Archives of Materials Science and Engineering

Volume 63
Issue 2
October 2013
Pages 58-67

International Scientific Journal
published monthly by the
World Academy of Materials
and Manufacturing Engineering

Transmission electron microscope studies on carbon nanostructured materials

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Received 21.06.2013; published in revised form 01.10.2013

ABSTRACT

Purpose: Carbon nanostructured materials are important and still not satisfactorily recognised products. Structure can be investigated with sufficient resolution using transmission electron microscopy but main difficulties are connected with low scattering of electrons by carbon atoms and destruction by knock-on damage caused by collisions of high energy electrons with specimen atoms.

Design/methodology/approach: Scanning/transmission electron microscopy (S/TEM) deliver a chance to improve the quality of performed investigations. BF, DF and HAADF detectors were applied for various carbon materials: carbon nanotubes, nano-onions, nanodiamonds and graphitized carbon black.

Findings: Obtained results confirmed the usefulness of applied microscopy techniques.

Research limitations/implications: Sample preparation is crucial for performed investigations. Because of ionization damage caused by collisions of high energy electrons, results obtained with high-voltage TEM have to be analysed with caution, hence low-voltage electron microscopy is strongly recommended.

Originality/value: New and not commonly used techniques were applied for carbon nanostructured materials studies. Advantages and disadvantages of them were compared.

Keywords: Nanomaterials; Electron microscopy; Low-voltage electron microscopy; Carbon nanostructured materials; STEM

Reference to this paper should be given in the following way:

M. Pawlyta, Transmission electron microscope studies on carbon nanostructured materials, Archives of Materials Science and Engineering 63/2 (2013) 58-67.

METHODOLOGY OF RESEARCH, ANALYSIS AND MODELLING

1. Introduction

The main task of material science is an improvement of materials. Spectacular progress of technical sciences at the area of forming materials result in obtaining a number of new materials which enable increasing of people living standards, guarantee growth of the production and storage of electric energy, make possible to collect, process and pass on a huge amount of information. Moreover, production of materials which can be used in extreme pressure and temperature conditions as well as materials which safely substitute parts of the human body became possible. As materials properties directly depend on their structure, it appears justified to aim at structure precise and in-depth analysis, including atomic level. The aim of the conducted researches is observation and unambiguous identification of single atoms. Although that result can be routinely obtained for most analysed materials, it still remains a big challenge to observe nanostructure of materials consisting of light elements. Among that group, because of its significance, especially important are

carbon-based nanostructural materials - nanodiamonds, nanotubes, graphene, fullerenes, nano-onions, carbon black and many others [1-4].

Carbon materials structure investigations have been conducted since a long time ago, however this was the first time that x-ray diffraction was applied with this end in view. X-ray diffraction confirmed that diamond and graphite are distinct carbon allotropes. At the same time it was observed that a significant part of carbon materials can not be considered as any of that form of carbon and theirs diffractograms have a shape only similar to the diffractogram of graphite or diamond. Shapes of peaks visible on diffractograms obtained for such carbon materials like coke, coal, carbon black and so on, are diffused and asymmetrical. Only approximately can their positions be attributed to (002) (100) and (110) positions for graphite. Differences in position and shape of peaks indicate that analysed materials don't have the structure of graphite (they don't consist of small crystallites of graphite) but include small packets of carbon planes (sheets) which are parallel, but not oriented into any relation to each other (carbon planes are not perfectly arranged one on top of the other but accidentally shifted). Such kind of structure was named a turbostratic structure (Fig. 1). It is characterised by the occurrence of (00l) (l=2,4,...) and (hk) peaks, while mixed peaks (hkl) are not present at all. Peaks (hk) form characteristic, asymmetrical bands, which intensity gradually decreases for higher angle values (Fig. 2).

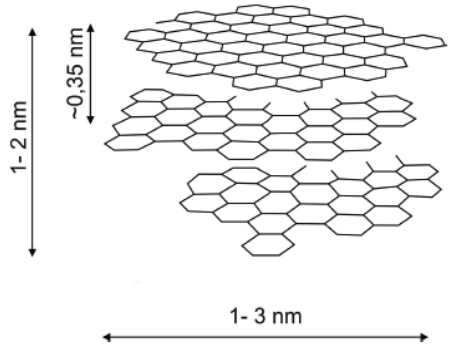


Fig. 1. Scheme of turbostratic structure (on the basis of [16])

The big contribution into researches of carbon material structure had Rosalind E. Franklin [5,6]. Her researches carried out in the forties of 20th century explained how temperature influences on carbon materials structure and made possible to classify them into two principal categories: non-graphitizing carbons and those which convert easily into graphite. Structure of graphitizing carbons, upon heating, becomes ordered, carbon planes connect and grow up, arranging in parallel with respect to each other while distance between them decreases to the value characteristic for graphite (0.335 Å). Elements different than carbon are removed outside, and the porosity vanishes. Non-graphitizing carbons have low density, large fine-structured porosity and are very hard. Even at a temperature equal to 3.000°C these materials don't transform into graphite. The unique behaviour of non-graphitizing carbons can be attributed to the formation of a strong system of cross-links between the crystallites (turbostratic domains), which prevent the rearrangement of material into graphite. Very soon Franklins' results found practical industrial applications. Glassy carbon (non-graphitizing carbon material) is used for melting-pots and heat-resistant wares production, denying the influence of high temperature and acids. In recent years obtaining of glassy carbon became especially important because of the potential use in medicine due to biocompatibility. The possibility to predict the behaviour of graphitizing carbons in high temperature found practical application for improvement of coking process (converting coal into coke).

