Graphene nanoplatelets size analysis based on sample transparency

Zofia Lorenc, Slawomir Tomczewski, Leszek Sałbut

Faculty of Mechatronics, Warsaw University of Technology, Boboli 8, 02-525 Warsaw

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Abstract—The paper presents transmission characteristics of different graphene samples. Predicting affiliation to groups characterized by different size nanoplatelets and describing character of pastes was the aim of the present work. To achieve this goal, the authors used a simple optical system in which a plane wave illumination of the sample and a telecentric imaging system were used. Analysis of intensity histograms and lowest transmission regions of nanaplatelets was done. To create a model from measured parameters, the authors applied a decision tree using leave-one-out cross-validation to fairly evaluate the results. The model allows to predict the size of nanoplatelets.

Graphene is a promising material with many interesting properties [1-3]. A monatomic layer of allotropic-carbon atoms in a honeycomb lattice [4-5] makes graphene a zero-gap semiconductor or a semimetal. The combination of graphene unique optical and electronic properties and the absence of a bandgap (in a single graphene layer) can be fully exploited in many applications. In photonics and optoelectronics graphene is being used in solar cells, organic light-emitting devices, touch screens, photodetectors and ultrafast lasers [1]. In several applications, graphene has better properties than normally used materials, e.g. ITO - indium tin oxide – a widely used material to prepare electrodes in transparent electronics, which is characterized by worse parameters like brittleness and wear resistance, chemical durability and toxicity [2]. The properties mentioned above make grephene a fascinating material.

Various techniques are used to measure the physical parameters of graphene nanoplatelets. Researchers use methods like optical differential interference contrast microscopy (DIC) [6], scanning probe microscopy (SPM)[6], atomic force microscopy (AFMs) [7-8] and scanning tunnelling microscopy (STM) [9] to examine nanoparticles of different nanomaterials, like graphene.

The aim of this research was to observe the tendency to create agglomerates by graphene nanoplatelets [10] of different size and to assess the methods for classifying the size of nanoparticles without using expensive equipment.

To call the material "nano", one of structure dimensions has to be smaller than 100nm. Tested samples contain graphene nanoplatelets with a thickness smaller than 25nm. Flakes diameters were 10μm in group A, 15μm in group B and 20μm in group C. The measured pastes consist of a nano material and a PMMA solvent, which were deposited on an elastic polyester PET substrate with a precise airbrush nozzle. Samples were prepared using spray coating methods. Polymer concentrations in a vehicle were selected with respect to rheology of compositions and electrical properties of composite layers. Optimal concentrations were from 0.18 to 0.32 wt.% (percentage by weight). The information about three types of pastes with different graphene nanoplatelets is shown in Table 1.

Table 1: Characteristic of measured pastes.

Designation	Producer	Diameter	Thickness
A	Angstron	10μm	< 1 nm
B	Cheap Tubes	15μm	10÷12nm
C	ITME	20μm	20nm

A custom-made optical system for transmission measurement was used to visualize the structure of pastes. The scheme of this system is presented in Fig. 1. The system consists of a pigtailed white light emitting diode LED as a light source (spectrum covered the range 440−650nm), a collimator (C), a microscope objective, a lens with a focal length of 200mm (L) and a CCD camera (Point Grey, Grasshopper, Sony ICX625). The collimator creates a parallel beam which evenly illuminates the plane of the sample (S). The lens and microscopic objective form a telecentric imaging system. Intensity distribution depending on sample transparency is registered by the CCD camera.

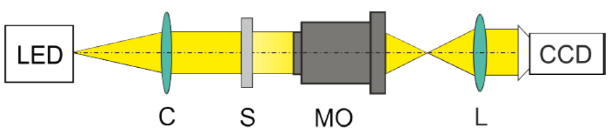

Fig. 1. The optical system for full-field sample transparency measurements. Light source – white LED, collimator (C), sample (S), microscope objectives (MO), lens (L), CCD camera.

