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Research Article

Effect of Electrochemical Treatment on Electrical Conductivity of Conical Carbon Nanotubes

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Interaction of conical carbon nanotubes (CNTs) with hydrogen during electrochemical treatment and its effect on their electronic properties was studied. The temperature dependencies of electroconductivity of initial and electrochemically hydrogenated conical CNTs were investigated by using four-probe van der Pauw method. The studies revealed that the electrochemical hydrogen absorption leaded to a significant reduction in the electroconductivity of conical carbon nanotubes. We assume that these changes can be associated with a decrease in the concentration of charge carriers as a result of hydrogen localization on the carbon π-orbitals, the transition from sp^2 to sp^3 hybridization of conical CNTs band structure, and, therefore, a metal-semiconductor-insulator transition.

1. Introduction

Carbon nanotubes (CNTs) attract considerable attentions due to their unique structural, electrical, and mechanical properties that make them suitable for various applications such as supercapacitors, catalyst supports, energy storage devices, and additives [1–5]. The investigations of carbon nanotubes' interaction with hydrogen are also of great interest [6–8]. A recent study [9] showed that graphene can react with atomic hydrogen, which, being localized on the carbon π-orbitals, leads to a transition from sp^2 to sp^3 hybridization of the graphite band structure and, hence, to a conductivity change. Considering the possible usage of carbon nanostructured materials and carbon based composites as lightweight microwave absorbers in the fields of communication, microwave devices, and electromagnetic pollution defense [10–14], the investigations on variation of the electrical and magnetic properties of carbon nanotubes are in the focus of interest.

In the present study conical carbon nanotubes were used as a testing material. Conical CNTs have a unique feature: the majority of their internal and external edges are open and this is favorable for hydrogen intercalation into their interplanar spaces. Previously, it was shown [15] that electrochemical hydrogen sorption leads to the structural changes occurring during hydrogenation in the conical walls of the CNTs. Such changes were associated with the hydrogen intercalation into the interplanar spaces of conical CNTs and its addition to the π-bonds of graphite layers. We assumed that localization of hydrogen on the carbon π-bonds should lead to electroconductivity reduction. A similar decrease in the electrical conductivity of carbon nanotubes by increasing the concentration of adsorbed hydrogen atoms was also theoretically described elsewhere [16].

The purpose of this work was to investigate temperature dependencies of electroconductivity of initial and electrochemically treated conical carbon nanotubes and to reveal hydrogen effect on the electronic properties of such structures.

2. Materials and Methods

Conical carbon nanotubes were grown by pyrolysis of granular polyethylene as described elsewhere [17]. The morphology

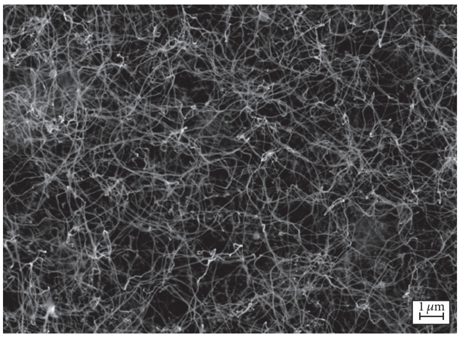

Figure 1: SEM image and schematic view of a fragment of conical carbon nanotube.

and geometrical parameters of carbon nanomaterial were investigated by electron microscopy techniques. Scanning electron microscopy (SEM) image of as-prepared sample is presented in Figure 1.

The sample consists mainly of carbon nanotubes and nickel nanoparticles. These nanotubes are several microns in length, with outer diameters ranging between 40 and 50 nm and inner channels varying between 9 and 20 nm. The fringe spacing is 0.34 nm. A characteristic feature of these tubes is their conical structure formed by the open graphite planes (Figure 2).

Acid treatment in 65% aqueous solution of chemically pure nitric acid for one hour at 60°C of conical CNTs was performed to remove residual catalyst particles. After that acid was evaporated and treated CNTs were rinsed with distilled water, filtered, and dried at 105°C. X-ray diffraction and electron spin resonance (ESR) experiments were carried out to study the as-prepared and treated with nitric acid CNTs. The results on X-ray diffraction experiments were the same as we described previously [15] and the effectiveness of acid treatment for the removal of residual catalyst particles was shown. Figure 4. presents the ESR spectra of carbon nanotubes composite.