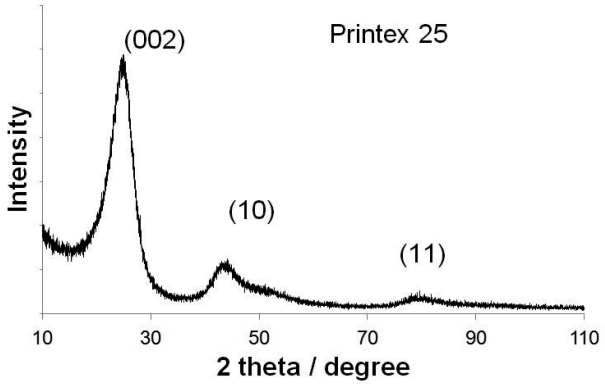


Fig. 2. X-ray diffractogram obtained for carbon material (Printex 25, carbon black made by Degussa Co.), λ_{Co}=1.79 Å

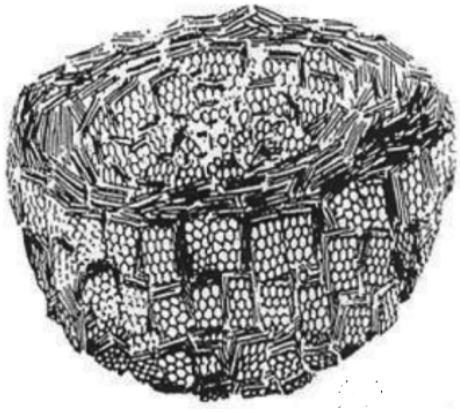


Fig. 3. Scheme of carbon black primary particle consisted on concentrically arranged BSU (on the basis of [17])

Rosalind E. Franklin's hypothesis turned out true but only after a few dozen years it was possible to show it directly using transmission electron microscopy (TEM) [7,8]. In an electron microscope elastic scattering is the main mechanism of electrons' deflection and is the main contribution to the image and diffraction patterns formation, while inelastic scattering forms the basis for EELS (Electron Energy Loss Spectroscopy) and characteristic X-ray emission is applied at EDS (Energy

Dispersive Spectroscopy). Signals mentioned above are generated at the same time and at the same small volume of sample. For these reasons transmission electron microscope offers amazing possibilities for materials (including carbon materials) investigations allowing to obtain wide spectrum of information.

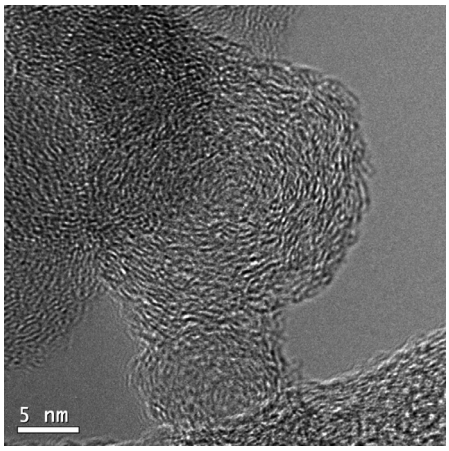


Fig. 4. TEM image of CB primary particle (Printex 25, carbon black made by Degussa Co.)

Although in recent years spectacular development of electron microscopy is observed (devices which are accessible on the market guarantee resolution expressed in picometers (1 pm=10^{-12} m), it is not equivalent to the possibility of observation all carbon materials with atomic resolution. Resolutions obtained for carbon materials are significantly smaller than values given at promotion brochures. Difficulties at imaging carbon materials result from the fact that light elements like carbon (Z=6) poorly scatter high energy electrons. An additional factor is that electron beam destroys the structure of these materials [9]. In case of carbon materials, observation of single atoms remain an enormous challenge - for example in graphene sheets or at nanotubes walls. That goal is becoming possible these days, but a lot of experience and very expensive equipment is required (high brightness field emission source, a monochromator, as well as an aberration corrector to correct the spherical aberration C_S of the objective lens). Moreover, lower accelerating voltage (HT) has to be applied [10].

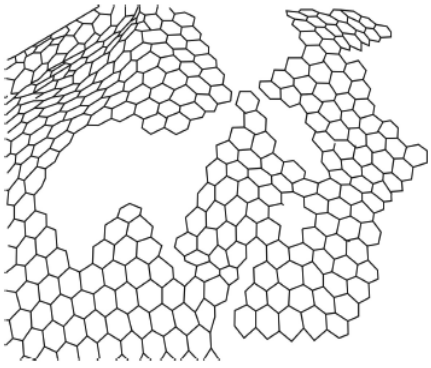


Fig. 5. Scheme of strongly defected carbon layer (on the basis [16])

In most cases of practical investigations of carbon materials it is not necessary to achieve atomic resolution. To obtain valuable information, knowledge of arrangement of carbon planes is required, which are situated in distance equal or insignificantly larger than 0.335 Å. On TEM images carbon planes are distinctly visible if they are parallel to electron beam - in case of polycrystalline materials that condition is met for at least part of material, in principle always.

