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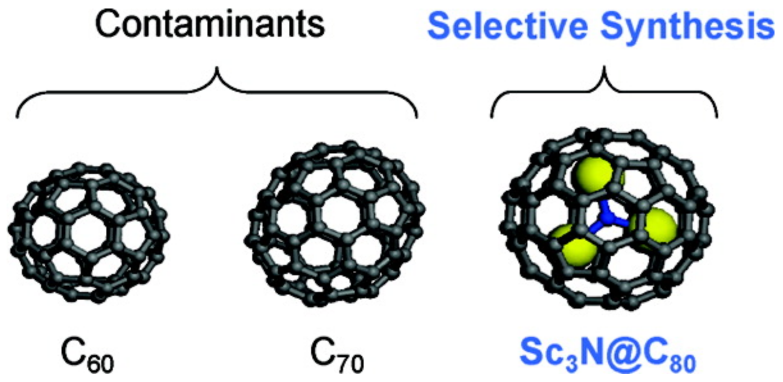

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Chemically Adjusting Plasma Temperature, Energy, and Reactivity (CAPTEAR) Method Using NO_x and Combustion for Selective Synthesis of $Sc_3N@C_{80}$ Metallic Nitride Fullerenes

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Abstract: Goals are (1) to selectively synthesize metallic nitride fullerenes (MNFs) in lieu of empty-cage fullerenes (e.g., C_{60}, C_{70}) without compromising MNF yield and (2) to test our hypothesis that MNFs possess a different set of optimal formation parameters than empty-cage fullerenes. In this work, we introduce a novel approach for the selective synthesis of metallic nitride fullerenes. This new method is "Chemically Adjusting Plasma Temperature, Energy, and Reactivity" (CAPTEAR). The CAPTEAR approach with copper nitrate hydrate uses NO_x vapor from NO_x generating solid reagents, air, and combustion to "tune" the temperature, energy, and reactivity of the plasma environment. The extent of temperature, energy, and reactive environment is stoichiometrically varied until optimal conditions for selective MNF synthesis are achieved. Analysis of soot extracts indicate that percentages of C_{60} and $Sc_3N@C_{80}$ are inversely related, whereas the percentages of C_{70} and higher empty-cage C_{2n} fullerenes are largely unaffected. Hence, there may be a "competitive link" in the formation and mechanism of C_{60} and $Sc_3N@C_{80}$. Using this CAPTEAR method, purified MNFs (96% $Sc_3N@C_{80}$, 12 mg) have been obtained in soot extracts without a significant penalty in milligram yield when compared to control soot extracts (4% $Sc_3N@C_{80}$, 13 mg of $Sc_3N@C_{80}$). The CAPTEAR process with $Cu(NO_3)_2 \cdot 2.5H_2O$ uses an exothermic nitrate moiety to suppress empty-cage fullerene formation, whereas Cu functions as a catalyst additive to offset the reactive plasma environment and boost the $Sc_3N@C_{80}$ MNF production.

Introduction

Discovered in 1999,[1] Metallic Nitride Fullerenes (MNFs) are molecules which, arguably, are more exciting than their empty-cage fullerene cousins (e.g., C_{60}, C_{70}) in that MNFs[1−6] have an entrapped trimetallic nitride cluster (Figure 1). The judicious selection of transition or rare-earth metal imparts a unique set of chemical and physical properties for MNFs. Examples include the use of $Gd_3N@C_{80}$ for MRI agents,[7,8] $Lu_3N@C_{80}$ for X-ray contrast agents,[9] $Ho_3N@C_{80}$ for radiotherapeutics, $Er_3N@C_{80}$ for optical properties,[10] and $Sc_3N@C_{80}$ for electronic[11] applications and as a "practice" molecule for chemical functionalization of MNF carbon cages.[7,8,12−19]

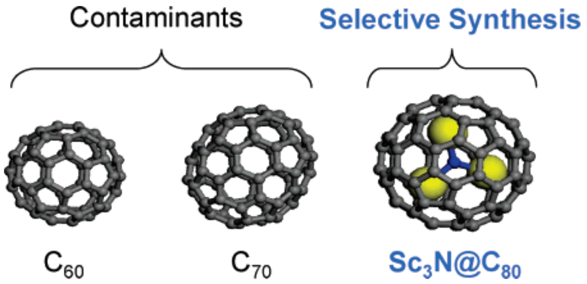

Figure 1. Structures of empty-cage and metallic nitride fullerenes produced in electric-arc soot.

