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Facile synthesis of carbon dots in immiscible system with excitation-independent emission and thermally activated delayed fluorescence

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Herein, we presented a one-pot microwave-assisted preparative method for water-soluble carbon dots (CDs) in immiscible system. The CDs demonstrated uniform morphology, high quantum yield and excitation-independent fluorescence emission. Moreover, we firstly reported the observation of thermally activated delayed fluorescence from CDs.

In recent years, emerging carbon dots (CDs) have generated growing excitement for their attractive characteristics, such as good biocompatibility, excellent aqueous solubility, low toxicity and high photostability.[1-4] CDs provide promising applications in bio-sensing, bio-imaging, drug delivery, photo-catalysis and other fields.[5-8] As a consequence, substantial research work has been concentrated on the simple fabrication of CDs.[9-13] Microwave-assisted pyrolysis of proper carbon precursors has become a rapid, green and economical methodology.[14,15] Nevertheless, the obtained CDs often possess weak fluorescence emission and low quantum yields (QYs). Additional surface passivation and/or heteroatom doping are developed to modify CDs and simultaneously augment their fluorescence.[16] However, poor reproducibility, multistep reaction, uncontrollable reaction conditions and complex purification steps hinder their wide applications. It is still an urgent desire to explore an efficient single-step approach for the fabrication of CDs with high QY via facile and rapid purification process.

Up to now, fluorescence and phosphorescence from CDs have been well studied and documented.[5,17] Thermally activated delayed fluorescence (TADF) from CDs has not been reported before. TADF materials, as the third generation-luminescent materials, have a small energy gap (ΔE_{ST}) between the lowest triplet excited state (T_1) and the lowest singlet excited state (S_1). In TADF process, highly efficient spin up-conversion from T_1 to S_1 excited states occurs, leading to

high radiative decay rates and fluorescence efficiency.[18-20]

By taking into account the above considerations, we describe herein a novel, facile and efficient pathway to attain CDs with high QY (~40%) from an immiscible system. The approach is cost-effective, less time-consuming and free of complex purification process (such as filtration, centrifugation and dialysis). Importantly, long lifetime TADF from CDs can be observed at low temperature.
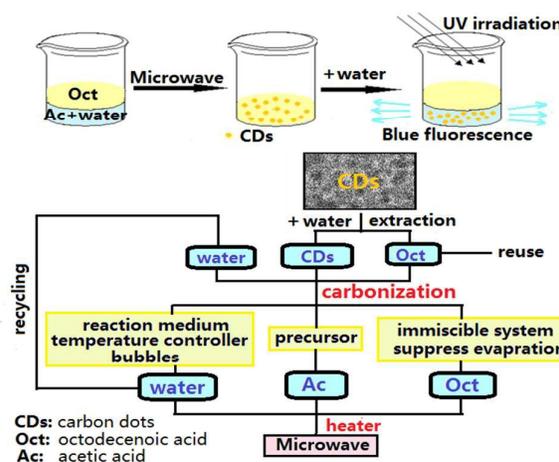
Scheme 1 Schematic illustration of the synthetic method

Scheme 1 illustrates the presentation of the reaction process. Briefly, acetic acid (13 mL) and distilled water (2 mL) were injected into 10 mL of octadecenoic acid. The mixture was heated in an ordinary household microwave oven at 375 W for 10 min. Finally, the CDs could be extracted directly from the system with water as extraction solution. In this open system, microwave irradiation could offer continuous, uniform and efficient heating to shorten the reaction time dramatically. Acetic acid, as the carbon precursor with simple structural component, could promote the formation of CDs with homogeneous surface defects and avoid complex by-products generated during the carbonization process. Moreover, excess

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acetic acid could be removed easily, and thus additional purification was not required. In this work, the carbonization reaction started and continued at a steady temperature (around 100 $^{\circ}$C) (Fig. S1). Water not only acted as reaction medium, but also restricted the reaction temperature at its boiling point. Furthermore, the nanobubbles generated from boiling water vapor could mix the reactants well and promote the uniform nucleation growth. Octadecenoic acid effectively suppressed the loss of acetic acid vapor due to its weak microwave absorption capability and high viscosity. Finally, pure CDs could be extracted directly from octadecenoic acid by water without intricate purification procedures. Overall, the preparative method was controlled by a series of conditions, such as simple carbon precursor, immiscible system, constant reaction temperature and continuous nanobubbles (see Experimental section for details, ESI†).

