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Multi-walled carbon nanotubes synthesized by methane pyrolysis: structure and magnetic properties

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Abstract. The structure and magnetic properties of multi-walled carbon nanotubes produced by catalytic pyrolysis of methane have been investigated by means of mutually complementary physical methods. The average sizes and number of carbon layers forming nanotubes, "smearing" of the density of states near the Fermi level, degeneracy temperature of gas of extrinsic current carriers, concentrations of localized spins and extrinsic two-dimensional current carriers have been determined. The conclusion has been drawn that ferromagnetic nanoparticles are present in the inner regions of nanotubes, including their tubular cavities. The difference in electronic structure near the Fermi level for carbon nanotubes and ordered graphite has been revealed. The possible reason is that the electronic states near zigzag-type sites of ends as well as edges of linear structural defects in nanotubes make greater contribution to the spectrum than that from similar sites of graphite.

Introduction

Carbon nanotubes are lengthy cylindrical structures consisting of one or several rolled up graphene planes which can be open-ended or close-ended (Fig. 1, *a-d*). Nanotube diameter ranges from one to several tens of nanometers, and the length can be up to several centimeters. Multi-walled carbon nanotubes (MWCNT) have a variety of configurations and shapes [1], in both longitudinal and transverse directions (see Fig. 1, *e-h*). The distance between the layers varies from 0.34 to 0.39 nm [2], which is more than distance between layers in crystalline graphite (0.335 nm). The specific configuration of a single MWCNT is largely determined by the synthesis conditions. In recent years the methods for producing nanotubes by thermal decomposition of various hydrocarbons in the presence of catalysts are of growing interest of researchers [3].

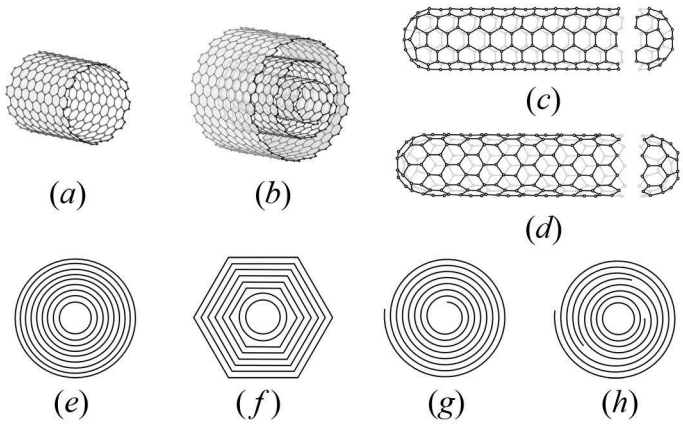

Fig. 1. *Nanotubes with open ends: (a) – single-walled, (b) – multi-walled. Possible models for single-walled nanotubes with closed ends: (c) – armchair type, (d) – zigzag type. Possible cross-sections for multi-walled carbon nanotubes: (e) – coaxial circles; (f) – coaxial polygons; (g) – scroll; (h) – papier-mache (alternating sections of coaxial circles and scrolls).*

Experimental

The carbon nanotubes were synthesized by pyrolysis of methane with using mixed nickel and iron containing oxides as catalysts. The purification of synthesis product was made by treating it in the strong sulfuric acid. The fluorination of the sample was performed by bromine trifluoride, which was formed as a result of thermal decomposition of sodium tetrafluoroborate.

The high-resolution transmission electron microscopy (HR TEM) images were recorded at accelerating voltage of 100 kV with a JEOL JEM-100C microscope in the Institute of catalysis SB RAS (Novosibirsk, Russia), and with a Carl Zeiss LIBRA 120 microscope in the Institute of Marine Biology FEB RAS (Vladivostok, Russia).

The static magnetic susceptibility was obtained using a Quantum Design MPMS-5S SQUID (superconducting quantum interference device) magnetometer in the International Tomography Center SB RAS (Novosibirsk, Russia) in the temperature range of 2–300 K and magnetic field 0.1 T. The sample was zero-field cooled from 300 to 2 K before the measurement.

