Synthesis of Carbon Nanomaterials by a Catalytic Disproportionation of Carbon Monoxide

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ABSTRACT

Low-temperature synthesis of multi-walled carbon nanofibers and nanocapsules using catalytic disproportionation of carbon monoxide is reported. The reaction products were studied by TEM, HRTEM, and...
XRD. In addition, we demonstrate that hot isostatic pressing of our carbon nanopowder furnishes a promising route for the controlled fabrication of novel graphite-like materials reinforced with multi-walled carbon nanofibers and nanocapsules.

INTRODUCTION

It has been known for over a century that in the presence of metals of the iron subgroup (Fe, Ni, Co) carbon monoxide (CO) may be catalytically decomposed forming solid carbon though the reaction:\[^{[1]}\]

\[
2\text{CO}_\text{(g)} \leftrightarrow \text{C}_\text{(s)} + \text{CO}_2\text{(g)} \tag{1}
\]

In 1952 Radushkevich and Luk’yanovich\[^{[2]}\] characterized a structure of carbon products of the reaction by transmission electron microscopy (TEM) and found that carbon particles have a hollow “elongated wormlike shape” with the catalyst particles at one end. In 1982 Nesterenko et al.\[^{[3]}\] using TEM and x-ray diffractometry (XRD) analysis suggested that the reaction products are carbon multi-layer tubular crystals formed by rolling graphene layers into independent cylinders. Furthermore, the authors speculated that in such rolling many different arrangements of graphene hexagonal nets are possible and suggested two particular structures: circular (an armchair tube) and helical (a chiral tube).

After the discovery of fullerenes\[^{[4]}\] and high resolution transmission electron microscopy (HRTEM) demonstration of structure of multi-walled carbon nanotubes (MWCNTs)\[^{[5]}\] and single-wall carbon nanotubes (SWCNTs)\[^{[6,7]}\] a serious research attention has been paid to the synthesis and characterization of MWCNTs and SWCNTs. In particular, SWCNT synthesis was demonstrated using reaction (1) at high temperature (up to 1,200°C) and high CO pressure (HiPco technology).\[^{[8,9]}\]

This paper presents mass-production, low-temperature synthesis of carbon nanomaterials through reaction (1) (LowTco technology) and detailed structural characterization of the reaction products. We also discuss a possibility of fabricating graphite-like materials reinforced with nanofibers and nanocapsules by hot isostatic pressing of the LowTco products.

EXPERIMENTAL DETAILS

Microcrystalline powders of metal oxides were placed in a Cu crucible and heated up to 400–600°C in (CO + H₂) gas floating through a quartz
tube reactor at a rate of 0.5 l/min. Particularly, the initial oxide materials were powders of Fe\textsubscript{2}O\textsubscript{3} and NiO of a specific surface area of 15 and 4.3 m\textsuperscript{2}/g, respectively. Structure of the synthesized materials was studied by TEM, HRTEM, XRD, and atomic force microscopy (AFM). Vickers hardness was measured using a Nano Indenter-II (MTS Systems Corporation).

RESULTS AND DISCUSSION

Structure of Main Nanocarbon Products of LowTco

Carbon nanoparticles grown at the surfaces of the initial porous catalyst sample and collected in the crucible were revealed to be a mixture of nanofilaments with an empty core and onion-like capsules (Fig. 1). All of them contain encapsulated catalyst inclusions and thus exhibit ferromagnetic properties. Diameter and length of the filaments are of 10–70 nm and 0.5–100 \(\mu\)m, respectively. The outer diameter of the onions are varied from 10 to 100 nm.

HRTEM clearly shows a layered structure of the filaments (Fig. 2). Many regions with graphite basal planes parallel to each other but not parallel to the central axis of the filament are in evidence. This structure is characteristic for multi-walled carbon nano-filaments (MWCNFs)\textsuperscript{[10,11]} and contrary to the arrangement of MWCNTs with zero-angle between the graphite basal planes and the central axis [such regions are also marked in Fig. 2(a)]. Formation of MWCNF structure may be attributed to presence of hydrogen in the reactive zone of CO disproportionation.\textsuperscript{[10,11]} Positive aspects of the defective MWCNF structure are discussed next.

