.M. Sorensen, and K.J. Klabunde, *J. Phys. Chem. B*, **105** (2001) 3353.

[8] F.X. Redl, K.S. Cho, C.B. Murray, and S. O'Brien, *Nature*, **423** (2003) 968.

[9] S. Narayanan, J. Wang, and X.M. Lin, *Phys. Rev. Lett.*, **93** (2004) 135503.

Figures:

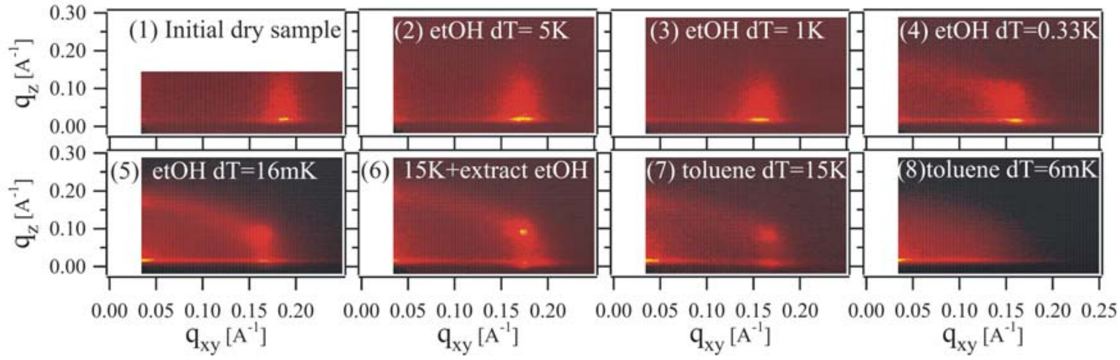

Figure 1 Grazing Incidence X-ray Diffraction patterns from a nanocrystal thin film under various equilibrium wetting conditions. (1) Initial dry monolayer. (2-3) Thin film of poor solvent: monolayer expansion. (4-5) Thick films of poor solvent: signature of oriented aggregates/superlattices. (6) Aggregate annealing and compaction by solvent thinning and drying. (7) Thin good solvent: partial aggregate disruption. (8) Thick good solvent: complete thin film dissolution.