ELECTRICAL CONDUCTIVITY AND MORPHOLOGY OF POLYANILINE/MONTMORILLONITE AND DERIVED GRAPHENE-CONTAINING NANOCOMPOSITES

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Abstract

Tapping mode atomic force microscopy (TM-AFM) and scanning spreading resistance microscopy (SSRM) were found to be useful scanning probe microscopy (SPM) techniques for the characterization of surface conductivity and morphology of the conductive ceramics-like and graphene-containing nanocomposite prepared from polyaniline/montmorillonite (PANI/MMT) nanocomposite. In this work, the changes in conductivity and morphology of PANI/MMT nanocomposites before and after heat treatment are studied. PANI/MMT nanocomposite was prepared using oxidative polymerization of anilinium sulfate by ammonium peroxydisulfate in the presence of MMT particles (size fraction < 40 μm). Prepared PANI/MMT powder was pressed into tablets using pressure 400 MPa. These tablets were calcined in dynamic argon atmosphere at temperature 1400 °C for 1 hour. The changes of local current on the surface and on the fractures (i.e. in the internal volume) of tablets were studied using SSRM and the local current maps of PANI/MMT nanocomposites before and after calcination were compared. SSRM shows that while after the calcination the conductivity in the internal volume of the sample strongly increased, the conductivity on the surface disappeared. Tapping mode is characterized by a less sample-tip interaction and, therefore, with respect to the nature of prepared nanocomposites, provides images without many visible artefacts.

Keywords: Polyaniline, montmorillonite, graphene, tapping mode atomic force microscopy, scanning spreading resistance microscopy

1. INTRODUCTION

Scanning spreading resistance microscopy (SSRM) is a scanning probe microscopy (SPM) technique used for the measurement of surface conductivity. This characterization method is useful technique and allows to locate the nonconductive and conductive areas of the sample surface, especially of semiconductor materials and devices [1, 2]. The **Figure 1a** shows the principle of SSRM. Constant bias voltage is applied between the conductive tip and the conductive sample and the flowing current is measured simultaneously when the tip scans the surface. The measurement takes place in contact mode and SSRM offers both two dimensional imagining of local current distribution and appropriate images of contact morphology. With respect to the nature of sample, the quality of the resulting images depends mainly on the value of the bias voltage applied between the tip and the sample, on the choice of the type of conducting layer on the tip, and on the probe with appropriate stiffness of the cantilever.

Tapping mode atomic force microscopy (TM-AFM) technique is method which is used for the characterization of surface morphology. Oscillated cantilever moves near the sample surface and tip touches the surface only for a short time. In contrast with contact mode, scanning with oscillated cantilever allows to work with softer and easy to damage materials such as polymers or bioorganics.

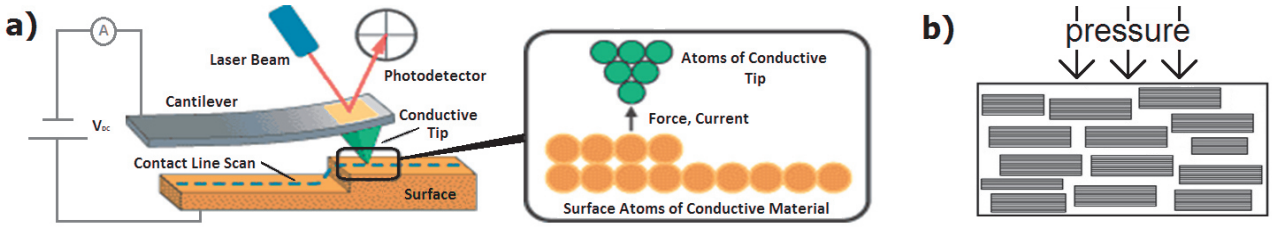

Figure 1a) The principle of SSRM measurement **b)** Arrangement of MMT particles intercalated by PANI in the pressed tablet (side view)

Graphene-containing nanocomposites, a group of synthetic conductive materials which have gained in importance in recent years, find great application such as anti-corrosive protective coatings, ultra-barriers for organic electronics or food and pharmaceutical packaging [3-6]. Graphene or graphene oxide can create nanocomposites with large scale of materials, for example polymers [3, 4], Al_2O_3 [5], or layered double hydroxides [6].

These materials usually containing commercial available graphene [3-5], or graphene synthetized using spark plasma sintering method [7]. Original method of preparation graphene from polyaniline was published by Čapková et al. [8]. Graphene-containing nanocomposite was prepared from polyaniline/montmorillonite (PANI/MMT) intercalate via high pressure (400 MPa) and high temperature (1400 °C) treatment [8]. The presence of graphene in final nanocomposite was confirmed by Raman spectroscopy (**Figure 2**) [8].

