

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 spectrophotometric 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

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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 to 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 possess 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 critical 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 350⁰C followed by refluxing in HNO₃. 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 refluxing 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 minutes 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 10min 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 $18\text{M}\Omega\text{ cm}$ was used throughout the experiments for the preparation of the aqueous solutions. A standard stock solution of nickel (1.7mM) was prepared by warming the 0.01g 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 100ml standard flask after cooling. The dimethylglyoxime reagent is prepared by dissolving 0.5g of dimethylglyoxime in 250ml of ammonia solution and diluting to 500ml 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 1nA at a sample bias voltage of +100mV. 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 0.1mg/ 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 200mg of raw soot of SWCNT was subjected to air oxidation by heating the sample in air at 350⁰C for 4 hours to oxidize the non-tubular forms of the carbon. The SWCNT sample was then treated with 6N nitric acid under reflux 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 50⁰C for 30 min. The filtrate obtained was transferred to a 100ml standard flask and made up to the mark using Millipore water and this solution is used for further spectrophotometric studies.

2.3.2 Spectrophotometric Analysis

Test for Iron

The presence of the iron in the CNT sample is analyzed by transferring 1ml of test solution to a 25ml graduated flask and the pH was adjusted to 3.5 by the addition of 0.2M sodium acetate. To reduce the Fe (III) species into Fe (II), 10% aqueous solution of hydroquinone was added followed by 2ml of 0.25% of 1,10-phenanthroline. The solution is made up to the mark and allowed to stand for 1hour in order to complete the reaction. No color formation is observed in this case. The absorbance of the sample was measured by a spectrophotometer after running a reagent blank. The absence of characteristic absorption peak in the spectra confirms that the carbon nanotube is free from iron.

Test for Cobalt

A test for cobalt is carried out by the addition of dimethylglyoxime reagent under appropriate conditions. There is no formation of brown colored Co-DMG complex indicating that cobalt metal is not present in the pristine SWCNT material.

Procedure for determination of the Nickel content

1 ml of the test solution was transferred to a 100ml standard flask containing water and shaken well so that the concentration of Ni^{2+} is uniform. On diluting the solution, the homogenously distributed nickel ions become more readily available for binding with the ligand. Since the molecular mass of dimethylglyoxime reagent is very high compared to nickel, it reacts with nickel in the stiochiometric ratio of 1: 2, and therefore a very small quantity of nickel could form a voluminous precipitate. The dilution process also helps in a facile extraction of the complex. Addition of

5g of citric acid to avoid the interference of any trace iron has brought down the pH of the solution from 4.5 to 2.1. The optimum pH of 7.5 for complexing nickel with DMG has been adjusted by the addition of dil. NH_3 . After cooling, it is transferred to a separatory funnel fitted with a Teflon stopcock, followed by the addition of 40ml DMG solution. After allowing it to stand for 3min, 6ml of chloroform was added and shaken well to dissolve the $\text{Ni}(\text{dmg})_2$ complex. The phases are allowed to settle out and the pale yellow colored nickel complex was extracted. Three more extracts in 4ml portions of chloroform were collected and all the extractions were combined. Care has been taken to avoid any viscous film or foam formed between two phases to get into the extractions. The extract is quantitatively transferred into a 25ml standard flask made up to the volume by chloroform. Since we find that the absorbance values increase slowly with time, each absorbance value had been recorded after 10 minutes of mixing. The absorbance of this yellow colored complex was measured in a 1 cm cell at a wavelength of 360 nm exactly after 10min of mixing, with reference to reagent blank.

The aforementioned procedure is employed for a series of standard nickel solutions of nickel concentration in a range of 1 to 20 $\mu\text{g}/\text{ml}$. From the absorbance data recorded by a spectrophotometer, a calibration graph of absorbance of the nickel dimethylglyoxime complex against the concentration of nickel was constructed.

