University of Pennsylvania
ScholarlyCommons

Departmental Papers (MSE) Department of Materials Science & Engineering

11-26-2001

Reproducible synthesis of C_{60}@SWNT in 90% yields

Brian W. Smith
University of Pennsylvania

Richard M. Russo
University of Pennsylvania, rrusso@seas.upenn.edu

Satishkumar B. Chikkannanavar
University of Pennsylvania, satishkb@seas.upenn.edu

David E. Luzzi
University of Pennsylvania, luzzi@lrsm.upenn.edu

Ferenc Stercel
University of Pennsylvania, stercel@seas.upenn.edu

Copyright Materials Research Society. Reprinted from MRS Proceedings Volume 706.
2001 Fall Meeting Symposium Z
Making Functional Materials with Nanotubes
Publisher URL: http://www.mrs.org/members/proceedings/fall2001/z/Z3_13.pdf

This paper is posted at ScholarlyCommons. http://repository.upenn.edu/mse_papers/18
For more information, please contact repository@pobox.upenn.edu.

Mat. Res. Soc. Symp. Proc. Vol. 706 © 2002 Materials Research Society

Reproducible synthesis of C_{60}@SWNT in 90% yields

Brian W. Smith, Richard M. Russo, S.B. Chikkannanavar, Ferenc Stercel, David E. Luzzi
University of Pennsylvania, Department of Materials Science and Engineering,
3231 Walnut Street, Philadelphia, PA 19104-6272, USA

ABSTRACT

In previous works, we have shown our discovery of C_{60}@SWNT and first described the general mechanism of filling, which involves the vapor phase transport of C_{60} molecules to openings in the SWNTs' walls. Here, we discuss the high-yield synthesis of C_{60}@SWNT by refinements to our method. Yields are measured by a calibrated weight uptake technique, a methodology that is not subject to many of the potential pitfalls inherent to other techniques that have been applied. At certain processing conditions, yields exceeding 90% were obtained and corroborated by transmission electron microscopy. From our data, we determine the parameters most important for creating endohedral SWNT supramolecular assemblies by the vapor phase method. Our results pave the way for successful single-tube measurements and for high-yield filling with non-fullerenes.

INTRODUCTION

In previous studies, we have shown that C_{60}@SWNT is synthesized by a vapor phase route, whereby the sublimation of solid C_{60} in the presence of open SWNTs caused the fullerenes to enter the SWNTs and self-assemble into 1-D chains [1]. Subsequently, these experiments were independently reproduced [2-5], although no one has yet rigorously quantified the high-yield filling of SWNTs with molecules. Not only does this prevent the study of C_{60}@SWNT with bulk characterization techniques, but also it increases the risk associated with attempts to measure directly the properties of an individual fullerene peapod. For example, such an experiment might require the spin-coating of SWNTs onto a substrate, and the TEM is of little use in assuring that the SWNTs are not empty. In the present work, we show by way of a parametric study how the filling fraction can be reliably measured and maximized.

EXPERIMENTAL DETAILS

We have devised a series of simple experiments to measure the yield of C_{60}@SWNT by calibrated weight uptake, a proven technique for determining the stoichiometry of a doped system. Although it was not feasible to comprehensively examine all permutations of the synthesis parameters, a number of representative examples are discussed.

In each experiment, samples of SWNTs were prepared for filling by prescribed processing steps, with the final step in each case being filtration to form a buckypaper that was dried in air at 110° C. The distal edges were trimmed from the buckypaper, which was then cut into samples weighing a few milligrams and uniquely identifiable by shape. Each sample was immediately weighed on a two-pan balance to ± 0.006 mg. The weighed samples were processed as quickly as possible, but whenever necessary they were stored in a desiccator evacuated to roughing vacuum to minimize atmospheric exposure.

