Preparation of functionalized water-soluble photoluminescent carbon quantum dots from petroleum coke

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ARTICLE INFO

Article history:
Received 9 May 2014
Accepted 11 July 2014
Available online 18 July 2014

ABSTRACT

Here we report a new strategy for preparation of water-soluble photoluminescent carbon quantum dots (CQDs) from petroleum coke. Petroleum coke was oxidized first in mixed concentrated H₂SO₄ and HNO₃, and then functionalized by hydrothermal ammonia treatment. The as-made CQDs and nitrogen-doped CQDs (N-CQDs) were characterized by UV–Vis absorption spectroscope, fluorescence spectroscope, transmission electron microscope, atomic force microscope, Raman spectrometer, X-ray powder diffractometer, X-ray photoelectron spectroscope and Fourier transform infrared spectrometer. The results show that the quantum yield of CQDs increases greatly from 8.7 to 15.8%, and the fluorescent lifetime increases from 3.86 to 6.11 ns after the hydrothermal treatment in ammonia. Moreover, the fluorescent color of N-CQDs can be tuned through the amount of doped nitrogen. Both CQDs and N-CQDs are water-soluble, and have uniform particle distribution, strong luminescence, and highly fluorescent sensitivity to pH in a range of 2.0–12.0. The uniform size distribution and nitrogen-doping of N-CQDs help to lead to high yield of radiative recombination, resulting in improved fluorescence properties. This work offers a simple pathway to produce high quality and enhanced photoluminescent CQDs from petroleum coke.

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1. Introduction

Carbon-based quantum dots (CQDs) were discovered in 2004 while separating single walled carbon nanotubes by etching electrophoresis [1]. It has been found that CQDs with novel optical properties, outstanding biocompatibility and robust chemical inertness are of potential as probes for high-contrast bioimaging and biosensing applications, and CQDs with intense and tunable photoluminescence (PL) and high water solubility are of special importance in catalysis and energy-related fields. As such, it is necessary to develop novel processes to make high quality CQDs with tuned properties in high yield. Up to now, various carbon precursors including graphite [2–5], graphene oxides [6–10], fullerene [11], carbon fibres [12] and organic carbon sources [13–17], have been used to prepare CQDs. Most carbon precursors mentioned above are relatively expensive, which results in a high preparation cost of CQDs to some degree. Petroleum coke is a by-product
in oil refining process, has high content of carbon and low content of ash, and has been demonstrated to be good starting material for production of porous carbons [18]. Petroleum coke is rich in benzene rings or aromatic domains, which make it possible to prepare high quality CQDs.

In terms of synthesis of CQDs, some methods including the chemical oxidation of candle soot [19], the thermal cracking of organic compounds [20], the microwave-assisted hydrothermal synthesis [21], the rapid plasma pyrolysis of egg [22], the alkali-assisted electrolysis of graphite [23] have been reported. Of these methods, the chemical oxidation is effective, convenient, and easy to scale-up [24,25], nevertheless, it is non-selective in terms of cutting the aromatic carbon framework smaller, this is especially the case for the precise control of the morphology and size distribution of CQDs with high fluorescence [26].

To improve the fluorescent performance of CQDs prepared by chemical oxidation, subsequent modifications or doping are required, which helps to tailor the electronic properties of the concerned CQDs by making use of strong electron-donating or electron-accepting molecules. Surface modification/passivation of CQDs by amine-containing agents via covalent bonding is a commonly used method to improve their PL performance [27,28]. Meanwhile, doping is another widely used approach to tune the PL properties of CQDs. N-doping can effectively enhance the PL emission performance of CQDs by inducing an upward shift of the Fermi level and electrons in the conduction band [29]. N-CQDs show nitrogen-content dependent PL intensities with multicolor [30]. Unfortunately, above mentioned works need complicated procedures or expensive passivating agents, which hinder their wide applications. It is reported that primary amine and carbon–nitrogen bonding can be introduced rapidly and easily to passivate CQDs. Tetsuka et al. [31] demonstrated that the molecular orbital resonance due to the delocalized π orbital of CQDs can be induced by direct bonding primary amino groups to the dots’ edges, yielding CQDs with high efficiency of narrow PL. Jin et al. [32] reported that the band gap of graphene quantum dots (GQDs) can be tuned by the charge transfer between amino groups and GQDs, leading to a shifted PL emission.