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Application development for MNFs by academia and industry has been hampered by poor sample availability. However, recent advances in nonchromatographic purification methods[20,21] and further advances in achieving isomerically purified[22,23] samples have led to a flurry of research activity in MNF fundamental research and application development. Historically, typical soot extracts[1,20,21] contain <10% MNFs with >90% of extract samples being contaminant empty-cage fullerenes (Figure 1).

There is literature precedence for using chemical additives in packed graphite rods for electric-arc generation of fullerene extracts. Additives to plasma can be introduced as solids (e.g., calcium cyanamide,[24] CoO,[3,25,26] Cu[27]) or gases (e.g., NH_3).[28−30] The ammonia method uses a reactive atmosphere[28−30] that suppresses empty-cage fullerene formation and provides MNF soot extracts with a high percent purity, but with a corresponding reduction in milligram MNF yield.

In this work, we introduce a new approach (CAPTEAR) that permits soot extracts of high MNF percent purity and without the typical, corresponding penalty in milligram yield. The CAPTEAR concept is based on the hypothesis that different types of carbonaceous nanomaterials (e.g., nanotubes, empty-cage fullerenes, metallic nitride fullerenes) have preferred temperatures of formation and stability in a given chemically reactive plasma (Figure 2). With CAPTEAR, we can “shift” or “tune” the type of fullerene produced by changing and optimizing the temperature, energy, and reactivity of the plasma environment.

Experimental Section

The cylindrical electric-arc reactor had dimensions of 25 cm diameter and a length of 43 cm. In preparation for vaporization, 1 in. (2.5 cm) diameter graphite rods (6 in. length) were core-drilled to 4 in. (10 cm) to leave an outer shell of 30 g of C as previously described.[27] These cored rods were then packed with Cu (Cerac), $Cu(NO_3)_2{\cdot}2.5H_2O$, or NH_4NO_3 (Aldrich) and various amounts of Sc_2O_3 powder (325 mesh, Stanford Materials, CA). For control experiments without these additives, 30 g of Sc_2O_3 were packed into cored, graphite rods. The reactor was vacuum pumped with subsequent backfilling of He gas to a reactor pressure of 300 Torr. An air flow of 6 Torr/min was introduced into the reactor, and experiments were conducted under a dynamic flow. Other reactor parameters were 220 A and a gap voltage of 38 V. Note that rods packed with $Cu(NO_3)_2{\cdot}2.5H_2O$ were NOT cured in a furnace prior to use to avoid premature thermal decomposition.

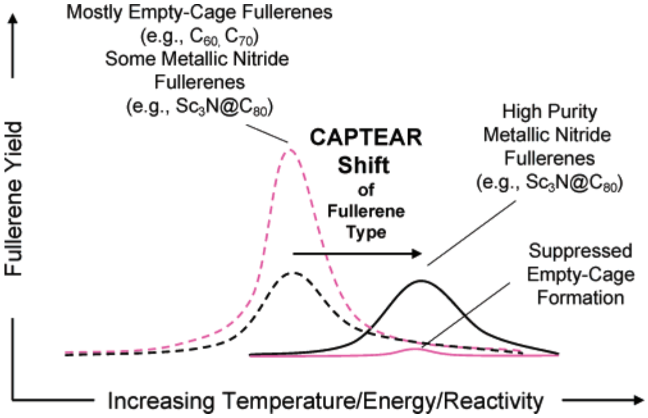

Figure 2. Concept of using the CAPTEAR method to adjust and optimize the temperature, energy, and reactivity of the plasma environment to “tune” the type of fullerene produced.

