



Photochemical vapor generation for removing nickel impurities from carbon nanotubes and its real-time monitoring by atomic fluorescence spectrometry



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ABSTRACT

A new method was proposed to remove trace nickel catalyst impurities from carbon nanotube (CNT) materials by the use of UV-induced photochemical carbonyl generation, and the process was real-time monitored by atomic fluorescence spectrometry. The CNTs were purified under mild optimal experimental conditions, and the characteristics of the purified CNTs were kept well. After purification, the content of nickel in the CNT materials was reduced from 1% to 0.4%, with a removal efficiency of 60%. The produced volatile nickel carbonyl was separated and introduced into an argon/hydrogen flame atomizer-atomic fluorescence spectrometer for measuring nickel atomic fluorescence signal to real-time monitor the purification process.

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1. Introduction

With their exceptional physical, chemical, electrical, and mechanical properties, carbon nanotubes (CNTs) are considered as one of the most attractive nanomaterials and widely studied and applied in basic science and technology. In order to obtain high-quality CNTs, various preparation methods have been developed. Although metal-free synthesis of CNTs is possible, transition metal catalysts such as Fe, Co and Ni are still frequently used in many CNT synthesis processes (chemical vapor deposition etc.) for the reason that the presence of the metal catalysts increases the conversion efficiency of hydrocarbons to nanotubular carbons and can better control over the tube structure [1]. Consequently, the metal impurities are inherently present in CNT products. Many characterization techniques have been applied for the purity evaluation of CNTs [2], such as scanning and transmission electron microscopy (SEM and TEM), thermogravimetric analysis (TGA) and Raman spectroscopy as well as near-infrared (NIR) spectroscopy; and some quantitative analytical methods have also been developed for the analysis of metal impurities in CNTs [3–8].

CNT samples may contain up to 30% (wt.) of residual metal impurities after production and up to 10% (wt.) after purification processes

[5,9,10]. Despite being encapsulated in the central canal in the case of multi-walled carbon nanotubes (MWCNTs) or surrounded by several carbon layers in the case of single-walled carbon nanotubes (SWCNTs), these residual metal particles might cause CNT structure defects and restrict their further applications; the presence of the metal impurities would also possibly cause problems associated with biocompatibility, toxicity and risk assessment of CNT materials. For example, it has been reported that the hydrogen uptake capacity of SWCNTs depends on the amount of residual nickel present in CNT samples [11]; the decreased thermal stability of CNT materials has also been found to result from the residues of cobalt nano-particles in CNTs [12]. Besides, it is widely accepted that the toxicological effects of CNTs could mainly be attributed to metal impurities [13–15]. The metal residue in CNTs might endanger the respiratory system [16,17] or contribute to cellular toxicity [18,19]. These metal impurities are bioavailable and even as low as 0.01% (wt.) of metal impurities can be redox-active [20], interact with the surrounding solution and bring about toxicological effects [21,22]. Therefore, removing residual metal impurities from CNTs is very important for high quality CNT materials. In fact, many approaches have been developed to remove metals and metal oxides especially for the purification of SWCNTs. These purification methods often involve aggressive oxidizing chemical treatments, such as gas-phase oxidation and nitric acid reflux [2,23,24], which may damage CNT structure [25–27], cut CNTs into shorter length [28,29] and even further introduce/break chemical functional groups [30]. Anik et al. [31] have reported the effect of nitric acid “washing” procedure on the electrochemical behavior of

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CNTs. After nitric acid “washing”, the electron transfer rate of CNTs significantly decreases. Thus, defensive purification procedure is expected. Chen et al. [32] have proposed a microwave-induced controlled method for the purification of SWCNTs, in which dilute acids and complexing agents were used instead of strong acids. They found that the SWCNTs retained their chemical and physical properties and were not functionalized. In addition, it has been reported that ultracentrifugation, with high centrifugal forces (typically in excess of 100 000 g), could be a nondestructive and non-oxidizing method for CNT purification [33, 34]. Recently, Meyer-Plath et al. have developed a very fast and entirely gas-phase based plasma-thermal purification technique for CNTs, neither acids nor other chemical reagents were used, and structural integrity of the purified CNTs was preserved [35].

Development of nondestructive and non-oxidizing methods for CNT purification that combine high yield removal of metal impurities and preservation of the CNT structure is of great importance and highly challenging. In this work, a new strategy was proposed to remove the residual nickel metal impurities from CNTs by using photochemical vapor generation (PVG); and the produced nickel-containing volatile species was simultaneously introduced to an atomic fluorescence spectrometer (AFS) to measure the nickel atomic fluorescence signal thus online monitoring the purification process. PVG is a new gaseous sample introduction method for analytical atomic spectrometry [36–38], with many advantages such as efficient matrix separation, high analyte transport efficiency, high selectivity and simple instrumentation; PVG–AFS has been applied in the detection of trace Fe, Co and Ni [39–42]. Since Fe, Co and Ni are the most common metal catalysts used in CNT synthesis, herein we proposed to remove nickel impurities from CNTs by the use of PVG, which involved formic acid ultrasonic pretreatment followed with UV-induced carbonyl generation. Without strong oxidizing chemical treatments or high temperature heating, this CNT purification process involves only mild chemical reactions.