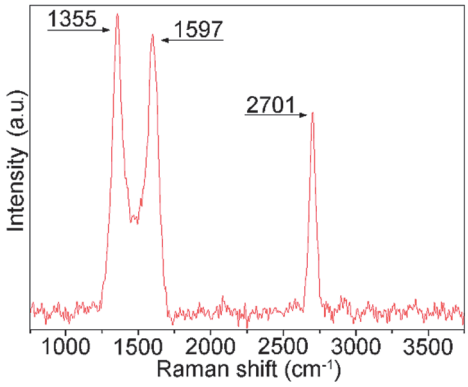

Figure 2 Raman spectrum of calcined PANI/MMT intercalate

Intensive band with maxima centered at 2701 cm^{-1} was found in spectrum of calcined sample. This band is generally ascribed to 2D (historically named G') overtone band of graphite, but high intensity of the band is typical for graphene [9, 10]. Raman spectrum (**Figure 2**) also contains the disorder band showing defects (1355 cm^{-1}) and the graphitic band determining orderliness of the carbon structure (1597 cm^{-1}). Presence of amorphous carbon is confirmed by broadness of the bands [9, 10]. Combination of Raman spectroscopy, molecular modeling and X-ray diffraction of both materials (i.e., PANI/MMT precursor and resulting graphene-containing nanocomposite) led to the conclusion that PANI→graphene transformation occurs in the interlayer space of MMT.

Only slight attention has been paid to SPM methods such as TM-AFM or SSRM which are capable to perform local conductivity measurements and detailed images of morphology.

Therefore, the main aim of this work is the use of TM-AFM and SSRM for study the influence of the heat treatment on the PANI/MMT nanocomposites and description of the changes in surface conductivity and morphology. Differences between the surface and internal volume (measured on fracture of tablets) of non-calcined and calcined samples are also compared.

2. EXPERIMENTAL

2.1. Materials and preparation of the samples

Aniline, ammonium peroxydisulfate and sulfuric acid were used as received from Lach-Ner, Czech Republic. Na-MMT Portaclay® was purchased from Ankerpoort NV, Netherland. Nanocomposite PANI/MMT was prepared by mixing the aniline solution in sulfuric acid and ammonium peroxydisulfate with aqueous

suspension of MMT particles (size fraction < 40 μm) at room temperature. Although the polymerization of aniline was completed within 40 minutes (blue color of suspension turned into dark emeraldine green - conduction form of PANI), the suspension was stirred for 6 hours. The green solid was collected on a filter by rinsing with distilled water and dried for 48 hours at 40 °C. Shift of MMT basal reflection (12.45 Å → 12.85 Å) suggested successful intercalation of MMT by PANI chains [8]. Powder samples were pressed into square tablets (28×28 mm, thickness 2.039 mm) using ZWICK 1494 press at room temperature, without any lubrication and binder. Applied pressure was 400 MPa. Increase in intensity of MMT basal reflection showed strong texture of PANI/MMT intercalate, i.e. MMT(001) planes are parallel to the tablet plane [8]. Schematic illustration is provided in **Figure 1b**. Non-calcined sample was denoted as P/M.

2.2. Thermal treatment

Tablet pressed from PANI/MMT powder was calcined in the furnace of the DIL 402 C/7 dilatometer (Netzsch GmbH, Germany) at the maximum temperature 1400 °C for 1 hour. The heating and cooling rate was 15 K·min^{-1} and the protective 99.999% Ar atmosphere with the constant flow rate 20 ml·min^{-1} was used. Calcined sample was denoted as P/M(1400), where the number means the temperature used.

2.3. Measuring methods

The surface morphology of non-calcined and calcined samples was studied using the TM-AFM with SolverNext (NT-MDT) atomic force microscope. For the measurement noncontact probes NSG30 (NT-MDT) were chosen. Local current maps of P/M and P/M(1400) sample were obtained using the same atomic force microscope operated in the mode of SSRM. During SSRM constant bias voltage +5 V was applied between the measured conductive sample and conductive tip. SSRM was performed in contact mode with the probes FMG01/Pt with platinum-coated tip (NT-MDT). The images of morphology and local current maps were evaluated using Gwyddion software.