Transmission electron microscopy (TEM) images in Fig. 1A show that the CDs are nearly spherical and mono-dispersed with an average diameter of 5.8 nm. High–resolution TEM image of a single dot displays clear lattice fringes with lattice spacing of 0.21 nm, which can be matched with the (102) facet of graphitic carbon (Fig. S2). The as-prepared CDs are more homogeneous than those obtained from conventional microwave-assisted pyrolysis and hydrothermal treatment method.[1,3,8] The X–ray diffraction (XRD) pattern exhibits two broad peaks at about 20.5° and 38.7°, associated with the graphitic structure (Fig. S3).
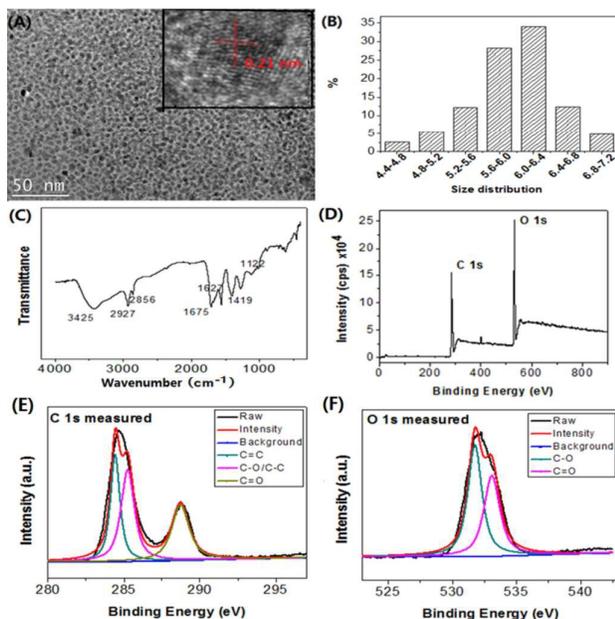

Fig. 1 TEM image (A), size distribution (B), FTIR spectrum (C), XPS spectrum (D), and high resolution XPS spectrum of C_{1s} (E) and O_{1s} (F) for the CDs

The Fourier transform infrared spectroscopy (FTIR) spectrum is shown in Fig. 1C. The broad absorption peak around 3425 cm^{-1} and the absorption peak at 1675 cm^{-1}

represent the –OH groups and C=O groups, respectively, revealing rich oxygen-containing groups on the surface of the CDs. The characteristic peaks at 2927 cm^{-1} and 2856 cm^{-1} are due to the stretching vibrations of sp^2 and sp^3 C–H. The peak at 1627 cm^{-1} corresponds to the C=C stretching vibration, indicating the formation of unsaturated carbon during the carbonization process. A crystalline G band at 1584 cm^{-1} and a disordered D band at 1343 cm^{-1} are presented in the Raman spectrum (Fig. S4), suggesting the co-existence of sp^2 and sp^3 carbon clusters in the CDs.[9]

X–ray photoelectron spectroscopy (XPS) was used to investigate the surface states of the CDs. The full scan XPS spectrum (Fig. 1D) reveals two prominent features of C_{1s} and O_{1s} with atomic contents of 62.34% and 37.66%, respectively. The typical C_{1s} spectrum (Fig. 1E) exhibits three distinct peaks located at 284.45, 285.27, 288.74 eV, which are attributed to C=C, C–O/C–C and C=O groups, respectively. The O_{1s} spectrum (Fig. 1E) can be resolved into two peaks at 531.79 and 533.11 eV, which correspond to C–O and C=O bands, respectively.[2,4] The data above are consistent with the FTIR results.

The UV–vis absorption spectrum, excitation and emission spectra of the water-soluble CDs are shown in Fig. S5. Strong absorption at 246 nm represents the π system transitions of aromatic sp^2 domains. Whereas the broad peak focused at 350 nm is related to the trapping of excited state energy by the surface states.[17] Accordingly, the excitation spectrum shows two peaks centred at 300 nm and 360 nm, which are due to the π–π* transition from the carbogenic core and n–π* transition from the surface state region, respectively.[16] The CDs show bright blue fluorescence under the UV illumination, which can be used as an 'invisible' ink for painting patterns and information encryption (Fig. S6).
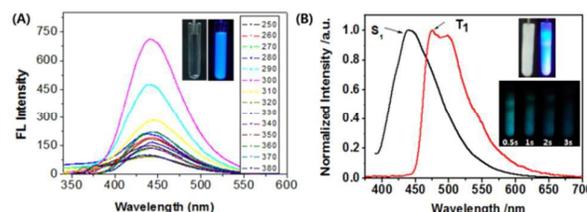
Fig. 2 (A) Fluorescence emission spectra of CDs: excitation wavelength starts from 250 nm to 380 nm and increases in 10 nm increments; inset: photos of the CDs dispersed in water under daylight light (left) and UV irradiation (right) (B) The emission spectra of CDs measured at 300 K (black line) and 77K (red line); the inset shows the photos of CDs at 77K under daylight (upper left), UV light (upper right) and the afterglow in air at time 0.5s, 1s, 2s and 3s after UV excitation.

