

Preparation and characterization of colloidal dispersions of graphene-like structures from different ranks of coals

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Abstract: This paper focuses on preparation of colloidal solution of graphene-like structures from different ranks of coals: brown coal, bituminous coal, low-volatile bituminous coal, anthracite. It was found that brown coal thermo-oxidative destruction leads to formation of small $d = 32$ nm ($V = 17\%$) and large $d = 122$ nm ($V = 11\%$) fractions of nanoparticles. The thermo-oxidative destruction of bituminous coal leads to formation of nanoparticles $d = 50$ nm ($V = 5.2\%$) and $d = 164$ nm ($V = 16\%$). Thermo-oxidative destruction of low-volatile bituminous coal and anthracite leads to formation of nanoparticles, predominantly, $d = 122$ – 190 nm. Carbon nanostructures obtained from coal are negatively charged at pH = 2–12. Colloidal solution of carbon nanostructures at dispersed phase concentration 0.01 mg/mL is stable for 1 month. Electron diffraction patterns and X-ray analysis of carbon nanostructures showed that nanostructure from brown coal is amorphous and nanostructure from anthracite is crystalline. Results of coal macromolecules modeling and graphene-like structures obtained from them are presented.

Key words: graphene-like structures; coal; colloidal dispersions; particle size distribution; electrokinetic potential

Carbon is the only natural element, which has many allotropic forms. These forms differ from each other by their properties. Allotropic forms of the carbon are classified by structural features and by nature of chemical bonds between atoms. Depending on structural features allotropic forms of carbon are divided into the following categories: crystalline, amorphous and partially crystalline. Crystalline forms include diamonds, graphite, carbene, lonsdaleite, nanodiamond, fullerene, fullerite, and nanotube. Amorphous and partially crystalline intermediate forms of carbon include carbon fibers, coke, pyrolyzed carbon, pyrolytic graphite, soot, glassy carbon and coal. Carbon forms are classified by nature of chemical bonds between atoms: sp^3 forms (diamond and lonsdaleite), sp^2 forms (graphite, graphenes, fullerenes, nanotubes, nanofibers, astralenes, and glassy carbon), sp forms (carbene) and mixed sp^3 and sp^2 forms (amorphous carbon). Nowadays the development of practical use of such carbon nanomaterials as graphene and its oxides became an object of research. These are used for preparation of polymer and composite materials, solar cells, super-condensers, membranes, adsorbents, quantum dots (which are used in biology and medicine), fluorescent materials^[1–3]. Main sources for production of these materials are graphite, methane and acetylene. However, not only graphene and its oxides are of

interest for carbon nanomaterials application, but also their derivatives, so-called graphene-like structures (GS). They can be produced by using physical and chemical methods for modification original graphene and its oxides^[4,5]. Nanomaterials, which contain graphene, graphene oxide (GO) and related structures are manufactured by mixing, dispersion and impregnation. For this purpose it is more convenient to use colloidal dispersion than powdered substance. Chemical methods are most commonly used for production of graphene oxide colloidal dispersions. Advantages of chemical methods are large-scale production possibility and relative simplicity of product surface modification^[6]. Appearance of new functional groups on the surface is a result of such modification. This paper offers preparation methods of graphene oxide colloidal solutions and other graphene-like structures from natural coals of different carbonization stages. Substantial world reserves of coal and variety of macromolecular structural fragments within its composition make coal preferable mineral for production process. Coal macromolecules differ not only by the structure of carbon skeleton but also by content of different functional groups. Study of composition, structure and properties of carbon nanomaterials from different ranks of coals can considerably increase application of cheap carbon raw material.

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1 Computational method

1.1 Coal characteristics

Donetsk and Dneper fields coals (Ukraine), namely brown coal (B, Dnieper field, “Alexandriaugol”, Protopopovskiy incision), bituminous coal (G, Donetsk Basin, “Dobropolieugol”, Belozerskaya mine), low-volatile bituminous coal (T, Donetsk Basin, “Luganskugol”, Artem’s mine), anthracite (A, Donetsk Basin, “Sverdlovantracite”, Sverdlov’s mine) were used for recovery of GS and GO. Humidity (W_a), ash content (A_d), volatile content (V_{daf}) and element composition of coal (% by weight) are shown in Table 1. Natural graphite (“Zavalevskiy Graphite” LLC, Ukraine, carbon content of 99.5%) with ordered crystalline lattice was used for comparison with coal. Initial coal with particle size of 1 mm was milled in porcelain ball mill ($V = 2 \text{ dm}^3$) within 2 h. Ceramic balls were used as grinding bodies. Coal powder with particle diameter $d < 40 \text{ }\mu\text{m}$ was obtained after screening through testing sieves SLM-200 (Russia). Structural and sorption characteristics of coal powder: density (ρ , g/cm^3), specific surface area (S , m^2/g), pore volume (V_{pore} , cm^3/g) and effective pore diameter (d_{pore} , μm) were calculated by Brunauer-Emmett-Teller method (BET), considering data of low-temperature nitrogen absorption (77 K) and using specific area analyzer Nova 2200 (Quantachrome, USA) as shown in Table 2. Distribution of surface functional groups by acidity was determined based on common exchange capacity (CEC) and sorption value of 0.1 mol/L NaOH, Na_2CO_3 , NaHCO_3 aqueous solutions^[7].

