Effect of copper metal on the yield of $Sc_3N@C_{80}$ metallofullerenes

Steven Stevenson,* Mary A. Mackey, M. Corey Thompson, H. Louie Coumbe, Praveen K. Madasu, Curtis E. Coumbe and J. Paige Phillips

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The yield of $Sc_3N@C_{80}$ metallofullerene and fullerene extract is dramatically increased *via* filling cored graphite rods with copper and Sc_2O_3 only; when compared to 100% Sc_2O_3 packed rods, improvements of factors of ~3 and ~5 have been achieved for $Sc_3N@C_{80}$ and fullerene extract produced, respectively, with the weight percent of Cu added to the rod affecting the type and amount of fullerene produced.

Since the recent discovery of metallic nitride fullerenes[1] (MNFs), an array of scientific disciplines have been eager to investigate their fundamental properties and application development, especially in the medical area.[2,3] However, fullerene experiments have been hampered by poor sample availability[4] due to low MNF yields in electric arc-produced soot and/or the difficulty of separating MNFs from other types of fullerenes (*e.g.*, empty cage, classical metallofullerenes, and other MNFs of various cage sizes and structural isomers).

Recent advances in MNF reactor research and development include the addition of reactive gases[5,6] (*e.g.*, NH_3) to suppress the electric arc yield and the formation of empty cage fullerenes. Although successful in terms of improved percent MNF purity, the overall mg yield of fullerenes decreases significantly.

Our motivation is to maximize the overall mg yield of MNFs per rod burned (*i.e.*, seek MNF quantity *in lieu* of percentage MNF in the extract). A consequence of maximizing the MNF mg yield is typically a concomitant increase in empty cage fullerene production at the expense of the percentage of MNF in the extract. However, with recent advances in non-chromatographic MNF purification techniques,[7–9] this consequence of more empty cage fullerenes is acceptable.

Our hypothesis is to use solid additives that can affect the yield, type and amount of fullerene produced. Prior attempts to use additives to improve MNF yield included CoO,[10] but with only marginal success. A mixture of Cu, Ni and Y was previously[11] added to an electric arc plasma to simultaneously synthesize nanotubes, empty cage fullerenes and metallofullerenes. Not desiring to make nanotubes for this study, we removed Y and Ni catalyst additives, and focused on maximizing MNF yield for $Sc_3N@C_{80}$. The Sc_2O_3 starting material is expensive, and the discovery of an inexpensive additive, such as Cu, that would permit less Sc_2O_3 in a packed rod and also improve the MNF yield is attractive. A schematic overview of this Cu additive approach is shown in Fig. 1.

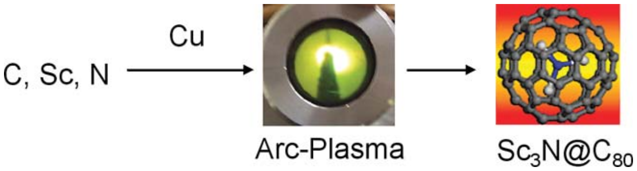

Fig. 1 Schematic overview of synthesizing $Sc_3N@C_{80}$ MNFs in an electric arc reactor.

In a typical electric arc[12,13] metallofullerene[14] synthesis, graphite rods are core-drilled and packed with a mixture of graphite and either a metal or a metal oxide for the desired metal encapsulant.† For MNF production, the selection of buffer gas is typically helium with minor quantities of N_2[1] or NH_3.[5,6] In a significant variation from traditional electric arc metallofullerene syntheses, which use much lower ratios of Sc : C (*i.e.*, 1 : 10), we use no packed graphite (*i.e.*, only Cu and Sc_2O_3) in the cored rods. Although it is common knowledge that air decreases fullerene production, another intentional deviation from typical metallofullerene synthesis was the use of air (6 torr min^{-1}), which was used as both the nitrogen source for MNF production and a "reactive gas". The primary source of C available for fullerene production is the shell of the cored graphite rod. Using this experimental design, a series of Cu/Sc_2O_3 rods were packed with arbitrary weight percentages of Cu relative to Sc_2O_3. These rods were vaporized in an electric arc reactor (Fig. 2), and the corresponding soot extracts were evaluated for fullerene type and yield in mgs.

