CATALYTIC EFFECTS OF HEAVY METALS ON THE GROWTH OF CARBON NANOTUBES AND NANO PARTICLES

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Abstract — The effects of bismuth, lead, and tungsten on the cobalt-catalyzed synthesis of single-layer carbon nanotubes and nanoparticles have been studied. When co-vaporized with cobalt in an electric arc, bismuth and lead increase the yield of single-layer nanotubes and broaden the range of tube diameters, compared to the case where only cobalt is used. Tungsten is found to reduce the nanotube yield and does not change the tube diameter distribution. Both tungsten and bismuth increase the graphitization of the carbon encapsulating the cobalt particles found in the soot, while lead does not. None of these three heavy metals catalyzes the formation of single-layer nanotubes without a transition metal present.

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Single-layer carbon nanotubes [1, 2] and metal-filled nanoparticles [3–8] are anticipated to have unique properties that may eventually lead to novel applications [9–11]. For example, nanotubes could be useful as strengthening fibers in composite materials, casings for metal nanowires, or atomic force microscope tips. Filled with metals or semiconductors, they might provide elements for nanoscale electrical or electronic devices such as amplifiers, switches, or electrical–mechanical converters. In addition to nanotubes, metal crystallites encapsulated in graphitic polyhedra have been produced by co-vaporizing metals and carbon. Typically these particles contain metals such as rare–earths in their carbide form [3–5], and have been found in the deposit that forms on the arc cathode. Examples of graphitic carbon encapsulation of pure transition metal crystallites of Ni or Co have also been reported [6–8]. One hope is that ferromagnetic nanoparticles can be produced with properties making them especially suitable for applications such as magnetic recording [12]. For that application, the chemical and magnetic isolation provided by graphitic encapsulation may be very desirable. Experimental studies of nanotubes and encapsulated nanocrystals have been hindered by the lack of samples containing high concentrations of these materials. Here we report that enhanced yields of both nanotubes and graphite encapsulated nanocrystals can be achieved by using heavy-metal promoters in the catalytic synthesis of these materials. The characteristics of the materials produced are in some cases dramatically modified by the heavy metals.

Our interest in improving the production efficiency of single-layer carbon nanotubes led us to consider various additives that might change the catalytic properties of cobalt, the primary catalyst we have been using [1, 7]. Bi and Pb were chosen as additives because they are thought to have exceptional ability to oxidize the carbon at the nanotube ends [13, 14]. The anode was vaporized by a DC arc under 400 Torr of helium flowing at 10–15 ml min⁻¹. The electrodes were 6 mm diameter graphite rods, with the anodes drilled out to 4 mm inside diameter and filled with mixtures of C, Co, and heavy metal (e.g. Bi and Pb). The metal concentrations were used 4% each for Co and the heavy metal (in atomic percent, relative to the carbon).

Shortly after the arc was struck, fine black threads rapidly aggregated to form a web-like material, which filled the reaction chamber. While this is a common phenomenon when nanotubes are grown catalytically in such an apparatus, the rate of thread formation and the final amount of web-like material was greatly enhanced when Bi or Pb was added to the anode. Soot collected from the chamber was sonicated in ethanol and a drop containing the suspended materials was placed on a holey carbon grid for
Fig. 1. Continued opposite.
TEM examination. The density of nanotubes was very high, and single-layer nanotubes with diameters exceeding 2 nm were abundant. Figure 1(a) is a typical TEM image of the soot produced using Co and Pb. One sees a network of nanotube bundles with nodules of amorphous carbon containing spheroidal cobalt particles with typical diameters around 10 nm and larger lead particles with diameters typically between 30 and 60 nm. Figure 1(b) and (c) shows high resolution images of bundles consisting of hundreds of single-layer nanotubes of various diameters, made using Co and Bi. In Fig. 1(b), the 3 nm diameter tube running vertically at the right edge of the bundle is larger than any single-layer carbon nanotubes produced to date with Co alone. The larger particle at the top-right of the image is a Bi particle about 60 nm in diameter. Figure 1(c) shows another image of a nanotube bundle, with a portion of the bundle bent sharply around. Bundles such as the ones shown in Fig. 1(b) and (c) were frequently observed when Bi and Pb were used. It is intriguing that even through Pb and Bi promote the Co catalytic efficiency for growing nanotubes, neither catalyzes nanotube growth when used alone.

