

AFM study of the supramolecular transformation of polyaniline and polyaniline/carbon nanotubes composite upon doping with dodecylbenzenesulfonic acid in the presence of a solvent

I A Lobov*, N A Davletkildееv, D V Sokolov

Omsk Scientific Center SB RAS, Omsk 644040, Russia

*LI__87@mail.ru

Abstract. In this work, we present a new approach for the formation of conducting polyaniline and polyaniline/carbon nanotube composite films with well-developed surface morphology. This approach consists in combined influence of solvent and dopant on the base form of the polymer film. The morphology of the films has been studied by atomic force microscopy. It has been found that polyaniline films possess the fiber structure, and polyaniline/carbon nanotube composite films have the island-like structure.

1. Introduction

Polyaniline (PANI) is one of the most extensively studied conducting polymers due to its unique electrical, optical, chemical properties, stability in air, easy of synthesis, and low cost. PANI is used in a wide range of applications, such as chemical sensors, supercapacitors, display devices, battery electrodes, fuel cells, etc. [1-3]. Physicochemical properties of the PANI may vary within wide ranges depending on synthesis conditions and dopants. The used dopants represent usually strong inorganic and organic acids, such as hydrochloric, sulfuric, camphor sulfonic, methane sulfonic, and dodecylbenzenesulfonic acid (DBSA). The usage of organic acids leads to formation of conductive PANI with increased strength, stability, and conductivity [4-6].

The PANI composites with nanoparticles demonstrate the improved electrical conductivity, tensile strength, and thermostability as compared with pure PANI [1,7]. The unique properties of carbon nanotubes (CNTs) [8] allow using them efficiently as a PANI polymer matrix filler, which leads to significant improvements of the polymer properties [9,10]. There are various methods to obtain PANI/CNTs composites: the introduction of the nanotubes in the polymer matrix by their direct mixing, nanotube surface modification by polymer layer, or in-situ chemical and electrochemical polymerization of aniline in the presence of CNTs [5,11,12]. Last two methods allow obtaining the most stable bond between polymer and nanotube.

Effective surface area plays a very important role in sensitivity of polymer layers, when PANI and composites on its basis are used for sensor devices. Therefore, the surface control of the obtained polymer film is important. Currently, there are a few basic methods to obtain PANI films and composites on its basis with high surface area [7,13,14]. The disadvantages of these methods are limitation of choice of the dopant and poor control of layer thickness needed for sophisticated equipment.



In this work, we propose to form the PANI films and composite of PANI with CNTs (PANI/CNTs composite) in conductive form by influence of a mixture of the solvent and the dopant on the polymer film in the basic form. This technique allows obtaining a well-developed surface morphology. We can produce films of controlled thickness using spin-coating method. The surface morphology of the PANI and PANI/CNTs composite films was examined by atomic force microscopy (AFM). This method allows obtaining 3D image of polymer layers with high resolution.

2. Experimental

2.1. Synthesis of multi-walled CNTs

Multi-walled CNTs were synthesized by chemical vapor deposition resulting from pyrolysis of toluene vapors at 850°C with added ferrocene as a source of catalyst Fe. CNTs were characterized by transmission electron microscopy and AFM [15].

2.2. Synthesis of polyaniline

Solution A: aniline $C_6H_5NH_2$ (2 ml), LiCl (3,2 g), 2-propanol (20 ml), and 3M HCl (21 ml) were mixed and cooled to -15°C. Solution B: ammonium persulfate $(NH_4)_2S_2O_8$ (APS) (1,25 mg), LiCl (1,6 g), and 3M HCl (12 ml) were mixed and cooled to -15°C. LiCl was added to the reaction mixture in order to avoid its congealing. Then, solution B was added slowly dropwise to the solution A with constant stirring in order to initiate the polymerization of the aniline monomer. During polymerization of aniline, the originally colorless mixture turned blue and later became dark green as a result of 1 h reaction. The dark green color indicated formation of the doped emeraldine salt. The product was washed thoroughly with 3M HCl to remove the unreacted monomer and oxidant, and was finally washed with acetone.

2.3. Synthesis of PANI/CNT nanocomposite

PANI/CNTs composite was synthesized by in situ chemical oxidative polymerization of aniline. The CNTs (wt-1% based on aniline monomer concentration) were previously dispersed in the 2-propanol, using sonication for 2 h. Then suspension was dispersed in aniline solution. The reaction mechanism was the same as for PANI.