ESR signal observed (line 1) is an asymmetric additive absorption curve. The obtained value of g-factor (2.017) is close to the typical g-factor for the metallic nickel $g = 2.2 \pm 0.02$ [18]. So this allows us to explain the ESR spectra of the as-prepared sample as a signal from residual catalyst nickel particles. As one can see (Figure 3, line 2), the signal's intensity reduces after acid treatment.

This confirms that the performed thermochemical treatment leaded to the removal of residual catalyst particles. Such catalyst-free samples were used as initial samples in order to eliminate the possible influence of Ni catalyst on electroconductivity of conical CNTs.

Hydrogenation of carbon nanotubes was performed using galvanostatic method in a three-electrode cell as described previously [15]. After hydrogenation the sample was rinsed with distilled water, filtered, and dried at 120°C for one hour to remove physically adsorbed molecules from the surface. After that carbon nanotubes (separately for initial and hydrogenated samples) were pressed into tablets (5 mg) for 6 hours to create a uniform structure. A set of 5 tablets for each of the samples was prepared. Ohmic contacts were made from 0.1 mm silver wire and fastened by silver paste. The temperature dependence of electrical conductivity of the conical CNTs was measured by using four-probe van der Pauw method at the temperature range from 77 K to 300 K.

To study the temperature dependence of the electrical conductivity of initial and hydrogenated samples a special setup was developed (Figure 4).

3. Results and Discussion

Figure 5 shows the temperature dependence of the electrical conductivity of initial and hydrogenated samples.

As one can see the electrochemical hydrogen absorption leads to a decrease in the electroconductivity of conical carbon nanotubes that can be associated with a decrease in the concentration of charge carriers as a result of hydrogenation. This can be explained as follows. The interaction of adsorbed hydrogen atoms with the surface of carbon nanotubes can be described using the periodic Anderson model. Since the geometric configuration of the CNTs determines their electroconductive properties, the proposed model is suitable to describe the adsorption on the surface of CNTs. In general, the periodic Anderson model [19] considers two groups of electrons: collectivized s-electrons and localized d-electrons. The collectivized particles are considered to be free, and localized particles interact with each other by Coulomb repulsion at the same site. The carbon atom in graphene layer forms three σ-type chemical bonds with the nearest neighbors. The fourth p-type orbital forms a π-type chemical bond describing states of collectivized electrons that determine the electroconductivity of carbon nanotube. A detailed analysis on the effect of adsorbed hydrogen atoms (adatoms) on the band structure of CNTs was presented in [20]. It was shown that a change in the band structure occurs near the energy level of the adatom, situated in the valence π-zone, and is expressed in the formation of an energy gap. Lowering the conductivity during hydrogen adsorption was due to the fact that some collectivized electrons of the crystal associated with hydrogen atoms and no longer participate in the charge transfer process.

Thus, it can be assumed that the electrochemical hydrogen treatment leads to hydrogen intercalation into the interlayer space of the nanotubes and its localization on the carbon π-bonds forming chemical C-H bonds. This in turn leads to a transition from sp^2 to sp^3 hybridization of graphite band structure and, therefore, to metal-semiconductor-insulator transition.

Temperature dependence of the electroconductivity of the samples subjects to the law

$$\sigma(T) = \sigma_1 + A \ln(T), \quad (1)$$

where σ_1 and A constants.

