

Work function tuning of the individual polyaniline/carbon nanotube nanostructures

I A Lobov, N A Davletkildiev and D V Sokolov

Omsk Scientific Center SB RAS, Omsk, 644040, Russia

LI__87@mail.ru

Abstract. Electrostatic force microscopy was used to study the dependence of the electron work function of individual polyaniline/nitrogen doped carbon nanotube (PANI/N-CNT) nanostructures on the duration of synthesis. The work function of nanostructures increases monotonically with the synthesis time increasing. These changes are interpreted as a result of the growth of the polymer layer thickness on CNTs and an increase in the degree of protonation of PANI during the synthesis of PANI/N-CNTs composite.

1. Introduction

Polyaniline (PANI) is the most important representative of the conductive polymers and attracts considerable interest due to its unique physicochemical properties, simplicity of synthesis, and resistance to environmental conditions. Carbon nanotubes (CNTs) are characterized by unique electrical and mechanical properties, which, in combination with their high specific surface area, underlie their use as matrices to create promising nanocomposites. The introduction of nanotubes into the PANI matrix leads to an improvement in the properties of the nanocomposite as a whole: electrical conductivity enhancement, thermal stability and mechanical strength improvement, redox capacity and stability of electrochemical activity increase [1,2]. It has been already shown [3-5] that such composites work well as elements of gas and electrochemical sensors, in energy storage systems, as protective coatings from microwave radiation, as fuel cells, etc.

In some applications of nanocomposites, it is necessary to reduce the size of the elements, up to the use of individual nanoobjects. The prospect of creating electronic components on single nanostructures requires the development of methods for obtaining nanostructures with specified properties. However, as a rule, the properties of massive nanocomposite samples differ from the properties of individual composite nanostructures due to the effect of dimensionality and heterogeneity of component distribution, and also due to the interface interaction of individual nanostructures in the array. Therefore, it is important to develop methods for studying the properties of individual nanostructures using high-resolution methods.

In this paper, we investigated the effect of the synthesis time of the PANI/nitrogen doped CNT (PANI/N-CNT) composite on the change in the electron work function in individual nanostructures using the methods of scanning probe microscopy.

2. Experimental

2.1. Synthesis of PANI/N-CNT nanocomposite

The PANI/N-CNTs composite were synthesized via in-situ chemical oxidative polymerization in the presence of nanotubes. 25 mg of N-CNT obtained by the method described in Ref. [6] were dispersed



in 20 mL of isopropyl alcohol and sonicated for 30 min. 2.5 mL of aniline and 25 mL of 3M HCl were added in this dispersion and sonicated for 30 min. To the N-CNT-aniline dispersed solution, 6 g of ammonium persulphate in 15 mL of 3M HCl were added drop wise at 0°C. The reaction product was taken from the reaction mixture after 5, 10, 20, 30, 40, and 60 minutes, and then the composite powders were dried at 60°C for 24 h.

To separate individual PANI/N-CNT nanostructures, the bulk PANI/N-CNT composite was dispersed in ethanol by sonication for 30 min. After that, the slurry was precipitated on SiO₂/Si substrate by spin-coating method for further studies.

On SiO₂/Si substrate, individual N-CNT and PANI/N-CNT films (40 nm thick) were planted to determine their work function and compare it with that of the PANI/N-CNT nanostructures.

2.2. Characterization

Morphologies of the PANI/N-CNT composite were characterized by scanning electron microscopy (SEM) on JSM-6610LV microscope, JEOL and atomic force microscopy (AFM) on MFP 3D microscope, Asylum Research.

Electrostatic force microscopy (EFM) was used to evaluate the work function of individual N-CNT, PANI/N-CNT nanostructure, and PANI/N-CNT composite film [6]. Voltage in the range from -7 to +7 V was applied. The HA_FM/Pt (NT-MDT SI) probes with Pt coating were used. Calibration of the probe material work function was carried out at HOPG ($W_f = 4.6$ eV).

3. Results and discussion

Figure 1a shows the SEM image of a massive PANI/N-CNT composite layer. As can be seen, N-CNTs are completely covered with a layer of polymer. Individual PANI/N-CNT nanostructures are densely packed in a layer and are interconnected by free PANI molecules. Morphology of individual PANI/N-CNT nanostructures was investigated by AFM method (Fig. 1b). Free PANI molecules were removed from PANI/N-CNT nanostructures after sonication. It can be seen that the surface of PANI/N-CNT nanostructure is covered by a polymer layer (Fig. 2a). There are no uncovered sections of N-CNTs.

