

COMPARATIVE STUDY OF PHYSICO-CHEMICAL PROPERTIES OF ULTRADISPERSE DIAMOND AND SHUNGITE NANOCARBON

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Introduction

Nanocarbon materials have attracted considerable interest of scientists in a wide range of disciplines due to a highly developed surface and reactivity. Since prospective applications of nanocarbons became visible the main accent was shifted to the general physical chemical problems of nanoparticles (NP), namely their aggregation. NPs aggregation takes place at the structure formation stage and under different treatment procedures. Aggregation could result in new properties of convenient materials when incorporating carbon NPs and unpredictable effect of NPs on the environment. Most of the ultradisperse systems formed are metastable, and it is, therefore, important to develop conditions under which they could be kept stable for a long time. The structure and dynamics of formation of a nanoscale carbon net can be described by comparative study of synthetic and natural nanocarbon materials if they are morphologically and genetically similar.

Different pathways have been employed for the synthesis of carbon NPs with different morphologies as well as size distribution but similar purification by wet methods. Water plays a role of a disperse medium and a regulator of intermolecular interactions among carbon NPs. Microdynamic properties of water molecules in the vicinity of NPs as well as the contribution of hydration to the structural and morphological characteristics and stability of nanocarbon clusters are the subject of intensive study [1,2].

Here the main attention is concentrated on two different forms of nanocarbon particles that could be combined by the way of their green synthesis, namely through stable aqueous dispersion. Shungite carbon (ShC) is originated from natural carbonaceous shungite rocks, otherwise ultradisperse diamond (UDD) is being produced from explosive (mixture of TNT ($C_7H_5N_3O_6$)-hexogen ($C_3H_6N_6O_6$)) using the expired stocks as the raw material [3,4].

It is challenging to compare nanocarbons of different origin that could be stabilized in water without using surfactants. The aim of the present paper was to study UDD and ShC in terms of their nanostructure and physico-chemical properties.

Experimental

Aqueous dispersion of ShC was prepared from shungite powder (less than 40 μm , carbon content ~ 98 wt.%) using ultrasonic treatment, filtration and centrifugation as described in [5]. The ShC dispersion was concentrated in vacuum evaporator at room temperature until carbon particles precipitated. An average particle size detected by TEM in the precipitated ShC dispersion was 10 - 100 nm, AFM and SEM showed aggregates with an average size 62 nm.

Nanodiamond (ND) was produced by NanoCarbon Research Institute, Japan from UDD by additional purification and ground in a stirred-media milling with zirconia beads less than 30 μm in diameter as described in detail elsewhere. As a result, stable aqueous dispersion with ND particles, ~ 5 nm in size with narrow size distribution of primary particles, is formed, as supported by DLS and TEM data [6].

The adsorption of molecules of different size, namely, carbon dioxide (0.33 nm), benzene (0.37 nm), and water (0.28 nm) was used to monitor the microporosity of ShC and ND. Measurements of these adsorptions were carried out by a static technique, using a gravimetric apparatus (McBain balance).

The sorption isotherms of nitrogen were obtained at 77K with an automatic device Quantachrome Instruments with Autosorb 1C analyzer. Samples were degassed at 323 K prior to every adsorption experiment. The isotherms of the other adsorbates were measured at 298 K and over the same relative pressure range. Pore distribution patterns were obtained based on Kelvin equation. Volume and radius of micropores were determined by Dubinine-Radushkevitch (DR) equation.

Results and Discussion

It was shown that ShC and ND are characterized by hierarchical system structure and presence of curved graphene shells or their fragments contribute to the formation of the structure [7]. Texture of nanomaterials could be determined by adsorption methods. An example of experimental nitrogen adsorption-desorption isotherms, obtained on ShC and ND, is shown in Fig. 1.

