Transport properties of carbon nanotube C_{60} peapods

C. H. L. Quay,[1] John Cumings,[1,*] S. J. Gamble,[2] A. Yazdani,[3] H. Kataura,[4] and D. Goldhaber-Gordon[1,†]
[1]*Physics Department, Stanford University, Stanford, California 94305-4060, USA*
[2]*Applied Physics Department, Stanford University, Stanford, California 94305-4090, USA*
[3]*Department of Physics, Princeton University, Princeton, New Jersey 08544, USA*
[4]*Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Central 4, Higashi 1-1-1, Tsukuba, Ibaraki 305-8562, Japan*
(Received 27 March 2007; published 3 August 2007)

We measure the conductance of carbon nanotube peapods from room temperature down to 250 mK. Our devices show both metallic and semiconducting behavior at room temperature. At the lowest temperatures, we observe single electron effects. Our results suggest that the encapsulated C_{60} molecules do not introduce substantial backscattering for electrons near the Fermi level. This is remarkable, given that previous tunneling spectroscopy measurements show that encapsulated C_{60} strongly modifies the electronic structure of a nanotube away from the Fermi level.

DOI: 10.1103/PhysRevB.76.073404 PACS number(s): 73.22.−f, 73.63.Fg, 71.10.Pm

In the 15 years since their discovery,[1] carbon nanotubes' electronic properties have generated considerable excitement in the physics and engineering communities. In addition to being ideal one-dimensional electronic systems, carbon nanotubes hold promise for use as transistors,[2] memory[3,4] and logic elements,[5] and field emitters.[6] In recent years, it has become possible to synthesize supramolecular structures by inserting smaller molecules such as C_{60} fullerenes into nanotubes to form "peapods."[7] Early experiments have shown that the inclusion of fullerenes modifies the electronic structure of a nanotube at energies far from the Fermi level[8] and that a peapod's conductance can depend on the choice of encapsulated species,[9,10] raising the prospect of novel transport phenomena in these molecules.

In this Brief Report, we report measurements of the conductance of carbon nanotube peapods at temperatures from 250 mK to room temperature. We were surprised to find that despite the addition of C_{60} molecules, our devices exhibit a range of low-energy transport behaviors similar to that previously seen in empty nanotubes. At room temperature, the nanotubes are semiconducting or metallic; at low temperature, we observe a Coulomb blockade and both spin-1/2 and spin-1 Kondo effects. Here, we discuss the overall behavior of our ensemble of devices and make some statistical statements about them. A detailed description of the Kondo effects will be published separately.

Our devices are carbon nanotube C_{60} peapods contacted by a palladium source and drain electrodes, 150–500 nm apart. The peapods lie on a 500 nm or 1 μm thick thermal oxide atop a highly doped silicon substrate, which acts as the gate. The peapods are synthesized by the sublimation technique described in Ref. 11. They are then dispersed by sonication in chloroform or orthodicholorobenzene. The dispersion is deposited on the substrate and allowed to dry. We locate the peapods relative to preexisting alignment marks using atomic force microscopy (AFM), and fabricate the electrodes using standard electron-beam lithography techniques. All nanotubes studied are 1–4 nm in diameter according to AFM measurements.

Figure 1 shows representative transmission electron microscopy (TEM) images taken of nanotubes deposited from our dispersion. We deposited electrodes on 20 different nanotubes, of which 7 were found to be conductive at room temperature. The other 13 nanotubes are discounted from the analysis that follows as they are likely not connected due to handling or alignment problems.[12]

Next, we perform a statistical analysis of our group of seven nanotubes in light of TEM images of many other nanotubes deposited from the same ensemble. Such a statistical analysis is crucial, as no synthesis method yields 100% filled peapods, and it is impractical to verify directly that a given nanotube in transport studies is filled with fullerenes—TEM is the only established method for differentiating between filled and unfilled carbon nanotubes, and the specimen requirements for TEM imaging are incompatible with the standard geometry of nanotube transistors. From images such as

