Evaluation of mechanical and electrical parameters of individual polyaniline nanoparticles

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The desire to reduce the size of electronic devices to the nanoscale makes new demands on the materials from which they are made. During the transition from the bulk structure to a separate nanoparticle, the properties of the material change significantly. 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 only 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. This paper presents the results of measurements of the electron work function, dielectric constant and elastic modulus of individual PANI nanoparticles containing a small number of molecules. The measurements were carried out in a single experiment using two methods of scanning force microscopy.

PANI was obtained via chemical oxidative polymerization of aniline [1]. The PANI nanoparticles were separated from the bulk polymer by sonication in ethanol. A suspension of nanoparticles was deposited on a freshly split HOPG. Measurements of individual PANI nanoparticles using electrostatic force microscopy (EFM) and contact atomic force microscopy (AFM) were obtained using AFM MFP-3D (Asylum Research). The electron work function was determined from the magnitude of the positive phase shift in the EFM images using the technique described in [2]. We are using the negative phase shift measured from EFM images and the model described by [3] to measure the dielectric constant for nanoparticles of PANI. 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.

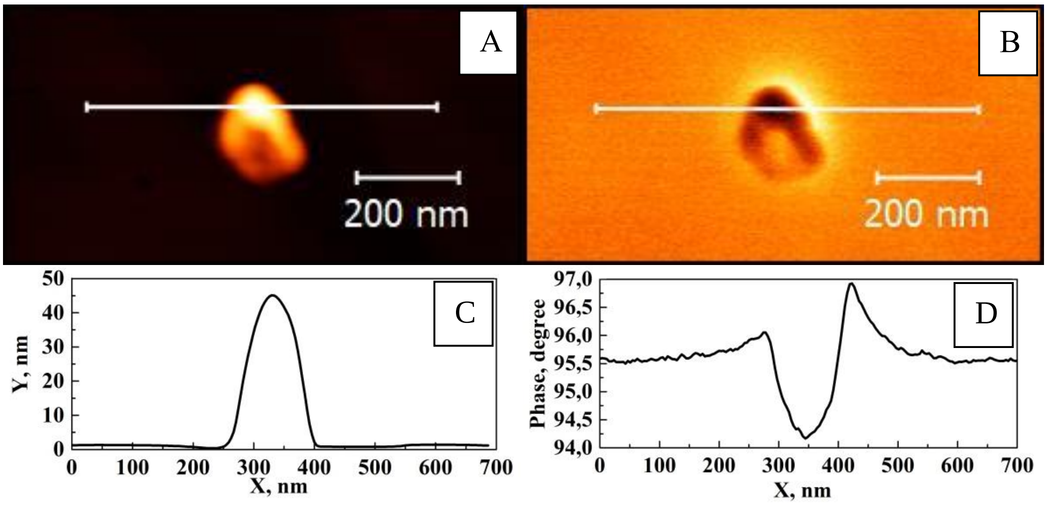

Figure 1. (a) AFM image, (b) EFM image of PANI nanoparticle, and (c,d) their cross-sections along line.

Figures 1a,b show an example of AFM and EFM images of a PANI nanoparticle 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). An increase in the EFM signal (oscillation phase of the cantilever) around the nanoparticle indicates the presence of conductivity in it.

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 nanoparticle. The average electron work function of PANI nanoparticles calculated on the basis of such dependences was $W = 4.88$ eV. This value is consistent with the magnitude of the work function we obtained earlier on the PANI monolayer films.

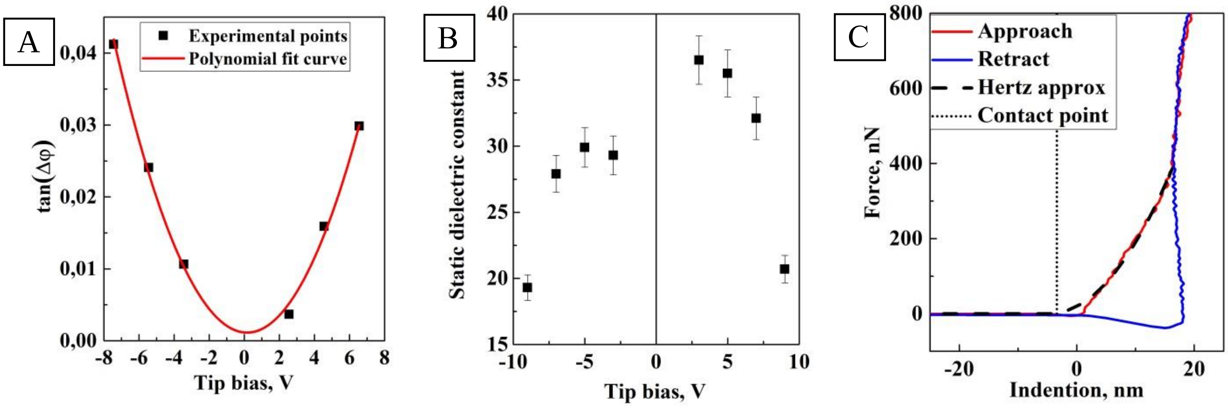

Figure 2. Typical dependences of the tangent of the EFM positive phase shift (a) and the dielectric constant (b) of the PANI nanoparticle on the applied tip voltage; (c) experimental indentation curve of a PANI nanoparticle and its approximation by the Hertz model.

Figure 2b shows the dependence of the calculated value of the static dielectric constant of the PANI nanoparticle on the applied voltage. With increasing voltage, the dielectric constant decreases, this shows a decrease in the polarizability of PANI molecules with increasing electric field strength. The obtained values of the PANI nanoparticles dielectric constant are in the value range of the PANI layers dielectric constant with different degrees of protonation [4].

Figure 2c shows a typical PANI nanoparticle 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 [5]. The average value of the Young's modulus of the PANI nanoparticles was $E = 4.42$ GPa. The obtained value corresponds to typical values of the elastic modulus of the PANI layers [6].

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