Benefit of porous silica nanoreactor in preparation of fluorescence carbon dots from citric acid

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Abstract

A facile and robust synthesis of carbon dots (CDs) emitting blue-light in water without activation and stabilization has been developed by pyrolysis of citric acid (CA) adsorbed in silica gel (SiO₂) pores. Effect of the host pore size on luminescent properties of SiO₂@CDs nanocomposite as well as water suspension of CDs has been studied. The synthesis conditions such as concentration of the precursor, duration of synthesis also have been investigated. It has been demonstrated that upon the thermal treatment of silica gels saturated with CA (60% of maximum loading) at 170 °C for 5–600 min, luminescent CDs are shaped inside the nanoreactor pores. These SiO₂@CDs emit photoluminescence centered at 450 nm. Silica-immobilized CDs can be separated from the source molecules and side-products by centrifugation, which allows avoiding the dialysis of the resulted mixture and so improve the scaling of the synthesis. The CDs can be easily released from SiO₂@CDs by washing it with water. Water-eluted CDs demonstrate photoluminescence at 447 nm. The smaller pore size of the host and longer time of thermal treatment promote the formation of the CDs with better photoluminescent peak symmetry and higher quantum yield up to 10.1%.

1. Introduction

Carbon dots (CDs) are a unique new class of water-soluble nanoobjects with strong photoluminescence (PL) in the visible range. Unlike other known nanomaterials, such as noble metal nanoparticles, semiconductor quantum dots and hybrids of organic metal halides, CDs exhibit numerous advantages such as high photostability, low toxicity, and low cost. Finally, the production and application of CDs are very sustainable. They can be obtained from various organic objects and degrade in a natural environment to CO₂. Due to their potential in energy conversion and storage [1], water disinfection [2], food safety [3] analytical chemistry [4–6] for development of chemical- and bio-sensors [6–8], biotechnology and nanomedicine [9–11] in cell imaging and biolabeling [12–15], for drug release [16], theranostics [9, 17], and photodynamic therapy [18], etc.

Carbon dots were first received in 2004 by the electrophoretic purification of oxidized single-wall carbon nanotubes [19]. Later, this approach was generalized as 'top-down' [20] and applied to graphite, graphene oxide [21] and nanodiamonds [22]. The top-down approach is based on the shredding of large carbon objects by using arc discharge [19], laser ablation [23], chemical or electrochemical oxidation [24]. The main problems of the top-down synthesis are low CDs yield and small quantum yield (QY) of photoluminescence for the resulting CDs. For example, CDs prepared from candle soot have QY about 2% [25]. In a two-step synthesis that included laser ablation of the carbon precursor and further passivation of the resulted CDs with diamine-terminated poly (ethylene glycol), QY was increased up to 10% [26]. In a one-step synthesis made by laser irradiation of carbon powder suspended in an organic solvent, CDs were obtained with a quantum yield of 5% [27].
Significant progress in CDs preparation has been achieved after an alternative ‘bottom-up’ approach has been developed several years ago. Particularly, it was demonstrated that organic compounds can generate CDs under thermal decomposition [28–32]. Various organic compounds, such as glucose, citric acid, ascorbic acid (CA), glycine, EDTA have been tested as carbonaceous precursors of CDs as individual components or in the mixture with different additives [33]. In contrast to the top-down approach, bottom-up CDs synthesis allows obtaining highly luminescent CDs (QY > 10%) in the one-step process, which not requires further activation and stabilization of the particles, can be performed under facile and mild conditions (150 °C–300 °C), such as hydrothermal treatment, ultrasonic reaction, microwave-assisted pyrolysis.

From both fundamental and applied perspectives, photoluminescence is one of the most appealing characteristics of CDs. For CDs obtained in bottom-up synthesis, the PL spectra are generally broad and dependent on the excitation wavelength (excitation-dependent photoluminescence). Quantum yield of CDs photoluminescence can vary from 1 to 99% depending on the precursors and pyrolysis conditions [34]. Due to the unclear mechanism of the bottom-up synthesis, a variation of the experimental conditions such as heating time and temperature cannot provide efficient control of CDs formation and their further aggregation [1, 7, 10, 30, 34]. Thus, at this point, such an approach has not been able to ensure reproducibility and scale-controlled yield of the luminescent CDs. Therefore, further procedures are often required to separate CDs from other residues [35]. For instance, size-exclusion chromatography [36], dialysis [37–39] and column chromatography [40] have been used for CDs purification and selection.