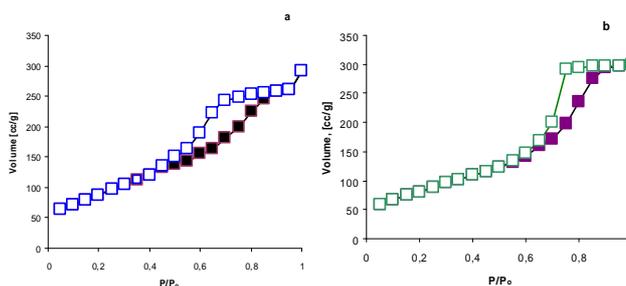


Fig.1 Nitrogen adsorption-desorption isotherms at 77K on ShC (a) and ND (b).

It can be seen that both samples are primarily mesoporous with a pronounced hysteresis in the desorption isotherm. The isotherms could be ascribed to type IV. A slight difference between hysteresis loops could be noticed. The loop on ShC is

thus similar to the one of nonrigid adsorbents (Fig.1a). The flexibility of pore walls could affect pore width: adsorption brings to increasing in pore width, while during desorption the pore size decreases, whereas the isotherm obtained on ND is typical of porous bodies consisting of rigid spherical particles. The BET surface area was found to be 283.8 and 325.0 m²/g for ND and ShC, respectively. An average pore size was close for both samples and equal to 6.3 -6.7 nm.

It is worth noting that the specific surface values of the samples are sensitive to the time and storage conditions of the powders due to remarkably high tendency to aggregate and great hygroscopicity. This is the main reason for scattering of data showed by different researchers for the same samples.

The largest total volume close for ND and nanoparticles of ShC was established for water adsorption. Thus, the specific surface area of ND and ShC for water molecule adsorption is equal to 503.2 and 577.7 m²/g, respectively.

Analysis of adsorption isotherms of molecules of different size resulted in calculations of specific surface (S) and volume adsorption (V) data using DR and BET equation (Table 1). V(CO₂) could be attributed to the ultramicropore volume with effective pore widths in the frames of 0.33 - 0.7 nm, while V(N₂) is often accepted as a measure of the total micropore volume (< 2 nm).

The surface area of mesopores was determined from the desorption branch of the benzene and carbon dioxide isotherms, assuming the split-like or cylindrical shape of the mesopores. Pore size distribution pattern of ND was calculated, based on both models. The split-like model fits better for mesopores 3-6 nm in size, while a cylindrical shape of pores is more preferable for the pore range 5-10 nm [7].

The flexibility of ShC pore walls (clapping) seems to be very promising for reservoir properties like of montmorillonites. Non planar grapheme segment (<1 nm) is the structural unit of ShC which could be easily transformed into water and formed the pore walls in dried powder.

The characteristic features revealed for the natural ShC were proposed to become apparent in morphologically similar ND. Thus the flexible aggregate of ShC could be opposed to the nondiamond shell with the characteristic thickness of 0.5 nm around diamond NPs (size ≈ 7 nm) determined by SANS using contrast variation method. The shell is responsible for the diffusive character of the ND surface and interpenetration of the aggregates as well as keeping water inside the aggregates [8].

One could suppose that removing of the shell could bring to decreasing stability of ND particles in concentrated aqueous dispersions and losing re-dispersibility in water. The work is in progress now.

Conclusions

Nanoparticles of ShC and ND stabilizing in aqueous dispersion without surfactants are characterized by similar texture in dried powder.

Both samples showed well-developed micro- and mesoporosity as revealed from the adsorption isotherms and

molecular probe technique. The difference in hysteresis loops allowed us to ascribe ShC to the nonrigid adsorbents, whereas ND is the one consisting of rigid spherical particles.

The BET surface area was found to be 283.8 and 325.0 m²/g for ND and ShC, respectively. An average pore radius was close for both samples and equal to 3.15 - 3.35 nm.

It could be supposed that a similar two-levelled structural pattern of both ShC and ND particles are responsible for surprising similarity in pore structure and adsorption characteristics.

Table 1. Specific surface and volume adsorption data of ND and ShC

	N ₂ (< 2 nm)		C ₆ H ₆ (0.37 nm)		CO ₂ (0.33 nm)	
	S, m ² /g	V, cm ³ /g	S, m ² /g	V, cm ³ /g	S, m ² /g	V, cm ³ /g
ND	283.8	0.48	324.2	0.46	172.5	0.066
ShC	325.4	0.45	34.9	0.24	144.2	0.055

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