

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/271217099>

Enhancing the luminescence of carbon dots by doping nitrogen element and its application in the detection of Fe(III)

ARTICLE *in* JOURNAL OF MATERIALS SCIENCE · JANUARY 2015

Impact Factor: 2.37 · DOI: 10.1007/s10853-015-8822-6

CITATIONS

4

READS

55

9 AUTHORS, INCLUDING:



Quan Xu

China University of Petroleum (Beijing), China

30 PUBLICATIONS 120 CITATIONS

SEE PROFILE



Hongjun Zhou

China University of Petroleum

38 PUBLICATIONS 386 CITATIONS

SEE PROFILE

Enhancing the luminescence of carbon dots by doping nitrogen element and its application in the detection of Fe(III)

Quan Xu · Jungang Zhao · Yao Liu ·
Peng Pu · Xuesong Wang · Yusheng Chen ·
Chun Gao · Jiarui Chen · Hongjun Zhou

Received: 6 October 2014 / Accepted: 3 January 2015 / Published online: 21 January 2015
© Springer Science+Business Media New York 2015

Abstract Carbon dots (CDs) attract great interests from scientists for their low toxicity and biocompatibility properties and their important applications in the fields of photocatalysts, batteries, bio-images and supercapacitors. Most strategies of making CDs contain several steps, which can be a time-consuming and costly procedure. In this study, nitrogen-doped CDs have been prepared by a one-step hydrothermal strategy with sodium citrate and ethylenediamine as precursors. It is found that fluorescence intensity of CDs is enhanced with the increased content of doped nitrogen, which implies that nitrogen-doped element plays an important role to improve the fluorescence intensity of CDs. Most importantly, those CDs yielded high selectivity of Fe^{3+} , with good linearity, precision and accuracy. Hence, the as-prepared nitrogen-doped CDs could be used as probes for quantitative analysis of Fe^{3+} in environmental applications.

Introduction

Carbon dots (CDs), since its discovery in 2004 [1], have attracted increasing attention due to their superior chemical

stability, low toxicity, high productivity and biocompatibility [2–4]. CDs have a potential as replacements for toxic metal-based quantum dots (QDs) and are proved to be promising candidates in many applications such as medical diagnosis [5], bio-images [4, 6–10], detection of metal ions [11–15] and catalysis [16, 17]. Recently, a variety of methods, including laser ablation of graphite [18, 19], electrochemical oxidation of graphite [20] and carbon nanotubes [21], thermal treatment of gelatin [22] or EDTA-2Na [23], acid treatment of sucrose solution or glucose [24–27] and microwaving of Ionic liquids [28] or chitosan [29] etc., have been adopted in the preparation of C-dots. Although the unique property of CDs has been studied and synthesis of CDs with different strategies has been reported extensively [30–35], the luminescence mechanism of CDs remains unclear. This is, however, fundamental in solving the puzzle of CDs and success of transferring CDs into practice applications. Previous studies have reported that gold particle [36], NaBH_4 [37], ZnS and ZnO [38] can enhance the luminescence of CDs. Most strategies of making CDs require complicated sample preparation and sophisticated instruments which limit their application in routine Fe^{3+} monitoring. Thus, it is still of great challenge to develop a simple method for aqueous Fe^{3+} detection. Here, we reported a one-step synthesis strategy to produce CDs. By adding certain amount of ethylenediamine into sodium citrate, nitrogen-doped CDs (NCDs) can be successfully synthesised and exhibited a strong fluorescence enhancement property. Furthermore, NCDs were found to be proportional to the fluorescent intensity, with the increase in nitrogen-doped element. Most importantly, the nitrogen-doped carbon dots (NCDs) were utilized as probes for the detection of Fe^{3+} . It is found that NCDs could detect Fe^{3+} in the range of 0.1–45 μM with a good linear correlation.

Q. Xu (✉) · J. Zhao · Y. Liu · P. Pu · X. Wang · H. Zhou
Institute of New Energy, State Key Laboratory of Heavy Oil
Processing, China University of Petroleum (Beijing),
Beijing 102248, China
e-mail: xuquan@cup.edu.cn

Y. Chen · C. Gao
Department of Chemistry, University of Akron, Akron 44325,
USA

J. Chen
Department of Chemical Engineering, Xi'an Jiaotong
University, Xi'an 710049, Shaanxi, China

Materials and methods

Materials

Sodium citrate and ethylenediamine were obtained from Tianjin Guangfu technology development Co., Ltd. Ferric trichloride was obtained from Sinopharm Chemical Reagent Co., Ltd. All the solutions were prepared using deionized water produced by BK-10B from Dongguanshi Qianjing environmental equipment Co., Ltd.

