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SYNTHESIS OF CARBON NANOSTRUCTURES UNDER INTENSIVE CAVIATION

Ph. D. Victor M. Dorokhov
Moscow Aviation Institute (National Research University), Russia
ORCID 0000-0003-4987-6751
dorokhovvm@mai.ru
Lic. Yulia Hauser
University of Stuttgart, Germany
ORCID 0000-0001-9279-022X
yulia.hauser@online.de

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Abstract

For aqueous disperse systems colloidal stabilization of the organic copper phthalocyanine pigment (CuPc), there were used series of homo- and block copolymers of methyl vinyl (MVE) and isobutyl vinyl (IBVE) ethers with a well-characterized molecular structure. It is shown that ultrasonic treatment of disperse systems is of great importance for their stabilization. The results are highly dependent on the hydrophilic-hydrophobic polymers and their structure balance. The temperature dependence of polymethylvinyl ether solubility makes it possible to control polymer stabilizers surface activity.

Keywords

Carbon – cavitation - hydrodynamic regime - nanoparticles

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Introduction

Recently, it was theoretically justified the possibility of synthesizing nanoparticles in a cavitating processes[1]. In that and more recent works, variants of the cavitation synthesis of diamonds in nature were discussed. The essence of the idea is as follows. When a fluid rises rapidly from the mantle to the ground through a narrow channel–crack formed by it, sharp pressure differences arise. According to the Bernoulli equation, pressure in the fluid flow is inversely proportional to the velocity squared. Therefore, pressure decreases in a narrow spot, which gives rise to the appearance of gas bubbles. When the fluid again enters a wide place, pressure is recovered and bubbles collapse. Calculation shows that pressure can increase by several orders of magnitude. As was calculated, pressure induced when bubbles filled with a carbon-containing gas collapse is sufficient for diamond synthesis[2]. It was assumed that the fluid contained CO_2, but a more recent analysis of diffusion velocities from the collapse medium showed that only hydrogen has a sufficiently high diffusion velocity[3].

Therefore, a hydrocarbon substrate such as methane must be the initial substance[4]. In this work, we aim to reproduce the cavitation synthesis in experiments. Benzene is used as the working substance. The saturated vapor of this low-viscous fluid has high pressure under normal conditions. In addition, it is characterized by a high carbon-to-hydrogen ratio (C_6H_6). The description of experimental setup is presented[5]. Theoretical approaches were also developed[6].

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[1] N. A. Bulychev; M. A. Kazaryan y E. S. Gridneva, “Plasma discharge with bulk glow in the liquid phase exposed to ultrasound”. Bulletin of the Lebedev Physical Institute, Vol: 39 num 7 (2012): 214-220; Yu. V. Ioni; S. V. Tkachev; N. A. Bulychev y S. P. Gubin, “Preparation of Finely Dispersed Nanographite”. Inorganic Materials, Vol: 47 num 6 (2011): 597-602 y N. A. Bulychev; E. L. Kuznetsova; V. V. Bodryshev y L. N. Rabinskiy, “Nanotechnological Aspects of Temperature-Dependent Decomposition of Polymer Solutions”. Nanoscience and Technology: An International Journal, Vol: 9 num 2 (2018): 91-97.

[2] V. F. Formalev; S. A. Kolesnik y B. A. Garibyan, “Heat transfer with absorption in anisotropic thermal Protection of high-temperature products”. Herald of the Bauman Moscow State Technical University. Series Natural Sciences, Vol: 86 num 5 (2019): 35-49; V. F. Formalev; S. A. Kolesnik y B. A. Garibyan, “Mathematical modeling of heat transfer in anisotropic plate with internal sinks”. Computational Mechanics and Modern Applied Software Systems (CMMASS’2019) AIP Conf. Proc., Vol: 2181 (2019), article 020003 y V. F. Formalev y S. A. Kolesnik, “On Thermal Solitons during Wave Heat Transfer in Restricted Areas”. High Temperature, Vol: 57 num 4 (2019): 498-502.

