

RESEARCH PAPER

Purification and Fractionation of Carbon Dots using pH-controlled Cloud Point Extraction Technique

Asadollah Beiraghi* and Seyed Ali Najibi-Gehraz

Faculty of Chemistry, Kharazmi University, Mofatteh Ave., No.49, Tehran, Iran

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ABSTRACT

In the present work a simple, fast, and green procedure is described for the purification and fractionation of carbon dots (CDs) coated by oxygen-containing groups. The CDs were synthesized by thermal pyrolysis of citric acid. The synthesis product was purified by separating them from the synthesis precursors. They also could be fractionated into two distinct kinds of CDs (f4 and f1) using pH-controlled cloud-point extraction (CPE) technique. The fractions f4 and f1 were characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), UV-Vis absorption, and FT-IR spectroscopy techniques. The results obtained were also used for studying and explaining the mechanism of the extraction procedure. It was revealed that the fractionation relies on the different surface chemistry of the CDs (i.e. the number or surface-density of oxygen-containing functional groups) which plays the main role in their different behavior at different pH values. Comparing fluorescence spectra of the separated fractions indicated that the surface-chemistry had also a marked effect on photoluminescence behavior of the CDs. The developed procedure can be used for the preparation of pure CDs or particular pure fractions of them for research laboratory purposes, or potentially for their industrial production, as well.

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INTRODUCTION

Owing to their immense promising prospects, carbon nanomaterials such as carbon nanotubes, graphene, nanodiamonds, fullerene, and CDs have intrigued many scientists. They have occupied a noticeable position in laboratory and industrial research with the aim of overcoming more and more problems by extending their applications. CDs are a new generation of carbon nanomaterials which were accidentally discovered in 2004 during an attempt to electrophoretic purification of carbon nanotubes [1]. CDs are easy to synthesize and there are a variety of methods to synthesize them. Moreover, CDs have some noteworthy properties

such as being fluorescent, being cheap, possessing excellent chemical and optical stability, solubility in and compatibility with biological systems, and non-toxicity. CDs also possess various surface functional groups which makes them capable of undergoing surface modifications. Taking all these into account, CDs has continuously been the subject of research in various fields such as bio-imaging [2], bio-sensing [3], chemical sensing [4,5], light emitting diodes [6,7], photovoltaic applications [8], and photocatalysis [9].

Synthetic approaches towards CDs can be divided into two main categories: (i) top-down methods in which CDs are prepared by crumbling and cutting various carbonaceous materials such

* Corresponding Author Email: beiraghi@khu.ac.ir
beiraghi3061@yahoo.com

as graphite carbon fibers [10], carbon nanotubes [11], black carbon [12] and soot [13]; and (ii) bottom-up methods in which suitable organic molecules containing functional groups such as -NH_2 , -OH , -COOH , and -C=O are dehydrated and carbonized at high temperatures. It is performed by using techniques such as microwave pyrolysis [14], combustion [15], thermal pyrolysis [16], and hydrothermal method [17] which ultimately result in the formation of CDs. The prepared CDs comprise a core carbon structure (with sp^2/sp^3 bonding) and a surface structure, rich in polar functional groups such as -C=O , -COOH , -OH , and epoxy group. Their optical properties depend on the size of the carbon core and surface density of the polar functional groups [18]. Thus separating and sorting CDs according to their size or surface-density of polar functional groups is of great importance with regard to both their application and understanding mechanism of their fluorescence.

Generally speaking, separation of nanoparticles is an essential preliminary step for their successful application. Various methods have been used for their separation, namely filtration, centrifugation, magnetic separation, precipitation, solvent extraction, and dialysis. As it comes to separation and purification of carbon dots (CDs), common separation methods of colloidal nanoparticles do not work satisfactorily. This can be ascribed to their minuscule particle size (< 10 nm) and also to the presence of plenty of polar functional groups on their surface. Due to the polar surface groups, CDs exhibit high colloidal stability in aqueous media which is their usual medium of synthesis. Thus far, dialysis is the predominant method used for purification of CDs. However this method is very time-consuming and somewhat expensive. Moreover, it is not suitable for large-scale preparation of pure CDs. Column chromatography [19] is another method capable of separating CDs which is also time-consuming and needs sophisticated and expensive equipment so that it is rarely used. Wang et al [20] used hydrophilicity gradient ultracentrifugation for size sorting of CDs and studying mechanism of their luminescence. Considering these all, proposing a simple, rapid, inexpensive, and, last but not least, green method for separating and sorting CDs can be of great importance.

Cloud point extraction is one of the methods widely used for the extraction of ionic [21]

molecular [22,23] and neutral ion pair [24]"ISBN" : "0003-2670", "ISSN" : "00032670", "PMID" : "18190807", "abstract" : "In the present study a cloud point extraction process using mixed micelle of the cationic surfactant cetyl-pyridinium chloride (CPC species because of low cost and lack of need for toxic solvents. During recent years CPE has been used for preconcentration and purification of some kinds of nanoparticles in various samples. Jiang et al [25] reported that the CPE by Triton X-114 can be used for separating and concentrating semiconductor quantum dots, C_{60} , carbon nanotubes, and Fe_3O_4 , Ag, Au, and TiO_2 nanoparticles. The separated particles can be re-dispersed in the solvent by re-adjusting the temperature at suitable level. Hartman et al [26] extracted and measured Au nanoparticles in a species-selective manner by using CPE. Hind et al [27] reported a method using CPE for extraction and analysis of metallic nanoparticles from soil.

In the present work, we reported a simple and effective procedure for the separation and fractionation of carboxylic CDs by pH-controlled CPE technique, based on different polarities of CDs at different pH values. The CPE was performed using the nonionic surfactant, Triton X 114 (TX-114). To the best of the authors' knowledge, this is the first report on using CPE for separating CDs. Furthermore we assume this is the first report on fractionating the synthesized CDs into two different fractions using the CPE technique. The method has very low cost and provides the separated CDs in very short time, as compared to the time-consuming purification with dialysis membranes or the high-cost HPLC technique. A series of comparative studies were made on the separated fractions to clarify the extraction mechanism and the differences in their characteristics, especially in terms of their optical properties.

