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Enhanced Solid-State Metathesis Routes to Carbon Nanotubes

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Ignition of three solids creates multiwalled carbon nanotubes in seconds. A solid-state metathesis (exchange) reaction between hexachloroethane (C_2Cl_6) and lithium acetylide (Li_2C_2) with 5% cobalt dichloride ($CoCl_2$) added as an initiator produces up to 7% carbon nanotubes, as observed via transmission electron microscopy. Using the concept that sulfur can promote nanotube growth, the reaction yield can be increased to 15% by switching to CoS as the initiator. The more readily available, inexpensive calcium carbide (CaC_2) can be substituted for lithium acetylide while maintaining comparable yields. Switching initiators to FeS can be used to further enhance the yield. A systematic study of the C_2Cl_6/CaC_2 reaction system indicates that a yield up to 25% can be realized by using 6% FeS as the initiator. Reaction temperatures for the C_2Cl_6/CaC_2 system of up to 3550 °C are calculated using thermodynamic data assuming quantitative yield and adiabatic conditions.

Introduction

The discovery of carbon nanotubes has sparked tremendous research efforts into the uses of nanostructured materials.[1] Current synthetic procedures focus on arc-discharge,[2] laser vaporization,[3] and chemical vapor deposition (CVD)[4] methods to produce multi- and single-walled carbon nanotubes. Applications ranging from high-strength composites[5] to hydrogen storage[6,7] could benefit from the development of a more-efficient and less-expensive synthetic route. Recent advances in the synthetic approach to the production of multiwalled carbon nanotubes focus on alternative routes such as water-assisted synthesis, plasma torch methods, reduction of metal carbonates, medial reduction, and explosive detonation.[8−14] Here we report a solid-state route to multiwalled carbon nanotubes. The potential advantages of solid-state metathesis (exchange) reactions include fast reaction times, simple experimental designs, and inexpensive starting materials.

Solid-state methathesis reactions have been developed as a simple and effective route to many materials that are difficult and/or costly to synthesize.[15,16] These highly exothermic reactions are self-propagating and can be initiated by a resistively heated filament. Metathesis reactions are driven by the formation of stable salt byproducts, which are then washed away to isolate the product of interest. A carbon-based exchange reaction between hexachloroethane (C_2Cl_6) and lithium acetylide (Li_2C_2) with 5 mol% cobalt dichloride ($CoCl_2$) added as an initiator produces up to 7% carbon nanotubes, based on transmission electron microscopy (TEM) images.[17]

Here we report several important improvements to the solid-state metathetical synthesis of carbon nanotubes. Calcium carbide (CaC_2) is found to be a better and more readily available alternative to the precursor lithium acetylide (Li_2C_2). Transition metal sulfides, e.g., CoS and FeS, are

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(1) Ajayan, P. M. *Chem. Rev.* **1999,** *99* (7), 1787−1799.
(2) Ebbeson, T. W.; Ajayan, P. M. *Nature* **1992**, *358*, 220−222.
(3) Thess, A.; et al. *Science* **1996**, *273*, 483−487.
(4) Maschmann, M. R.; Amama, P. B.; Goyal, A.; Iqbal, Z.; Gat, R.; Fisher, T. S. *Carbon* **2005** *44* (1), 10−18.
(5) Schaffer, M. S. P.; Windle, A. H. *Adv. Mater*. **1999**, *11*, 937−941.
(6) Ye, Y.; et al. *Appl. Phys. Lett.* **1999**, *74*, 2307−2309.
(7) Liu, C.; et al. *Science* **1999**, *286*, 1127−1129.
(8) Hsin, Y. L.; Hwang, K. C.; Chen, F. R.; Kai, J. J. *Adv. Mater*. **2001**, *13*, 830−833.
(9) Zhu, H. W.; Li, X. S.; Jiang, B.; Xu, C. L.; Zhu, Y. F.; Wu, D. H.; Chen, X. H. *Chem. Phys. Lett.* **2002**, *366*, 664−669.
(10) Liu, J.; Shao, M.; Tang, Q.; Zhang, S.; Qian, Y. *J. Phys. Chem. B* **2003**, *107*, 6329−6332.
(11) Lu, Y.; Zhu, Z.; Liu, Z. *Carbon* **2004**, *42*, 361−370.
(12) Smiljanic, O.; Larouche, F.; Sun, X.; Dodelet, J.-P.; Stansfield, B. L. *J. Nanosci. Nanotechnol.* **2004**, *4* (8), 1005−1013.
(13) (a) Lou,Z.; Chen, C.; Chen, Q. *J. Phys. Chem. B* **2005,** *109* (81), 10557−10560.
(14) Lou, T.; Liu, J.; Chen, L.; Zeng, S.; Qian, Y. *Carbon* **2005**, *43* (4), 755−759.
(15) Gillan, E. G.; Kaner, R. B. *Chem. Mater*. **1996**, *8*, 333−343.
(16) Wallace, C. H.; Reynolds, T.; Kaner, R. B. *Chem. Mater*. **1999**, *11*, 2299.
(17) O'Loughlin, J. L.; Kiang, C.-H.; Wallace, C. H.; Reynolds, T.; Rao, L.; Kaner, R. B. *J. Phys. Chem. B* **2001**, *105*, 1921.