Spatial isolation of the CDs precursors before their carbonization can be an alternative approach to the post-synthesis separation of CDs. It can be achieved, for example by adsorption the precursor in the pores of an appropriate host material with further pyrolysis of guest-host composite. In such an approach the pores will serve as quantum confinement nanoreactors and will limit the growth and shape of the CDs.

The synthesis of C-dots in nanoreactors is a very attractive approach. In contrast to conventional chemical reactors, the confined space of nanoreactors can increase the probability of reaction collision and the mass transfer of reactive chemical molecules, thereby greatly improving the efficiency of chemical reactions [1, 10]. Information about the application of porous nanomaterials as thermal-resistant nanoreactors for the production of CDs is limited. The first proof-of-concept of size-controlling approach was made in [41], where carbon precursor (citric acid) was introduced into the pores of an inorganic framework before pyrolysis. The resulted CDs were received by the dissolution of silica shell in NaOH with very low QY [41]. Several attempts to use microporous materials in CDs synthesis were published [42–45], but mesoporous materials with pore size larger than 2 nm are more appropriate for templated synthesis of CDs. The latest results in this subject summarized in table S1 is available online at stacks.iop.org/NANOX/1/010011/mmedia (in the ESM). Among mesoporous materials, silica gels have the most appropriate properties to serve as a nanoreactor for CDs preparation. They have suitable pore size (from 1.5 to 11 nm) and hydrophilic surface, about 99% of the total silica gel surface is the area of mesopores. Thus, templated synthesis of CDs using mesoporous silicas attracts the most attention [46–51].

Nevertheless, information on the application of silica gels as nanoreactors for CDs synthesis if very segmental and insufficient. Particularly, no information available on the effect of the host pore size on the size and luminescent properties of the CDs. Also, the methodology for matrix-assisted CDs preparation, such as precursor loading, optimum duration of synthesis, conditions of CDs removal from the nanoreactor requires further development.

In the current study, four sets of silica gel (SiO₂) samples having a different diameter of pores (from 4 to 11 nm) have been studied as nanoreactors for the preparation of CDs from citric acid. To ensure localization of CA strictly in the template pores, samples of silica gels with adsorbed CA (SiO₂@CA) were obtained with 60% of CA maximum loading. Silica gel composites with embedded CDs (SiO₂@CDs) were prepared at 170 °C–200 °C during 15–600 min Conditions of CDs elution from the host have been also studied. The results were compared with the conventional bottom-up preparation of CDs from CA. Solid SiO₂@CDs nanocomposites and water suspension CDs have been characterized by various methods such as SEM, AFM, FTIR, XPS, UV–vis, luminescence spectroscopy (including 3D photoluminescent spectra and excitation-emission map).

2. Experimental section

2.1. Materials

Citric acid (99.5%) was purchased from Proquimios (Brazil), sodium hydroxide (99%) was from Dinamica (Brazil), sodium bicarbonate (99%) was supplied by Synth (Brazil). Four sets of silica gel (all from Sigma–Aldrich) were used. Their different porous characteristics, particle size, and geometry are presented in table 1. Calcium hydride (95%), toluene (99.8%), and molecular sieves (3 Å, 4–8 mesh) were purchased from Sigma–Aldrich (USA). Toluene was dried by distillation over calcium hydride and stored in a dark bottle with molecular
| ID  | Sigma-Aldrich ID | Particles type       | Particle size (μm) | Average pore size (nm) |
|-----|------------------|----------------------|--------------------|------------------------|
| SiO₂(4) | SKU 60735 (SAFC) high-purity grade for column chromatography | irregular | 63–200 | 4.0 |
| SiO₂(6) | SKU 717185 (Supelco) technical grade | irregular | 40–63 | 6.0 |
| SiO₂(9) | SKU 60745 (SAFC) high-purity grade for column chromatography | irregular | 63–200 | 9.0 |
| SiO₂(11) | SKU 80442 (Supelco) 0.7–0.9 cm³/g pore volume | spherical | 40–75 | 11 |
sieves. All aqueous solutions were prepared with ultra-pure water from a water purification system (The PURELAB Classic, Elga, UK).