The data for these experiments are shown in Fig. 3 and Fig. 4. As a control, with no Cu added, a cored graphite rod packed only with Sc_2O_3 produced an extract containing relative percentages of 47% C_{60}, 26% C_{70} and 15% $Sc_3N@C_{80}$, with the remainder being higher mass fullerenes (*e.g.*, C_{76}, C_{78} and C_{84}) and metallofullerenes (*e.g.*, $Sc_3N@C_{68}$ and $Sc_3N@C_{78}$). The corresponding mass of the overall fullerene extract (Fig. 4) was 130 mg, of which 19 mg of

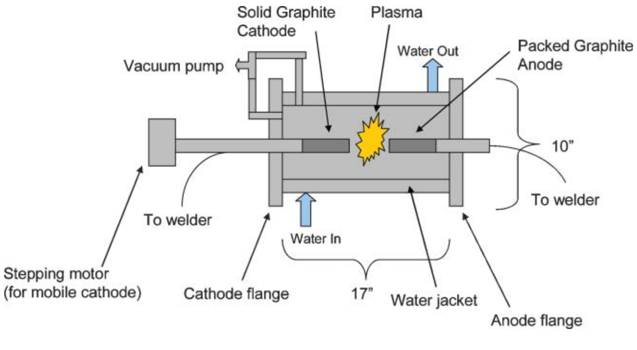

Fig. 2 Electric arc fullerene reactor and dimensions.

Department of Chemistry and Biochemistry, University of Southern Mississippi, 118 College Drive, #5043, Hattiesburg, MS, 39402, USA. E-mail: steven.stevenson@usm.edu; Fax: +1 601-266-6075; Tel: +1 601-266-5142

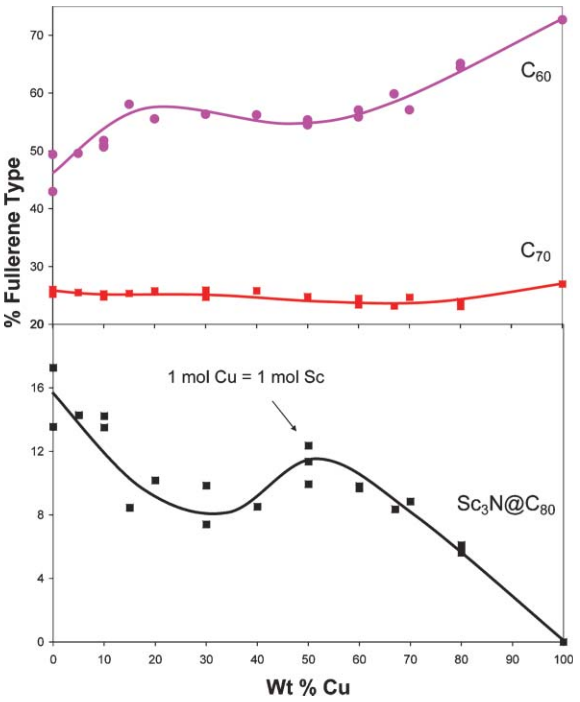

Fig. 3 Effect of Cu additive on fullerene type (%).

$Sc_3N@C_{80}$ (I_h and D_{5h} mixture) was available for subsequent purification.

Another striking feature in Fig. 3 is the rise in percent MNF yield at a peak maximum of *ca.* 50 weight percent Cu added. There is an overall decline in MNF percentage in the extract with increasing Cu added to the packed rod. This feature is to be expected, as there is a decreasing amount of Sc_2O_3 in the rod. There is also a comparable negative slope from 0–30% Cu and 60–100% Cu, which corresponds to a MNF loss of *ca.* 1% per each 3.5 weight percent Cu added. Although the reason for the rise in MNF percent yield at 50% Cu is unknown, the peak maximum corresponds to approximately equimolar amounts of Cu and Sc. Further inspection at 50% Cu reveals that the percent $Sc_3N@C_{80}$ peak maximum corresponds to a minima in the percent C_{60} produced. In contrast, the percent C_{70} in the extract is not as adversely affected as C_{60} in the 0–50% range. This inverse relationship between C_{60} and $Sc_3N@C_{80}$ may suggest that the electric arc synthesis of these two types of fullerene is linked.