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determined to be superior initiators when compared to their halide counterparts. Combining the metal sulfide FeS with calcium carbide dramatically improves the yield of carbon nanotubes up to 25%.

Experimental Section

Lithium acetylide (Li_2C_2, Alfa), hexachloroethane (C_2Cl_6, Aldrich, 99%), and calcium carbide (CaC_2, Fluka, <0.1 μm pellets) were ground into fine powders prior to use. Cobalt metal (Cerac, 99.8%), iron metal (Mallinckrodt Chemical Works, reduced), nickel metal (ESPI), sulfur (Fisher), cobalt chloride ($CoCl_2$, Alfa), nickel sufide (NiS, Alfa), cobalt disulfide (CoS_2, Alfa), cobalt sulfide (CoS, Alfa), and iron sulfide (FeS, Alfa) were used as received.

The synthesis of carbon nanotubes was carried out in a helium-filled glovebox (Vacuum Atmosphere MO-40). Stoichiometric amounts of the reactants were weighed and ground together with an agate mortar and pestle. The reactants were then transferred to a stainless steel pan and placed within a larger capped stainless steel reaction vessel, modeled after a bomb calorimeter. This allows for partial containment of any gases produced. The reaction is initiated using a resistively heated Nichrome wire. The reaction is complete in less than a second. The reaction products are removed from the drybox and washed with water to remove the salt byproduct.

Powder X-ray diffraction was performed on the washed products using a PANalytical XPert Pro powder diffractometer with Cu K_α radiation with $\lambda = 1.5418$ Å. The scans were taken between 10° and 100° 2θ at 0.1° intervals with a scan speed of 0.5°/s.

TEM was performed using a JEOL 2000FX. Samples were dispersed onto lacey carbon grids for analysis. The product yields were estimated by counting the number of carbon nanotubes on randomly selected grids. Scanning electron microscopy was carried out using a JEOL JSM-6700F FE-SEM.

Results and Discussion

A carbon-based metathesis (exchange) reaction between hexachloroethane (C_2Cl_6) and lithium acetylide (Li_2C_2) produces crystalline graphite and the byproduct salt lithium chloride as given in eq 1.[17]