Multiple samples from each processing condition were split into control and experimental groups. The control group was sealed within a Pyrex or quartz ampoule at a vacuum of ~5×10^{-6} torr. The experimental group was similarly sealed, only C_{60} powder was also added to the ampoule in excess such that sufficient C_{60} was present to completely fill all the SWNTs in the sample. Experimental and control ampoules were annealed together in a muffle furnace for the desired time. Following annealing, the ampoules were broken, and the samples were annealed at 800° C under a dynamic vacuum of ~5×10^{-6} torr for one hour to remove residual exterior C_{60}. Control and experimental samples were annealed separately during this last step, and all temperature ramps were carefully controlled. It was visually confirmed that each sample was situated well within the furnace heat zone. Immediately after this last step, samples were re-weighed to ± 0.006 mg.

In order to determine the yield, the percent retained mass (ρ) of each control and experimental sample was calculated. Differences in weight retention between these two groups cannot be due to residual exterior C_{60} molecules, which would have sublimed during the last processing step (800° C annealing). Similarly, they cannot be due to atmospheric exposure, which was uniform and minimal across samples. Thus, differences in weight retention are attributed to the filling of SWNTs with C_{60} in the experimental ampoule. As will be discussed, this hypothesis is borne out by the data: in all of our experiments, the weight retention of each experimental sample was always greater than or equal to that of any corresponding control sample to within the error of the experiment. From this information, the implied C_{60}:SWNT weight ratio in each experimental sample can be calculated:

$$\eta_{exp} = \frac{\rho_{exp} - |\rho_{cont}|}{|\rho_{cont}|} \tag{1}$$

where $|\rho_{cont}|$ is the average retained mass of the control samples. (This equation can be understood by considering that a 1 mg SWNT sample processed without C_{60} should weigh $|\rho_{cont}|$ but actually weighs ρ_{exp} when processed with C_{60}. Then $\rho_{exp} - |\rho_{cont}|$ is the amount of C_{60} taken up, and the remaining $|\rho_{cont}|$ is the mass of SWNT material.) In the case of a C_{60}@(10, 10) SWNT with the C_{60} molecules spaced c.a. 1 nm center-to-center, the C_{60}:SWNT weight ratio for perfect filling is 3/8. Therefore, the implied filling fraction of each experimental sample is $8/3 \times \eta_{exp}$ (i.e. the filling fraction is expressed as a percentage of perfect filling).

The SWNTs utilized in this study were synthesized by the pulsed laser vaporization technique using a Ni/Co catalyst, purified by a 12 hour reflux in 2.6 M HNO_3, rinsed in a weakly basic (pH 8.0) solution, and extracted with toluene to yield a stock suspension (provided by R.E. Smalley, Rice Univ., through Tubes@Rice). Two groups of samples were examined:

<u>Group A</u>: The stock suspension was filtered onto PTFE to form a buckypaper, which was then annealed at 225° C under dynamic vacuum of ~5×10^{-6} torr for 15 hours. Samples were filled for 64.5 hours at 350, 450, and 550° C, with four control and four experimental samples at each condition (24 samples in total).

<u>Group B</u>: A recipe similar to one proposed by Kataura [5] was followed. A buckypaper was prepared from the purified stock suspension as above and cut into small pieces. The pieces

were refluxed with mild stirring at 125° C for 2 hours in 15 vol.% H_2O_2 at a ratio of 1 mL per 1 mg of starting material. The refluxed SWNTs were washed repeatedly with water and then sonicated for 20 minutes in 12.1 N HCl at a ratio of 1 mL/mg. The acidic solution was approximately neutralized with NaOH, and the SWNTs were recovered by filtration onto a 1 μm pore nylon membrane. Nanotubes were immediately washed from the membrane with ethanol and were redispersed in toluene by sonication for 30 minutes. Filtration onto a PTFE membrane yielded the processed material at weight loss of ~1/3. Samples were filled for 64.5 hours at 350, 450, 550, and 650° C, with two experimental and two control samples each (16 samples), and at 750° C°, with eight experimental and eight control samples each (16 additional samples).