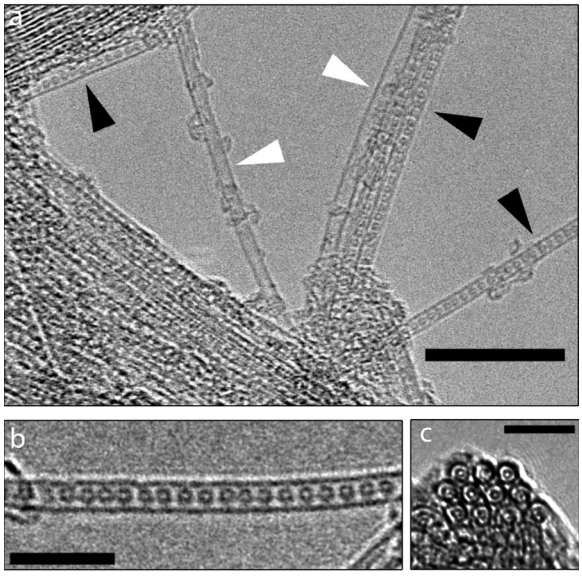

FIG. 1. (a) TEM image of bundles of carbon nanotubes deposited from our chloroform suspension, mostly filled with C_{60}. Arrows point to unobscured single nanotubes representative of those counted in our analysis—black arrows to filled tubes, white ones to unfilled. The scale bar is 30 nm long. (b) A single nanotube filled with C_{60} peas. The scale bar is 5 nm long. (c) A bundle of nanotubes viewed at an angle, showing the C_{60} molecules inside. The scale bar is 5 nm long.

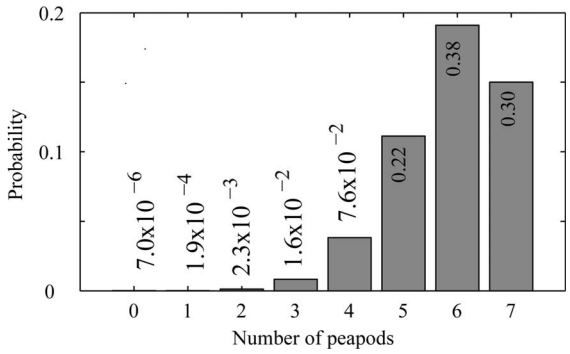

FIG. 2. Calculated probabilities, using Bayes's theorem, for the number of filled nanotubes in our sample of seven, taking into account the proportion of filled nanotubes in our TEM images (92 out of 109).

those in Fig. 1, we identify 109 single nanotubes, which are unobscured and in focus. Of these, 92 nanotubes are filled, and 17 empty. We observe no partially filled tubes. We also note that these tubes were deposited in the same way as those in the devices, i.e., by drop casting from solution.

Taking into account the frequency of filling in the nanotubes examined by TEM and assuming no prior knowledge of the fraction of filled tubes, we use Bayes's theorem for continuous probability distributions[13,14] to evaluate the probability that our seven measured nanotubes included any specific number of filled tubes from 0 to 7. This information is presented in Fig. 2. The expected number of filled tubes is found by this method to be 5.86. Details of these calculations are included in the Appendix; however, we would like to emphasize here that our approach is more conservative than simply taking 92/109 as the fraction of filled nanotubes, yielding a higher calculated probability that many of our nanotubes are unfilled.

Returning to the transport properties, Figs. 3 and 4 show representative measurements of the conductance of our devices as a function of gate voltage at room temperature and at 250 mK.

In the room-temperature measurements, we observe devices with conductances significantly modified by the gate as well as the ones that are unaffected by it [Fig. 3(a)]: "semiconducting" and "metallic," respectively, in the conventional description of carbon nanotubes.[15,16] Only a few devices with rather low overall conductances are completely depletable [Fig. 3(b)].

At 250–350 mK, two of the seven nanotubes in our ensemble have undetectably low conductance. The question naturally arises as to whether these, and only these, are peapods. As seen in Fig. 2, we find that the probability that three or more of our tubes in this sample of seven are filled is 99.75% (see Appendix for details). It is therefore practically a certainty that one or more of our quantum dot devices are formed on peapods.

