Synthesis of Fullerene–Rhodium Nanocomposites via Aerosol Decomposition

Abhijit S. Gurav,[†] Zhibang Duan,[‡] Lumin Wang,[§] Mark J. Hampden-Smith,[*,§] and Toivo T. Kodas[*,†]

Departments of Chemical Engineering, Chemistry, and Geology, University of New Mexico, Albuquerque, New Mexico 87131

Received September 16, 1992. Revised Manuscript Received November 30, 1992

Highly disperse (20–100 nm) powders consisting of nanophase fullerenes and their nanocomposites with rhodium were generated by aerosol decomposition. Solutions of mixed fullerene extract (C_{60}, C_{70}) and $[(1,5\text{-COD})RhCl]_2$ in toluene were atomized and passed through a hot-wall reactor in N_2 carrier gas where toluene evaporation and thermal decomposition of $[(1,5\text{-COD})RhCl]_2$ to form Rh occurred. Nanocomposite particles were formed at a reactor temperature of 550 °C which was sufficiently low to avoid C_{60} and Rh grain growth in each particle but sufficiently high to thermally decompose $[(1,5\text{-COD})RhCl]_2$. Transmission electron micrographs of pure fullerenes showed lattice fringes corresponding to the prominent *d* spacing of 8.2 Å in C_{60}. TEM of the 50/50 wt % fullerene/Rh composite showed 3–5-nm Rh crystallites, consistent with the value of 4 nm calculated from X-ray diffraction peak broadening. Aerosol decomposition allows reasonable production rates of such nanophase materials at the laboratory scale and has the potential for scale up to larger levels.

Introduction

The recent synthesis of macroscopic quantities of C_{60} and C_{70} (fullerenes)[1] has stimulated a variety of studies on their chemical and physical properties.[2] Fullerene-based materials have many potential applications[3,4] including optical limiters, superconducting and nanoscale devices, catalysts, carbon fibers, and carbon composites. Although there are numerous reports[2,5] on spectrochemical studies of C_{60} and its chemical reactions with alkali and other metals such as La, Y, Sc, Os, and Pd, there are few reports about processing of fullerene-based composites. C_{60} is perhaps the perfect nanoscale structural unit and can be used to develop pure nanophase or nanocomposite materials.[4] At the nanophase level, such composites and even single-phase materials may exhibit entirely new or highly enhanced properties.[4,6] In this paper, we describe the first report of processing of nanophase fullerenes and their nanocomposites with rhodium metal via aerosol decomposition.

Aerosol decomposition is a promising approach for generation of unagglomerated ceramic and metal powders with submicron particle size.[7] This aerosol technique involves generation of aerosol droplets from a solution of precursors. Solvent evaporation, precursor precipitation, and decomposition of precursors take place within individual droplets/particles as they are carried through a hot-wall reactor. This approach has several advantages over traditional processing methods. High-purity powders can be produced because milling is not required to reduce particle size. A more homogeneous chemical composition or controlled-phase distribution (composite materials) can be obtained because segregation during precursor precipitation is limited to the submicron scale of each particle. In addition, particle size, morphology and microstructure can be controlled.[7–9]

Commercially available fullerene powders often have a broad particle size distribution and irregular morphology. Thus, aerosol routes could be used to obtain spherical, submicron, uniform-size fullerene particles from solutions. Composites and compounds of fullerenes may be synthesized by adding metal precursors to the solution. Also, by optimizing the reactor temperature, residence time, and solution concentration, it may be possible to achieve complete decomposition of precursors and minimize grain growth to obtain nanophase powders as demonstrated for several ceramics.[9] We have used this approach to produce 3–5-nm grain-size fullerene–rhodium composites using solutions of mixed fullerene extract (MFE) and $[(1,5\text{-COD})RhCl]_2$ (1,5-COD = 1,5-cyclooctadiene) in toluene.

Experimental Section

The mixed fullerene extract was purchased from Texas Fullerene Corp. and contained about 85 wt % C_{60} and 15 wt % C_{70}. The mixture was used as-received without further purification. The compound $[(1,5\text{-COD})RhCl]_2$ was synthesized by the procedure reported in the literature.[10]

[†] Department of Chemical Engineering.

[‡] Department of Chemistry.

[§] Department of Geology.

[*] To whom correspondence should be addressed.