Diameter distributions for nanotubes produced with Co and Bi or Pb, each measured by high resolution TEM examination of over 150 tubes, are shown in Fig. 2. The ranges of nanotube diameters are 1–5 nm and 1–4 nm, respectively, for tubes produced with Bi and Pb, compared with 1–2 nm for tubes produced with Co alone [7]. Clearly the nanotube diameter distributions are dramatically modified by the addition of the heavy metals. Many tubes produced using the heavy metal promoters have diameters well outside the range accessible using only transition metals or mixtures of transition metals [2, 5, 7]. The histograms show some fine structure, in particular peaks at about 1.2 and 1.5 nm, that are similar to peaks in the diameter distributions obtained using only Co or Co
Fig. 3. Co crystallites encapsulated in graphitic polyhedra, produced with Co and Bi. The crystallite marked A is a 20 nm diameter fcc-Co crystallite encapsulated in 17 layers of graphene sheets, which have a constant spacing comparable to that of bulk graphite. The particles marked B, C, and D are also fcc-Co crystallites, similar to those produced without Bi, and the large particle at the bottom-right is a pure Bi particle.

with sulfur as a promoter [7]. These features suggest that some aspect of the nanotube nucleation process is insensitive to the presence of the catalyst promoters.

Motivated by these observations, we have studied the influence of other heavy elements on the growth of various carbon structures in the arc. Xenon was tried because it is similar in physical size to Bi and Pb, but is chemically inert. However, when we used a Xe:He (1:2) mixture as a buffer gas, the arc was unstable and the formation of nanotubes was greatly reduced. Another heavy metal, tungsten, was tried, but it reduced the nanotube yield, and the diameter distribution for the tubes that were produced was essentially the same as that obtained using Co alone. It has been reported [15] that using platinum with Co increases the nanotube yield, and produces nanotubes with diameters of 1–2 nm, similar to those made with only Co. The enhancement of the yield and extension of the diameter range are not effects particular to heavy metals, as shown by our finding that a non-metal element, sulfur, has similar effects on the growth of nanotubes when it is used with Co [7]. This strongly suggests that the chemical properties of the promoters, rather than physical properties such as size or mass, are responsible for these effects.

In addition to affecting the production and characteristics of single-layer nanotubes, we found that Bi and W also affect the structure of the carbon surrounding the transition metal particles in the soot. For example, high resolution TEM images show that many of the Co particles produced with

Fig. 4. Carbon-encapsulated Co crystallites produced using W. While the graphitic layers of the carbon shells surrounding the particles in the two panels are quite well ordered, defects in the layering are evident, particularly in the carbon surrounding the particle in the lower panel.

Bi present are encapsulated in well-graphitized, multilayer carbon polyhedra. Figure 3 is a typical image of enclosed Co particles found in soot made using Co and Bi. The crystallite marked A is a 20 nm diameter fcc-Co crystallite encapsulated in 17 layers of graphene sheets, which have a constant spacing comparable to that of bulk graphite. The particles marked B, C, and D are also fcc-Co crystallites, similar to those produced without Bi, and the large particle at the bottom-right is a pure Bi particle. Tungsten also seems to enhance the graphitization of the carbon surrounding Co particles, but to a lesser extent than does Bi. In Fig. 4, for example, layers of carbon encapsulate Co crystallites produced with Co and W are shown. While the graphitic layers of the carbon shells surrounding the particles in the two panels are quite well ordered, defects in the layering are evident, particularly in the carbon surrounding the particle in the lower panel. Our observations indicate that Bi and W share with S [7] the catalytic ability to significantly increase the production of fcc-Co crystallites tightly wrapped in graphitic polyhedra. In contrast, lead does not noticeably increase the formation of graphite encapsulated metal particles. In the case of lead, as
in the case where no promoter element is used, the carbon surrounding the cobalt crystallites typically appears amorphous in the TEM.

The variability of the effectiveness of different promoters for catalyzing formation of nanotubes and nanoparticles is perhaps worth emphasizing. While Bi and S enhance both nanotube yield and graphitic encapsulation of Co crystallites, Pb enhances nanotube formation but does not seem to affect Co encapsulation, and W suppresses nanotube formation but increases the yield of encapsulated Co particles. This variability suggests that the role of these promoters may be fairly complicated. If in analogy to the transition metal catalyzed formation of vapor grown carbon fiber (VGCF) [16–18], we suppose that nanotubes nucleate on and grow from Co catalyst particles, then Bi, Pb or S residing on the surface of these particles could facilitate sp² carbon–carbon bond formation, enhancing growth rates for the nanotubes, and possibly as the temperature drops, graphitization of carbon coatings on the metal particles. This model has the problem that, unlike the case of VGCF formation, no correlation has been found between the diameter of the single-layer nanotubes (1–5 nm) and the size of the Co particles ultimately found in the soot (with diameters 5–50 nm). Furthermore, TEM observations typically show no metal particles at free ends of the tubes, which usually are closed with single-layer carbon caps, and the carbon surrounding the metal particles obscures their surfaces so that we find very few images showing nanotubes that appear to terminate on metal particles. Therefore the growth model for VGCF may not apply directly to the case of single-layer nanotube formation.

The discovery of catalyst promoters provides a key to mass production of single-layer carbon nanotubes and metal encapsulated graphitic polyhedra. Catalytic production allows high efficiency and selectivity. More efficient synthesis of tubules with a wider range of diameters will facilitate investigations of nanotube properties and applications that depend on the diameter, such as electric conductivity [20], hydrogen storage media [21], and super strong crystals [22].

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REFERENCES