Resulting soot was extracted with *o*-xylene, and the solvent was removed under reduced pressure to furnish a dried extract, which was washed with solvent (e.g., diethyl ether, acetone). Soot extracts were weighed and characterized by HPLC to determine the type and amount of fullerene material present. HPLC peak areas were obtained using standard chromatographic integration software (Vernier, Logger Pro), which did not account for variations of extinction coefficients. Nevertheless, calculated amounts of fullerenes (e.g., $Sc_3N@C_{80}$) obtained from peak integrations were comparable to isolated amounts. The reactor and analysis methods had an error of ~10%. HPLC separations used a PYE column (Phenomenex, 4.6 mm × 250 mm) with a 50 μL injection, 1.0 mL/min toluene mobile phase, and 360 nm UV detection.

Results and Discussion

By adjusting the amounts and reagents supplied to the reactor, the temperature, energy, and reactivity of the plasma can be “tuned” toward the selective synthesis of one type of fullerene (i.e., $Sc_3N@C_{80}$) versus empty-cage fullerenes (e.g., C_{60}, C_{70}). The goal then is finding the optimal convergence of temperature, energy, and reactivity for selective synthesis. We have selected the thermal decomposition of $Cu(NO_3)_2{\cdot}2.5H_2O$, whose reactive byproducts have been previously investigated.[31,32] Significant heat release, chemical reaction, and subsequent decomposition products have been reported[31,32] and are shown in Scheme 1. In our experimental design, we adjust the temperature, energy, and amount of reactive, oxidizing NO_x vapor by stoichiometrically varying the amount of copper nitrate hydrate packed in the Sc_2O_3 filled graphite rod.

The mechanism, formation, and combustion reactions of NO_x have also been reported.[33−36] A review of kinetics, mechanisms, and roles of NO and N_2O from N_2 and O_2 combustion is available.[35] The thermal mechanism of NO formation has been

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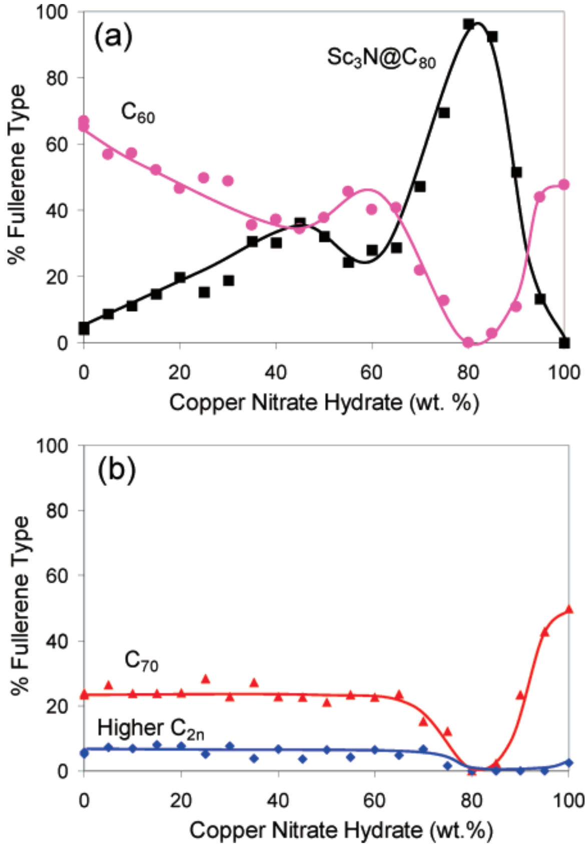

Figure 3. Comparison of percent fullerene versus weight percent of added $Cu(NO_3)_2$•$2.5H_20$ for (a) C_{60}, $Sc_3N@C_{80}$ and (b) C_{70}, higher fullerenes, C_{2n} (e.g., C_{76}, C_{78}, C_{82}, C_{84}).