Here we report the synthesis of nitrogen-doped CQDs (N-CQDs) from petroleum coke by an ultrasonic-assisted chemical oxidation method. Under the combined synergistic effect of H2SO4, HNO3 oxidation, and ultrasonic wave energy, petroleum coke with cheap price and stacked graphitic layers has been selectively converted to well-dispersed CQDs. The as-made water-soluble fluorescent CQDs are further functionalized by ammonia under hydrothermal conditions, yielding tuneable PL N-CQDs with uniform size and high quantum yield (QY).

2. Experimental

2.1. Chemicals and materials

All chemical agents used in the present study were analytical pure, sulfuric acid of 98.0 wt.%, nitric acid of 65.0 wt.%, ammonia of 28.0 wt.%, hydrochloric acid of 37.0 wt.%, and sodium hydroxide were bought from Sinopharm Chemical Reagent Co. of China, and used without further treatment. Quinine (97.0 wt.%) was purchased from Aladdin Industrial Corporation at Shanghai of China. Inorganic filter membrane (0.22 μm) and 3500 Da molecular weight cut off (MWCO) dialysis membranes (Amicon Ultra-4, Millipore) were purchased from Shanghai Green Bird Science & Technology Development Co. of China. The water used throughout the experiments was deionized water.

2.2. Synthesis and purification of CQDs

Petroleum coke (2.0 g) was added into a mixture of concentrated H2SO4 (45.0 mL) and HNO3 (15.0 mL) in a flask under ultrasonic conditions (KQ-700DE, operated at 700 W) for 2 h, then heated under constant stirring in an oil bath at 120 °C for 12 h in reflux. After the reaction, the mixture was cooled to room temperature (RT), and diluted 10 times with deionized water, and neutralized with ammonia till pH = 7.0. The neutralized mixture was filtered by a filter membrane (0.22 μm) to remove the larger fractions, yielding a solution containing CQDs that was further dialyzed with 3500 Da MWCO for 72 h to remove the salts and tiny fragments. Finally, a deep yellow CQDs solution was obtained, exhibiting yellow emission under 365 nm UV light.

2.3. Synthesis and purification of N-CQDs

The as-made CQDs were treated hydrothermally in ammonia to make N-CQDs. For a typical run, 10 mL of as-made CQDs homogeneously dispersed in water (0.1 mg/mL) was mixed with 3 mL of ammonia in a glass vial, and sonicated for 20 min, yielding a mixture that was transferred to a Teflon lined autoclave and heated at 180 °C for 12 h. After cooling back to RT, the solution was filtered again using a 0.22 μm filter membrane to remove the insoluble larger fragments, yielding a supernatant containing N-CQDs that was heated at 100 °C for 1 h to get rid of excess ammonia. Then, the supernatant was dialyzed by the same procedure mentioned before for treating the CQDs, yielding a light yellow N-CQDs solution with a blue emission excited at 365 nm UV light.

2.4. Charaterizations

X-ray photoelectron spectroscopy (XPS) was recorded on ESCALAB 250Xi spectrometer equipped with a pre-reduction chamber. The position of the Cls peak (284.5 eV) was used to correct the binding energies for other groups due to the possible charging effect. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer. Raman spectroscopy was recorded using an Ar+ ion laser at 514.5 or 633 nm (Renishaw inVia 2000 Raman microscope, UK). X-ray powder diffraction (XRD) measurement was performed on a PANalytical X-ray Diffractometer (Cu Kα radiation, λ = 0.15406 nm, 40 kV, 40 mA). The transmission electron microscopy (TEM) images were obtained by JEOL JEM-2100UHR microscope operated at 200 kV. Field emission scanning electron microscopy (FESEM) images were taken in a Hitachi S-4800 scanning electron microscope operated at 5.0 kV. The height profiles of CQDs and N-CQDs were
investigated by an atomic force microscope (AFM, Nanoscope V D3100, Veeco Instruments, USA). UV–Vis absorption spectra were measured at RT by a UV/Vis spectrophotometer (Gold Spectrumlab 54, Shanghai Lengguang Technology Co. Ltd., China). Fluorescence spectra were measured at RT by a spectrofluorometer (F-97 Pro, Shanghai Lengguang Technology Co. Ltd., China). For the excitation dependent emission spectra and PL excitation (PLE) spectra, a Xe lamp was used as an excitation source. The time decay was measured on a Fluoro Max-4 fluorometer (Horiba Jobin Yvon Inc., France). An excitation wavelength of 405 nm was used and emission was collected at 510 nm of CQDs and 475 nm of N-CQDs, respectively.