TEM investigations of carbon materials take advantage of fact that most of them consist of volumes where carbon planes are parallel. For such volumes the name basic structural unit - BSU is commonly adopted [11]. Extent of BSU can be very diverse - from very large to very small. In the second case extent can equal 2-3 nanometers merely. This can be observed in case of carbon black CB which is obtained by incomplete combustion of hydrocarbons. Formerly CB was presented as an example of perfect amorphous material. In reality, primary soot particles consist of concentrically arranged small packets of carbon sheets (a few nanometers in diameter, Fig. 3). If these planes are arranged parallel to microscope optical axis then electron beam gets strongly scattered on numerous atoms at these sheets and strong contrast is visible on TEM images. In case of layers being arranged at some angle to microscope optical axis, electron beam gets scattered at least on one (or none) atom of each layer. As a result, very weak contrast is obtained. In case of carbon materials consisting of a huge amount of accidentally arranged BSU, a part of them is always arranged parallel to electron beam and only these are visible on TEM images. In Fig. 4. TEM image of primary CB particle built of concentrically arranged BSU is presented. Carbon layers parallel to microscope optical axis are visible as dark lines.

These days it is commonly accepted that basic elements of many carbon materials are not carbon planes but strongly defected carbon layers (Fig. 5) [12,13]. Thanks to ordered domains, observed during high resolution trasmission electron microscopy (HRTEM) investigations, it has been stated that size of observed carbon layers surpassed its estimation calculated from width of diffraction peaks in terms of size. Strongly defected carbon layers model is also confirmed by results of diffraction profile analysis obtained during thermal treatment. In that model it is assumed that diffraction line broadening is not connected to small size of ordered domains but with structure defects mostly. This allows to deduce that parameters of crystallographic structure determined by diffraction method are a measure of defects inside carbon layers. Width of (hk) peak on diffraction pattern is a measure of an average size without defects (instead of size of carbon layers). Similarly, width of (002) peak is a measure of continuity of parallel layers without defects. TEM imaging of single carbon layers, especially strongly defected layers, is considerably more difficult than non-defected layers arranged parallel.

The aim of this paper is to present research potentials and preliminary results of carbon nanostructured materials imaging with techniques accessible in transmission electron microscope S/TEM TITAN 80-300 from FEI Co., installed in 2012 year at the Institute of Engineering Materials and Biomaterials of Silesian University of Technology. This device allows to set an accelerating voltage from the range between 80 and 300 kV. Additionally, it can operate in both transmission (TEM) and scanning transmission electron microscopy (STEM) modes [14].

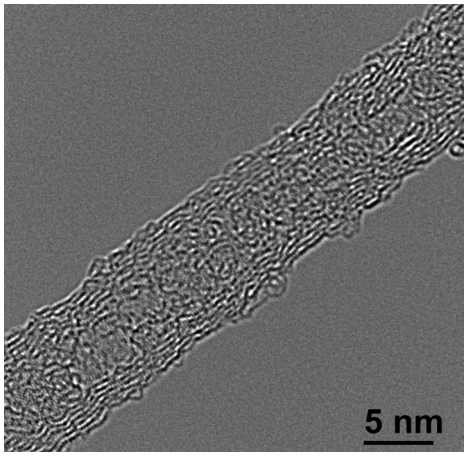


Fig. 6. HRTEM image of carbon nanotubes (acceleration voltage 300 kV)

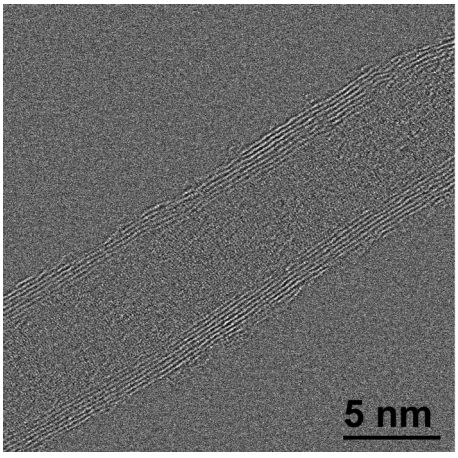


Fig. 7. STEM-BF image of carbon nanotubes (acceleration voltage 300 kV)

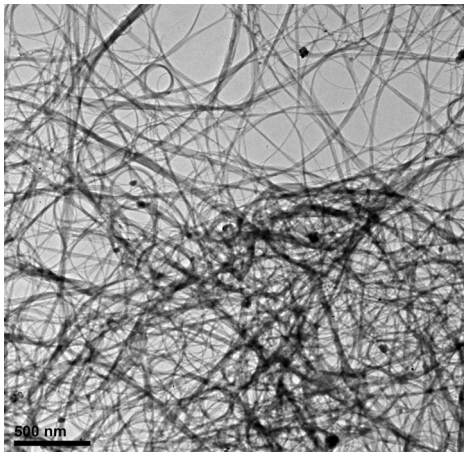


Fig. 8. TEM image of carbon nanotubes (acceleration voltage 80 kV) - low magnification

