Synthesis and Functionalization of Endohedral Metallofullerenes

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Introduction

Fullerenes are a novel allotrope of carbon that consist of empty, spherical carbon cages of varying size, Figure 1. Metallic nitride fullerenes (MNFs), $M_3N@C_{2n}$, are an especially stable family of endohedral metallofullerenes (EMFs), fullerenes with encapsulated metal compounds, that have been shown to have unique electronic and chemical properties relative to empty fullerenes and other EMFs[1].

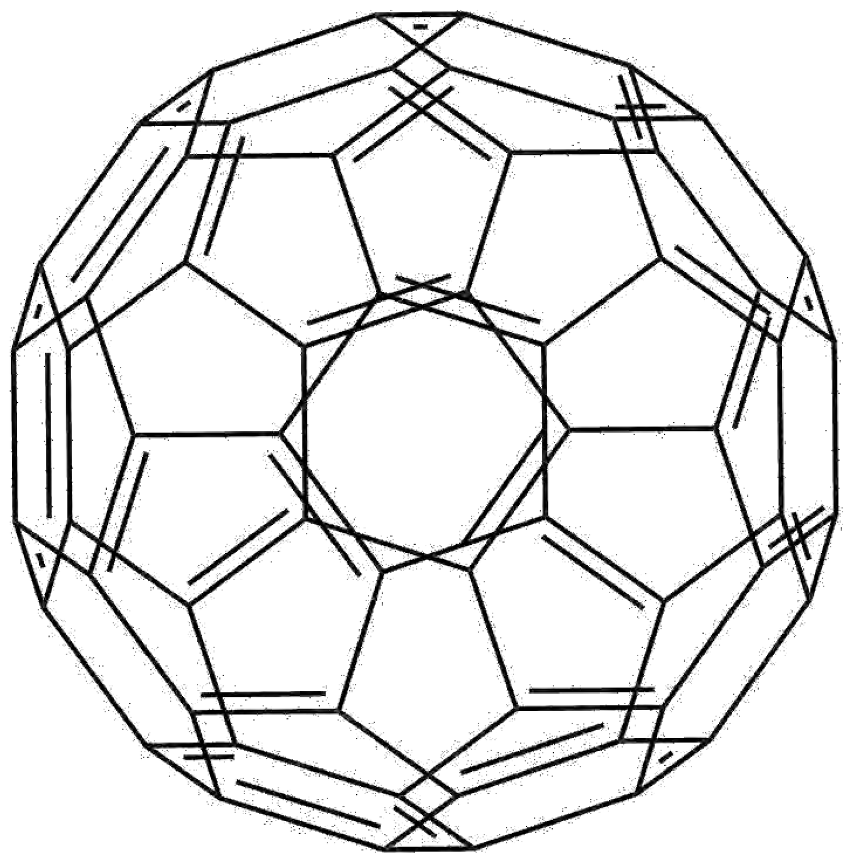

Figure 1: Structure of C_{60}, the most prevalently synthesized and studied empty fullerene.

Functionalizing, or "decorating", the exohedral surfaces of MNFs has been shown to enhance the physical properties of the compounds, especially in regard to their medicinal[2] and electronic[3] application. However, successful functionalization is relatively limited due to the variance in electronic properties exhibited by different encapsulated metal species and different carbon cage sizes. Furthermore, MNF species are relatively expensive and must be synthesized in lab. As such, the goals of this research were to:

1. Synthesize MNFs in workable quantities through the arc vapor deposition of packed graphite rods. MNF species with M=Sc,Gd were respectively selected due to their relative ease of synthesis and ability to function as a better MRI contrasting agent relative to those currently employed[2].
2. Create novel functionalized MNF species through chemical reaction of synthesized EMFs with various reagents.

Methods

Metal oxide M_2O_3 (M=Sc,Gd) powders were mixed with graphite dust in a 1:10 (m/m) ratio and were homogenized and subsequently packed into respective cored ¼" graphite rods, Figure 2.

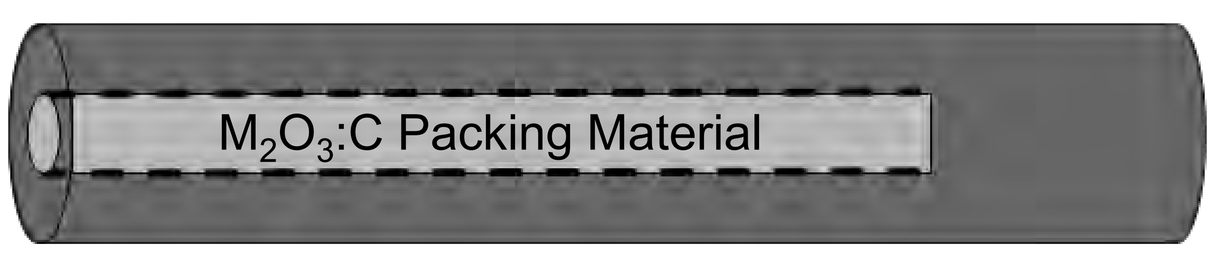

Figure 2: Diagram of a packed graphite rod. Figure not to scale.