(1) Kratchmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(2) For recent reviews: (a) *Acc. Chem. Res.* **1992**, *25*, 97–176. (b) Hammond, G. S., Kuck, V. J., Eds. *Fullerenes: Synthesis, properties and chemistry of large carbon clusters*; ACS Symp. Series 481; American Chemical Society, Washington, DC, 1992.

(3) Ismail, I. M. K.; Rodgers, S. L. *Carbon* **1992**, *30*, 229.

(4) Ball, P.; Garwin, L. *Nature* **1992**, *355*, 761.

(5) (a) Yannoi, C. S.; Hoinkis, M.; de Vries, M. S.; Bethune, D. S.; Salem, J. R.; Crowder, M. S.; Johnson, R. D. *Science* **1992**, *256*, 1191. (b) Nagashima, H.; Nakaoka, A.; Saito, Y.; Kato, M.; Kawanishi, T.; Itoh, K. *J. Chem. Soc., Chem. Commun.* **1992**, 377.

(6) (a) Gleiter, H. *Prog. Mater. Sci.* **1989**, *33*, 223. (b) Siegel, R. W.; Eastman, J. A. *Mater. Res. Soc. Symp. Proc.* **1989**, *132*, 3.

(7) For review: Kodas, T. T. *Adv. Mater.* **1989**, *6*. 180.

(8) Ortega, J.; Kodas, T. T.; Chadda, S.; Smith, D. M.; Ciftcioglu, M.; Brennan, J. E. *Chem. Mater.* **1991**, *3*, 746.

(9) (a) Carim, A. H.; Doherty, P.; Kodas, T. T.; Ott, K. *Mater. Lett.* **1989**, *8*, 335. (b) Lyons, S. W.; Wang, L. M.; Kodas, T. T. *Nanostruct. Mater.*, in press.

0897-4756/93/2805-0214$04.00/0

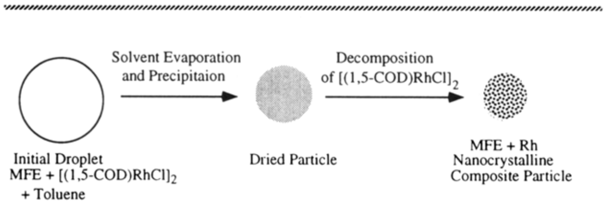

Figure 1. Schematic of generation of fullerene–rhodium nanocomposite powders via aerosol decomposition.

The aerosol decomposition apparatus has been described previously.[8] During the present study, humidifying columns were not used and nitrogen was used as the carrier gas. The system was purged with nitrogen before and after the experiments. A modified Collison (BGI Inc.) aerosol generator was used. Aerosol carrier gas flow rate was 10.0 ± 0.1lpm. The powders were collected on a nylon filter which was kept at 47 ± 2 °C to prevent condensation of the solvent and possible clogging at the filter. Two solutions were used to generate powders.[11] The first consisted of a toluene solution of MFE and was processed at 200 °C. The second solution contained MFE and [(1,5-COD)RhCl]$_2$ in toluene and was processed at 550 °C.

Results and Discussion

The process of forming pure fullerene and fullerene–rhodium composite powders by aerosol decomposition consists of drying micron-size droplets followed by intraparticle reactions as the particles flow through the reactor (Figure 1). Solvent evaporation is accompanied by precipitation of C_{60} and the precursor in the particle to form solid phases and is followed by thermal decomposition of [(1,5-COD)RhCl]$_2$. Since both the C_{60} and rhodium precursor are initially mixed at the molecular level and the solutions are dilute, ultrafine particles having a nanoscale dispersion of the composite phases are formed. A $^{13}C\{^1H\}$ NMR spectrum of the mixed solution of MFE and [(1,5-COD)RhCl]$_2$ in deuterated benzene showed no extra peaks that could be attributed to any reaction between the two precursors. This confirmed that the solution droplets entering the reactor were composed of a mixture of unreacted precursors. The criterion for the choice of the Rh precursor was that it should thermally decompose under inert atmosphere to form Rh metal at a temperature where C_{60} is thermally inert. In a recent survey[12] of the thermal stability of a series of [L_2RhCl]$_2$ compounds, L_2 = 1,5-COD, NBD (2,5-norbornadiene), and (ethylene)$_2$, only L_2 = 1,5-COD gave Rh metal directly at low temperatures (~335 °C) under N_2 atmosphere. In the experiments reported here, a reactor temperature of 550 °C was necessary to achieve complete decomposition of the rhodium precursor because the residence time was only 15 s. However, these conditions did not result in C_{60} decomposition or cause excessive grain growth.

