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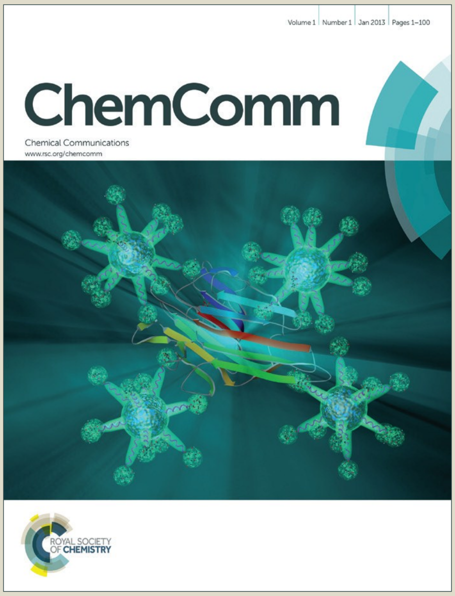

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Electrochemical Exfoliation of Carbon Dots with the Narrowest Full Width at Half Maximum of Fluorescent Spectra in Ultraviolet Region Using Only Water as Electrolyte

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Here, a novel kind of CDs was electrochemically exfoliated from graphite rods in distilled water as the only electrolyte. The as-exfoliated CDs showed two significant features: the narrowest fluorescence spectra with FWHM of only 10 nm and the ultraviolet fluorescence spectra in the region up to 360 nm.

For the last decade, Carbon Dots (CDs) have attracted considerable attention for various applications, especially for biological probe or image, due to their fascinating optical properties, excellent biocompatibility, environment friendly nature, small size and water solubility [1], which was also considered as the most potential substitution to traditional semiconductor Quantum Dots (QDs) in the applications of biological probe for monitoring physiological processes in living cells, tissues, and organisms[2]. Up to now, fluorescence (FL) spectra of CDs were reported to be usually broad with full width at half maximum (FWHM) of at least several dozens or a hundred of nanometers [3], which is similar to other common fluorescent materials (QDs and organic dyes). It is well known that the properties of biological probes (organic dyes, QDs or CDs) will directly affect the quality of final results. As one of the most important behavior of CDs, the FWHM of FL spectra from biological probe plays a vital role in improving the contrast of bioimaging. The material with narrower FWHM always has sharp FL emission spectra, indicating that it possesses pure color or excellent monochromaticity which is significant factor for the improvement of higher-contrast bioimaging [4]. The narrower FWHM material is used as probe, the higher contrast FL imaging is to be obtained. In order to obtain QDs with narrower FWHM, several groups had implemented a few investigations on the topic and have synthesized samples with the FWHM of 20~40 nm [5], which were competitive for QDs due to achieving pure color. However, the synthesis of CDs with narrow FWHM less than 20 nm of FL spectrum is still a big challenge and no relevant investigations have been reported. Besides, the FL spectra from most of current CDs usually range from the visible into near-infrared region[1c, 6], and there are rare CDs with FL emission spectra approaching ultraviolet area (approximately at 360 nm). As a comparison, QDs with ultraviolet emission spectra have been synthesized and applied in various light-emitting diodes (LEDs) as emission layer[7]. Thus the successful synthesis of CDs with FL spectra in UV region will inspire us to use it as a new kind of UV source for LEDs or other future applications in high density versatile disk, medical and environmental tools, etc.

Up to now, much effort have been devoted to investigate various synthesis and properties of CDs, such as microwave synthesis, ultrasonic treatment, reverse micelles, hydrothermal treatment, electrochemical method and so on [1c, 6, 8 9]. Nevertheless, these approaches have some limitations in terms of economical and large-scale production because they usually involve harsh synthesis conditions, complex process or needing expensive starting materials. Besides, many of the reported routes rely heavily on environmentally and biologically hazardous agents. Thus, in this paper, a one-step approach, with only water and cheap graphite rods as the starting materials, was proposed to inexpensively and largely-scale synthesis of CDs for commercial usage and, moreover, this approach appears to be great well agreement with concept of “green chemistry”.

In this work, a very facile approach was introduced to electrochemically exfoliate CDs from graphite rods, only using distilled water as electrolyte and graphite rods as carbon resource. The as-grown CDs showed the narrowest FWHM of FL emission spectra only 10nm, which was largely less than any of previously reported CDs [3]. Moreover, the obtained CDs have another striking feature emitting in UV region, of which behavior may open a new route using CDs as UV resource.