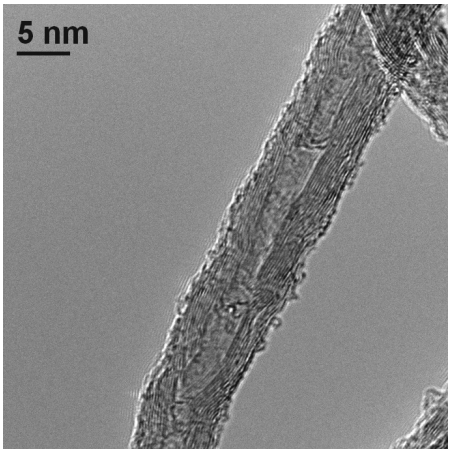


Fig. 9. TEM image of carbon nanotubes (acceleration voltage 80 kV) - high magnification

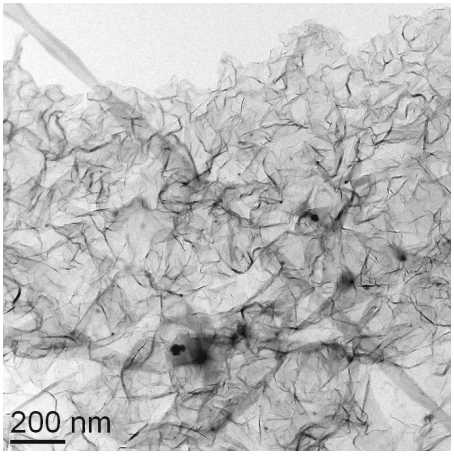


Fig. 10. TEM image of activated carbon (acceleration voltage 300 kV) - low magnification

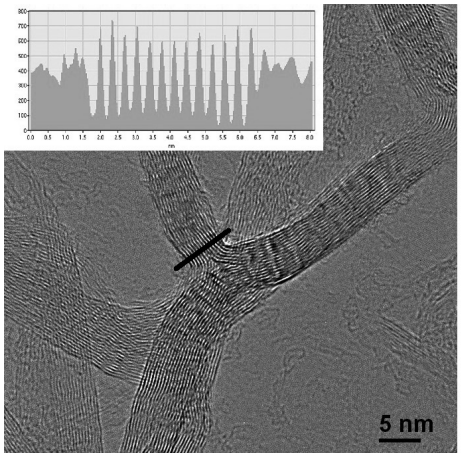


Fig. 11. HRTEM image of activated carbon (acceleration voltage 300 kV). In upper part intensity profile obtained at dark line is present

The main difference between these modes are the way the electron beam illuminate the sample. In TEM mode beam is wide, parallel and static. In STEM mode beam is convergent and scans the samples surface. For carbon materials the main advantage of STEM is that electron beam illuminate any point at sample for a very short time and expected damage is smaller.

In transmission electron microscope working in TEM mode, image is formed in four stages:

- sample is illuminated by wide and parallel beam;
- first image is formed by the objective lens,
- obtained image is magnified by intermediate lens;
- magnified image is projected on the screen.

In STEM mode sample is illuminated by convergent electron beam, focused on the sample surface. In transmission electron microscope working in STEM mode, image is formed in two stages:

- convergent electron beam is focused by the objective lens on the sample surface while sample surface is scanned by using deflecting coils;
- signals formed as a result of interaction of high energy electrons with sample are recorded and processed.

Signals can be simultaneously recorded by two detectors (BF and HAADF or DF and HAADF). Probe corrector enables the operator to form a beam which is adequately convergent and has minimal diameter (0.1 nm) on the sample surface. BF and DF detectors collect electrons scattered at small angles (comparable to values in Bragg low) and diffraction and mass/thicknes contrast can be obtained this way. HAADF detector collect electrons scattered at higher angles, which makes that intensity is proportional to Z^2 and composition contrast can be obtained.

2. Experimental

2.1. Sample preparation

For hereby presented investigations, five carbon materials, characterised by different structure, were chosen:

- multi-walled carbon nanotubes;
- activated carbon;
- graphene;
- graphitised carbon black;
- nanodiamonds and nano-onions.

Commercial multi-walled carbon nanotubes were created by Chengdu Organic Chemicals Co. Their outer diameter was about 8 nm and surface area was close to 500 m^2/g. Activated carbon was obtained from cellulose. Graphitized carbon black was obtained from commercial carbon black (PRINTEX 25 from Degussa Co.). It was heated at 2600°C under an argon flow. The initially rounded nanoparticles (diameter about 50 nm) became polyhedral and partially graphitized. Other examples of nanostructural materials are nanodiamonds and nano-onions.