[3] I. S. Burkhanov; L. L. Chaikov; N. A. Bulychev; M. A. Kazaryan y V. I. Krasovskii, “Nanoscale metal oxide particles produced in the plasma discharge in the liquid phase upon exposure to ultrasonic cavitation. 2. Sizes and stability. Dynamic light scattering study”. Bulletin of the Lebedev Physical Institute, Vol: 41 num 10 (2014): 297-304.

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[5] N. A. Bulychev; W. Van Camp; B. Dervaux; Y. Kirilina; K. Dirnberger; T. Schauer; V. Zubov; F. E. Du Prez y C. D. Eisenbach, “Comparative Study of the Solid-Liquid Interface Behaviour of Amphiphilic Block and Block-like Copolymers”. Macromolecular Chemistry and Physics, Vol: 210 (2009): 287-298.

[6] K. V. Pushkin; S. D. Sevruk; N. S. Okorokova y A. A. Farmakovskaya, “The most efficient corrosion inhibitors for aluminum anode of electrochemical cell used as a controlled hydrogen generator”. Periodico Tche Quimica, Vol: 15 num 1 (2018): 414-425; Yu. P. Aleksandrova; N. S. Budanova; A. A. Farmakovskaya; N. S. Okorokova; G. N. Ustyuzhaninova; N. P. Zharova y V. Kohlert, “The effect of ultrasonic treatment on the stability of aqueous dispersions of inorganic and organic pigments in the presence of surfactants”. Revista Inclusiones, Vol: 7 num Especial (2020):

Examination of carbon nanoparticles

The working regime in the experimental setup adequately simulates the second stage of the cavitation process, i.e., the cavitation collapse of bubbles that occurs in cavity under the conditions corresponding to the recovery of pressure after the outflow of bubbles from the Venturi tube. After the experiment, the fluid was poured out of the working cylinder. Suspended particles were precipitated by centrifugation, placed in a Petri dish, and studied under a microscope. A considerable part of the precipitated substance is a dark shapeless paste. However, this paste contained bright micron particles. In crossed nicols of the analyzer of the optical microscope, many of these particles provided a pronounced polarographic pattern in the form of a cross (Fig. 1). In reflected light, a noticeable brown inclusion was always observed in the central part of these particles. This inclusion is clearly seen in the far right particle in Fig. 1.

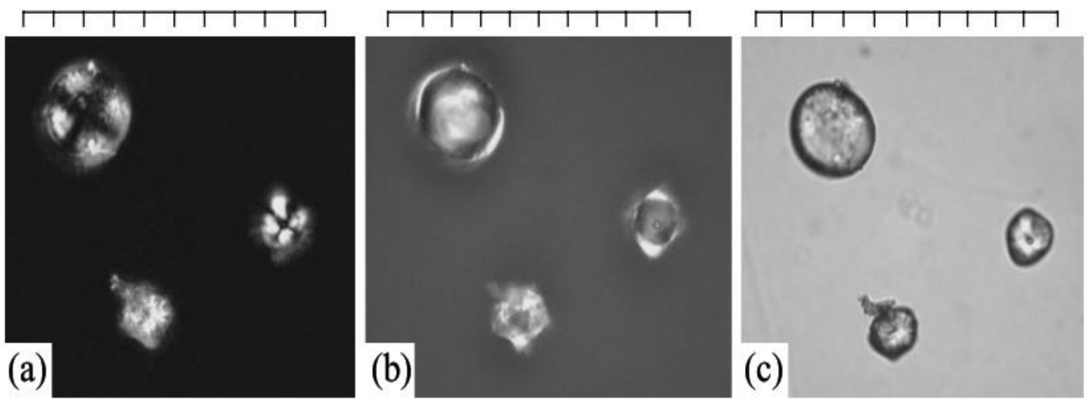

Figure 1
Microscopic image of particles obtained in the cavitation experiment by using (a) crossed nicols, (b) reflected light, and (c) passing light. One scale division is equal to 1 μm.