Preparation of carbon dots

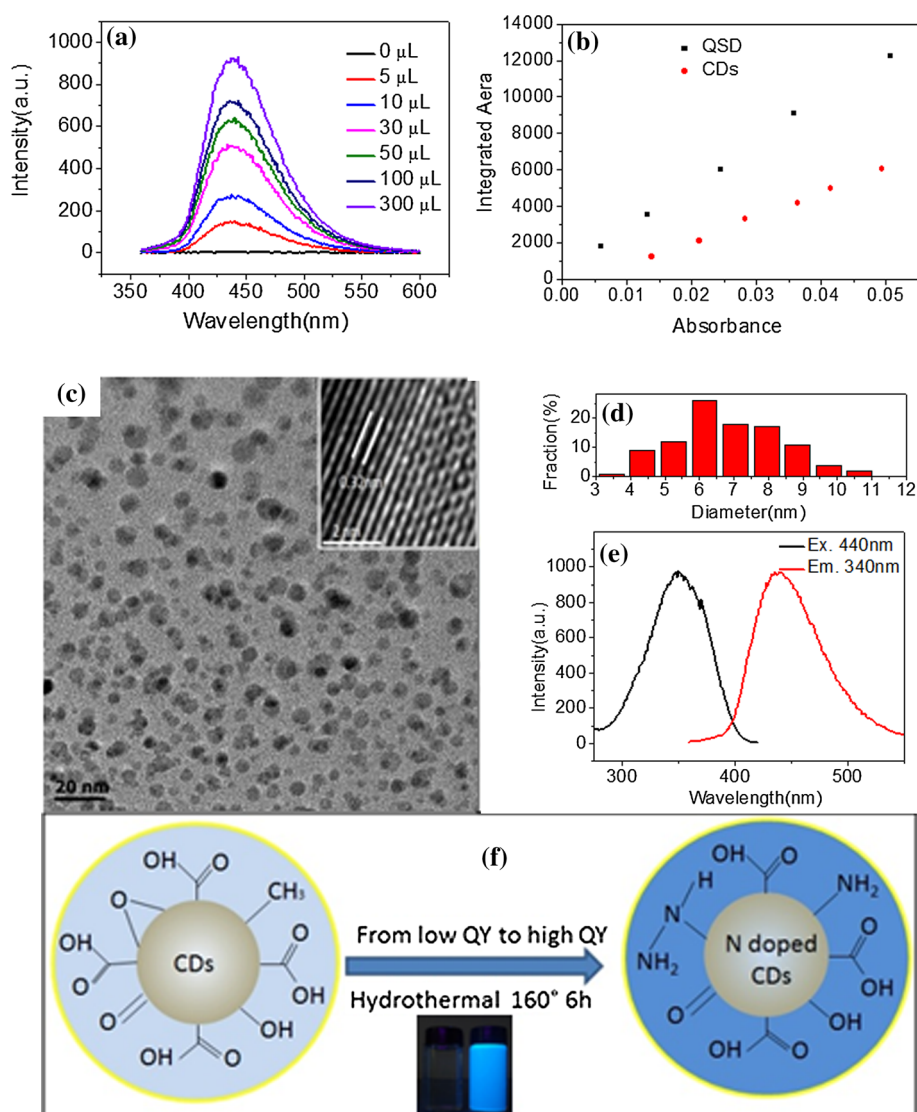
Briefly, 25 mL sodium citrate solution (0.1 M) and ethylenediamine (0, 5, 10, 30, 50, 100, 300 μL) were loaded

into a 50-mL Teflon-lined stainless steel autoclave. After that, the autoclave was kept at 180 $^{\circ}\text{C}$ for 6 h. The product could be used after filtering with cylinder membrane filter (0.22 μm).