Figure 2 shows an example of the morphology, the EFM signal, and the section profile along the EFM signal line of the individual PANI/N-CNT nanostructure at a probe potential of 5 V. The bright contrast around the nanostructure in the EFM image indicates its conductive character. The contact potential difference between the probe and the nanostructure was determined and the electron work function was calculated from the profile analysis of the EFM image section of individual nanostructures using the procedure described in Ref. [6].

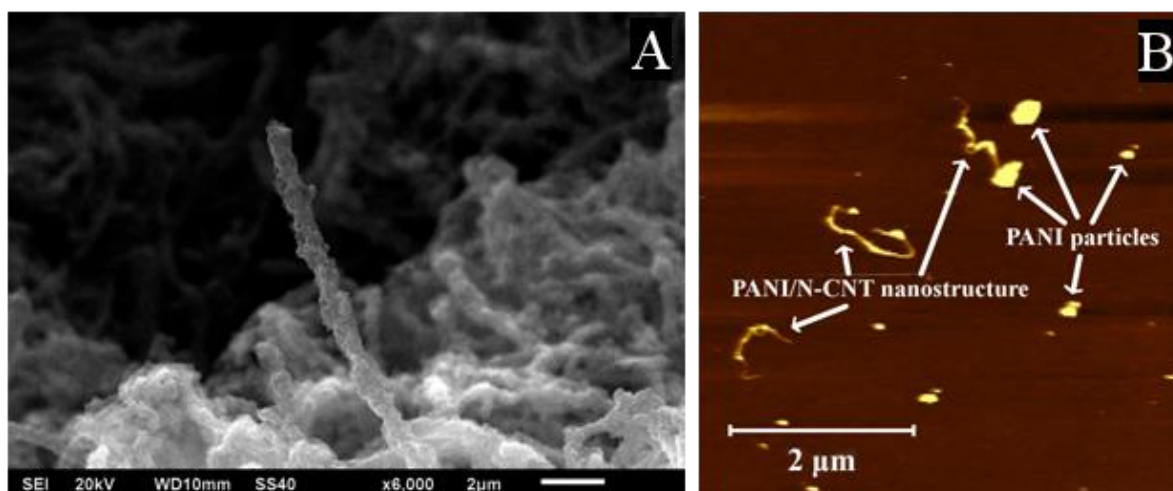


Figure 1. (a) SEM image of PANI/N-CNT bulk composite and (b) AFM image of individual PANI/N-CNT nanostructures on SiO₂/Si substrate.

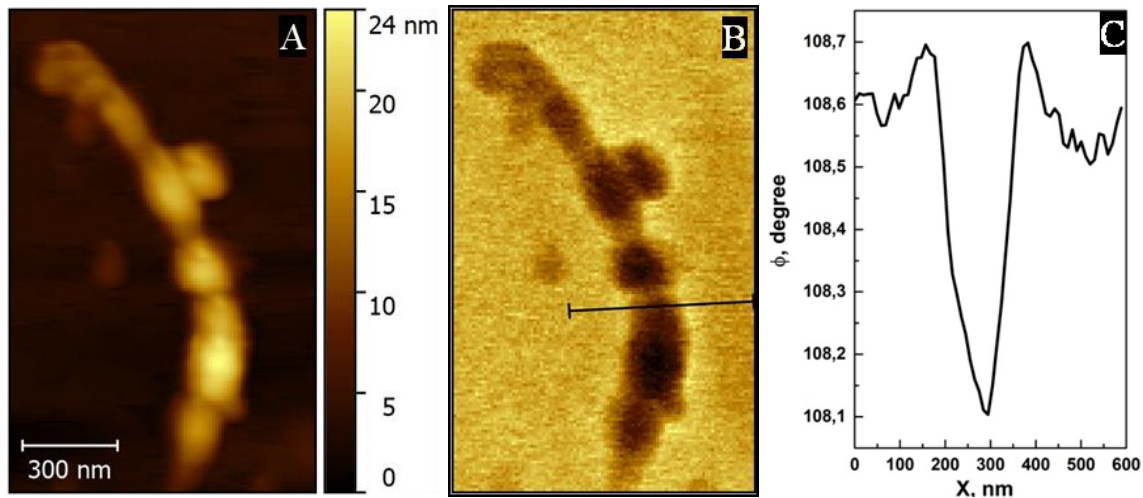


Figure 2. The PANI/N-CNT nanostructure: (a) AFM topography, (b) EFM image, and (c) cross section profile along the line marked at (b).

