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Reconstruction of volume structure of carbon-based conductive polymer composites

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Abstract. Conductive polymer composites with different carbon fillers are under intensive investigation nowadays due to their unique properties and possible applications in different areas of science and technology. The percolation character of the conductivity behaviour in these materials and influence of nanoscale structure of conductive filler on macroscopic characteristics of composites make it important to determine the 3D structure of the components. Various electrical methods of atomic force microscopy (AFM) are efficient tools for visualization of a conductive network on a sample surface. In this work, we use a combination of AFM methods and ultramicrotomy for the 3D reconstruction of the filler structure in graphene-polystyrene and carbon black-epoxy-amine composites. Common features of the various composites, such as the formation of clusters with similar conductivity and limited number of filler particles forming a conductive network, are discussed.

1. Introduction

During the last two decades a new class of the conductive materials based on carbon fillers and nonconductive polymers was discovered and intensively investigated [1-4]. Various carbon materials were used as a conductive filler: carbon nanotubes (CNT), graphene (Gr), and carbon black (CB). The percolation character of the electrical conductivity in such composite materials provides a low value of resistance at very small amount of filler (usually parts of percent). Such composites are promising for using them as conductive coatings, paintings, transparent electrodes, sensors, etc. [5]. Knowledge of the nanoscale filler structure and its influence on the macroscopic properties is necessary for the development of new functional composite materials and improvement of their properties. The conductive filler inside a polymer forms a three-dimensional network. The structure of such a network can be visualized by various microscopy methods, including the various forms of atomic force microscopy (AFM) [4, 6] and electron microscopy [7]. The advantage of AFM is that it is possible to detect a range of electrical properties, such as conductivity, surface potential, and local charges, with nanometer resolution, which is important for reconstruction of the conductive network. Since AFM is a surface sensitive technique, additional sample treatment is needed for reconstruction of the 3D filler structure [8]. Controllable removal of a thin layer of material from the surface by methods, like ultramicrotomy, etching, and AFM probe scratching, is required for volume structure reconstruction by AFM. A combination of conductive-AFM (C-AFM) and ultramicrotomy was used for the 3D



reconstruction of nanoscale conductivity in CNT-polystyrene (CNT-PS) composites [9]. Clusters with a similar conductivity level were observed inside the sample volume. It was concluded that these clusters were linked by high resistance connections, which determined the overall current in a single cluster. The possibility to distinguish between the conductive network of graphene and electrically isolated flakes using different modes of AFM was demonstrated in Ref. [10]. In this article, we use a combined AFM-ultramicrotome device for the 3D reconstruction of the filler network in conductive Gr-polystyrene (Gr-PS) and CB-epoxy-amine (CB-EA) composites and compare results obtained for different carbon-based composites.

2. Experimental

Samples of a PS-Gr composite with 2% Gr were prepared using latex technology. Details of preparation route are described elsewhere [4]. CB-EA composites with 2.5% CB were prepared by mixing CB particles into epoxy matrix. All composites had filler concentration well above the percolation threshold.

The device combining AFM and ultramicrotomy (Ntegra Tomo, NT-MDT) was used for measurements and 3D reconstruction [11]. The probes were Au-coated CSG10 (NT-MDT) and NSC12 (Micromash). C-AFM was performed in contact mode, in which the voltage applied to the probe typically was in the range 0.1-1 V, while the samples were grounded. Electrostatic force microscopy (EFM) was performed in tapping mode using the two-pass technique. 3D reconstruction was performed with ImagePro software.

3. Results and discussion

The procedure of data acquisition and subsequent 3D reconstruction was the same as described before [9-11]. The topography and current distribution of a PS-Gr sample after microtoming are shown in Figure 1. The surface is rather flat (typical rms is 3-4 nm on $10 \times 10 \mu\text{m}^2$ area), except some pores and nearly vertical scratches due to the ultramicrotome knife. Since the topography is nearly flat, it is approximated by a plane for 3D reconstruction. This approximation is valid as we use a relatively large z -step of 180 nm. Combining 9 images separated by z -step of 180 nm leads to a reconstructed volume element of $15.7 \times 13.6 \times 1.5 \mu\text{m}^3$ (Fig. 1c). Figure 1 shows the presence of conductive domains of filler with different current levels, similar to results obtained on carbon nanotubes-PS composites [9]. Such clustering of nanoscale current pathways inside the composite is confirmed by Figure 1c. Unfortunately, it is not possible to see connection between the domains inside sample volume, since the size of graphene flakes is too large in comparison with the depth available with the method used for measurements. The z -range available for reconstruction using the AFM-ultramicrotome approach with reasonable z -resolution is usually limited by a maximum of 20-30 slices, leading to a thickness of $\sim 20\%$ from the x - and y -size [11]. Penetration of domains with similar current level inside the sample volume is additional proof for the clustering of current pathways in Gr-PS.