RESULTS AND DISCUSSION

For convenience, each condition is designated by the processing group and annealing temperature, i.e. A350 indicates samples from group A, annealed at 350° C. The retained masses of the control and experimental samples are plotted as a function of temperature and filling preparation in Figure 1. The one spurious data point at the A350 condition is due to the fact that the sample was not situated in the heat zone during 800° C annealing and is omitted from all further calculations. Error bars are omitted for clarity, although the *absolute* error due to measurement is calculated to be only 2-3%. Although the spread in the data cannot be statistically quantified due to the small number of samples at each condition, the results are clearly reproducible. The corresponding average filling fractions, assuming a C_{60} center-to-center separation of 1 nm, and their errors are plotted in Figure 2. Notice that the measured filling fractions are approximately linear with temperature.

We must be open to the possibility that the evidenced weight uptake in the experimental samples is not due to the filling of SWNTs with C_{60}. Other imaginable explanations include the retention of impurities due to a change in the SWNTs induced by the presence of C_{60} in the ampoule, the reaction or decomposition of C_{60} in the ampoule to yield a residue that is not easily removed by annealing, or the intercalation of C_{60} into rope channels and buckypaper pores such that they are not sublimed at 800° C. Fortunately, all of these scenarios are unlikely at the pressure-temperature processing conditions. In general, we conclude that our yield measurements are legitimate to within a reasonable error.

In order to aid in interpreting the yield measurements, representative material from the A450, B650, and B750 conditions, having 22%, 56%, and 90% calculated yields, were examined by TEM. Sections were prepared from the central and edge regions of the materials. Our observations qualitatively support the calculated yields, showing homogeneously distributed C_{60}@SWNT in low and moderate abundance in A450 and B650, respectively. The control samples were confirmed to have comparatively negligible yields. Figure 3 shows representative micrographs of A450 and B650 samples. Our general impression is that B is a cleaner material than A, containing less amorphous carbon and physisorbed contaminants.

These results demonstrate the importance of both chemical and thermal processing in producing high-yield material. Chemical methods afford control over impurity fractions and the density of entrance defects, while the subsequent heat treatment pertains to the activation barrier separating solid C_{60} from its encapsulated state.

For the treatments discussed in this letter, our hypothesis is that B is a superior material due to the H_2O_2 reflux imposed prior to filtration. It is well known that temperature (or light)

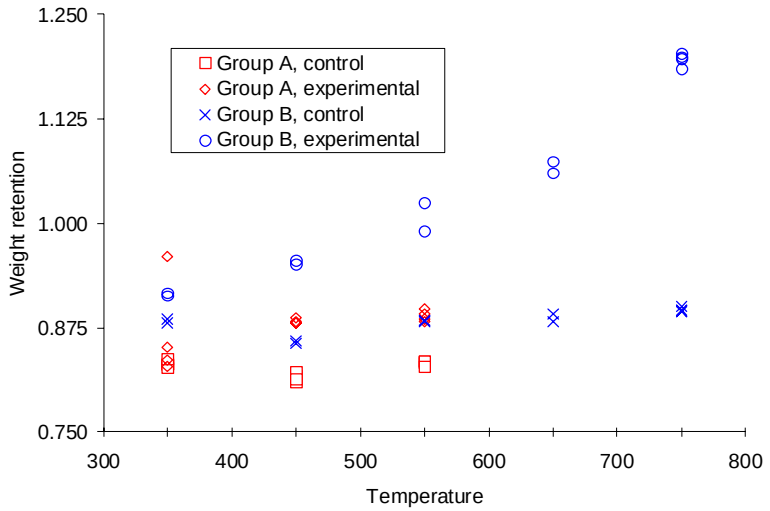

Figure 1. Retained masses of control and experimental samples from our weight uptake study, plotted as a function of filling temperature. In general, experimental samples retained more mass during processing than control samples. The spurious data point at the A350 condition is not included in further calculations.