Figure 3a shows the change in the average value of the electron work function in individual nanostructures with an increase in the synthesis time of the composite. It can be seen that with an increase in the duration of synthesis, the work function in the nanostructures increases monotonically. The mean values and scatter of the electron work function in individual N-CNTs and in continuous thin layer of PANI/N-CNT composite can be also observed in Figure 3. The change in the work function in nanostructures occurs within the limits of these values and reaches a value of 0.4 eV.

We believe that increase of the work function with increasing of the synthesis time is due to two reasons. The polymer layer thickness on the CNT grows with increasing the synthesis time. The change in the work function with increasing thickness of the PANI layer can be demonstrated using the energy diagram of the PANI/N-CNT structure (Fig. 3b). At the polymer/nanotube junction, a space-charge region (SCR) is formed in the polymer. PANI band bending down leads to a decrease in the work function. Therefore, with decreasing thickness of the polymer layer on CNT, the work function of PANI/N-CNT nanostructure decreases. The work function of the bulk layer of PANI/N-CNT composite considerably exceeds the work function of nanostructure. This is due to the fact that the main contribution in the work function is provided by thick polymer layers on the CNTs or unrelated polymer particles.

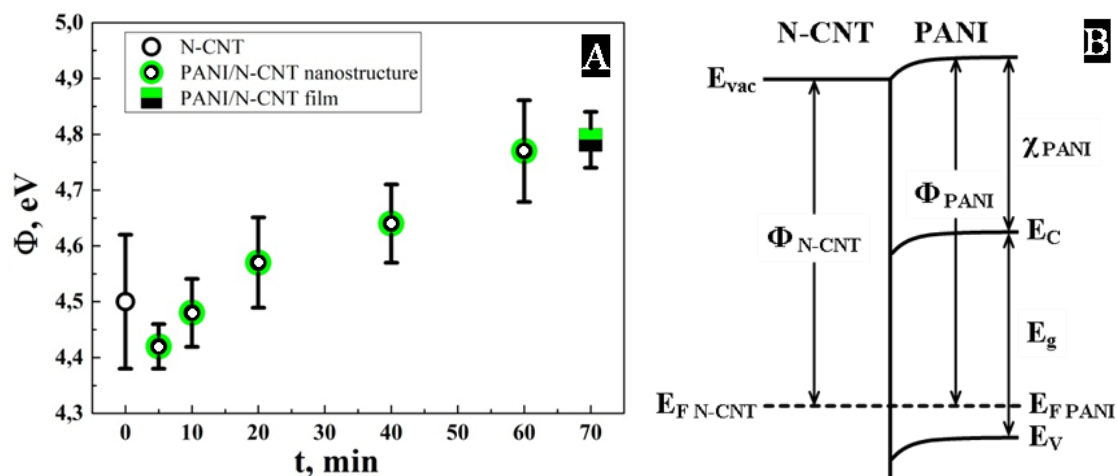


Figure 3. (a) Work function of PANI/N-CNT nanostructure vs. synthesis time and (b) energy diagram of PANI/N-CNT junction.

