In summary, we reported a catalytic method for production of giant fullerene cages ranging generally from C_{1140} to C_{4570} with a single- or a double-wall structure. This was achieved by heat treatment of amorphous carbon containing uniformly distributed Fe nanoparticles at low temperatures of 1000–1350 °C. We anticipate that our study might be a starting point for catalytic synthesis of giant fullerene cages and induce investigations of this sort of material in wide areas such as information technology, diagnostics, pharmaceuticals, environmental and energy industries.

Acknowledgement

We appreciate the Outstanding Youth Fund from The National Natural Science Foundation of China.

References


Spontaneous charging of single-walled carbon nanotubes in the gas phase

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Received 6 April 2006; accepted 7 April 2006
Available online 19 May 2006

The discovery of the spontaneous charging of single-walled carbon nanotubes (CNTs) during their aerosol (floating catalyst) synthesis is reported. The charging phenomenon was surprisingly correlated to the process of the CNT bundle formation in the gas phase, while individual tubes remained electrically neutral.

CNTs were synthesized using two different methods described in detail elsewhere [1,2]. In the first method, ferrocene was vaporized by passing room temperature CO (with a flow rate of 300 cm³/min) through a cartridge filled with ferrocene powder [1]. The flow containing ferrocene vapor (0.7 Pa) was introduced into the high temperature zone of the ceramic tube reactor through a water-cooling probe and mixed with an additional CO flow (100 cm³/min).

In the hot wire generator (HWG) method for the synthesis of CNTs, Fe particles were produced from a resistively heated catalyst wire in a H₂/Ar (with a 7/93 mol ratio) flow (400 cm³/min) and, subsequently, introduced into a ceramic tubular reactor, mixed with a carbon monoxide (CO) flow of 400 cm³/min, and heated to induce CNT formation [2]. Additionally, 12 cm³/min of CO₂ was introduced into
the reactor as an etching agent to maintain the conditions for the growth of CNTs [3]. Experiments were carried out at reactor temperatures from 700 °C to 900 °C. The aerosol product was collected downstream of the reactor on a holey carbon coated copper grid, using an electrostatic precipitator, for transmission electron microscopy (TEM) observations.

In order to determine the charging of CNTs in the gas phase, we used a differential mobility analyzer (DMA) [1]. A DMA is a standard tool in the field of aerosol science for the determination of the electrical mobility distribution of charged aerosol particles [4]. Commonly, for the DMA measurements, a radioactive bipolar charger is used for the artificial charging of the aerosol. However, we have observed that the CNTs synthesized in both ferrocene and HWG systems were naturally electrically charged. In order to remove the charged CNT fraction from the gas phase, we used a 10 cm long electrostatic filter (ESF) with an electric field of 4000 V/cm. Aerosol size distribution measurements of charged and non-charged CNTs showed that almost all the CNTs (up to 99%) coming from the reactor were charged (Table 1). Furthermore, CNTs were found to be charged both positively and negatively. Importantly, TEM observations of the CNTs produced in the ferrocene

(Fig. 1a and b) and HWG (Fig. 1c and d) systems showed that the nanotubes were single-walled and clearly aggregated in bundles.

From the experimental results, it can be speculated that the charging phenomenon is directly correlated to the process of formation of bundles. In order to examine this hypothesis, we collected neutral CNTs produced in the HWG reactor by filtering out charged nanotubes at the reactor outlet by using the ESF. Experimental conditions were selected to maintain a small concentration of CNTs and, thereby, to minimize their bundling. This was accom-

![Fig. 1. TEM images of the as-grown CNT bundles in the (a, b) ferrocene and (c, d) HWG systems.](image-url)
achieved by reducing the heating power applied to the wire, which, in turn, results in lowering the concentration of the introduced catalyst clusters and, subsequently, CNTs grown in the gas phase. Surprisingly, TEM observation of the electrically neutral CNTs revealed the presence of only individual CNTs (Fig. 2a and b).

Analysis of possible mechanisms for the charging of CNTs revealed that the observed phenomenon might be explained by the van der Waals energy release during the bundling process. For instance, the bundling of two armchair (10,10) nanotubes leads to an energy decrease as high as about 1 eV/nm [5]. Considering that the average length of our bundles is around 100 nm, bundling is expected to result in a very high energy release. Thus, the bundle can become charged due to the emission of electrons and ions [6] via dissipation of the released van der Waals energy.

In summary, the spontaneous charging of single-walled CNTs synthesized using aerosol (floating catalyst) methods was observed. Bundles of CNTs were found to be naturally positively and negatively charged. Individual nanotubes were observed to be neutral. The origin of this phenomenon is believed to be due to the high energy release during the CNT bundle formation. It is worth noting that the discovered charging phenomenon can be used in applications requiring the presence of charged CNTs. In addition, the charging effect can be used for the separation of individual CNTs from bundles in the gas phase. Further, the extracted individual CNTs can be collected at ambient temperature on any type of substrate, including temperature-sensitive substrates, to be integrated into silicon-based electronics as well as into the rapidly developing area of flexible electronics.

Acknowledgements

This work was supported by the Academy of Finland and the European Community Research Training Network “Nanocluster” (Grant No. HPRN-CT-2002-00328). One of the authors (S.D.S.) acknowledges the European Commission for its financial support through a Marie Curie Individual Fellowship (No. MIF1-CT-2005-022110).

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