1.2 Preparation of colloidal solution of carbon nanostructures

Since the initial coals contain considerable amount of ash (Table 1), gravity and density floatation was carried out in water solution of sodium salt of silicon-tungstic acid $\text{Na}_8[\text{Si}(\text{W}_2\text{O}_7)_6] \cdot n\text{H}_2\text{O}$ ($\rho = 2.3 \text{ g/cm}^3$, $\text{pH} = 7.2$). To dissolve the ash residue, HF (70%) was added to the coal and the resulted mixture was mixed on a magnetic stirrer within one day. After repeated washing with distilled water the ash content of coal powder was as follows: B ($A_d = 0.8 \%$), G ($A_d = 0.8\%$), T ($A_d = 0.7\%$), A ($A_d = 0.7\%$). To recover the carbon nanostructures from coals B and G, initial deashed coal

powder ($d \leq 40 \text{ }\mu\text{m}$) passed through thermal processing ($T = 120^\circ\text{C}$, time: 2 h) in H_2SO_4 (98%) and HNO_3 (98%) acid mixture (1:4 ratio). To recover the carbon nanostructures from coals T and A, modified Hammers method was used^[8]. The structure of high carbonization coals may be destroyed only by using strong oxidizers. Coal (10 g) was mixed with NaNO_3 (10 g) and concentrated H_2SO_4 (350 mL). The resulted mixture was cooled up to 0°C in an ice water bath. Then KMnO_4 (30 g) was added and reaction temperature was maintained at the level of not higher than 20°C . The final solution was heated up to 35°C and mixed within 3 h. The resulted mass was cooled down and flashed with solution of H_2O_2 (3%) and distilled water. Light-brown sludge was separated in a glass funnel with a glass porous membrane (S4, $d_{\text{pore}} = 16 \text{ }\mu\text{m}$) by vacuum filtration method and repeatedly flashed with KOH (1.0 mol/L) alcohol solution. Then it was dried in air at temperature of 50°C . The water suspension of the carbon nanostructures was treated by ultrasonic disintegrator UD-11 (TechPAN, Poland) within 20 min at maximum power of generator (100 W, 22 kHz). The colloidal solution of the carbon nanostructures was centrifuged in LMC-4200R centrifuge (Biosan, Latvia) at 4000 r/min rotor rotation speed within 40 min to settle out large particles. The schematic diagram of process is shown in Figure 1.

1.3 Spectroscopic analysis of coals and graphene-like structures

X-ray phase analysis of the deashed coal and carbon nanostructures was carried out by X-ray diffractometer DRON-2 (Cu $K\alpha$ -radiation, Co filter, $\lambda = 0.1542 \text{ nm}$). The sample plane was on goniometer axis with 0.1 mm accuracy. The error did not exceed 1 mm upon determining meter zero. X-ray diffraction patterns were made in automatic angular movement mode with increment of 0.1° . Exposure interval was equal to 10 min in each point with rotation of the sample in its own plane. Operation voltage was 30 kV and anode current power was 20 mA. Samples for analysis were prepared in form of flat disks pressed in a cuvette. Infrared spectra (IR) of coals and carbon nanostructures in matrix from KBr were recorded by FT-IR Spectrometer “Vector 22” (Bruker, USA) within frequency range ($400\text{--}4000 \text{ cm}^{-1}$) and resolution of 4 cm^{-1} .

Table 1 Proximate and ultimate analyses of coal

Coal	Proximate analysis w/%			Ultimate analysis w _{daf} /%				
	W_a	A_d	V_{daf}	C	H	N	O	S
B	51	20	48.5	70.1	5.0	1.2	19.7	4.0
G	7.8	17.5	37.7	80.0	5.0	1.4	10.5	3.1
T	5.1	25.0	14.9	88.5	3.8	0.67	5.33	1.7
A	5.0	17.0	7.5	95.6	2.1	0.4	1.2	0.7

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