Charging of Aerosol Products during Ferrocene Vapor Decomposition in N₂ and CO Atmospheres

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Received: December 16, 2007; In Final Form: February 12, 2008

Decomposition of ferrocene vapor in CO and N₂ atmospheres in the temperature range from 800 to 1150 °C leading to the formation of single-walled carbon nanotubes (CNTs) and maghemite (γ-Fe₂O₃) particles, respectively, was investigated by means of a differential mobility analyzer (DMA) and Fourier transform infrared spectroscopy, transmission electron microscopy, and laser desorption ionization time-of-flight spectrometry. This allowed us to produce aggregated iron oxide particles with mobility diameters of 20–60 nm and bundles of single-walled CNTs with mobility diameters of 60–100 nm. The DMA measurements of iron oxide particles revealed an equal negative and positive natural single charging with similar bimodal size distributions. Increasing the temperature resulted in the increase of the total particle concentration and a slight decrease in the fraction of charged particles from 30% to 20%. It was found that CNTs form spontaneously charged (92–99%) bundles carrying up to five elementary electrical charges. The concentration ratio between positively and negatively charged CNTs decreased from 6 to 1, increasing the temperature in the system from 800 to 1150 °C. The charging phenomenon can be explained by electron and ion emission owing to the surface minimization processes in both particles and CNTs, resulting in high-energy release.

Introduction

Carbon nanotubes (CNTs) in general and single-walled CNTs in particular have recently caused tremendous scientific interest owing to their remarkable and intriguing properties. A few different techniques, such as carbon arc discharge, laser ablation, and chemical vapor deposition (CVD), were successfully utilized to synthesize this material in the lab scale quantity. The CVD process, and especially the aerosol (catalyst floating) CVD technique, is one of the most powerful methods for the development of a high-yield synthesis at controlled conditions (e.g., HiPco process and other techniques). Additionally, this method enables continuous production of relatively clean CNTs compared with physical techniques, thus eliminating the need for chemical purification of the produced CNTs.

Recently, we have reported a method for the synthesis of high-purity single-walled CNTs based on the ferrocene vapor decomposition in the atmosphere of carbon monoxide. This method allowed us to synthesize a novel carbon material, NanoBuds, where single-walled CNTs and fullerenes were combined in a single hybrid structure. In spite of the successful utilization of the experimental ferrocene–CO system, there are still many uncertainties clouding our understanding of nucleation, growth, and post-growth behavior of CNTs. Our previous investigations of this system, together with another aerosol synthesis method based on the introduction of catalyst particles generated by a hot wire, allowed us to discover the phenomenon of spontaneous CNT charging in the gas phase. The charging process was clearly correlated with the bundling of CNTs; i.e., it was found that post-growth processes played a very important role in the morphology of the collected CNTs. Consequently, we elaborated a method for the room temperature deposition of individual CNTs onto any substrate, which can present an interesting nanotechnological application, for instance, in manufacturing individual tube electronic devices, such as single-electron and field effect transistors and memory devices.

This paper is devoted to investigation of the growth of CNTs in the presence of carbon monoxide and iron-containing particles in a nitrogen atmosphere on the basis of aerosol measurements together with transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, and laser desorption ionization time-of-flight (LDI-TOF). The post-growth process mechanisms of charging of CNTs and particles have been thoroughly examined.

Experimental Methods

Description of Experimental Setup. The reactor for the investigations of single-walled CNT and iron-based particle formation utilized in this work has been described in detail elsewhere. It consisted of a reactor and catalyst precursor feed and sample collecting systems (Figure 1). For the reactor, a ceramic tube with internal diameter of 22 mm inserted inside a furnace was used. Ferrocene was vaporized by passing room temperature gas with a flow rate of 300 cm³/min through a cartridge filled with ferrocene powder. 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 gas flow (100 cm$^3$/min). In order to produce CNTs or iron-based particles, either CO or N$_2$ was used as a carrier gas in the reactor. The reactor was maintained at set temperatures of 800, 1000, and 1150 °C. It is worth noting that the maximum temperature in the reactor was about 50 °C higher than the set temperature determined on the basis of thermocouple measurements inside the reactor.