$$C_2Cl_6 + 3Li_2C_2 \rightarrow 8C + 6LiCl \qquad (1)$$

The enthalpy released in this reaction (ΔH_{rxn}) is -2056 kJ/mol, yielding a theoretical maximum temperature (T_{max}) of 2029 °C. The maximum temperature for any metathesis reaction can be calculated from standard thermodynamic data, i.e., heat capacities and heats of transition, assuming complete reaction and adiabatic conditions.[15,18] After the LiCl byproduct was washed away, powder X-ray diffraction reveals graphite as the only crystalline phase present. The creation of crystalline graphite in seconds from a solid-state metathesis reaction makes sense when one considers that T_{max} for the C_2Cl_6/Li_2C_2 reaction approaches the reported graphitization temperature for bulk carbon (2200 °C)[18] and this reaction produces nanoscale carbon. The addition of 5 mol% (based on carbon) cobalt dichloride ($CoCl_2$) as an initiator to the C_2Cl_6/Li_2C_2 reaction yields graphite and face-centered cubic cobalt metal after washing with water. Face-centered cubic cobalt is the high-temperature phase since cobalt converts from the hexagonal to the cubic phase above 450 °C.[20] With reaction temperatures exceeding 2000 °C, the formation of the cubic phase is not surprising. The yield of carbon nanotubes is 7%, based on TEM images.

The precursors (Li_2C_2, CaC_2, and C_2Cl_6) and initiators (Co, $CoCl_2$, CoS, CoS_2, Ni, NiS, and FeS) were varied systematically to determine the optimum parameters for synthesizing carbon nanotubes from these solid-state metathesis reactions. The use of sulfur as a promoter for nanotube growth was thoroughly investigated since elemental sulfur has been identified as a promoter for carbon nanotube formation.[21] When combined with iron or cobalt, the catalytic activity for nanotube production is known to improve.[22] Sulfur is believed to promote the growth of large carbon clusters, thus stabilizing the intermediate species for nucleation and subsequent evolution of carbon nanotubes.

Elemental sulfur was added first to a reaction between hexachloroethane (C_2Cl_6) and lithium acetylide (Li_2C_2) with a transition metal initiator since this reaction is known to produce carbon nanotubes.[17] When 2.5% sulfur was added to a reaction with 5% Ni as the initiator, no nanotubes were observed. When 2.5% sulfur was added to a reaction with 5% Co as the initiator, only a few carbon nanotubes were observed. These low nanotube yields can be attributed to the high temperatures reached in these extremely exothermic reactions. Since sulfur sublimes at 445 °C, it is not surprising that elemental sulfur is ineffective in promoting nanotube growth in a metathesis reaction between C_2Cl_6 and Li_2C_2. Therefore, it was important to search for an initiator that could release sulfur at elevated temperatures. Transition metal sulfides with melting points ranging from 1182 °C for CoS to 1188 °C for FeS were considered good candidates since they are known to decompose at temperatures greater than their melting points.[20]

The addition of cobalt sulfide (CoS) as an initiator to the reaction between Li_2C_2 and C_2Cl_6 dramatically increases the yield of carbon nanotubes up to 15%. This is a significant improvement in the 7% yield obtained in earlier work with a 5 mol% $CoCl_2$ initiator.[17] Varying the concentration of CoS initiator from 0.5 to 20 mol% (based on moles of carbon) indicates that 5 mol% initiator produces the highest yield of nanotubes (Table 1). Figure 1 shows a typical transmission electron micrograph of a multiwalled carbon nanotube synthesized by the metathesis reaction of Li_2C_2 and C_2Cl_6 with the optimal 5 mol% CoS initiator.

Another parameter that can affect the yield of carbon nanotubes is the choice of reactants. Lithium acetylide is not an ideal precursor since it is now difficult to obtain due to safety considerations and, hence, somewhat expensive. Calcium carbide, on the other hand, is a readily accessible and inexpensive alternative. Therefore, metathesis reactions

(18) *JANAF Thermochemical Tables*, 3rd ed.; Lide, D. R., Ed.; American Chemical Society and American Institute of Physics: New York, 1985.
(19) Saito, R.; Dresselhaus, G.; Dresselhaus, M. S. *Physical properties of carbon nanotubes*; Imperial College Press: London, 1998.
(20) *CRC Handbook of Chemistry and Physics*, 76th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1995.
(21) Kiang, C.-H.; Goddard, W. A.; Beyers, R.; Bethune, D. S. *Carbon* **1995**, *33*, 903−914.
(22) Kiang, C.-H. *J. Phys. Chem. A* **2000**, *104*, 2454−2456.