3. Results and discussions

The spectrophotometric procedure developed here is used to determine the amount of nickel in inhomogeneous bulk soot without modifying the

structure of the nanotubes. The proposed method does not consume any specific quantity of the sample because it is an integral part of purification steps. This is due to the fact that the filtrate with metal nitrates obtained during the purification process is used for the analysis. The stability of this test solution, which is used for spectrophotometric analysis, is indicated by its constant pH value (1.41) up to 100 days. When dimethyl glyoxime is used as a sequestering agent, one of the acidic hydrogen in DMG is replaced by one equivalent of Ni^{2+} ion and two molecules of DMG reacts with Ni^{2+} to give red voluminous precipitate. Ammonical citrate medium is employed to prevent the co-precipitation of other ions, which would generally form their hydroxides. Being a bidentate ligand, DMG forms a strong coordinate covalent bond through oxygen and nitrogen atoms. The color intensity of the Ni-DMG complex strongly depends on OH^- ion concentration. The stability of the complex is widely studied in various solvents and optimum pH for chelating is reported to be 7.5. This optimum pH is brought about by the addition of dil. NH_3 solution. The use of dil. NH_3 prevents the formation of crystalline $\text{Ni}(\text{OH})_2$. Under the experimental conditions employed, the absorption spectrum of Ni-DMG complex obtained is as shown in Fig1. The absorption maximum at 360nm characterizes a typical metal to ligand charge transfer (MLCT) spectra which arises from the transition of an electron from one of the orbital of nickel into a π^* orbital of DMG generally represented as $\text{M-L} \rightarrow \text{M}^+ - \text{L}^-$.

3.1 Analytical characteristics

Since the analytical application of spectrophotometry rely on the proportionality between absorbance and concentration , a calibration curve was constructed with the data obtained from spectrophotometric

measurements. Figure 2 shows the calibration graph illustrating the validity of Beer's law up to a concentration of 20 μ g/ml for Ni-DMG complex at 360nm.

A linear regression analysis of the data yields a correlation coefficient of 0.999. The obtained apparent molar absorbance coefficient was $\epsilon = 5.206 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. From the calibration graph the concentration of nickel in the test solution is found to be 14.1 μ g/ml that corresponds to the nickel content of 17.5% in a given CNT sample. Three replicate analysis of the test solution containing the nickel by the aforementioned procedure gave a variation coefficient of $\pm 1\%$.

The above-described procedure was repeated for the second stage purification of already once purified CNT sample. Due to the efficiency of our purification process there is an almost complete removal of metallic impurities. This has been confirmed by the analysis of the filtrate obtained during the second stage purification. From the calibration graph of Figure 3, it can be observed that the test solution containing residual nickel shows an absorbance value corresponding to 1.5 μ g/ml, which constitutes a nickel content of 0.234% in purified SWCNT sample.

The scanning tunneling microscope images of the SWCNT on HOPG surface both before and after purification treatment are shown in Figure 4. The constant current STM image of the sample before purification can be seen to contain tight bundles of SWCNT where the individual nanotubes could be barely resolved as shown in Figure 4 (a). It can also be seen from Figure 4 (b), some clusters of nanoparticles probably encapsulated with carbon is imaged at a different location of the unpurified sample. The sizes of the nanoparticle clusters are about 10 –12 nm. Presumably these clusters

contain several individual nanoparticles. Figures 4(c) and 4 (d) show the STM images of the purified samples at two different scan ranges of (c) 15nm x 15 nm and (d) 6 nm x 6 nm from which individual CNTs can be clearly resolved. The scanning was carried out at a tunneling current of 1 nA and a bias voltage of +100 mV (substrate positive) in the constant height mode of imaging. The 15nm x 15 nm image of Figure 4 (c) shows a bundle of SWCNT in which the individually resolved nanotubes can be clearly seen. The separation of the nanotubes are effected by the acid treatment which also functionalises the nanotubes with carboxylic groups. The diameter of the individual CNT is about 1.4 nm as can be seen from higher resolution image of Figure 4(b). No Ni nanoparticle could be seen on different regions of the scanned surface showing the effectiveness of purification procedure adopted in this work.

Conclusions

We have obtained highly pure SWCNT with minimum structural deformation by following a purification procedure combining air oxidation at 350⁰ C for 4 hours as an initial step and nitric acid refluxing. The optimum conditions to obtain pure and defect-free SWCNT involve acid refluxing for 30 min at 60⁰C. This reproducible procedure also permits the quantitative spectrophotometric analysis of nickel content. The procedure followed for determining the nickel content in a CNT sample is based on simple spectrophotometry, which involves the sequestration of trace amount of nickel in ammoniacal citrate medium. The method employed here is simple and rapid and does not need sophisticated instrumentation facilities. The amount of nickel measured is in good agreement with the amount of the catalytic nickel used during the synthesis of CNT as reported in the

literature. The second stage purification of SWCNT and the subsequent determination of nickel, validate the efficiency of our purification procedure, besides optimizing the conditions employed. Quantitative determination of nickel content in SWCNT sample opens a way for the systematic study of nickel-influenced properties of SWCNT. We have demonstrated the application of this method for the determination of nickel content of up to 0.24% with good reproducibility. We have also shown clearly resolved individual carbon nanotubes on the HOPG surface by the scanning tunneling microscopic studies.

