SIR – Single-walled carbon nanotubes (SWNT) have been produced in a carbon arc [1–3] and in amazingly high yield by laser vaporization [4] where, in both cases, a small amount of transition metal has been added to the vaporized graphite rod. Whereas the diameters of metal-catalyzed *multiwalled* nanotubes are clearly correlated with the size of the attached metal particle [5], the same diameter $d \approx 1.2$ nm has been observed in SWNT under varying conditions and with different metal catalysts and concentrations. This suggests that the above diameter value reflects a property of condensed carbon rather than of a particular metal/carbon aggregate. More important, this observation proves to be the missing key towards understanding the initial nucleation and growth mechanism of single-walled nanotubes.

Whereas fullerenes are formed in $\lesssim 30-40\%$ yield by laser vaporization of graphite, a mere $\approx 1\%$ addition of metal atoms to the condensing carbon vapor leads to the formation of SWNTs as the prevalent product under otherwise identical conditions. The role of metal atoms M in tube nucleation, even though crucial, is limited to saturating the dangling bonds at the open edge and thus preventing closure of a hemifullerene by a dome; the $M-C$ bond energy is irrelevant for the diameter of the hemifullerene. A carbon nanotube starts forming as soon as additional carbon atoms start forming a cylinder attached to the hemifullerene (Fig. 1). This "tubelet" is initially free to anneal into its optimum structure, given by the tube diameter. Beyond a critical cluster size of $N_{crit} \approx 200-400$ atoms this tubelet is kinetically fixed, leaving only lengthening or closure as available reaction branches with additional carbon feedstock. Here, we present an amazingly simple quantitative explanation for the observed constant value of the tube diameter $d = 1.2$ nm which is based on energetic arguments involving the strain and the dangling bond energy of the tubelet with a critical size N_{crit}.

The lowest energy structure of an open capsule with N carbon atoms results from balancing the strain energy of a cylinder attached to a hemifullerene of the same diameter (which favors larger diameters) with the dangling bond energy at the open edge of the capsule (which favors smaller diameters). The total strain and edge energy of the tubelet in Fig. 1 is

$\Delta E = E_h + E_c + E_e$, where E_h and E_c are the respective strain energies of the hemifullerene and the cylinder, and E_e is the energy of the dangling bonds at the open cylinder edge. The strain energy of a hemifullerene, E_h, is, to a very good approximation, independent of its diameter [6]. The strain energy of the attached cylinder of diameter d and length L is $E_c = \epsilon_c L/d$, where $\epsilon_c = 15.1$ eV [6]. Finally, the energy stored in the dangling bonds at the open cylinder edge is $E_e = \pi d \epsilon_e$, where ϵ_e has been estimated to be 21 eV/nm based on *ab initio* density functional calculations of a graphene sheet edge [7].

Minimizing ΔE with respect to the cylinder diameter d for a constant number N of carbon atoms in the tubelet yields the relation $d_{eq} = \alpha N^{1/3}$, with $\alpha = 0.16$ nm for the above values of ϵ_c and ϵ_e. The weak dependence of the equilibrium tube diameter d_{eq} on N_{crit} is strongly suggestive of a narrow range of expected tube diameters. We find equilibrium tube diameters of 0.73 nm, 0.92 nm, 1.05 nm, 1.16 nm, and 1.25 nm for tubelets with 100, 200, 300, 400 and 500 atoms, respectively. The weak dependence of $\alpha \sim \epsilon_c/{\epsilon_e}^{1/3}$ on ϵ_e indicates that a partial saturation of the edge by a few chemisorbed metal atoms (effectively reducing ϵ_e) cannot significantly alter the equilibrium diameter; there is only a 10% increase in the diameter if the effective dangling bond energy is lowered by 25% due to adsorbed metal atoms. The calculated diameter in the range of $N = N_{crit} \approx 200 - 400$ atoms is in excellent agreement with observed tube diameters.

The excellent agreement between the predicted and the observed tube diameters supports the idea that the role of the metal in determining the nanotube diameter is kinetic, rather than energetic. Metal atoms initially inhibit closure of the fullerene, allowing time for annealing to the equilibrium structure predicted above. As more carbon adds to the growing tube, which is now kinetically fixed in diameter, metal accumulates at the growing edge and aggregates to a larger particle which can more effectively prevent closure. Indeed, we believe that growth stops when the metal particle becomes so large that it catalyzes the closure and falls off the tip. This suggests the possibility of sustaining growth indefinitely by intercepting supply of metal atoms and feeding nucleated tubes *pure* carbon feedstock. Such experiments are currently underway.

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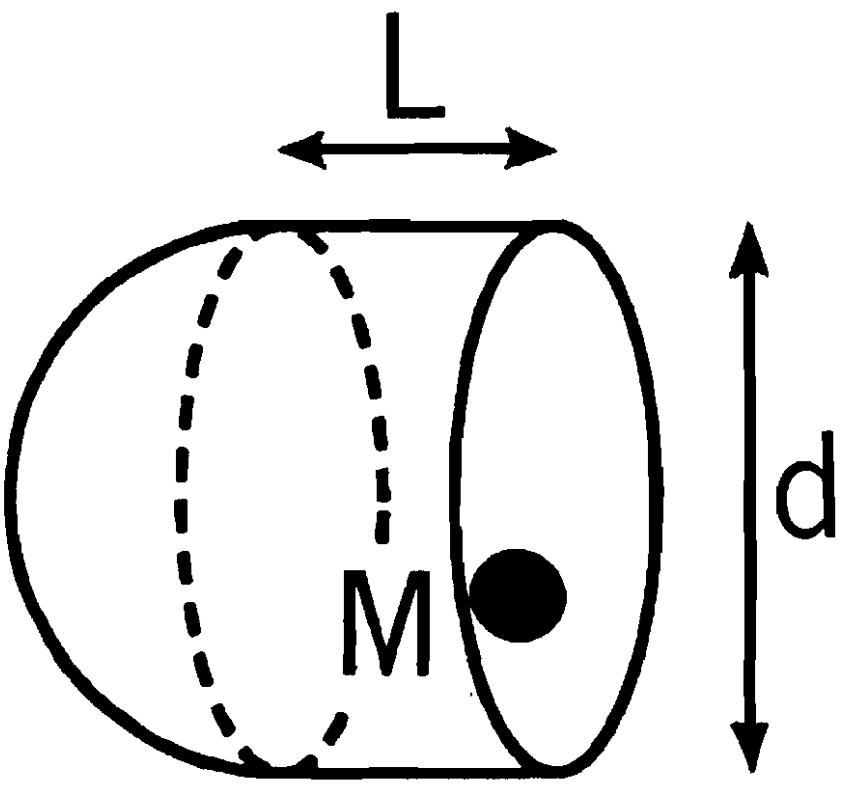
FIGURES

FIG. 1. Schematic view of the critical nucleus of a single-walled nanotube of length L and diameter d, with a metal atom M saturating some dangling bonds at the open edge. Beyond a critical size N_{crit}, this nucleus can no longer anneal completely to modify the tube diameter.


L
d
M