The Kuzbass Basin coals as a raw material for the preparation of carbon quantum dots

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Abstract. The article discusses a promising method for producing carbon quantum dots (C-dots) from coal. Coal grades A (anthracite), K (coking), OS (lean-sintered) were used as raw materials. The separated particles were investigated by X-ray diffraction and optical methods of analysis. The interplanar distances in C-dots and the phase ratio in the samples are determined. The intrinsic absorption region was determined from the optical spectra and the band gap of the obtained C-dots was estimated. Lines of photoluminescence were found in the UV and visible ranges.

1. Introduction
Carbon quantum dots (C-dots) are of interest in view of their potential applications. This forces us to search for less costly and efficient methods of obtaining them. One of the promising areas of modern research is the production of quantum dots from coal. Coal is the best known and most widely used modification of carbon. The structure of coal, as a rule, is presented in the form of an irregular polymer-like substance, where structural configurations such as aromatic, aliphatic, heterocyclic fragments are in fusion with carbon clusters. This feature is expressed in the inheritance of the functional properties of C-dots, which are isolated from coals of various classes of metamorphism.

Mainly high-tech methods and pure reagents are used in the process of obtaining carbon nanomaterials. This affects the final cost of such materials and their areas of application. The use of more accessible methods and raw materials will expand the scope of application of C-dots, for example, in such areas as: the development of molecular probes in biology, luminescent sensors, supercapacitor materials, sensitizers for photostimulated processes, etc.

Basically, quantum dots were obtained from semiconductor materials, until in 2004 C-dots were accidentally discovered during electrophoretic cleaning of single-walled carbon nanotubes (CNTs) synthesized by an arc discharge [1]. They are considered as a special transition state of carbon, which differs from graphite, graphene, graphene oxide, CNTs, fullerene, etc. [2-4]

Graphite quantum dots (CQDs) are synthesized using various carbon materials, for example, fullerenes [5], glucose [6], graphene oxide [7-10] and carbon nanotubes [11]. Physical separation of graphene layers is expensive and impractical to generate significant amounts of CQD. Hydrothermal [12,13] and electrochemical [11,14] methods can effectively synthesize CQDs, but the starting materials (fullerenes, graphene, carbon nanotubes, carbon fibers) are still expensive for mass production.
One of the promising methods for the synthesis of carbon quantum dots is the use of small organic molecules controlling the structure of the resulting particles at the stage of the initial carbon skeleton of the molecule. But this method has not received the desired result and widespread use [15]. Separation of the extracted quantum dots by the method of gradient centrifugation or ultrafiltration requires a significant investment of time and energy [16].

To obtain C-dots, a precursor containing nano-sized $sp^2$ carbon structures is required. This can be a coal containing graphite crystallites, and their number and size are variable in different coals. This makes it possible to control the properties of the extracted quantum dots [17, 18]. These particles in aqueous solutions showed stable size-dependent and pH-dependent photoluminescence. Moreover, the degree of graphitization of coals (stage of metamorphism) is a key factor affecting the formation of C-dots. Coals with too high or too low degree of graphitization are not optimal for this process [19].

Another raw material for the production of C-dots can be coal tar pitch, which is a by-product of the coke industry. The structure of coal tar pitch is similar to graphene quantum dots, including an aromatic core and several side bonds. By acting on the pitch with hydrogen peroxide, it was possible to isolate particles with a size of $1.7 \pm 0.4$ nm and containing from one to three graphene layers, while the product yield reached more than $80 \text{ wt\%}$. According to the authors, this technique opens up the possibility of commercial synthesis of C-dots. [20]. In the next work [21], the same authors, using carbon quantum dots isolated from coal tar pitch, used TiO$_2$ to modify the photocatalyst, thus expanding the sensitivity region to the visible region. In the visible range, the rate of photocatalytic decomposition of radomin B increased 23 times as compared to pure TiO$_2$.

Nitrogen doped fluorescent carbon dots (N-CQD) were synthesized by a hydrothermal method using anthracite in the presence of dimethylformamide (DMF), with a yield of 25.6 wt\%. As a result, colloidal $sp^2$ carbon structures exhibited strong photoluminescence with a quantum yield of 47.2%. [22]

In [19], C-dots were also isolated from anthracite and ligated with nitrogen, phosphorus, and sulfur in a one-step method. The content of ligating impurities was 5.6%, 3.7% and 3.7% mole fractions, respectively. The resulting quantum dots demonstrated luminescence quenching by some microelements and were used to detect Pb$^{2+}$ ions in a solution in the range of 1–20 $\mu$M, with a limit of 0.75 $\mu$M.

