174d Assembly of Structurally Ordered Nanoparticle Thin Films Utilizing a CO2-Expanded Liquid Deposition Strategy

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A major challenge in the production of ordered nanoparticle arrays and assembled nanoparticle thin films involves precisely controlling the deposition and placement of nanoparticles on specific surfaces over wide areas with low defects. Much of the recent work on the assembly of nanoparticles into ordered and wide area thin films has been driven by several prospective applications including electronic devices, optical materials, sensors, molecular catalysis, and others. A common method for the fabrication of nanoparticle thin films involves deposition, or drop casting, by simple evaporation of an organic solvent containing dispersed (stabilized) nanoparticles to leave structurally ordered 2-D superlattice structures. Unfortunately, the very surface tensions and wetting effects inherent to the evaporating vapor/liquid interface that are commonly used to maneuver the particles into the ordered arrays also inevitably lead to random film defects such as interconnected lattices and areas of inconsistent particle deposition and assembly.

We have developed a novel nanoparticle deposition technique utilizing carbon dioxide (CO_2) as an anti-solvent to target low defect, structurally ordered and wide area metallic (Au, Ag) nanocrystal thin films without the detrimental surface tension effects inherent to the evaporation of normal liquids systems. Ligand (e.g. alkane thiols, carboxylic acids) stabilized metallic nanoparticles (Au, Ag, Pt, Pd) were precipitated from organic solvent by controllably expanding the solution with carbon dioxide. The addition of CO_2 to the organic liquid mixture results in a reduced solvation of the ligand tails thus inducing nanoparticle precipitation and targeted deposition onto a specified surface. Subsequent addition of CO_2 and heating into the supercritical state provides for the removal of the organic solvent thereby avoiding the wetting effects and surface tensions that commonly exist in the evaporating solvent methods. These wetting and interfacial effects can be very detrimental to the supramolecular assembly of nanoparticles into low-defect and wide area nanocrystal thin films. Careful control over the expansion of the liquid solution via CO_2 injection allows for precise manipulation of the thermophysical properties that govern this deposition and assembly process. The influence of various factors on the quality of the thin films will be discussed including the rate of CO_2 pressurization, stabilizing ligand type and length, various organic solvents, and the effects of temperature.

A critical factor in the deposition of these nanoparticles into structurally ordered thin films using this new technique involves the need for very monodisperse ligand stabilized nanoparticles in the organic solvent. Ordered thin film arrays of Au nanoparticles were successfully produced using this CO_2-expanded liquid technique provided that the original dispersion of nanoparticles was fairly monodispere. For this purpose, we have employed two new particle synthesis and separation techniques that yield very monodisperse ligand stabilized nanoparticle dispersions in simple processing steps. The first method involves the synthesis of β-D glucose stabilized nanoparticles in an aqueous solution with subsequent extraction of a monodisperse fraction (5nm, $\sigma = 1$nm) into an organic phase by dodecanethiol capping ligand while leaving the β-D glucose in the aqueous phase. It should be noted that this method does not require the use of expensive phase transfer catalysts, provides complete recycle of the β-D glucose and solvents, and does not require the need for elaborate post synthesis processing to narrow the size distribution. In addition, we have developed a rapid and precise nanoparticle size selective fractionation technique that utilizes the pressure tunable solvent properties of CO_2-expanded liquids. By pressurizing and expanding a single organic solution with CO_2 gas, ligand stabilized metal nanoparticles of a desired mean size were size selectively precipitated and separated for further use in ordered thin film formation. The monodisperse nanoparticles obtained through the two synthesis/separation techniques were successfully applied in the assembly of structurally ordered, low defect and wide-area nanocrystal thin films using this CO_2 expanded liquid strategy. The thin films obtained were characterized by transmission electron microscopy (TEM), FTIR spectroscopy, EDS and EDX techniques.