MATERIALS AND METHODS

Materials and instrumentation

All the chemicals and reagents were of the highest purity available and obtained from Merck (Darmstadt, Germany) or Sigma-Aldrich. The solutions were prepared with triply distilled water. The nonionic surfactant Triton X-114 was from Sigma-Aldrich (St. Louis, MO, USA). UV-Vis spectra were recorded by a double-beam in-time spectrophotometer (Perkin-Elmer, model Lambda 25, U.S.A.) with 1 cm quartz cell. Fluorescence spectra were obtained by a JASCO fluorescence

spectrophotometer (FP8500). FT-IR spectra were recorded by a Perkin-Elmer RXI spectrometer using KBr disks. Zeta potential of the prepared CDs was measured by Nanobrook Zetaplus zeta potential analyzer and an AXIS Ultra DLD spectrometer was used for recording XPS spectra. TEM measurement was made using a Philips CM120 transmission electron microscope. All pH measurements were performed using a Metrohm 827 pH meter.

Preparation of CDs

CDs were prepared according to the literature [28]. In brief; 4 g citric acid was dissolved in 5 mL distilled water within a beaker with the aid of heating until a clear solution was obtained. The solution was heated at 200 °C until a juicy solution was formed. The synthesized CDs were dissolved in 200 mL distilled water and subjected to CPE procedure.

Purification of CDs using cloud point extraction procedure

Purification of CDs by using CPE technique included two steps. In the first step 8 mL of the CDs dispersion was transferred into each of 12 centrifuge tubes (15 mL). The pH of each tube content was adjusted at the desired level (in the range of 1-12) using HCl (1 mol L⁻¹) or NaOH (1 mol L⁻¹) solutions. After adding 2 mL of 4% (w/v) solution of Triton X-114 to each of the tubes, they all were placed in a thermostatted water bath for 10 min at 40 °C. Separation of the aqueous and surfactant-rich phase was accelerated by centrifugation for 10 min at 3000 rpm in each case. After cooling the contents of each of the tubes in an ice bath, the surfactant-rich phase was separated by decantation. In the second step a certain amount of water was added to each of the surfactant-rich phases and their pH were then set at 7. CPE procedure was performed in each case once again and the supernatants obtained from this stage were submitted to the subsequent experimental analysis.

Fractionation of CDs

In order to fractionate the prepared CDs, 8 mL of the synthesized CDs dispersion was transferred into a beaker (20 mL) and its pH was adjusted at 4 using NaOH solution (1 mol L⁻¹). The content of the beaker was transferred into a centrifuge tube and then 2 mL 4% (w/v) Triton X-114 solution was added. CPE was performed as before and the

supernatant was separated from the surfactant-rich phase and was named supernatant 1. CDs extracted into the surfactant-rich phase were extracted back into distilled water in the same way as described beforehand. The obtained aqueous solution was named as the fraction f_4 (the 4 subscript referring to the pH 4). The pH of supernatant 1, obtained from the first step of the CPE, was adjusted at pH 1 and the CDs within it were extracted into micellar phase by applying the CPE procedure for the second. Again, the extracted CDs were back-extracted into an aqueous medium and the obtained aqueous dispersion was called fraction f_1 . Both f_1 and f_4 fractions were subjected to the TEM, XPS, UV-Vis absorption, FT-IR spectroscopy, and fluorescence spectroscopy.

RESULTS AND DISCUSSION

Extraction and purification of CDs

In the present work, carbon quantum dots with oxygen-containing functional groups were synthesized by thermal pyrolysis of citric acid. The obtained carboxylic CDs were used as an illustrative type for studying applicability of CPE technique for extraction and purification of CDs. CPE was performed using Triton X-114 surfactant, and relied on the fact that upon elevation of the temperature of an aqueous solution of the surfactant to higher than its critical temperature, surfactant molecules form globular micelles. This was followed by a phase separation between the micellar and aqueous phase. The internal environment of the formed micelles was nonpolar and showed higher affinity to species which were less soluble in water, therefore such species tended to migrate into their internal space [29]. On the other hand, the solubility and dispersivity of CDs depended on the dissociation degree of the hydroxyl and carboxyl groups which, in turn, depended on the pH of the environment. Considering all these, it was deduced that different kinds of CDs can be extracted and purified using CPE upon adjusting pH of the dispersion. With the aim of doing this, in the first step, 8 mL of the CDs dispersion was transferred into each of 12 centrifuge tubes and their pH was adjusted at various levels (1-12) according to the Experimental section and the first CPE was performed on the tubes' content. The results can be seen in Fig. 1a. Note that one can use color intensity of the sedimented phase as a qualitative indicator of the efficiency of extraction. Fig. 1a shows that at pH values above 6, no significant