### 2.2. Characterization

The textural properties of silica gel samples were determined by means of the low-temperature nitrogen adsorption-desorption method at 77 K on an ASAP 2020 (Micromeritics, USA). The total pore volume was determined at the maximal adsorption point and specific surface area was calculated through the BET method. The pore size distribution was calculated through the Nguyen-Do approach modified by Gun’ko (MND) [52–55]. The pH values and the electrical conductivities of supernatant liquids were measured using a PHS-3E meter with a BioTrove lab glass membrane electrode (Hamilton, USA) and HI 8633 conductivity meter (HANNA instruments, UK), respectively. Fourier transform infrared spectroscopy (FT-IR) spectra, recorded within the 4000–400 cm⁻¹ range, were collected on a FT-LA-2000 spectrophotometer (Thermo Scientific Nicolet). Electronic (UV–vis) absorption spectra (in 200–450 nm range) were measured on a Cary 100 UV–vis spectrophotometer (Agilent, USA). X-ray photoelectron spectroscopy (XPS) was used to analyze the surface composition with the help of a Kα, X-ray photoelectron spectrometer (Thermo Fisher Scientific, UK) equipped with a high-performance hemispherical electron analyzer with a 128-channel detector and an aluminum anode. X-ray source (Kα = 1486.6 eV), providing an energy resolution of about 1 eV. Photoluminescence measurements were realized using LS 55 luminescence spectrometer (Perkin-Elmer, UK) with 1 cm optical path length quartz cuvettes and with a solid substrate measurement accessory.

The 3D photoluminescence emission spectra were recorded at room temperature and in ultra-high vacuum (10⁻⁷ mTorr) conditions at the Toroidal Grating Monochromator (TGM) beamline of the Brazilian Synchrotron Light Laboratory (LNLS). Photons within the energy range of 4.5–8 eV (276–155 nm) were used as a source of exciting light after filtering on a quartz window. Light emission was transferred by an optical fiber line (aperture: 600 μm) and measured on an R928 Hamamatsu photomultiplier (PMT). The spectra were corrected for the variation in the incident flux of the excitation beam using the excitation and emission spectra of sodium salicylate as standard.

The morphology of the samples was studied by means of a low-vacuum JSR-6490LV (JEOL, Japan) scanning electron microscope (SEM). Atomic force microscopy (AFM) images were obtained using a Bruker MultiMode 8 microscope. A Si tip with a force constant of 0.4 N m⁻¹ and a resonance frequency of 70 kHz were used in tapping the peak force method. The samples were diluted in deionized water, ultrasonicated and a single drop was dried on a clean mica surface in a nitrogen flux for 2 h. Statistical analysis of the thickness distribution was performed using Gwyddion 2.53 software.

The powder X-ray diffraction (XRD) pattern of the CDs product was collected at room temperature using a X’Pert PRO (Panalytical, UK) diffractometer equipped with a PIXcel one-dimensional hybrid pixel technology position-sensitive device detector and operated with Ni-filtered CuKα radiation (λ = 1.54178 Å).

Quantum Yield (QY) of CDs was determined from single-point methods [56]. Quinine sulfate in 0.1 M H₂SO₄ has been used as a standard. Before the measurements, CDs suspensions and quinine sulfate were diluted to the absorption level below 0.1 at the excitation wavelength (344–360 nm) in order to minimize reabsorption effects. Both absorbance and photoluminescence emission spectra were measured for these samples. QY of CDs was measured for two excitation light, at 340 and 350 nm and calculated using equation (1).