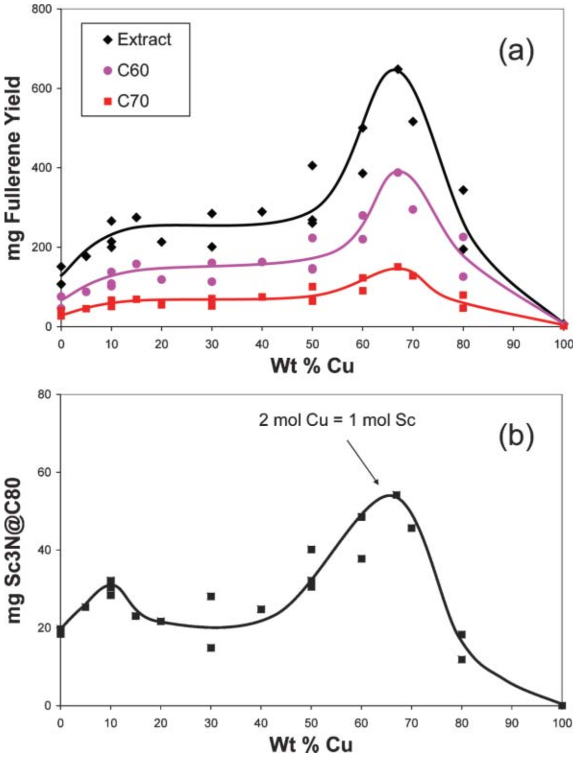

Fig. 4 Effect of Cu additive on the mg quantity produced of (a) extract, empty cage fullerenes, and (b) $Sc_3N@C_{80}$.

Another surprising finding (Fig. 3) is that although there is a maximum peak in the percentage MNF at 50% Cu, there is no corresponding maximum at 50% Cu in terms of the mg yield of fullerene produced (Fig. 4). Unexpectedly, there are two peak maxima—at 10 and 67% Cu added—but no mg maximum at 50% Cu. At only 10% Cu, the extract yield doubles and the mg MNF increases from 19 to 31 mg. At 67% Cu, the extract yield increases from *ca.* 130 to 650 mg—a ∼500% increase. The corresponding MNF yield enhancement is from 19 to 55 mg per rod—a ∼300% increase. It should also be noted that this fullerene peak maximum at 67% Cu corresponds to a molar ratio of 2 : 1 Cu/Sc.

In summary, the peak maximum for the percent MNF yield occurred at ∼50% Cu, which corresponds to 1 mol Cu = 1 mol Sc. The peak maximum for MNF yield (mg) and fullerene extract yield (mg) occurred at ∼67% Cu (*i.e.*, 2 mol Cu = 1 mol Sc). Further studies are under way to address the question of why the Cu metal additive affects the yield so dramatically. Also of interest is the effect of other transition metals (*e.g.*, Fe, Ni and Co) on $Sc_3N@C_{80}$ production, as well as the effect of Cu additive on synthesizing yttrium and rare earth metallic nitride fullerene extracts. Other interesting experiments would be the effect of Cu additive on MNF and fullerene yield for reactors using other nitrogen sources (*e.g.*, N_2[1] and NH_3)[5,6] or other geometrical designs. Although the MNFs were not explored, copper has been shown to boost the carbon nanotube yield by 5 times over traditionally-used Fe and Co nanotube catalysts.[15] Curiously, our factor of ∼5 improvement in fullerene yield (mg) is comparable.

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Notes and references

† *Experimental details*: The electric arc reactor used in this study was cylindrical (*ca.* 43 cm long, 25 cm diameter). Graphite rods of 25 mm diameter and 150 mm length were core drilled to a depth of 90 mm (= 30 g of shell carbon) and packed with various weight percentages of Cu metal relative to Sc_2O_3. Packed rods were cured in a furnace at 1050 °C under a helium flow for 8 h prior to use and placed inside the reactor. Upon evacuation of the reactor with a vacuum pump, helium was introduced until a 300 torr pressure was achieved. Air was introduced into the chamber at 6 torr min^{-1}. The electrical parameters were 220 A and 38 V. The collected soot was extracted with *ortho*-xylene. The dried extract was washed with solvent (*e.g.*, diethyl ether or acetone). HPLC analysis was used to characterize the fullerene extracts. Peak areas were obtained using standard HPLC integration software, which did not account for variations in extinction coefficients. Calculated amounts (*e.g.*, of $Sc_3N@C_{80}$) obtained from this methodology were comparable to isolated weighed amounts. Chromatographic conditions were as follows: PYE column (Phenomenex,

4.6 mm × 250 mm), 1.0 mL min^{-1} toluene mobile phase, 360 nm UV detection and 50 μL injection.

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