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Filling of single-walled carbon nanotubes by CuI nanocrystals via capillary technique

M.V. Chernysheva[a], A.A. Eliseev[a,*], A.V. Lukashin[a], Yu.D. Tretyakov[a], S.V. Savilov[b], N.A. Kiselev[c], O.M. Zhigalina[c], A.S. Kumskov[c], A.V. Krestinin[d], J.L. Hutchison[e]

[a]*Department of Materials Science, Moscow State University, Moscow 119992, Russia*
[b]*Chemical Department, Moscow State University, Moscow 119992, Russia*
[c]*Institute of Crystallography, Moscow 119333, Russia*
[d]*Institute of Problems of Chemical Physics, Chernogolovka 142432, Moscow Region, Russia*
[e]*Department of Materials, University of Oxford, Oxford OX1 3PH, UK*

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Abstract

The present study is focused on the synthesis and investigation of the nanocomposite CuI@SWNT obtained by the filling of metallic single-walled carbon nanotubes (SWNTs) (inner diameter 1–1.4 nm) by wide-gap semiconducting CuI nanocrystals using so-called capillary technique. The method is based on the impregnation of pre-opened SWNTs by molten CuI in vacuum with subsequent slow cooling to room temperature. SWNTs and CuI@SWNT nanocomposites were studied by nitrogen capillary adsorption method, EDX microanalysis, HRTEM microscopy and Raman spectroscopy. The changing of electronic properties of CuI@SWNT as compare to row nanotubes was observed.

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Keywords: Single-walled carbon nanotubes; 1D nanostructure; Raman spectroscopy; Electronic band structure

1. Introduction

Single-walled carbon nanotubes (SWNTs) first produced in 1991 by arc-discharge evaporation method nowadays draw close attention of scientific community worldwide due to their unique electronic and structural properties accompanied by extraordinary mechanical behavior depending on the diameter and conformation of tubes [1,2]. Well-defined atomic structure, ultra-small diameter (from 0.4 nm) and the highest length to diameter ratio makes SWNTs extremely attractive as the perfect templates for the formation of one-dimensional (1D) nanocrystals inside the channels [3]. Chemical design of SWNTs via filling of tubes with favorable conductive, optical or magnetic compounds impulses development of novel class of nanotube architectures and nanoscale materials. For instance intercalation of the electron donors (with Fermi level located in the conductance band) to the metallic tubes will lead to increase of electron density on carbon walls resulting in better conductance through the composite wire while intercalation of electron acceptors (with Fermi level below one of SWNT) may cause the decrease of carrier density (and Fermi energy) in the system [4]. This concept allows to tune electronic structure of SWNTs by intercalation of metallic, semiconductor or dielectrics materials. Recently a shift of Fermi level of SWNTs intercalated by CrO_3, Ag and C_{60} was demonstrated by Raman spectroscopy [4–6]. On the other hand mechanical properties of SWNTs (e.g., tensile strength and elastic bending modulus) depends strongly on the interatomic distance in graphitic layer, which can be varied by applying (positive or

*Corresponding author. Tel.: +7 495 9395931; fax: +7 495 9390998.
E-mail address: eliseev@inorg.chem.msu.ru (A.A. Eliseev).

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negative) internal pressure originating from intercalation of substances with cell parameters (or d spacing) slightly different from the channel diameter.

The usual way for filling SWNTs employs so-called capillary technique involving impregnation by molten salts or salt solutions with subsequent temperature treatment [7]. However, guest materials used for the intercalation should meet a number of requirements. First, to wet the nanotube surface it should possess low surface tension ($\gamma = 100-200\,\mathrm{mN/m}$) [8]. This obviously denies direct filling of SWNTs with majority of melted compounds, but allows using most of organic or inorganic solvents like water ($\gamma = 72\,\mathrm{mN/m}$ at 25 °C) or benzene ($\gamma = 28.9\,\mathrm{mN/m}$). Second, the melting point of guest materials or the treatment temperature should not exceed ~900 °C to prevent the destruction of carbon nanotubes. Besides, as the nanotube channels are normally filled with adsorbed molecules and at least one of their ends is usually closed with fullerene half-sphere the opening stage and vacuum treatments are highly required [8].

At present a great number of studies report filling of carbon nanotubes (SWNTs and MWNTs) with metals (Au, Ag, Pt, Pd, etc.), metal oxides (La_2O_3, Sm_2O_3, NiO, MoO_2, ZrO_2, CdO, etc.), halides (KI, AgCl–Br–I, $ZrCl_4$, $CdCl_2$, $TbCl_3$, $ThCl_6$, etc.) and fullerenes [3,9–11]. However, most of these works are focused on the structure of incorporated materials or the deformation of nanotube walls, while only a few of them concentrate on the electronic properties of modified SWNTs. In the same time these characteristics are of main importance for their practical application.

