J. Am. Chem. Soc. **2000,** *122,* 4245−4246

Steric Stabilization of Nanocrystals in Supercritical CO_2 Using Fluorinated Ligands

Parag S. Shah, Justin D. Holmes,[†] R. Christopher Doty,
Keith P. Johnston,* and Brian A. Korgel*

Department of Chemical Engineering and
Texas Materials Institute
The University of Texas, Austin, Texas 78712-1062

Received December 15, 1999

Hydrocarbon monolayer-passivated silver nanocrystals consist of a metal core coated by an adsorbed layer of alkanethiol capping ligands and can readily be dispersed in a variety of hydrocarbon solvents.[1−3] Carbon dioxide has far weaker van der Waals forces than hydrocarbons, as reflected in the low polarizability per volume and refractive index.[4−7] The key to designing surfactants suitable for stabilizing water-in-CO_2 microemulsions[8,9] and for dispersions in CO_2 of organic[10] and inorganic[11] solids has been to find a suitable "CO_2-philic" molecular group that provides a steric barrier to aggregation. To date, surfactants with fluorinated tails have proven to be the most effective stabilizers. Here, we report a new synthetic method to make robust fluorocarbon-coated nanocrystals that disperse in liquid and supercritical (sc) CO_2. This is the first account of sterically stabilized nanocrystals in pure sc-CO_2. Furthermore, these fluorinated ligands provide steric stabilization in acetone, a polar solvent with significantly different dielectric properties than sc-CO_2.

Silver nanocrystals were synthesized at room temperature using a single-phase arrested growth method in a polar solvating medium. A thiolated fluorocarbon molecule, 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol from Oakwood Products Inc., ($C_{10}H_5F_{17}S$) was used as the stabilizing ligand. Water was deionized before use. Initially, 36 mL of an aqueous silver ion solution (0.03 M $AgNO_3$) was combined with 24.5 mL of an acetonic solution of phase transfer catalyst (0.20 M $(C_8H_{17})_4NBr$). After stirring the solution vigorously for 1 h, 250 μL of perfluorodecanethiol was added and stirred for 5 min. An aqueous sodium borohydride solution (30 mL, 0.44 M $NaBH_4$) was then added. After stirring overnight, the capped silver nanocrystals flocculated in the water/acetone solution. The precipitate was isolated and re-dispersed in acetone.[12] Size-selective precipitation using acetone/water as the solvent/nonsolvent pair narrowed the particle size distribution.[2,13]

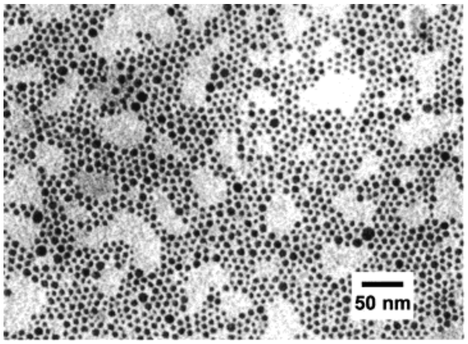

Figure 1. TEM image of silver nanocrystals coated with fluorinated ligands. TEM images were obtained using a Phillips EM 208 transmission electron microscope with 4.5 Å point-to-point resolution operating with an 80 kV accelerating voltage. ($d_p \approx 55$ Å, $\delta \approx 22$ Å)

The fluorinated thiol-capped silver nanocrystals could be re-dispersed in acetone and liquid and sc-CO_2. Dispersibility measurements in carbon dioxide were performed in a temperature-controlled stainless steel, high-pressure, variable-volume view cell equipped with sapphire windows in the front and on opposing sides. CO_2 was used as received from Matheson Gas Products. Nanocrystals were loaded into the cell by evaporating a drop of the particle suspension. The cell was then sealed and filled with a known volume of CO_2 and subsequently pressurized externally, using a computer-controlled ISCO model 100DX syringe pump. Particle dispersibility was verified when the CO_2 inside the cell became yellow. The fluorocarbon-coated particles dispersed in liquid CO_2 at pressures as low as 62 bar and 25 °C.