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Methods (cont.)

Packing material was sealed using colloidal graphite and rods were then heat treated in a He atmosphere at 1000 °C for 8 hours in a tube furnace, Figure 3.

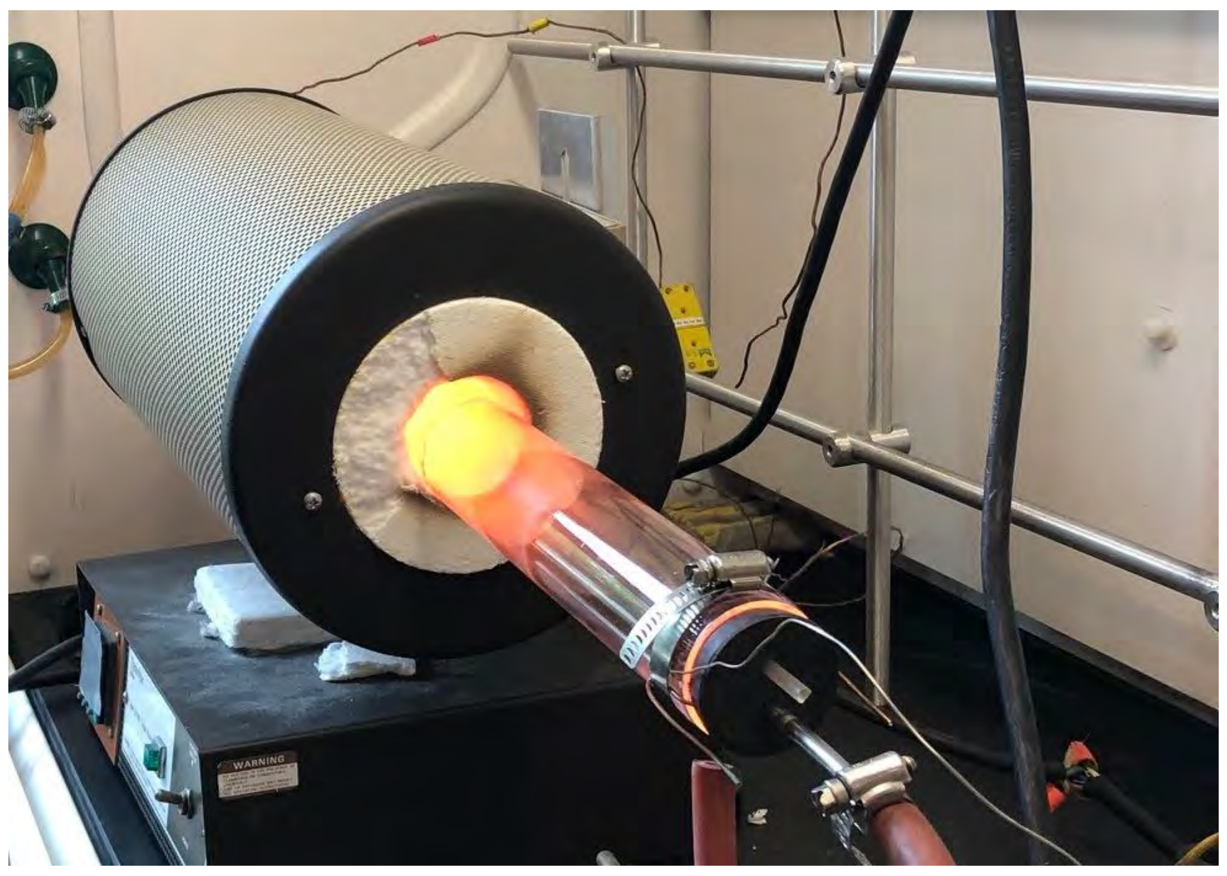

Figure 3: Tube furnace setup for curing packed rods. The gas inlet fills the quartz tube with helium gas in order to maintain an inert atmosphere and prevent oxidation of the graphite.