For the aerosol measurements of the product coming from the reactor, we utilized a dilutor with a flow rate of 12 L/min of ambient temperature N$_2$. An electrostatic filter (ESF) located downstream of the reactor enabled us to filter out all charged aerosol particles from the gas phase by applying an electric field. It comprised two metallic plates with dimensions of 15 cm in length and 1.5 cm in width separated from each other by a distance of 1 cm. Electric field was created by connecting one of the plates to high voltage (4 kV) while the other one was kept grounded. Two different DMA measurement systems were utilized in the aerosol experiments. The first DMA system consisted of a modified Hauke DMA classifier with length 11 cm and a TSI 3027 ultrafine condensation particle counter (CPC). Sample flow rate of 0.3 L/min and sheath flow rate of 12 L/min (N$_2$) allowed measurements in the range 3–200 nm. The second DMA system consisted of a TSI 3081 DMA coupled with a TSI 3022 CPC. The sample flow rate of 0.3 L/min and sheath flow rate of 6 L/min of air allowed us to do the measurements in the range 10–400 nm.

The mobility diameter, $D$, was calculated assuming a spherical shape and a single charge of aerosol particles on the basis of the Millikan equation.

Usually, for DMA measurements, a radioactive charger is used for the charging of the aerosol particles. In our case, the aerosol products coming from the reactor were partially naturally charged. We have therefore presented our aerosol mobility size measurements in two different ways: as distributions and spectra. The mobility size distributions were measured by passing the aerosol containing flow through a radioactive charger, and then a typical inversion procedure was performed to calculate the real aerosol concentration assuming equilibrium charging in the charger.

The spectra data, in which the concentration of the naturally charged aerosol was not subjected to the inversion procedure, were obtained without the charger.

The aerosol product was collected downstream of the reactor (commonly without using diluter) on TEM grids by an electrostatic precipitator and was investigated with a field emission gun transmission electron microscope (TEM, Philips CM200 FEG). On-line measurements of the gaseous composition were carried out by a Gasmet FT-IR gas analyzer. LDI-TOF measurements were carried out with a Voyager-D STR MALDI-TOF mass spectrometer. For this purpose, CNT samples were collected on a silver filter as a powder and transferred to LDI-TOF steel sample substrate.

**Ferrocene Decomposition in CO Atmosphere.** Investigations of the ferrocene vapor decomposition leading to the CNT formation were carried out at 800, 1000, and 1150 °C in the CO atmosphere. TEM observation of the product synthesized at these temperatures revealed that it consisted of bundled single-walled CNTs.

The fraction of charged CNTs was determined on the basis of DMA size mobility measurements using a $^{85}$Kr charger (Figure 2a,c,e). Electrically neutral and all (neutral and charged) aerosol CNTs were measured after the ESF, where potential was or was not respectively applied. As can be calculated from Figure 2a,c,e, the concentration of charged CNTs is very high (92% at 800 °C; 99% at 1000 °C; 98% at 1150 °C). In order to examine the morphology of the noncharged fraction of aerosol, we collected the product onto TEM grids. TEM observation of the collected noncharged fraction revealed that it consisted of a mixture of bundles and inactive catalyst and carbon aggregated particles.

The mobility size spectra of naturally charged CNTs produced at different temperatures are presented in Figure 2b,d,f. At the temperature of 800 °C the concentration of negatively charged ions is about 6 times higher than that of positive CNTs. Increasing the reactor temperature to 1000 °C resulted in the increase of the fraction of positively charged CNTs: the difference decreased to the factor of 2. At 1150 °C, the spectra of both negative and positive polarities were very similar.

