MEASURING OF THE STRUCTURAL CHARACTERISTICS AND ADHESION OF THE POLYANILINE THIN LAYERS BY THE ATOMIC FORCE MICROSCOPY

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Abstract

Polyaniline (PANI) is the most studied conducting polymer exhibiting unique electrical and optical properties, high environmental stability, and good redox reversibility. Taking into account the wide availability of aniline and its derivatives and the low cost, PANI is an ideal candidate in many practical applications such as sensors, displays, transistors etc. In this work, the structural characterization and adhesion properties of the PANI thin layers formed by in-situ polymerization on the glass substrate is presented. The structural characteristics like a morphology, roughness and thickness of the PANI layers and their adhesion to the gold and silica were analyzed by the atomic force microscopy. Adhesion of PANI to the gold was found to be significantly higher than to the silica. Depending on the deposition time (immersion of the glass slides in the reaction mixture), the single steps of the formation of a continuous PANI film can be very well observed. Creation started by the growth and rounding of individual PANI grains on glass substrate. During the first 20 minutes, the thickness and roughness of the layer increased. In the further 10 minutes, the gaps between them were filled with additional PANI chains, coming from the surrounding solution, the roughness of the layer decreased and the thickness didn't change considerably. Finally, continuous PANI film was formed with height about 70 nm. Surface characterization of PANI layers as well as the determination of their adhesion, has a great influence on their further use and application.

Keywords:

polyaniline, thin layers, atomic force microscopy, structural characteristics, adhesion

1. INTRODUCTION

Polyaniline (PANI) belongs to the group of the polymers containing conjugated π-electrons system, i.e. conducting polymers. PANI is one of the very promising materials with unique properties including controllable electrical conductivity, good environmental stability and redox reversibility. Therefore this polymer finds application in many fields, especially in electronics, sensors, catalysis, energy, or electrorheological fluids [1].

Atomic force microscopy (AFM) is the scanning probe microscopy technique based on the detection of interatomic forces between the atoms of the tip and the sample. The very sharp tip (curvature radius is in the order of tens of nanometres) scans the sample's surface to image and measure properties of different kind of materials. The cantilever is bending due acting the attractive or repulsive forces between the tip and the sample. The cantilever deflection is detected by a laser beam that is reflected and subsequently analyzed by the detector (**Fig. 1**). AFM provides 2D and 3D images in nanoscale. Using AFM we can observe the thickness, morphology and roughness of surface layer, the shape of the particles and their size. Also the presence of adhesion forces acting between the tip and the surface of the sample of studied sample can be determined. Typical force-distance (F-D)

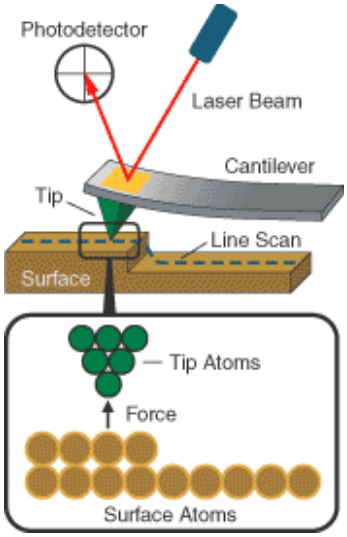

Fig. 1 Principle of the AFM measurement [2]

curve for tip with gold coating and PANI layer is showed in **Fig. 2**. The presence of adhesion forces is proved with the existence of difference in runs of both F-D curves (pull-on and pull-off). In our case the gold coated tip placed at the end of the AFM cantilever is approaching to the surface of polymer sample, when attractive as well as repulsive forces acts between the cantilever tip and sample surface with respect to the mutual tip-surface distance. During the retraction of the tip from surface a contribution of the adhesion attractive forces causes the delay in pull-off of tip from surface, which is proved by different course of F-D curve in comparison to F-D curve registered during landing of the tip to the surface. Adhesion forces are determined from the pull-off curves [3].