All devices measurable at low temperature show a Coulomb blockade behavior, but with widely varying peak conductances. Representative data are shown in Fig. 4. Devices on all five tubes show Coulomb diamonds in measurements of conductance versus gate and bias voltages [Fig. 4(c) is representative], indicating that each device acts as a single or a double quantum dot.

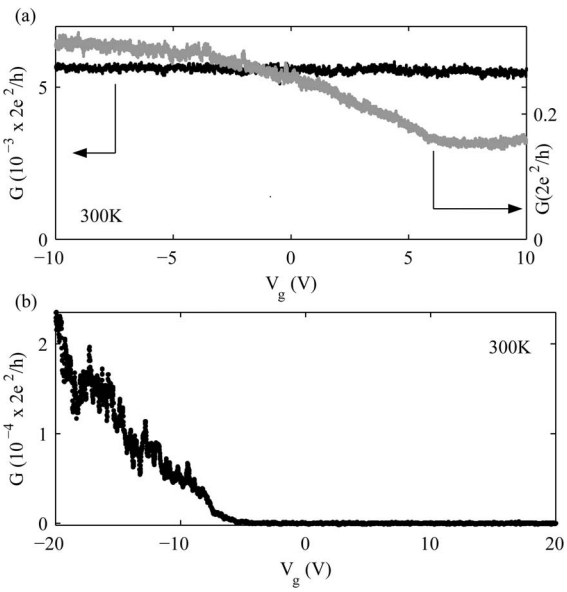

FIG. 3. Our devices, which include some peapods (see Fig. 2), show a range of room-temperature transport properties indistinguishable from those of unfilled nanotubes. (a) Room-temperature linear conductance traces for devices exhibiting some (gray line, right axis) and no (black line, left axis) change as the gate voltage is swept. (b) Room-temperature linear conductance of a completely depletable semiconducting device.

In Table I we summarize results from devices on the five tubes which conduct at low temperature. We compare measure charging energies to estimates obtained by using the classical expression for capacitance between a metallic wire and a metallic plane, $C=2\pi\epsilon L/\ln(4h/d)$, and $U=e^2/C$.[17] Here, d is the tube diameter, L is the distance between contacts, h is the oxide thickness, and $\epsilon=3.9\epsilon_0$ is the dielectric permittivity for SiO_2.

For two of the five tubes, our measured and calculated values agree; however, in three tubes (four devices), the measured charging energies are lower than what would be expected if the quantum dot or double dot were delimited by the contacts. The most likely explanation is that in those cases, the contacts do not break the tube into electrically separate regions—rather, the quantum dots extend beyond the contacts, as was observed in one previous experiment in which a tube was draped across multiple contacts.[19] Assuming for tubes A and E that electrons are delocalized over the entire length of the tube, and for tube D that the entire length of the tube acts as a double dot, yields predicted charging energies consistent with our measured values (Table I).[18] As delocalization of electrons in a nanotube beyond a junction with a metal contact deposited on top of the tube is previously unknown, we speculate that intercalation of C_{60} makes nanotubes more radially rigid and more difficult to crush.

This possibility of a structural effect of C_{60} intercalation is intriguing and deserves further study, but it does not impact the main conclusions of our work on the electrical effects. If, as argued above, some of the devices in Table I are formed from peapods, the observation of Coulomb diamonds leads to the conclusion that the encapsulated C_{60} does not introduce substantial backscattering of electrons passing through