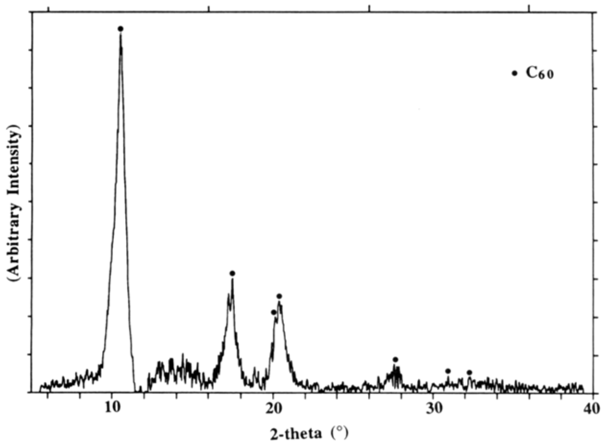

Figure 2. XRD pattern for fullerene powder made at 200 °C in nitrogen.

Figure 3. TEM bright field micrograph of pure fullerene powder.

Figure 2 shows the X-ray diffraction spectrum (Scintag, USA; Cu Kα) of the aerosol-generated pure fullerene powder made in nitrogen at 200 °C. Extensive peak broadening indicated a small crystallite size of roughly 10 nm in the particles. These particles were solid as shown by a TEM (JEOL 2000FX, 200 kV) bright-field micrograph of pure fullerene powder (Figure 3). Some of the regions showed lattice fringes with a spacing of about 8.2 Å which corresponds to the prominent (002) *d* spacing of C_{60}. A selected-area electron diffraction pattern (Figure 3), indicated that the particles were polycrystalline. These results demonstrate that aerosol decomposition is a useful route for generation of submicron fullerene powders.

Rh-fullerene powders with 50/50 wt % composition were produced at 550 °C. A scanning electron micrograph (Hitachi Model S-800) of these powders showed the presence of 20–50-nm agglomerated particles (Figure 4). The corresponding XRD pattern is shown in Figure 5. Peaks corresponding to C_{60} and rhodium metal are marked;

---

(10) (a) Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 4735. (b) Abel, E. W.; Bennett, M. A.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3178. (c) Cramer, R. *Inorg. Synth.* **1990**, *28*, 86. (d) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, *28*, 88.

(11) The MFE solution was prepared by dissolving 400 mg of MFE in 308 mL of toluene. Pure fullerene powders were prepared by drying aerosol droplets of this solution. Batches of 85–95 mg of fullerene–rhodium composites having compositions (wt %) MFE/Rh = 50/50 were made using a solution containing both the precursors in toluene. *Note*: During the experiments, the reactor contains toluene vapor and chlorine gas at high temperatures (200–550 °C). Care is necessary to check the system for leaks and with the exhaust gases.

(12) Duan, Z.; Hampden-Smith, M. J.; Sylwester, A. P., submitted to *J. Organomet. Chem.*

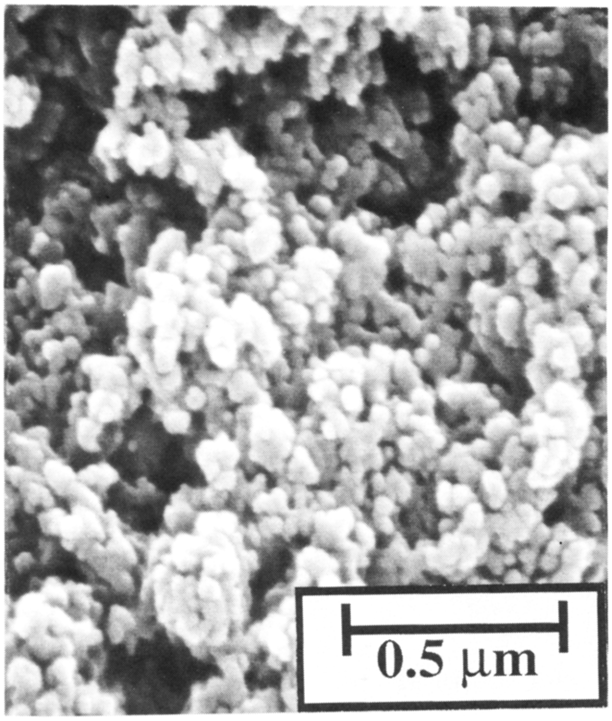

Figure 4. SEM micrograph of 50/50 fullerene–rhodium composite powder made at 550 °C in nitrogen.