3. RESULTS AND DISCUSSION

3.1. Measurement of morphology

The results of TM-AFM scanning are presented in **Figure 3** for P/M and **Figure 4** for P/M(1400) sample. **Figure 3** shows the morphology on the surface (**Figure 3a**) and in the internal volume (**Figure 3b**) before calcination. In comparison with the surface of P/M sample (**Figure 3**) in the internal volume the layers of MMT oriented perpendicular to direction of pressure can be clearly seen (compare with **Figure 1b**).

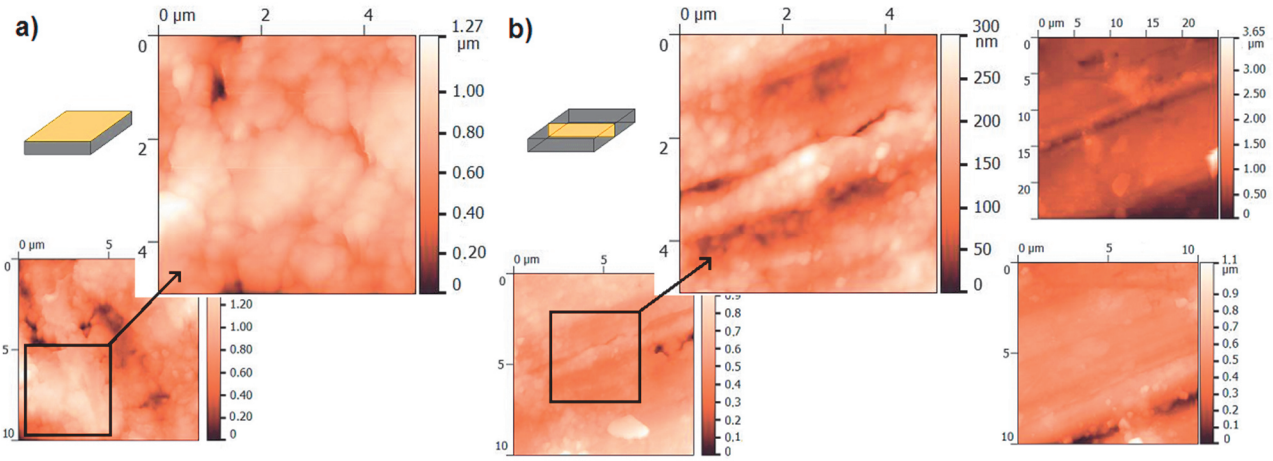

Figure 3 Tapping mode AFM images of P/M sample, a) morphology of the surface, b) morphology in the internal volume (measured on the fracture)

After the calcination the surface of the sample P/M(1400) changed (**Figure 4**). The surface of sample (**Figure 4a**) sintered and shows significantly different character in comparison with P/M. The average surface roughness decreased from 955 nm (P/M) to 257 nm (P/M(1400)). In some areas the bubble-like structures were created. In the internal volume the layers perpendicular to direction of pressure are less visible (**Figure 4b**). This fact confirms that during calcination the transformation of P/M occurred both on the surface and in the entire volume. **Figures 3** and **4** demonstrate how clear images of morphology can be obtained using TM-AFM.

