474d Size Selective Fractionation of Nanoparticles Using the Tunable Solvent Properties of Co_2 Gas Expanded Liquids

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This paper presents a process for rapid and precise size separation of polydisperse nanoparticle populations into mondisperse fractions using the pressure tunable physico-chemical properties of CO_2 gas expanded liquid solutions (Nanoletters, 5, 461, 2005). While solution based nanoparticle formation techniques are attractive due to their simplicity, they often result in synthesis of particles with a wide size range (e.g. 1 to 20 nm). As such, post synthesis processing is required to further refine the size distribution to the desired monodisperse range. This work utilizes the highly tunable solvent properties of organic/CO_2 solvent mixtures to selectively precipitate and size separate dispersions of polydisperse silver, gold or semiconductor nanoparticles (2 to 12 nm) into multiple, monodisperse fractions (± 0.5 nm). This work demonstrates that by controlling the addition of CO_2 (pressurization) to an organic dispersion of nanoparticles, the ligand stabilized nanoparticles can be size selectively precipitated within a novel high pressure apparatus that confines the particle precipitation to a specified location on a surface. The dispersibility of the ligand-stabilized nanoparticles is controlled by altering the ligand-solvent interaction (solvation) through the addition of the CO_2 gas as an antisolvent, thereby tailoring the bulk solvent strength. As such, the solvent interaction with the ligand tails can be diminished to a value below a threshold interaction energy necessary for dispersion of particles of a given size. Below this solvent strength, particles of that size or larger will precipitate. Therefore, the solvent strength of the medium can be tuned through CO_2 pressurization to provide sequential precipitation of increasingly smaller particles in a simple, controllable process. Compared to current techniques, this CO_2 expanded liquid approach provides for faster and more efficient particle size separation, reduction in organic solvent usage, and pressure tunable size selection in a single process.

This study also details the influence of various factors on this size separation process including the pressure ranges required for nanoparticle separation from various organic solvents (variations in solvent length), the impact of various material types (e.g. silver, gold, semiconductors), the impact of the alkyl stabilizing ligand length, as well as the use of recursive fractionation. Changes in ligand or solvent length were found to have a significant effect on the interaction between the solvent and the nanoparticles and therefore the pressure range required for precipitation of the nanoparticles. Stronger interactions between solvent and ligands require greater CO_2 pressure to precipitate the particles. A comprehensive examination of these factors has resulted in an optimization of the operating parameters necessary for efficient separation of a given nanomaterial type including the choice of solvent length, ligand length and the CO_2 pressure range required. The separation achieved using this CO_2 expanded liquid technique is impressive in that an initial polydisperse nanoparticle solution can be narrowed to populations with greater than 60% of the nanoparticles having $\sigma < 5\%$ in a single pressurization step. Furthermore, we have shown that recursive fractionation of particles collected within a given pressure range results in further reduction in the polydispersity of the sample, where populations with greater than 80% of the nanoparticles having $\sigma \leq 5\%$ have been achieved in three steps. In addition to providing efficient separation of the particles, this process also allows all of the solvent and antisolvent to be recovered, thereby rendering it a green solvent process.