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Q_y = \frac{I_S}{I_R} \cdot \frac{A_R}{A_S} \cdot \frac{\eta_S^2}{\eta_R^2},
\]

where \(Q_y\) = quantum yield of CDs; \(Q_R\) = quantum yield of reference; \(I_S\) = integrated fluorescence intensity of CDs; \(I_R\) = integrated fluorescence intensity of reference; \(A_S\) = absorbance of CDs at 350 nm (340 nm); \(A_R\) = absorbance of reference at 350 nm (340 nm); \(\eta_S\) = refractive index of the solvent of CDs; \(\eta_R\) = refractive index of the solvent of reference.

The integrated intensity of PL was determined using software SpectraGryph 1.2. The refractive index of water is 1.33.

### 2.3. Conventional bottom-up synthesis of CDs

Conventional synthesis of CDs was performed by the pyrolysis of bulk citric acid in the inert atmosphere [57]. Briefly, 10 g of CA was placed into 250 ml two-neck round-bottomed flask and heated to 170 °C under nitrogen atmosphere using graphite bath. The transparent liquid became orange after 30 min of heating, which implied the formation of CDs [57]. The resulted liquid was poured out into 130 ml of NaOH (10 mg mL⁻¹) solution under vigorous stirring. The obtained mixture was filtered through a 0.45 μm filter to remove large particles and stored for further analysis in the refrigerator (at 4 °C).
2.4. Preparation of SiO$_2$@CA composite

General scheme of SiO$_2$@CA preparation, thermal treatment, and CDs elution is presented in figure 1.

A set of silica-based composites having CA adsorbed was prepared from bulk silica SiO$_2$@CA. The set consists of four silica samples with different porosity and was prepared using a similar procedure by adding 1.0 ml of CA aqueous solution (1.5 g ml$^{-1}$) to 1.0 g of silica. The mixture was sonicated for 10 min and the excess of liquid was removed by blotting it with filter paper until dry. Then 2 mL of diethyl ether was added to silica composite and shaken for 20 min. Excess of ether was removed by decantation and the procedure was repeated twice. Finally, the samples were dried under vacuum (0.1 Torr) at 60$^\circ$C producing a loose powder.

An additional sample of SiO$_2$@CA was prepared as a reference (rSiO$_2$@CA) by following the experimental procedure, recommended in [41]. Briefly, 200 mg of silica gel SiO$_2$ (11) and 100 mg of CA were mixed and sonicated in 0.5 ml of water. The mixture was dried (without filtration and washing) in an oven at 60$^\circ$C, producing an agglutinated powder.

2.5. Thermal treatment of SiO$_2$@CA

All silica gels samples were heated at 170$^\circ$C and 200$^\circ$C under nitrogen atmosphere. Portions of the samples were collected at different treatment time ($\tau$), from 15 to 720 min, to obtain SiO$_2$@CDs-$\tau$.

2.6. Releasing CDs from SiO$_2$@CDs

The conditions of CDs releasing from SiO$_2$@CDs were studied in three consecutive steps: (1) the composites were suspended in 5 ml of water and shaken for 15 min. The solid phase was separated by filtration and the washing procedure was repeated till no fluorescence was observed for the filtrate. Alternatively, SiO$_2$@CDs were washed in Soxhlet apparatus with water. The supernatant was collected, filtrated through a 0.22 $\mu$m filter and stored at 0$^\circ$C. (2) The samples were washed with 0.1 mol l$^{-1}$ NaHCO$_3$ solution (portions of 5 ml) in the same manner as it is described for the first step. The supernatant was collected and stored equally. (3) Finally, the silica scaffold was dissolved in 3 ml of NaOH solution (3 mol l$^{-1}$) at room temperature.

3. Results and discussion

3.1. Morphological properties of host silicas

For proper preparation of CDs under the nanoreactor approach, it is critical to use the hosts with suitable pore size. It is generally accepted that CDs have a particle size of less than 10 nm [5, 7, 58]. Therefore, in contrast to earlier publications where microporous zeolites with small particle size have been used, silica gels with 4–11 nm nominal pore diameter and large particles (40–200 $\mu$m) is used in the current research, table 1. The latter shall
reduce CA adsorption on an external area of the particles and so prevent the formation of CDs outside of the pores.