Scheme 1. Reactions and Decomposition Products of Volatile[31] and Nonvolatile[32] Species of Copper Nitrate Hydrate

(Volatile) ***CAPTEAR Goal 1*****: Exothermic and Reactive NO_x Vapor to Suppress Empty-Cage Fullerenes**

$$Cu(NO_3)_2{\cdot}xH_2O \longrightarrow Cu(OH){\cdot}NO_3 + HNO_3 + H_2O \quad (1)$$

$$HNO_3 \longrightarrow H_2O + 2NO_2 \quad (2)$$

$$NO_2 \xrightarrow{CuO} NO + O_2 \quad (3)$$

(Non-Volatile) ***CAPTEAR Goal 2*****: Generation of Copper to Boost Metallic Nitride Fullerene Yield**

$$Cu(NO_3)_2{\cdot}xH_2O \longrightarrow CuNO_3 \longrightarrow Cu(NO_3)_2 \longrightarrow CuO \longrightarrow Cu \quad (4)$$

Scheme 2. NO_x Formation[33,35,36] in Combustion Process

$$N_2 + O \longleftrightarrow NO + N \quad (5)$$

$$N + O_2 \longleftrightarrow NO + O \quad (6)$$

$$N_2 + O + M \longleftrightarrow N_2O + M \quad (7)$$

$$N_2O + O \longleftrightarrow NO + NO \quad (8)$$

$$N_2O + O \longleftrightarrow N_2 + O_2 \quad (9)$$

described as a sequence of reactions (5)−(9) and are shown in Scheme 2.[35,36]

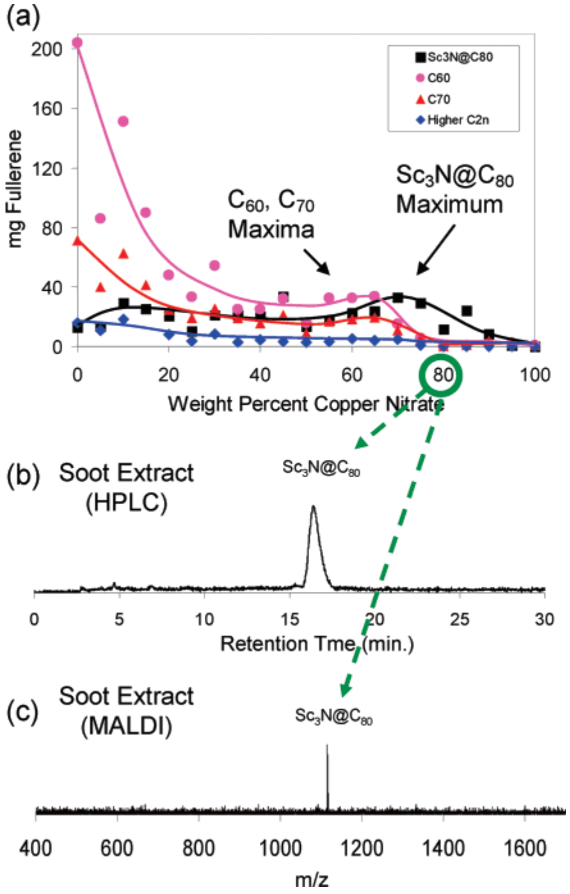

Figure 4. Results from CAPTEAR experiments: (a) milligrams of fullerene type produced versus weight percent of added $Cu(NO_3)_2$•$2.5H_2O$, (b) HPLC chromatogram, and (c) MALDI mass spectrum of fullerene soot extract corresponding to 80% copper nitrate hydrate/20% Sc_2O_3.