Characterization

Transmission electron microscopy (TEM) (Model JEM-2100 and JEM-2100F, JEOL) was used to characterize the surface morphology of the as-prepared C-dots. The fluorescence measurements were measured with a Cary Eclipse fluorescence spectrophotometer (Varian, Inc.). The samples were placed in a 10 mm optical path length quartz fluorescence cuvette. The sample was excited at 350 nm, and the range of emission spectra was 360–660 nm. The

Fig. 1 **a** The fluorescence emission spectra of carbon dots prepared with different volume of ethylenediamine; **b** the calculation of the fluorescence quantum yield of NCDs, Here QSD refers to quinine sulphate; **c** low and high magnified (*inset*) TEM images of NCDs; **d** size distribution of NCDs corresponding to **c**; **e** photoluminescence spectrum of NCDs; **f** graphical of the synthesis of NCDs with blue luminescence. *Inset* photographs of aqueous solutions of CDs (*left*) and NCDs (*right*) under UV light (330 nm)

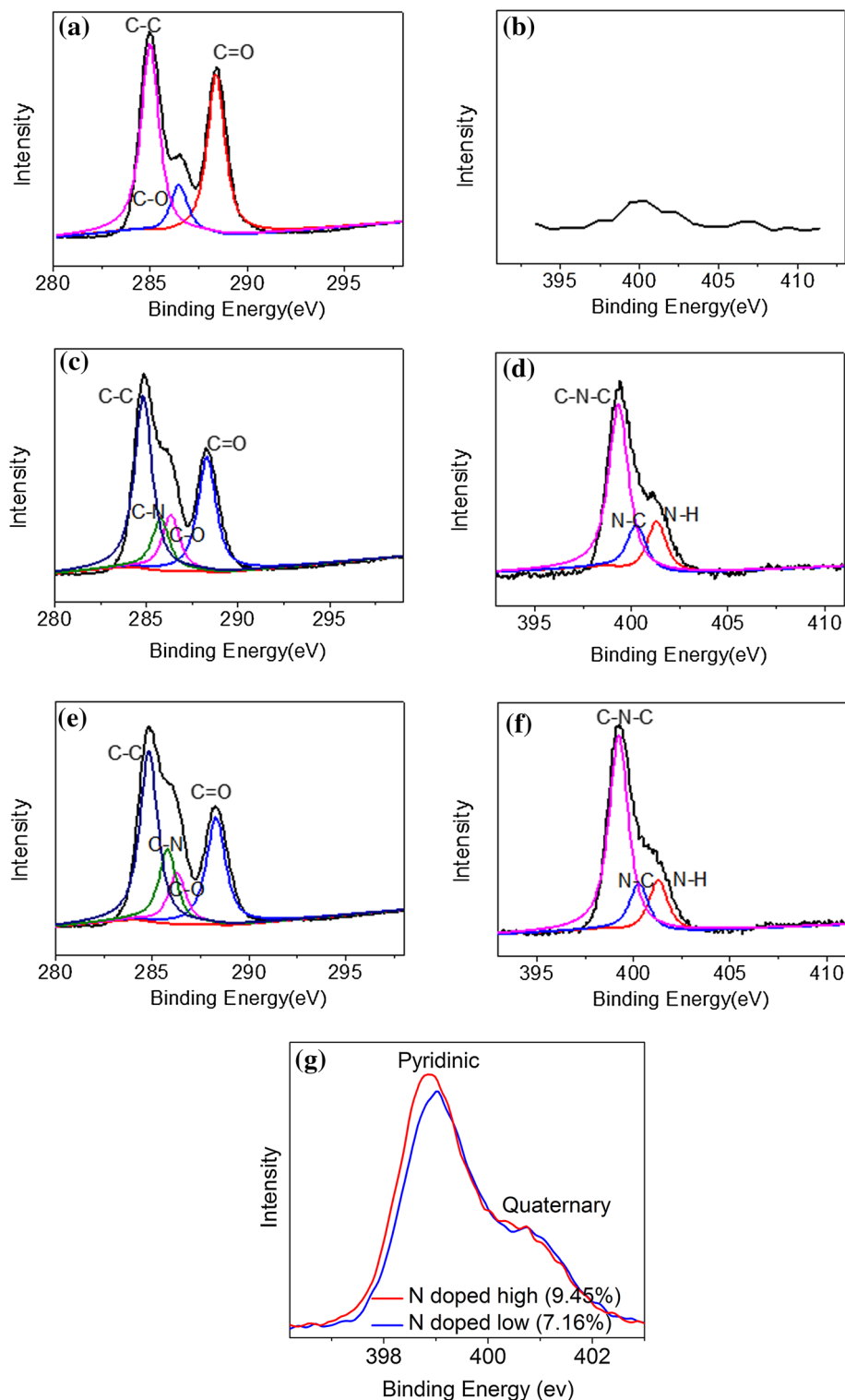


emission slit and the exciting slit were both 2.5 nm. X-ray Photoelectron Spectroscopy (XPS) was recorded using ESCALAB 250 spectrometer with a mono X-Ray source Al K α excitation (1486.6 eV). Binding energy calibration was based on C_{1s} at 284.6 eV.