Since porous characteristics of the host are essential for the nanoreactor approach, they were justified from nitrogen adsorption experiment. It was confirmed that the selected silica samples have the desirable pore sizes from 5.5 to 10.2 nm, with 0.7–1.25 cm³ g⁻¹ pore volume, table 2. Accordingly, the mesopores contribute more than 95% (commonly 99.7 ± 0.3) to the overall porosity of the silica gels, table 2. Selected samples of the host have a unimodal and narrow distribution of the pores (figure 2), which allows expecting the narrow distribution of hosted CDs particles.

### 3.2. Preparation of SiO₂@CA

A crucial aspect of the nanoreactor synthesis of CDs is verification that a major part of the precursor is localized in the host pores. To ensure this, the volume of CA solution used for the preparation of SiO₂@CA composites was limited by pore volumes of the silica gels. Also, high loading of hydrophilic silanol groups on the silica surface ensures good affinity of CA to the host. Taking into account the pore volume of silica gel samples and solubility of CA in water (1.5 g ml⁻¹) maximum loading of the precursor was estimated, table 2. For example, 1 g of silica SiO₂(11) can hold up to 1.9 g of CA inside of the pores. Nevertheless, after the treatment of silica gel even with a small volume of liquid, wet material is always obtained due adsorption of some part of the water solution on inter-particle space. In order to obtain SiO₂@CA having the precursor in the pores only, this interparticle liquid having dissolved compounds must be removed before the pyrolysis. To prove the importance of such pre-treatments, a sample labeled as rSiO₂(11)@CA was prepared according to the procedures recommended in [41, 42, 59]. By comparison of mass the silica sample before and after treatment with CA, it was found that loading of CA on rSiO₂(11)@CA constitute of 112% of maximum pore capacities for this material. Therefore, after drying rSiO₂(11)@CA is a compact glued agglomerate. After two consecutive rinsings of rSiO₂(11)@CA with ether, CA loading is reduced to 60% of maximum pore capacity. Such samples of SiO₂@CA present itself as a loose dry powder. The SEM images confirm the difference between rSiO₂@CA particles and SiO₂(11)@CA particles (figure 3), demonstrating a lot of CA microcrystals located on the external surface of rSiO₂@CA and absence of those on SiO₂(11)@CA.

### Table 2. Porous characteristics of silica gel hosts.

| Silica denoted | Maximum Loading of CA on SiO₂ (g g⁻¹) | Average pore size (nm) | Pore volume (cm³ g⁻¹) | S_{BET} (m² g⁻¹) | S_{meso} / S_{BET}, MND (%) |
|----------------|--------------------------------------|------------------------|-----------------------|------------------|--------------------------|
| SiO₂(4)        | 1.1                                  | 5.5                    | 0.72                  | 360.3            | 94.9                     |
| SiO₂(6)        | 1.2                                  | 6.0⁴                   | 0.80                  | —                | —                        |
| SiO₂(9)        | 1.5                                  | 6.9                    | 1.01                  | 387.4            | 99.8                     |
| SiO₂(11)       | 1.9                                  | 10.2                   | 1.25                  | 400.2            | 99.6                     |

* data from the manufacturer.

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![Figure 2.](image) The incremental pore size distribution by surface area of silica gels used for SiO₂@CDs preparation.

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**Figure 2.** The incremental pore size distribution by surface area of silica gels used for SiO₂@CDs preparation.
Thus, the importance of the procedure for removing CA excess from an outer surface of silica composite was considered. In order to do so, wet samples of as-prepared SiO$_2$@CA were blotted with filter paper until dry and then were washed out with two portions of diethyl ether. The ether is not miscible with water, therefore it was expected that ether will not penetrate the pores of wet SiO$_2$@CA filled by water and so will remove the excess of CA from the external surface of the particles only. It could get samples of SiO$_2$@CA with high loading of CA in the poses and clean outer surface as it is demonstrated in figure 3.