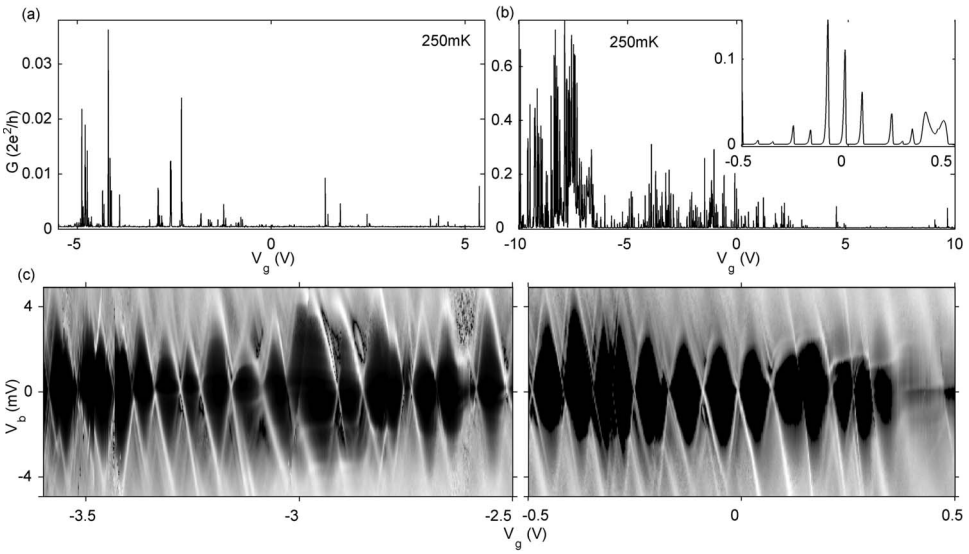

FIG. 4. (a) At 250 mK, device showing Coulomb blockade. (b) Also at 250 mK, device with higher conductance showing Coulomb blockade. (Inset) Detail showing a regularity of peaks, which continues over the whole range. (c) Conductance versus bias and gate voltage of device in (b). The color scale is black (low) to white (high conductance). Regular diamonds indicate that this is a single quantum dot.

a nanotube: electrons are delocalized over hundreds of peas. This somewhat surprising result is consistent with data from recent photoemission studies.[20] The absence of backscattering in peapods may be due to the long wavelength of the perturbation introduced by the encapsulated C_{60}. Due to an unusual band structure, backscattering in single-walled carbon nanotubes is expected to require a very large momentum transfer, which can only be produced by a nearly atomically sharp perturbation or a perturbation so large that it locally depletes the tube.

To our knowledge, there have been only two previous or contemporaneous reports of transport measurements on nanotubes believed to contain C_{60} molecules (though several studies have been published on metallofullerene peapods). (1) Yu *et al.* found modulation of conductance by gate and bias voltages on large energy scales and weak conductance at zero bias, suggesting the formation of multiple dots in series within the nanotube.[21] In contrast, we always see conductance at zero bias and a Coulomb blockade behavior consistent with the formation of single or double dots. These differences between our results and theirs may be due to the irregular spacing of C_{60} peas in their nanotube, in contrast to the regular spacing in our tubes (Fig. 1). (2) Since the first submission of this manuscript, Utko *et al.* have reported measurements which substantially agree with ours. They found a single dot behavior in several tubes from an ensemble of peapods. Their observed charging energies are consistent with electrons in a dot delimited by metal contacts—unlike in our study, in which contacts are narrow (250 nm) palladium strips that cross the tubes, Utko *et al.* covered each tube entirely with palladium metal, except for a small portion through which they measure transport.[22]

In conclusion, we have measured the transport properties of carbon nanotube samples, including some C_{60} peapods at room temperature and at 250–350 mK, and have done a careful statistical analysis of such an assembly of devices. Our results indicate that C_{60} peapods do not differ collectively from nanotubes in their electronic transport characteristics. We note that this complements earlier scanning tunneling microscopy work,[8] where C_{60} peas were found to induce

TABLE I. Correlation of energy scales with device geometry. Each letter corresponds to a different tube. For tube E, results are reported for transport between two different pairs of contacts (E1 and E2). Charging energies are experimentally determined from intersection of lines with opposite slopes in Coulomb diamond plots such as Fig. 4(c). For comparison, charging energies are predicted for electrons confined to a stretch of nanotube between two neighboring metal contacts, assuming a tube diameter of 1–4 nm (Ref. 17). These predictions are dramatically off for some devices—in those cases charging energy is instead consistent with electrons delocalized over the entire tube. Whichever prediction is consistent with our measured value is shown in bold. Note: When we observe a double dot behavior (tubes B and D), each of the two predictions assumes that the relevant tube is divided into two equal segments, each acting as one dot. See text and supplementary information for details and discussion (Ref. 18).