This dependence of the conductivity is typical for two-dimensional conductors with local disorder. Similar results on studying the electronic structure of multiwalled nanotubes were presented by Kotosonov and Shilo [21]. It was shown that the electronic structure of multiwalled nanotubes (diameter > 20 nm, as in our case) matches that

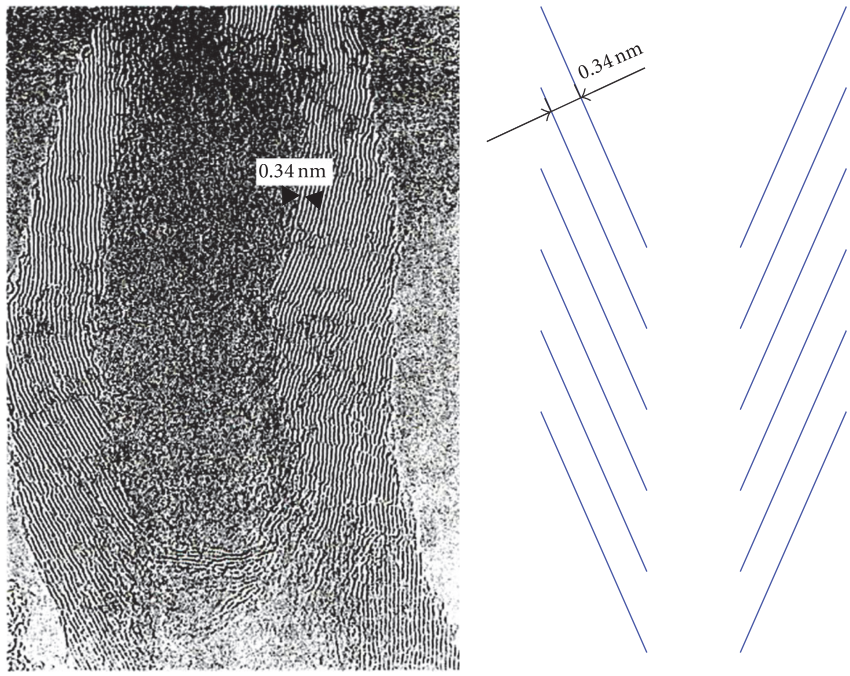

Figure 2: TEM image and schematic view of a fragment of conical carbon nanotube.

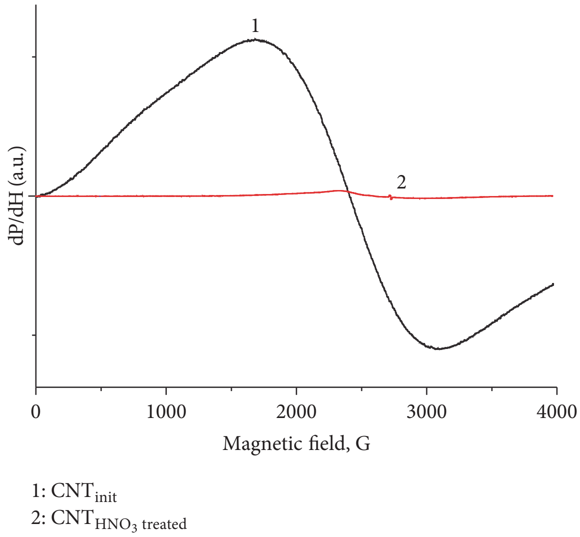

Figure 3: ESR spectra of as-prepared (1) and treated with nitric acid (2) carbon nanotubes composite.

of a two-dimensional graphite structure. Romanenko et al. [22] investigated the effects of different atmospheres on the temperature dependence of the resistivity of multilayer carbon nanotubes. The authors also observed an increase in resistance as the temperature decreased. It was suggested that physical and chemical adsorption of hydrogen leads to an increase in resistance. Temperature dependence of the conductivity of multiwalled carbon nanotubes annealed at different temperatures was investigated in [23]. It was found that the temperature dependence of the conductivity for multiwalled carbon nanotubes with a diameter of 20–22 nm are typical for the two-dimensional conductors with a local disorder. Mechanism of hydrogen adsorption on a single graphene was studied in [24]. Our investigations on hydrogen interaction with conical carbon nanotubes are similar to the above-mentioned work, since such type of nanotubes can be regarded as an agglomeration of conductive carbon planes, and the total effect on the conducting properties of hydrogenated carbon nanotubes reflect the physical and chemical fundamentals of graphene-to-graphane transformation. Indeed, the results obtained indicate that the electrochemical hydrogen absorption leads to a significant reduction in the conduction of conical carbon nanotubes that can be associated with a decrease in the concentration of charge carriers as a result of hydrogen absorption due to hydrogen localization on the carbon π-orbitals and the transition from sp^2 to sp^3 hybridization of conical CNTs band structure.