Detection of Fe³⁺ using carbon dots as probes

The detection of Fe³⁺ was carried out at room temperature. In the typical assay, the as-prepared CDs (5 μ L) were diluted to 1 mL with deionized water, followed by the

Fig. 2 High-resolution C_{1s}, N_{1s} XPS spectra of C_{1s}, N_{1s}. Here samples are for sample A: CDs (a, b), B: low N-doped NCDs (c, d), 100 μ L ethylenediamine and high N-doped NCDs (e, f), 300 μ L ethylenediamine, respectively; g comparison of the high-resolution N_{1s} XPS for different nitrogen-doped contents



addition of Fe^{3+} solution at different concentrations. The fluorescence emission spectra before and after the addition of Fe^{3+} were recorded, respectively. The change in fluorescent intensity of CDs at 440 nm (ΔF) was calculated.

Results and discussions

The fluorescence emission spectra of CDs were prepared by adding different volumes of ethylenediamine (Fig. 1a). The fluorescence intensity was increased with the increasing amount of ethylenediamine. The fluorescence quantum yield of NCDs (300 μL ethylenediamine) was calculated as 32 % (Fig. 1b) using quinine sulphate as fluorescence standard [15], and all the following characterization was carried out for NCDs (300 μL ethylenediamine). Figure 1c shows the NCDs are well separated from each other. The high-magnified TEM picture in Fig. 1c reveals an observable core with a lattice spacing of approximately 0.32 nm, which reflects the (002) facet of graphite [39]. The diameters of most obtained CDs are distributed in the range of 3–11 nm (Fig. 1d), with an average diameter value of 6.9 nm. To evaluate the optical properties of NCDs, the emission and excitation spectra (Fig. 1e) were investigated. The fluorescence excitation spectrum shows a peak centred at 340 nm upon emission at 440 nm. The synthesis procedure of NCDs is illustrated in Fig. 1f. NCDs lead to strong fluorescence as observed in the inset picture of Fig. 1f [CDs (left) and NCDs (right)].

For comparison, three kinds of CDs were prepared: for sample A, NCDs were prepared without ethylenediamine; for sample B, NCDs were prepared with 100 μL ethylenediamine; for sample C, NCDs were prepared with 300 μL ethylenediamine. Figure 2 gives C_{1s} and N_{1s} for these three samples: sample A (a, b), sample B (c, d) and sample C (e, f). According to the XPS spectrum of C_{1s} (Fig. 2a, c, e), as the amount of ethylenediamine increased, the peak of C–N exhibited an increasing trend, which implies N is gradually doped on the surface of CDs. The XPS spectrum of N_{1s} provides a consistent evidence to prove the existence of doping N after ethylenediamine treatment (Fig. 2b, d, f). The quantitative analysis further shows that the content of N doping is 0, 7.46 and 9.45 %, for samples A, B and C, respectively (Table 1). Interestingly, besides N doping content, the chemical state of N

also changes with the treatment of different amounts of ethylenediamine. According to the XPS N_{1s} spectrum (Fig. 2g), the peak of pyridinic N gets broader and higher when compared with the peak of quaternary N. This result indicates that as the N doping content increases, there is a change in the chemical state of N. High N doping tends to form pyridinic N, accompanied with high-luminescence intensity. Previous researches found that higher content of pyridinic N can provide favourable conditions for oxygen/reduction reaction (ORR) on the surface of CDs, which can further passivate carbon dot surface and enhance the intensity of luminescence [40–43]. This could be one of the reasons for fluorescence improvement of NCDs by increasing the nitrogen-doped content.