3. Results and discussion

3.1. Preparation of CQDs and N-CQDs

Fig. 1 is the synthesis schematic of CQDs and N-CQDs derived from petroleum coke. The weight yield of CQDs is about 24.0 wt.% in the chemical oxidation step. The QY of CQDs is about 8.7% (Table S1), which is much higher than most CQDs prepared by traditionally chemical oxidation reported in literature [19,24,25]. The results show that petroleum coke with irregular size and shape distributions (Fig. S1) has been oxidized by the mixture of concentrated nitric acid and sulfuric acid to small CQDs that are rich of oxygen-containing functional groups. Low concentration ammonia in the hydrothermal step functions as a chemical knife to polish the edges of CQDs, and have N atoms anchored on the surface of CQDs [33]. The as-made N-CQDs with hydrophilic groups resulted from the chemical oxidation show an excellent solubility and stability in water and other polar organic solvents such as acetone, DMF and DMSO.

3.2. Physical structure of CQDs and N-CQDs

Fig. 2 is the TEM images of CQDs and N-CQDs, showing clearly that the as-made N-CQDs are quasi-spheres, and dispersed well. N-CQDs have a narrow size distribution centering at ca. 3.0 nm, with an average size of 2.7 nm, which are smaller than CQDs with a wider size distribution centering at ca. 4.5 nm, and an average size of 5.0 nm. The insets in Fig. 2a and c are the typical HRTEM images of CQDs and N-CQDs, indicating certain crystallinity with a lattice space of 0.332 and 0.334 nm, respectively. Both are in good agreement with the 002 planes of graphite, evidenced in the XRD patterns discussed below [34,35].

Fig. 3a is the AFM image of CQDs with a topographic height in a range of 0.5–4.5 nm (Fig. 3c) and an average height of 1.8 nm (Fig. 3b), suggesting that most CQDs consist of ca. 1–8 graphene layers [36]. The heights of N-CQDs are in a range of 1–10 nm (Fig. 3f), with an average height of 3.7 nm (Fig. 3e), indicative of the presence of graphene-like structures in the N-CQDs [35]. This result is similar to the results of N-CQDs made from other carbon precursors in literature [33,37,38].

XRD is a powerful tool for examining the structure of CQDs. Fig. 4a shows that petroleum coke has a very sharp diffraction peak at 25.8° (2θ), while CQDs and N-CQDs show a broader diffraction peak in the whole range. Both CQDs and N-CQDs show a small sharp peak at 26.7° (2θ), which is a little bit higher than that of petroleum coke. The interlayer spacing (ca. 0.334 nm) in CQDs and N-CQDs are more compact than those in the original petroleum coke (ca. 0.346 nm), which is consistent with the TEM observations (Fig. 2). The smaller interlayer spacing in CQDs and N-CQDs can be attributed to the effective π–π stacking of graphene sheets with few structural defects [33]. On the other hand, the formation of hydrogen bonds among the O-containing functional groups at the edges of graphene layers in CQDs and N-CQDs may also help to facilitate the compact stacking of graphene layers [39,40].

Raman spectra of petroleum coke, CQDs, and N-CQDs are shown in Fig. 4b, further demonstrating the defects with unsaturated bonds in CQDs. The peak around 1600 cm⁻¹ (G) corresponds to the E₂g mode of graphite due to the vibration of the sp²-bonded carbon atoms in the 2D hexagonal lattice, while the peak around 1370 cm⁻¹ (D) exhibits disorder characteristic due to scattering at the edges. The I_D/I_G ratio of N-CQDs is 1.20, higher than that of CQDs (0.98) and petroleum coke (0.72). The hydrothermal treatment of CQDs in ammonia...
not only cuts sp$^2$ clusters in graphite sheets into CQDs but also has N atoms anchored to the surface of carbon skeleton, thus, the highest value of $I_D/I_G$ ratio of N-CQDs may be caused by the increased disorder due to the introduction of C-N bands and amino groups on the surface of N-CQDs [33]. All of the results have suggested that the CQDs derived from petroleum coke are mainly composed of sp$^2$ graphitic carbons with sp$^3$ carbon defects and oxygen-rich edges such as hydroxy and carbonyl/carboxylate groups that are abundant on the surface [22]. Raman spectrum of N-CQDs shows a broader D and G bands, suggesting that the intercalation of N atoms into the exterior conjugated carbon backbone has resulted in more disordered structures [31]. In comparison with petroleum coke, blue shifts of D and G bands in CQDs and N-CQDs can be seen, which is consistent with the results reported before [41].