4. Conclusions

In this paper the investigation of the electrochemical treatment effect on electroconductivity of conical carbon nanotubes is presented. A successful attempt to change the conductivity of conical CNTs by hydrogen intercalation into their interplanar space was performed. The temperature dependencies of the electroconductivity of initial and hydrogenated conical carbon nanotubes were studied. The results obtained were typical for the electrical conductivity of two-dimensional conductors with local disorder. It was found that the electrochemical hydrogen absorption leads to a significant reduction in the conductivity of carbon nanotubes. It could be caused by the decrease in concentration of charge carriers due to the localization of hydrogen on the carbon

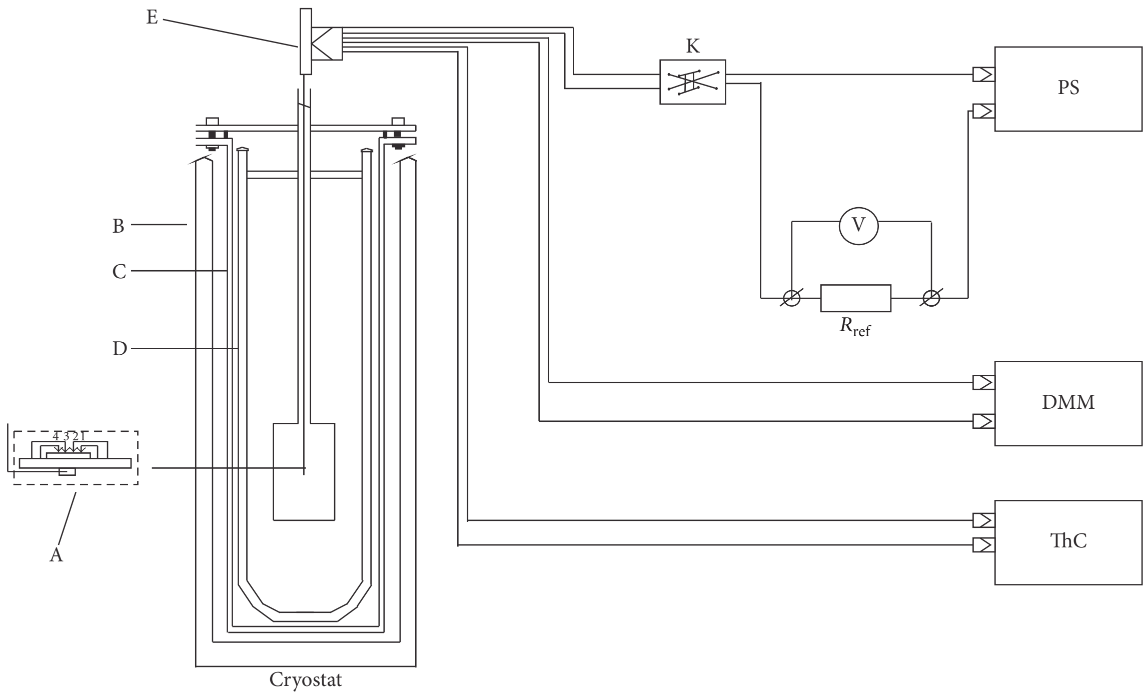

FIGURE 4: Experimental setup for the conductivity of the carbon nanotubes investigation. PS: power source, DMM: digital multimeter, ThC: thermocouple, K: key-commutator allowing to change the direction of current, A: plate with sample and thermocouple, B: case, C: metal frame, D: glass capsule, E: holder with electrical contacts.