Using perchloric acid and hydrogen peroxide, carbon quantum dots were isolated from bituminous coal, with a yield of 30 wt\%. The size of particles obtained by oxidation with hydrogen peroxide was 3.26 nm, and their specific capacity, determined by galvanostatic cycling, was 200 F / g, and their charge-discharge cycle stability was more than 15,000, while maintaining 90% of the capacity [23].

Using the method of pulsed laser ablation in ethanol from carbon (0.03 g / ml), quantum dots with sizes ranging from 5 to 30 nm were obtained. The particles thus obtained were highly photostable, had low toxicity and biocompatibility, and were used in bioimaging. Their use has been demonstrated as highly efficient photoluminescent molecular probes for obtaining bioimaging of pancreatic cancer cells [24].

Thus, most researchers point to the possibility of mass production of carbon quantum dots from coals due to the simplicity and easy scalability of the synthesis processes. The functionalization of the resulting particles is no different from the particles obtained from other precursors. Moreover, functionalization is often not required, since coal crystallites already contain impurities and structural defects. Naturally, carbon quantum dots obtained from coals of various deposits and stages of metamorphism will have different physicochemical properties inherited from their predecessor. The prospect of such studies, in our opinion, remains relevant.

2. Experiment details
The study used coal samples from most deposits of the Kuzbass Basin coal of grade A (anthracite, Bungurskiy open pit), K (Berezovskaya mine), OS (Tomusinskiy open pit). We have proposed a method consisting of the following stages: wet grinding of coal in a planetary ball mill; peroxidation
with ultrasonic activation; stabilization and sedimentation of the suspension; evaporation and drying for extraction of carbon quantum dots from coal of the Kuzbass Basin.

The initial coal was ground in the Planetary Micro Mill "PULVERISETTE 7". The starting material (2 g of charcoal and 5.5 ml of water) was placed in agate mortars together with 3 large agate balls 7.5 mm in diameter and 6 small ones 2.5 mm in diameter. Grinding was continued for 5 hours at 400 rpm. The samples were subjected to additional grinding (dispersion) by ultrasound with an energy released of the order of about 100 kJ / h during the experiment. The mixture preheated in a thermostat to 80 °C (0.2 g of crushed coal and 20 ml of H₂O₂) was sonicated for 40 min. During this time, 5 ml of H₂O₂ was poured into the reaction mixture every 10 min. A centrifuge was used to remove unreacted components of the mixture (impurities). Centrifugation was carried out at a frequency of 3500 rpm (acceleration 10746 m / s) for 20 minutes. After centrifugation, the centrifuge was separated from the solid sediment and placed in an oven at a temperature of 60 °C. The dried sample visually appears dark brown in transmission and black in reflection (see Figure 1 left and right, respectively).

Figure 1. A sample of C-dots obtained from K grade carbon in white light transmission (left) and in white light reflection (right).

X-ray diffraction patterns of coal materials obtained in the course of the experiments were recorded with an X-ray diffractometer DR-02 "Radian". The sample under study was scanned in the following mode: scanning step (0.02 ° / step) over the angular range from 7 ° to 60 ° in Kα radiation of copper (25 kV, 6 mA) when recording diffraction patterns. The diffracted radiation was recorded with a semiconductor (Si) detector. The obtained diffraction patterns were processed using the Origin Lab Pro software package.

The study of the obtained samples for the absorption of electromagnetic radiation in the wavelength range (λ) from 190 to 900 nm was carried out with a UV-2550 spectrophotometer.

The apparatus FLYUORAT-02-PANORAMA was used to measure the luminescence spectra and luminescence excitation. The light source of the analyzer is a high pressure xenon lamp, which provides excitation in the mode of short pulses (of the order of 1 μs). The working wavelength range of the analyzer is 210-860 nm. The device contains two monochromators, one of which is aimed at registration of excitation, and the other at registration of luminescence. The obtained spectra were processed using the Origin Lab Pro software package.

3. Results and discussion

The physical impact on the organic part of coals causes structural changes, in particular, the crystallite size, interplanar distances and the ratio of amorphous and crystalline carbon, the so-called "graphitization", can change. In this case, the reverse process of disordering of the graphite structure due to the intensification of oxidation and separation of crystallites is not excluded.