3.3. Chemical structure of CQDs and N-CQDs

The high-resolution C1s XPS spectra of petroleum coke, CQDs, and N-CQDs are shown in Fig. 5a–d. For petroleum coke (Fig. 5a), it has sp$^2$ C=C bands at 284.9 eV and sp$^3$ C-C bands at 284.2 eV. The C1s spectrum of CQDs (Fig. 5b) can be resolved as follows [42,43]: C=C/C=C at 284.8 eV, C=O at 285.7 eV, C=O at 288.3 eV and O−C=O at 289.0 eV.
The full-range XPS spectrum of N-CQDs in Fig. S2 shows N1s peak at ca. 400.7 eV, C1s peak at ca. 284.8 eV and O1s peak at ca. 531.9 eV, the atom contents of which are 7.82, 44.38 and 47.80%, respectively. The existence of N1s confirms the incorporation of N atoms to CQDs in the hydrothermal treatment step in ammonia. As seen in Fig. 5d, the N1s spectrum of N-CQDs has three main peaks centering at 399.3, 400.6 and 401.6 eV, which can be attributed to pyridine-like N, pyrrolic N and N–H, respectively [38,44]. A shoulder peak around 406.3 eV is also observed, which may be due to nitrogen oxides [45]. In addition to C–N bond at 284.3 eV, the high-resolution C1s spectrum of N-CQDs (Fig. 5c) further confirms the presence of oxygen-containing groups [46], such as C–O (285.2 eV), C=O (286.3 eV) and O–C=O (288.1 eV), which is further confirmed by the FT-IR results discussed below.

The FT-IR spectra of CQDs and N-CQDs are shown in Fig. 5e. The typical band at 3441 cm⁻¹ is assigned to –OH group, the small peaks at 2918 and 2857 cm⁻¹ are due to the vibration of –CH₂ groups, the peaks at 1608 and 1763 cm⁻¹ are due to the stretching vibration of C=O groups in carboxylic moiety, the 1439 cm⁻¹ peak is due to C–OH or C–H stretching vibration, and the 1128 cm⁻¹ peak can be assigned to C–O stretching vibration. After the hydrothermal treatment in ammonia, the bands at 2918, 2857, 1763 cm⁻¹ disappear while the C–O stretching peak around 1100 cm⁻¹ still exists. New peaks at 1614, 1384 and 3153 cm⁻¹ are assigned to C=O

Fig. 4 – XRD patterns (a) and Raman spectra (b) of petroleum coke, CQDs and N-CQDs. (A color version of this figure can be viewed online.)

Fig. 5 – High-resolution C1s XPS spectra of petroleum coke (a), CQDs (b), N-CQDs (c), N1s XPS spectrum of N-CQDs (d), and FT-IR spectra (e). (A color version of this figure can be viewed online.)
strectching vibration, C=O and N–H in-plane stretching vibrations of amine groups [16,48], indicating the doping of nitrogen in N-CQDs. Both CQDs and N-CQDs are rich of hydrophilic groups such as carboxyl and hydroxyl groups that are formed in the chemical oxidation step of petroleum coke in concentrated H2SO4 and HNO3. The abundant hydrophilic groups help to greatly improve aqueous solubility of the CQDs, which are beneficial for the applications of the CQDs in fields such as biochemistry, diagnostics and drug delivery.

All of the results presented above including TEM, AFM, XRD, Raman, XPS and FT-IR results have confirmed that N-CQDs with more defects have been prepared by the hydrothermal treatment in ammonia. N-CQDs with a uniform size and diversity surface groups show an improved optical properties than the untreated CQDs, as discussed below.

3.4. Optical properties of CQDs and N-CQDs

The optical properties of CQDs and N-CQDs are measured by UV–Vis absorption and PL spectroscopy. Fig. 6a is the UV–Vis spectrum of as-prepared CQDs, showing an absorption band at 228 nm that can be attributed to π–π* electron transition of graphitic sp2 domains. This result is consistent with CQDs prepared by the electrolysis of graphite rod [34]. Fig. 6b is the UV–Vis spectrum of N-CQDs, with no obvious absorption band. A broad and weak absorption shoulder peak in the range of 250–420 nm can also be seen in Fig. 6a and b, which may be due to the n–π* transition of C=O or C–N groups in CQDs and N-CQDs [49,50].