To investigate CAPTEAR variables (i.e., plasma temperature, energy, reactivity), experiments were performed using an array of cored, graphite rods with increasing packing material content of $Cu(NO_3)_2$•$2.5H_2O$ relative to Sc_2O_3. These rods were vaporized under comparable conditions, the soot was collected, and their extracts were analyzed for fullerene type, percent abundance (Figure 3), and milligram yield (Figure 4). Results were compared to control experiments having only Sc_2O_3 packed (i.e., no $Cu(NO_3)_2$•$2.5H_2O$) in the cored graphite rods. The data shown in Figure 3 indicate an inverse relationship between the empty-cage C_{60} and $Sc_3N@C_{80}$ metallic nitride fullerene (MNF). In contrast, the percentages of C_{70} and higher cage fullerenes, C_{2n}, appear to be largely unaffected for extracts prepared from rods packed with 0 to 70 wt % added copper nitrate hydrate. When conditions are optimized for MNF formation (i.e., 80% copper nitrate hydrate), the percentages of C_{70}, higher C_{2n}, and C_{60} are at their peak minima (∼0%). Beyond 80% copper nitrate hydrate, MNF purity declines steadily to zero. Empty-cage fullerene production, however, increases to comparable amounts of C_{60} and C_{70} (i.e., $C_{60}/C_{70} = 1{:}1$) relative to control experiments where $C_{60}/C_{70} = 3{:}1$. With CAPTEAR, MNF purity increases from 4% in the control to 96% $Sc_3N@C_{80}$ at 80% copper nitrate hydrate. The remaining 4% of this soot extract is predominantly $Sc_3N@C_{78}$, with only traces of empty-cage fullerenes observable. Also at 80% copper nitrate hydrate additive, the amount and percent of C_{60} produced in the soot extract decreased from 67% C_{60} (control) to ∼0%.

Note that when a rod packed with 80% copper nitrate hydrate was vaporized, the plasma became noticeably larger. The pressure in the reactor rose steeply due to the reactive gases formed from CAPTEAR decomposition and combustion reactions. Reactor flanges and electrode assemblies were significantly hotter relative to control experiments. The amount of heat generated was proportional to the amount of copper nitrate

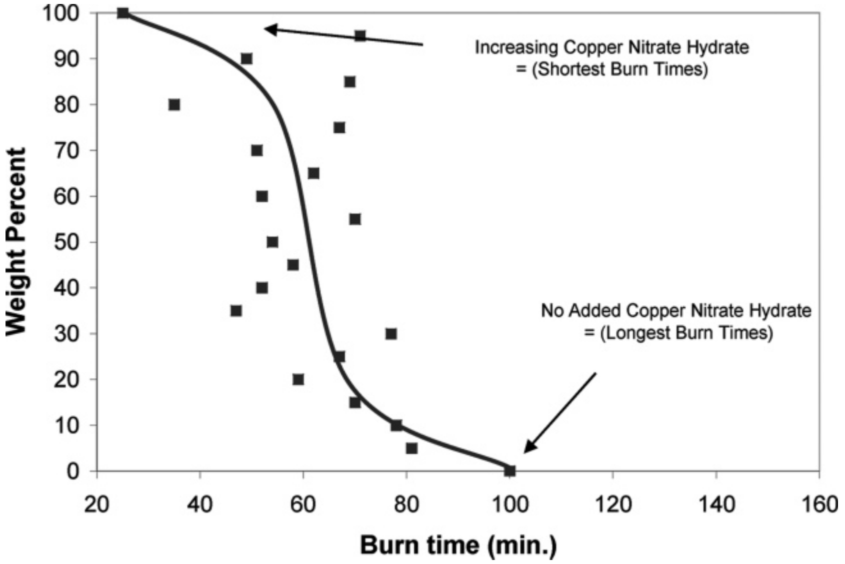

Figure 5. Correlation of weight percent added $Cu(NO_3)_2$•$2.5H_20$ versus burn time.

hydrate added to the rod. Hence, we were able to "adjust" the temperature in the reactor by controlling the amount of copper nitrate hydrate (Scheme 1) added to the packing material. We are attributing this CAPTEAR shift to extra temperature, energy, and reactivity from the copper nitrate hydrate to the plasma, which, as a result of the additive, is more optimal for selective MNF synthesis (Figure 2). Too much copper nitrate, however, results in a plasma unoptimized for MNFs, and the yield of $Sc_3N@C_{80}$ drops precipitously.