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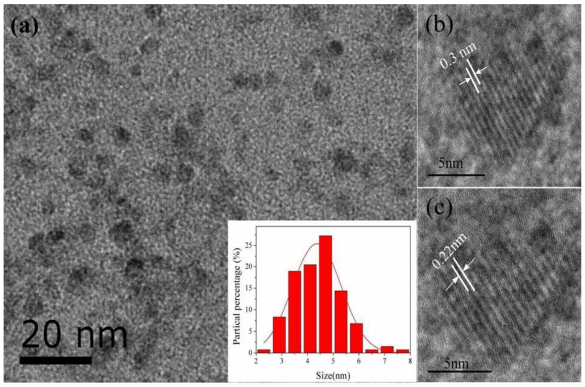
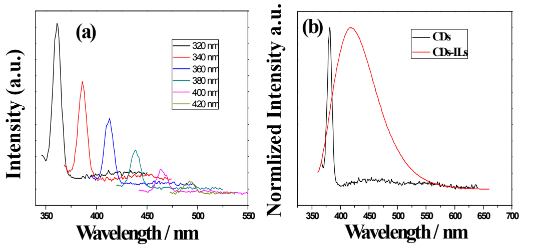
The TEM and HRTEM images of as-grown CDs were shown in Fig. 1. The statistical analysis of CDs' size and corresponding fitting Gaussian distribution were also shown in the inset of Fig. 1 (a). It can be easily found that the CDs were monodispersed and quasi-spheres in shape and had an average size of 4.4 nm from the fitting Gaussian curve. Two kinds of distinct crystal lattice with the spacing of 0.3 and 0.22 nm were observed from the HRTEM images as shown in Fig.1 (b) and (c), respectively. The lattice spacing of 0.22 nm was agreed well with the (100) lattice plane of graphite (in-plane) and the other spacing of 0.3 nm may be due to the inter-plane of graphite [9, 10]. These results provided enough evidence that the as-grown CDs are carbon genic materials. Besides, the better crystal structure may facilitate broaden of energy band in the CDs due to quantum size effect.

The FL emission spectra of as-grown CDs were shown in Fig. 2(a) excited at different wavelengths from 320 to 420 nm with the increment of 20 nm. It can be easily observed that one very sharp peak existed in each spectrum with symmetric and nearly Gaussian shape. Besides, as-grown CDs also showed the obvious excitation-dependent red-shift FL behaviors. As the excitation wavelength increased, the FL emission peaks shifted to longer wavelengths from 361 nm (violet) to 493 nm (green), and meanwhile the intensity of FL peaks deceased. The variations of peak shift and peak intensity in FL spectra of as-grown CDs were well in agreement with previous reports [1a, 11]. When excited at 320 nm, the FL emission peak centered at 360 nm in UV region, which was of distinct difference from that of previous CDs, usually emitting at blue region [12]. This significant FL behavior imparts CDs to be used as UV resource, as much as QDs acting in UV LEDs as emission layer [7].



- Fig. 1 (a) TEM image andcorresponding size distribution (inset) of as-grown CDs. HRTEM images of CDs with lattice parameters of 0.3nm(b)and 0.22nm(c), respectively.

As the most fascinating and important property, the FL behaviors of CDs have been deeply investigated. However, as the best our knowledge, there was no specialized investigation on how to improve FWHM of FL spectra for CDs. As a vital parameter, FWHM of FL materials will directly affect the contrast and pure color (monochromaticity) of obtained bioimaging. In this article, the as-grown CDs showed a sharp FL peak with only a FWHM of approximately 10 nm as shown in Fig. 2(a), which was narrower than any of reported CDs [3]. In order to give a more clear discrimination, we showed the comparison of the normalized FL emission spectra of as-grown CDs and our previously synthesized CDs in Fig. 2(b), which were also electrochemical exfoliation of graphite rods under almost the same condition except of mixed electrolyte of distilled water and ionic liquids (donated as CDs-ILs) [13]. It can be easily observed that the FWHM of as-grown CDs was significantly narrower than those of CDs-ILs (45nm). Generally, the FL spectra of reported CDs synthesized by various approaches were broad with dozens or more than one hundred of nanometers. For example, Sun's [1a] group synthesized the fluorescent CDs with FWHM of 90nm; Yang Bai*et al* prepared CDs with FWHM of 60 nm [14] and so on[1b, 1c, 2]. Therefore, the CDs with the narrowest FL emission peak have been successfully synthesized by a very facile method of electrochemical exfoliation of graphite rods in distilled water. We also recorded PL excitation of the CDs (shown in the Electronic Supplementary Information Fig S1). It can be easily observed that the maximum excitation wavelength at 286 nm and the maximum emission wavelength is 320 nm. The distinct property of PL excitation peak was as narrow as the emission one with the FWHM of about 10 nm. Although the exact mechanisms responsible for FL in CDs remain to be elucidated, it is believed that the narrowest FWHM of FL spectra may be close related to the structure or functional groups on surface of the CDs. It is obviously necessary to study the surface or structure of as-grown CDs.



- Fig. 2 (a) FL spectra of as-grown CDs under different excitation wavelengths, (b) the comparison of normalized FL spectra of as-grown CDs and CDs-ILs (excited at 340 nm).