It is known that the optical properties of CQDs and N-CQDs are related to their concentration in the solution to some degree. Slight blue-shifts can be observed in the maximum emission wavelengths of CQDs and N-CQDs when the aqueous solutions were gradually diluted (Fig. S3), which is due to the reduced particle aggregation of CQDs and N-CQDs in the diluted solutions, leading to higher band gaps [51]. The self-quenching phenomena take place in high concentration due to the aggregation quenching effect resulted from the stacking of polyaromatic structures.

Fig. 6 also shows the fluorescence emission spectra of CQDs and N-CQDs, which were measured at different excitation wavelengths with the concentrations being optimized. The CQDs excited at 340 nm UV light show strong yellow PL centering at 510 nm (Fig. 6a). When the excitation wavelength increases from 320 to 580 nm, the PL peaks correspondingly red-shift from 480 to 600 nm. The excitation-dependent PL behavior of the CQDs is similar to the CQDs reported in literature [17,48,52,53]. The excitation-dependent emission may be associated with the aromatic C=C bonds and surface defects resulted from C=OH and C=O groups in the CQDs [49,52–54].

To explore the PL mechanism of CQDs, quantum confinement effects and the surface functional groups should be addressed here. It is known that the as-made CQDs have narrow particle distributions, abundant sp2 structures as well as hydroxyl and carboxyl moieties on their surface, which act as energy traps that make CQDs exhibit strong fluorescence.

In the case of N-CQDs, an excellent blue PL at UV light was observed, as shown in Fig. 6b. Despite the excitation wavelength increasing from 320 to 400 nm, the maximum emission wavelength of N-CQDs remains at 475 nm, which may be due to a new kind of surface state resulted from the doped nitrogen atoms [35]. As the excitation wavelength further increases to 520 nm, the maximum emission wavelength shows a red-shift from 480 to 540 nm. The corresponding PL excitation (PLE) spectrum of N-CQDs (475 nm) shows a blue-shift compared to that of CQDs (510 nm) (Fig. S4). It should be noted that the as-made CQDs and N-CQDs solutions are transparent, and exhibit strong PL even after 6 months in air at RT, indicating good fluorescent stability.

The optical performance of N-CQDs is affected by the amount of N content, and it can be tuned from blue to the greenish yellow region through decreasing amount of doped nitrogen, which can be confirmed in Table S2, Figs. S5 and S6. The level of doped nitrogen can be easily controlled by changing the hydrothermal temperature (Fig. S5), and this is consistent with the literature [31].

The PL properties of CQDs and N-CQDs in aqueous solutions are partly related to the pH value of the solutions. Fig. 7a shows the variation trend of the CQDs from petroleum coke. For CQDs, the PL intensity increases significantly as the pH increases from 2 to 5, then levels off in a neutral range with the pH from 5 to 9, and drops quickly in strong alkaline solution with the pH increasing from 9 to 12 (Fig. S7a). Because of this, the maximum emission wavelength red shifts from 493 to 509 nm as the pH decreases (Fig. S7b). This
is due to the narrowed band gap resulted from the reduced deprotonation effect of carboxyl groups from high to low in pH value [17].

In the case of N-CQDs (Fig. 7b), the variation trend of the PL intensity differs from the CQDs as discussed before, which increases gradually as the pH increases from 2 to 8, then levels off in a range of pH from 8 to 12 (Fig. S7c). Because of this, the maximum emission wavelength of N-CQDs remains at 475 nm with the pH at 6–12 (Fig. S7d). This strong and stable PL of N-CQDs can be attributed to the amide groups on the surface of N-CQDs, which make the N-CQDs have a stable surface chemistry in neutral and alkaline conditions [55]. It should be noted that at pH below 5, the emission spectra of N-CQDs blue shift, with the PL intensity drops gradually as the pH decreases. Anyway, the fluorescence emission of N-CQDs solution can be easily tuned by adjusting the pH, which may be a protonation-driven effect in acid solutions [56]. It is believed that the pH-sensitive fluorescence property of CQDs and N-CQDs will be helpful to their applications in the field of pH-sensitive molecular sensing.

![Fig. 7 – Effect of pH value on the PL intensity of CQDs (a) and N-CQDs (b) (λex = 350 nm). (A color version of this figure can be viewed online.)](image1)

The obvious difference in the PL behaviors of CQDs and N-CQDs is closely related to the PL enhancement after the nitrogen doping, in which the mechanism involved needs to be addressed.

