Solvent Mediated Assembly of Nanoparticles Confined in Mesoporous Alumina


1DEAS, Harvard University; 2Center for Nanoscale Materials, Argonne National Laboratory; 3Department of Physics, Harvard University; 4ASRP, Argonne National Laboratory; 5Department of Polymer Science and Engineering, University of Massachusetts, Amherst; 6Department of Materials Science and Engineering, MIT; 7Center for Functional Nanomaterials, Brookhaven National Lab

Abstract

In-situ small angle x-ray scattering measurements of the solvent mediated assembly of 2 nm diameter Au-core colloidal nanoparticles inside mesoporous alumina are presented. The evolution of the self-assembly process was controlled reversibly via solvent condensed from vapor. Measurements of the absorption & desorption of solvent showed strong hysteresis upon thermal cycling. In addition, the capillary transition for the solvent in the nanoparticle-doped pores was shifted to greater under-saturation by a factor of four relative to the expected value for the same system sans nanoparticles. Analysis indicated that a cylindrical shell super-structure of the nanoparticles is maintained throughout the addition and removal of liquid solvent. Nanoparticle nearest-neighbor separation increased and the in-shell order decreased with the addition of solvent. The process was reversible with the removal of liquid. Isotropic clusters of nanoparticles were also observed to form temporarily during desorption of the liquid solvent and disappear upon complete removal of liquid.

Motivation

- Understanding self-assembly of nanoparticles important for both fundamental physics and technological viewpoints.
- Applications: magnetic storage, catalysis, electro-optical devices, etc.
- Quasi-1D systems of particular interest: nanowires, similarity with biological systems such as virus protein coating and cell microtubules.
- Some experiments on end product in cylindrical geometry, no in-situ.
- There have been several experiments of nanoparticle self-assembly on flat substrates using bulk methods, i.e. dropcast evaporation.
- These methods not possible for 1D systems which require templates.
- Need reversible, method for condensing liquid into the system
- This is achieved via our AT method to sub-mm film thickness.
- Need non-destructive, non-invasive, in-situ method for measuring the evolution of the nanoparticle evolution as function of condensation.
- Small Angle X-Ray scattering perfect for this investigation!

Experimental

Figure 1a: (Left) SEM image shows well ordered 2D hexagonal packing of alumina nanoparticles prepared under similar conditions to samples used for x-ray experiments.

Figure 1b: (Right) Bright-field TEM image of the nanoparticles (arrow) on the walls (tangent diagonal lines) of alumina pores. The nanoparticles are Au-core with octahedral coating. Crosssections of the hybrid sample were prepared by the ultramicrotome method followed by the sample used for x-ray experiments.

Results

Figure 2: Scheme of the experimental chamber used for in-situ SAXS experiments. The outer (inner) cell was kept at 25(4)°C (5)°C during the experiment. The sample temperature T was controlled independently from the inner cell and liquid solvent reservoir temperatures. The sample was reacted by the sample where the long axis of the pore can be related to (C) the horizontal plane. The capillary transition was controlled by liquid condensation on the sample via the vapor.

Figure 3: Saxsometry for SAXS measurements: X-rays were incident at 0°-12° from the normal to the nanoparticle long axis. Intensified scattering intensity was monitored with a fixed position CCD detector 1.8 m downstream. The angle describes the scattering space and wavevector transfer of the nanoparticle, respectively. Note that the geometry shown here has been rotated about the incident beam by 10° for clarity.

Figure 4: Typical CDF image of scattering intensity. Two different scattering regions were observed: intense small angle peaks for the 2D ordering of the nanopores and at higher angles of (WAXS) a broader, weak annihilation ring from the local nanoparticle packing. The dark blue region in the lower left corner is due to an attenuator.

Figure 5: Volume absorption (AUA) desorption (ADO) curves as a function of AT. Dashed lines are added as a guide for the eye. Note the strong hysteresis upon cycling. Vertical dashed lines indicate locations of capillary transition for empty (no nanoparticle) pores predicted by the Kelvin equation, AT = YR. Data is normalized for liquid saturation volume of the pores. (Inset) Plot showing the powder diffraction peaks from the 2D nanoparticle packing. Volume information was extracted from the CDF peaks.

Figure 6: Scattering intensity distribution at representative AT. (Top) Left) Data from AT = 9 K (adsorption curve): note the ring is broader with a smaller radius. (Lower) Right) Data from AT = 9 K (desorption curve): note the ring is broader with an even smaller radius. (Bottom) Left) Data from AT = 12.8 K (desorption curve): note the presence of an isotropic scattering ring just inside the nanoparticle ring.

Figure 7: To model the scattering a monolayer of nanoparticles around the pore wall is assumed. The monolayer is broken into nearly flat films and powder averaged over all thin film orientations at a given AT. This scattering curve is modeled using the Lorentzian ring. r i form factor for the nanoparticles. The total scattering is given by the integration over all q.

Conclusions

Solvent Mediated Self Assembly in pores

- Shift in capillary transition due to nanoparticle, strong hysteresis
- Suggests Cohahn mechanism
- May explain clusters as well
- Dry case: nanoparticle monolayer
- Add Solvent: particle separation increases, ordering decreases
- Remove Solvent: particle separation decreases, ordering increases
- Additionally evidence for isotropic particle clusters is observed.

Acknowledgements

This work was supported in part by the National Science Foundation Grant No. 03-4916.