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One-Step Synthesis of Highly Luminescent Carbon Dots in Noncoordinating Solvents

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Luminescent semiconductor quantum dots (QDs) are nanometer-sized particles with size-dependent optical and electronic properties that have been under intensive research and development for a broad range of applications, such as energy-efficient displays and lighting, photovoltaic devices, and biological markers.[1−6] The estimated market size for QD-based products is \$721 million by 2013.[2] However, the intrinsic toxicity and potential environmental hazards associated with many of these materials represent considerable challenges to their practical applications. The emerging light-emitting, quantum-sized carbon dots (CDs)[7] appear to be a promising alternative to semiconductor QDs in many of applications because of their advantages in low toxicity and cheaper cost.[6]

Following the laser ablation method,[7] various methods have been established to produce quantum-sized carbon nanoparticles,[8−12] like electrochemical release or exfoliation from a graphitic source, separation of combusted carbon soot,[13,14] carbonizing polymerized resols on silica spheres,[15] thermal oxidation of suitable molecular precursors,[16−18] and dehydration of carbohydrates using concentrated sulfuric acid.[19] However, most of these synthesis methods need several steps.[7−14] In addition, the photoluminescent quantum yields (QY) of these resultant carbon dots are very low,[7−14,16−18] usually below 6%. The highest quantum yield[6] reported until now reached 20%, where the laser ablated carbon dots were conjugated with PEG$_{1500N}$ in neat SOCl$_2$. In view of the significant potential of this zero-dimension carbon nanomaterial in various fields, a facile and scalable synthetic approach for luminescent carbon dots is highly desired.

Here, we report a novel strategy to synthesize highly luminescent oil-soluble carbon dots (OCDs) by carbonizing carbon precursors, e.g., citric acid, in hot noncoordinating solvent. This one-step method is inspired by the synthesis of various monodispersed and size-controlled semiconductor and magnetic nanocrystals.[20−22] The obtained OCDs possess a maximum QY at room temperature up to 53% (excited at 360 nm), which is the best result reported so far. Furthermore, as a natural extension of this facile method, we also synthesized water-soluble CDs (WCDs) via changing the reaction solvent and capping agent. The QY of the WCDs is lower than the OCDs, yet it still can reach 17% (excited at 360 nm). In this communication, we focus on the synthesis of OCDs, whereas the details of WCDs are presented in the Supporting Information.

The OCDs was prepared using octadecene (ODE) as the noncoordinating solvent, 1-hexadecylamine (HDA) as the surface passivation agent, and citric acid anhydrous as the carbon precursor. Typically, a mixture of 15 mL ODE and 1.5 g of HDA loaded in a three-neck flask was heated to 300 °C under argon flow, and then 1 g of citric acid was quickly injected into the reaction flask. Aliquots were taken at different time intervals for the optical and

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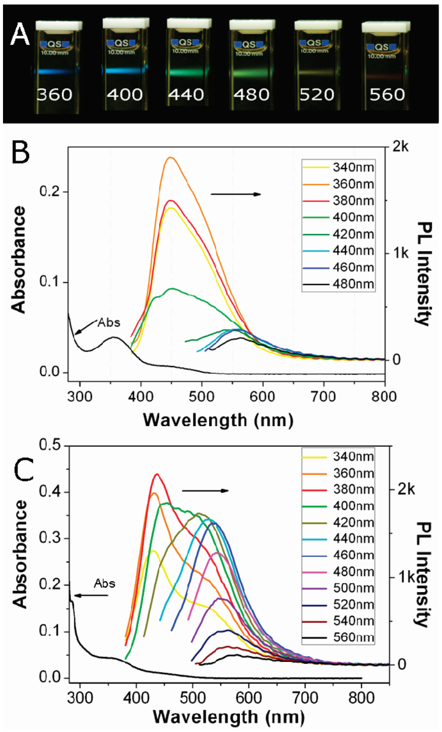

Figure 1. (A) Photograph of the toluene solution of OCDs after 180 min reaction excited by the fiber of the fluorescent spectrometer, and the absorption and photoluminescence emission spectra of the OCDs reacted after (B) 5 min (C) 180 min.

morphology measurements. After being purified by precipitating with acetone three times, about 0.1 g of product was obtained. For comparison, bare carbon dots (CDs) were also prepared without adding the HDA.