The role of doped nitrogen atoms in N-CQDs might be reorganized, leading to new surface states of CQDs, which further results in an efficient radiative recombination [46]. A complex heteroaromatic π system may be resulted from the nitrogen doping in CQDs [57]. In order to figure out the mechanism involved in this system, the as-obtained CQDs were treated by the same hydrothermal procedure in the absence of ammonia, yielding CQDs (termed as C-CQDs). Fig. 8 shows the PL spectra of CQDs, C-CQDs and N-CQDs, showing clearly that the maximum emission wavelength changes from 510 nm of the untreated CQDs to 440 nm of C-CQDs. The average size of C-CQDs is 1.6 nm (Fig. S8), which is much smaller than those of CQDs and N-CQDs (Fig. 2). The HRTEM of C-CQDs is given in Fig. S8. The lattice space of C-CQDs is 0.341 nm, indicating C-CQDs have certain crystallinity. This means that the hydrothermal treatment helps to tune CQDs to smaller size with an enhanced quantum confinement effect. It is noted that N-CQDs show much stronger PL intensity than C-CQDs excited at 365 nm. The QY of C-CQDs is 5.6%, which is much lower than 15.8% of N-CQDs (Table S1). The low PL quantum yield of C-CQDs is most probably ascribed to the fluorescence quenching caused by the aggregation of carbon dots without doped nitrogen. With the formation of the differences in particle size and surface functional groups between CQDs and N-CQDs, it is possible for one to assume that the strong blue emission of N-CQDs is related to two factors. First, new amide-containing fluorophores may be formed in the hydrothermal treatment in ammonia [50]. Second, the optical band gap of N-CQDs increases with decreasing sp² domain size due to the quantum confinement effects [58]. Finally, a synergistic effect due to the combined contribution from the doped nitrogen atoms and size effect results in an improved PL properties of N-CQDs.

![Fig. 8 – PL spectra of CQDs, C-CQDs and N-CQDs (λex = 350 nm). (A color version of this figure can be viewed online.)](image2)

Based on the results discussed above, a schematic mechanism for fluorescence of CQDs and N-CQDs made from petroleum coke is proposed (Fig. 9). The CQDs with larger particle size and less surface states have a relative wide distribution of energy levels in comparison to the N-CQDs, showing an
excitation-dependent emission behavior and a relative weak PL signal. For the concerned CQDs and N-CQDs in the present work, a quantum confinement of emissive energy traps exist [53], i.e., a large surface-to-volume ratio is necessary for the passivated nanoparticles to exhibit strong photoluminescence. The nitrogen bonding to carbon may cause disorder in the carbon hexagonal rings and create new luminescent centers by trapping the radiative electron–hole pairs. As N-CQDs are enriched with primary amine, which can act as the electron-donating groups to enhance the conjugation degree of conjugated systems [59]. In a word, the doped nitrogen, the adsorbed primary amine [31] at the edges of N-CQDs, and the varied size of the sp² domains all contribute to narrowed optical band gaps of N-CQDs with blue-shift in the PL emission. The radiative recombination of excitons [53,60] between the delocalized π orbital and the doped nitrogen atoms in N-CQDs results in high photoluminescent QY, i.e. 15.8%, which is much higher than 8.7% of CQDs. The time decay of N-CQDs is 6.11 ns, much longer than 3.86 ns of CQDs (Fig. 10), which is agree with the PL enhancement.

The PL performance of CQDs and N-CQDs made from petroleum coke can be further improved by optimizing the preparation process, for example, by electrochemical and plasma treatments of the coke, and by co-doping other non-carbon atoms such as B/P/S in the matrix of CQDs. The work is in progress now, and the results will be reported soon.

4. Summary

In sum, water-soluble photoluminescent CQDs are produced from petroleum coke for the first time by ultrasonic-assisted chemical oxidation method. The as-made CQDs and N-CQDs with graphene-like structures are rich of oxygen-containing functional groups, and have a uniform size and good dispersion, and excellent water solubility. Both CQDs and N-CQDs are sensitive to pH in a wide range of 2.0–12.0, and have a high QY. The QY of N-CQDs is 15.8%, much higher than 8.7% of the CQDs without N-doping by hydrothermal treatment in ammonia. This work offers a new way for producing high quality and tunable PL CQDs from petroleum coke.

Acknowledgements

This work was partly supported by the NSFC of China (Nos. 51372028, 21302224, 51372277); the Fundamental Research Funds for the Central Universities (14CX02060A, 13CX02066A). The authors wish to thank Prof. Zhenhui Kang and Prof. Yang Liu at Soochow University of China for fruitful discussion and Dr. Xiaojuan Wang at China University of Petroleum for assistance in AFM and PL analyses.
Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2014.07.029.

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