After cooling, a given ¼" packed rod was loaded into the arc vapor deposition reactor, Figure 4. The reactor utilizes an arc welder and a 1:3 $He:N_2$ atmosphere to generate a plasma that consumes the anode (the packed rod) and ultimately enables fullerene and MNF formation. Packed anodes were driven into the plasma manually and were combusted until all packing material was spent. The resulting carbonaceous soot that lined the reactor lid, Figure 5, was collected and processed via Soxhlet extraction with toluene to specifically isolate fullerene species in solution.

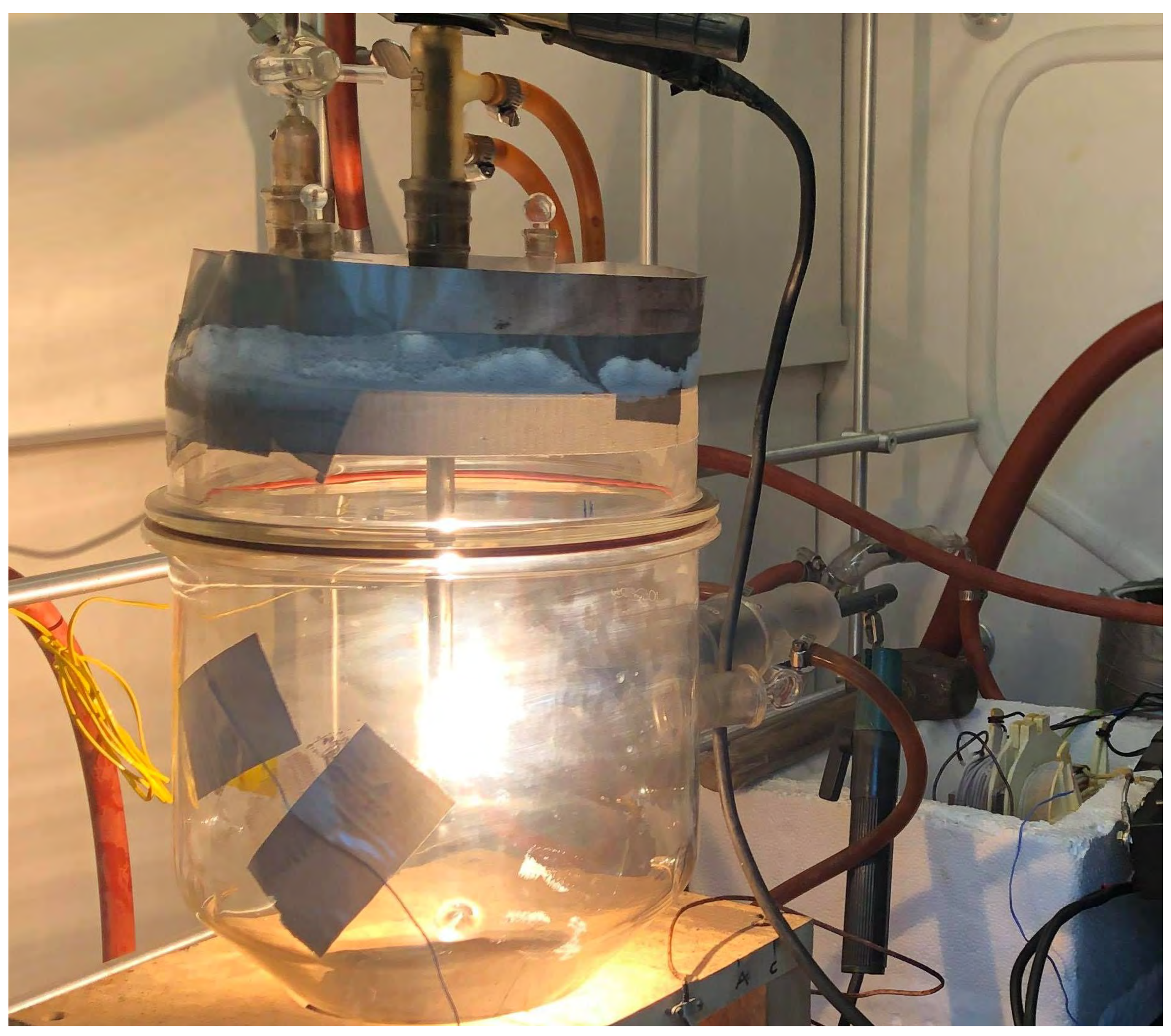

Figure 4: Arc vapor deposition reactor. The packed graphite rod (anode) is parallel to the ground, while a simple graphite cathode is perpendicular to the ground. A plasma arc is observable between the two electrodes. This method produces both empty and filled fullerenes.

Figure 5: Soot deposit from the combustion of a Sc_2O_3 packed rod.

