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COMMUNICATION

## Carbon Dots with Aggregation Induced Emission Enhancement for Visual Permittivity Detection†

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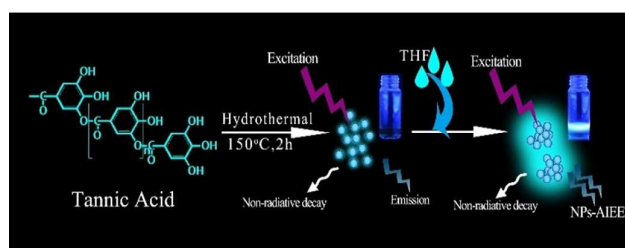
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Photoluminescent carbon dots (CDs), hydrothermally prepared with tannic acid (TA), show visual aggregation induced emission enhancement (AIEE) properties at 455 nm when excited at 350 nm owing to the rotation hindering of the surface groups on CDs such as aromatic rings and phenolic hydroxyl ones, making an exponential decay between the ratio of the photoluminescent intensity in organic solvent to that in water and the permittivity of the solvent, and thus dazzling emissions of the CDs in the presence of solvents with small permittivity, tetrahydrofuran (THF), for instance, could be visually observed.

Aggregation is an interesting topic, which generally involves in the assembly of small molecules or polymer, or even if cell fragments such as blood platelet<sup>1</sup>, during which interesting information or signals disclose. Aggregation-caused signal change (ACSC) strategy has found widely applications in the fields of, for example, developing new optical probes and sensors<sup>2</sup>, making the two opposite processes of aggregation and disaggregation could be interesting and applicable since the emission signals of chromophores either fluorescent organic small molecules (OSMs) or photoluminescent nanoparticles (PLNPs) turn off or on.<sup>3</sup>

In principle, aggregation of OSMs or PLNPs generally depends on the functional groups of the aggregation unit and the environmental conditions such as pH, ionic strength and the polarity etc.<sup>3</sup> The aggregations of PLNPs are interesting since ACSC strategy with functional-groups decorated PLNPs has been identified to be very effective to design new optical



Scheme 1 Schematic of the synthesis of TA-CDs and the CDs-AIEE effect by tetrahydrofuran (THF), which has very small permittivity.

devices and nanoprobe. For example, Mirkin and co-workers using the colour change in DNA-modified gold-nanoparticle aggregation to develop a sensitive and selective sensor of Cu<sup>2+</sup>.<sup>4</sup> With the ACSC strategy, we also developed an off-on fluorescent probe of europium (Eu)-adjusted carbon dots (CDs), which were prepared by condensation reaction between citric acid and 11-aminoundecanoic acid. Since a lot of carboxylate groups on the surface of CDs, the sensitive recognition of phosphate ion (Pi) in complicate water sample from wetland could be successfully realized depending on the binding ability difference between the carboxylate and phosphate groups.<sup>2</sup>

As the same as the aggregation induced emission enhancement (AIEE) of fluorescent OSMs proposed by Tang et al.,<sup>5-8</sup> the aggregation of PLNPs induced emission enhancement (PLNPs-AIEE) effect, as identified by Gao *et al.* by using the CDs prepared from C60, occurred in a variety of solvents such as dioxane, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), acetone, isopropanol, methanol,<sup>9</sup> still needs to be investigated for further understanding the unclear aggregation mechanism,<sup>10, 11</sup> namely, the features of PLNPs-AIEE is dependent on the physical nature of solvents such as viscosity, polarization, refractive index or hydrogen bond.

Up to now, there is no good way to assign the surface groups of CDs prepared from different raw carbon materials even if it have been reported<sup>12</sup> and reviewed<sup>13</sup> involving the surface functional group engineering of the CDs. So, investigations of the functional activities of the surface groups of CDs are

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necessary. Though surface states of CDs are not clear, CDs show more stable optical properties comparing with OSMs and metal nanomaterials in AIEE systems. In this contribution, we found that the CDs prepared with tannic acid (TA) display permittivity dependent AIEE properties in the presence of organic solvents, especially in the solvents with small permittivity, such as tetrahydrofuran (THF, Scheme 1), which has been widely used in organic synthesis and pharmaceutical engineering but exerts a great harm to human health<sup>14</sup>. Comparing with other AIEE systems such as OSMs and metal nanomaterials, our system was established for physical constant of different organic solvents instead of detection for single objects.