Nanodiamonds and nano-onions used in the present work were also obtained from the same carbon black (PRINTEX 25) [14]. Nanodiamonds were obtained as a result of carbon black heating at 1500°C under 15 GPa for 30 min. Conversion of nanodiamonds to nanoonions is a result of heat treatment (1700°C). Shape of aggregates as well as size of primary particles of both materials remained unchanged while internal structure changed drastically.

All the materials mentioned above were powders. TEM samples preparation was run according to the following schedule: small amount of material was prepared by dispersing in ethanol, placed in an ultrasonic bath for 5 minutes, then droplets were put onto 3 mm copper microscopy grid coated with lacey amorphous carbon film and dried in the air at room temperature. TEM samples of carbon nanostructural material preparation is simple but requires much care. The most serious threat is contamination, which makes difficult or even impossible to apply some microscopy techniques (for example EELS, STEM). For that reason it is crucial to prevent deposit of hydrocarbons on the surface of the holders and at microscope column. Sample preparation and storage should protect from introducing contamination, among other things thanks to using clean chemical reagents. It is also very helpful to use anticontaminant trap regularly and cool the holder using liquid nitrogen during observation. Moreover, it is recommended to apply short (about 3 sec.) plasma cleaning or illumination with infra red IR radiation (20 minutes). Good results can be obtained thanks to 20-30 minutes of illumination with intensive electron beam, what causes contamination to gather outside the beam-illuminated area.

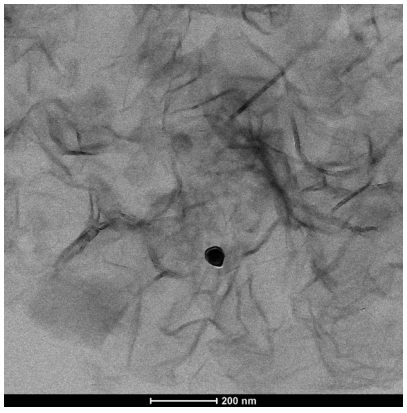
TEM TITAN 80-300 equipped with Schottky-type field emission gun, CETCOR Cs-probe corrector from CEOS Company, a Gatan Energy Filter Tridiem 863, EDS detector and hardware and software for 3D Tomography were used for investigations. Microscope is not equipped with image corrector so the state of the art resolutions are not expected to be obtained in TEM mode, but probe corrector makes it possible to obtain optimal resolution in STEM mode.

2.2. Results and discussion

Images obtained during examination present how imaging parameters like accelerating voltage, chosen mode and used detectors influence final results. In case of carbon nanotubes difficulty results from nanometric size (diameter below 10 nm, which requires to apply high magnification) and high value of shape factor (length is even thousand times higher than diameter, which forces to apply low magnification if considerable part of nanotube should be visible on the image). Application of high accelerating voltage has two main disadvantages: images are characterized by poor contrast (especially at low magnifications) and the structure of investigated samples can be destroyed (knock-on damage) (Fig. 6). Investigations performed in STEM mode (BF) not influence on observed carbon nanotube structure (Fig. 7). Its walls remain visible as straight, parallel lines. Reduction of acceleration voltage (80 keV) improves the contrast and decreases structure damage (Figs. 8 and 9), but deteriorates resolution.

Microscope S/TEM TITAN 80-300 can operate between 80 and 300 kV accelerating voltage, but because of required lenses stabilisation it is necessary to wait at least a few hours before starting new investigations. For that reason optimal parameters for all necessary magnifications cannot be applied and it always comes down to choosing the least disturbing factor (resolution deterioration, contrast deterioration, knock-on damage).

a)



b)

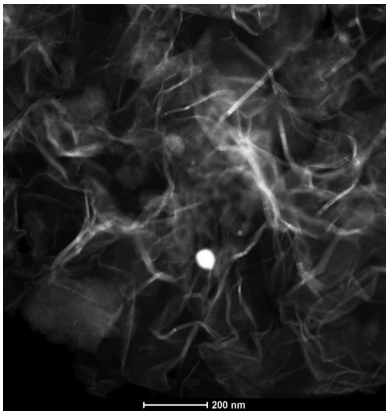


Fig. 12. Comparison of STEM images of activated carbon obtained with BF (a) and HAADF (b) detectors (acceleration voltage 300 kV)

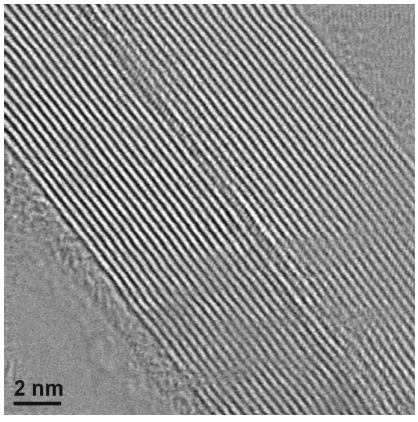


Fig. 13. HR STEM-BF image of activated carbon (acceleration voltage 300 kV)

