Evaluation of mechanical and electrical parameters of individual polyaniline nanoparticles

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Abstract. The work function, the static dielectric constant, and the elastic modulus of individual polyaniline nanoparticles in the base form deposited on HOPG were determined. Electrostatic force microscopy was used to determine the electrical parameters. The value of the work function is 4.66 eV. The dielectric constant is 2.2. Contact atomic force microscopy was used to determine Young's modulus. The modulus of elasticity is 4.42 GPa. The obtained values differ from the typical values obtained on bulk samples of the base form polyaniline. In the case of electrical parameters, this is due to contact phenomena between the conductive substrate and the dielectric nanoparticle. The Young's modulus of a polyaniline nanoparticle depends on the packing density of the macromolecule, while the Young's modulus of a compressed tablet depends mainly on the intermolecular forces.

1. Introduction

The desire to reduce the size of electronic devices toward submicron and even nanoscale lengths generates new requirements to the materials they are made of. The accurate measurement of electronic materials properties with high spatial resolution has become increasingly important. During the transition from the bulk structure to a separate nanoparticle, the properties of the material change significantly. Since standard characterization techniques are not capable of addressing the electronic properties of thin films or nanoparticles, new techniques are needed to achieve both higher accuracy and higher spatial resolution.

Polyaniline (PANI) is one of the most important conductive polymers, which is widely used in various electronic applications. The most important characteristics of conductive polymers are mechanical and electrical parameters, the magnitudes of which largely depend on the production conditions. The properties of PANI have been investigated basically with respect to its bulk state. Measurements, as a rule, are carried out on the polymer massive layers. Therefore, the results are influenced by the contact interactions between PANI molecules.

Scanning probe microscopy (SPM) is widely used to study the morphology and physical properties of 2D, 1D, and 0D materials. The method is based on the physical (mechanical, electrical, etc.) interaction of the probe with the sample. A variety of techniques that allow extracting different characteristics of the sample have been developed. Thus, mechanical interaction allows obtaining 3D surface morphology, elastic and adhesive properties. Electrical interaction allows identifying the sample portions with different resistance, revealing magnetic and ferromagnetic features, and calculating electronic properties. Most of the information obtained by SPM methods is the result of modelling and requires an understanding of the physics and the interaction nature in order to apply various models.
correctly. In respect of PANI nanoscopic methods of research, SPM is not so widespread. However, they can clarify many controversial issues, for example, related to the conduction mechanism.

The mechanical properties of PANI are mainly measured on compressed tablets [1]. The elastic properties of the polymer depend on the preparation conditions. Therefore, in order to obtain the mechanical properties of PANI itself, it is necessary to study them on a native sample. The measurement of PANI base form Young's modulus is the most appropriate, since PANI salts with various acids can affect the packing density of polymer molecules, hydrophobic properties (including the water content in the polymer), etc. SPM allows measuring Young's modulus both on films and on nanoscale particles. For this purpose, the measured indentation curve can be used in different models. The choice of a certain model depends, for example, on the shape of the probe or on the ductility of the material.

The electron work function (WF) is a fundamental thermodynamic property of the material. SPM allows measuring this parameter by various methods, such as scanning tunnelling microscopy, Kelvin probe force microscopy, or electrostatic force microscopy (EFM) [2,3]. PANI WF can vary from 4 to 5 eV. WF depends on protonation level, type of dopant acid, film preparation, and others.

Broadband Dielectric Spectroscopy is usually used to determine the dielectric characteristics of polymers. This technology allows measuring both static and dynamic permittivity. It can be used both for bulk materials and for thin films [4]. However, the study of 1D and 0D objects is not possible. SPM allows measuring the static dielectric constant of not only thin films, but also nanoscale objects [5].

This paper presents the results of measurements of the electron work function, dielectric constant, and elastic modulus of individual PANI nanoparticles (PANI-NP) in the emeraldine base form containing a small number of molecules. The measurements were carried out in a single experiment using two methods of scanning probe microscopy.

2. Experimental

2.1. Preparation of PANI-NP
PANI was obtained via chemical oxidative polymerization of aniline [6]. Ammonium persulphate (APS) was used as an oxidizing agent. Two solutions were prepared. The first of them contained 3 ml of aniline, 25 ml of 3M HCl, and 40 ml of isopropyl alcohol. The second one included 7.5 g of APS and 15 ml of 3M HCl. The molar ratio of aniline monomer to APS is 1:1. Both solutions were cooled to 0°C in an ice bath. Then a solution containing an oxidizing agent was added dropwise to the first solution with constant stirring. The reaction flask was placed in an ice bath to maintain a constant synthesis temperature. Synthesis time is 40 min. Then PANI was transferred in an emeraldine base form by stirring a 1 M NH₃ for 24 h. The PANI-NP was separated from the bulk polymer by sonication in ethanol. A suspension of nanoparticles was deposited on a freshly split HOPG.

