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Short communication

Simultaneous purification and spectrophotometric determination of nickel present in as-prepared single-walled carbon nanotubes (SWCNT)

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Abstract

The quality of single-walled nanotubes (SWCNT) is usually assessed by means of electron microscopic techniques or Raman spectroscopy. However, these sophisticated techniques are not widely available and do not reliably estimate the impurities in highly heterogeneous samples containing metal particles, fullerenes and other carbonaceous materials. We have developed a simple, inexpensive and convenient spectrophotometric method to assess the purity of arc-discharge grown as-prepared SWCNT. Purification process consists of initial gas phase oxidation and refluxing with nitric acid at the optimal conditions including short time period during acid refluxing. We have shown that this method could remove the metal particles effectively with a good yield of high quality SWCNTs, as shown by the spectrophotometric and scanning tunneling microscope studies described here. The extent of removal of the nickel present in as-prepared carbon nanotube sample is followed by spectrophotometeric analysis of the dissolved nickel analyte. The composition of nickel in the SWCNT sample is found to be 17.56%. The method is based on the chelating of Ni^{2+} with dimethylglyoxime in ammoniacal citrate medium to form nickel dimethylglyoxime complex. A second stage purification of SWCNT eliminates the residual metal particles. The purified SWCNT has been studied using scanning tunneling microscopy which shows clearly resolved individual carbon nanotubes.

Keywords: Single-walled nanotubes purification; Nickel nanoparticles; Spectrophotometric determination; STM of single-walled nanotubes

1. Introduction

The potential applications of single-walled carbon nanotube (SWCNT) both in basic science and technology originate from its exceptional physical and chemical properties [1,2]. The advanced technological application envisaged for SWCNTs mainly rely on the purity of the material. Most of the presently known techniques for production of SWCNT quote the purity of the sample to be about 10–90%. The as-produced SWCNT (AP-SWCNT) generally contains carbon encapsulated metal particles along with the non-tubular carbon forms (amorphous carbon particle, fullerenes, polyaromatic shells). A measurement of the metal content in as-produced SWCNT samples is important in realizing many of its potential applications. For example, the hydrogen uptake capacity of SWCNT shows a strong dependence on the amount of residual nickel present in nanotube sample [3]. The unusual magnetic properties of SWCNT form the basis of nanoscale electronic devices. Obviously ferromagnetic nickel particles can have a significant influence on the magnetic behavior of CNT. In order to realize the potential applications of the magnetic properties of SWCNTs, the sample under investigation should be either free of nickel particles or should posses a known quantity of the metal. In other words, the efficiency of a purification process on the extent of the removal of nickel has to be monitored carefully.

The arc-discharge method of synthesizing SWCNT is a principal technique used for large-scale economic production of high quality SWCNT. Electric arc-derived AP-SWCNT contains significant amount of metallic impurities, predominantly nickel, which is used as a catalyst in its preparation. Although SEM and TEM methods are regularly used to evaluate the sample purity, these methods become highly unreliable when bulk samples are under investigation. For example, within one SEM frame, the amount of the material that can be seen and analyzed is of the order of a few micrograms and consequently only the materials with high homogeneity can be studied by SEM analysis. A crit-

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ical step involved in TEM studies is the preparation of nanotube dispersion while in Raman and IR spectroscopic measurements, interpretation of the spectral data is rather complex and quantitative estimate of the metal content cannot be obtained [4]. Though thermo gravimetric analysis (TGA) is one of the widely used analytical tools for the determination of the metal content in SWCNT, the complications involved in TGA studies are, exothermic oxidation during the measurements and the dependence of the data on the temperature ramp rate.

In this communication, we report a simple and sensitive spectrophotometric method for the quantitative analysis of catalytic nickel present in as-prepared single-walled carbon nanotubes. The proposed method is a macro scale technique, which may readily be applied to purify several gram quantities of raw product. The purification procedure employed here involves initial gas phase oxidation of SWCNT sample at 350 °C followed by refluxing in HNO_3. There are several methods based on different oxidising temperatures and sequences for gas phase oxidation and acid refluxing that are available in literature [5,6]. In our procedure, the air oxidized SWCNT is subjected to acid refluxing in 6N nitric acid to dissolve metal particles. A long time acid reluxing procedure usually employed attacks the defective sites of nanotube surface, which results in shortening or eventual destruction of SWCNT. We have employed a significantly short time period of 30 min for acid refluxing treatment in 6N nitric acid and we observe that this could effectively dissolve the metal nanoparticles without causing significant structural deformations to SWCNT. Owing to their nanometre size, the metal particles dissolve fast and the development of intense green color after 10 min of heating is indicative of the formation of nickel nitrate.