3.3. Preparation and characterization of SiO$_2$@CDs composites

3.3.1. Synthesis of SiO$_2$@CDs

Four samples of silica-based material were used as a host for CDs precursors. After impregnation with the precursor and pre-treatment, samples of SiO$_2$@CA were thermally treated in an inert atmosphere at 170 °C for 5–600 min and then subsequently washed with water, NaHCO$_3$, and NaOH to release CDs, table 3.

Earlier it was shown that appropriate temperature for conventional CDs synthesis from CA is 150 °C–200 °C [34, 60]. The temperature in 170 °C was chosen as the middle of the optimal interval and maintained constant in order to compare the results of pyrolysis for different samples. Conventional CDs were also obtained by pyrolysis of CA at 170 °C for 180 min. After the thermal treatment SiO$_2$@CDs had light brown, and conventional CDs black color, figures S1–S2 in the ESM. Under UV light, SiO$_2$@CDs demonstrated bright blue photoluminescence, figure 4. The reference sample rSiO$_2$@CDs has a brown color with randomly-distributed photoluminescence, figure S2 in the ESM.

3.3.2. FT-IR spectra

The FTIR spectrum of silica gel host exhibits several peaks related to silanol groups: at 3750 cm$^{-1}$ for isolated Si-OH; 3670–3220 cm$^{-1}$ for hydrogen-bonding Si-OH; at 1640 cm$^{-1}$ deformation vibration Si-OH. Also, FTIR spectra of silica host demonstrate two peaks at 1800–2000 cm$^{-1}$ that corresponds to overtones from Si–O–Si

Table 3. Overview of the host samples used for the preparation of CDs from citric acid precursor.

| Host   | Pore diameter, nm | Time of pyrolysis, min | Post-treatment          |
|--------|-------------------|------------------------|-------------------------|
| SiO$_2$ | 5.5, 6.0, 6.9, 10.2 | 5, 15, 30, 60, 120, 240, 360, 600 | H$_2$O, NaHCO$_3$, NaOH |
| —      | n.a.              | 180                    | H$_2$O, NaHCO$_3$       |

Thus, the importance of the procedure for removing CA excess from an outer surface of silica composite was considered. In order to do so, wet samples of as-prepared SiO$_2$@CA were blotted with filter paper until dry and then were washed out with two portions of diethyl ether. The ether is not miscible with water, therefore it was expected that ether will not penetrate the pores of wet SiO$_2$@CA filled by water and so will remove the excess of CA from the external surface of the particles only. It could get samples of SiO$_2$@CA with high loading of CA in the poses and clean outer surface as it is demonstrated in figure 3.

![Figure 3. SEM images of rSiO$_2$@CA (a), SiO$_2$(11)@CA (b), and pristine SiO$_2$(11) (c).](image-url)
stretching vibrations, figure 5. Spectrum of SiO$_2$(6)@CDs-180 reveal itself as a superposition of the host and the guest (CDs) and in addition to the bands of silica, SiO$_2$(6)@CDs-180 sample demonstrates well-defined peaks at 1775 cm$^{-1}$ and 1702 cm$^{-1}$ that can be attributed to stretching vibration of C=O fragments in –C(=O)(OR) and –COOH functional groups of silica-adsorbed CDs [51, 59].

3.3.3. XPS spectra
The XPS survey spectra for the SiO$_2$(6)@CDs-180 (figure 6(a)) indicate predominantly O1s, C1s, Si2s and Si2p peaks centered, respectively, at 532, 286, 155 and 103 eV.

The high-resolution C1s XPS spectra of samples revealed different types of carbon atoms in CDs. Curve-fitting analysis of high-resolution XPS of C1s reveals bands at 284.5 eV, 286.3, 287.5 and 289 eV that can be assigned to C–C (44%), C–OH (24%), carbonyl (26%) and carboxyl (6%) groups, correspondingly [24], figure 6(c). This kind of XPS is very typical for CDs and demonstrates the formation of partly decarboxylated CDs. A weak band at 551.5 eV attributed to carbonyl fragments in CDs can be seen in high-resolution O1s XPS spectrum of SiO$_2$(6)@CDs-180, figure 6(b). This kind of group is common for CDs obtained earlier [1].