In order to study the charging state of the naturally charged CNTs, tandem DMA measurements were carried out. For this purpose, the first DMA was used to extract fractions of 80, 100, or 130 nm mobility-sized CNTs, which were then introduced into the second TSI DMA via a $^{85}$Kr charger. The standard geometric deviation of individual ions ($\sigma_g = 1.08$) was determined on the basis of tandem DMA measurements without the chargers in prior to both DMAs (Figure 3a). The results of the Gaussian function fittings with the measured standard geometric deviation showed that the CNTs possessed from 1 to 5 elementary charges (Figure 3b–d). Also, at least three additional experimental facts can be stated on the basis of the analysis of the tandem measurement results: (i) small mobility diameter CNTs possess higher charge state; (ii) the larger mobility size, the more charging occurs in the charger; (iii) the smaller the size, the more effective the ion discharge in the charger. All these facts are evidence of the nonequilibrium charging of CNTs. According to the equilibrium charge distribution, only 50% of 80 nm sized particles possess a single charge and about 4% can carry two charges, and the fraction of particles with three or more charges is negligibly small.
In order to examine the nature of ions that can be emitted from the CNTs and can be responsible for the CNT ionization, we carried out LDI-TOF measurements of the CNT samples placed on an LDI substrate without any matrix and solvent. During the measurements, the power of the laser was varied from 0 to 3500 arbitrary units. It was found that positively charged ions started to be detected at the power of about 2900 units (Figure 4a). There are three strong peaks at \( m/z = 91.07, 119, \) and 149 amu, which can be designated as \( \text{C}_6\text{OH}_3^+ \), \( \text{C}_7\text{O}_2\text{H}_3^+ \), and \( \text{C}_9\text{O}_2\text{H}_9^+ \), respectively. Negatively charged ions appeared only at the power as high as 3200 power units, when the process of CNT destruction was already observed (Figure 4b). At the laser power \( \geq 3200 \) units, in both negative and positive modes one can observe the formation of carbon clusters: \( \text{C}_5 (m/z = 60 \text{ amu}), \text{C}_6 (72), \text{C}_7 (84), \text{C}_8 (96), \text{C}_9 (108), \) and \( \text{C}_{10} (120) \). The ionization of positive ions therefore occurs at much lower laser power, while no negative ions were detected before the CNT destruction happened.

**Ferrocene Decomposition in N\(_2\) Atmosphere.** The formation of particles was examined by replacing CO by \( \text{N}_2 \). The mobility spectra of charged particles were measured without charger; therefore, the inversion procedure was not applied to these data (Figure 5a). As we can see from the figure, positively and negatively charged particle distributions are very similar. The mobility spectra are bimodal in nature with peaks at about 20 and 60 nm. TEM observations of the collected particles with

![Figure 2](image_url)

**Figure 2.** Number size distributions of all and noncharged fraction of CNTs at (a) 800, (c) 1000, and (e) 1150 °C. Mobility spectra of negatively and positively naturally charged CNTs at (b) 800, (d) 1000, and (f) 1150 °C.
selected mobility sizes of 20 and 60 nm (Figure 6a,b) showed that the particles were crystalline, clearly aggregated, and can be easily distinguished by a different degree of agglomeration: the larger the particles, the higher the aggregation. The 20 nm sized particles look like clusters consisting of about 10 nm sized primary particles, while many 60 nm particles are completely sintered into one particle. Estimations of the number of charges indicate that the charged particles typically possess only one elementary charge.

The number size distribution of neutral particles was measured after filtering out the charged fraction of the particles (ESF on) and calculated assuming an equilibrium charging (Figure 5b). Interestingly, the distributions of neutral particles are unimodal with the mean diameter of 20 nm. Comparing parts a and b of Figure 5, one can calculate that the catalyst particles are partially charged (30% at 800 °C and 20% at 1150 °C).

Surprisingly, our TEM crystallographic investigations (Figure 6c,d) revealed that the particles formed during the ferrocene vapor decomposition in an inert nitrogen atmosphere had maghemite (γ-Fe₂O₃) crystalline phase. The observed particles were freshly prepared and exposed to the ambient conditions only for 5–10 min to carry the sample from the reactor to the TEM. The possibility of the formation of crystalline oxide particles at ambient conditions can therefore be excluded. Figure 6d shows experimental and simulated electron diffraction patterns revealing γ-Fe₂O₃ crystallinity of the particles. Apparently, the reason for the formation of the maghemite particles was oxygen-containing impurities in nitrogen carrier gas. It is known that even high-purity gas carriers might contain impurities such as O₂, H₂O, and CO₂ at a level of a few parts per million (ppm). Those impurities can play a very important role in the formation of the product and also in post-growth processes, including charging. We therefore performed on-line FT-IR measurements of the gaseous products coming from the reactor to analyze their chemical composition. We also studied the maturity of the ferrocene decomposition reaction on the basis of the FT-IR measurements and carried out on-line CPC and DMA monitoring of the concentration of aerosol particles at the outlet of the reactor. During the experiments the reactor was heated with an interval of 50 °C every 30 min at a rate of 10 °C/min.