We have used gas phase purification, acid refluxing and vacuum filtration for separating the SWCNT from the metal impurities. A second stage purification of once purified SWCNT ensures the effectiveness of our purification process and spectrophotometric studies confirm the purity of CNT to be above 99% with respect to metal content. Finally, we have characterized the purified SWCNT by scanning tunneling microscopy.

2. Experimental

2.1. Reagents

All the chemicals used in this study are of analytical grade. The Millipore water with the resistivity of 18 MΩ cm was used throughout the experiments for the preparation of the aqueous solutions. A standard stock solution of nickel (1.7 mM) was prepared by warming the 0.01 g of nickel strip in 6N nitric acid at 60° C for 25 min. The dissolved solution is evaporated to expel any oxides of nitrogen, transferred quantitatively to a 100 ml standard flask after cooling. The dimethylglyoxime reagent is prepared by dissolving 0.5 g of dimethylglyoxime in 250 ml of ammonia solution and diluting to 500 ml with water. A freshly prepared solution of DMG is used in all the experiments as the oxime group tends to get oxidized in air to form furoxane compound. The dilute ammonia solution was prepared by mixing the aqueous ammonia with water in the volume ratio of 1:1.

The SWCNT purchased from Carbolex Inc. (USA) consists of single-walled close-ended carbon nanotubes, prepared by arc-discharge synthesis using nickel and yttrium as catalysts. Though the arc-discharge method of producing SWCNT promises to be a convenient and relatively less expensive one, the pristine nanotube sample is generally associated with the metallic impurities. It is well known that arc-derived CNT is difficult to purify from the metal catalytic particles. There are some procedures described in the literature for the purification of SWCNTs grown by arc-discharge method [7,8].

2.2. Instrumentation

A spectrophotometer model SD 2000 (Ocean Optics, USA) fitted with a tungsten lamp source and a cell having a path length of 1 cm was employed to measure the absorbance spectra and analysis. The pH was measured with a digital hand held pH meter (Hanna Instruments), which is calibrated with a standard buffer solution before each measurement.

A home built scanning tunneling microscope (STM) in high-resolution mode described elsewhere [9] was used to probe the SWCNT dispersed on a highly oriented pyrolytic graphite (HOPG) surface. The STM images were obtained at room temperature in air and the instrument was operated in constant current mode of 1 nA at a sample bias voltage of +100 mV. Higher resolution images were acquired at constant height mode of operation. Prior to these experiments, the instrument was calibrated with highly oriented pyrolytic graphite (HOPG) (ZYA grade, Advanced Ceramic). A mechanically cut tungsten tip was used as the probe. The images shown here were plane corrected and in some cases Fourier filtered using scanning probe image processor (SPIP) software (Image Metrology, Denmark). To ensure that the images shown were representative of the CNT, multiple images were taken at different locations and scan ranges.

The STM studies of both the purified and as-prepared SWCNT samples were carried out. The SWCNT is dispersed in ethanol at a typical concentration of 0.1 mg/ml and a drop of the solution is spread on to a freshly cleaved HOPG substrate and used as a specimen for imaging.

2.3. Procedures

2.3.1. Purification

The 200 mg of raw soot of SWCNT was subjected to air oxidation by heating the sample in air at 350° C for 4 h to oxidize the non-tubular forms of the carbon. The SWCNT sample was then treated with 6N nitric acid under reflux at 60 °C for 30 min in order to dissolve the metal particles. After cooling, the sample was filtered using a cellulose nitrate filter paper with 0.2 μm pore size by applying vacuum suction. A clear green colored supernant acidic solution was collected at the bottom of filtering unit; successive washing with Millipore water removes the substantial amount of trapped acid from the sediment. The SWCNT collected in the filter paper was dried in an oven at 50° C for 30 min. The filtrate obtained was transferred to a 100 ml standard flask and made up to the mark using Millipore water and this solution is used for further spectrophotometric studies.