The electron magnetic resonance (EMR) and X-ray photoelectron spectroscopy (XPS) measurements were performed in the Institute of Chemistry of FEB RAS (Vladivostok, Russia). The EMR spectra were acquired on a Bruker EMX-6/1 X-band spectrometer in temperature range from 100 to 300 K. The EMR intensities and *g*-factors of the signals were calibrated using the intensity and value $g = 2.002293 \pm 0.000003$ of the EMR signal of a Li:LiF reference sample, respectively.

The electronic structure of the samples was studied by XPS of the valence electrons measured on an ES-2401 electron spectrometer (EZAN, Chernogolovka, Russia) with the use of nonmonochromatic Al$K\alpha$ radiation. The vacuum level in the energy analyzer of the spectrometer was maintained at $\approx 6 \times 10^{-8}$ Torr.

Results and discussions

From the HR TEM data it follows that the product of reaction consists of MWCNT whose length is less than 2.5 μm and diameter is less than 70 nm (Fig. 2, *a*). The dark areas in the bright field of HR TEM image are referred to structures with larger electron density compared to surrounding ones [4]. Therefore, the small dark spots on image (Fig. 2, *a*) correspond to elements being heavier than carbon and they have been attributed to the nanosized particles of catalyst, which was used in the synthesis of the investigated material. According to the literature [5], the acid treating is one of the most available techniques for purification of nanotubes. In our case the catalyst particles on the surface of nanotube and thin nanotubes have mostly disappeared after treating with the strong sulfuric acid within several days (Fig. 2, *b*). Additionally, after purification both inner and outer layers have been partially dissolved.

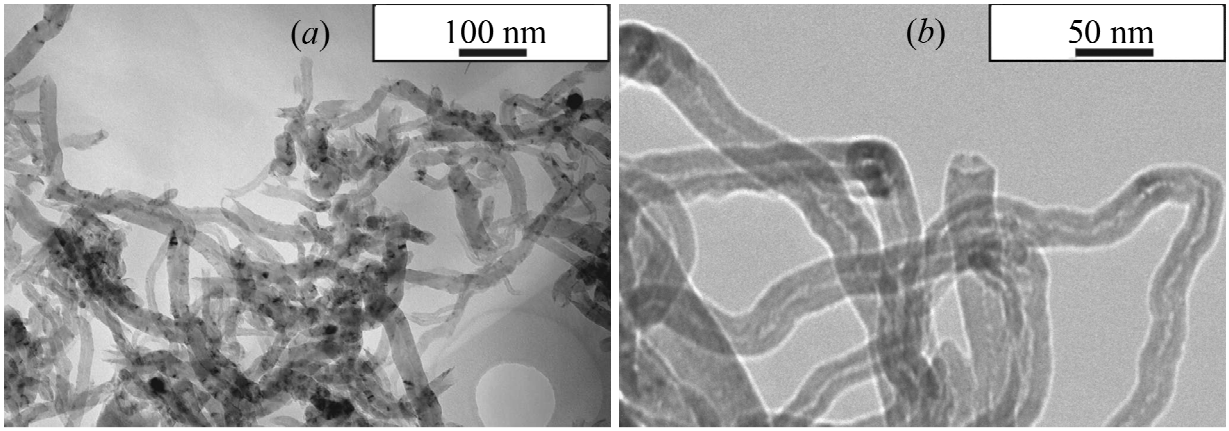

Fig. 2. *HR TEM images of MWCNT powder:* (*a*) *– initial,*
(*b*) *– after ≈ 10 days in the strong sulfuric acid.*