The hypothesis of different optimal reaction conditions for empty-cage fullerenes versus MNFs is also supported in Figure 4a. For the first time, we have experimentally shown a separate, discrete peak maximum for MNF production relative to empty-cage fullerenes. This optimal convergence at 80% copper nitrate hydrate (20% Sc_2O_3) has resulted in an extracted soot sample consisting of 12 mg of $Sc_3N@C_{80}$ at 96% purity. The corresponding HPLC trace and MALDI mass spectrum are shown in Figure 4b and c, respectively.

In a control experiment using no added copper nitrate(Figure 4a), the percent purity of MNF in the extract is only 4% $Sc_3N@C_{80}$, corresponding to 13 mg of $Sc_3N@C_{80}$ in the extract (305 mg). With only 10% added copper nitrate hydrate, the percentage of $Sc_3N@C_{80}$ MNF tripled (12%), and the milligram yield increased from 13 mg to 30 mg of $Sc_3N@C_{80}$. This factor of 2.5 increase in MNF milligram yield is attributed to the Cu metal from the $Cu(NO_3)_2$•$2.5H_2O$ (Scheme 1). A similar boost in MNF milligram yield by a factor of 2.5 from Cu metal additive has recently been reported.[27] With CAPTEAR, however, the MNF purity increases dramatically from 4% to 96%. This remarkable boost in MNF yield is attributed to the effect of the nitrate hydrate moiety of the $Cu(NO_3)_2$•$2.5H_2O$ and its subsequent decomposition and combustion products (Schemes 1 and 2).

Also of interest is the correlation of burn time to the amount of copper nitrate hydrate. Figure 5 shows that increasing amounts of copper nitrate hydrate correspond to faster "burn times," as defined by the time needed to vaporize the graphite rods packed with Sc_2O_3/copper nitrate hydrate. The more rapid burn times are associated with higher loadings of copper nitrate hydrate and are consistent with rod vaporization under more oxidizing and reactive environments. Note that control rods with only Sc_2O_3 packing material needed 100 min to vaporize compared to only 35−50 min for packed rods with high nitrate content.

When the percent purity (Figure 6a) and milligram yield (Figure 6b) are plotted versus burn time, another startling discovery is made. The data suggest different optimal burn times for various fullerene types. For extracts with higher MNF purity, decreased burn times are optimal. Note the MNF purity drops exponentially from 96% $Sc_3N@C_{80}$ (35 min) to only 4% $Sc_3N@C_{80}$ (100 min) at longer burn times. In contrast to the decay curve for $Sc_3N@C_{80}$, the percentage of empty-cage fullerenes (e.g., C_{60}, C_{70}, higher C_{2n}) exponentially increases to a plateau with increasing burn time. Figure 6b shows the corresponding milligram yields of soot extracts relative to burn time. In contrast, the peak maximum for making the highest milligram yield of $Sc_3N@C_{80}$ is not at 35 min (12 mg) of burn time. Rather, the peak maximum occurs at 50−60 min (33 mg of $Sc_3N@C_{80}$) followed by a steady decline in MNF yield beyond 60 min. During the 60−100 min time frame, in which $Sc_3N@C_{80}$ MNF yield is declining, empty-cage fullerene production increases dramatically. This 60−100 min time frame also corresponds to decreasing copper nitrate hydrate, which is otherwise clearly deleterious for empty-cage fullerene production. In general, increasing copper nitrate hydrate results in (1) shorter burn times, (2) higher MNF percent purity, and (3) suppression of empty-cage fullerenes.

Data for specific regions are summarized in Table 1. CAPTEAR maximum enhancements in percent purity for soot extracts are 4% $Sc_3N@C_{80}$ (control) to 96% $Sc_3N@C_{80}$ (80 wt % copper nitrate hydrate). CAPTEAR maximum enhancements in milligram yield for soot extracts are 13 mg of $Sc_3N@C_{80}$ (control) to 33 mg of $Sc_3N@C_{80}$ (70 wt % copper nitrate hydrate). Although a higher yield of $Sc_3N@C_{80}$ (33 mg) was obtained using 70 wt % additive, the corresponding purity was only 47% $Sc_3N@C_{80}$, but still a factor of 10 improvement in purity relative to the control (4% $Sc_3N@C_{80}$).