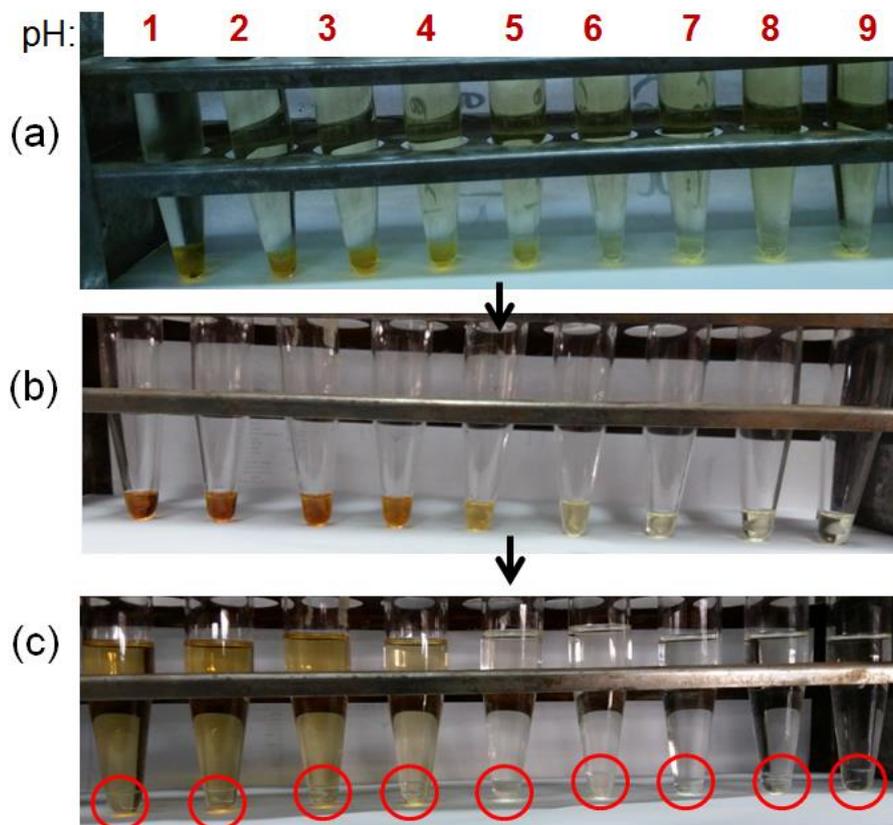


Fig. 1. Steps of CPE of CDs: (a) The two phases separated during the first step of extraction; (b) The separated micellar phase containing CDs; (c) The second step of purification which returns CDs to the aqueous phase.

amount of extraction was achieved; whereas at pH values lower than 6, the extraction efficiency of the CDs was increased, and maximized at pH range of 1-2. Then the separated aqueous phase was decanted

(Fig. 1b), and the obtained surfactant-rich phases was dissolved in distilled water and subjected to the CPE procedure again, but this time at pH 7. This resulted in the back-extraction of the CDs into aqueous phase (Fig. 1c). Thus, the first step led to the separation of CDs from polar impurities such as unreacted citric acid molecules or short-chain polymeric species formed during the CDs synthesis, because they were all expelled by the micelles and remained in the aqueous phase. In the second step (back-extraction), upon changing pH, CDs were released from micellar phase into the aqueous phase, whereas all nonpolar impurities were entrapped within the micellar phase. The net result of the consecutive CPEs was separation of the synthesized CDs from the synthesis precursors. For quantitative

assessment of the extraction efficiency at various pH values UV-Vis absorption intensities of diluted solutions of the extracted CDs were also measured. As it can be seen in Fig. 2, by decreasing pH values the extraction recoveries were increased, whereas using neutral or higher pH levels lead to a decrease in extraction efficiencies. The proposed separation method enjoys the fact that the surfactant molecules, upon formation and dissociation of micelles, act as CD-conveyors which are "filled" with and "emptied" out of CDs, so that they can be used for repeated extraction procedures; in other words, the only substance consumed during the extraction is water and that is why the proposed method can be considered as a green method of separation. Moreover it is not only possible to use the method for research laboratory preparation purposes, but it can be potentially used for large-scale preparation of pure CDs.

Thin layer chromatography (TLC), as an efficient technique for the detection of organics was applied to the as-prepared and purified CDs.

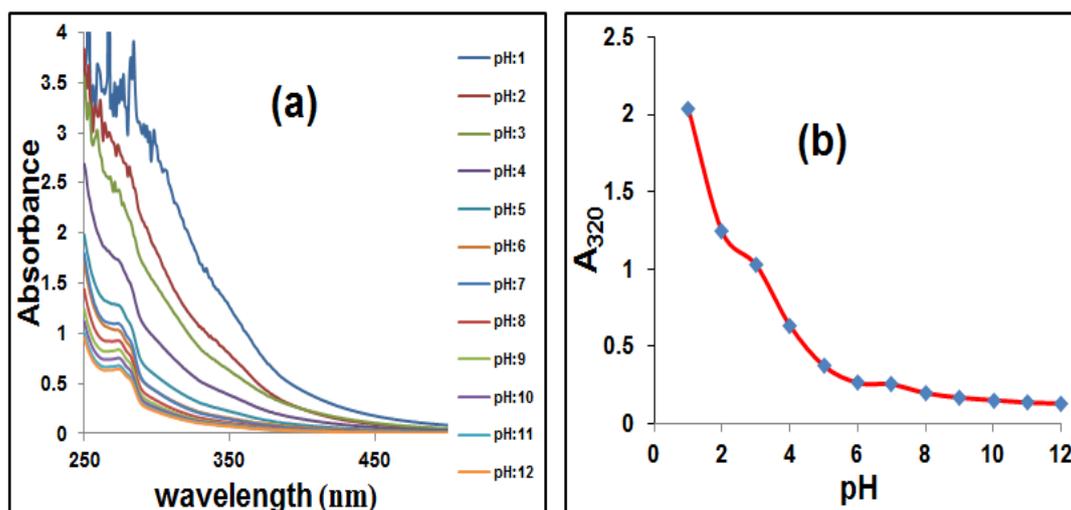


Fig. 2. UV-Vis absorption spectra of the CDs extracted by CPE at different pHs (a) and their corresponding absorbance values at 320 nm (b).