Figure 1 shows a typical transmission electron micrograph (TEM) of the fluorocarbon-coated silver nanocrystals on a carbon-coated copper TEM grid. The average particle diameter is 55 Å. The fluorocarbon coating prevents the silver surfaces from touching and maintains an edge-to-edge interparticle separation of 22 Å. This is significantly larger than what is found for decanethiol-coated silver nanocrystals (∼12.5 Å),[2] most likely due to the rigidity of self-assembled fluorocarbon monolayers (FSAMs).[14] The capping molecules cannot flex and bend as effectively as the hydrocarbons to accommodate nanocrystal core packing in the monolayer.[2]

Fourier transform infrared (FTIR) spectroscopy confirmed the presence of the fluorinated ligands on the particle surfaces (see Figure 2). FTIR spectra were recorded using a Perkin-Elmer Spectrum 2000 spectrometer at 20 °C by depositing silver nanocrystals onto a ZnSe IR window. Prior to performing these measurements, the samples were thoroughly washed to remove all unbound ligands. The four peaks in the dodecanethiol capped nanocrystals correspond to the asymmetric and symmetric methylene stretching modes—$\nu_a(CH_2) = 2928$ cm^{-1} and $\nu_s(CH_2) = 2855$ cm^{-1}, respectively—and to the asymmetric in-plane and symmetric stretching modes of the terminal methyl groups—$\nu_a(CH_3,ip) = 2954.5$ cm^{-1} and $\nu_s(CH_3,FR) = 2871$ cm^{-1}, respectively.[15] For the fluorinated thiol capped nanocrystals, the $\nu_s(CH_3,FR)$ and the $\nu_a(CH_3,ip)$ stretches are not present, and other features appear, possibly as a result of the increased electrone-

---

* To whom correspondence should be addressed. Telephone: (512) 471-5633. Fax: (512) 471-7060. E-mail: korgel@mail.che.utexas.edu.

[†] Present address: Department of Chemistry, University College Cork, Ireland.

(1) See for example, Korgel, B. A.; Fitzmaurice, D. *Phys. Rev. B* **1999**, *59*, 14191−14201 and references therein.

(2) Korgel, B. A.; Fullam, S.; Connolly, S.; Fitzmaurice, D. *J. Phys. Chem. B* **1998**, *102*, 8379−8388.

(3) Korgel, B. A.; Fitzmaurice, D. *Phys. Rev. Lett.* **1998**, *80*, 3531−3534.

(4) O'Shea, K.; Kirmse, K.; Fox, M. A.; Johnston, K. P. *J. Phys. Chem.* **1991**, *95*, 7863.

(5) McClain, J. B.; Londono, D.; Combes, J. R.; Romack, T. J.; Canelas, D. A.; Betts, D. E.; Wignal, G. D.; Samulski, E. T.; DeSimone, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 917−918.

(6) O'Neill, M. L.; Yates, M. Z.; Johnston, K. P.; Smith, C. D.; Wilkinson, S. P. *Macromolecules* **1998**, *31*, 2838.

(7) Hoefling, T. A.; Beitle, R. R.; Enick, R. M.; Beckman, E. J. *Fluid Phase Equilib.* **1993**, *83*, 203.

(8) Johnston, K. P.; Harrison, K. L.; Clarke, M. J.; Howdle, S. M.; Heitz, M. P.; Bright, F. V.; Carlier, C.; Randolph, T. W. *Science* **1996**, *271*, 624.

(9) Nanocrystals were recently synthesized in water-in-CO_2 microemulsions: Holmes, J. D.; Bhargava, P. A.; Korgel, B. A.; Johnston, K. P. *Langmuir* **1999**, *15*, 6613−6615. Ji, M.; Chen, X.; Wai, C. M.; Fulton, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2631−2632. Holmes et al. found the CdS particles were not redispersible in CO_2 without water due to weak surfactant binding to the nanocrystal surface.

(10) DeSimone, J. M.; Maury, E. E.; Menceloglu, Y. Z.; McClain, J. B.; Romack, T. J.; Combes, J. R. *Science* **1994**, *265*, 356.

(11) Calvo, L.; Holmes, J. D.; Yates, M. Z.; Johnston, K. P. *J. Supercrit. Fluids* **2000**, *16*, 247−260.