To extend the application of the NCDs, the NCDs were utilized as probes for the detection of Fe^{3+} . Firstly, the changes in fluorescence intensity at 440 nm (ΔF) of different metal ions at the same concentration (50 μM) were detected, including Zn^{2+} , Ni^{2+} , Fe^{2+} , Fe^{3+} , K^{+} , Mn^{2+} , Ca^{2+} and Ba^{2+} . As shown in Fig. 3a, the fluorescence intensity of the as-prepared CDs was quenched by the addition of Fe^{3+} , while there was no significant change with the other metal ions, which exhibited a higher resolution for Fe^{3+} detection. The selectivity of the prepared CDs for the Fe^{3+} can be attributed to the faster chelating process between CDs and Fe^{3+} through “N” and “O” [16].

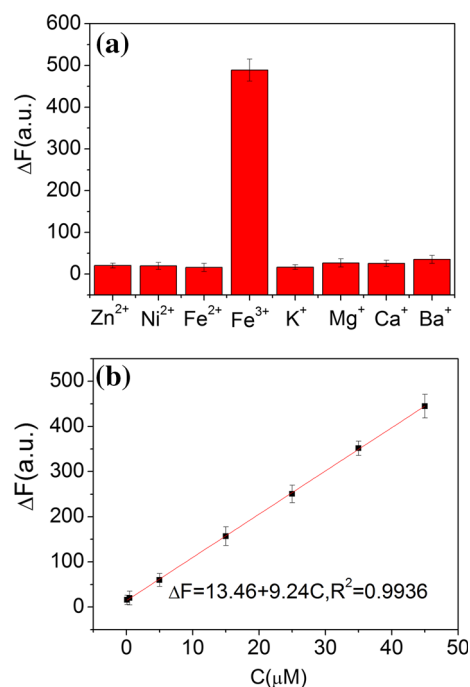


Fig. 3 **a** Selective PL response of NCD solution towards different metal ions, **b** plot of absolute change of the fluorescence intensity of NCDs versus the concentration of Fe^{3+} . (Error bars represent the SD of five independent measurements.)

Table 1 XPS results

	C_{1s}	N_{1s}	O_{1s}
Sample A-CDs	50.08	0	49.92
Sample B-N-doped-low	50.78	7.16	42.06
Sample C-N-doped-high	50.89	9.45	39.66

As a result, the excellent selectivity of NCDs for Fe^{3+} renders it the potential for the detection of Fe^{3+} .

In order to study the sensitivity of NCDs for Fe^{3+} , different concentrations of Fe^{3+} were added into the aqueous solution of NCDs and the change in fluorescence intensities at 440 nm was measured. Figure 3b shows the change in fluorescence intensity of the solution of the CDs in the presence of different concentrations of Fe^{3+} . It is found that the change in fluorescence intensity of CDs (ΔF) is sensitive to Fe^{3+} concentration and increases with the concentration of Fe^{3+} . Calibration plots were generated for Fe^{3+} and it can be seen that there is a good linear correlation ($R^2 = 0.9936$) between ΔF and Fe^{3+} concentration in the range of 0.1–45 μM with the following equation: $\Delta F = 13.46 + 9.24C$.

Conclusions

In summary, NCDs were simply prepared using a simple hydrothermal method with sodium citrate and ethylenediamine as precursors. Based on the XPS and fluorescence emission spectra analysis, the enhanced fluorescence intensity in CDs could be attributed to nitrogen doping. Specially, when nitrogen doped amount increased, the fluorescence intensity increased continually. Furthermore, the as-prepared NCDs were successfully utilized as probes for the detection of Fe^{3+} in the range of 0.1–45 μM with a good linear correlation.

Acknowledgements We thank Science Foundation of China University of Petroleum Beijing (No. 2462014YJRC011) for the support.