The surface functional groups of CDs were measured by XPS and the obtained spectra were shown in Fig. 3. The XPS survey spectrum (Fig. 3(a)) showed only two predominant peaks of C1s and O1s, indicating that only two elements can be detected in as-exfoliated CDs. It can be found that the CDs were composed of C and O elements and the corresponding atomic percentages are 78% and 22%, respectively, which implied the simple surface composition of the CDs. The C1s core level peak, as shown in Fig.3 (b), can be fitted into three components centered at 284.5, 285.5 and 288.5 eV, respectively, corresponding to C=C, C-OH and C=O bonds[15]. It can be inferred that oxygen has connected to the carbon surface through the above chemical bonds, which can be estimated from O1s spectra. Fig. 3(c) exhibited the high-resolution XPS spectrum of O1s, which can be also resolved into three components. The peak at 531.6 eV could be assigned to C=O, which was related to C1s spectra. The peak at 532.4 eV was associated with C-O and the peak at 533.4 eV can be attributed to C–OH [15b, 16], which was well agreed with the above C1s spectrum. The functional groups were also characterized by FTIR spectroscopy and the compared spectra of as-grown CDs and CDs-ILs were shown in Fig. 3(d). Compared with CDs-ILs, as-grown CDs had fewer absorption bands in spectrum and showed a smoother curve, indicating that CDs had less functional surface groups. It can be found that only two peaks located at 3451 and 1640 cm^{-1}, respectively. The broad peak at around 3451cm^{-1} may be due to the O–H stretching vibration [17], exhibiting the presence of abundant hydroxyl groups. The peak at 1640 cm^{-1} could be assigned to C=O stretching vibrations [17]. These peaks in FTIR spectra were well consistent with the above XPS analysis. Based on above results of XPS and FTIR spectra, it can be concluded that only some very simple functional groups of C-OH and C=O existed on the surface of as-grown CDs, which may be reason for the narrowest FWHM and pure color FL emission.

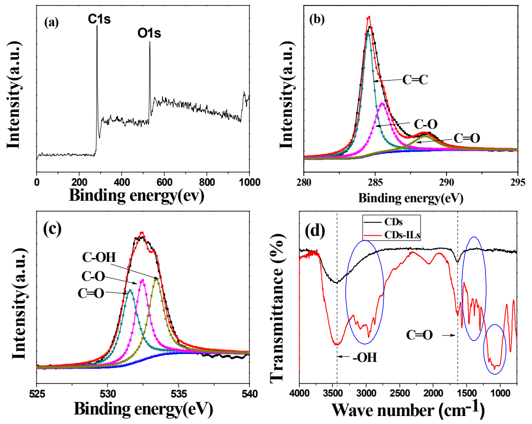


Fig. 3 (a)XPS spectra of CDs,(b) the high-resolution XPS spectrum of C1s, (c) the high-resolution XPS spectrum of O1s, (d) FT-IR spectra of CDs and CDs-ILs.

The UV-vis absorption spectrum of the CDs was measured and was shown in the Electronic Supplementary Information Fig S2. A UV absorption peak centered at 223 nm and a shoulder at 260 nm were observed from Fig S2. The peak at 223 nm is attributed to the π-π* transition of C=C band and the shoulder at 260 nm may be assigned to the *n*-π* transition of C=O bands [18], which were well agreement with the results of XPS and FTIR. ^{13}C NMR spectrum was usually used to verify the type of carbon centers in the CDs. We recorded the ^{13}C NMR spectrum and it was shown in the Electronic Supplementary Information Fig S3. According to the Fig S3, ^{13}C NMR spectrum of the CDs showed two main signals in the range of 120 to 200 ppm corresponding to sp^2 carbons. The signals in the range of 120 to 150 ppm arose from aromatic carbon, while the signals in the range of 170 to 200 ppm were attributed to carboxylic carbon [19]. The signals of 134 and 170 ppm represented C=C and C=O in the CDs, respectively, which were well agreement with and were also evidenced by the XPS and FTIR results.

Although a lot of approaches have been developed to synthesize CDs, there are many differently possible origins of PL emission, such as quantum size effect, defect-derived origins and radiative recombination of electron and holes. In our case, a possible origin of PL emission in the CDs is a consequence of recombination of localized e-h pairs in sp^2 clusters, and the energy gap between the π and π* states generally depends on the size of sp^2 clusters or conjugation length [20]. During the exfoliation, the oxygen radicals from dissociation of water can bond with near carbon atoms and form carboxyl (C=O) groups on the surface of CDs, which can be evidenced by the results of XPS and FTIR. The C=O groups are sp^2 hybridized structure in the CDs, which are structurally analogous to sp^2 islands in a large carbon sheet. As a result, the recombination of e-h pairs in sp2 can be implemented. Besides, the obtained sp^2 of carboxyl (C=O) groups may be one or two aromatic rings in the conjugation state, which are small enough to induce large bandgaps for PL emission in UV region.

In conclusion, CDs with the narrowest FWHM of FL emission spectra in ultraviolet region have been successfully exfoliated from graphite rods using a very facile electrochemical approach. The TEM images showed as-grown CDs were monodispersed and the HRTEM images revealed that it possessed crystal lattice of carbon materials. FL emission spectra exhibited not only very sharp peaks with the narrowest FWHM of 10 nm but also emission in the ultraviolet region. The narrower FWHM of FL spectra may be used to improve the contrast of bioimaging and the UV emission behavior enable as-grown CDs used as UV resource. XPS and FTIR results exhibited less and very simple functional groups on the surface of CDs, which may be contributed to the narrowest FWHM of FL spectra.

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