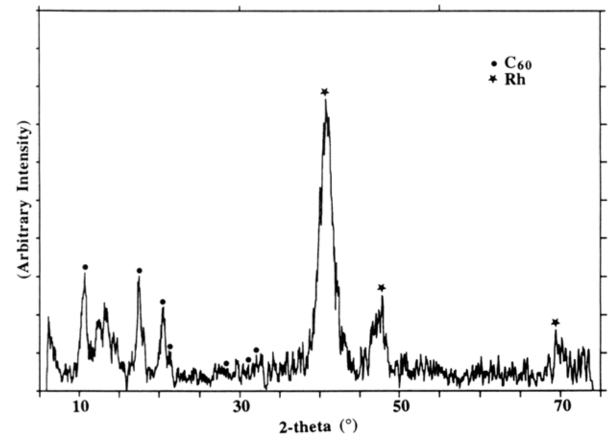

Figure 5. XRD pattern for 50/50 fullerene–rhodium composite powder made at 550 °C in nitrogen.

however, a few peaks in the pattern could not be indexed. These peaks could be due to the presence of C_{70} or unique $C_{60}/C_{70}/Rh$ structures in the powders. The peaks were quite broad indicating crystallite sizes of 4 and 11 nm, respectively, for rhodium and C_{60}. A TEM micrograph of the MFE/Rh = 50/50 composite powder (Figure 6) showed dark rhodium particles dispersed in the fullerene matrix. The rhodium particles had a size of 3–5 nm consistent with the crystallite size observed by XRD peak broadening.

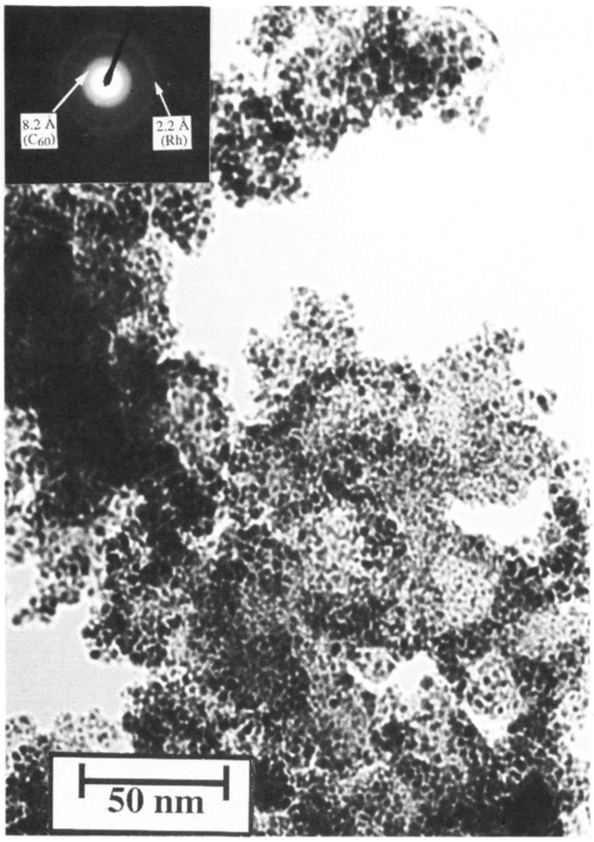

Figure 6. TEM bright-field micrograph of 50/50 fullerene–rhodium composite powder made at 550 °C in nitrogen.

The selective area diffraction patterns (Figure 6) showed rings corresponding to the prominent *d* spacings of C_{60} and rhodium. Thus, XRD and TEM showed that phase segregation can be controlled at the nanometer-scale to form ultrafine particles consisting of a nanocomposite of C_{60} and Rh. This new method for processing C_{60}-based composites is being extended to other systems and the subsequent processing of the powders is being examined.

Acknowledgment. The authors are grateful to Xiaomei Qiu for help with TEM micrographs. T.T.K. thanks the NSF (Grant PYI CTS-9058538) for support. M.H.S. thanks the NSF Chemical Instrumentation Program for the purchase of a low-field NMR spectrometer. TEM was carried out in the Electron Microbeam Analysis Facility, Department of Geology at the University of New Mexico, which is supported by NSF, NASA, DOE-BES, and the State of New Mexico.

Registry No. C_{60}, 99685-96-8; C_{70}, 115383-22-7; toluene, 108-88-3; nitrogen, 7727-37-9; 1,5-cyclooctadiene, 111-78-4.