(12) The phase-transfer catalyst was required in the synthesis to obtain nanocrystals that were redispersible.

(13) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706−8715.

(14) Chidsey, C. E. D.; Loiacono, D. N. *Langmuir* **1990**, *6*, 682−691.

(15) Ulman, A. *An introduction to ultrathin organic films: from Langmuir−Blodgett to self-assembly*; Academic Press: Boston, 1991.

10.1021/ja9943748 CCC: $19.00

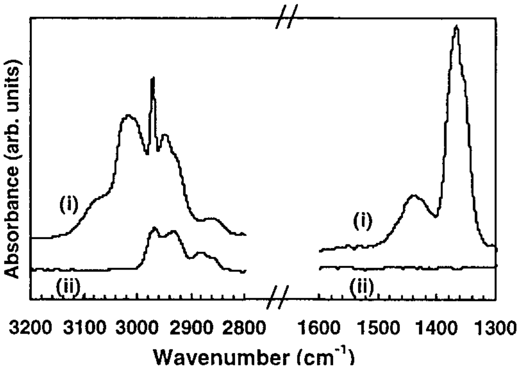

Figure 2. FTIR spectra of silver nanocrystals capped with (i) fluorinated ligands and (ii) dodecanethiol.

gativity near the neighboring C−H and C−F bonds of the $-(CH_2)_2(CF_2)_7CF_3$ group that could affect their vibrational motion. The $\nu_s(CF_3)$ stretches appear as expected in the range from 1300 to 1500 cm^{-1}.[14] The hydrocarbon ligands do not give rise to stretching frequencies in this range.

The key to sterically stabilized systems is to have well-solvated ligand tails that extend out into the solvent and provide the necessary repulsive force to overcome the van der Waals attraction between the nanocrystals.[16−18] The dispersibility of the partially fluorinated nanocrystals in polar solvents such as acetone and ethanol can be rationalized in terms of the large dipole moment of the CH_2-CF_2 group, which produces substantial dipole−dipole interactions with polar solvents leading to chain extension from the particle surfaces.[19] In terms of dipole moment and refractive index, sc-CO_2 is very different from acetone, yet the fluorocarbon-coated nanocrystals also dispersed in sc-CO_2. O'Neill et al. showed that polymer solubility in CO_2 correlates with the surface tension of the polymer, γ, which is a measure of the cohesive energy density.[20] Since hydrocarbon molecules, such as decane, dissolve in sc-CO_2,[21] one might expect that the hydrocarbon-coated nanocrystals would exhibit at least minimal dispersibility. However, dodecanethiol-capped silver nanocrystals did not disperse in sc-CO_2. It was found that by adding hexane in significant quantities as a cosolvent to sc-CO_2 (volume fractions greater than 50%) dodecanethiol-capped nanocrystals could be dispersed. This finding is consistent with the expectation that the lower surface tension of perfluorodecane (14.0 mN/m) relative to dodecane (24.5 mN/m)[22] leads to much greater dispersibility of fluorocarbon-coated nanocrystals than hydrocarbon-coated nanocrystals in CO_2.

UV/vis absorbance measurements of silver nanocrystals dispersed in sc-CO_2 were taken using the variable volume view cell setup described above. The windows on the cell were made of sapphire with a path length of 3 cm, and all of the measurements were taken on a Beckman DU-40 UV−vis spectrophotometer. The peak in the absorbance spectra (Figure 3) corresponds to the lowest order surface mode resulting from a plasma oscillation with uniform polarization across the volume of a nanocrystal.[23] The resonant frequency of this oscillation, called the Fröhlich frequency, ω_F, depends on particle size, the dielectric properties of the surrounding medium, and the plasmon energy for silver, ω_P. In the limit of small particle size, ω_F relates to the optical dielectric constant of the surrounding medium (which is the refractive index squared), by the following equation: $\omega_F^2 = \omega_P^2/\sqrt{1+2\epsilon_m}$. On the basis of the fact that ϵ_m(hexane) > ϵ_m(acetone) > $\epsilon_m(CO_2)$, λ_{max} is expected to be the lowest for CO_2 suspensions, followed by acetone and then hexane. However, λ_{max} was largest for nanocrystals dispersed in sc-CO_2. This peak shift to longer wavelength is characteristic of an increase in particle size. TEM measurements, however, showed that the primary nanocrystal size did not increase after suspension in sc-CO_2. Reversible particle "sticking" resulting from slight interparticle attractions in sc-CO_2 most likely explains the increase in λ_{max}.[2,23,24] The absorbance peak for fluorocarbon-coated silver nanocrystals in acetone was significantly broader than the peak for similarly sized hydrocarbon-coated nanocrystals in hexane. Using the Drude free electron model as a guideline, the absorbance peak width for silver nanocrystals relates inversely to the free electron path length.[23] This seems to indicate that the electronegative fluorocarbon coating decreases the electron mean free path in the silver nanocrystals.

