

Synthesis of carbon nanoflasks

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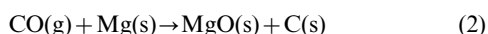
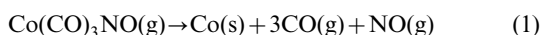
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The catalytic reaction of Co(CO)₃NO and Mg at 900 °C has led to the formation of multi-walled carbon nanoflasks.

Since the discovery of the buckminsterfullerene molecule (C₆₀),¹ a variety of novel structures with trigonally bonded carbon have been discovered: multi- and single-walled nanotubes^{2,3} (MWCNT and SWCNT), nested spheroidal shell (onions),⁴ giant fullerene shells,⁵ interconnected fullerene-like cages,⁶ cross-linked graphitic cages,⁷ flattened nanotubes and flattened carbon nanoshells.^{8,9} Strong interest in these materials appeared in the field of nanotechnology¹⁰ when it was shown to be possible to insert different kinds of materials with potentially interesting properties into the core volume of nanotubes or carbon nanoparticles. Lead was the first material introduced into a CNT.¹¹ Cobalt-filled carbon nanoparticles or nanotubes were recently prepared and studied by several groups.^{12–20} Guerret-Plecourt and co-workers reported the preparation of cobalt nanowires encapsulated in nanotubes.¹² They used the arc-discharge method for their fabrication. The same group later demonstrated that a sulfur impurity (of approximately 0.25%) was the cause for the filling of nanotubes with various materials.²⁰ Their cobalt nanowires, however, were short, having only a 200 nm length.

Here we report the existence of multi-shelled, flask-shaped carbon nanostructures whose overall geometry differs from those of carbon nanotubes or carbon nanoparticles. Such carbon vessels we call here carbon nanoflasks. The nanoflask has an ovoid or a spherical bulbous base with a “plus end” from which the nanotube grows, lengthening one-dimensionally. The protective carbon coating ensured that the inserted cobalt was in a fcc phase. We anticipate that the cobalt-filled carbon nanoflasks will have novel magnetic properties.

Carbon nanoflask samples were prepared by a catalytic reaction. The synthesis was carried out in a 2 ml closed vessel cell, which was assembled from stainless steel Swagelok parts. A 3/8" union part was capped from one side by a standard plug. For this synthesis, 400 mg of magnesium powder and 700 mg of Co(CO)₃NO were placed in a cell at room temperature. The vessel was then immediately closed tightly because Co(CO)₃NO is an air-sensitive material, and was heated at 900 °C for 3 hours. The reaction takes place at the autogenic pressure of the precursors. The proposed reactions are as follows:



After cooling down to room temperature, there was no pressure inside the vessel. The products were treated with 50 ml of 8 M HCl at 70 °C for 1 hour, and then left in the acidic solution overnight at room temperature. During this acid treatment the MgO and the Co metallic particles reacted with HCl, and were removed from the outer surface of the CNT. At the end of the reaction, the precipitate was centrifuged, repeatedly washed with distilled water, and dried under

vacuum. Finally, using a permanent magnet the cobalt-filled carbon nanoparticles can be easily separated from the products. The X-ray diffraction patterns were recorded by employing a Rigaku X-ray diffractometer (Model-2028, Cu K α). Samples were also analyzed on a JEOL JEM-1220 transmission electron microscope (TEM).

The X-ray diffraction patterns (Fig. 1) shows that the samples contain small amounts of Co, even after their long-time treatment with concentrated HCl (Fig. 1b). This implies that Co was encapsulated inside the carbon shells. Based on the results of X-ray powder diffraction, we find that encapsulated materials are fcc metallic cobalt (JCPDS 15-806) rather than the stable hexagonal phase. We consider that the walls of nanoflasks and nanotubes hinder the conversion of the fcc Co to the stable hexagonal phase.

Our TEM observations reveal that the majority of the structures are cobalt-filled carbon nanotubes (nanotubes and nanoflasks). The conversion of the Co(CO)₃NO into carbon was approximately 100%. The percentage of the nanoflasks of all the observed TEM structures is approximately 15%. Fig. 2a shows some of these nanoflasks. All of them were filled with Co in the ball part. The approximate inside diameter distribution of the base of the nanoflasks was 50–400 nm, while the inside diameter of the tubular neck of the flasks was approximately 20–80 nm. The number of carbon layers of the nanoflasks was in the range 30–70. For some flasks, the wall at the bottom is slightly thicker than in the neck.