Table 1. Initiators Used in the Reaction between Li_2C_2 and C_2Cl_6 To Produce Carbon Nanotubes (CNTs)[a]

initiator (mol%)[b]	CNT yield estimation
5% $CoCl_2$	7%
5% Co	low
5% Co + 2.5% S	low
5% Ni	none observed
5% Ni + 2.5% S	none observed
5% NiS	none observed
5% CoS_2	none observed
0.5% CoS	low
5% CoS	15%
10% CoS	12%
15% CoS	10%
20% CoS	5%

[a] The carbon nanotube yield is estimated from the transmission electron micrographs. [b] Based on moles of carbon.

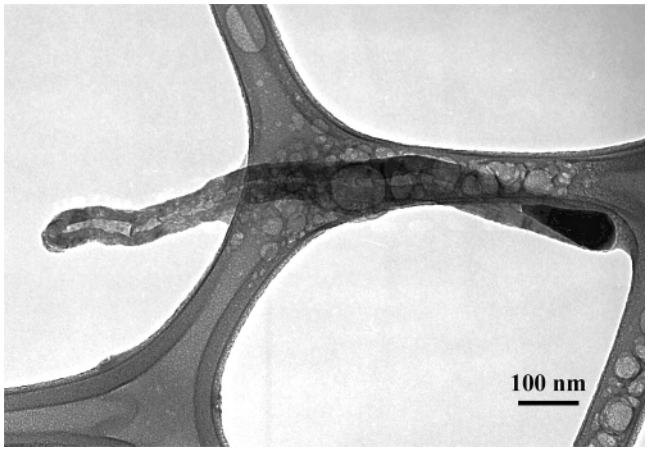

Figure 1. Transmission electron micrograph of a multiwalled carbon nanotube formed by the reaction of lithium acetylide and hexachloroethane with 5 mol% CoS added as an initiator. The weblike structure in the background is the lacey carbon grid support.

were performed using calcium carbide (CaC_2) as the starting reagent, as given in eq 2.

$$3CaC_2 + C_2Cl_6 \rightarrow 8C + 3CaCl_2 \qquad (2)$$

The reaction of calcium carbide with hexachloroethane (C_2Cl_6) yields graphite as the only crystalline material after washing with water to remove the byproduct calcium chloride salt. The heat of formation for this reaction (ΔH_{rxn}) is −1992 kJ/mol, yielding a theoretical maximum temperature (T_{max}) of 3550 °C. Attempts to determine T_{max} experimentally were inhibited by the thermocouple materials available. When C-type thermocouples (5% W/26% Re) were inserted into the reactants, they melted during the reaction. Since a 5% W/26% Re thermocouple has a melting point of 3130 °C, but a practical measurement range up to 2320 °C, clearly the reaction between calcium carbide and hexachloroethane reaches a maximum temperature well above 2320 °C and likely above 3130 °C.[23] Therefore, the formation of crystalline graphite (Figure 2) in the CaC_2/C_2Cl_6 reaction is consistent with the high reaction temperature.

Many materials were tested as initiators for the synthesis of carbon nanotubes in the reaction between CaC_2 and C_2Cl_6 (Table 2). Cobalt sulfide produced 15% carbon nanotubes, consistent with the C_2Cl_6/Li_2C_2 reaction. Iron sulfide (FeS) was found to be even more effective as an initiator (Table 3). By varying the FeS concentration from 0.5 to 20 mol%, an optimal ratio of 6 mol% FeS was determined for the production of carbon nanotubes with a yield of 25%. Figure 3 presents typical transmission and scanning electron micrographs of multiwalled carbon nanotubes produced in the reaction between CaC_2 and C_2Cl_6 when 6 mol% FeS is used as an initiator. The multiwalled carbon nanotubes have an average diameter of 50 nm and an average length of 1 μm. Most tubes are capped at one end by a metal nanopar-

(23) *The Temperature Handbook*, Z203-Z246; Omega Engineering: Stamford, CT, 1999.