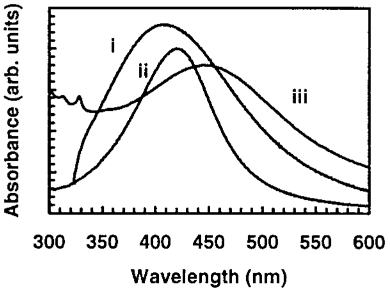

Figure 3. UV−visible absorbance spectra of 55 Å diameter silver nanocrystals (i) coated with fluorinated ligands dispersed in acetone; (ii) coated with hydrocarbon ligands dispersed in hexane; (iii) coated with fluorinated ligands dispersed in sc-CO_2.

In conclusion, fluorocarbon-coated nanocrystals disperse in CO_2 at moderate temperatures and pressures, providing an environmentally benign medium for nanocrystal processing and synthesis. The use of fluorinated ligands could prove to be important for memory storage applications, for example, where the low dielectric constant material helps to insulate active charge-storing device structures. Additionally, these fluorocarbon-coated nanocrystals might prove to be very useful for coatings applications due to their unique wettability.

Acknowledgment. We acknowledge support from DOE, the Welch Foundation, and the Separations Research Program at UT Austin and thank the ISCO Corporation for their donation of a high-pressure syringe pump. We also thank the Institute for Cell and Molecular Biology at UT Austin, for their TEM assistance. B.A.K. thanks DuPont for a Young Professor Grant and NSF for support.

JA9943748

---

(16) Hiemenz, P. C.; Rajagopalan, R. *Principles of Colloid and Surface Chemistry*, 3rd ed.; Marcel Dekker: New York, 1997.

(17) Hamaker, H. C. *Physica* **1937**, *4*, 1058−1072.

(18) Israelachvili, J. *Intermolecular & Surface Forces*, 2nd ed.; Academic Press: San Diego, 1992.

(19) *Fluorine Chemistry: A Comprehensive Treatment*; John Wiley & Sons: New York, 1995.

(20) O'Neill, M. L.; Cao, Q.; Fang, M.; Johnston, K. P.; Wilkinson, S. P.; Smith, C. D.; Kerschner, J. L.; Jureller, S. H. *Ind. Eng. Chem. Res.* **1998**, *37*, 3067.

(21) Knapp, H.; Doring, R.; Oellrich, L.; Plocker, U.; Prausnitz, J. M. *Vapor-Liquid Equilibria for Mixtures of Low Boiling Substances*; Schon & Wetzel: Frankfurt, 1982.

(22) The surface tension can be estimated using $\gamma = A/24\pi\delta_0^2$, where δ_0 is a "universal constant" determined to be 0.165 nm in ref 18 and A is the Hamaker constant in a vacuum.[18] A for silver in a vacuum is 2.2 eV.[18] To calculate A_{131} for silver interacting across CO_2, the relationship $A_{131} \approx (A_{11} - A_{33})^2$ was used: A_{11} is silver in a vacuum and A_{33} is CO_2 in a vacuum.[18]

(23) Bohren, C. F.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles*; John Wiley & Sons: New York, 1983.

(24) Mattoussi, H.; Cumming, A. W.; Murray, C. B.; Bawendi, M. G.; Ober, R. J. *J. Chem. Phys.* **1996**, *105*, 9890.