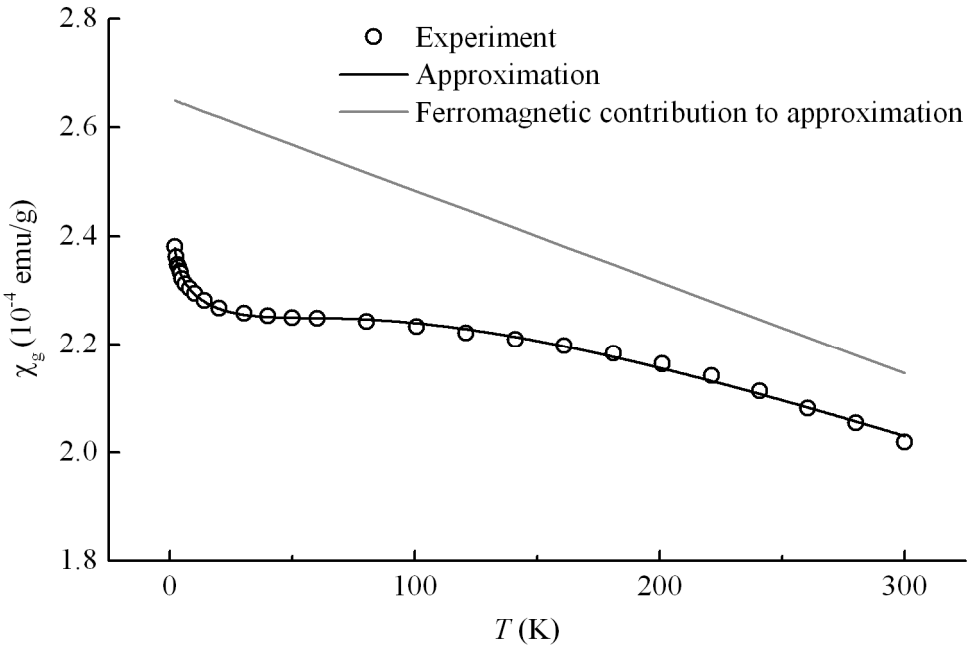

Fig. 3. *The temperature dependence of the static magnetic susceptibility of initial MWCNT powder.*

The temperature dependence of the static magnetic susceptibility of the investigated material before and after purification consists of two components (Fig. 3): one arising from MWCNT and another from ferromagnetic impurities, respectively. The last one can be approximated by the linear function of absolute temperature [6]. It was assumed that the static magnetic susceptibility of MWCNT is composed of paramagnetic and diamagnetic susceptibilities. The former was fitted by Curie law and the latter was computed in terms of the band model of quasi-2D graphite with 2D band parameter $\gamma_0 = 3$ eV [7]. The best fit was obtained with Curie constant 1.4×10^{-5} emu K/g, degeneracy temperature of extrinsic carriers $T_0 = 164$ K and parameter which takes into account

