SELF-ASSEMBLAGE AND SELF-ORGANIZING OF NONEQUILIBRIUM CARBON NANOGELS

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Introduction

Studying hydrosol of ultradisperse diamonds (UDD) in the early nineties shown that UDD in the water environment are aggregated [1]. Thus primary particles in the size of 2 nanometers form secondary units in the size of 20 nanometers. On the basis of investigation of hydrosol (C <5 %) have been established that fractal dimension for units makes 2,1–2,3. Exceeding 5 % concentration UDD nanogel solutions were investigated by a method small angle X-ray scattering. For them it has been established that fractal dimension of UDD received in the explosive chamber ("volume" type of a fractal) changes within 2,2–2,84 and 2,2–2,94 for the diamonds received at blasting of charges in pool ("superficial" type of a fractal). It has been thus shown that nanoparticles, whose size exceeds 3 nanometers, keep the form and stick together sides, forming fractal cluster structures in the sizes about 30–40 nanometers. Presence of steady levels of aggregation at detonation carbon was also revealed by results of adsorption measurements.

Objective of this research was theoretical definition of morphological structure of UDD nanogel solutions in a mesopore of materials. For achievement of this purpose a number of modelling problems, as follows, were solved.

1. Some computer models for description of formation of atomic nanoclusters in “limited diffusion aggregation approach”, and formation of nano-aggregates of clusters with varied their concentration within the limits of the “cluster-cluster aggregations approach” were constructed [2].
2. Parameters of interpartical interactions were calculated by a nonlocal density functional method and self-organizing relaxation models of fractal nanostructures were constructed by using of a method of molecular mechanics.
3. Common theory of fractal dimensions, the Shannon information, and the theory of thermodynamic functions were applied to the description of carbon nanogels generated by algorithm “cluster-cluster aggregations” of carbon nanoparticles.

Mathematical modelling

Concentration of N nanoparticles in system of V cells of space of a material is given by:

$$C = \frac{N}{V} \cdot 100\%$$

It sets porosity of a material under the formula

$$P = 100\ \% - C.$$

Calculation of thermodynamic functions and fractal dimensions of system of atoms is under construction as follows.

Internal energy of nanosystem being composed of n atoms is given in pair approach by:

$$E = \sum_{i=1}^{n}\sum_{j=1}^{n} S_{ij}\varepsilon_{ij}(R_{ij})$$

Here S_{ij} - a matrix of a contiguity of atoms with numbers i, j, accordingly.

Entropy of placing N nanoparticles in system q cells of space of a material is given by the known formula of combination theory:

$$S = k_B \ln \frac{N!}{\prod_{i=1}^{q} N_i!}$$

Here N_i – number of nanoparticles in i cell.

Free Helmholtz energy of nanoparticle system is set, as usually, the formula:

$$F = E - TS.$$

Fractal dimension of the nanosystem is set:

$$N(L) = \frac{b}{L^D}$$

where L is a length of a grid cell; D is a fractal dimension; N is a number of the occupied cells in a grid; b is an empirical constant.

For calculation of the Shannon information of virtual nano-aggregates of clusters the signature principle is used.

The structure is represented a bond graph, in which some vertexes denote monomers making cluster, and a set of edges presents bonds of monomers among themselves. Thus set of bonds is formed by only next particles. Each pair of particles is connected only by one edge.

A number of the edges incidental with vertex defines its degree. It is possible to allocate 26 types of the vertexes differing with a number of edges connected them.

For calculation of Shannon information the known formula is used:

$$I_s = -\sum p_i \cdot \log_2 p_i,$$

where $p_i = N_i / N$ is a probability of occurrence of i-th type of vertex. Here N is a total number of vertexes. N_i is a number of vertexes of the given type.

Results and discussion

Inside a mesopore in the size 100x100x100 nm^3 properties of nanogel, which is "cluster-cluster" aggregated from UDD nanoparticles in the linear size 3.33x3.33x3.33 nm^3, correspond to a grid (30x30x30) of 27000 cells. Earlier we had been obtained results of computer modelling of filling of such system of cells [3].

Calculations of "cluster-cluster aggregation" of fractal nanogels of diamond-like particles in a mesopore have shown existence of three main forms of morphology of aggregate structures: «loose nanogel» (P > 50 %), «cellular-matrix nanogel» (50 %> P> 20 %), and «solid nanogel» (P <20 %), Two of them are shown on Fig. 1, 2.

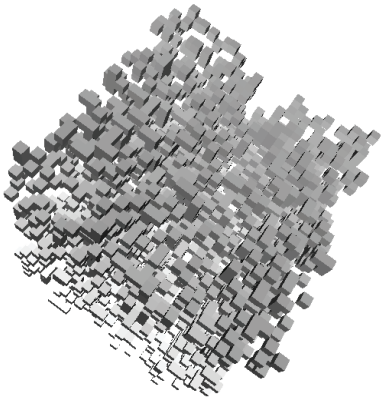

Fig.1. «Loose nanogel», porosity 90%.

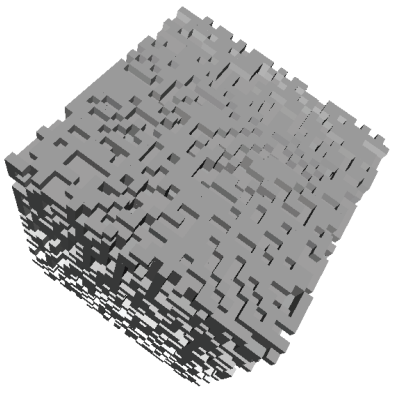

Fig.2. «Cellular-matrix nanogel», porosity 30%.

In Tab. 1 morphological parameters of carbon nanogels are resulted.

Table 1. Porosity P, the Shannon information I_S, fractal dimension D depending on a number N of nanodiamond particles in a mesopore

N	P, %	I_S, bit	D
2700	90	2.628	2.454
5400	80	3.105	2.658
8100	70	3.404	2.753
10800	60	3.606	2.816
13500	50	3.713	2.862
16200	40	3.753	2.898
18900	30	3.765	2.929
21600	20	3.659	2.956
24300	10	3.275	2.979
27000	0	0.764	3

Conclusions

1. For nonequilibrium processes of synthesis in a mesopore of diamond nanoparticle's nanogel correlation between the Shannon information of topological nanostructural interpartial bonds and morphological parameters, such as fractal dimension and porosity, has nonlinear character.

2. In case of "cellular-matrix" nanogel in self-assembling nano-aggregate there are maximum values of "dome-shaped" Shannon information. Besides of intricate system of nanopores these nanosystems, at the same time, possess a strong diamond-like skeleton comparable with «solid nanogel» and permeability (porosity up to 50 %) that is comparable with «loose nanogel». As a result "cellular-matrix" nanogels present some new adaptive multifunctional nanomaterials.

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