Plasma generation of ultradispersed carbon nanoparticles in liquids

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Abstract: The article presents new approach to synthesis of carbon nanoparticles - nanodiamonds, carbon onions and fullerenes. Ultra dispersed carbon nanoparticles have been generated by pulse plasma discharge in liquid. Some results of tribological tests are presented.

Keywords: Carbon nanoparticles, ultradispersed nanomaterials, nanodiamonds, fullerenes

1. Introduction and target setting

Carbon nanoparticles, such as nanodiamonds and fullerenes, can be used in different areas of technology, e.g. electronics, chemical industry, construction, medicine etc. Use and importance of nanomaterials in industry will continue to grow, but nowadays there are a great number of limits for this growth [1].

First, this is high cost of production. Secondly, there is technical issue of nanoparticle coagulation and formation of conglomerates. It is especially important when we deal with dry powder of nanoparticles which should be then uniformly homogenized in liquids; in many cases this is hardly doable if possible at all. Our approach may allow to remove both of these limitations of nanomaterials by this new approach of nanomaterials manufacturing by pulse electric discharge in liquid.

Plasma system with controllable and adjustable parameters have been optimized for creation of ultradispersed nanodiamonds, carbon onions and fullerenes mixture with similar nanoscale sizes. These materials can be used for various practical applications such as lubricants, paints and plastics, surface modification and polishing, for medical use and many others.

2. Experimental setup

Experimental setup based on special discharge chamber and pulse power supply. Picture of discharge chamber is presented in Fig.1.

Fig.1 Picture of discharge chamber.

Nanoparticles are generated by electric discharge in liquids. From the start of the process nanomaterial forms suspension in liquid while concentration of nanoparticles is controlled by the process time and electric discharge power. Organic liquids such as xylene, benzene and ethanol were used. The power supply generates high voltage pulses with adjustable pulse parameters and frequency. Electric power input to plasma was up to 200W which corresponds to nanomaterial production capacity up to 2 g/hour per single electrode.

3. Experiments description

Before the experiments, system was filled by the treated liquid, then desirable pulse parameters and repetition frequency were set. During the experiment flow rate and composition of gas, generated by electric discharge, were controlled. When the experiment was finished, suspension generated nanoparticles in liquid was removed from the reactor. Produced materials were analysed both in suspension and in dried form after evaporation of liquid.

4. Experimental results

Dried powders produced were grey or brown colour, and showed low electric conductivity. Specific resistance of powder was 10^5- $5*10^7$ ohm*cm.

Element analysis shows that carbon nanomaterial produced is quite pure and admixtures are not exceeding 1%.

Types of generated nanomaterials has been studied by X-ray diffraction. Typical X-ray diffractogram in 2-Theta region 5-30^o is presented on Fig.2.

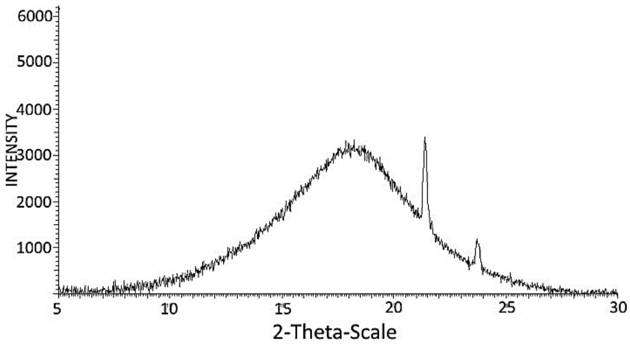

Fig. 2. X-ray diffractogram of nanomaterial powder with background subtraction in 5-30^o 2-Theta region shows fullerene mixture and carbon onions.

Diffractogram presented in Fig.2 shows sharp and diffused peaks, which are typical for carbon onions and fullerenes mixture. High resolution TEM image of generated material presented on Fig.3.

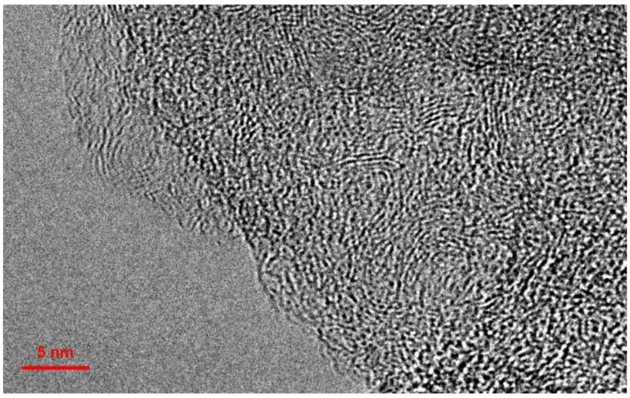

Fig.3. High resolution TEM image of material containing fullerenes and carbon onions with different numbers of layers.