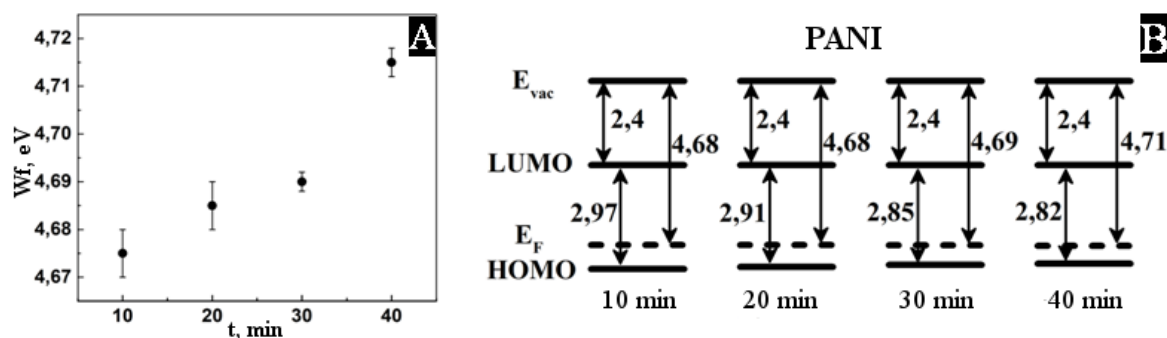


Figure 4. (a) Work function of PANI vs. synthesis time and (b) energy diagram of PANI for different durations of synthesis.

We estimate the thickness of the SCR in PANI using the expression:

$$W = \sqrt{\frac{2\varepsilon\varepsilon_0\Delta\Phi}{eN}} \quad (1)$$

where ε is the permittivity of the PANI, which we take as 6.6 Fm^{-1} [7]; ε_0 is the electric constant; $\Delta\Phi = \Phi_{\text{PANI}} - \Phi_{\text{N-CNT}}$ is the barrier height equal to 0.3 eV; e is the electron charge; N is the concentration of charge carriers, taken as 10^{24} m^{-3} [8].

The estimated value of the SCR width in the PANI is 15 nm. According to this estimate, when the thickness of the polymer layer on an N-CNT is less than this value, the work function of the nanostructure will decrease and tends to a value for N-CNTs with a decrease in the thickness of the PANI. Thus, the variation of the work function in the nanotubes and the thickness of the PANI coating on the CNT makes it possible to adjust the work function in the individual PANI/CNT nanostructures.

Another reason for changing the work function with an increase in the duration of the synthesis may be a change in the electronic properties of the polymer. Earlier, we showed that with an increase in the synthesis time of pure PANI, the work function was increasing [9]. Figure 4a shows the change in the work function in the pure PANI layer depending on the duration of synthesis, as well as change of the band structure of the polymer at different durations of synthesis (Fig. 4b). This change is attributed to the increasing degree of protonation of the polymer, increasing concentration of charge carriers, and the shift of the Fermi level toward the valence band.

4. Conclusion

The electron work function in individual PANI/N-CNT nanostructures was determined by EFM method. It is shown that the work function of nanostructures monotonically increases with the duration of synthesis. This value lies in the range from the work function of N-CNT to that of the bulk PANI/N-CNT composite layer. These changes in the work function of PANI/N-CNT nanostructures are associated with an increase in the thickness of the polymer layer on CNTs and an increase in the degree of protonation of PANI with an increase in the synthesis time of PANI/N-CNTs composite.

Acknowledgments

The work was carried out according to the state task of the OSC SB RAS (project registration number AAAA-A17-117041210227-8) and partially supported by the Russian Foundation for Basic Research (grant 18-48-550009 p_a).

References

- [1] Kumar A M and Gasem Z M 2015 *Surf. Coat. Tech.* **276** 416-23
- [2] Mariano L C, Salvatierra R V, Cava C E, Koehler M, Zarbin A J G and Roman L S 2014 *J. Phys. Chem. C* **118** 24811-8
- [3] Ji T, Tu R, Mu L, Lu X and Zhu J 2018 *Appl. Catal. B: Environ.* **220** 581-8

- [4] Liu P, Han J-J, Jiang L-F, Li Z-Y and Cheng J-N 2017 *Appl. Surf. Sci.* **400** 446-52
- [5] Ramana G V, Srikanth V V S S, Padya B and Jain P K 2014 *Eur. Polym. J.* **57** 137-42
- [6] Davletkildeev N A, Stetsko D V, Bolotov V V, Stenkin Y A, Korusenko P M and Nesov S N 2015 *Mater. Lett.* **161** 534-7
- [7] Zakrevskii V A, Kuz'min S V and Sudar' N T 2008 *Polym. Sci. Ser. A* **50** 411-6
- [8] Toušek J, Toušková J, Chomutová R, Křivka I, Hajná M and Stejskal J 2017 *Synth. Met.* **234** 161-5
- [9] Lobov I A and Shulus I K 2018 *Omsk Scientific Bulletin* **159** 98-101