Brief Communications

Electrochemical preparation of colloidal fluorescent graphite

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Colloidal graphite having nano- and microparticles and exhibiting fluorescence properties was prepared by the destruction of the glassy carbon anode in the electrolyte containing hydrochloric acid and α-olefin C_{16}—C_{18}.

Key words: electrosyntesis, colloidal graphite, fluorescence.

Many methods for the preparation of carbon nanoparticles and nanocrystals are known, including laser ablation of graphite,[1,2] carboxylation of candle soot,[3] irradiation of nanodiamonds with a proton beam,[4,5] and using other laborious methods.[6—8] Carbon nanocrystals have recently[6] been obtained from multilayer carbon nanotubes by the electrolysis of a MeCN solution. However, they turned out to be unstable in both aqueous solutions and carbon material bulk.

Fluorescent semiconducting nanocrystals, which are widely used due to photostability and other remarkable optical properties, are of special interest for biology and medicine.[9—12] They are not cytotoxic, unlike, *e.g.*, CdS.

We have previously[13] reported the electrochemical halogenation of paraffins from technical fractions of higher α-olefins. The comparison of the results obtained on various electrodes showed that the glassy carbon electrodes decomposed under these conditions and produced a stable suspension of carbon particles in olefin. The suspension can be stored for years, which suggested the formation of carbon particles of micro- or nanometers in size. The purpose of the present work is to determine the size of carbon particles formed upon the decomposition of glassy carbon anodes and to elucidate their nature and fluorescence properties.

Experimental

Preparative electrolysis was carried out using a V5-71 dc source in a temperature-controlled cylindrical undivided 100-cm^3 electrolyzer (three-electrode cell). A saturated calomel electrode (Hg/Hg_2Cl_2) was used as a reference electrode. The electrolyte was magnetically stirred during electrolysis. Electrosynthesis was carried out in the thermostatic mode at 20 °C using a circulation thermostat (MLW, Germany). After the end of electrolysis, the electrolyte represented a two-phase system (aqueous and organic phases). The organic phase represented a suspension of chloroparaffin and particles of the destroyed glassy carbon anode.

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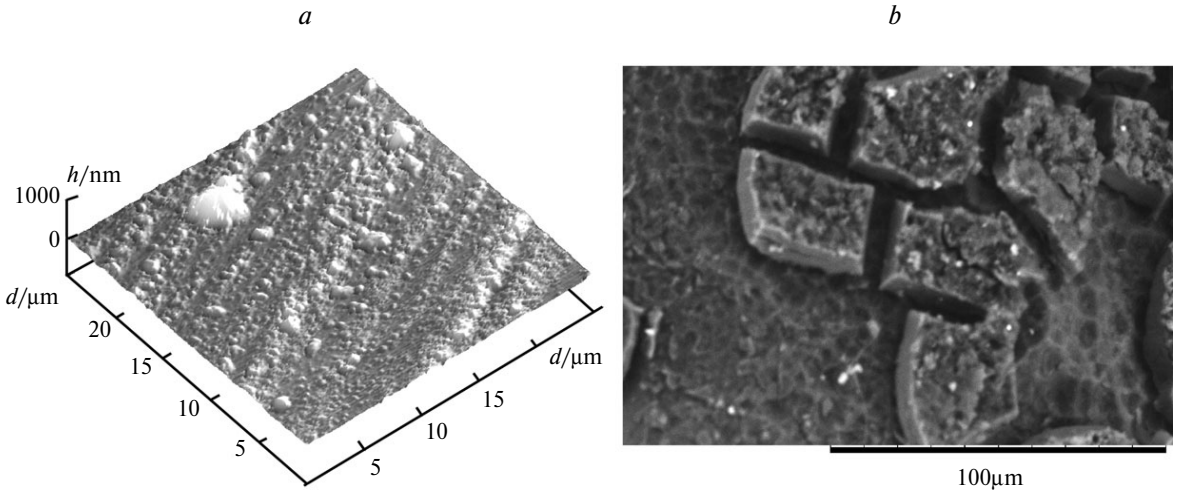

Fig. 1. Surface of the glassy carbon anode before (*a*) and after electrolysis (*b*).

α-Olefins of the C_{16}—C_{18} fraction (OAO Nizhnekamskneftekhim) and hydrochloric acid (reagent grade) were used in the synthesis.

Colloidal graphite was prepared from the glassy carbon cylindrical electrode (SU-2500 trade mark) of the total surface area 40 cm^2 during the electrolysis for 5 h of a 4 *M* solution of HCl in the presence of α-olefin C_{16}—C_{18} taken in an amount of 20% of the electrolyte volume. The coaxially mounted titanium cylinder with the surface area 22 cm^2 served as a cathode. The current density at the anode was 900 A m^{-2}.