Figure 1 demonstrates the distribution of graphene flakes forming a conductive network, since the current is going through the sample volume between the conductive probe and the grounded sample holder with a total distance between the electrodes in the range of ~ 0.2 -1 mm. However, as was shown before [10], there are electrically isolated flakes, which can be visualized by EFM. It is not obvious that EFM can be used for 3D reconstruction, since there are different sources of EFM contrast: tip-sample capacitance and Coulomb interaction. As shown before [10], the penetration depth of EFM signal in Gr-PS composite is within 50-100 nm, which roughly corresponds to d_{air}/ϵ , where d_{air} is the distance from the surface, when the EFM contrast disappears, and ϵ is the permittivity of the polymer. From this observation, it can be concluded that the main source of contrast in EFM imaging of Gr-PS composites is the Coulomb interaction between the tip and the charged Gr flakes. Thus, relatively short range Coulomb interaction makes it possible to reconstruct the volume structure of electrically isolated graphene flakes inside composites by EFM. Figure 2 shows a 3D reconstruction of the graphene network inside a composite basing on 7 EFM images in a volume of $3 \times 2.2 \times 0.2 \mu\text{m}^3$ with a z -step of 30 nm. It is clear from Figure 2c that z -step of 30 nm is sufficient to get information on volume shape of graphene flakes. At the same time, both lateral resolution and z -resolution of 3D EFM reconstruction are worse

than those of C-AFM shown in Figure 1. Thus, both C-AFM and EFM can be used for 3D graphene network reconstruction, giving complementary information on the conductive network and the electrically isolated Gr flakes distribution.