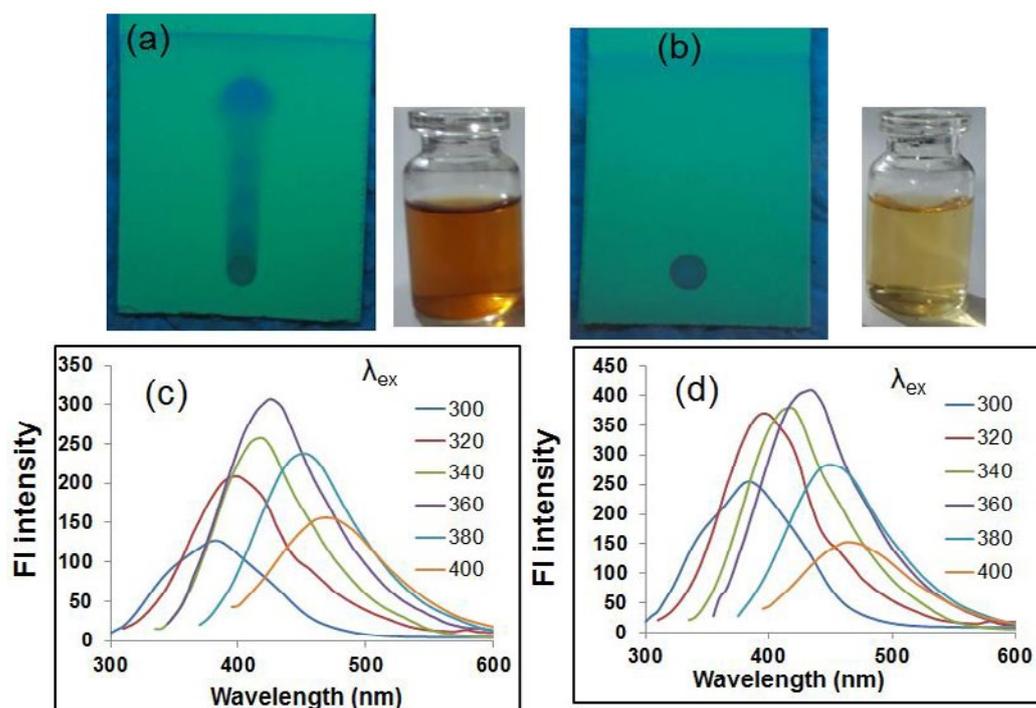


Fig. 3. (a) TLC layer and solution of as-prepared CDs; (b) TLC layer and solution of purified CDs; fluorescence spectra of the as-prepared CDs (c) and purified CDs (d) after excitation at different wavelength.

The TLC results using organic solvents as eluent (n-hexane/ethyl acetate: 2/1), before purifying indicated the existence of some spots on the top of layer related to organic compounds (by-products or unreacted starting materials), in the

as-prepared CDs (Fig. 3a), while, as can be seen in Fig. 3b, TLC result of purified CDs clearly showed a single spot at the bottom of layer related to the CDs and removal of organic impurities. These results indicated that all organic impurities were

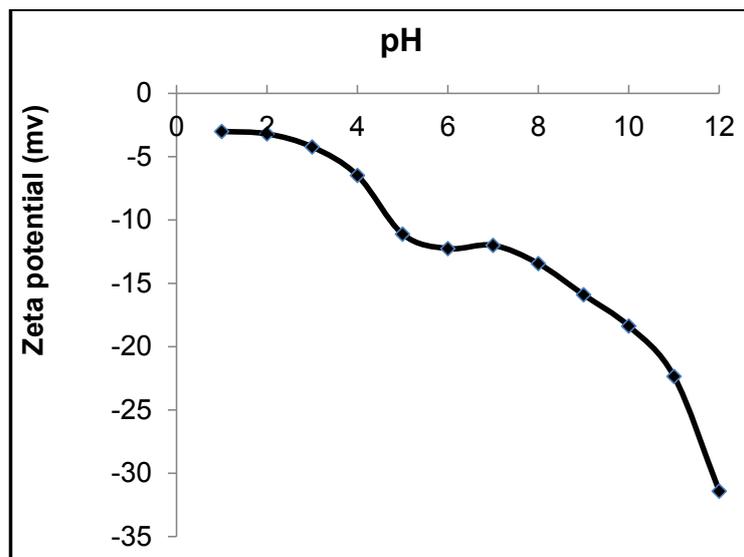


Fig. 4. Zeta potential analysis of dispersion of CDs at various pH values.

well removed during the purification of CDs by proposed CPE method. In order to investigate the effect of purification on the fluorescence properties of CDs, the fluorescence spectra of the as-prepared and the separated CDs were recorded under different excitation wavelengths (Fig. 3c and 3d). Both the as-prepared and purified CDs showed similar excitation wavelength-dependent fluorescence emissions. The photoluminescence quantum yields (PLQYs) of purified and unpurified CDs at 360 nm were calculated to be about 10.5% and 8.2%, respectively. All these results displayed the efficiency of the described method for purification of the synthesized CDs and enhancement of their PLQY using.

Optimization of CPE process

In order to evaluate and optimize the parameters affecting the extraction, a series of as-prepared CDs samples were extracted under different conditions according to the one-at-a-time approach. The results of the experiments showed that extraction efficiency reached its maximum value at 45 °C (Fig. S1a) and extraction equilibrium was reached in 20 min (Fig. S1b). Extraction of CDs at optimum temperature and time with various concentration of Tx-114 displayed that the maximum extraction achieved with 0.4 % (w/v) of surfactant (Fig. S1c). Further experiments showed that salinity of the solution did not significantly influence the extraction efficiency of CDs (Fig. S1d).

Mechanism of extraction

In order to study and explain the mechanism of the above-mentioned behavior, the surface charge of CDs was determined by zeta potential measurements. As it can be seen in Fig. 4, the magnitude of the zeta potential was directly proportional to the pH of the solution and increased by rise in the pH. At pH < 5 the zeta potential has lesser negative magnitude which is due to protonation of the surface carboxylic groups at the acidic medium. Upon increasing pH to > 5 the zeta potential exhibited greater negative values because of the ionization of the carboxylic groups to form more surface carboxylate anions. At pH values > 9 the zeta potential indicated even more negative values which could be attributed to the dissociation of the surface –OH groups to –O⁻ due to the harsher basic conditions. Taking all these results into account it was concluded that the determining factor in extraction of the prepared CDs by CPE technique was their surface chemistry and the oxygen-containing functional groups on their surface, such as –COOH and –OH. At acidic pH these groups are protonated and the CDs tend to reside in the micellar phase, whereas at neutral or basic pH they transform to their negative form so that the CDs show further affinity towards the polar aqueous phase.