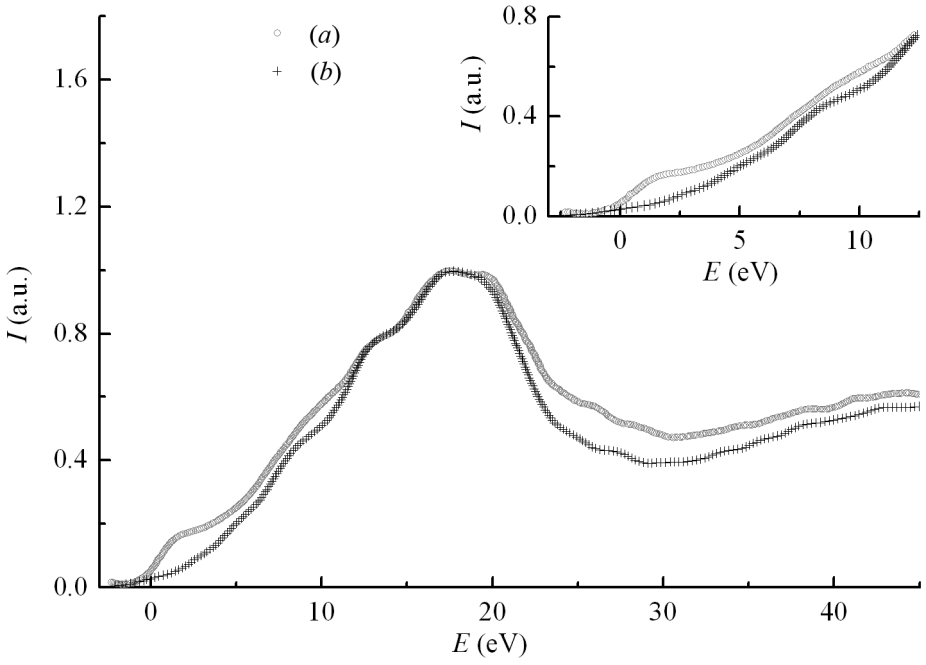

Fig. 4. *XPS of the valence electrons for MWCNT powder* (*a*) *and highly oriented pyrolytic graphite* (*b*).

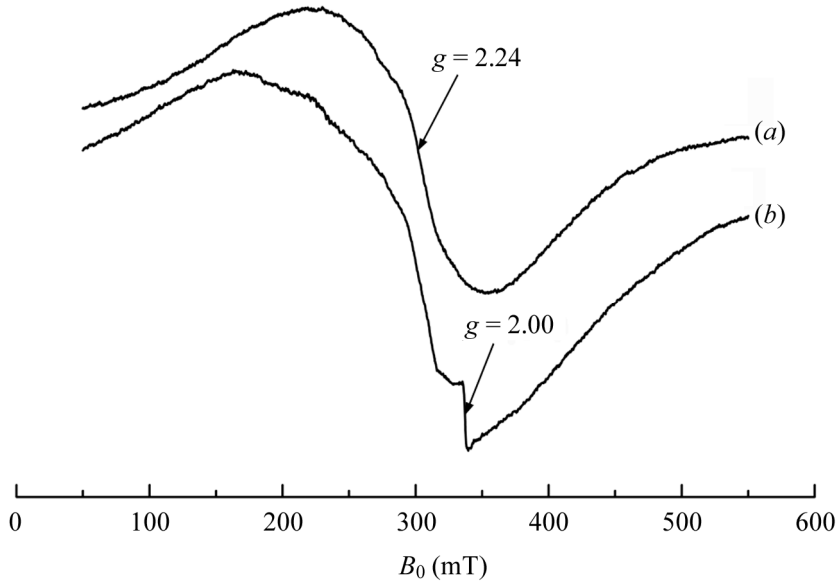

Fig. 5. *EMR spectra for MWCNT powder before* (*a*) *and after* (*b*) *fluorination. X-band; T = 300 K.*

"smearing" of density of states near the Fermi level $\delta = 73$ K. The value of Curie constant corresponds to one paramagnetic center per ≈ 2200 carbon atoms. According to [8], large value of ratio $T_0/\delta \approx 2$ indicates the presence of linear structure defects in nanotubes. The concentration of extrinsic carriers in MWCNT was estimated as 1.6×10^{10} cm^{-2}.

The XPS of valence electrons of MWCNTs powder shows a noticeable peak near the Fermi level (Fig. 4, *a*), which does not occur in the corresponding spectrum of highly oriented pyrolytic graphite (Fig. 4, *b*). Taking into account the literature data [9, 10], this peak can be attributed to the photoelectrons emitted from the regions near the zigzag positions of carbon nanotube ends and edges of their linear defects.

The EMR spectrum of investigated material consists of the slightly asymmetrical line with width ≈ 1.38 mT, characterized by the effective value of *g*-factor ≈ 2.24, and barely visible narrow line with width ≈ 0.32 mT, superimposed on the former near its center (Fig. 5, *a*). The shape of EMR spectrum preserves down to the temperature about 100 K. The observation of slightly asymmetrical EMR signal from powder indicates the location of paramagnetic ions in high symmetry crystal field positions, for instance, in field of cubic symmetry. The presence of the central line in the EMR spectrum allows interpreting it as corresponding to the trivalent iron ions. The difference of g-factor value for catalyst nanoparticles from that for ions of trivalent iron in a diamagnetic matrix ($g \approx 2$) can be explained by the contribution of intrinsic (induced) field of ferromagnetic particle to the resonance magnetic field. After treating the initial sample in strong sulfuric acid the intensity of EMR spectrum decreases by ≈ 12 times.