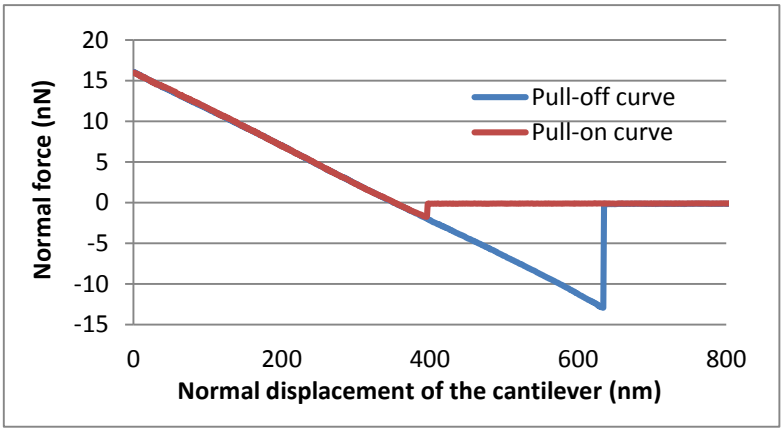

Fig. 2 Typical adhesion curve for tip with gold coating and layer PANI_10

All these characteristics at the nanoscale and below play a crucial role in determining the functional performance of many devices and greatly affect the resulting mechanical, optical, electrical and chemical properties of the surface of the investigated materials such as light scattering and X-ray radiation or conductivity [4].

2. EXPERIMENTAL

2.1. Samples preparation

In-situ polymerization of aniline is the most common method for preparation of PANI. In present work, PANI samples were prepared by mixing two solutions according to [5]. The first solution containing 0.2 M anilinium sulfate prepared in 0.5 M sulfuric acid and the second solution containing 0.1 M ammonium peroxodisulfate dissolved in distilled water at room temperature.

The glass slides (76 mm x 26 mm x 1 mm) were properly cleaned with soap solution, rinsed with distilled water and ethanol, dried and attached by clips on the rack. After mixing of the two reaction solutions, the glass slides were immersed into the beaker and the PANI thin layer started to grow on the glass slides. During the polymerization process, the glass slides were pulled out from the reaction mixture one by one after 10, 20 and 30 minutes, rinsed with 0.2 M hydrochloric acid then with ethanol and finally dried.

All prepared samples are denoted as PANI_T, where T is the deposition time (i.e. length of the immersion of glass slide in the reaction mixture).

2.2. Measuring methods

The surface morphology, roughness and thickness of the PANI layers were studied using SolverNEXT (NT-MDT) atomic force microscope (AFM) operated in semicontact (tapping) mode with the noncontact probes NSG10 and NSG30.

The adhesive forces were measured in the contact mode using the probes with either gold coated silicon tip (CSG01/Au), or uncoated silicon tip (CSG01).

The images and F-D curves were evaluated using Gwyddion software.

3. RESULTS AND DISCUSSION

3.1. Characterization of morphology

The morphology of the surface of PANI_10 sample (the sample prepared with 10 minutes long immersion of glass slide in reaction mixture) can be seen in **Fig. 3**. Because the glass with this layer was in the reaction mixture the shortest time, the image shows the beginning of the formation of the layer. PANI grains have only negligible tendency to aggregation into the large clusters, do not cover entire surface and do not create complete layer. However the distribution of the PANI on the glass is homogeneous.

The complete coverage of the glass slides with PANI particles is shown on the images of PANI_20 sample (**Fig. 4**). The grains are ceasing to be separated, which leads to their merging with the subsequent formation of the layer.

On the images of PANI_30 (**Fig. 5**) the changes that occurred during the last ten minutes of deposition time are observed. The gaps between the grains are filled by additional PANI chains coming from the surrounding solution causing the formation of more coherent PANI layer.