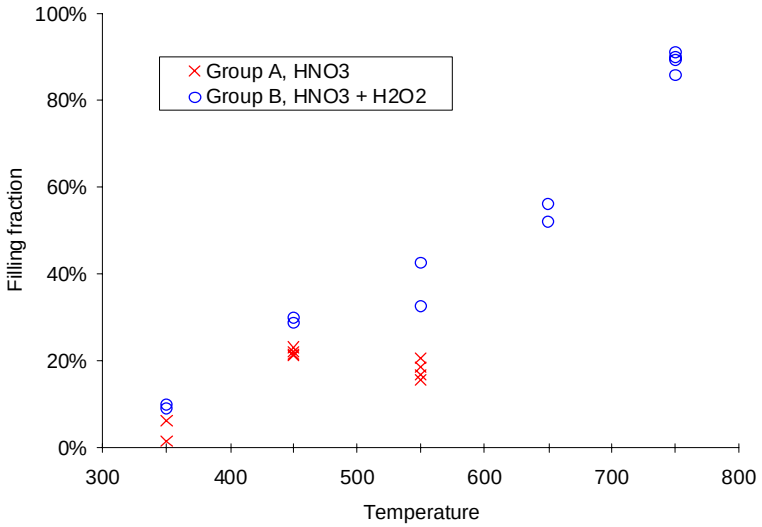

Figure 2. Implied C_{60}@SWNT yields from the data of Figure 1, plotted as a function of filling temperature for both group A and group B processing.