3.3.4. Photoluminescence of solid composites SiO$_2$@CDs-τ.
The incipience of CDs has been monitored by measuring the photoluminescence from solid samples of SiO$_2$@CDs obtained for different time of thermal treatment, figure 7. Evidently, the CDs are formed in silica pores very quickly. At least, luminescence of SiO$_2$@CDs can already be detected after 5 min of SiO$_2$@CA treatment at 170 °C. However, the position of PL maximum (420 nm) for SiO$_2$@CDs obtained after such a short
Figure 6. Survey (a) and high resolution fitted XPS spectra (b, c) of SiO$_2$(6)@CDs-180 in O1s (b) and C1s (c) regions.

Figure 7. Normalized PL spectra of SiO$_2$(d)@CDs-τ.
time (5–60 min) does not match to PL of CDs obtained from CA by conventional methods (445 nm) [28]. Together with the peak at 420 nm, PL spectra of all SiO$_2$@CDs exhibit a peak at 450 nm, figure 7. Thus, PL spectra of SiO$_2$@CA commonly show a wide band, which consists of two peaks at 420 and 450 nm.

While the peak positions do not substantially depend on the time of SiO$_2$@CDs thermal treatment and the size of the host pores, the relative intensity of long-wave emission rises with time for all studied SiO$_2$@CDs that can manifest the development of CDs with enhanced decarboxylation degree.

The absolute intensity of SiO$_2$@CDs reaches its maximum for 15–30 min of SiO$_2$@CA thermal treatment and then sharply declines for all studied samples, figure 8(a). After 100 min of the treatment, no further depression of PL was observed, figure 8(b).

The photoluminescence spectra of SiO$_2$@CDs clearly exhibit the formation of CDs captured in silica pores. Apparently, those CDs also have different sizes and shapes since they are characterized by multiple maxima in PL spectra of SiO$_2$@CDs. The nature of the PL band at 420 nm calls for further investigations.

The SiO$_2$@CDs composites also demonstrate photoluminescence that occurs under excitation with high energy radiation (165–276 nm, 7.5–4.5 eV). For example, SiO$_2$(6)@CDs generates wide emission with a maximum at 525 nm, figure 9(b). From two-dimensional mapping, as a function of the excitation energy, it can be seen that the peak position of photoluminescence emission almost does not change in the function of excitation energy, figure 9(a). The most intense photoluminescence for SiO$_2$(6)@CDs is observed at 4.0–4.2 eV (310–295 nm). Presumably, SiO$_2$(6)@CDs can be useful for adsorption and transformation of short wave UV radiation.

### 3.4. Elution of CDs from the host

To elute the resulted CDs from the silica host three consecutive steps were applied. First, they were thoroughly washed with water until the conductivity of the washing solution dropped down essentially and absorption at 300 nm was about zero, figures 10(a), (b).
Then, 0.1 mol l\(^{-1}\) of NaHCO\(_3\) water solution was exploited for the same purposes. Finally, SiO\(_2\) scaffold was dissolved in NaOH. It has been found that water elutes strongly luminescent CDs from all samples of SiO\(_2@CDs\)-\(\tau\). Four washing cycles were enough to remove most of the trapped CDs, figure 10(a). Further washing of SiO\(_2@CDs\)-\(\tau\) with NaHCO\(_3\) and even solubilization of the host in NaOH do not reveal an essential quantity of the CDs, except for the samples treated for 600 min, figures 10(c), (d). The fact of a weak affinity of the CDs to the SiO\(_2\) host can be concluded from this experiment. It also can be assumed that silica gel is more appropriate host for confining of CDs particles then earlier used zeolites because it releases the CDs through treatment with water and does not require solubilization of the host in alkali solution.