The working solution (100 mL) was prepared by mixing of a 4 *M* solution of HCl (80 mL) and α-olefin C_{16}—C_{18} (20 mL). Electrolysis was carried out in the galvanostatic mode with strong emulgation.

Nanostructures were studied using a MultiMode V scanning probe microscope (Veecco), TM-1000 electron microscope (Hitachi), and Photocor-FC and UF-Vid-BIK instruments (dynamic light scattering method).

The ion ionization mass spectra were obtained on a MAT-212 mass spectrometer with the ionization energy 70 eV with the gradual temperature increase from room temperature to 450 °C. The MALDI mass spectra were recorded on a ULTRAFLEX-III mass spectrometer on a metallic plate.

Colloidal graphite. UV, λ_{max}/nm: 375. ^{13}C NMR ($CDCl_3$), δ: 134.9, 135.5, 136.0, 136.8, 142.6, 143.7.

Results and Discussion

The surface of the glassy carbon anode in a scanning probe microscope before electrosynthesis is shown in Fig. 1, *a*; roughness does not mainly exceed 50 nm.

After electrolysis the roughness of the anode surface increases strongly (see Fig. 1, *b*); a part of carbon is washed out to the solution and forms a suspension in the organic part (olefin). The suspension is easily separated from the aqueous phase by decanting. An insignificant amount of carbon particles (larger in size) in the system is unstable and precipitates. We failed to obtain the image the anode surface in a scanning probe microscope because of its strong loosening.

Colloidal graphite particles in a solution with olefin (chloroparaffin) were studied by ^{13}C NMR and UV spectroscopy and dynamic light scattering. The ^{13}C NMR spectrum of colloidal graphite contain signals in the region characteristic of aromatic compounds at δ 134.9, 135.5, 136.0, 136.8, 142.6, and 143.7. The UV spectrum exhibits an absorption band at 375 nm, which also corresponds to aromatic compounds. Three main narrow regions were found by the dynamic light scattering method when studying the size distribution of carbon particles in the non-filtered solution (Fig. 2).

The dispersion and histogram of the particle distribution are retained when the solution is filtered through the ceramic Schott filters nos 3 and 4. After filtration through the micronic filters (0.45 μm), only the particles with an average size of 0.44 nm (97% of the overall amount of the remained particles) are determined in the solution (Fig. 3).

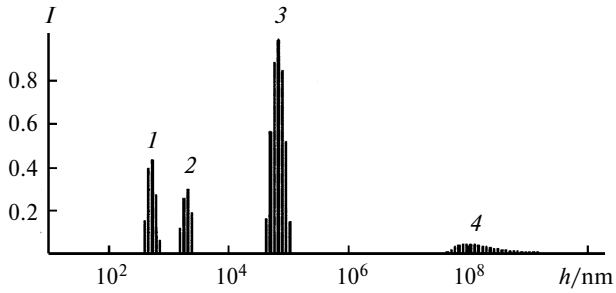

Fig. 2. Size distribution of the carbon particles in a non-filtered solution in chloroparaffin after electrolysis. Here and in Fig. 3, *I* is the intensity, and *h* is the hydrodynamic radius. The peak surface area and the corresponding particle size (nm) are 0.266, 620.1 (*1*); 0.060, 5154.0 (*2*); 0.600, $6.7 \cdot 10^4$ (*3*); 0.075, $8.2 \cdot 10^7$ (*4*).

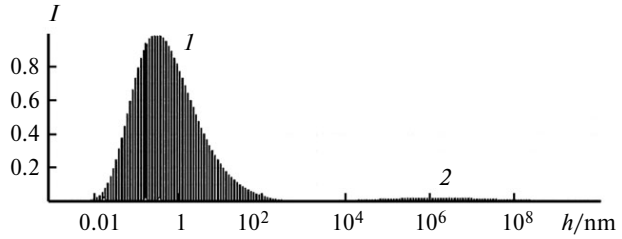

Fig. 3. Size distribution of the carbon particles after filtration of the solution in chloroparaffin through the micronic filter (0.45 μm). The peak surface area and the corresponding particle size (nm) are 0.966, 0.436 (*1*); 0.024, $1.2 \cdot 10^6$ (*2*).

Green fluorescence was observed upon the UV irradiation of the initial solution of the carbon particles (organic phase after electrolysis) and the solution filtered through the Schott filters nos 3 and 4.

It should be noted that no emulsion of carbon particles is formed in the absence of olefin in the electrolyte. The glassy carbon is destroyed when active chlorinating agents are generated on it, but larger carbon particles immediately precipitate.

We have found that the electrolytic destruction of the glassy carbon under the conditions of chloride ion oxidation in the presence of higher olefins affords nano- and microsize carbon particles of aromatic nature (possible graphene analogs) and possessing the fluorescence properties. Under such an anodic destruction, a strongly loosened surface from which nano- and microparticles are washed out is formed.

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