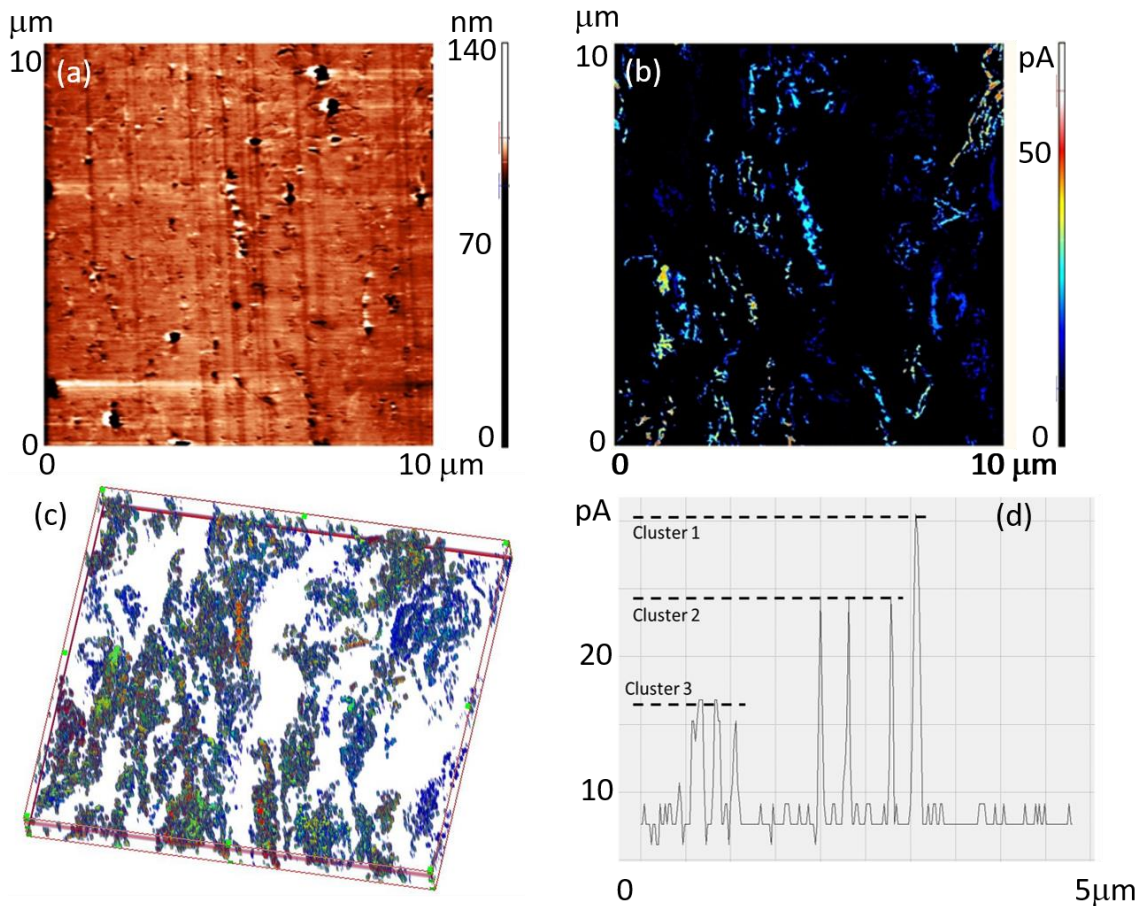


Figure 1. Gr-PS composite: (a) topography, (b) current distribution on the same area, (c) reconstructed volume structure of current inside a composite volume, (d) section of the current image.

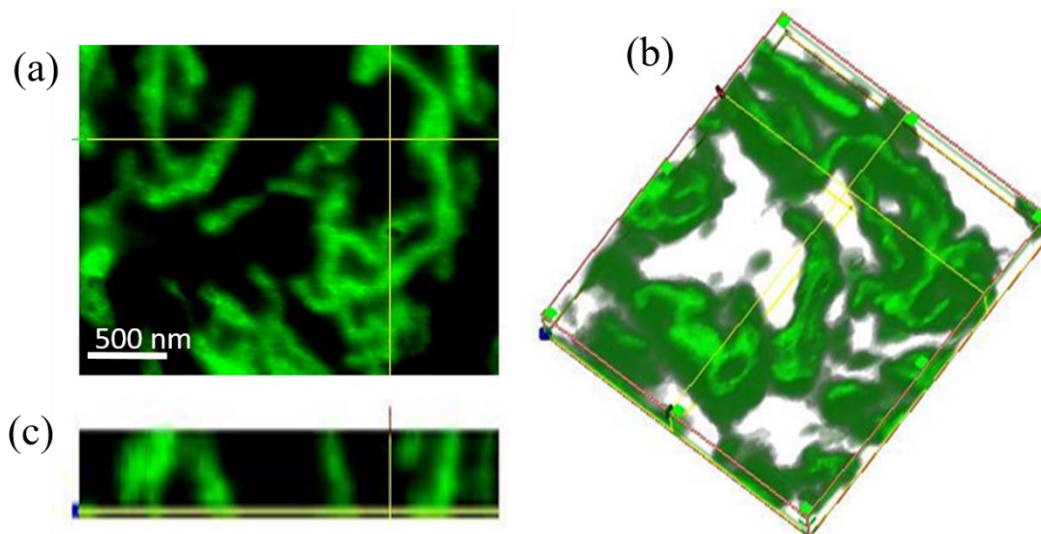


Figure 2. 3D reconstruction of Gr-PS based on EFM images: (a) top view (one of EFM images), (b) 3D EFM image, (c) vertical cross-section of (b) scaled for better visibility.

Another composite material studied by 3D AFM imaging is CB-EA. We used C-AFM for reconstruction of the nanoscale current inside a volume of this composite. The results of a reconstruction based on 28 slices and a z-step of 20 nm resulting in a volume of $4.5 \times 4.5 \times 0.54 \mu\text{m}^3$ are shown in Figure 3. Several conclusions can be drawn from these results. First, from a comparison of the topography and the current distribution measured on the same area (Figs. 3a,b), it is clearly seen that only part of the CB particles is connected to the conductive filler network, while many particles are electrically isolated. The particles are clearly visible in the topography image due to the different mechanical properties of the matrix and the filler, which leads to a different surface deformation during cutting. Second, again clustering of the current pathways inside the composite is observed. Since the z-step used for 3D reconstruction was comparable with the size of the CB particles, several connections between particles were obtained within the z-range used. Analysis of the obtained 3D data revealed the locations, where changes of current level occur (Figure 3d). In Figure 3d, the transition from a low current cluster (blue color) to a cluster with a higher current level can be observed. The current level is indicated by the color bar in Figure 3b. Thus, these locations are interpreted as “bottle necks” with a high resistance between two neighboring clusters inside the sample volume. The size of the conductive clusters is directly related to the size of the filler particles: clusters of current pathways in CB-based composite are much smaller than those in Gr- or CNT-filled materials and more connections between particles are observed in the same volume. The probability to find a transition between clusters is higher just below the surface, since the number of conductive branches increases with increasing distance from tip and then a “bottle neck” should be expected after a few connections between the particles.