References

- Xu X, Ray R, Gu Y, Ploehn HJ, Gearheart L, Raker K et al (2004) Electrophoretic analysis and purification of fluorescent single-walled carbon nanotube fragments. *J Am Chem Soc* 126:12736–12737
- Zhu S, Meng Q, Wang L, Zhang J, Song Y, Jin H et al (2013) Highly photoluminescent carbon dots for multicolor patterning, sensors, and bioimaging. *Angew Chem Int Ed Engl* 52:3953–3957
- Baker SN, Baker GA (2010) Luminescent carbon nanodots: emergent nanolights. *Angew Chem Int Ed Engl* 49:6726–6744
- Song Y, Zhu S, Yang B (2014) Bioimaging based on fluorescent carbon dots. *RSC Adv* 4:27184–27200
- Kong B, Zhu A, Ding C, Zhao X, Li B, Tian Y (2012) Carbon dot-based inorganic-organic nanosystem for two-photon imaging and biosensing of pH variation in living cells and tissues. *Adv Mater* 24:5844–5848
- Michalet X, Pinaud FF, Bentolila LA, Tsay JM, Doose S, Li JJ et al (2005) Quantum dots for live cells, in vivo imaging, and diagnostics. *Science* 307:538–544
- Ruan S, Zhu B, Zhang H et al (2014) A simple one-step method for preparation of fluorescent carbon nanospheres and the potential application in cell organelles imaging. *J Colloid Interface Sci* 422:25–29
- Bhunia SK, Pradhan N, Jana NR (2014) Vitamin B1 derived blue and green fluorescent carbon nanoparticles for cell-imaging application. *ACS Appl Mater Interfaces* 6:7672–7679
- Cheng LK, Li Y, Zhai X et al (2014) Polycation-b-polyzwitterion copolymer grafted luminescent carbon dots as a multifunctional platform for serum-resistant gene delivery and bioimaging. *ACS Appl Mater Interfaces* 6:20487–20497
- Luo PG, Yang F, Yang S et al (2014) Carbon-based quantum dots for fluorescence imaging of cells and tissues. *RSC Adv* 4:10791–10804
- Yang X, Luo Y, Zhu S, Feng Y, Zhuo Y, Dou Y (2014) One-pot synthesis of high fluorescent carbon nanoparticles and their applications as probes for detection of tetracyclines. *Biosens Bioelectron* 56:6–11
- Yang S, Sun J, Li X et al (2014) Large-scale fabrication of heavy doped carbon quantum dots with tunable-photoluminescence and sensitive fluorescence detection. *J Mater Chem A* 2:8660–8667
- Li S, Li Y, Cao J, Zhu J, Fan L, Li X (2014) Sulfur-doped graphene quantum dots as a novel fluorescent probe for highly selective and sensitive detection of Fe^{3+} . *Anal Chem* 86:10201–10207
- Ju J, Chen W (2014) Synthesis of highly fluorescent nitrogen-doped graphene quantum dots for sensitive, label-free detection of Fe(III) in aqueous media. *Biosens Bioelectron* 58:219–225
- Guo Y, Zhang L, Zhang S, Yang Y, Chen X, Zhang M (2015) Fluorescent carbon nanoparticles for the fluorescent detection of metal ions. *Biosens Bioelectron* 63:61–71
- Zhuo S, Shao M, Lee S-T (2012) Upconversion and downconversion fluorescent graphene quantum dots: ultrasonic preparation and photocatalysis. *ACS Nano* 6:1059–1064
- Li H, He X, Kang Z, Huang H, Liu Y, Liu J et al (2010) Water-soluble fluorescent carbon quantum dots and photocatalyst design. *Angew Chem Int Ed Engl* 49:4430–4434
- Hu SL, Niu KY, Sun J, Yang J, Zhao NQ, Du NW (2004) One-step synthesis of fluorescent carbon nanoparticles by laser irradiation. *J Mater Chem* 19:484–488
- Sun YP, Zhou B, Lin Y et al (2006) Quantum-sized carbon dots for bright and colorful photoluminescence. *J Am Chem Soc* 128:7756–7757
- Zhou J, Booker C, Li R et al (2007) An electrochemical avenue to blue luminescent nanocrystals from multiwalled carbon nanotubes (MWCNTs). *J Am Chem Soc* 129:744–745
- Lu J, Yang J, Wang J, Lim a, Wang S, Loh KB (2009) One-pot synthesis of fluorescent carbon nanoribbons nanoparticles, and graphene by the exfoliation of graphite in ionic liquid. *ACS Nano* 3:2367–2375
- Liang Q, Ma W, Shi Y, Li Z, Yang X (2013) Easy synthesis of highly fluorescent carbon quantum dots from gelatin and their luminescent properties and applications. *Carbon* 60:421–428
- Zhou L, Lin Y, Huang Z, Ren J, Qu X (2012) Carbon nanodots as fluorescence probes for rapid, sensitive, and label-free detection of Hg^{2+} and biothiols in complex matrices. *Chem Commun* 48:1147–1149
- Zhu H, Wang X, Li Y, Wang Z, Yang f, Yang X (2009) Microwave synthesis of fluorescent carbon nanoparticles with electrochemiluminescence properties. *Chem Commun* 51:18–20
- He X, Li H, Liu Y, Huang H, Kang Z, Lee ST (2011) Water soluble carbon nanoparticles: hydrothermal synthesis and excellent photoluminescence properties. *Colloid Surface B* 87:326–332
- Li H, He X, Liu Y et al (2011) One step ultrasonic synthesis of water-soluble carbon nanoparticles with excellent photoluminescent properties. *Carbon* 49:605–609
- Chandra S, Das P, Bag S, Laha D, Pramanik P (2011) Synthesis, functionalization and bioimaging applications of highly fluorescent carbon nanoparticles. *Nanoscale* 3:1533–1540