Fractionation of CDs

Two main factors determine the optical

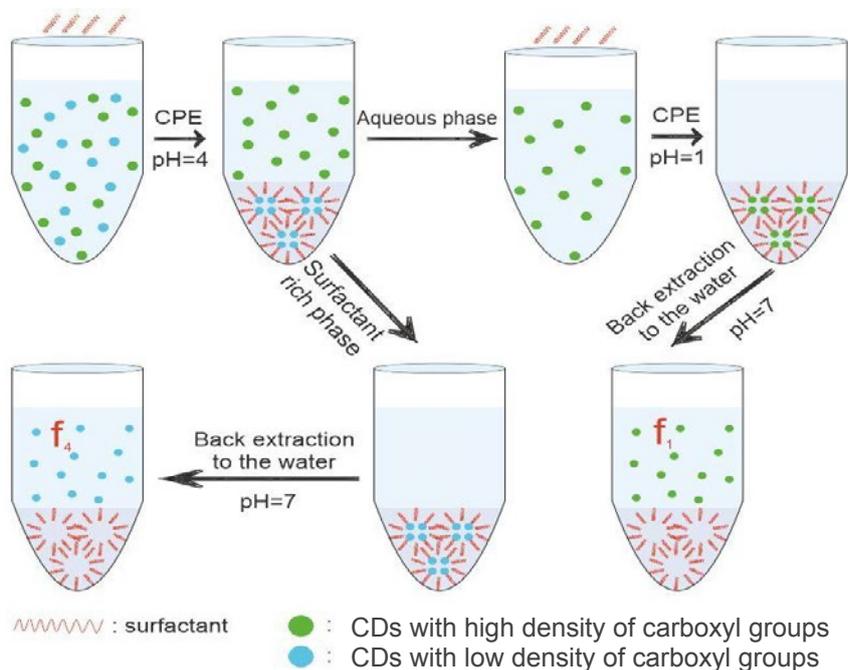


Fig. 5. Schematic illustration of the f_4 and f_1 fractionations of CDs via the CPE processes.

properties of CDs. The first factor is their particle size which is also referred to as the quantum confinement effect [18]. CDs of different sizes show different absorption and luminescence behaviors so that the larger the particle size, the longer their fluorescence emission wavelength. The second factor is called surface state related emissive trap. Surface state is based on the functional groups attached to the surface of CDs which interact with the π bonding system of the carbon core of CDs and affects their UV-Vis absorption and fluorescence properties. The larger the surface density of polar functional groups on CDs, the greater the number of surface defects, which consequently results in red shift in the emission spectrum [18].

In order to further examine the factors affecting extraction of CDs with the proposed method, the synthesized CDs were fractionated into two distinct fractions (f_4 and f_1) as described in the experimental section and illustrated in Fig. 5. The fractions were studied by using TEM, FT-IR, UV-Vis spectroscopy, XPS and fluorescence spectroscopy.

It should be noted that dispersity of colloidal nanoparticles in aqueous media depends on their particle size and on the nature of their surface functional groups. With the same surface functional groups, the smaller particles have more

stability and more dispersivity than the larger particles. So it might be reasonable to assume that the particle size may affect the result of the proposed CPE procedure. In order to assess this idea, the TEM image of the fractions f_4 and f_1 were taken (Fig.s 6a and 6b). As it can be seen in Fig. 5, CD particles in both of the fractions are spherical with similar size distribution of average diameter ca. 5 nm. Therefore it was concluded that particle size of the CDs does not play determinative role in extraction and fractionation of them by the proposed CPE method.

The FT-IR spectra of the fractions f_4 and f_1 shown in Fig. 7a demonstrate that they have similar surface functional groups. The broad peak at 3406 cm^{-1} is due to stretching vibrations of $-\text{OH}$ group and the small peak observed at 2926 cm^{-1} can be attributed to the stretching vibrations of the $-\text{C-H}$ bonds [29]. The stretching vibrations of the $-\text{COOH}$ groups are emerged as a sharp band at 1743 cm^{-1} while the peak observed at 1568 cm^{-1} is related to the stretching vibrations of $\text{C}=\text{C}$ bonds [30]. The peak of stretching vibrations of $-\text{C-O-C}$ can be seen at 1097 cm^{-1} and that of asymmetric stretching vibrations of $-\text{COO}^-$ can be seen at 1394 cm^{-1} [31]. These spectra prove that the prepared CDs have a sp^2 carbon body with $\text{C}=\text{C}$ bonding and