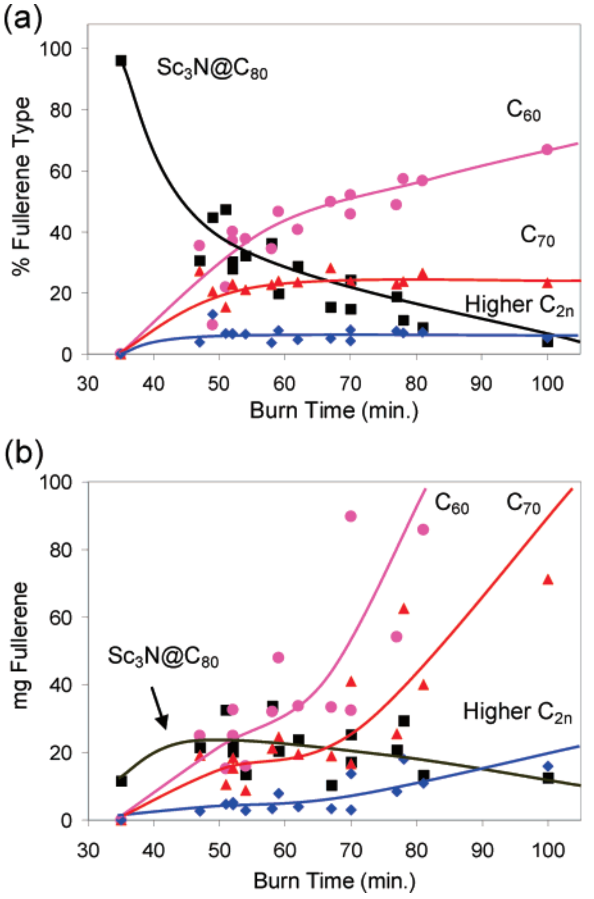

Figure 6. Comparison of (a) percent type and (b) amount of fullerene produced versus burn time.

Table 1. Summary of Fullerene Yield Data from Soot Extracts Obtained from Vaporizing Rods Packed with Various Amounts of $Cu(NO_3)_2{\cdot}2.5H_20$

	0% added (control)	70% copper nitrate hydrate	80% copper nitrate hydrate	90% copper nitrate hydrate
% $Sc_3N@C_{80}$	4	47	96	52
mg $Sc_3N@C_{80}$	13	33	12	8
mg C_{60}	204	15	∼0	2
mg C_{70}	70	11	∼0	4
mg higher fullerenes, C_{2n}	16	5	∼0	<1
mg $Sc_3N@C_{78}$	2	5	<1	<1
mg extract	305	69	13	16

To investigate our hypothesis that the nitrate moiety permits higher MNF purity while the Cu moiety of the copper nitrate hydrate boosts MNF yield, we performed a set of experiments using three types of additives, each containing copper and/or a nitrate. Figure 7 compares soot extracts from rods packed with Cu metal, $Cu(NO_3)_2{\cdot}2.5H_2O$, and NH_4NO_3. The data indicate that all rods packed with nitrates permitted high MNF purities for $Sc_3N@C_{80}$. A purity of 96% $Sc_3N@C_{80}$ was achieved from rods packed with 80 wt % $Cu(NO_3)_2{\cdot}2.5H_2O$. A similar purity of 98% $Sc_3N@C_{80}$ was obtained from rods packed with 80 wt % NH_4NO_3, but only 1 mg of $Sc_3N@C_{80}$ was obtained. In contrast, all rods packed with a copper source had significantly higher $Sc_3N@C_{80}$ MNF yields (mg). In summary, 16 mg of $Sc_3N@C_{80}$ (only 6% purity) were produced in soot extracts from packed rods with 80% Cu, and 12 mg of $Sc_3N@C_{80}$ (96% purity) were obtained from rods packed with 80 wt % $Cu(NO_3)_2{\cdot}2.5H_2O$.