Organic compounds including polymeric compounds are naturally produced when cavitation is induced in benzene, and their presence is indirect evidence of the realization of the cavitation regime in the setup used in this work[7]. However, we are primarily interested in the nature of bright particles that are mentioned above and observed under the microscope. The substance precipitated from benzene was processed in hydrochloric acid at 80–218°C for ten hours for the removal of the organic component and was analyzed with a JEM-100CX scanning electron microscope. Data calculated from electron diffraction patterns for the samples under consideration in comparison with reference data for diamond and graphite show that the diamond phase is identified with a high probability in certain sections of particles being studied. In other sections, carbon is instead in the graphite phase.

387-397 y Yu. P. Aleksandrova; N. S. Budanova; A. A. Farmakovskaya; N. S. Okorokova; G. N. Ustyuzhaninova; N. P. Zharova y V. Kohlert, "Theoretical and experimental studies of the spectral characteristics of doped semiconductors on the example of zinc oxide and sulfide". Revista Inclusiones, Vol: 7 num 3 (2020): 453-463.

[7] A. V. Rudnev; N. G. Vanifatova; T. G. Dzherayan; E. V. Lazareva y N. A. Bulychev, "Study of stability and dispersion composition of calcium hydroxyapatite in aqueous suspensions by capillary zone electrophoresis". Russian Journal of Analytical Chemistry, Vol: 68 num 8 (2013): 700.

Whole particles are an aggregate of nanocrystallites[8]. The dimension of diamond crystals is equal to 10–30 nm. Figure 2 shows diffraction patterns from diamond particles, which also include an unidentified line that does not refer to the diamond phase. Certain ring reflections are split due to lattice distortion caused possibly by impurities. A number of aggregates provide the diffraction pattern shown in Fig. 2. The interplanar spacings calculated for this case correspond to graphite.

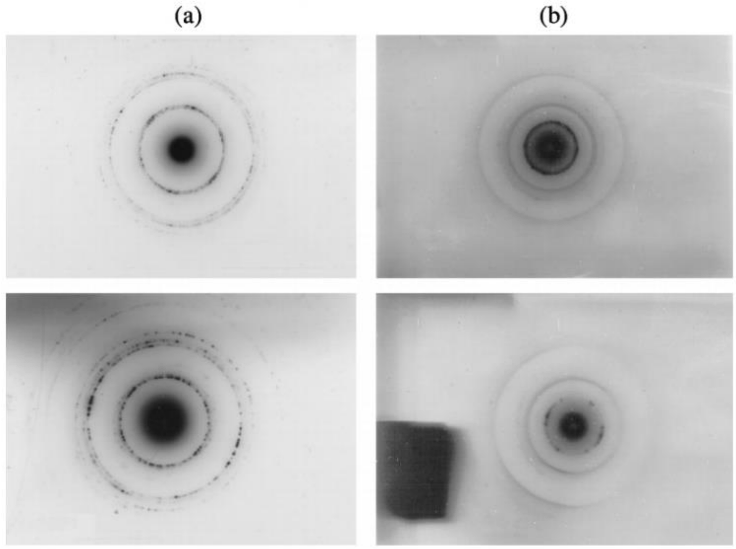

Figure 2

Electron diffraction pattern (negative) of the structure of sections of cavitation-synthesized particles containing (a) the diamond phase and (b) predominantly graphite.

Individual particles were mechanically transported under the microscope to the sample table and analyzed by Raman spectroscopy[9]. Raman scattering spectra were detected with a T64000 triple spectrograph Jobin Yvon on a silicon photoreceiver (CCD matrix) cooled by liquid nitrogen[10]. The Raman scattering spectrum was excited by a 5145-Å argon laser. Exciting radiation supplied on a sample through the microscope was focused on a spot with a diameter of about 2 µm and had a power of 10 mW. Although the spectrum of particles extracted from the products of cavitation processing of benzene included a line close to the characteristic 1330 cm^{-1} diamond line, this spectrum is more complicated and this line is broader[11]. Figure 3 shows the typical Raman spectrum for particles synthesized in the experiment. It is known that the broadening of the Raman spectrum can be caused by both the small size of diamond clusters as was observed, e.g., in the Raman spectrum of a diamond film and the presence of nondiamond impurity

[8] A. V. Ivanov; V. N. Nikiforov; S. V. Shevchenko; V. Yu. Timoshenko; V. V. Pryadun; N. A. Bulychev; A. B. Bychenko y M. A. Kazaryan, “Properties of Metal Oxide Nanoparticles Prepared by Plasma Discharge in Water with Ultrasonic Cavitation”. International Journal of Nanotechnology, Vol: 14 num 7/8 (2017): 618-626.