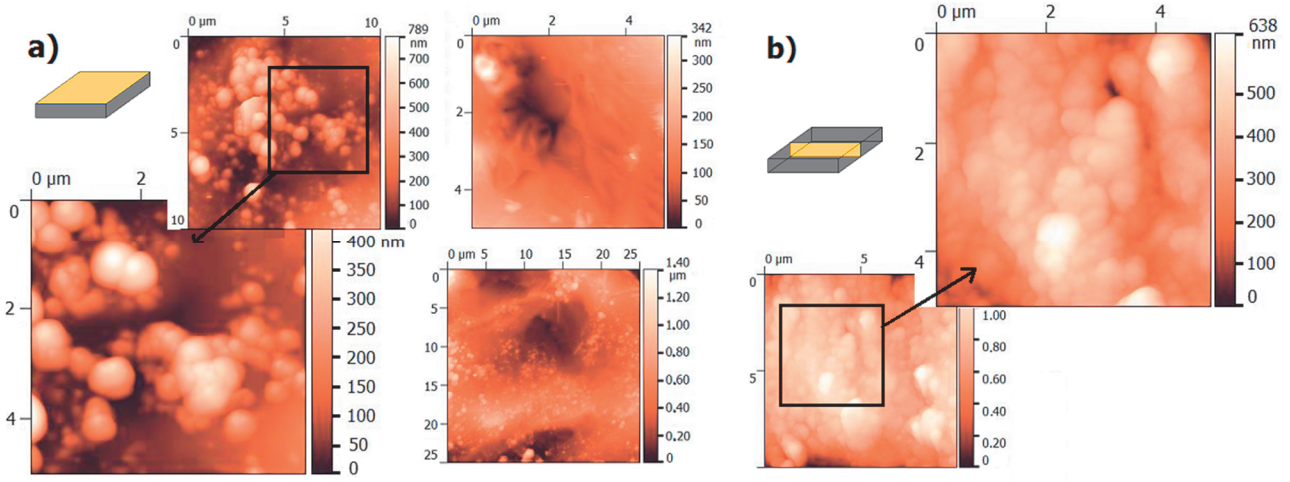

Figure 4 TM-AFM images of P/M(1400) sample, **a)** morphology of the surface; **b)** morphology in the internal volume (measured on the fracture)

3.2. Measurement of surface conductivity

The distribution of local current was studied using SSRM on the surface and in the internal volume of the samples. The changes in the surface conductivity of P/M and P/M(1400) samples were compared and all results can be seen in **Figure 5** and **Figure 6**, respectively.

Figure 5 shows the local current map in the internal volume (**Figure 5a**) and on the surface (**Figure 5c**) of P/M sample, i.e. before the heat treatment. On this typical local current map the maxima of the current achieved the value 34.7 nA and 15.4 nA. The average value of the current is ~ 5.9 nA (measured on the fracture) and ~ 1.1 nA (measured on the surface).

The morphology of the surface measured simultaneously in contact mode can be seen in **Figures 5b** and **5d**. In contrast with TM-AFM, the contact mode is characterized by a strong sample-tip interaction and with the respect to the nature of samples it provides images with many visible

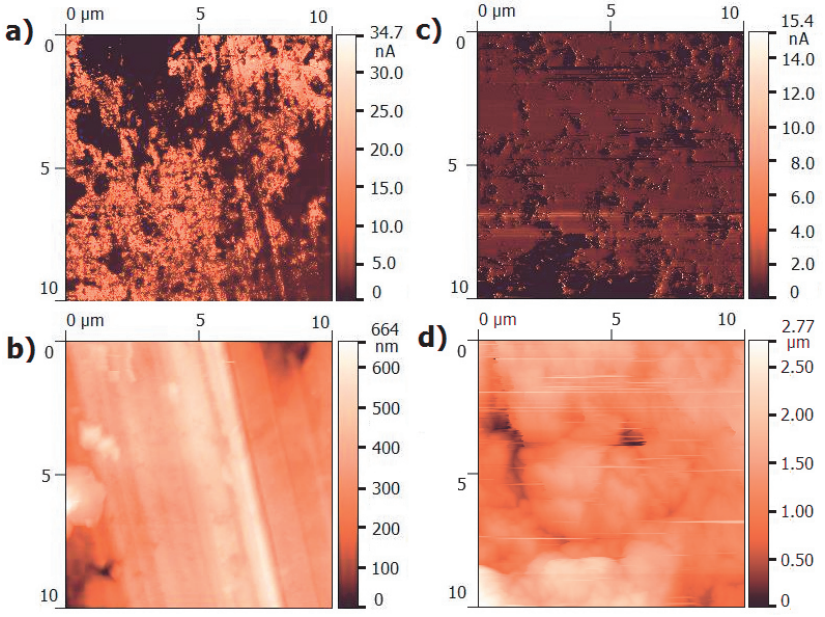

Figure 5 SSRM images of the P/M sample, **a)** local current map and **b)** respective morphology of surface; **c)** local current map and **d)** respective morphology in the internal volume

artefacts. This is the reason why TM-AFM lacking this deficiency was chosen for the imaging of the morphology in **Figures 3** and **4**.

After the calcination the surface conductivity of P/M(1400) sample disappeared (**Figure 6a**). Measured values of current in the order of pA are typical for the nonconductive sample (e.g. glass).

On the other hand, the conductivity in the internal volume increased and the maximum of the current is 536 nA. Current maxima are detected on the edge of large particles as shown by arrows in **Figures 6c** and **6e**. Average value of the current is 27.2 nA which is almost five times higher than for P/M sample. It means that the thermal treatment caused the changes resulting to decrease in conductivity on the surface, but strongly increase in conductivity in the internal volume of P/M(1400) sample. This result suggests importance of MMT particles for the PANI→graphene transformation occurring in the MMT interlayer space.

The morphology of the surface measured simultaneously with current maps in contact mode can be seen on **Figures 6b, 6d** and **6f**.

