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An atomic force microscopy mode for nondestructive electromechanical studies and its application to diphenylalanine peptide nanotubes

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ABSTRACT

Nondestructive scanning probe microscopy of fragile nanoscale objects is currently in increasing need. In this paper, we report a novel atomic force microscopy mode, HybriD Piezoresponse Force Microscopy (HD-PFM), for simultaneous nondestructive analysis of piezoresponse as well as of mechanical and dielectric properties of nanoscale objects. We demonstrate this mode in application to self-assembled diphenylalanine peptide micro- and nanotubes formed on a gold-covered substrate. Nondestructive in- and out-of-plane piezoresponse measurements of tubes of less than 100 nm in diameter are demonstrated for the first time. High-resolution maps of tube elastic properties were obtained simultaneously with HD-PFM. Analysis of the measurement data combined with the finite-elements simulations allowed quantification of tube Young's modulus. The obtained value of 29 ± 1 GPa agrees well with the data obtained with other methods and reported in the literature.

1. Introduction

Determination and characterization of functional properties of individual nanoscale objects, such as two-dimensional (2D) materials, nanowires, nanotubes, and nanoparticles, becomes of increasing need for understanding and tailoring their properties, search for novel materials and assembly strategies. Scanning probes with various scanning probe microscopy modalities are indispensable tools in this research field. However, the existing techniques and recipes of scanning probe measurements frequently turn out to be destructive; poorly controlled mechanical contacts and contact forces between probes and nanoscale objects are harmful to the samples. This demands development of new techniques based on a refined control of the mechanical probe-sample interactions during acquisition of signals characterizing functional properties of nanoscale objects. In response to this demand, AFM imaging using high-speed force spectroscopy allowing a fine control over the probe-sample mechanical force has been implemented by a number of AFM manufacturers: Bruker (PeakForce mode), WITec (Digital Pulsed Force Mode), Asylum Research (Fast Force Mapping) and NT-MDT (HybriD mode). However, the ability of parallel piezoresponse measurements has not been implemented and demonstrated thus far. Such measurements are extremely important for studies of soft and fragile objects (e.g., ferroelectric polymers [1,2] and graphene [3]). They are also indispensable for characterization of loose nanoscale objects with pronounced piezoelectricity such as nanopowders, nanofibers, nanowires, and nanotubes [4–14]. In this work, we present a novel approach to nondestructive measurements of piezoresponse with simultaneous mapping of quantitative nanomechanical properties and demonstrate its application to piezoresponse and Young's modulus studies of diphenylalanine peptide nanotubes (PNTs) as a model system.

Self-assembly of bioorganic materials is a convenient tool for the fabrication of micro- and nanodevices with emergent functional properties [15,16]. Peptides are of particular importance as molecular building blocks because of their unique characteristics that can be tuned by changing the amino acid sequence and conjugating chemical groups to achieve targeted functionality [17]. Assembly mechanisms based on various noncovalent intermolecular interactions allow peptides to adopt a range of diverse 3D architec-

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tures such as vesicles, micelles, monolayers, bilayers, fibers, tubes, ribbons, spheres, and tapes [18]. In the recent decade, nanotubes of short aromatic peptides (as exemplified by diphenylalanine, FF, which consists of two molecules of amino acid phenylalanine, F) have attracted significant attention due to their outstanding physical and chemical properties, which are of importance from both the fundamental and application points of view [19]. Along with inherent biocompatibility, they possess high aspect ratios, strong piezoelectricity [20,21], notable pyroelectricity [22], and interesting optical properties related to quantum confinement of charge carriers. These useful functional properties are considered to be important for the design of novel biosensors and bioelectronic and biomolecular devices. For example, it has been shown that microtubes of FF (self-assembled bundles of the nanotubes) exhibit clear piezoelectric resonance in the MHz range with high quality factors and, thus, can serve as piezoelectric sensors and actuators in micromechanical systems (MEMS) [23]. Special attention was paid to the remarkably rigid structure of FF nanotubes that allowed high frequency modulation. Its experimentally measured transversal Young's modulus varies from 9 to 27 GPa [24,25]. Piezoelectric and quantitative mechanical studies of FF peptide tubes were recently performed by means of atomic force microscopy (AFM). Contact Piezoresponse Force Microscopy (PFM) was used for mapping of polarization direction and quantifying the d_{15} piezoelectric constant. However, a review of literature on contact PFM studies of FF peptide tubes reveals that the lateral force acting between the tubes and mechanical probes during scanning results in tube displacement and damage.