Fig. 2b shows an individual carbon nanoflask, which is almost fully filled with Co. Only a small part near the top is empty. The inset depicts a close-up of the top for this flask. It is found that two caps cover this nanoflask. One is an inner cap, which is on the end of nanowires and covers the tip tightly. The other is an outer cap that covers the tube end at the top of the flask. Only some of the nanoflasks have inner caps. When the as-prepared sample is further treated with H₂SO₄ and H₂O₂ solution under ultrasonic irradiation for two hours, some of the

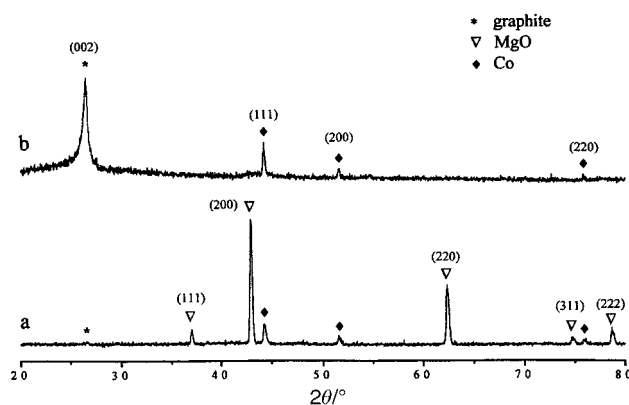


Fig. 1 X-Ray diffraction patterns of the samples: (a) as-prepared; (b) after treatment with concentrated HCl.

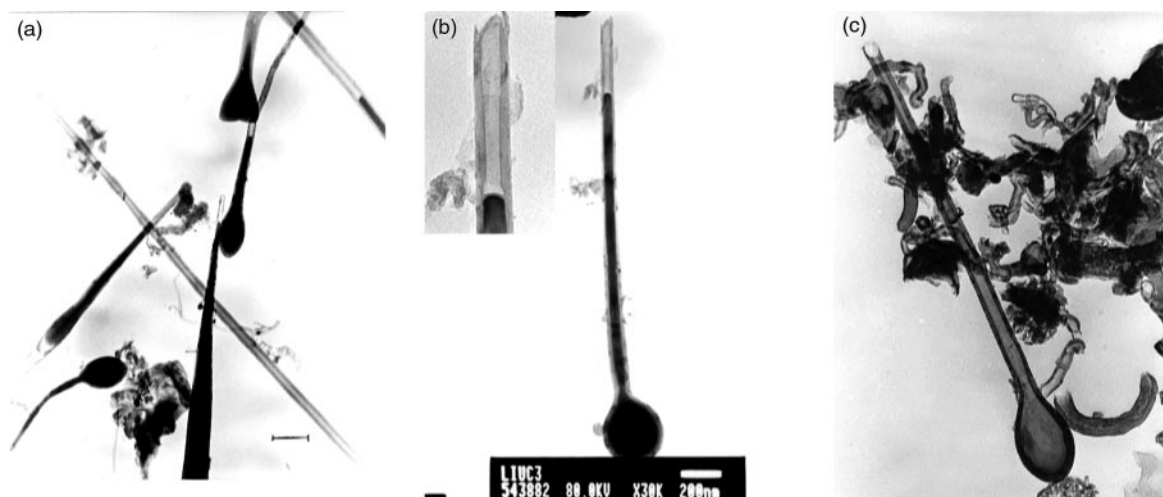


Fig. 2 TEM images of carbon nanoflasks. (a) Carbon nanoflasks filled with metallic cobalt. Scale bar 500 nm. (b) An individual carbon nanoflask filled with Co. Inset is a close-up of the top part of this flask. Scale bar 200 nm. (c) An empty nanoflask which was formed after treatment with H_2SO_4 and H_2O_2 solution under ultrasonic irradiation.

flask caps are removed. The bodies of the nanoflasks still seem perfect. After this process most flasks are empty. Fig. 2c shows an empty nanoflask whose top is apparently opened. This figure shows many fragments of nanotubes, which are the result of damage from the H_2SO_4 and H_2O_2 treatment. The nanoflasks that sustained the sonication and remained intact might be firm nanovessels. Considering that the caps of the nanoflasks react first, both the strain at the cap and the presence of C_5 rings might help to initiate the oxidation process. The degree of curvature, *e.g.* the strain, between the caps and bodies of the nanoflasks is different. So although C_5 rings might play a role, strain must be the key factor in the onset of oxidation at the top of the nanoflasks.

To explain the observation of both flasks and nanotubes in these experiments the following model is proposed. The decomposition of the gas phase cobalt precursor occurs at the elevated temperature. It leads to the formation of a small nanoparticle of cobalt. Small cobalt clusters must either coagulate with other cobalt clusters or interact with initial carbon atoms to reduce their energy. This cobalt cluster serves as a nucleation center for the carbon, which is formed by the reduction of the CO residue by the magnesium atoms. When this process occurs, the growth proceeds by the addition of carbon as atoms, chains and rings.¹⁸ The formation of the filled nanoflasks happens because the cobalt clusters coagulate very fast at the beginning. However, midway through the process the coagulation is slowed down and the carbon wraps most of the base. At this moment, only a slight edge of the cobalt cluster that is not wrapped by carbon protrudes from the coated particle, so that when the cobalt is further deposited, it causes a wire to grow in one dimension. The carbon follows the wire, and the tube continues growing onto the base along the cylindrical axis. To form a nanotube neck seems to require a suitable diameter of catalytic particles. Only when the diameter is smaller than a certain value, can the nanotube necks be formed. In our case, the diameter of cobalt nanowires in the necks is smaller than 80 nm.

A method by which MWCNT are prepared is described in this manuscript. In addition to obtaining empty MWCNT and cobalt-filled MWCNT, carbon flasks filled with cobalt were also detected. These nanoflasks might be useful nanoelements due to their large base, which makes it easy to manipulate them.

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