Scheme 1 displayed the syntheses schedule of CDs with TA, which is very easy by a thermal synthesis route. UV-vis spectra and PL spectra were measured to confirm there was few influence of remaining TA (Fig.S1 and S2, ESI†). The as-prepared TA-CDs have a uniform dispersion without apparent aggregation and the average diameter is 4.57 nm with lattice spacing of about 0.24 nm (Fig.1a), which is similar to the (002) facet of graphitic carbon and corresponding to the X-ray diffraction (XRD) pattern (Fig.S3, ESI†) with a broad peak at around 25° and Raman spectrum (Fig.S4, ESI†) with D and G band at 1373 cm<sup>-1</sup> and 1598 cm<sup>-1</sup> respectively. X-ray photoelectron spectroscopy (XPS) (Fig.1b, Fig.S5a and Fig.S5b, ESI†) and Fourier Transform infrared spectroscopic (FTIR) (Fig.S6, ESI†) analysis indicate that the as-prepared TA-CDs mainly contain carbon and oxygen, and there are amount of aromatic rings, carboxyl and phenolic hydroxyl groups on the surface of TA-CDs. The appearance of aromatic rings, carboxyl and phenolic hydroxyl groups is very critical to the AIEE properties of TA-CDs in organic solvents since they might be hindered during their rotation in the solvents.

The as-prepared TA-CDs had a UV absorption band in UV-vis region with a shoulder peak at 275 nm, which should be ascribed to the  $\pi$ - $\pi^*$  transition of the nanocarbon.<sup>15</sup> When excited at 350 nm, the TA-CDs showed a PL emission centred at 455 nm (Fig.1c) with a quantum yield (QY) of 7.16% against quinine sulphate as reference (Fig.S7, ESI†), and the maximum excitation band was mirror symmetric with the maximum emission band. The average PL lifetime of the as-prepared TA-CDs was calculated to be 1.85 ns (Fig.S8 and Table S1, ESI†). Such a short lifetime indicates a possible mechanism of the radioactive recombination nature of excitations.<sup>15, 16</sup> Also, the as-prepared TA-CDs show excitation wavelength dependent emission (EDE) features (Fig.1d), which are in accordance with previous reports.<sup>17, 18, 19</sup>

The as-prepared TA-CDs were very stable in a medium of high salt concentration (Fig.S9, ESI†) and under continuous excitations of light (Fig.S10, ESI†). An interesting phenomenon is that the PL emission of the as-prepared TA-CDs gets greatly enhanced in organic solvents as concerned (Fig.2a) in ethanol, acetone, DMF, isopropanol, DMSO, acetonitrile, methanol, acrylic acid, 1,2-dichloroethane (DCE), pyridine, glycol and THF (Fig.2b). The most interesting is that the enhanced emission of TA-CDs is greatly dependent the permittivity ( $\epsilon$ ) of the tested organic solvents. As shown in Fig.2b, the PL

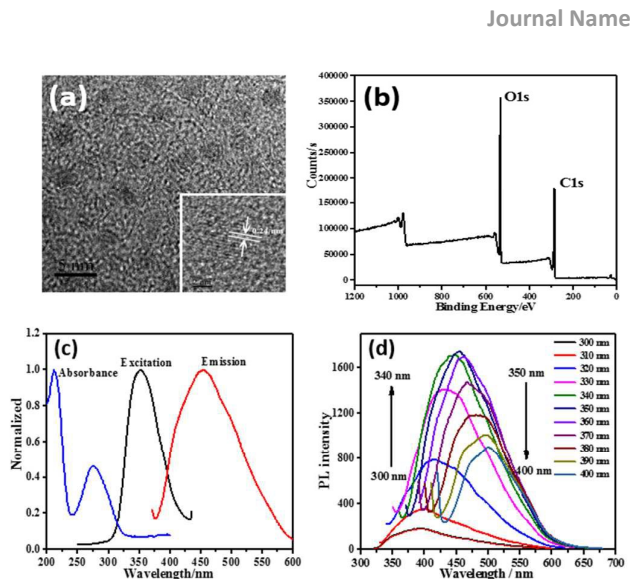


Fig.1 Characterization of TA-CDs. (a) high resolution transmission electron microscope (HRTEM) of TA-CDs. Insert: lattice spacing of the CDs. (b) XPS spectra of CDs. (c) UV-vis absorption spectrum and PL spectra. (d) Emission spectra of CDs recorded for progressively longer excitation wavelengths with 10 nm increments from 370 nm to 500 nm.

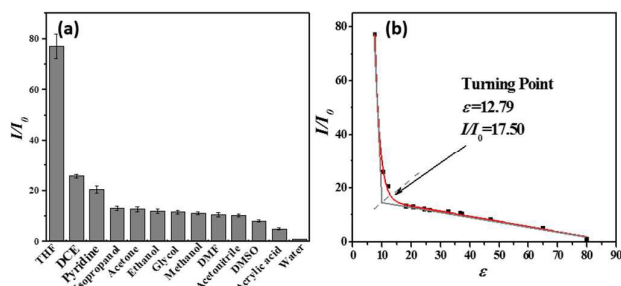


Fig.2 Permittivity-dependent AIEE of TA-CDs in organic solvents. (a) Emission intensity of TA-CDs measured at 455 nm in different solvents when excited at 350 nm. (b) The relationship between PL intensity and permittivity ( $\epsilon$ ). The first and the second term of the turning point was calculated to be -2.529 and 20.029, respectively.