Two typical kinds of carbon nanomaterials with sp2 hybridization (mix of fullerenes and carbon onions) and sp3 hybridization (ultra-dispersed nanodiamonds) has been produced in the experiments, their proportion in the mix was dependent upon pulse parameters.

Diffractogram of the material containing diffused peak in 18-33^o area typical for carbon with sp2 hybridization, and diffused peaks about 43^o and 80^o typical for sp3 carbon hybridization, is presented on Fig.4.

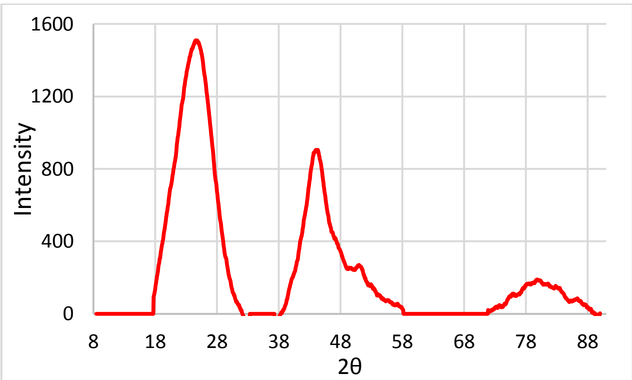

Fig.4. Diffractogram of the nanopowder after solvent removal.

There are two strongly diffused diffraction peaks close to diamond lattice planes (111) and (220) shown at Fig.4. Peak's half width correlates with particle size about 2 nm which is 2.5 times smaller than typical detonation nanodiamond particles [2].

Lattice zones with parameters that are typical for diamond, with dimensions about 2 nm, often observed on high resolution TEM image (Fig.5). Unfortunately, observed small structures were unstable in electron beam of TEM.

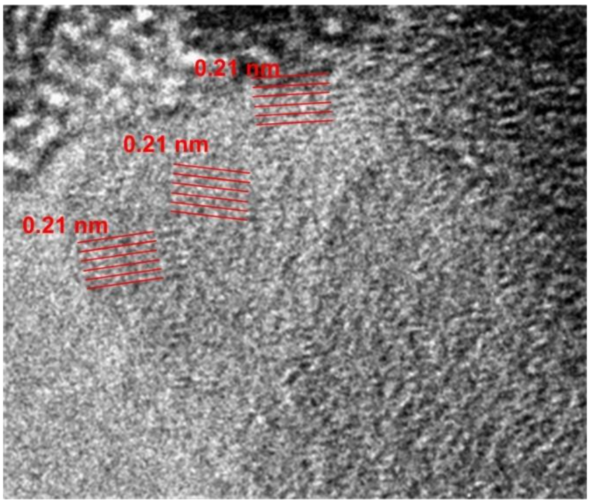

Fig.5. Zones with lattice has 0.21 A interplanar distances.

Larger crystals of about 5 nm in size and more were observed, but not so often as the small ones (Fig. 6).

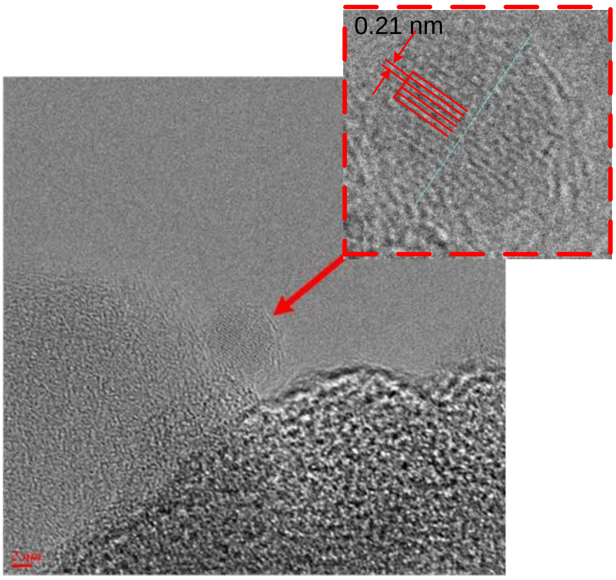

Fig.6. 6 nm crystal particle TEM image.

Diffractograms of the materials in 2-Theta interval 7-60^o were studied to estimate proportion between sp2 and sp3 particles in the material (Fig.7) depending on time of heating the material in hydrogen.