28. Zhao A, Zhao C, Li M, Ren J, Qu X (2014) Ionic liquids as precursors for highly luminescent, surface-different nitrogen-doped carbon dots used for label-free detection of $\text{Cu}^{2+}/\text{Fe}^{3+}$ and cell imaging. *Anal Chim Acta* 809:128–133
29. Xiao D, Yuan D, He H, Lu J (2013) Microwave-assisted one-step green synthesis of amino-functionalized fluorescent carbon nitride dots from chitosan. *Luminescence* 28:612–615
30. Zhang X, Wang S, Xu L, Feng L, Ji Y, Tao L et al (2012) Biocompatible polydopamine fluorescent organic nanoparticles: facile preparation and cell imaging. *Nanoscale* 4:5581–5584
31. Jia X, Li J, Wang E (2012) One-pot green synthesis of optically pH-sensitive carbon dots with upconversion luminescence. *Nanoscale* 4:5572–5575
32. Yang Z-C, Wang M, Yong AM, Wong SY, Zhang X-H, Tan H et al (2011) Intrinsically fluorescent carbon dots with tunable emission derived from hydrothermal treatment of glucose in the presence of monopotassium phosphate. *Chem Commun* 47:11615–11617
33. Wang F, Xie Z, Zhang H, Liu C, Zhang Y (2011) Highly luminescent organosilane-functionalized carbon dots. *Adv Funct Mater* 21:1027–1031
34. Wang J, Wang C, Chen S (2012) Amphiphilic egg-derived carbon dots: rapid plasma fabrication, pyrolysis process, and multicolor printing patterns. *Angew Chem Int Ed Engl* 51:9297–9301
35. Xu Q, Pu P, Zhao J et al (2015) Preparation of highly photoluminescent sulfur-doped carbon dots for Fe(III) detection. *J Mater Chem A* 3:542–547
36. Zong J, Yang X, Trinchì A, Hardin S, Cole I, Zhu Y et al (2013) Photoluminescence enhancement of carbon dots by gold nanoparticles conjugated via PAMAM dendrimers. *Nanoscale* 5:11200–11206
37. Zheng H, Wang Q, Long Y, Zhang H, Huang X, Zhu R (2011) Enhancing the luminescence of carbon dots with a reduction pathway. *Chem Commun* 47:10650–10652
38. Sun YP, Wang X, Lu F, Cao L, Mezzani MJ, Luo PG et al (2008) Doped carbon nanoparticles as a new platform for highly photoluminescent dots. *J Phys Chem C* 112:18295–18298
39. Li H, He X, Kang Z, Huang H, Liu Y, Liu J et al (2010) Water-soluble fluorescent carbon quantum dots and photocatalyst design. *Angew Chem Int Ed Engl* 122:4532–4536
40. Gao S, Fan H, Chen Y, Li L, Bando Y, Golberg D (2013) One stone, two birds: gastrodia elata-derived heteroatom-doped carbon materials for efficient oxygen reduction electrocatalyst and as fluorescent decorative materials. *Nano Energy* 2:1261–1270
41. Niwa H, Horiba K, Harada Y et al (2009) X-ray absorption analysis of nitrogen contribution to oxygen reduction reaction in carbon alloy cathode catalysts for polymer electrolyte fuel cells. *J Power Sources* 187:93–97
42. Bao L, Zhang Z, Tian Z et al (2011) Electrochemical tuning of luminescent carbon nanodots: from preparation to luminescence mechanism. *Adv Mater* 23:5801–5806
43. Chen Y, Xu X, Perry K et al (2013) Achieving diameter-selective separation of single-walled carbon nanotubes by using polymer conformation-confined helical cavity. *ACS Macro Lett* 1:701–705