The nondestructive method proposed in this work is based on the HybriD AFM mode (NT-MDT Spectrum Instruments), i.e., on a high-speed force spectroscopy with real-time processing of the force-distance curves [26]. With use of this method, we demonstrate nondestructive PFM measurements of the FF nanotubes for piezoresponses both along and normal to the tube axes. Moreover, simultaneously with the PFM characterization and imaging, transversal Young's moduli of the tubes were obtained by means of AFM Force Spectroscopy. It is worth noting that previously, quantitative mechanical properties of suspended and substrate-fixed FF tubes were measured via indention of AFM probes [27,28]. The results are controversial with values 19 ± 1 GPa in [28] and 27 ± 4 GPa [27]. Also, to the best of our knowledge, there are thus far no reports on mapping the tube mechanical properties with nanometer-level spatial resolution while they can vary along the tube axis. Therefore, further investigation of FF peptides in terms of nondestructive piezoresponse studies and quantitative nanomechanical measurements are required. In this work, we present quantitative mapping nanomechanical properties of the FF peptide tubes as well.

2. Method: HybriD PFM imaging

The method of the compositional analysis of the self-assembled peptide tubes is based on the HybriD (HD) imaging mode. This imaging mode implements a high-speed force spectroscopy via a tip-sample distance modulation following a sinus law with simultaneous real-time processing the force-distance curves. The mode allows fast quantitative measurements of sample local mechanical properties nondestructively, combining advantages of resonance-enhanced non-contact and non-resonant contact AFM probing. Such a combination opens up a path to a realization of nondestructive PFM measurements and imaging.

For simultaneous force spectroscopy and measurements of the sample piezoresponse, an AC bias voltage U_{sin} is applied to the conducting probe within the time window when the probe is in contact with the sample surface during the fast force spectroscopy. Vertical, *DFL(t)*, and lateral, *LF(t)*, piezoresponse signals are measured (Fig. 1), when the AC bias is applied. The method was implements with use of a fast-force spectroscopy controller HybriD 2.0 (NT-MDT Spectrum Instruments).

When compared with traditional PFM measurements, the HD approach has several key advantages. The probe is retracted from the sample while moving to the next pixel of the scan line, which minimizes the lateral probe-sample interaction and allows studies of fragile, soft, and weakly attached objects on a substrate. The parallel acquisition of the force spectroscopy and PFM signals provides simultaneous measurements of the Young's modulus, probe-sample adhesion force, and piezoresponse at a pixel. The method is insensitive to thermal drifts or drifts in the microscope causing parasitic changes of the AFM Deflection (*DFL*) signal. Therefore, in particular, the measurements can be straightforwardly performed while varying sample temperature.

In order to calculate the amplitude and phase of the vertical and lateral piezoresponses, digital synchronous detection of the *DFL(t)* and *LF(t)* signals is carried out within the in-contact time window followed by averaging the signal values over the unit force-distance curve. An analytical model of the synchronous detector indicated significant distortions in the calculations of the amplitude and phase associated with the shape of the *DFL(t)* and *LF(t)* curves at the U_{sin} frequencies below 100 kHz. Close inspection revealed several reasons for the distortions. First, abrupt changes of the *DFL(t)* and *LF(t)* signals at surface touch and probe liftoff contain frequencies comparable to that of U_{sin} in their frequency spectra. Second, the high-frequency filter, bandwidth of which is limited from below by the performance of the Programmable Logic Device (PLD), passes higher harmonics of the *DFL(t)* and *LF(t)* signals, which contain components at the frequency of the tip-sample distance modulation, f_{pz}. To minimize these distortions, only the amplitude and phase signals corresponding to the in-contact window are taken into account. The signals outside this window are set to zero to remove abrupt changes associated with the probe touch/liftoff. Since zeroing leaves abrupt changes of *DFL(t)* and *LF(t)* signals at the beginning of the in-contact window and introduces distortions into the averaged signal due to a phase delay in the HF filter of the synchronous detector, the *DFL(t)* and *LF(t)* signals are also offset within the in-contact window so that the values of the signals at the first point of the window equal to zero. Additionally, components at the frequency f_{pz} are subtracted from the *DFL(t)* and *LF(t)* signals before the synchronous detection. Analytical modeling of the synchronous detector showed that these steps allow performance improvements at the bias frequencies below 100 kHz (Fig. S1, Supplementary materials). Therefore, after the preliminary signal filtration to reduce the distortions associated with the shape of the force-distance curve, the method can be applied to samples demanding frequencies below 100 kHz for measurements of the piezoresponse.

The method was validated with use of a periodically-poled $LiNbO_3$ single-crystal (PPLN). The test sample consists of ferroelectric domains with a strictly vertical polarization and a width of about 5 µm. Imaging the sample using the proposed HD PFM showed a piezoresponse domain-to-domain phase change of 178 ± 4^{o} (compared to 180° in the ideal case), which demonstrates correctness of the measurement and signal processing (Fig. S2, Supplementary materials). To test the noise performance of the method, it was compared with that of the standard in-contact PFM using the same PPLN sample and identical imaging parameters: probe, probe-sample contact force, scan rate, feedback gain, bandwidth and phase of the synchronous detector reference signal (Fig. S3, Supplementary materials). RMS deviations of the phase signal within one ferroelectric domain were found identical for both the methods, while the RMS deviation of the amplitude signal was ca. 20% larger in the HD PFM than in the standard PFM. This increase stems from a shorter effective signal acquisition time in the HD