Device label	Tube length (μm)	Intercontact distance (nm)	Oxide thickness (μm)	U, charging energy (meV)	Predicted U (meV)	Predicted U for entire tube (meV)
A	2	500	0.5	3–5	9–11	**2.3–2.8**
B[a]	5.5	500	0.5	5–10	**9–11**	1.7–2
C	4	250	0.5	15–40	**18–23**	1.1–1.4
D[a]	2	250	0.5	1–5	18–23	**4.6–5.6**
E1	4	250	1	3–4.5	20–24	**2.2–2.4**
E2	4	150	1	1–3	34–41	**3–4.1**

[a]These devices act as double dots.

significant perturbations in the electronic structure of a nanotube only at much higher energies than are accessed in our present measurements.

Photoemission studies nevertheless suggest that other peapod species may yield more exotic behavior in transport—for example, a Tomonaga-Luttinger to Fermi-liquid transition with increased potassium doping.[23] A more detailed picture of the range of transport properties of peapods may emerge when transport measurements can be combined with *in situ* structural characterization. Meyer *et al.*[24] have commenced work in this direction.

We thank Rafael de Picciotto for technical assistance and scientific advice, Robert Tibshirani for invaluable advice on statistical matters, and Yi Qi for technical assistance. This work was supported by U.S. Air Force Grants No. FA9550-04-1-0384 and No. F49620-02-1-0383, and a Grant-in-Aid for Scientific Research by the MEXT of Japan. It was performed in part at the Stanford Nanofabrication Facility of NNIN supported by the National Science Foundation under Grant No. ECS-9731293. C.H.L.Q. acknowledges support from Gabilan Stanford Graduate and Harvey Foundation, and D.G.-G. acknowledges the Packard and Sloan Foundations.

APPENDIX: BAYES'S THEOREM

Bayes's theorem for continuous probability distributions[13,14] states

$$f(x|y) = [f(y|x)f(x)] / [\int_{-\infty}^{\infty} f(y|x)f(x)dx]. \quad \text{(A1)}$$

Here, $f(x)$ is the marginal density of the random variable $\mathbf{x}$, and $f(y|x)$ is the conditional density of the random variable $\mathbf{y}$, given $\mathbf{x}=x$. For us, $\mathbf{x}$ is the fraction of filled nanotubes in our ensemble and $\mathbf{y}$ is the probability of finding 92 filled tubes in a sample of 109 drawn from that ensemble.

Equation (A1) thus gives us $f(x|y)$, the posterior distribution of $\mathbf{x}$, given that we found 92 filled nanotubes out of 109. $f(y|x)$ is simply the binomial distribution given any particular $\mathbf{x}=x$,

$$f(y|x) = \binom{109}{17} x^{92}(1-x)^{17}. \quad \text{(A2)}$$

To guard against overestimating the number of filled nanotubes in our sample, we assume a uniform prior distribution of $\mathbf{x}$, i.e., $f(x)=1$, making our calculations more conservative than if we had simply used "92/109" as the fraction of filled nanotubes in our ensemble.

As Eq. (A1) gives a "probability distribution," the conditional expected value for any function $g(x)$ is

$$\bar{g} = \int_{-\infty}^{\infty} f(x|y)g(x)dx, \quad \text{(A3)}$$

i.e., $g(x)$ multiplied with the probability of each x and integrated over all x.

For example, for a given value x of the random variable $\mathbf{x}$, by definition, the probability that any particular nanotube in the ensemble is filled is $g(x)=x$. Putting this into Eq. (A3), which accounts for the earlier 92 out of 109 observation, we find that the likelihood that any randomly chosen nanotube is filled is $\bar{g}=31/37$. Thus, the expected number of filled tubes in our sample of seven is 5.86.

Similarly, to obtain the probability that a specific number n of our seven nanotubes are filled, we substitute

$$g(x) = \binom{7}{n} x^{n}(1-x)^{7-n} \quad \text{(A4)}$$

into Eq. (A3) to produce Fig. 2.

*Present address: Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742-2115.
†goldhaber-gordon@stanford.edu

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