2.4. Formation of PANI and PANI/CNT nanocomposite developed layers

Emeraldine base (EB) PANI and EB PANI/CNTs composite were dissolved in N-methyl-2-pyrrolidone C_5H_9NO (NMP) and deposited on the Si/SiO₂ substrate via spin coating. To convert EB films into the emeraldine salt (ES) they were doped with dodecylbenzenesulfonic acid $C_{12}H_{25}C_6H_4SO_3H$ (DBSA), mixed with NMP. After that, the film was carefully washed with deionized water and dried in air.

2.5. Measurements

The surface morphology of the PANI and PANI/CNTs composite films was examined by an atomic force microscope MFP-3D SA (Asylum Research) in tapping mode in air. The cantilevers NSG01 (NT-MDT) were used, with resonant frequency 150 kHz, spring constant 5 N/m, and tip curvature radius 10 nm.

3. Morphology studies

Figure 1 shows AFM image of the EB PANI (Fig. 1a) and EB PANI/CNTs composite (Fig. 1b) films. The surface roughness of these films is 3.1 and 4.6 nm for the polymer and composite, respectively. The films structure has a granular appearance. The granule size is 60 ± 7 and 80 ± 12 nm for EB PANI and EB PANI/CNT films, respectively (Fig. 2). The presence of the granules indicates that the polymer molecules are coiled into a ball, which is typical for many macromolecules.

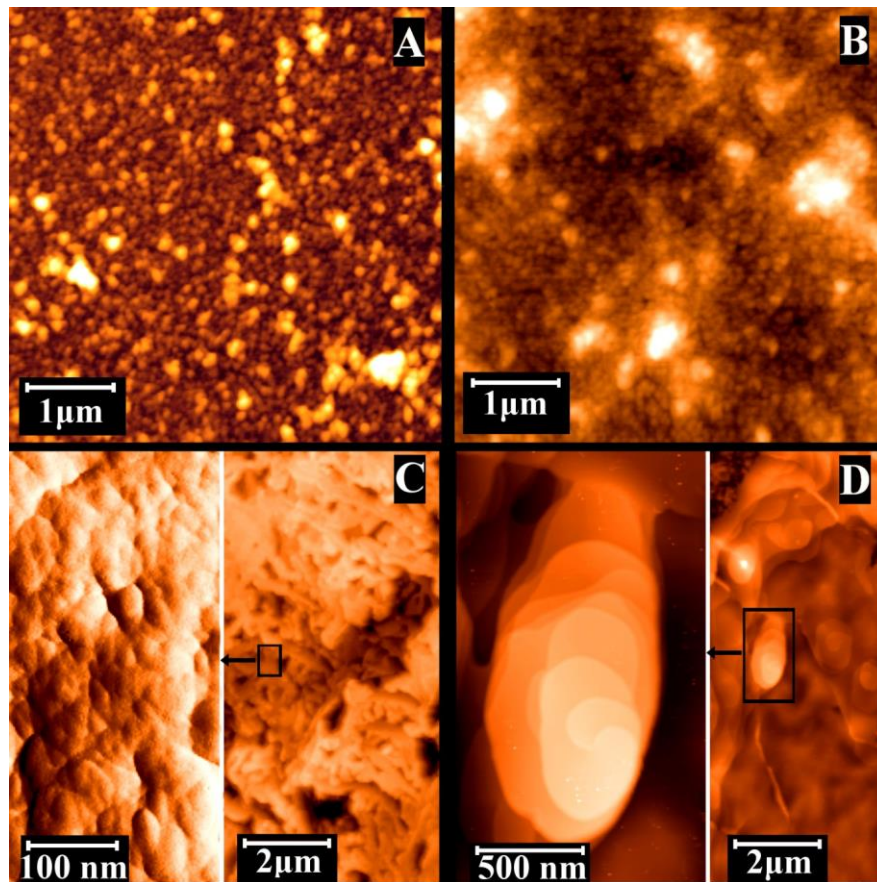


Figure 1. AFM images of: (a) EB PANI, (b) EB PANI/CNTs composite, (c) ES PANI, and (d) ES PANI/CNTs composite films.

After doping EB PANI film, a layer of chaotic interwoven fibers is formed (Fig. 1c). The width of these fibers varies from 200 to 350 nm. The surface roughness of ES PANI film has increased almost by an order of magnitude (22 nm) in comparison with EB PANI film. The observed granular structure of the fibers (Fig. 1c, left part of the image) has an average granule size of about 40 ± 4 nm (Fig. 2). Reducing of the granule size is associated with both an increased packing density of the PANI molecules due to electrostatic force and the transition from hydrophilic to hydrophobic state, which leads to displacing water molecules from the polymer.