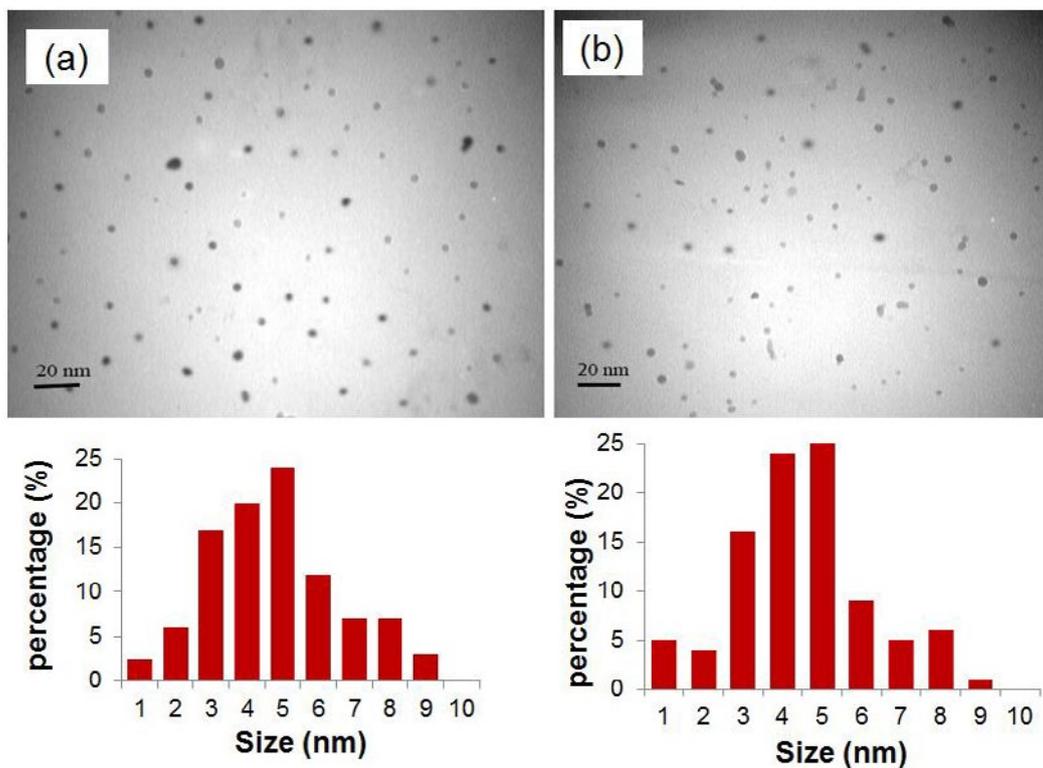


Fig. 6. TEM image of fractionated CDs with the size distribution diagram of each fraction: f_4 (a) and f_1 (b).

there are oxygen-containing functional groups such as $-\text{COOH}$, $\text{C}=\text{O}$, $-\text{OH}$, and epoxy on their surface. A comparison made between FT-IR spectrum of f_4 and f_1 reveals that the peaks relating to $-\text{COOH}$ and $-\text{OH}$ groups are stronger in the spectrum of f_1 than that of f_4 and this indicates higher surface density of these functional groups in fraction f_1 as compared to f_4 . So, it can be deduced that the CDs present in f_4 have less $-\text{COOH}$ groups so that upon a decrease in pH, their dispersivity decreases more effectively than f_1 in a way that they are extracted into the micellar phase at $\text{pH} = 4$. That is why at the same conditions the CDs present in f_1 retain their dispersivity in aqueous phase and do not get extracted into the micelles. Upon further decreasing the pH from 4 to 1, the f_1 carboxylate groups undergo further protonation and f_1 CDs lose much of their dispersivity and are extracted into the micelles as well as f_4 CDs. Thus oxygen-containing functional groups play a profound role in the extraction and fractionation of CDs by the proposed method.

UV-Vis absorption spectra of the f_4 and f_1 fractions were also recorded (Fig. 7b). The

absorption spectra of both of the fractions show a peak at about 280 nm, which corresponds to $\pi \rightarrow \pi^*$ electronic transitions of $\text{C}=\text{C}$ bonds of carbon structure of the CDs [32], and another peak at about 320 nm, which can be attributed to the $n \rightarrow \pi^*$ electronic transitions of polar oxygen-containing functional groups, i.e. $-\text{OH}$, $-\text{COOH}$, and $-\text{C}=\text{O}$. A comparison of the absorption spectra shows that the $n \rightarrow \pi^*$ transition peak at f_1 is stronger than f_4 which is an indication of the fact that there are more polar functional groups on the surface of f_1 than f_4 CDs. Thus the absorption spectra confirm the results deduced from the FT-IR spectra which in turn also proves that oxygen-containing functional groups have an important role in the CPE of the CDs.

Raman spectroscopy is a useful technique to provide information on structural properties of CDs. Raman spectra of the CDs generally consist of two prominent bands namely G-band (G for graphitic) and D-band (D for defect) that are attributed to the presence of sp^2 and sp^3 carbons, respectively. Fig. 7c shows the Raman spectra of the f_1 and f_4 fractions obtained from