Surprisingly, the fluorescence emission wavelength of the CDs is around 445 nm, showing no significant shift upon different excitation wavelengths (Fig. 2A). This phenomenon is quite different from the usually observed multicolour emissions of CDs prepared by other methods.[14,15] It is generally agreed that the presence of different sizes and multiple surface emissive trap status may lead to inter-system crossing

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and adjacent vibrational relaxation of excited electrons, thereby triggering FL emission with corresponding energy.[21,22] By summarizing the spectroscopic observations, both the intrinsic band state from the carbogenic core and the surface state account for the strong fluorescence emission at 445 nm. It is hypothesized that non–radiative transitions (electron transfer/thermal relaxation) between the carbogenic core and surface state are likely to occur (Fig. S7).[23] Consequently, the FL emissions are irrespective of the excitation wavelengths.

Using quinine sulfate in 0.1 M H_2SO_4 as a standard, the QY of the CDs in water is measured up to be 40.1% (Table S1), which is much higher than that of previously reported CDs without doping and surface passivation. Such high QY may be attributed to the highly crystalline structure of the CDs and uniform surface states.[24] Fig. S8 depicts the fluorescence decay profile of the CDs dispersed in water at room temperature. The decay curve can be fitted using a two-exponential function with lifetimes of 20.8 ns (96.7%) and 120.7 ns (3.3%). It is clear that the CDs with a shorter lifetime dominate the fluorescence emission, suggesting relatively uniform FL radiative process. This also agrees with the observation of excitation–independent emission.[22,23]

Then, the effects of continuous UV exposure, ionic strength and long time storage on the FL intensity of the CDs were investigated (Fig. S9 and Fig. S10). There is no apparent change in both FL intensity and peak position, suggesting the excellent photo-, time- and ions-stability of CDs. However, the CDs demonstrate a pH-sensitive FL feature. As illustrated in Fig. S11, a significant decrease of the FL intensity is recorded within pH 3-11 and the pH-dependent behaviour has good reversibility. This observation is related to the protonation-deprotonation of carboxyl groups on the surface of the CDs.[13] Notably, the fluorescence intensity exhibits good linearity with pH variation from 5.0 to 9.0. Common cations, anions or compounds have no effect on the FL emission (Fig. S12). Therefore, the CDs show good selectivity towards pH and can be served as the potential pH sensor in environmental or biological systems, as evidence in Table S2.

At room temperature, the CDs exhibit a broad emission band at 445 nm, which is attributed to the intramolecular charge-transfer transition. Interestingly, the CDs can emit cool white light at 77K under the same UV light excitation. A green afterglow of the CDs can be observed for seconds by naked eyes when we turn off the UV beam (inset in Fig. 2B). The phosphorescence spectrum measured at 77K with 10 ms delay shows emission bands at 471 nm and 498 nm, which can be assigned to the decay of a locally excited triplet state.[18,20] Accordingly, the CDs provide a small ΔE_{ST} of 0.16 eV (S_1=2.79 eV and T_1=2.63 eV), which is favourable for a reverse intersystem crossing from the T_1 to S_1 states (Fig. S7). To further confirm that the delayed fluorescence originated from TADF, we conducted the temperature dependence of the transient FL decay (Fig. S13). The CDs show two-component decays, that is, a fast decay with a lifetime of 20.6-22.0 ns and a slow decay with a lifetime of 676-810 ns, which can be assigned to the fluorescence and TADF decay, respectively. The ratio of the delayed component increases monotonically with

increasing the temperature from 100 K to 250 K. This phenomenon is due to the acceleration of reverse ISC rate from T_1 to S_1 states by heat activation.[18] Generally, the aromatic carbonyl groups are considered the origin of the triplet state emission.[21] It is prospected that the oxygen-containing functional groups on the surface of CDs realize the TADF due to the efficient spin-orbit coupling. In fact, oxygen is a strong quencher of the triplet state emission, so the slow decay component cannot be observed at room temperature due to the oxygen quenching (Fig. S8). At low temperature, the solution is frozen and the C=O bonds on the CDs are rigidified, hiding the direct collisions between oxygen atoms and aromatic carbonyl groups, which promotes the TADF emission. The study on TADF from CDs is a brand new area in infancy. The luminescent mechanism of CDs may be very complicated and requires further exploration. Taking good advantages of the long-lifetime TADF emission will open up new opportunities for biochemical imaging/sensing, as well as highly efficient photovoltaic devices design.

In short conclusion, we have synthesized water-soluble CDs by microwave heating of acetic acid in immiscible system within 10 min. The preparative method is facile, low-cost and free of complex purification process. The CDs possess uniform morphology, excitation-independent fluorescence emission and high quantum yield (QY: ~40%). Moreover, the CDs have a very small ΔE_{ST}, and obvious TADF performance can be observed at low temperature. Preliminary investigation on the luminescence from CDs may bring promising applications.

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