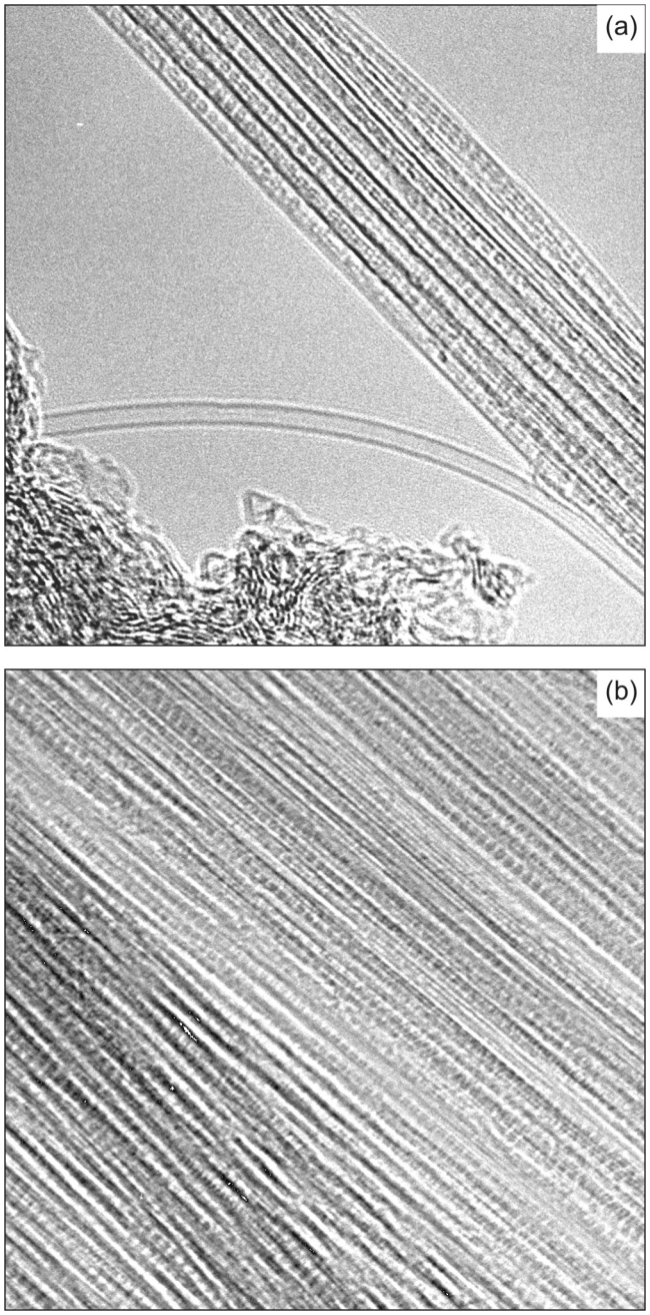

Figure 3. (a) Representative micrograph of the A450 (22% yield) sample. C_{60}@SWNT appears in moderate abundance, although impurities sometimes decorate the surfaces of nanotubes, as seen in the lower left of the image. (b) Representative micrograph of the B650 (56% yield) sample. This micrograph is intended to show a large region of the material, and because SWNT samples have substantial depth, there is a focus gradient. Nevertheless, the conspicuous periodic contrast of C_{60}@SWNT is easily detected at both underfocus and overfocus conditions. C_{60}@SWNT appears in high abundance.

causes homolytic cleavage of H_2O_2 into two highly reactive free radicals (·OH). Therefore, H_2O_2 is potentially an effective oxidizer, resulting in the extensive hydroxylation of amorphous carbon, polycyclic impurities, SWNT defects, etc. Hyrdoxylation improves the solubility of these components in neutral or slightly basic polar solvents (i.e. H_2O). The obstructing impurities can be easily washed away from the insoluble SWNTs, thereby increasing the surface area of the SWNTs that is directly accessible to the C_{60} vapor during heat treatment.

The best yields are expected when the fullerenes have the greatest flux onto the SWNTs. In the closed environment of the ampoule, this means that the partial pressure of C_{60} (P_{C60}) should be maximized. Heating occurs isochorically, and the pressure inside the ampoule (i.e. the external pressure acting on the solid C_{60}) will increase due to gas expansion and the vaporization of additional molecules from the solid. Thus, provided excess solid C_{60} is present, the best P_{C60} that can be attained at *any* temperature is the equilibrium vapor pressure over the solid.

In this way, heating the ampoule to higher temperature will promote intermixing, provided that the C_{60} does not degrade. Increasing temperature also has the detrimental effects of healing defects and impairing surface diffusion processes that might serve to channel C_{60} molecules into defects [1]. However, our experiments suggest that these detriments are insignificant for the tested annealing time up to even moderately high filling temperatures, in contrast to our initial belief. Apparently, the benefit of increasing P_{C60} outweighs all other costs associated with high temperature.

Therefore, it is expected that the kinetics of filling are determined primarily by the arrival rate of C_{60} to the nanotubes, so long as the nanotubes are properly prepared. Filling should occur more slowly at lower temperatures, resulting in lower yields for isochronal experiments that are terminated before the SWNTs are saturated. Alternatively, it may be that heating the SWNTs to higher temperatures during filling causes a simultaneous decomposition and removal of impurities bonded to entrance defects. We note that the A450 and A550 samples had identical yields (see Figure 2), potentially because the filling rate was limited not by arrival rate but by impurities that could not be removed at these temperatures.

CONCLUSION

In this work, we have shown the high-yield synthesis of C_{60}@SWNT, reliably measured by weight uptake and confirmed by TEM observation. Under the tested conditions, SWNT purity and annealing temperature have the most significant effect on the obtained yield. Perhaps most importantly, we have demonstrated and quantified a recipe for the synthesis of C_{60}@SWNT in abundance, facilitating both bulk- and local property measurements. Funded by ONR N00014-00-1-0482 and NSF DMR98-02560.

REFERENCES

1. B.W. Smith D.E. Luzzi, *Chem. Phys. Lett.*, **321,** 169 (2000).
2. K. Hirahara et al., *Mat. Res. Soc. Symp. Proc.*, **633** (in press, 2001).
3. K. Hirahara et al., *Phys. Rev. Lett.*, **85,** 5384 (2000).
4. S. Bandow et al., *Chem. Phys. Lett.*, **337,** 48 (2001).
5. H. Kataura et al., *Synth. Metals*, **121,** 1195 (2001).