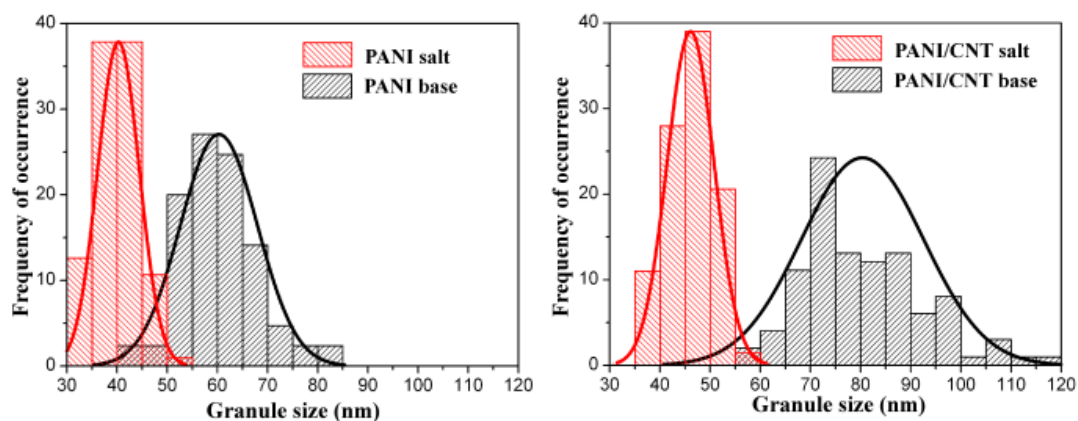


Figure 2. Histograms of the PANI and PANI/CNTs granule size distribution.

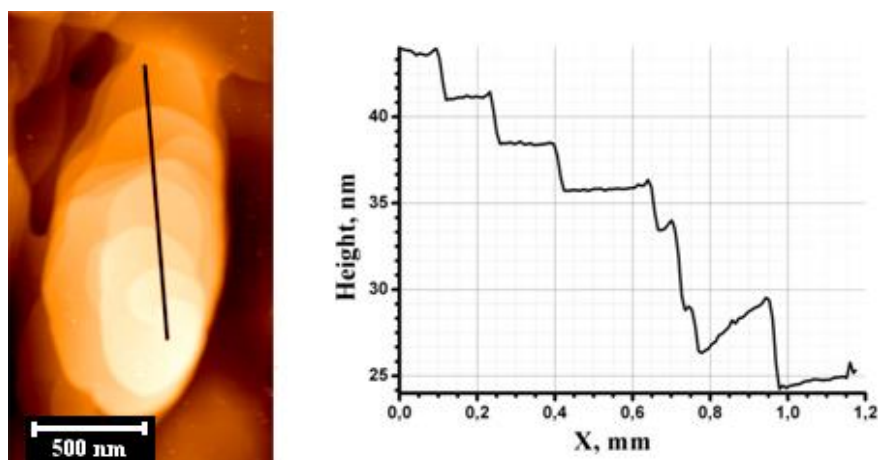


Figure 3. AFM image of island-like structure of PANI/CNT composite and cross section along the line.

After doping EB PANI/CNTs composite film, a developed layer with an island-like structure is formed (Fig. 1d). The islands have a layered structure and consist of superposed circular planes (Fig. 1d, left part of the image). Lack of granular structure indicates that polymer molecules unfold completely. The steps with height from 3 to 45 nm can be observed on the edges of the planes (Fig. 3). A quite large DBSA molecule with a long hydrocarbon tail is used as a dopant. It is interesting, that the height of the steps on the edge of the planes is multiple of length of DBSA molecules. It may indicate the incorporation of the dopant molecules between polymer planes.

It should be noted that the obtained films have areas of the discontinuity of the developed polymer layer (Fig. 4). These areas have a granular appearance (Fig. 4, upper parts of the images). The granule size is 40 ± 4 and $45 \pm 4,7$ nm for the polymer and composite, respectively (Fig. 2). The surface roughness of such area increases in comparison with EB films (4.2 and 12 nm for PANI and PANI/CNTs composite, respectively). This granular layer is an intermediate layer between the substrate and the developed polymer layer. It occurs due to the strong adhesive interaction between the polymer and the substrate. The layer provides a large contact area and high adhesive force of the developed polymer layer with the substrate.