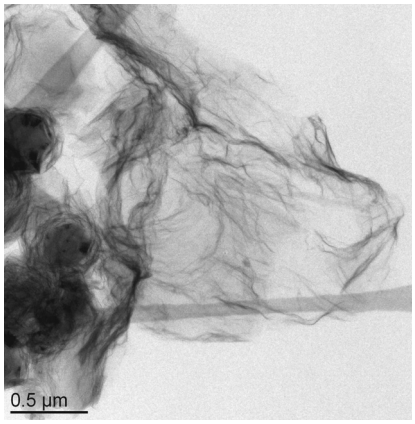


Fig. 14. STEM-BF image of graphene (acceleration voltage 300 kV)

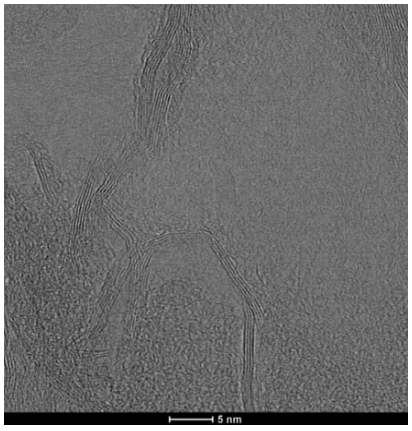


Fig. 15. HR STEM-BF image of graphene (acceleration voltage 300 kV)

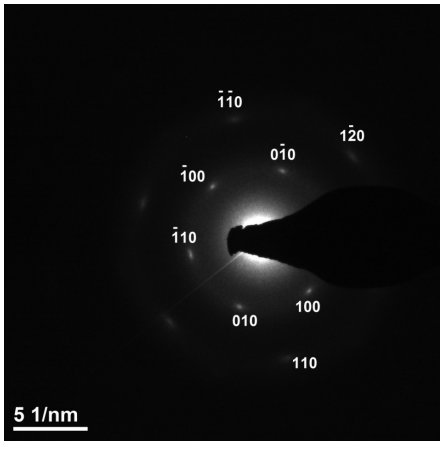


Fig. 16. SAED pattern of graphene

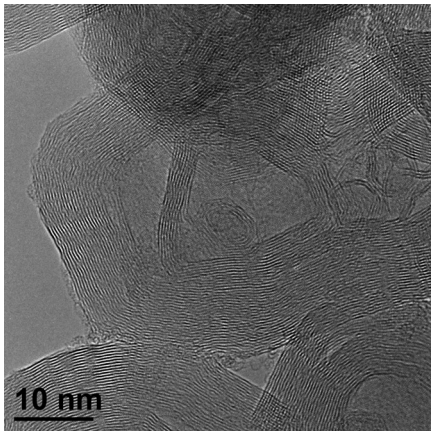


Fig. 17. HRTEM image of graphizited carbon black (acceleration voltage 300 kV; L=160 mm)

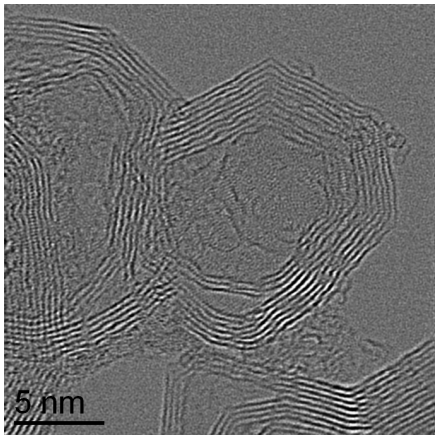


Fig. 18. STEM-BF image of graphizited carbon black (acceleration voltage 300 kV; L=300 mm)

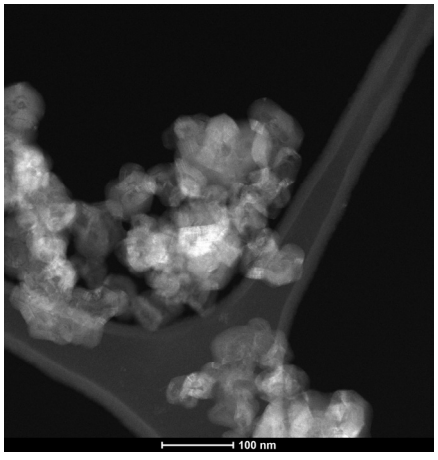


Fig. 19. STEM-HAADF image of graphizited carbon black (acceleration voltage 300 kV; L=300 mm)

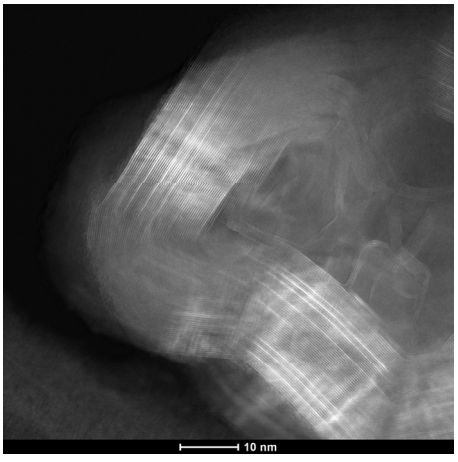


Fig. 20. STEM-HAADF image of graphizited carbon black (acceleration voltage 300 kV; L=300 mm)