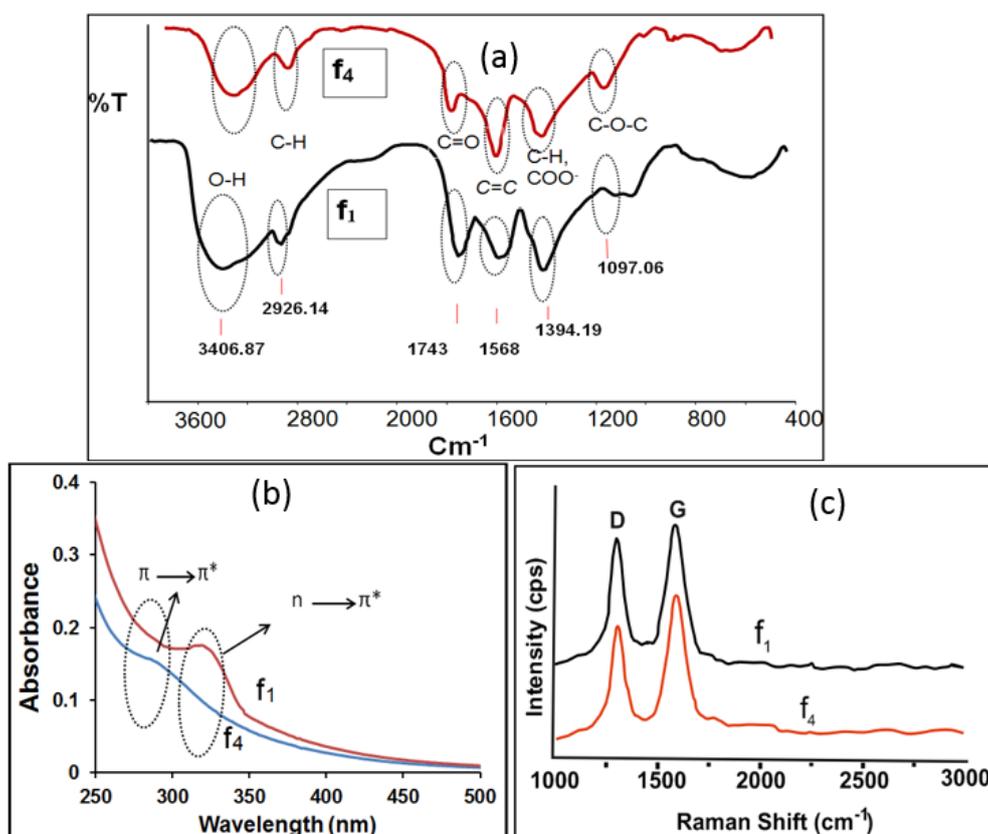


Fig. 7. (a) FT-IR spectra of the two CDs fractions, f_4 and f_1 . (b) UV-Vis absorption spectra of the two CDs fractions, f_4 and f_1 . (c) Raman spectra of the f_1 and f_4 .

the synthesized CDs. As can be seen, both f_1 and f_4 displayed characteristic D (1365 cm^{-1}) and G bands (1586 cm^{-1}) related to the sp^3 and sp^2 carbon atoms. The ratio of the intensities of D band to G band (I_D/I_G) are 1.08 for f_1 and 0.92 for f_4 , indicating the amorphous structure of CDs in both fractions. The larger I_D/I_G of f_1 revealed that it contains more sp^3 carbons than f_4 that is related to the presence of more $-\text{COOH}$, $\text{C}=\text{O}$ and $-\text{OH}$ functional groups in the structure of f_1 CDs as compared to f_4 fraction.

XPS analysis of the CDs can provide us with information about the identity and abundance of the surface functional groups of the particles. The comparison of the survey spectrum of the two fractions (Fig. 8a and 8c) demonstrates that the surface oxygen abundance of the f_1 fraction is larger than that of f_4 which is reflected in the smaller carbon-to-oxygen ratio of f_1 (1.14) as compared to f_4 (1.41). Fig. 8b and 8d show the C 1s high resolution XPS spectra of f_1 and f_4 fractions. As can be seen, f_1 CDs produce C=C, C-C, C-O, C=O and O-C=O peaks of intensities 26.13, 18.87,

16.42, 15.60 and 22.98, respectively, while f_4 CDs yield 32.71, 26.44, 13.12, 11.85 and 15.88 comparatively. It can be concluded that in spite of similarity of the surface functional groups of f_4 and f_1 , f_1 contain more carboxylic moieties than f_4 while f_4 have more hydrophobic regions as compared to f_1 fraction. These results show the influence of surface groups on extractability of CDs. So this difference can make it practical to extract and fractionate CDs by a combination of CPE and pH adjustment.

With regard to the very small particle size and very large surface area of CDs, their fluorescence is affected by their size [33] and their surface states (i.e. the functional groups present at their surface) [34,35]. TEM analysis of f_4 and f_1 proved that they are not very different in terms of particle size and their XPS analysis indicated that surface density of $-\text{OH}$ and $-\text{COOH}$ functional groups of f_4 and f_1 were different. The fluorescence spectra of the fractions f_4 and f_1 with different excitation wavelengths (λ_{ex}) were recorded in order to compare their

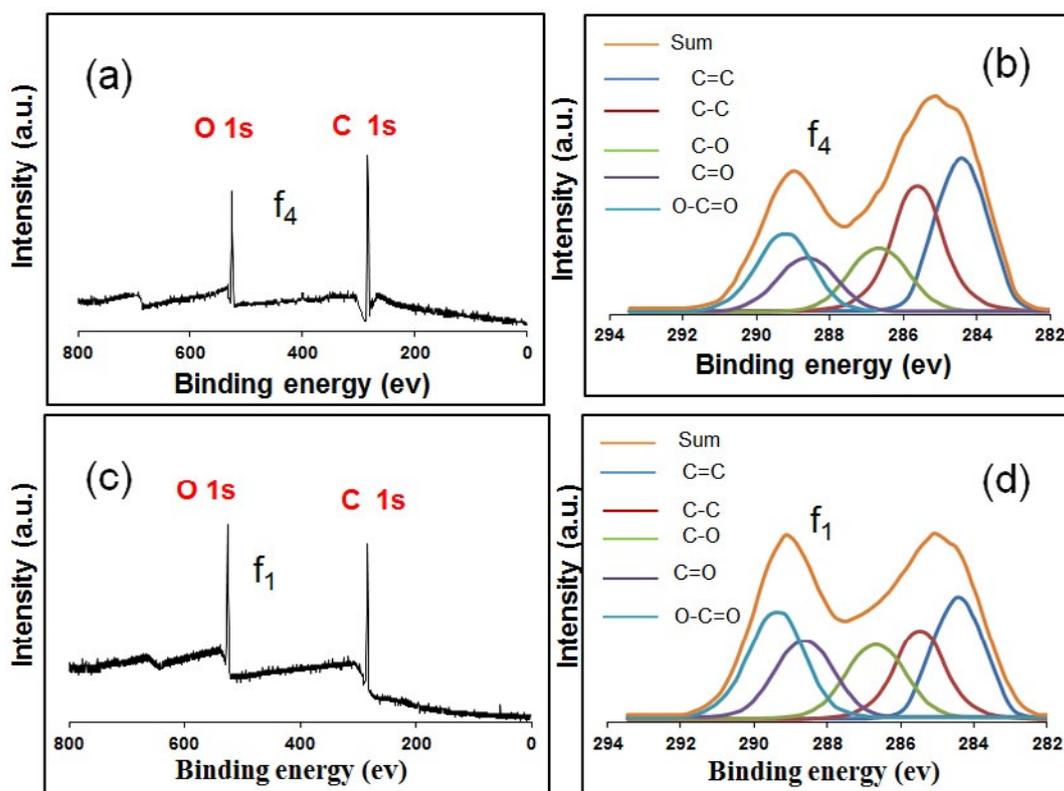


Fig. 8. XPS survey spectrum of f_4 (a) and f_1 (c). High-resolution XPS C 1s spectra of f_4 (b) and f_1 (d).