As shown in Figure 1A, bright and colorful photoluminescence (PL) emissions are observed from as-made OCDs, and the emission maxima shift bathchromically as the excitation wavelength increased (Figure 1B), comparable to previous reports on CDs.[7−18] The full-width at half−maximum intensity of the PL peaks are around 100 nm, much larger than other semiconductor QDs. Moreover, the excitation wavelength of OCDs is increased with reaction time. When the reaction was proceeded to 5 min, the OCDs can only be excited in a narrow range of excitation light (from 340 to 480 nm), however, when the reaction was proceeded to 3 h, the excitation broadened significantly into longer wavelength. This was accompanied by an enhanced emission intensity at longer wavelengths (Figure 1C). A similar optical behavior was also observed in the WCDs (see Figure S1 in the Supporting Information). Several mechanisms have been proposed to explain these unique optical characteristics, such as the size distribution of the CDs particles within the sample,[7,13,14] a distribution of different emissive trap sites[7,13,14] and the pyrolytic formation of several different polyaromatic fluorophores within the carbogenic core.[16] However, lacking clear experimental evidence, the relative contribution of these mechanisms and the possible existence of additional effects is still an open question.

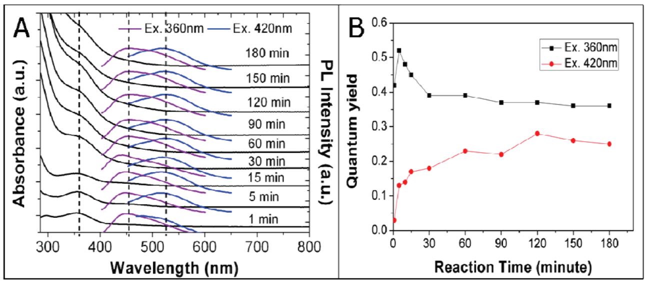

Figure 2. (A) Temporal evolution of the absorption and normalized photoluminescent spectra of OCDs pyrolyzed in ODE, and (B) relationship between quantum yield and reaction time excited at 360 and 420 nm using Quinine sulfate in 0.1 M H_2SO_4 and Coumarin 6 in ethanol as standard references (see the Supporting Information), respectively.

To understand the temporal evolution during the reaction time, we measured absorption and PL spectra of the OCDs solutions by taking out aliquots at different reaction time and diluted with toluene. As shown in Figure 2A, the PL maxima of OCDs excited at 360 and 420 nm do not show obvious shift along the reaction time. However, the distinct absorption peak around 360 nm gradually broadened and eventually disappeared as the time increases. As mentioned above, The emission of OCDs at the longer wavelength was enhanced as the reaction time extended. This can be confirmed by calculating the QY as a function of reaction time for different excitation wavelengths. As shown in Figure 2B, the QY excited at 360 nm reaches a maximum in the beginning of the reaction (about 5 min) and then decreases, reaching a plateau around 30 min. Conversely, the QY excited at 420 nm increased at a much slower pace, the steady increase of QY appeared to reach the maximum around 120 min, followed by a slight decrease thereafter. It should be mentioned that the WCDs shows a similar behavior (see Figure S2 in the Supporting Information).

Such a reaction-time-dependent phenomenon was also observed in other QDs,[23,24] and ascribed to the effects of size change during the nanocrystal growth.[25] To verify the applicability of this theory to this carbonization route, wase characterized the morphology of the OCDs extracted at 5 and 180 min (Figure 3) by high-resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM). The results reveal that the OCDs are mostly spherical dots with diameters in the range of 4−7 nm. Correspondingly, as shown in Figures S4 and S5 in the Supporting Information, the WCDs and CDs have a size and morphorlogy similar to the OCDs. This leads to our speculation that it was not the size change that has altered the QY of the OCDs over the reaction time, whereas it may be the OCDs surface that has continuously evolved, which may have resulted in changes at the emissive sites. This outcome also confirms that the CDs formation by "hot injection" method in noncoordinating solvent undergoes a depolymerization, decomposition, and pyrolysis process accompanied by formation of gas