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[11] N. A. Bulychev; M. A. Kazaryan; A. Ethiraj y L. L. Chaikov, “Plasma Discharge in Liquid Phase Media under Ultrasonic Cavitation as a Technique for Synthesizing Gaseous Hydrogen”. Bulletin of the Lebedev Physical Institute, Vol: 45 num 9 (2018): 263-266.

(graphite, amorphous carbon, hydrocarbon formations)[12]. We note that some particles exploded when irradiated by a laser beam for a comparatively long time (100 s), which is probably associated with the presence of gas–liquid inclusions[13].

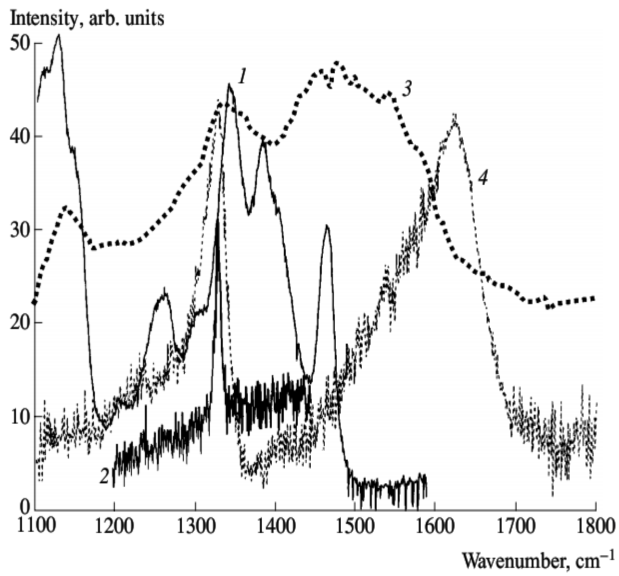

Figure 3
Raman spectrum of the (1) experimental particle, (2) diamond crystal, (3) diamond film, and (4) explosion-produced microdiamonds. The particle under investigation was a 14-µm aggregate; exposition time is equal to 100 s.
The excitation wavelength was equal to 632.8 nm.

The Raman spectrum of a particle obtained in the cavitation experiment was compared to the Raman spectrum of a new carbon-containing formation synthesized in a high-pressure setup. The spectra were almost identical. Since a pressure of 70 kbar and a temperature of 1700°C in the high-pressure setup were in the region of the thermodynamic stability of diamond, the above new formation likely contained the diamond phase[14].

Conclusions

The conclusions of this work are as follows: the excitation of cavitation in the working hydrocarbon fluid (benzene) is accompanied by the appearance of new formations that consist primarily of organic polymers and include solid carbon particles; particles are aggregates of nanocrystalline structures; at least some of such aggregates contain the diamond phase. Thus, the possibility of synthesizing the diamond phase when exciting cavitation in a carbon-containing fluid has been experimentally corroborated.

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[12] Yu. P. Aleksandrova; N. S. Budanova; A. A. Farmakovskaya; N. S. Okorokova; G. N. Ustyuzhaninova; N. P. Zharova y V. Kohlert, "Surface modification of organic pigments by isobutyl vinyl ether copolymers under the action of ultrasonic". Revista Inclusiones, Vol: 7 num Especial (2020): 11-21.
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[14] V. N. Nikiforov; N. A.Bulychev y V. V. Rzhevskii, "Elastic properties of HTSC ceramics". Bulletin of the Lebedev Physical Institute, Vol: 43 num 2 (2016): 74-79.

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