Registered images gave information about intensity distribution. Every image was normalized to 0-1 scale. In that case the comparison between them was possible. Histograms were generated from each picture. Afterwards, a specific threshold was established. In that experiment the best results were visible with a threshold equal to 0.7 of maximum intensity. This assumption allows to observe the lowest transmission areas of measured samples. The authors called them agglomerates of graphene nanoplatelets because only a huge number of connected graphene nanoparticles could be characterized by such a low transmission level of light. Different parameters from histograms and distribution of agglomerates were calculated. The results were subjected to different statistical operations.

Histograms were generated from normalized distribution of light intensity. Representative examples from groups A, B and C are shown in Fig. 2. Every chart was described by a number of parameters like FWHM (full-width at half maximum), standard deviation of populated bin, HRMS (histogram root mean square - rms of the values in a histogram), mode of histogram and Y value of the highest point of the histogram, skewness and roughness parameters like Ra (arithmetic average of absolute values). Group A exhibited the largest amount of dark spots, which resulted in a shift of histograms to the left. It means that the smallest nanoplatelets (diameter - 10μm) tend to agglomerate more than nanoparticles in the other two groups. Histograms do not fit to a Gaussian curves. Even after an increase in camera exposure time, the dark spots did not let the histogram to fit to normal distribution.

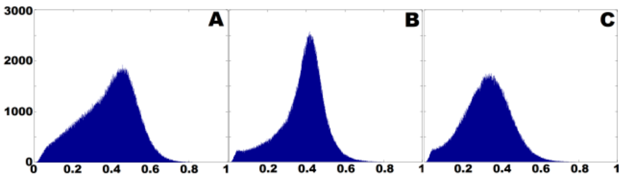

Fig. 2. Exemplary histograms of registered light intensity calculated from groups A, B, C.

Every parameter was statistically analyzed. Standard deviation of histograms and roughness parameter – Ra after one-way analysis of variance (ANOVA [11] on significant level: alfa=0.01 and alfa=0.05, respectively) are statistically significant (Fig. 3). After using Bonferroni correction it is possible to see that every value in tables is much smaller than alfa=0.01. It means that the difference between each group is statistically significant (Fig. 3). Hence, these parameters could be useful to predict affiliation to different size nanoplatelets groups.

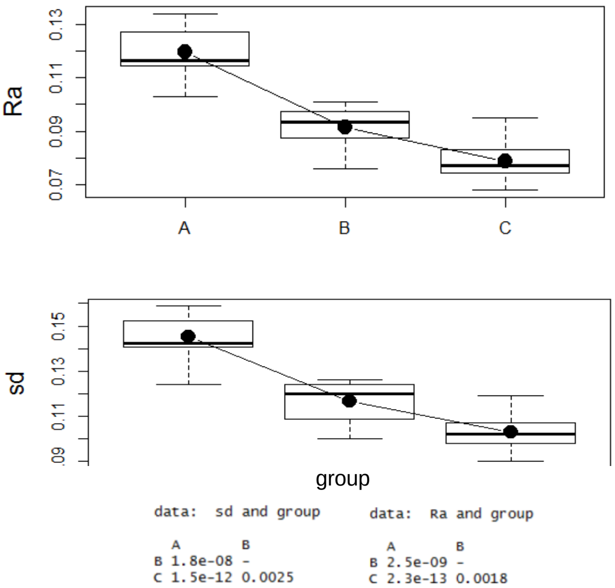

Fig. 3. Box and whiskers plot of the roughness parameter – Ra and standard deviation of histogram for groups A, B and C (black spots show means of parameters) and results of Bonferroni correction for standard deviation of histogram (left) and roughness parameter - Ra (right) for groups A, B and C.

The information about the arrangement of graphene nanoplatelets agglomerates describes the paste character, which is important for the production process.

Each sample has a number of agglomerates. Their size depends on nanoplatelets diameter. Agglomerates are represented by the darkest areas in registered intensity distributions. Every agglomerate was classified to one of the three classes. The first class covered the values from 0 to 0.2 of normalized intensity, the second class – the values from 0.2 to 0.4 of normalized intensity and the third class – the values from 0.4 to 0.6 of normalized intensity (the scheme of these classes is shown in Fig. 4). This type of division means that the agglomerates from the first class were the least transparent. Exemplary images of classified agglomerates from groups A, B and C are shown in Fig. 5.