2.2. Characterization
Measurements of individual PANI-NP using EFM and contact atomic force microscopy (AFM) were obtained using AFM MFP-3D (Asylum Research). Measurements were performed at room temperature in air. We used a HA_FM/Pt probe (TipsNano) with a resonant frequency of 108 kHz and a radius of curvature of 35 nm. Second pass height was 100 nm. The voltage was varied in the range from -9 to +9V. The electron work function was determined from the magnitude of the positive phase shift in the EFM images using the technique described in [7]. We are using the negative phase shift measured from EFM images and the model described by [5] to calculate the dielectric constant for PANI-NP. In the model used, the probe was taken as a sphere, and the sample was taken as a flat disk. The magnitudes of the Young’s modulus were determined by fitting the model curve constructed using the Hertz model for a conical probe to the force-indentation curves using the Asylum Research MFP-3D Hertz analysis tool.
3. Results and discussion

Figures 1a,b show an example of AFM and EFM images of a PANI-NP consisting of several polymer macromolecules, as well as their cross-sectional profiles showing the characteristic particle size of PANI (Fig. 1c) and the contrast feature of its EFM image (Fig. 1d). PANI-NP sizes range from 100 to 300 nm, and heights from 40 to 65 nm. The light contour (positive phase shift) around the nanoparticle and the negative phase shift inside it are clearly visible in the EPM image.

The electron work function was determined from the magnitude of the positive phase shift [7]. HOPG with a known work function of 4.6 eV was used in the work. Before measuring, the probe was calibrated on pure freshly split HOPG for goal determinate of tip WF (4.82 eV). Figure 2a shows the parabolic dependence of the tangent of the EFM positive phase shift on the magnitude of the tip voltage. The position of the dependence minimum on the voltage axis corresponds to the contact potential difference between the tip and the PANI-NP. Value of this difference $\Delta U_{\text{PANI-NP/tip}}=0.16$ V. The average electron work function of PANI-NP calculated on the basis of such dependences was $W_{\text{PANI-NP}}=4.66$ eV. Work function PANI measured on bulk structures lies in the range from 4 to 5 eV [2,8]. Such a large variation is due to the fact that many parameters influence the value of the work function. The obtained WF value is close to the values of the protonated forms of PANI. This is possible due to the presence of contact phenomena between the conductive substrate and the sample. Depending on the ratio of the WF PANI and HOPG, the formation of an ohmic contact or an energy barrier for charge carriers is possible.

Figure 2. (a) Typical dependences of the tangent of the EFM positive phase shift and (b) the dielectric constant of the PANI-NP on the applied tip voltage; (c) experimental indentation curve of a PANI-NP and its approximation by the Hertz model.
We are using the negative phase shift measured from EFM images to calculate the dielectric constant of PANI-NP. The phase shift of the EPM signal is associated with the capacitance according to the formula given in [9]. In our model, the probe was taken as a sphere, and the sample was taken as a flat disk. Figure 2b shows the dependence of the calculated value of the static dielectric constant of the PANI-NP on the applied voltage. The average dielectric constant of PANI-NP is $\varepsilon_{\text{PANI}}=2.2\pm0.6$. The value of static dielectric constant for volume PANI is about 4 [10]. The small value of $\varepsilon_{\text{PANI}}$ in our experiment confirms the presence of contact phenomena.

Figure 2c shows a typical PANI-NP indentation curve with an AFM probe, built on the basis of force curves, its approximation by a model curve constructed on the basis of solving the Hertz model for a conical probe. When calculating the elastic modulus, we used the Poisson’s ratio for PANI $\nu=0.38$ from [11]. The average value of the Young's modulus of the PANI-NP was $E = 4.42$ GPa. Typical values of the elastic modulus of the base form PANI layers is 1 GPa [11,12]. When measuring Young's modulus on pressed tablets or on polymer films, the main contribution is made by intermolecular interactions. When a probe is identified in a nanoparticle consisting of one or two layers of polymer molecules, the packing density of the macromolecule makes the main contribution to the Young’s modulus.

4. Conclusion
In the work in a single experimental cycle, the electrical and mechanical properties of PANI-NP are investigated. It is shown that due to the small size of the object of study and the need to use a conductive substrate, the electrical properties of the nanoparticles differ from the similar parameters of the bulk PANI samples. To reduce or eliminate the influence of contact phenomena, it is necessary to use a different type of substrate. Further work will be aimed at studying this issue. The obtained value of Young's modulus corresponds to the elastic properties of an individual polymer macromolecule.

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