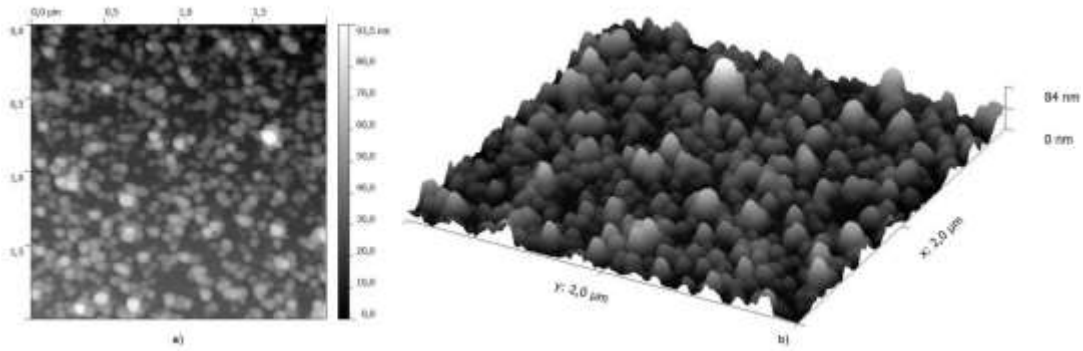

Fig. 3 AFM image of topography of layer PANI_10, 5x5µm, a) 2D, b) 3D

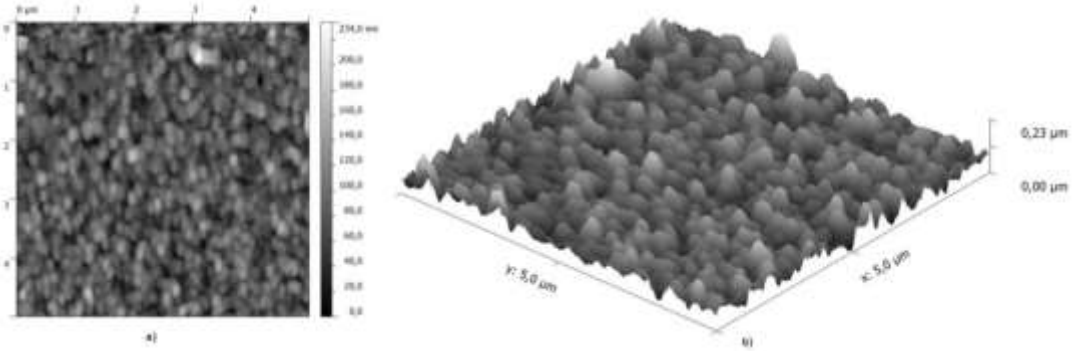

Fig. 4 AFM image of topography of layer PANI_20, 5x5µm, a) 2D, b) 3D

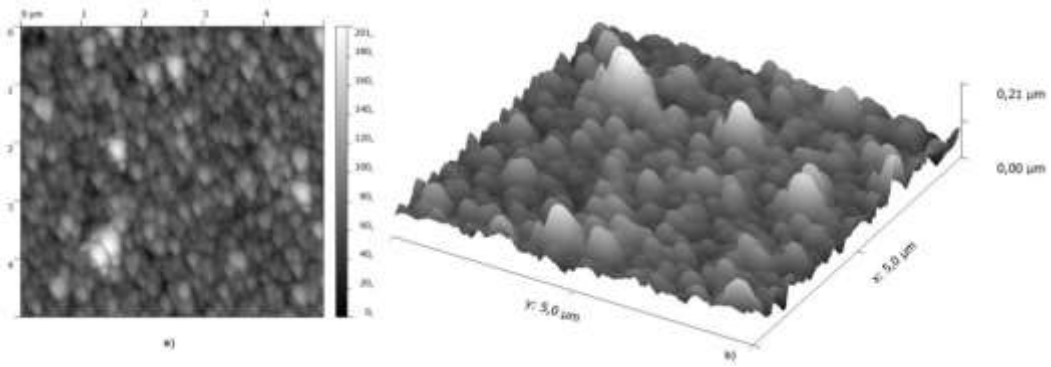

Fig. 5 AFM image of topography of layer PANI_30, 4.9x4.9µm, a) 2D, b) 3D

3.2. Measurement of layers thickness and surface roughness

The profiles of the roughness confirm the facts mentioned above. For profile of PANI layer deposited for 10 minutes each separated grain can be seen in **Fig. 6a**, unlike the profiles of PANI_20 where bonding the grains, creating continuous layer and increasing of roughness can be observed (**Fig. 6b**). In comparison with PANI_20, decreasing of roughness and filling the gaps between the grains can be seen on the roughness profile of PANI_30 (**Fig. 6c**). The values of roughness average (R_a) and root mean square roughness (R_q) were determined and calculated by software Gwyddion (**Table 1**).