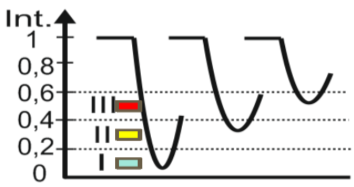

Fig. 4. Scheme of classifying agglomerates in three classes. Blue - class 1, yellow - class 2, red - class 3.

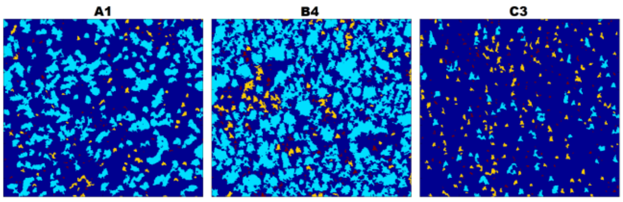

Fig. 5: Exemplary images of classified agglomerates of nanoparticles. Blue - class 1, yellow - class 2, red - class 3.

To describe these results numerically, the authors calculated some parameters like the number of agglomerates per area, mean agglomerates area, standard deviation of agglomerates area, mean distances between the centers of agglomerates and standard deviation of distances between the centers of agglomerates. Statistical analysis shows that the most useful parameter during the size nanoplates categorization process is a parameter representing number of agglomerates. Pairs of groups BC and AC are statistically significant and pair AB is not.

Homogeneity of tested pastes can be described by a level of standard deviation of distances between the centers of agglomerates. The smaller is the value of the parameter, the more uniform is the sample. In the present research the difference between the homogeneity of 3 groups of samples is not statistically significant. However, there is a trend for groups B and C (15µm and 20µm) to have lower values of the discussed parameter.

The authors use a decision tree to create a numerical size graphene nanoplatelets categorization model. Modeling based on parameters from histograms only was not as satisfactory as modeling based on parameters describing the lowest transmission areas. However, when all calculated parameters were considered together, the resubstitution error rate (indicates only results on the training data) was 6%, but the decision tree with cross validation indicated about 11% of error rate estimation. It is a good result for 36 samples (12 in each group). The decision tree with the numbers of samples from groups (A B C) in each leaf is shown in Figure 6[12]).

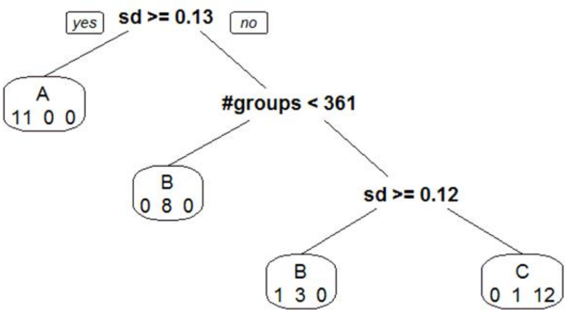

Fig. 6. Decision tree. sd - standard deviation from histogram, #groups - number of agglomerates (the lowest transmission areas, smaller than threshold - 0.7 of maximum intensity).

In conclusion, the performed analysis did not show explicitly differences in the homogeneity of the tested groups of samples. However, there is a visible trend for nanoplatelets of small diameters (like 10µm) to agglomerate while their uniformity is not on a high level. On the other hand, large nanoparticles (like 15µm, 20µm) are more likely to lie down in order, providing good homogeneity of printed layers. This information, as well as the rest of measured parameters, might be useful for technologists who work with graphene. The numerical model provides quite a good prediction about affiliation to groups characterized by different size of nanoplatelets. More samples could provide better understanding of analysis results. The presented model proved the possibility to estimate the size of nanoplatelets in graphene paste using only a very simple optical system. The information which is useful in this model is based only on transmission intensity distribution. It means that the idea of an optical transmission system for characterization of transparent samples can be very useful and provide a lot of advantageous parameters, especially for technologists. Using such an analysis they can obtain increased control over the product, make little changes in the production process and monitor the results on the fly.

The presented method could be used in different branches of science and technology, where it is important to analyze sample homogeneity, as well as the size and many different parameters describing agglomerates of nanoparticles.

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