Even though the ferrocene concentration was close to the FT-IR detection limit (around 1 ppm) from Figure 7, one can see that ferrocene decomposition starts at about 300 °C and occurs nearly completely at 650 °C. Similar behavior was obtained for the aerosol concentration coming from the reactor. The main gaseous products coming from the reactor during ferrocene decomposition in N₂ atmosphere are CO₂ and H₂O. One can estimate that the level of oxygen impurities was around 80 ppm, which is an order of magnitude higher than the total iron concentration in the reactor and would explain the formation of iron oxide particles in a nitrogen atmosphere.

Discussion
Experimental results showed that iron oxide particles partially and CNTs almost completely were charged at the outlet of the reactor. Let us examine possible reasons for the observed self-charging phenomenon. In general, the natural charging of aerosol particles according to the energy input needed for the ionization can be divided into chemical and physical ionizations.29–34
According to the chemical ionization model, the particles are charged by emission of ions and electrons under high-energy release of chemical reactions on the surface of particles. In consequence, it can be speculated that exothermic reactions of ferrocene decomposition or CO disproportionation might be responsible for the electrical charging. Most likely ferrocene and its fragment decomposition reactions do not dominantly affect the charging, since the charging state of particles and CNTs is not equivalent. Also, our previous experimental results gave evidence that CO disproportionation reaction is not directly involved in the charging process.

We believe that the observed self-charging phenomenon originates from the physical ionization. In principle, this type of ionization can take place in different processes such as collisions of particles or particle aggregation leading to energy release owing to the minimization of the surface energy. At high temperatures another possible origin for the charging is an excess of thermal energy, resulting in the emission of ions (atoms/molecules or electrons) from the particle surface. Since the thermal charging efficiency exponentially depends on temperature, this dependence is supposed to be seen in the wide experimental temperature range. Experimental results showed that the total charging efficiency does not depend totally on temperature: charging varied from 92% at 800 °C via 99% at 1000 °C to 98% at 1150 °C. Most likely the thermal charging is not the determinative process in the charging.

Our previous works suggested that the charging of CNTs occurred because of the bundling and van der Waals energy release. For instance, a bundling process of two armchair (10,10) CNTs results in a free energy decrease of as much as 0.95 eV/nm compared with two isolated tubes. This energy can be released owing to the thermal dissipation and emission of ions from the surface of the formed bundle.

Speaking of iron oxide particles, the charging can occur also because of the surface energy minimization during the aggregation process. The charged aggregated particles had a bimodal distribution with a mean diameter of 20 and 60 nm. The 20 nm sized particles are formed by partial sintering of primary particles and as a result have a low-energy release. This can explain why 20 nm catalyst particles are mostly not charged (Figure 5). Even though the total concentration of 60 nm sized particles is lower than that of 20 nm particles, the concentrations of the charged 20 and 60 nm sized particles are the same. This can be interpreted by higher energy release during the sintering and 60 nm sized particle formation.

Simple estimations of the surface energy release during particle aggregation and CNT bundling give very high values of 100–1000 eV. If, however, this energy were evenly spread among all the atoms, the energy release would be only 0.01–0.03 eV/atom. Thus, the energy dissipation should be a slow process to explain the fact that 20–30% of iron oxide particles and up to 99% of CNTs are charged. It is most likely that the energy released during agglomeration or bundling is dissipated via the emission of ions before the system achieves its equilibrium condition.