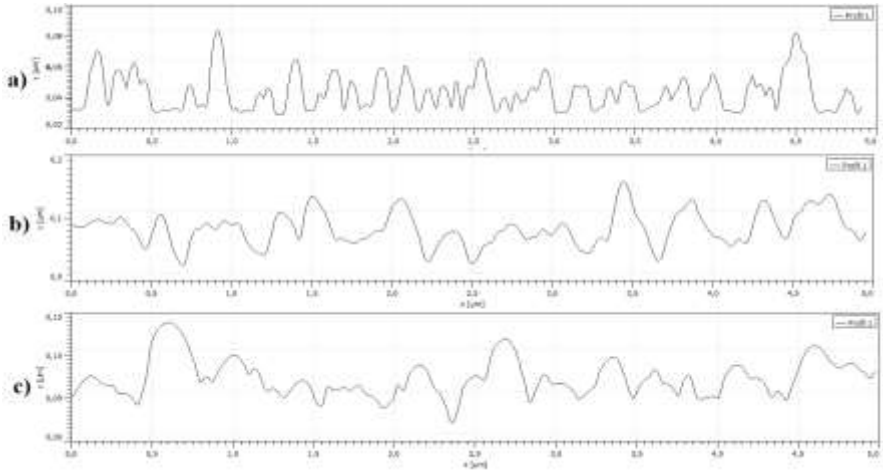

Fig. 6 The profiles of roughness, a) PANI_10, b) PANI_20, c) PANI_30

The thickness of the PANI layers was evaluated as a height of the step which was obtained after the scratching of the PANI layer using sharp scissor. The groove is extending to the glass substrate and using the AFM to scan just this transition (step) between the layer and the clear surface of glass (**Fig. 7** and **Fig. 8**). The thicknesses of the prepared layers are shown in **Table 1**.

During the first 10 minutes creation started by the growth and thickness of the layer was the smallest (**Fig. 8a**). After next 10 minutes, the thickness and roughness of the layer increased (**Fig. 8b**). In the last 10 minutes, the thickness did not change considerably (**Fig. 8c**). Finally, continuous PANI film was formed with height about 70 nm.

Table 1 The values of roughness average (R_a), root mean square roughness (R_q) and thickness of the layers

Sample	Thickness (nm)	R_a (nm)	R_q (nm)
PANI_10	11	9.8	13.0
PANI_20	70	23.6	34.5
PANI_30	68	20.4	29.5

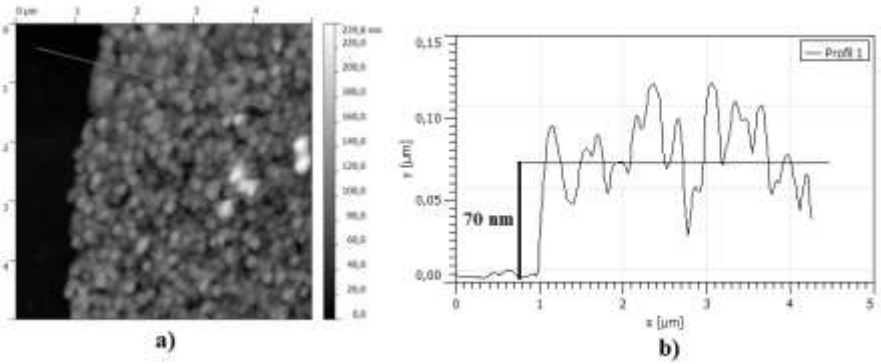

Fig. 7 AFM image of transition between the layer and glass of PANI_20, a) 2D image, 5x5μm, b) profile of this step