The EMR spectrum of fluorinated MWCNT powder (Fig. 5, *b*) contains the additional resonance signal with width ≈ 5 mT and the g-factor value very close to the free electron one. This signal is attributed to the electrons localized on p_z-orbitals of carbon atoms near the atoms "attacked" by fluorine.

Conclusions

According to HR TEM the initial material is powder of MWCNT with a considerable amount of catalyst particles attached to their surfaces. HR TEM images show that there are no catalyst particles on the surface of MWCNT treated in the strong sulfuric acid within several days. However, the preservation of both the character of the temperature dependence of the static magnetic

susceptibility and the shape of EMR spectrum of MWCNT powder after treating in the strong sulfuric acid denotes that the ferromagnetic impurities remain in the volume of nanotubes. The most probable positions for them are in the inner tubular cavities and interlayer spacings of nanotubes. Therefore, the final product in considered technique of synthesis is a powder of magnetic nanocomposites.

Basing on analysis of magnetic properties of MWCNT powder, the concentration of paramagnetic centers and extrinsic 2D carriers, the degeneracy temperature of extrinsic carriers and the "smearing" of levels near the Fermi energy have been estimated.

The electronic structure near the Fermi level for MWCNT powder differs from that for ordered graphite. The reason for that may be greater density of electronic states near the zigzag sections of both nanotube ends and edges of linear structural defects of nanotubes.

The EMR spectra of initial and purified MWCNT powders correspond to the trivalent iron in ferromagnetic particles. The EMR spectrum of fluorinated MWCNT powder contains the additional narrow signal from electrons localized on p_z-orbitals of carbon atoms near the positions "attacked" by fluorine.

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References

[1] S. Amelinckx, D. Bernaerts, X.B. Zhang, G. Van Tendeloo, J. Van Landuyt, A structure model and growth mechanism for multishell carbon nanotubes, Science 267 (1995) 1334-1338.

[2] C.-H. Kiang, M. Endo, P.M. Ajayan, G. Dresselhaus, M.S. Dresselhaus, Size effects in carbon nanotubes, Phys. Rev. Lett. 81 (1998) 1869-1872.

[3] E.G. Rakov, Methods for preparation of carbon nanotubes, Russ. Chem. Rev. 69 (2000) 35-52.

[4] S.L. Flegler, J.W. Heckman, K.L. Klomparens, Scanning and transmission election microscopy: an introduction, Oxford University Press, USA, 1993.

[5] F.H. Ko, C.Y. Lee, C.J. Ko, T.C. Chu, Purification of multi-walled carbon nanotubes through microwave heating of nitric acid in a closed vessel, Carbon 43 (2005) 727-733.

[6] T. Holstein, H. Primakoff, Field dependence of the intrinsic domain magnetization of a ferromagnet, Phys. Rev. 58 (1940) 1098–1113.

[7] A.S. Kotosonov, S.V. Kuvshinnikov, Diamagnetism of some quasi-two-dimensional graphites and multiwall carbon nanotubes, Phys. Lett. A 230 (1997) 377-380.

[8] A.S. Kotosonov, Texture and magnetic anisotropy of carbon nanotubes in cathode deposits obtained by the electric-arc method, JETP Letters 70 (1999) 476-480.

[9] S. Suzuki, Y. Watanabe, T. Ogino, S. Heun, L. Gregoratti, A. Barinov, B. Kaulich, M. Kiskinova, W. Zhu, C. Bower, and O. Zhou, Electronic structure of carbon nanotubes studied by photoelectron spectromicroscopy, Phys. Rev. B 66 (2002) 035414.

[10] M. Fujita, K. Wakabayashi, K. Nakada, K. Kusakabe, Peculiar localized state at zigzag graphite edge, J. Phys. Soc. Jpn. 65 (1996) 1920-1923.