During the thermal treatment of SiO\(_2@CA\), most of CDs are growing inside of the host pores without essential interaction with the surface of silica. Such a type of CDs particles can be eluted with water from the hosts. Immersing of SiO\(_2@CDs\) into NaHCO\(_3\) solution promotes ionization of silanol groups of silica surface and carboxylic fragments on CDs surface. Next, negatively charged silica surface stimulates elution of the negatively charged CDs.

3.5. Characterization of CDs
3.5.1. Microscopy
AFM technique was utilized to probe the sample topography and measure particle height. AFM image of CDs prepared from rSiO\(_2@CDs\) according to the procedure [41] shows the wide distribution of the particle’s height mainly from 5 to 8 nm, figure 11(a). The CDs obtained from SiO\(_2@CDs\)-180 have a smaller height (2–4 nm) and narrower distribution profile, figure 11(b).

These data support the results reflected on the SEM images of rSiO\(_2@CA\) particles (figure 3), suggesting the possible formation of CDs on the outer surface of the silica template. If so, the growth of such particles is not confined by the template, and CA pyrolysis can lead to formation CDs with size, larger than the size of silica pores. On the contrary, the experimental procedure proposed in current research demonstrates a narrow distribution of the CDs particle height. Thus, the importance of the pre-treatment of SiO\(_2@CA\) nanocomposites for removing CA excess that can be adsorbed on the outer surface of silica is feasible.

Figure 10. (a) Electroconductivity of supernatant solution obtained after immersing of SiO\(_2(4)@CDs\)-60 (0.5 g) to 10 ml of water with further filtration and cycling the procedure; (b)–(d) UV–vis spectra of the supernatant solutions, obtained by successive treatment of SiO\(_2(4)@CDs\)-60 with water (b), 0.1 mol l\(^{-1}\) NaHCO\(_3\) (c), 3 mol l\(^{-1}\) NaOH (d) after different time of the thermal treatment.
3.5.2. The x-ray diffraction of CDs.
XRD pattern of CDs washed out from SiO$_2$-NH$_2$@CDs-120 with water shows a broad peak centered at $2\theta = 23.2^\circ$ (0.34 nm), which is commonly attributed to the amorphous highly disordered carbon atoms in CDs [56], figure S3 in the ESM.

3.5.3. Photoluminescence of CDs obtained in nanoreactors
All CDs eluted from SiO$_2$ hosts exhibit emission band centered at 447 nm, figure 12. The band intensity essentially depends on the time of SiO$_2$@CA thermal treatment and reaches its maximum for CDs obtained from SiO$_2$@CDs-60 (figures 12(a)–(c)). The PL band symmetry of CDs deteriorates with increasing of the maternal host pore size, reviling short-wavelength shoulder, figure 12(d).

This observation is consistent with those obtained for SiO$_2$@CDs (figure 7) and can indicate the formation of less decarboxylated CDs for short treatment time (less than 60 min) in silica gel with larger pores.

Quantum yield was determined for CDs from SiO$_2$@CDs-r thermally treated for 60–600 min. The results presented in table 4 demonstrate that the CDs obtained in silica host with narrow pores have higher QY (up to 10.1%) than those obtained in larger porous (8.0%). It seems that prolonged time of the thermal treatment increases QY of CDs, at least for those obtained in silicas with narrower pores.
4. Conclusions

It was proven that rinsing of SiO$_2$@CA with ether allows manipulating with CA loading into the host pores. XPS spectra of silica-embedded CDs suggest the formation of partly decarboxylated carbon nanoparticles. In silica gel with larger pores, a short time (less than 100 min) of SiO$_2$@CA pyrolysis resulted in the formation of particles, which exhibit strong blue-shifted PL with a maximum at 420 nm. Increasing of pyrolysis time leads to the formation of luminescent solids with red-shifted (450 nm) PL. These particles eluted with water demonstrate PL at 447 nm. Time of SiO$_2$@CA thermal treatment has no visible effect on CDs PL, except those obtained for very short (less than 60 min) time of the pyrolysis.

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### Data availability

The raw data required to reproduce these findings are available to download from [http://doi.org/10.17632/9md6ykhnks.1](http://doi.org/10.17632/9md6ykhnks.1).

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