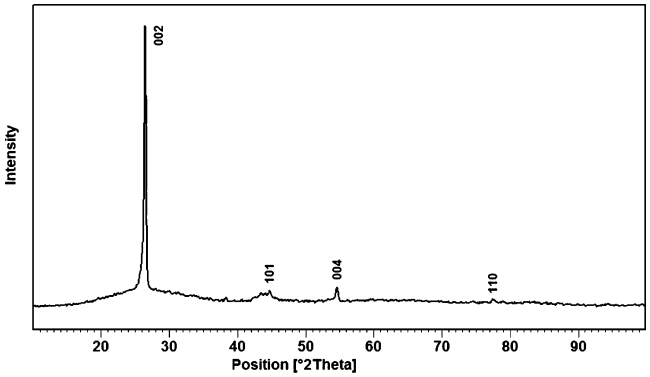

Figure 2. Powder X-ray diffraction pattern of the product from the solid-state metathesis reaction between CaC_2 and C_2Cl_6 with the addition of 6 mol% CoS used as an initiator. The Miller indices for the graphitic peaks are given.

Table 2. Initiators Used for Optimum Production of Carbon Nanotubes (CNTs) in the Reaction between CaC_2 and C_2Cl_6

initiator (mol%)[a]	CNT yield estimation
5% CoS	15%
5% FeS	23%
5% Co	low
5% Co + 5% S	low
5% CoS_2	none observed
2.5% Co + 2.5% Ni	none observed
2.5% Ni + 2.5% S	none observed

[a] Based on moles of carbon.

Table 3. Percent FeS Initiator Used to Optimize the Synthesis of Carbon Nanotubes (CNTs) in the Metathesis Reaction between CaC_2 and C_2Cl_6

initiator (mol%)[a]	CNT yield estimation
0.5%	none observed
1%	low
2%	10%
3%	15%
4%	20%
5%	23%
6%	25%
7%	22%
8%	20%
9%	15%
10%	15%
11%	10%
12%	7%
13%	low
14%	low
15%	low
20%	low

[a] Based on moles of carbon.

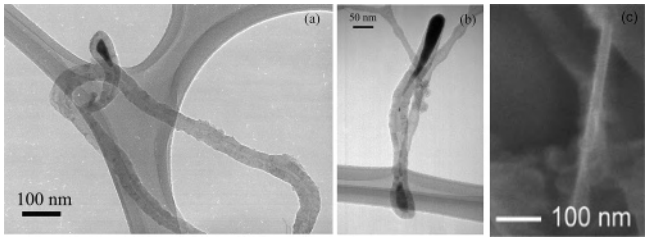

Figure 3. (a−b) Transmission and (c) scanning electron microscopy images of multiwalled carbon nanotubes formed in the solid-state metathesis reaction between CaC_2 and C_2Cl_6 with 6 mol% FeS used as an initiator. The lighter structure in the background of the TEMs is the lacey carbon grid.

ticle. These nanoparticles appear to be metallic cobalt formed from the reduction of cobalt sulfide during the metathesis reaction that then provides a surface on which the carbon nanotubes can grow. In some cases, the nanotubes are capped at both ends by metal nanoparticles (Figure 2b). The metal nanoparticles affect the diameter of the nanotubes, with larger nanoparticle caps producing larger tube diameters. Therefore, it may be possible to control tube diameter by controlling the initiator particle size distribution prior to reaction.

Conclusions

Solid-state metathesis reactions could provide an alternative, rapid route to the synthesis of carbon nanotubes. By simply reacting two solids in the presence of a metal initiator, multiwalled carbon nanotubes can be produced. The yield of carbon nanotubes is enhanced by using the metal sulfides CoS or FeS as initiators. Since sulfur has been shown to improve the catalytic ability of both cobalt and iron metal, the metal sulfide is believed to act as both initiator and promoter for production of carbon nanotubes. The metathesis reaction was further improved by substituting calcium carbide for lithium acetylide. The reaction between calcium carbide and hexachloroethane was optimized by systematically varying the initiator and the percentage used. The addition of 6 mol% FeS produces a yield of 25% carbon nanotubes, as estimated from the transmission electron micrographs. Future work will focus on increasing the reaction scale to produce larger amounts of carbon nanotubes without sacrificing yields.

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