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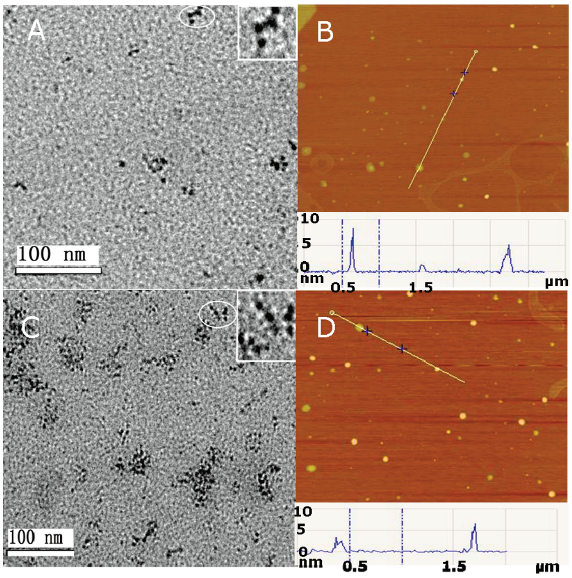

Figure 3. (A, C) HRTEM images and (B, D) AFM topography images on mica substrates of OCDs reacted (A, B) after 5 min and (C, D) after 180 min. The inset of A and C are enlarged images of selected areas.

and condensable vapors,[26] which is a starkly different reaction compared to the semiconductor QDs.

The addition of surface passivation agents in the one-step synthesis is essential for both the OCDs and WCDs to attain highly photoluminescent emission. Although the as-made bare CDs showed similar optical property and morphology, the QY is quite low (less than 10% excited at 360 nm, emission spectra in Figure S3 in the Supporting Information). Additional passivation procedure was undertaken to the bare CDs by adding 1.5 g of HDA into the reaction thereafter and maintaining 5 min, the QY of resulted product reaches 38%, given a further evidence that the passivation step is extremely important. Elemental analysis reveals that the bare CDs are composed of C 57.33 wt %, H 6.03 wt % and O 36.64% (calculated). The surface state of the bare CDs was characterized by means of Fourier-transform infrared spectroscopy (see detail in Figure S6 in the Supporting Information). Carboxyl groups were clearly identified, through both the broad O−H stretching vibration (3100 cm^{-1}) and the sharp C=O stretching vibration (1706 cm^{-1}). In the case of HDA-modified OCDs, two sharp peaks at 1707 and 1658 cm^{-1} indicate the appearance of $\nu_{(C=O)}$ and $\nu_{(CONR)}$ vibrations, suggesting that carbonyl group have been converted into amide group during the passivation process. This result is consistent with the decreased oxygen content and the appearance of nitrogen, as observed in the elemental analysis: C, 80.79 wt %; H, 12.79 wt %; N, 1.65%; O, 5.77 wt % (calculated). This set of comparative experiments suggest that the introduction of N atoms on the surface may be responsible for the significantly enhanced PL; however, this is not the prerequisite for the light emission, which is evidenced by the WCDs that do not contain N atoms in their chemical composition, characterized by the elemental analysis: C, 42.70 wt %; H, 8.29 wt %; O, 49.01(calculated). Attempts to obtain Raman spectra of OCDs and WCDs were unsuccessful due to the fluorescence of the nanoparticles; however, a typical X-ray diffraction (XRD) pattern expressed a broad peak located at $2\theta = 25°$ (Figure S7 in the Supporting Information), suggesting an amorphous nature.[27]

In conclusion, we have introduced a novel one-step approach for synthesizing highly luminescent OCDs and WCDs by injecting carbon precursors such as citric acid in hot noncoordinating solvents. The method is versatile, allowing a broad range of carbon hydrates as the carbon precursor as well as carbon precursors with heteroatoms, such as N, B, etc. The highest QY of OCDs reached 53% (excited at 360 nm) and it can stay at least 2 months with negligible decrease. The temporal evolution study of the PL characteristics versus reaction time indicates that it may be the chemical composition rather than the particle size that has the dominant effect on the optical properties of the CDs formed by this method. The superior luminescence efficiency, together with the simple, rapid, and reproducible synthesis method, will facilitate fundamental studies and practical applications of these carbon-based quantum dots.

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Supporting Information Available: Details of experiment; the optical property and morphology of WCDs and CDs; XRD of OCDs and WCDs; FT-IR of OCDs, WCDs, and CDs (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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