

291j Advantages of Tunable CO₂ Solvent Systems in Metallic Nanoparticle Deposition and Separation Processes

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Many applications often require solvent based processing. As an example, nanoparticle thin films and arrays can be drop-cast by simply evaporating liquid solvents with dispersed particles. However, solvent dewetting and capillary forces at the liquid/vapor interfaces can lead to film defects and destruction of nanoscale features. Here we present the application of CO₂-based solvent systems as a means of controlling particle dispersion, deposition, and separation utilizing the tunable solvent properties in these systems. The implementation of CO₂-expanded liquids, as example, for the deposition of uniform nanoparticle thin films overcomes destructive wetting instabilities and surface tensions while also allowing solvent recovery. We have developed a novel particle deposition technique which utilizes CO₂ as a non-solvent for low defect, wide area nanoparticle film formation employing monodisperse metal nanoparticles. Ligand stabilized particles were precipitated from organic solvents by controllably expanding the solution with CO₂. Subsequent addition of CO₂ as a dense fluid then provides for removal and recovery of the organic while avoiding detrimental wetting effects common to evaporating solvents. The influence of factors such as pressurization rate, substrate, temperature, and ligands will be described. Application of nanoparticles in the CO₂-based systems often require very monodisperse starting materials. A new method for nanoparticle synthesis has been developed. This two-phase procedure reduces a metal salt in an aqueous phase, forming particles capped with β-D Glucose. These particles are then transferred into an organic phase by extraction. These particles were then extracted into an organic phase with the glucose molecules displaced by thiol ligands resulting in very monodisperse particles without the need for further processing steps. Additionally, the particles are stabilized by inexpensive, nontoxic ligands in a nontoxic solvent, making the particle dispersion extremely environmentally benign. Films of these particles were then made by the CO₂-based method described previously, resulting in a wide area, ordered array of monodisperse nanoparticles. CO₂-expanded liquids were also used in a technique designed to narrow the size distribution of ligand stabilized nanoparticles. We have shown that multiple monodisperse nanoparticle populations can be easily isolated from one another and from the organic solvent through controlled pressurization and deposition. Polydisperse Au and Ag particles (2 to 20 nm) were fractionated into +/- 2 nm monodisperse fractions. Compared to current liquid techniques, this CO₂-expanded liquid approach provides for faster and more efficient size separation, a reduction in organic solvent usage, tunable size selection, and controllable deposition. The influence of factors such as settling time, recursive fractionation, temperature, pressurization rate, and ligands will be described. Another alternative to organics for nanoparticle applications involves using CO₂ only as the processing solvent. Unfortunately, CO₂ is a weak solvent that requires fluorinated ligands to achieve particle dispersability. Since these fluorinated ligands are both expensive and environmentally persistent, the industrial viability of these processes has been severely hampered. By replacing fluorinated ligands with highly branched, methylated carboxylic acids able to interact with CO₂, we have stably dispersed metal nanoparticles in neat CO₂. This should greatly aid in nanoparticle technology as CO₂ offers many processing advantages, while the fluorine free ligands are both inexpensive and far more environmentally acceptable.