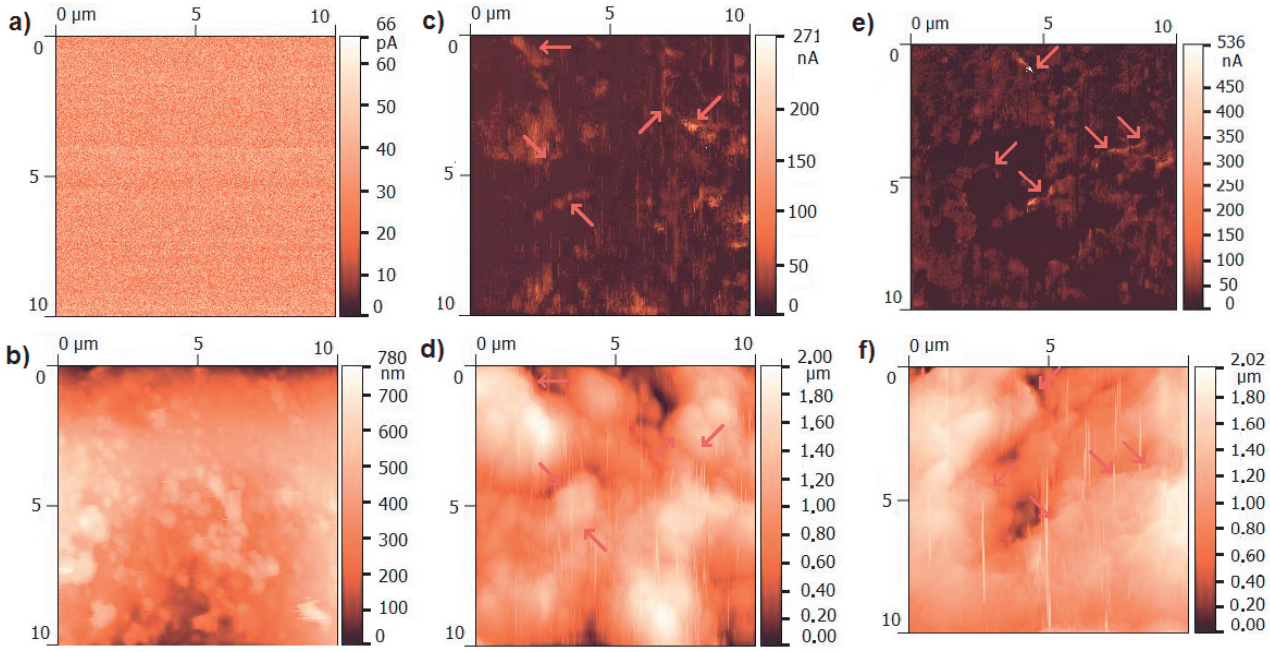

Figure 6 SSRM images of the P/M(1400) sample, **a)** local current map and **b)** respective contact morphology of surface; **c), e)** local current maps and **d), f)** respective contact morphologies in the internal volume

4. CONCLUSION

This work was focused on the application of the SPM techniques, TM-AFM and SSRM, for the characterization of PANI/MMT and derived graphene-containing nanocomposites. The PANI/MMT nanocomposites were prepared using oxidative polymerization of anilinium sulfate by ammonium peroxydisulfate in the presence of MMT particles, pressed into tablets using pressure 400 MPa and calcined in dynamic argon atmosphere at temperature 1400 °C for 1 hour to form ceramics-like graphene-containing nanocomposite. Presence of graphene in calcined sample was confirmed by Raman spectroscopy. The surface conductivity and morphology were measured using TM-AFM and SSRM on the surface and in the internal volume and differences between non-calcined and calcined samples were compared. Before the heat treatment in the internal volume the layers of MMT were oriented perpendicular to direction of pressure and the average of current measured on the fracture was 5.9 nA. After the heat treatment the surface of tablet sintered and in the

internal volume the MMT layers were less visible. The conductivity on the surface disappeared, but in the internal volume the conductivity strongly increased and the maximum of current is fifteen times higher than the maximum of the current in the case of non-calcined sample. The maxima of current were detected on the edge of large particles. Present results clearly demonstrate that the TM-AFM and SSRM is a highly suitable technique for characterization of the morphology and conductivity and localization of the conductive and nonconductive areas of the solid samples.

ACKNOWLEDGEMENTS

The study was supported by Ministry of Education, Youth and Sports of the Czech Republic (projects no. SP2015/50 and SP2016/63) and by the NPU II - IT4Innovations excellence in science (project no. LQ1602).

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