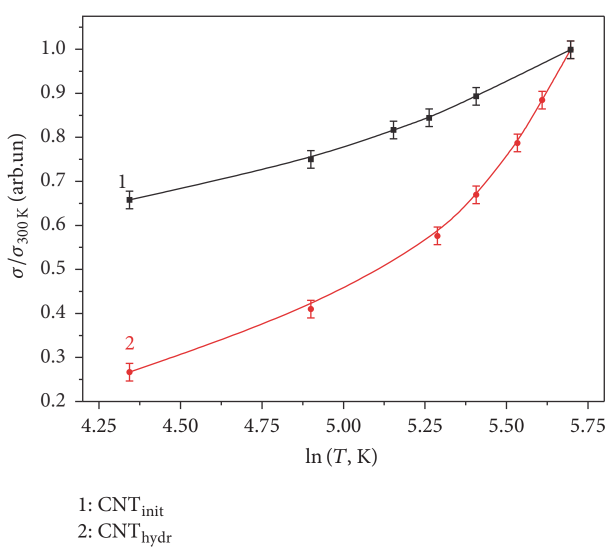

FIGURE 5: Temperature dependencies of the electroconductivity of conical carbon nanotubes. Line 1 (CNT_{init}): averaged line with errors for 5 initial samples, Line 2 (CNT_{hydr}): averaged line with errors for 5 electrochemically hydrogenated samples, $\sigma_{300\,K}$: electroconductivity at 300 K.

π-orbitals and the transition from sp^2 to sp^3 hybridization of the band structure of conical CNTs.

The obtained results can be used to study hydrogen interaction with carbon nanostructured materials for the development of the carbon based materials with controllable electrophysical properties, nanoelectronic devices, and effective hydrogen containers.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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References

[1] W. Zhang, P. Sherrell, A. I. Minett, J. M. Razal, and J. Chen, "Carbon nanotube architectures as catalyst supports for proton exchange membrane fuel cells," *Energy and Environmental Science*, vol. 3, no. 9, pp. 1286–1293, 2010.

[2] H. Pan, J. Li, and Y. P. Feng, "Carbon nanotubes for supercapacitor," *Nanoscale Research Letters*, vol. 5, no. 3, pp. 654–668, 2010.

[3] A. Malak, K. Fic, G. Lota, C. Vix-Guterl, and E. Frackowiak, "Hybrid materials for supercapacitor application," *Journal of Solid State Electrochemistry*, vol. 14, no. 5, pp. 811–816, 2010.

[4] S. M. Khantimerov, E. F. Kukovitsky, N. A. Sainov, and N. M. Suleimanov, "Fuel cell electrodes based on carbon nanotube/metallic nanoparticles hybrids formed on porous stainless steel pellets," *International Journal of Chemical Engineering*, vol. 2013, Article ID 157098, 4 pages, 2013.

[5] A. Allaoui, S. Bai, H. M. Cheng, and J. B. Bai, "Mechanical and electrical properties of a MWNT/epoxy composite," *Composites Science and Technology*, vol. 62, no. 15, pp. 1993–1998, 2002.

[6] C. N. R. Rao, U. Maitra, K. S. Subrahmanyam et al., "Potential of nanocarbons and related substances as adsorbents and chemical storage materials for H_2, CO_2 and other gases," *Indian Journal of Chemistry—Section A*, vol. 51, no. 1-2, pp. 15–31, 2012.

[7] Y. L. Chen, B. Liu, J. Wu, Y. Huang, H. Jiang, and K. C. Hwang, "Mechanics of hydrogen storage in carbon nanotubes," *Journal of the Mechanics and Physics of Solids*, vol. 56, no. 11, pp. 3224–3241, 2008.

[8] G. Krishnamurthy, R. Namitha, and S. Agarwal, "Synthesis of carbon nanotubes and carbon spheres and study of their hydrogen storage property by electrochemical method," *Procedia Materials Science*, vol. 5, pp. 1056–1065, 2014.

[9] D. C. Elias, R. R. Nair, T. M. G. Mohiuddin et al., "Control of graphene's properties by reversible hydrogenation: evidence for graphane," *Science*, vol. 323, no. 5914, pp. 610–613, 2009.