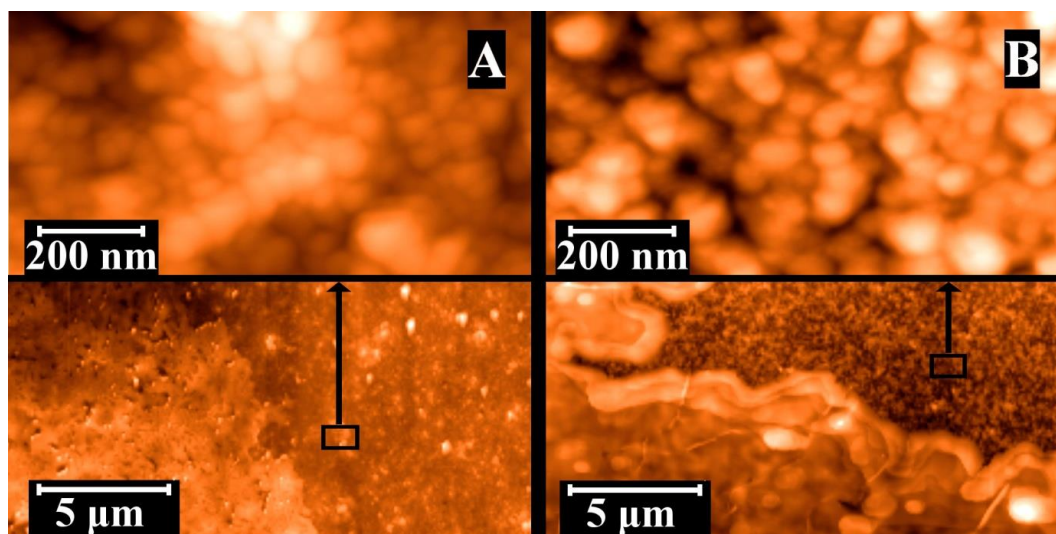


Figure 4. AFM images of ES PANI (a) and ES PANI/CNTs composite (b) films in the areas of the discontinuity of the developed polymer layer.

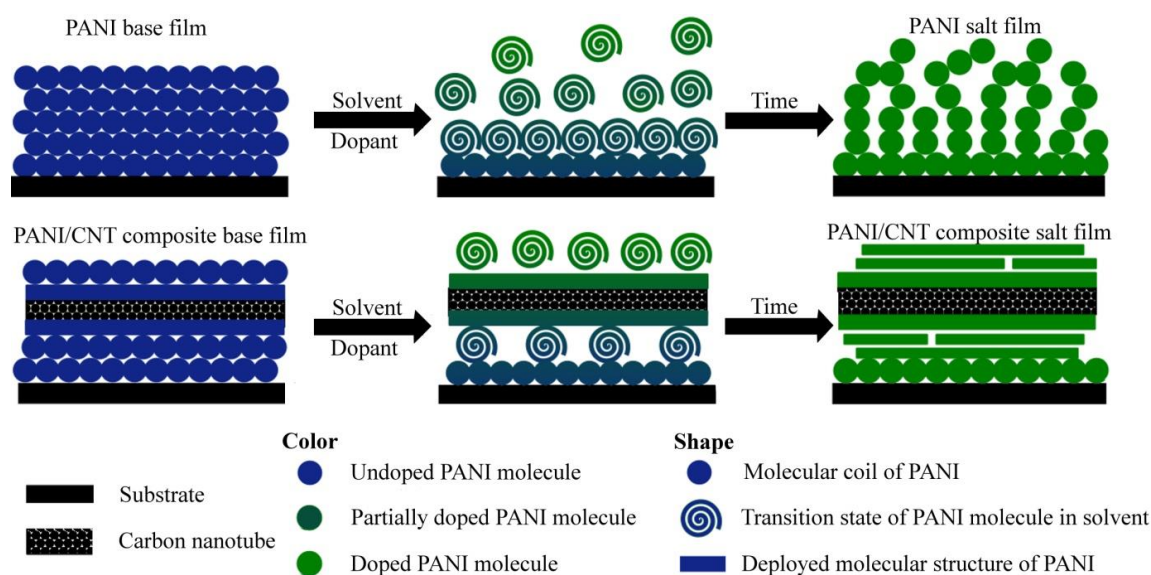


Figure 5. The formation scheme of the developed surface structure. The effect of the solvent on the polymer leads to a change of the molecule shape. The effect of the dopant on the polymer leads to a change of color (from blue to green).