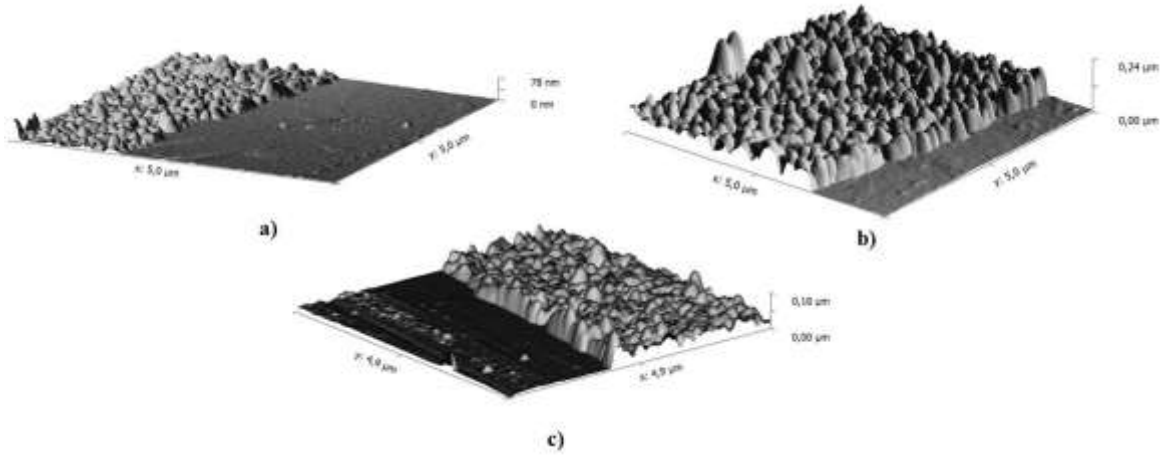

Fig. 8 3D AFM images of transition between the layer and glass, a) PANI_10, b) PANI_20, c) PANI_30

3.3. Measurement of adhesion

Experimental F-D curves were analyzed, the average pull-off forces were gathered and noted in **Table 2**. Measurement results of adhesive forces show that each of the PANI layers has a specific adhesion to the gold. Although PANI_10 exhibits the strongest adhesion, this value differs minimally from the others. Comparing adhesive forces for gold coated tip on a clean glass substrate with the results for PANI layers, it can be observed, that for PANI layers the measured values are two times higher than in the case of clear glass substrate.

Regarding on silicon tips without a gold layer, the measured adhesive forces are negligible and in fact do not differ from the values measured on a clean glass. Therefore it may be noted, that the PANI layers do not show adhesion to the silicon.

Table 2 Measured adhesion forces for the layers PANI_T and clear glass substrate

	Adhesion forces (nN)			
Type of probe/Sample	PANI_10	PANI_20	PANI_30	Clear glass substrate
CSG01/Au	**13.73**	**13.18**	**11.61**	**7.28**
CSG01	**2.28**	**2.12**	**1.89**	**2.33**

However, there is one important fact about measuring the adhesive forces. Whereas the measurements in microscope do not take place in vacuum, but in certain ambient conditions including also very important moisture, the capillary forces acting between the sample and the tip must be taken into account. These forces are created by the formation of meniscus of the water vapor layer adsorbed on the sample surface, which prevents "unstick" of the tip from the surface (**Fig. 9**). Arising high surface energy contributes to the adhesive forces [6]. Although the capillary forces are minimal when measured at about 35% of moisture, the results in **Table 2** are affected by the humidity. Nevertheless, all of them have been obtained under the same conditions and as such provide information about the adhesion of PANI on these substrates.

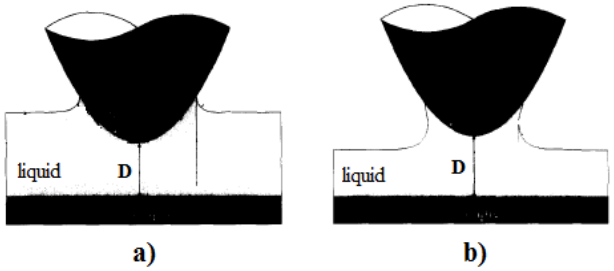

Fig. 9 The meniscus of the water vapor layer adsorbed on the sample surface onto a paraboidal tip, during a) approach and b) retraction, where D is the distance from the sample [6]

4. CONCLUSION

This work was focused on the study of the topography, thickness and adhesion of PANI films using the atomic force microscopy. Present results showed that the morphology, roughness and thickness of the PANI layers were changing with the deposition time. In the case of adhesion measurement the deposition time doesn't affect the value of adhesion forces.

ACKNOWLEDGEMENT

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LITERATURE

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