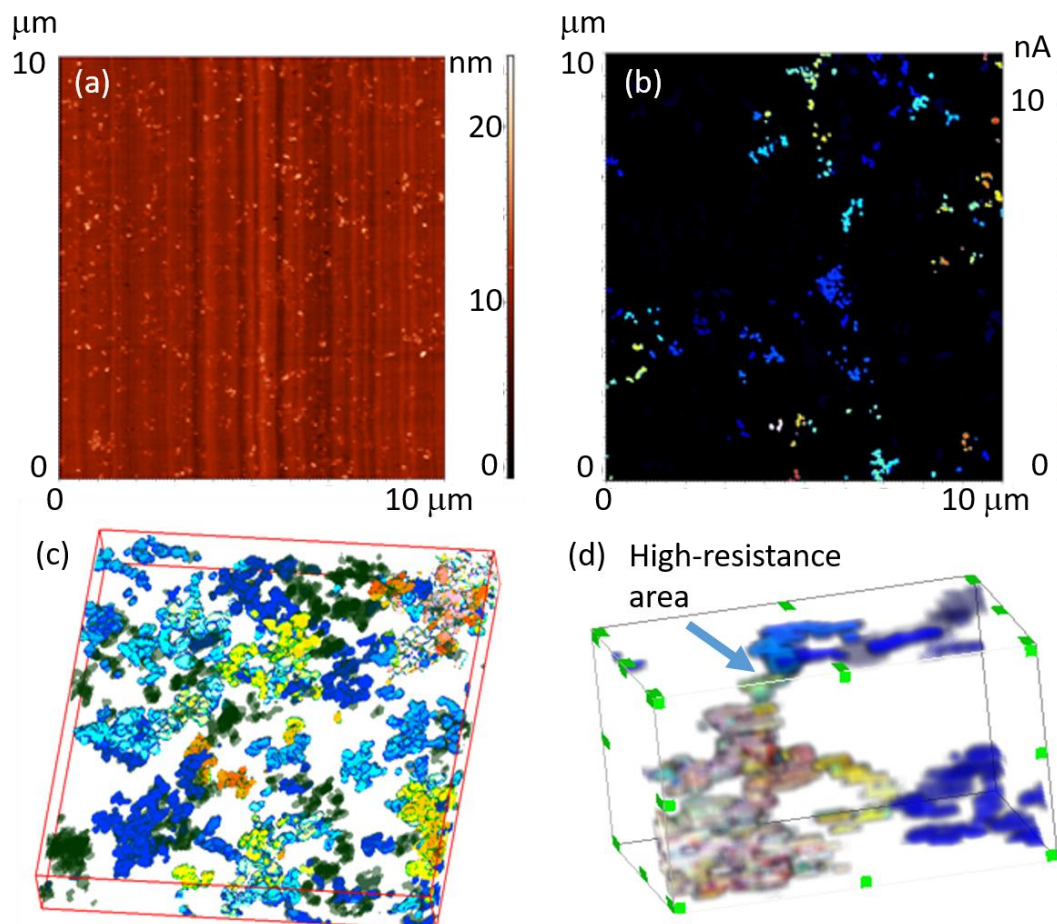


Figure 3. CB-EA composite: (a) topography, (b) current distribution on the same area, (c) reconstructed volume structure of current inside the composite volume, (d) zoomed part of (c).

The results obtained for three conductive composites (CNT-PS, Gr-PS, and CB-EA) made by different technologies with three types of fillers and different matrixes are very similar in general and have common features. This similarity is also present in the local I-V curves measured by C-AFM: in all composites both linear and nonlinear I-V characteristics were observed, possibly reflecting the existence of a tunneling conductivity mechanism between the filler particles. It may be thought that the existence of “bottle necks” is due to the dispersion methods used for realizing these composites. However, conductive composites realized by infiltration of CNT networks by a polymer [12] demonstrate very similar characteristics.

4. Conclusion

The nanoscale volume structure of conductive fillers in conductive Gr-PS and CB-EA composites was reconstructed using a combination of AFM and ultramicrotomy. The similar character of conductivity in all measured samples as well as in previously investigated CNT-PS composites shows the universal character of the revealed peculiarities. In all investigated carbon-based conducted composites, the filler particles form clusters with similar conductivity level, separated by connections with high resistivity. Only a part of filler particles forms a conductive network, while others remain electrically isolated. The size of the domains in CB-based composites is smaller than that for Gr- and CNT-based composites, which makes it possible to directly visualise highly resistive connections between clusters in a volume. 3D reconstruction of Gr-PS structure by EFM is possible due to strong influence of Coulomb interaction on the measured contrast between the AFM probe and the charged graphene flakes.

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