2. Experimental

2.1. Instrumentation

A dual-channel non-dispersive atomic fluorescence spectrometer (AFS-2202E, Beijing Haiguang Instruments Co., Ltd., Beijing, China) equipped with a hollow cathode lamp of nickel (General Research Institute of Non-Ferrous Metals, Beijing, China), a quartz argon–hydrogen flame atomizer and a quartz gas–liquid separator (GLS) was utilized to detect the AFS signal of nickel. High purity (99.99%) Ar was purchased from Qiaoyuan Gas Co. (Chengdu, China). Hydrogen was generated using a hydrogen generator (SPGH-300, Zhongya Gas & Instrument Research Institute, Beijing, China). A UV lamp (15 W, CnLight Co., Ltd., Foshan, China), a pump (BT100-02, Baoding Qili Precision Pump Co., Ltd., Baoding, China), an electrochemical workstation (CHI 760E, Chen Hua Instrument Co., Ltd., Shanghai, China), glassy carbon (GC) electrodes (3 mm in diameter), a high speed centrifuge (HC-3018, Anhui USTC Zokia Scientific Instruments Co., Ltd., China) and a microwave oven (Master 40, Shanghai Sineo Microwave Chemistry Technology Co., China) were also used in this work.

2.2. Reagents and materials

All chemicals used in this work were of at least analytical grade. The chemicals formic acid (>88%), ammonia (25–28%), concentrated nitric acid (guaranteed reagent, 65–68%), hydrogen peroxide (>30%), hydrochloric acid (37%) and N,N-dimethyl formamide (DMF, >99.5%) were all purchased from Kelong Chemical Reagent Factory (Chengdu, China.). High purity deionized water (DIW, 18.2 MΩ cm resistivity) from a Milli-Q Millipore water purification system (Millipore, USA) was used to prepare solutions throughout this work. All vessels used in the experiments are soaked in 5% (v/v) nitric acid at least overnight and cleaned sequentially with tap water and DIW prior to use. CNTs

(short and purified MWCNTs, SM5, o.d. 20–30 nm, i.d. 5–10 nm, 0.5–2 μm in length) were purchased from Chengdu Organic Chemicals Co., LTD. (Chengdu, China).

2.3. Procedure of removing Ni impurities from CNTs

The purification procedure was carried out by photochemical vapor generation, with online AFS monitoring. As shown in Fig. 1, it mainly consisted of an atomic fluorescence spectrometer and a purification cell. The purification cell (used for carbonylation reaction, about 70 mm i.d. and 150 mm in height) was connected with AFS via a gas–liquid separator, and it was wrapped with aluminum foil and immersed in the ultrasonic water bath. The UV lamp inserted into a quartz tube was put deep into the solution approaching to the bottom of the purification cell. The radiation from the UV lamp, together with the radiation reflected back by the aluminum foil, irradiated onto the CNT suspension to effectively induce carbonyl generation of Ni from the CNT sample. A flow of carrier gas Ar (300 mL min⁻¹) and H₂ (100 mL min⁻¹) passed through the catheter to the bottom of the solution and purged the gaseous nickel carbonyl to the argon–hydrogen flame atomizer for the atomization and AFS detection.

CNTs (5–10 mg) were mixed with 100 mL formic acid in the purification cell, after being ultrasonic pretreated 2–10 h with formic acid, 100 mL ammonia solution was pumped into the purification cell to adjust suitable pH condition for the carbonylation reaction. After mixing, the UV lamp was turned on, and carbonyl nickel was generated under the UV irradiation, which was separated from the CNT sample and then on-line determined by AFS. The current for HCL of Ni was set at 50 mA, the voltage for the photomultiplier tube was –290 V, the atomizer height was 10.0 mm, and the flow rate of shielding gas (Ar) was 500 mL min⁻¹.

2.4. Quantitative determination of Ni impurities in CNTs before/after purification

In order to investigate the removal effect of Ni impurities from CNTs, Ni impurities in SM5 CNTs were quantitatively determined before/after purification. After purification, the CNT suspension was washed with water to neutrality, centrifugalized, dried and then the purified products were collected. With 3 mL concentrated nitric acid and 1 mL hydrogen peroxide, 5 mg CNT sample (before/after purification) was completely digested in a Teflon digestion cell by microwave digestion (digestion power 1200 W, digestion temperature 200 °C and digestion time

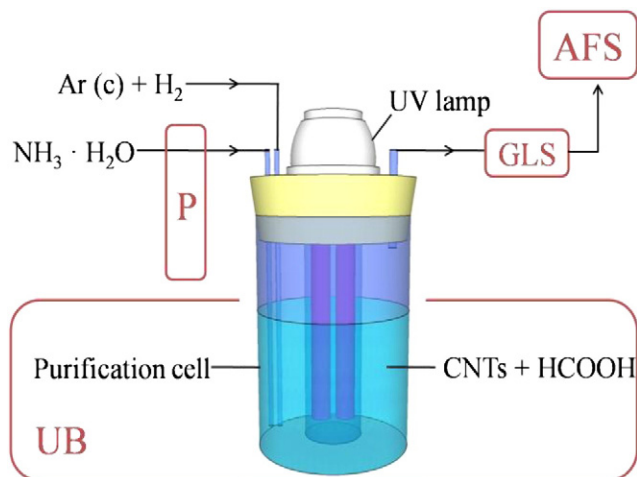


Fig. 1. The experimental setup for removing nickel impurities from CNTs, with online monitoring by atomic fluorescence spectrometry. Ar(c): argon as the carrier gas; P: pump; and UB: ultrasonic bath.

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