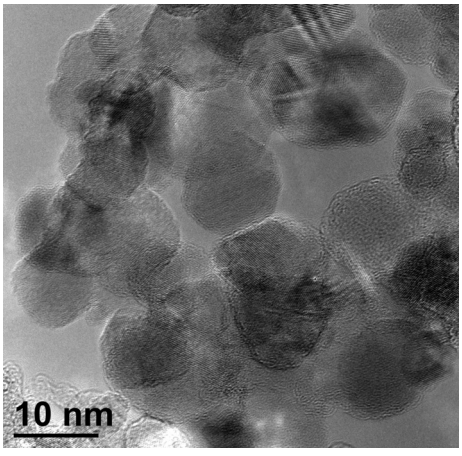


Fig. 21. TEM image of nanodiamonds (acceleration voltage 300 kV)

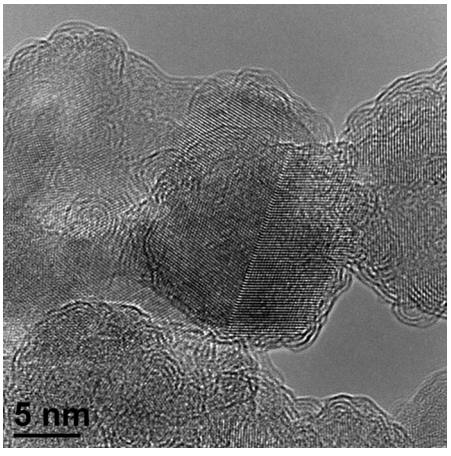


Fig. 22. HRTEM image of nanodiamonds (acceleration voltage 300 kV)

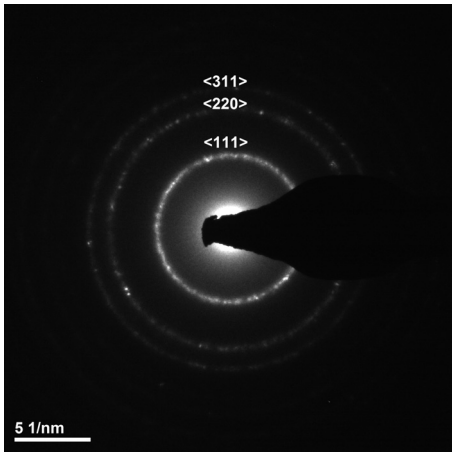


Fig. 23. SAED pattern of nanodiamonds

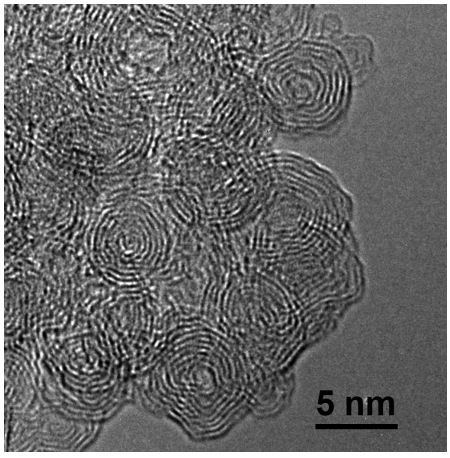


Fig. 24. HRTEM image of nanoonions (acceleration voltage 300 kV

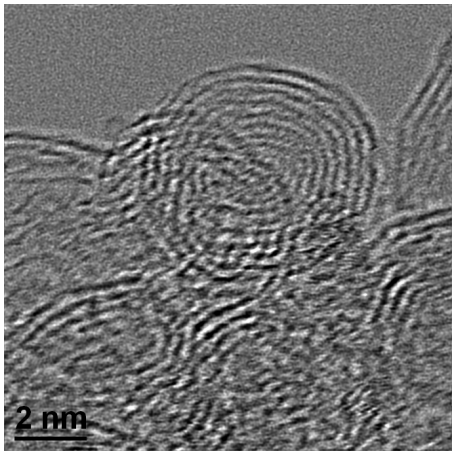


Fig. 25. STEM-BF image of nanoonions (acceleration voltage 300 kV; L=245 mm)

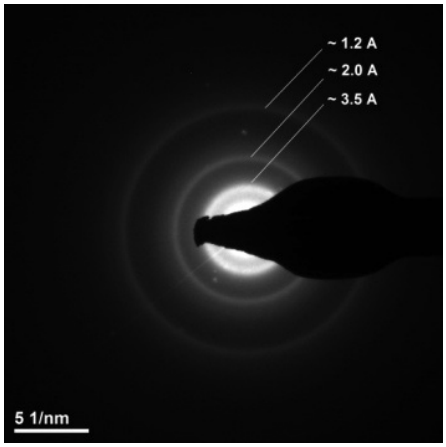


Fig. 26. SAED pattern of nanoonions

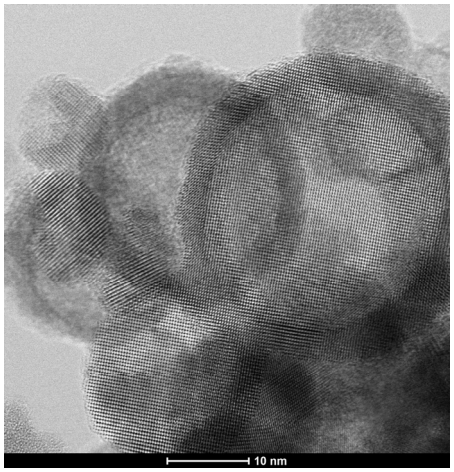


Fig. 27. STEM-BF image of tantalum nanoparticles (acceleration voltage 300 kV)