Results

High-performance liquid chromatography (HPLC) with a Buckyprep column was used to analyze a sample of mixed empty fullerene standards, providing the Figure 6A chromatogram. Concentrated fullerene samples from the combustion of Sc_2O_3 and Gd_2O_3 packed rods were subsequently analyzed with the same HPLC parameters, providing Figures 6B and 6C, respectively.

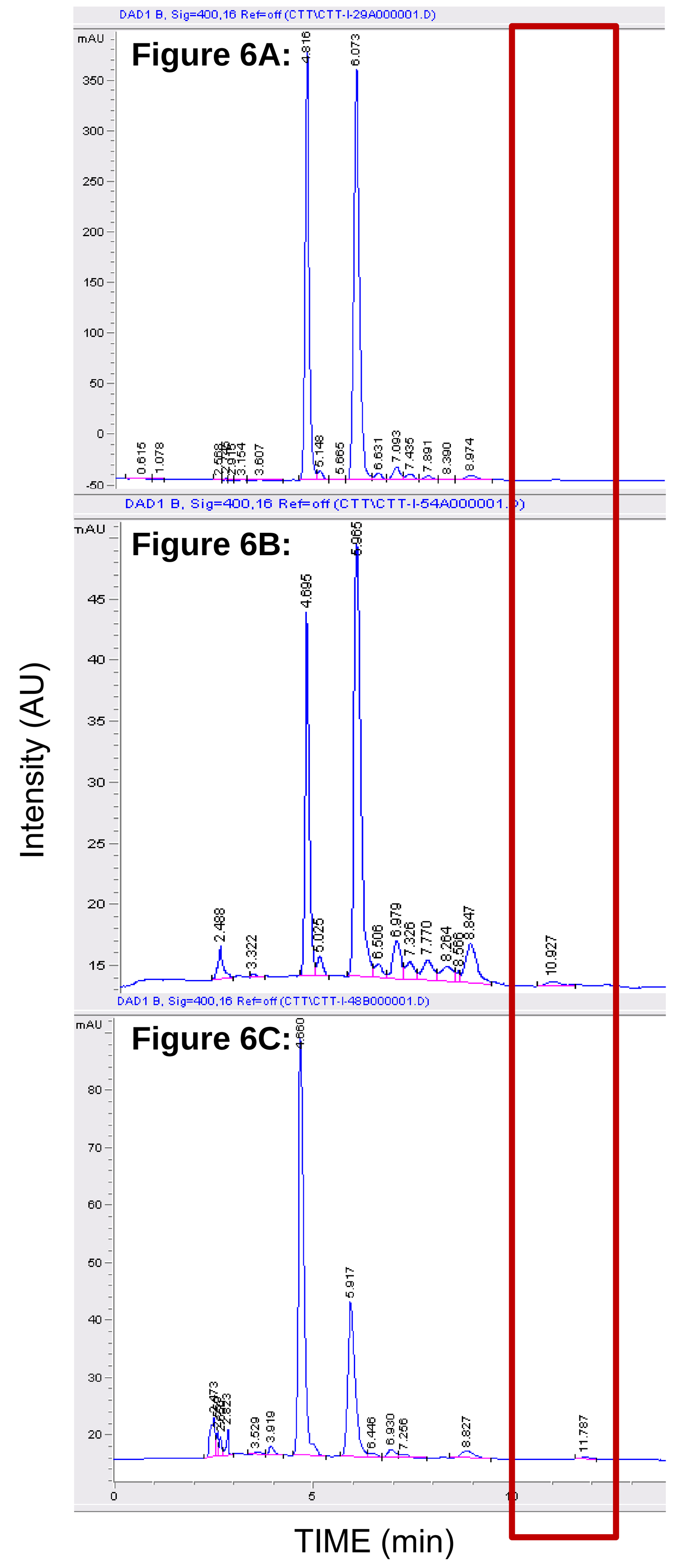

Figure 6: HPLC chromatograms for a mixed empty fullerene standard (Fig. 6A), Sc_2O_3 composite rod soot (Fig. 6B), and Gd_2O_3 composite rod soot (Fig. 6C).

The observation of the two major peaks (belonging to C_{60} and C_{70}) with similar retention time in all chromatograms demonstrate the reactor's success in producing empty fullerenes that are comparable to the standard. Within the red box in Figure 6, the t=10.927 min peak in Figure 6B and the t=11.787 min peak in Figure 6C went unobserved in the standard, and therefore may belong to an MNF species.

Conclusion

Unknown fullerenes, potentially EMF/MNF species, have been synthesized with the given methods. These compounds are to be identified via MALDI-ToF Mass Spectrometry and functionalized once significant quantities are produced.

References

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