Carbon-Encapsulated Magnetic Nanoparticles

Carbon nanotubes produced by various catalytic methods are known to be decorated by catalyst metal particles and quasi-spherical carbon nanocapsules with a catalyst metal core.\textsuperscript{[1]} Carbon particles of all shapes (tubular and spherical) and sizes are collected all together and their separation constitutes a serious technological challenge and certainly will increase final prices of carbon nanotubes and nanopsheres. Here we report the serendipitous discovery of the fact that in the LowTco process, with Fe\textsubscript{2}O\textsubscript{3} initial oxide powder, quasi-spherical highly crystalline magnetic\textsuperscript{[12]} nanoparticles can be effectively synthesized as a side-product of MWCNF synthesis and collected separately from the other products of the reaction. In particular, we revealed an extensive deposition of nanoparticles onto cooled parts of a quartz reactor on both left and right sides from the reaction zone.
Figure 1. TEM (a) and AFM (b) images of carbon nanoparticles produced by LowTco.
Figure 2. HRTEM images of multi-walled carbon nano-filaments.

(a) MWCNT
(b) MWCNF

Figure 2. HRTEM images of multi-walled carbon nano-filaments.
XRD pattern for this deposited material (Fig. 3) was found to include reflections from polycrystalline magnetite (Fe$_3$O$_4$) together with [0002] graphite peak from the carbon shells (see later). So, this material is mostly Fe$_3$O$_4$. HRTEM revealed that the material consists of quasi-spherical nanoparticles with a diameter of 5–30 nm, some of which are encapsulated by 1–2 carbon shells [Fig. 4(a)]. Lattice imaging demonstrated defect-free crystalline structure of the nanoparticles [Fig. 4(a) and (b)]. Selective area electron diffraction (SAED) supports the conclusion that every such nanoparticle is a Fe$_3$O$_4$ single nanocrystal. Energy dispersive spectrum (EDS) analysis confirmed presence of iron, oxygen, and carbon.

We may explain the results assuming that the following processes occur under the experimental conditions. In the presence of CO initial Fe$_2$O$_3$, placed in a Cu crucible in a hot zone of the reactor, is reduced successively to Fe$_3$O$_4$ and Fe:

$$3\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2 \quad (2)$$
$$\text{Fe}_3\text{O}_4 + 4\text{CO} \rightarrow 3\text{Fe} + 4\text{CO}_2 \quad (3)$$

Some of the Fe$_3$O$_4$ and Fe clusters continue to stay in the reaction zone and catalytically contribute to the synthesis of nanostructured carbon through reaction (1). This leads to a volume increase and subsequent disintegration of the initial oxide sample. The latter in turn results in the formation

![Figure 3. XRD pattern for nanoparticles deposited onto cooled parts of LowTco quartz reactor.](image)
Figure 4. HRTEM images of nanoparticles: carbon-encapsulated (a) and uncovered (b) Fe₃O₄ particles deposited onto cooled parts of LowTco quartz reactor; Fe₅C₂@C core-shell particles produced by LowTco with Fe₃O₄ nanoparticles as initial catalysts (c).

(continued)
of new catalytically active surfaces at which this scenario repeats until all of the surfaces are covered by the nanostructured carbon. At the same time, other Fe₃O₄ clusters are sublimated, vapor transported and then deposited onto the cooled parts of the quartz tube. Movement of aerosol particles with sizes less than 100 nm is known to be governed mostly by diffusion rather than gravitation or aerodynamic principles.⁹¹⁵ Indeed, in our experiment, the aerosol Fe₃O₄ particles was transported from the reaction zone against the temperature and concentration gradients in both directions, i.e., along and even against CO gas flow. During their movement in CO atmosphere the Fe₃O₄ particles could catalytically instigate the formation of encapsulating carbon shells. Apparently, experimental conditions may control the fractions of condensed and sublimed as well as carbon encapsulated [Fig. 4(a)] and uncovered [Fig. 4(b)] Fe₃O₄ particles.

In the next experiment we used Fe₃O₄ deposits as an initial catalyst for the LowTco process. Using the same LowTco conditions as those described previously we have demonstrated the corresponding growth of the MWCNFs and core-shell nanospheres with additional 6–10 concentric graphite-like
quasi-spherical shells [Fig. 4(c)]. XRD patterns of this material (not shown) consist of the pronounced (0 0 0 2) graphite peak from the nanostructured carbon and intensive reflections from the iron carbide (Fe₃C₂).

Some slow peaks of Fe₃O₄ are also in evidence. It means that in this LowTco product iron presents mainly in the form of carbide with trace amounts of Fe₃O₄ (later we refer to this material as Fe₃C₂@C). We can conclude therefore that the change of the initial microcrystalline Fe₂O₃ catalyst powder by the nanocrystalline Fe₃O₄ strongly influences the scenario of the chemical–physical processes occurred under the same LowTco conditions.