On the basis of the AFM studies, the model of the formation of the developed surface structure can be proposed (Fig. 5). There are processes of dissolution of the polymer surface layer and the doping of polymer chains under the joint impact of solvent (NMP) and dopant (DBSA) on PANI and PANI/CNTs composite films. Under the influence of the solvent, an area with the polymer concentration gradient in the direction of the substrate is formed. The presence of the dopant in the solvent leads to the formation of conductive polymer complexes with DBSA. These complexes are not soluble in NMP. Due to the high concentration of PANI in the subsurface layer of films, active interaction occurs between the polymer molecules, as a result a developed surface morphology of the films is formed. The main contribution to these interactions is made by electrostatic forces. These forces are generated because of the dipoles in the polymer chains appeared by implantation of an acid molecule in the polymer chain. The adhesive force of the polymer molecules to the substrate is high enough that prevents removing the polymer completely from the substrate. In this regard, the layer adjoining the substrate retains the granular appearance and does not undergo changes in supramolecular structure.

It is believed that the chemical oxidative polymerization of aniline in presence of CNTs leads to the formation of PANI with a flat polymer chain configuration. This is mainly due to the interaction between the aromatic structure of polymer and the graphene plane of CNTs due to π -stacking [16,17]. Thus, the CNTs surface is covered by polymer molecules with a deployed molecular structure [18]. Flat polymer chain structure facilitates the transition of molecular coils into ribbons upon doping. We believe that the growth centers of the islands are the CNTs. A polymer layer covering the nanotubes serves as a template.

4. Conclusion

We propose a new approach for the formation of a developed surface of polyaniline (PANI) and polyaniline/carbon nanotubes PANI/CNTs composite films, doped with dodecylbenzenesulfonic acid (DBSA). Initially non-developed emeraldine base (EB) layers transform in fiber and island-like structure for PANI and PANI/CNTs composite, respectively. The developed surface morphology of the films is achieved through simultaneous processes of dissolution of the PANI in the N-methyl-2-pyrrolidone C_5H_9NO (NMP) and doping with DBSA. Polymer films have areas of the discontinuity of

the developed polymer layer with a granular appearance. Granule sizes of PANI fibers and non-developed layers are equal.

Acknowledgments

This work was partially supported by the Russian Foundation for Basic Research (grant 16-08-00763a).

References

- [1] Ciric-Marjanovic G 2013 *Synth. Met.* **177** 1-47
- [2] Song B, Tuan C-C, Huang X, Li L, Moon K-S and Wong C-P 2016 *Mater. Lett.* **166** 12-5
- [3] Ansari M O, Khan M M, Ansari S A, Amal I, Lee J and Cho M H 2014 *Mater. Lett.* **114** 159-62
- [4] Babu V J, Vempati S and Ramakrishna S 2013 *Mater. Sci. Appl.* **4** 1-10
- [5] Jelmy E J, Ramakrishnan S, Rangarajan M and Kothurkar N K 2013 *Bull. Mater. Sci.* **36** 37-44
- [6] Li J, Fang K, Qiu H, Li S and Mao W 2004 *Synth. Met.* **142** 107-11
- [7] Patil D S, Pawar S A, Devan R S, Ma Y R, Bae W R, Kim J H and Patil P S 2014 *Mater. Lett.* **117** 248-51
- [8] Ruoff R S, Qian D and Liu W K 2003 *C. R. Phys.* **4** 993-1008
- [9] Gajendran P and Saraswathi R 2008 *Pure Appl. Chem.* **80**(11) 2377-95
- [10] Bal S and Samal S S 2007 *Bull. Mater. Sci.* **30**(4) 379-86
- [11] Yun S and Kim J 2007 *Synth. Met.* **157** 523-8
- [12] Kulkarni M V and Kale B B 2013 *Sens. Actuators B* **187** 407-12
- [13] Ma X, Wang M, Li G, Chen H and Bai R 2006 *Mater. Chem. Phys.* **98** 241-7
- [14] Lin Q, Li Y and Yang M 2012 *Sens. Actuators B* **161** 967-72
- [15] 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
- [16] Huang J-E, Li X-H, Xu J-C and Li H-L 2003 *Carbon* **41** 2731-6
- [17] Wang R-X, Huang L-F and Tian X-Y 2012 *J. Phys. Chem. C* **116** 13120-6
- [18] Wang Q, Yao Q, Chang J and Chen L 2012 *J. Mater. Chem.* **22** 17612-8