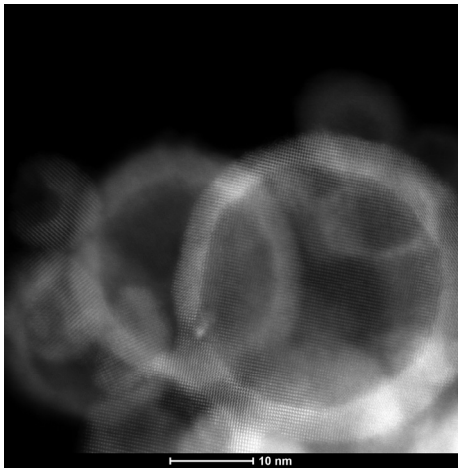


Fig. 28. STEM-HAADF image of tantalum nanoparticles (acceleration voltage 300 kV)

Figs. 10 and 11 present TEM and HRTEM images of activated carbon. On Fig. 12 STEM-BF and STEM-HAADF images are compared. The advantage of STEM-HAADF imaging is possibility easily detect any impurities (high Z contrast). Perfectly aligned carbon layers are visible on HRSTEM obtained with BF detector (Fig. 13).

The same conclusion can be obtain for graphene as long as atomic resolution is not required. Most commercial graphene sample contain more than one carbon layer, which are strongly curved. It can be imaged in STEM-BF (Figs. 14 and 15). Structure can be analysed by electron diffraction (Fig. 16).

In the Figs. 17-20 images of graphitised carbon black are presented. In comparison to raw carbon black (Fig. 4) large change of structure is visible. As a result of graphitisation, pieces of carbon layers, forming BSU, are ordering and arranging closer to parallel.

Layers growth is limited by initial size of primary particles. Moreover, volumes consisting of parallelly arranged carbon layers are formed. These volumes meet the requirements for electron diffraction. Planes parallel to optical axis are distinctly visible on TEM (Fig. 17) and STEM images, obtained with BF (Fig. 18) and HAADF (Figs. 19 and 20) detectors. In case of BF detector, optimal results are obtained for larger value of camera length L, when diffraction contrast dominate. Carbon layers which satisfy Bragg law scatter electrons in large angle and as a result are visible as dark lines on STEM-BF images. As analysed samples consist almost only of carbon, contrast on HAADF images depends on the amount of scattering materials- layers parallel to electron beam scatter stronger and are visible as light lines on STEM-HAADF images. Volumes without carbon layers and volumes were angled and are visible as darker. This effect can be intensified by applying larger value of L.

Aggregates of nano-onions and nanodiamonds consist of primary particles with a diameter of between a few to few dozen nanometers (size is limited by initial diameter of primary particles of CB, from which they were manufactured). Nanodiamonds are characterised by distinct crystallographic structure (Figs. 21 and 22). 3D order was also confirmed using SAED observation (Fig. 23).

Primary particles of nano-onions consist of spherical carbon layers (fullerenes) placed one inside another. Distance between layers is constant and equals (like in graphite) 3.35 Å. On both TEM (Fig. 24) and STEM-BF (Fig. 25) images spherical layers are visible as dark circles. Crystallographic and electronic structure is different than for nanodiamonds (Fig. 26, respectively). Others interesting nanostructures can be found in almost pure carbon samples. Figs. 27 and 28 present aggregates of tantalum nanoparticles (probably catalyst residue) with morphology very similar to carbon black, but structure and chemical composition is quite different.

3. Conclusions

1. High voltage electron microscopy (300 kV) allows to obtain satisfactory resolution, but obtained results are not completely reliable. High energy electron beam strongly modifies the structure of investigated carbon materials. For that reason (if high resolution is not indispensable) low-voltage electron microscopy is strongly recommended. If high resolution is required observations in STEM mode are more credible.
2. For carbon materials decorated with noble metals' nanoparticles, STEM mode is very useful. For lower magnification, HAADF detector facilitates unequivocal assessment of distribution and homogenity of deposited nanoparticles, while for higher magnification - the best (atomic) resolution can be obtained.

Acknowledgements

Author is very grateful to Dr. J.N Rouzaud (Laboratoire de Géologie, Ecole Normale Supérieure) and Dr. S. Duber (University of Silesia) for providing her with nanoonions and nanodiamonds samples. This work was realised with using apparatus purchased within the framework of the Project „Śląska BIO-FARMA. Centrum Biotechnologii, Bioinżynierii i Bioinformatyki" founded by EFRR within PO IG, 2007-2013.

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