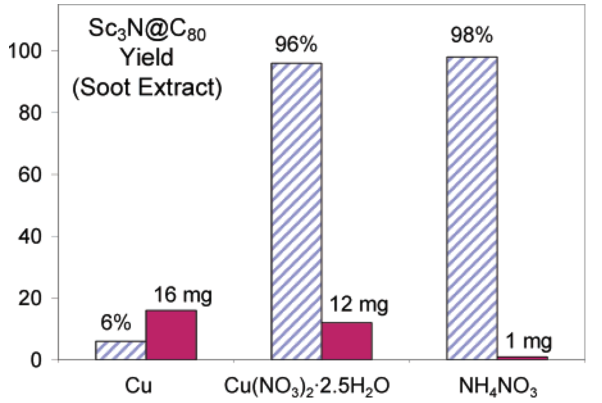

Figure 7. Comparison of $Sc_3N@C_{80}$ purity (%) and $Sc_3N@C_{80}$ yield (mg) from three soot extracts prepared from vaporizing packed rods containing 80 wt % of each of the following additives: Cu, $Cu(NO_3)_2{\cdot}2.5\ H_2O$, and NH_4NO_3.

Based on these results, we conclude that two types of plasma additives promote the selective synthesis of $Sc_3N@C_{80}$ while simultaneously maintaining comparable milligram yields of MNFs. The high $Sc_3N@C_{80}$ MNF purity arises from a reactive moiety (e.g., NO_x from the copper nitrate), whereas the copper boosts the milligram yields of MNFs. In this experimental design, note that both the reactive moiety and catalyst additive are contained within a single compound (copper nitrate hydrate). Alternatively, another experimental design for MNF synthesis could, in principle, introduce the plasma additives separately. For example, a rod containing Cu metal additive (i.e., no nitrate) could be vaporized in an atmosphere of NH_3 (e.g., a different type of reactive gas).

Conclusions

We have investigated our hypothesis of different optimal plasma conditions for empty-cage fullerenes versus MNFs. Intuitively, optimal reactor conditions for C_{60} and other empty-cage fullerenes should be different compared to MNF formation, which requires encapsulation of a trimetallic nitride cluster. To pursue the selective MNF synthesis idea, our experimental design sought to chemically modify the plasma environment until optimal MNF formation parameters (i.e., temperature, energy, and reactivity) were obtained. We stoichiometrically varied amounts of solid-phase reagent (i.e., copper nitrate hydrate) to "tune" exothermicity and combustion in the plasma reactor, thereby adjusting the corresponding temperature, energy, and reactivity. Results indicate the percent composition of C_{60} and $Sc_3N@C_{80}$ in CAPTEAR soot extracts were inversely related, whereas the percentages of C_{70} and other empty-cage C_{2n} fullerenes were relatively unaffected from 0 to 70% copper nitrate hydrate additive. This finding suggests a "competitive nature" for C_{60} and $Sc_3N@C_{80}$. With the CAPTEAR method, purified $Sc_3N@C_{80}$ MNFs (96% purity, 12 mg) have been achieved in soot extracts, while maintaining a comparable yield (mg) relative to control soot extracts (4% $Sc_3N@C_{80}$, 13 mg of $Sc_3N@C_{80}$). We believe the CAPTEAR process with copper nitrate hydrate uses a twofold approach. First, the exothermic nitrate moiety and decomposition vapors (i.e., experiments using

NH_4NO_3 and $Cu(NO_3)_2{\cdot}2.5H_2O$) suppress empty-cage fullerene formation to obtain soot extracts with high MNF purity. Second, the Cu moiety functions as a catalyst additive for MNFs, offsets reactive plasma conditions, and boosts $Sc_3N@C_{80}$ MNF production.

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