Fe₃O₄ nanoparticles produced by the LowTco process form very stable suspensions in toluene, acetone, alcohol, and water. For example, for the suspensions with concentration less than 10 mg/l no change has been observed for 2 years.

**Hot Isostatic Pressing of the LowTco Products**

Fig. 5(a) displays an XRD pattern of the Ni-catalyzed LowTco product that consists only of the nanostructured carbon decorated with Ni nanoparticles. This LowTco product was compressed by hot isostatic pressing (HIP) under 1000 Bar at temperature of 1,150°C during 1.5 hr. The compressed sample is shown by the inset in Fig. 5(b). XRD (Fig. 5) and HRTEM (Fig. 6) characterization of the compressed sample revealed that such structural transformation as graphitization and coagulation of metal particles occur under the HIP conditions. The compressed sample represents very inhomogeneous material that consists of at least three different phases [Fig. 6(a)]: 1—sphere-like carbon grains with diameter of 0.3–1.0 µm; 2—large (~0.1–1.0 mm) inclusions of Ni; 3—small inclusions that are situated mostly near the boundaries between carbon grains.

Lattice imaging [Fig. 6(b and c)] shows that most of carbon grains have a structure of bulk graphite. This statement is confirmed by a predominance of a narrow and intensive [0 0 0 2] peak from bulk graphite in the XRD pattern of the powder obtained from the compressed sample and boiled in HCl for 6 hr (in order to remove metallic contaminations) [Fig. 5(b)].

Temperature of the HIP processing (1150°C) was significantly lower than that is required for a graphitization of bulk samples of pure carbon but the process may be driven by the nano-size origin of the carbon LowTco samples and the presence of Ni nanoparticles. Graphitization was observed at similar temperatures but under extremely high pressure (~1–10 GPa) treatment of C₆₀ and SWCNTs. It is still not clear why the above-mentioned dramatic structural transformation of LowTco MWCNFs occur under such low pressures. We may speculate, however, that the process is stimulated...
Figure 5. XRD pattern of the Ni-catalyzed LowTco products in as-produced state (a) and after hot isostatic pressing (~1000 Bar, 1,150°C, 1.5 hr) and etching in boiling HCl during 6 hr. (b) The inset shows a splinter of the compressed sample.
Figure 6. HRTEM images of the compressed sample: (a) sphere-like carbon grains (1), large (~0.1–1 mm) inclusions of Ni (2), small Ni inclusions (3); (b and c) lattice imaging of carbon grains; (d) giant carbon nanocapsule; (e) lattice imaging of carbon shells for the nanocapsule shown in (d).

(continued)
by a fishbone structure of our MWCNFs, which is unstable without hydrogen stabilization.\cite{10,11}

Nanoindentation measurements demonstrated that hardness in the compressed sample strongly depends on the number of Ni inclusions in the measured area. However, even for the carbon grains completely free of

**Figure 6.** Continued.

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Nanoindentation measurements demonstrated that hardness in the compressed sample strongly depends on the number of Ni inclusions in the measured area. However, even for the carbon grains completely free of
inclusions, the recorded hardness values (0.7–1.0 GPa) were significantly higher than those for graphite.\cite{14} Furthermore, our compressed LowTco-HIP sample was shown to exhibit viscoelastic behavior that is not characteristic for graphite. Although the details of these nanoindentation measurements will be published elsewhere, we suppose here that these results are attributed to the fact that some of the graphitic grains in the compressed sample are reinforced by MWCNFs [Fig. 6(c)] and carbon nanocapsules [Fig. 6(d) and (e)]. Properties of the compressed materials would be controlled by the ratio of graphitic and nanocarbon faces. It is evident that in order to fabricate graphite-like materials reinforced with MWCNFs and nanocapsules, further research aimed to an optimization of such ratio by the control of HIP conditions is required.

**CONCLUSIONS**

LowTco technology for mass production of MWCNFs and carbon nanocapsules by low-temperature catalytic disproportionation of carbon monoxide has been developed. Carbon-encapsulated and uncovered nanoparticles of single-crystalline Fe$_3$O$_4$ have been revealed to be deposited at the reactor sites spatially separated from the sites of deposition of the other LowTco products. Hot isostatic pressing of the other LowTco products at relatively low values of pressure furnishes a promising route for the controlled fabrication of novel graphite-like materials reinforced with MWCNFs and nanocapsules.

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Polymerization of single-wall carbon nanotubes under high pressures and