Figure 2 shows a diffractogram of coal of grade K and C-dots obtained from it. The analysis of the data obtained from the diffractometer was carried out according to the following algorithm: smoothing...
of the spectrum lines; decomposition of the spectrum into Gaussians / Lorentzians; estimation of the phase relationship with the comparison of areas at 10, 20 and 23 ° to 20.

Thus, a peak at 10 ° to 20 characterizes the presence of C-dots; a peak 20 ° to 20, also called a γ-pattern, allows you to characterize the presence of carbon in the resulting material in the amorphous phase; the 002 pattern at 23 ° to 20 makes it possible to assess the presence of an ordered carbon structure.

**Figure 2.** Diffraction patterns of grade K coal and C-dots obtained from it (a), decomposition of the diffractogram into Lorentzians in the Origin Lab Pro software package

The calculation of the interplanar distance \( d \) for the obtained C-dots was carried out on the basis of the Wolff-Bragg formula for a diffraction grating at an X-ray wavelength of 1.54 Å and the corresponding angles of incidence of X-rays on the plane of the sample under study \( \Theta \); the phase ratio \( S \) was estimated by comparing the peak areas and the yield in % of the starting material; product yield in %. The calculation results are shown in Table 1.

**Table 1.** Parameters of C-dots samples from coal grades A, K and OS

| Coal grades | Angle 2Ø (°) | \( d, \) Å | Phase ratio \( S \), % | Product yield, % |
|-------------|-------------|---------|-----------------|-----------------|
| A           | 10.9        | 8.11    | 56              | 29              | 16              | 3-8             |
| K           | 10.9        | 8.11    | 49              | 38              | 12              | 25-35           |
| OS          | 10.7        | 8.28    | 88              | 9               | 3               | 1-5             |
The optical absorption spectra (Figure 3) of the C-dots samples demonstrate that the highest absorption is observed in the near UV range (from 190 to 300 nm). The highest absorption is observed in the sample obtained from OS coal grade; The least absorption is observed for the sample obtained from A coal grade.

Based on the results of optical absorption spectroscopy, the band gap was calculated for each of the C-dots samples. The calculation was performed according to the following algorithm: calculation of the frequency of the incident radiation; calculation of the energy of the incident radiation; calculation of absorption coefficient (if optical density $D \sim 1$, then the absorption coefficient is $\alpha = \frac{D}{d}$, if $D > 1$, then $\alpha = \frac{1}{d} \ln \left(10^{-D}\right)$); plotting graphical dependencies $\alpha^2 = f(h\nu)$; from the constructed graphical dependence for a given sample, sections of the graph with a linear dependence are selected. Extrapolating the selected linear section to the intersection with the energy axis ($h\nu$) shows the value of the band gap for direct (optical) allowed transitions. Thus, the band gap $\Delta E$ for a sample from A coal grade is 2.3 eV, from K coal grade: 3.5 eV, from OS coal grade: 3.7 eV.

The study of the photoluminescence of the C-dots samples was carried out for all the samples under study, having previously been dispersed in water by ultrasound for 10 min. The concentration of the samples in the solution was 50 $\mu$g / ml. Figure 4a shows the photoluminescence spectrum of a C-dots sample obtained from anthracite. The maximum luminescence was observed upon excitation by light with a wavelength of 210 nm. In this case, the absorbed radiation energy relaxes to re-radiation at a wavelength of 460 nm. Upon excitation with a UV laser, greenish-blue C-dots luminescence was observed (Figure 4b).
Figure 4. Photoluminescence spectrum of C-dots obtained from anthracite (a); photoluminescence C-dots with UV laser excitation (b)

For the samples, in addition to the peak at 460 nm, there is a weak peak at 300 nm obtained from K coal grade. The luminescence of the C-dots samples is possibly due to the presence of impurities of heavy metals, nitrogen, sulfur present in the form of structural or adsorbed impurities in the particles.

Conclusions
It can be stated that high metamorphic coal from the Kuzbass Basin is suitable for obtaining C-dots. Moreover, for this, you can use simple methods that can be implemented on an industrial scale. The resulting C-dots should be classified as wide-gap semiconductors with a band gap of 2.3 eV (anthracite), 3.5 eV (coking), 3.7 eV (lean-sintered). The resulting particles exhibit photoluminescence with a main maximum at 460 nm. Of course, the purity and homogeneity of the separated particles is insufficient and they have a significant proportion of carbon in other solid phases, which limits their application in fields such as biology and nanoelectronics. But, nevertheless, coal can be used as a cheap raw material for producing quantum C-dots.

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