[10] B. Wen, M. Cao, M. Lu et al., "Reduced graphene oxides: lightweight and high-efficiency electromagnetic interference shielding at elevated temperatures," *Advanced Materials*, vol. 26, no. 21, pp. 3484–3489, 2014.

[11] B. Wen, M.-S. Cao, Z.-L. Hou et al., "Temperature dependent microwave attenuation behavior for carbon-nanotube/silica composites," *Carbon*, vol. 65, pp. 124–139, 2013.

[12] W.-Q. Cao, X.-X. Wang, J. Yuan, W.-Z. Wang, and M.-S. Cao, "Temperature dependent microwave absorption of ultrathin graphene composites," *Journal of Materials Chemistry C*, vol. 3, no. 38, pp. 10017–10022, 2015.

[13] R. C. Che, L.-M. Peng, X. F. Duan, Q. Chen, and X. L. Liang, "Microwave absorption enhancement and complex permittivity and permeability of fe encapsulated within carbon nanotubes," *Advanced Materials*, vol. 16, no. 5, pp. 401–405, 2004.

[14] Y. Yang, M. C. Gupta, K. L. Dudley, and R. W. Lawrence, "Novel carbon nanotube-polystyrene foam composites for electromagnetic interference shielding," *Nano Letters*, vol. 5, no. 11, pp. 2131–2134, 2005.

[15] S. M. Khantimerov, V. A. Shustov, N. V. Kurbatova et al., "Effect of electrochemical treatment on structural properties of conical carbon nanotubes," *Applied Physics A: Materials Science and Processing*, vol. 113, no. 3, pp. 597–602, 2013.

[16] S. A. Sudorgin and N. G. Lebedev, "Influence of atomic hydrogen adsorption on the transport properties of semiconducting carbon nanotubes," *Khimicheskaya Fizika*, vol. 33, no. 8, pp. 69–75, 2014.

[17] N. A. Kiselev, J. Sloan, D. N. Zakharov et al., "Carbon nanotubes from polyethylene precursors: structure and structural changes caused by thermal and chemical treatment revealed by HREM," *Carbon*, vol. 36, no. 7-8, pp. 1149–1157, 1998.

[18] S. M. Bhagat and P. Lubitz, "Temperature variation of ferromagnetic relaxation in the 3 d transition metals," *Physical Review B*, vol. 10, no. 1, pp. 179–185, 1974.

[19] P. W. Anderson, "Localized magnetic states in metals," *APS Journals Archive*, vol. 124, no. 1, p. 41, 1961.

[20] A. V. Pak and N. G. Lebedev, "Model of multiple hydrogen atoms adsorption on the surface of carbon nanotubes," *Chemical Physics*, vol. 31, pp. 82–87, 2012.

[21] A. S. Kotosonov and D. V. Shilo, "Magnetic properties of boron-doped carbon nanotubes," *Molecular Materials*, vol. 13, no. 1–4, pp. 113–116, 2000.

[22] A. I. Romanenko, O. B. Anikeeva, V. L. Kuznetsov, T. I. Buryakova, E. N. Tkachev, and A. N. Usoltseva, "Influence of helium, hydrogen, oxygen, air and methane on conductivity of multi-walled carbon nanotubes," *Sensors and Actuators A: Physical*, vol. 138, no. 2, pp. 350–354, 2007.

[23] S. D. Borodanov, A. I. Romanenko, O. B. Anikeeva, V. L. Kuznetsov, K. V. Elumeeva, and S. I. Moseenkov, "Temperature dependences of conductivity and magnetoconductivity of multiwall carbon nanotubes annealed at different temperatures," *Journal of Siberian Federal University. Mathematics & Physics*, vol. 4, no. 2, pp. 143–148, 2011.

[24] D. W. Boukhvalov, M. I. Katsnelson, and A. I. Lichtenstein, "Hydrogen on graphene: electronic structure, total energy, structural distortions and magnetism from first-principles calculations," *Physical Review B*, vol. 77, no. 3, Article ID 035427, 2008.