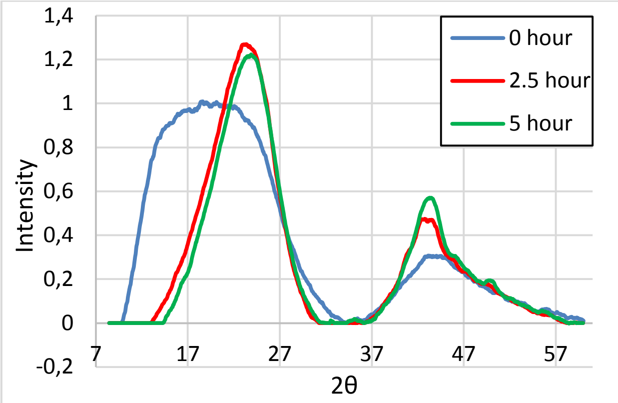

Fig.7. 2-Theta scale diffractograms of material depending on time of heating in hydrogen at 550 C^o.

Calculated ratio between sp2 and sp3 hybridized carbon nanomaterial is shown at Fig.8.

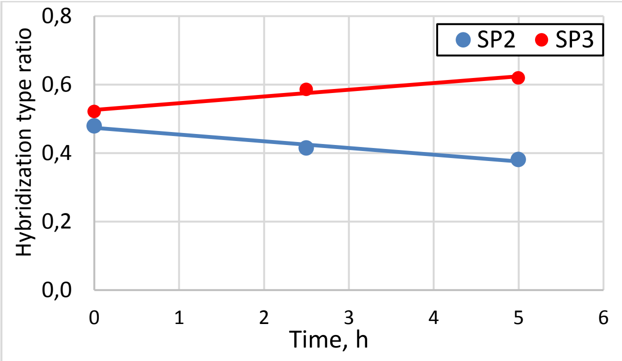

Fig.8. Dependence of ratio between sp2 and sp3 hybridized carbon particles content and heating time in hydrogen at 550 C^o

5. Experimental results: discussion and theoretical model.

Experimental results demonstrate possibility of efficient generation of ultra-dispersed carbon nanoparticle suspension directly in liquid, thus avoiding re-dispersing problems typical for detonation nanodiamond materials. Suspension contains ultra-dispersed nanodiamonds with particle size mostly about 2 nm as well as fullerenes and carbon onions mixture of 0.7 nm – 5 nm size range.

Simple semi-empirical model of the process has been developed to estimate temperature and pressure in plasma and gas buble, and shock wave propagation velocity by plasma pulse electric parameters. The model helps to predict necessary pulse conditions for selective generation of desirable carbon nanoparticles.

6. Tribological tests of nanomaterial produced

Nanomaterial suspension was tested as antifriction additive to lubricants. The friction coefficient between rotating steel cone which was inserted into the steel cylindrical tube with controllable force has been measured. The results of experiments for pure and modified oil are presented on Fig. 9. The cylinder rotation frequency was 900 s^{-1}. Nanomaterial content in oil was 0.5%.

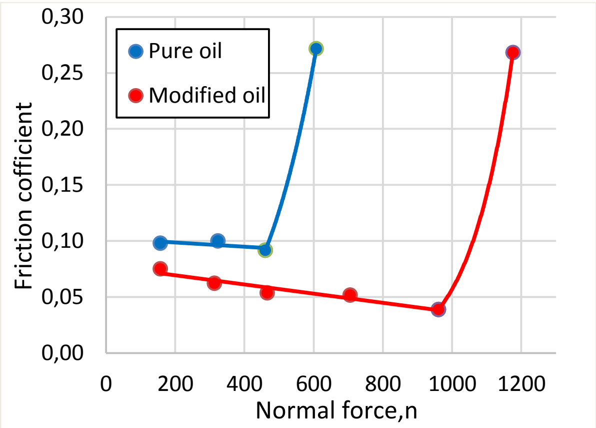

Fig.9. Dependence of friction coefficient on rotating cylinder pressing force for pure and modified oil.

Fig.9 shows that small addition of produced nanomaterial to oil leads to reduction of friction coefficient and more than double maximal pressing force.

7. Conclusions

Possibility of efficient generation of ultradispersed carbon nanoparticles including nanodiamonds, fullerenes and carbon onions directly in liquid has been demonstrated.

Nanomaterial can be generated in the form of stable suspension in organic liquids.

Production process is energy efficient, safe and doesn't require special explosion facilities and equipment.

The process can be easily scaled up to desirable capacities.

Material was tested as additive to lubricants and demonstrated promising results.

8. References

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