Nanocrystal and Nanowire Synthesis and Dispersibility in SCFs

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Supercritical fluids (SCFs) provide a very useful solvent medium for nanomaterials synthesis, separation, and assembly. Organic SCFs, like toluene heated and pressurized above its critical point, offer a high temperature solvent environment amenable to a wide range of synthetic nanomaterials reactions that are not easily carried out in conventional solvents at ambient pressure. High temperature SCFs have demonstrated a particularly important role in solution-phase semiconductor nanowire synthesis. For example, vapor-liquid-solid (VLS) like growth of semiconductor nanowires using metal nanocrystals as seeds can be accomplished in SCFs. VLS-like growth requires reaction temperatures that exceed the metal:semiconductor eutectic, which are 360°C for Au:Si and ~590°C for Au:GaAs for example. These temperatures are easily reached in supercritical toluene. We have synthesized a wide variety of nanowires, including silicon, germanium, GaP, and GaAs using this approach. Solid-phase seeding of semiconductor nanowires from nanocrystals of transition metals like Co and Ni has also been demonstrated in SCFs. Even carbon nanotubes can be made in solution-from supercritical toluene at reaction temperatures of 625°C with metallocene reactants as catalysts. In addition to their high temperatures, SCFs exhibit density-tunable solvation strength, which is a very useful property for the synthesis and processing of organic ligand-coated nanocrystals. The size-dependent steric repulsion between ligand-coated nanocrystals can be tuned reversibly by adjusting solvent density, thus providing the ability to size-selectively separate nanocrystals and tune to some extent their size during synthesis. Compressed solvents at their vapor pressure can also be used to deposit nanocrystal monolayers at controlled evaporation rates without dewetting to form uniform coatings over relatively large substrate areas.