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Legends for the figures

Figure 1

The absorption spectra of dimethylglyoxime complex of Nickel prepared from the filtrate obtained during the purification of SWCNT.

Figure 2

The calibration graph of concentration of nickel vs. absorbance of nickel-dimethylglyoxime complex, illustrating the validity Lambert-Beer's Law.

(a) After first stage purification. The dotted lines correspond to the measured nickel concentration of 14.1 $\mu\text{g/ml}$ in the test solution.

(b) After second stage purification. The dotted lines correspond to the measured nickel concentration of 1.5 $\mu\text{g/ml}$.

Figure 3

Scanning tunneling microscope images of SWCNT on HOPG

(a) and (b) constant current mode images before purification .

(c) and (d) constant height mode images after purification.

The scanning parameters are Tunneling current : 1 nA , Bias voltage : +100 mV (Substrate positive).

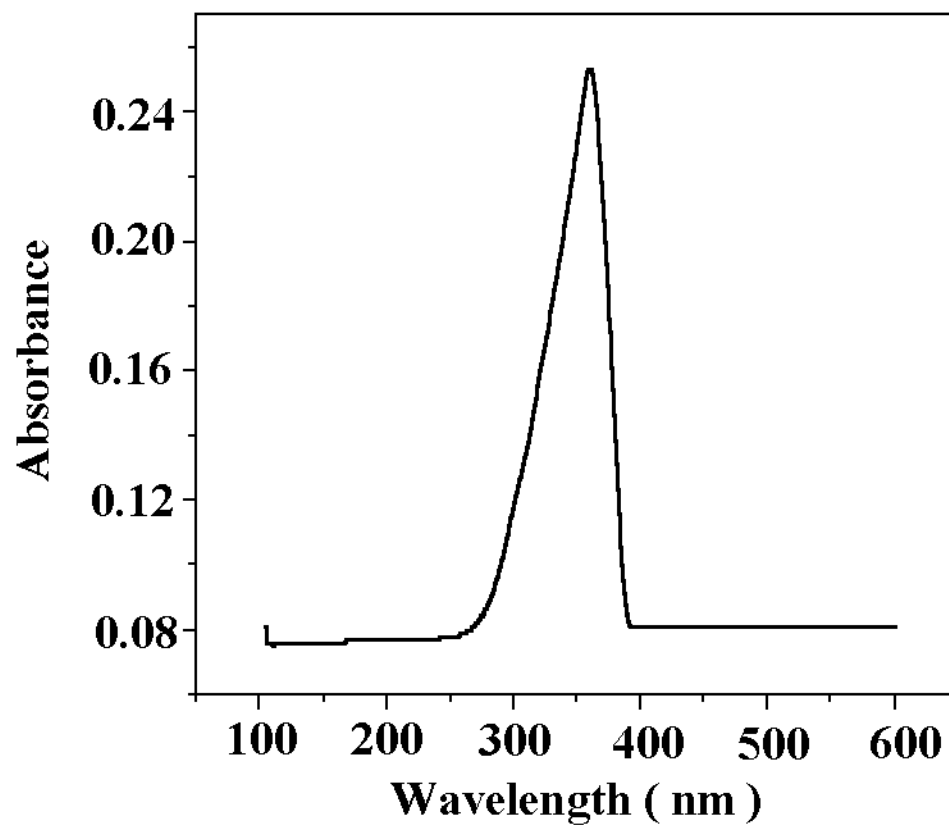


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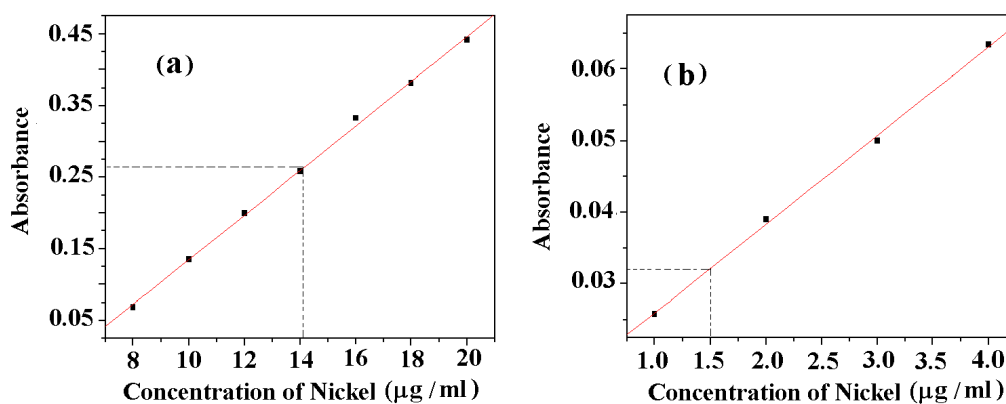


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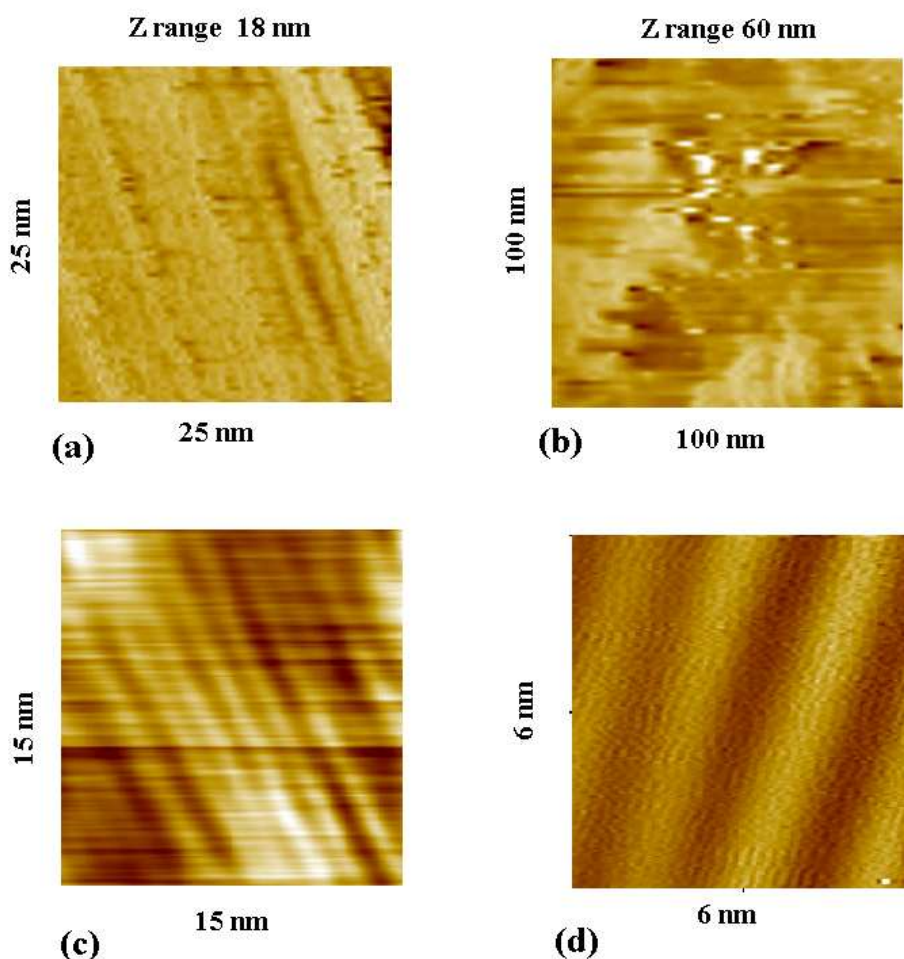


Figure 3

Scanning tunneling microscope images of SWCNT on HOPG

(a) and (b) constant current images before purification at two different scan ranges and different regions of the surface.

(c) and (d) constant height images after purification for two different scan ranges.

The scanning parameters are Tunneling current : 1 nA , Bias voltage : +100 mV (Substrate positive).