Another important aspect that should be discussed here is the nature of the emitted ions during CNT bundling. Our previous Raman measurements revealed almost no D-band features in the spectra, verifying the fact that the CNTs are quite clean. In order to explain the charging phenomenon, however,
we have to accept the presence of impurities with low adsorption energy. As was revealed during the LDI-TOF measurements, positively charged ions (with masses of 91.07, 119, and 149 amu) can be emitted from the surface of CNTs at relatively low laser power. Chemically, these ions (C$_6$OH$_3$, C$_7$O$_2$H$_3$, and C$_9$O$_2$H$_9$) can be presented as long chain carbon structures being intermediates in the CNT growth. It is most likely that these ions were responsible for the negative charging of CNTs. Since our ILD-TOF measurements could not detect negative ions emitted from the surface of CNTs under laser irradiation, we believe that the CNT positive charging during the bundling occurs because of the electron emission.

Interestingly, the concentration ratio between positively and negatively charged CNTs decreased from 6 to 1, increasing the temperature in the system from 800 to 1150 °C (Figure 2b,d,f). This can be explained in the framework of the surface minimization mechanism: during the CNT bundling two competing processes for the dissipation of the released energy, emission of either electrons or positive ions takes place. Apparently, at similar conditions the emission source is determined by the availability and amount of species responsible for the emission of positive ions, i.e., unreacted carbon chain species found in the LDI-TOF measurements. Obviously, the

Figure 6. TEM images of nanoparticles with selected mobility diameter of (a) 20 nm and (b) 60 nm. (c) A high-resolution TEM image and (d) experimental and simulated electron diffraction ring patterns from the nanoparticles revealing their maghemite (γ-Fe$_2$O$_3$) crystalline phase.

Figure 7. Results of FT-IR measurements of gaseous species and CPC and DMA measurements of the concentration of aerosol particles coming from the reactor at different temperatures.
relative amount of these incompletely reacted hydrocarbon-containing compounds is higher at lower temperatures, resulting in the privilege emission of positive ions and negative charging of CNT bundles at 800 °C.

Another source of the ion emission that should also be discussed here is the reactor walls, since the walls are covered by the deposited material (CNTs, iron- and carbon-containing particles), and they have a higher specific surface area than the particles and CNTs in the reactor. The leading role of the reactor particles), and they have a higher specific surface area than the particles and CNTs in the reactor. The leading role of the reactor walls will be not be restricted to nonequilibrium charging.

It is important to note that the synthesized iron oxide magnesium (γ-Fe2O3) nanoparticles have many interesting applications in biosciences and medical sciences owing to their biocompatibility, nontoxicity, chemical activity, and magnetic properties. For instance, γ-Fe2O3 particles were found to behave as a room temperature superparamagnetic. The method described here allowed us to produce 20 nm maghemite particles and could easily be optimized for the synthesis of the desired particle size of this superparamagnetic material.

Conclusions

On-line DMA measurements of ferrocene vapor decomposition in carbon monoxide atmosphere revealed the formation of positively and negatively charged (up to 99%) single-walled CNT bundles. Tandem DMA measurements showed nonequilibrium charging of the CNT bundles with 1–5 elementary charges. On the basis of the analysis of the LDI-TOF experimental data, it was proposed that the positive charging of CNTs occurs because of the electron emissions, while negative charging is caused by emission of impurities from the surface of CNTs.

Ferrocene vapor decomposition in nitrogen atmosphere resulted in the formation of maghemite (γ-Fe2O3) phase as a result of the oxidation of iron by the carrier gas oxygen containing impurities. The aerosol measurements of iron oxide particles revealed that 30% at 800 °C and 60% at 1150 °C are electrically charged.

The charging phenomenon of the iron oxide particles and CNTs can be explained in the framework of aggregation processes leading to the energy release owing to the minimization of the surface energy and emission of electrons and positive adsorbing molecules.

Acknowledgment. The authors thank Dr. Gyula Eres for fruitful discussions and Dr. Ulrich Bergmann for his assistance in the LDI-TOF measurements. This work was supported by the Academy of Finland (grant No. 118445). S.D.S. acknowledges the European Commission for financial support through a Marie Curie Individual Fellowship (No. MIFI-CT-2005-022110).

References and Notes

Nasibulin et al.