fluorescence properties and to examine the effect of surface states on their fluorescence. Both of the fractions had fluorescence emissions dependent on the λ_{ex} in a way that the maximum emission wavelength and the fluorescence intensity were both dependent on the λ_{ex} . Upon changing λ_{ex} towards longer wavelengths, a parallel red shift was observed in the fluorescence spectra of both of the fractions which can be attributed to the variety of emissive moieties on the surface of the CDs so that each λ_{ex} excites only parts of the particle surface compatible with that particular wavelength [36]. Therefore a comparison of fluorescence spectra of f_4 and f_1 can reveal the difference between the fractions in terms of abundance and distribution of the existing emissive functional groups. As to the CDs belonging to f_4 the optimal emission wavelength was 410 nm (Fig. 9a) while that of f_1 showed a 25 nm red shift and was observed at 435 nm (Fig. 9b). This red shift confirms that the more the number of oxygen-containing surface functional groups, the more the number of surface states, so that fluorescence emission of CDs is dominated by the

surface states with concomitant red shift in their fluorescence. The fluorescence examinations also lead to the conclusion that the oxygen-containing hydrophilic functional groups on the surface of CDs are a deciding factor in their extraction by CPE technique and this can be used as a basis for their fractionation.

CONCLUSION

A green, low-cost and highly effective procedure for purification and fractionation of synthesized CDs into two different fractions f_4 (at pH = 4) and f_1 (at pH = 1) was developed. The method was based on the different surface chemical properties of CDs combined with the CPE technique performed under appropriately controlled pH. The proposed technique offers many advantages, namely it is simple, inexpensive, fast, and capable of readily being used in large industrial scales. The method also excludes any toxic solvents or reagents. Taking advantage of the method, the CDs can not only be separated, but also fractionated into fractions of quite uniform optical behavior. Studies of the two

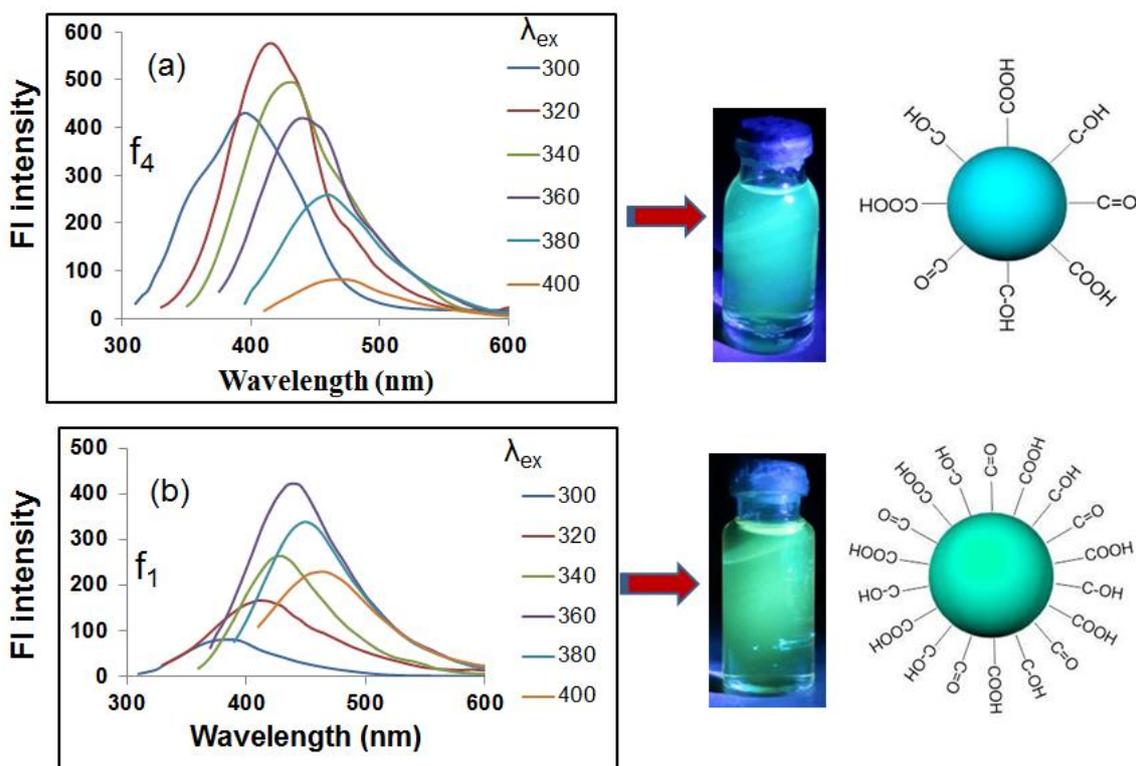


Fig. 9. Fluorescence spectra of CDs at various excitation wavelengths: (A) f_4 ; (B) f_1 . The photos placed at right hand of the graphs show the f_1 and f_4 CDs solutions under irradiation of 360 nm UV light.

fractions with TEM, FT-IR spectroscopy, UV-Vis absorption spectroscopy, and XPS proved that the prepared CDs were purified and assorted in terms of the abundance of hydrophilic functional groups on their surface and their particle size does not play a determining role. Meanwhile, the optical study of two extracted fractions of f_1 and f_4 proved that they have different fluorescence behavior. To the best of the authors' knowledge, this is the first report on a CPE technique used for both purifying synthesized CDs and fractionating them regarding their surface aspects.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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