As the most significant changes in electronic structure of nanocomposites compared to raw materials can be expected either in case of encapsulation of wide-gap semiconductor into metallic tubes or metal compounds into semiconducting ones here we report growth and investigation of CuI nanocrystals in the channels of metallic SWNTs with inner diameter 1–1.4 nm.

2. Experimental details

SWNTs were obtained by catalytic arc-discharge method using 0.8 cm diameter graphite rods with Y/Ni powder catalyst at 73.3 kPa helium pressure and a current of 100–110 A [12]. The SWNTs were purified by multistage procedure consisting of controllable oxygenation in air and rinsing by HCl for the catalyst removal [13]. The purified nanotubes with SWNT content of 78 wt% and catalyst content of 0.12 wt% were pre-opened by temperature treatment at 500 °C in dry air for 0.5 h.

The oxidized SWNTs (0.025 g) were grinded with 0.4 g of CuI (Aldrich, 99 wt%) in agate mortar, vacuumized at 1 Pa for 1 h and sealed into quartz ampoule. The sample was treated at 705 °C (100 °C above the melting point of CuI) for 6 h and slowly cooled (0.02 °C/min) to room temperature to induce better crystallization.

SWNTs and CuI@SWNT nanocomposites were studied by nitrogen capillary adsorption method, Raman spectroscopy, HRTEM and EDX. The surface properties were characterized with QuantaChrome NOVA 4200E instrument (working gas N_2, 77 K). The Raman spectra were registered on Equinox 55/S (Bruker) spectrometer equipped with FRA 106/S Raman module using the 1064 nm excitation line of Nd:YAG laser (350–500 mW) at room temperature in air. High resolution transmission electron microscopy (HRTEM) was performed using JIM JEOL 4000EX microscope with acceleration voltage of 400 kV. Energy dispersive X-ray (EDX) spectra of CuI@SWNT composite were collected at high-resolution scanning electron microscope LEO Supra 50 VP with microanalytical system INCA Energy + Oxford.

3. Results and discussion

Capillary adsorption data for SWNTs recalculated using Barret–Joyner–Halenda (BJH) approach illustrate the value of specific surface area of 635 m^2/g. Pore size

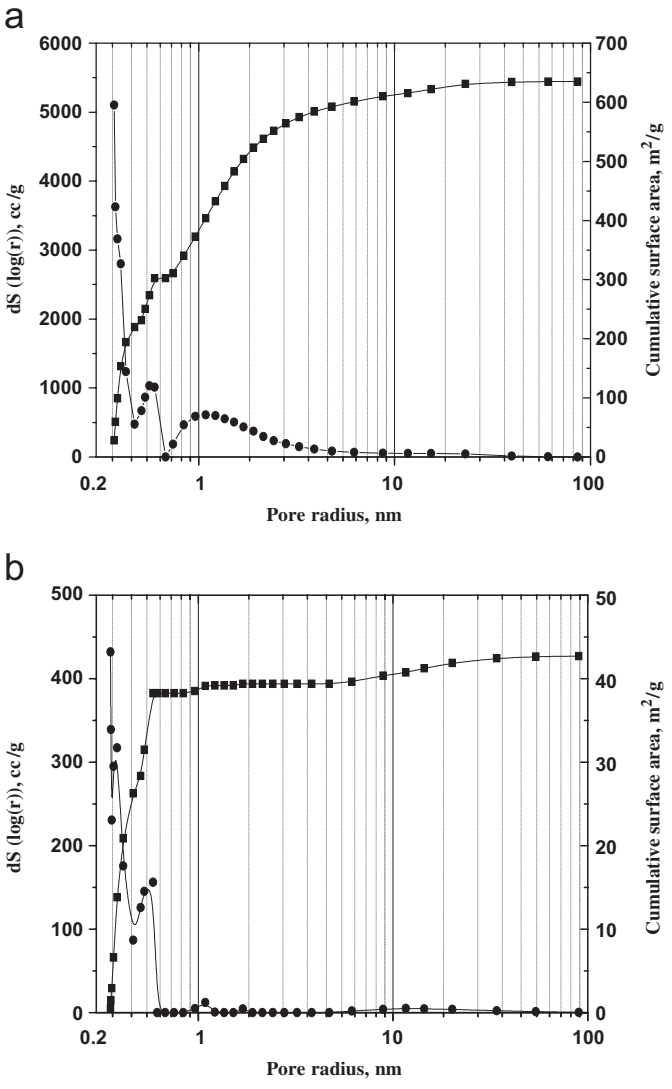

Fig. 1. BJH pore size distribution and cumulative surface area plots for (a) SWNTs and (b) CuI@SWNT nanocomposites.