intensity of TA-CDs decreased in different organic solvents with permittivity ranging from 7.6 to 80. The curve could be fitted as follows:

$$\frac{I}{I_0} = 9.53 \times 10^5 \left[ e^{-\frac{\epsilon}{4.82 \times 10^6}} - 1 \right] + 5.52 \times 10^3 e^{-\frac{\epsilon}{1.68}} \quad (1)$$

with  $r^2=0.998$ , wherein  $I$  and  $I_0$  represent the PL intensity of TA-CDs in different organic solvents and in water, respectively, indicating that an exponential decay obeyed between the ratio of the PL intensity in organic solvent to that in water and the permittivity of the solvent. The equation (1) consists in two items, and the first one is always negative only if  $\epsilon \geq 4.82 \times 10^6$ , which is impossible in reality (Table S2, ESI†). Furthermore, the first terms stands out only after the turning point in Fig 2B, where  $\epsilon=12.79$ . In the case of  $\epsilon < 12.79$ , sharp decrease of the

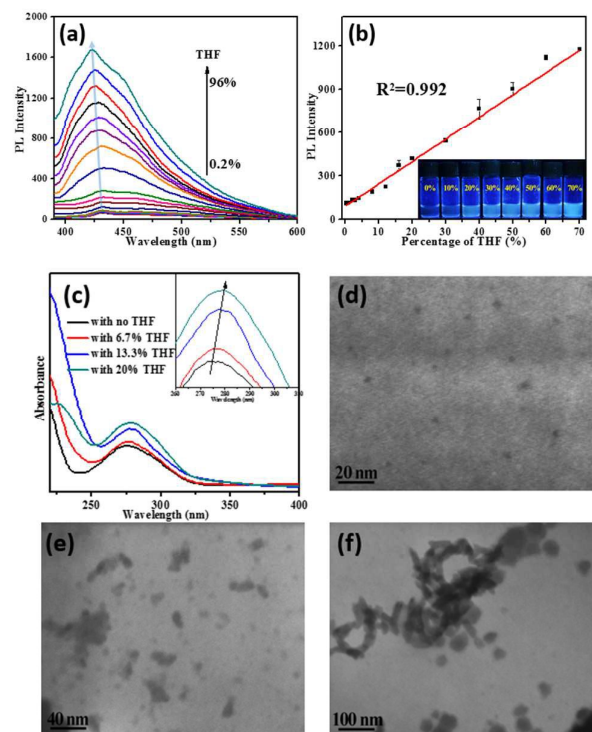


Fig.3 Aggregation features of TA-CDs in the presence of THF. (a) Emission spectra of TA-CDs with the increase of THF from 0.2% to 96%; (b) Linear dependence of AIEE intensity on the content of THF, and the inserted are the photos for TA-CDs with different content of THF taken under UV light; (c) absorption spectra, and the inserted shows the red shift of the characteristic band with increasing content of THF; (d)-(f) TEM of aggregated TA-CDs in the aqueous medium of 10%, 30% and 50% THF.

PL intensity ratio of TA-CDs in organic solvents with very small permittivity and in water is available, showing that the ratio is mainly depends on the second item in equation (1) and the TA-CDs thus could be applied for highly sensitive sensing of very small permittivity (Fig.2b). Solvents with smaller permittivity than THF was also considered, but because of steric hindrance effect, aggregation ratio of TA-CDs could not increase any more. So the PL do not enhance where permittivity of solvents is smaller than THF (Fig.S11, ESI†). It worth to be mentioned that PL of TA-CDs did not enhance in benzene solution because of high symmetry and electric neutrality. It can be easily understood that the charge on the surface of the as-prepared TA-CDs was screened by the solvent partly when the TA-CDs dispersed in different solvents, since the solvent with lower permittivity show weaker ability of screening charge<sup>20</sup>. Thus the solvents with low permittivity, as a result of charge interaction, make TA-CDs aggregated to different degrees depending on the permittivity of the solvents.

The strong emission of the as-prepared TA-CDs in organic solvents with low permittivity should have to be ascribed the nanoparticles aggregation-induced emission enhancement (NPs-AIEE) effect, the same as our previous reports<sup>9</sup>. For example, THF-induced aggregation of TA-CDs (Movie S1, the AIEE of TA-CDs with increasing THF in water) stands out

Table 1 Rate constants of CDs in aqueous solution and 80% THF solution.

	In aqueous solution	In 80% THF solution
$\phi\%$	7.16	42.65
$\tau/\text{ns}$	1.85	1.21
$k_r/10^6\text{s}^{-1}$	38.7	352.5
$k_{nr}/10^8\text{s}^{-1}$	5.02	4.74

Wherein  $\tau$  stands for the average lifetime of CDs measured with excitation wavelength of 375 nm and emission wavelength of 455 nm,  $\phi$  stands for the PL QY of TA-CDs using quinine sulfate as reference,  $k_r$  and  $k_{nr}$  refer to the radiative and non-radiative rate constant.

from all the tested organic solvents (Fig. 2a, Fig. 3a and Fig. 3b). With THF contents increased, the PL wavelength of TA-CDs in THF had a slight blue shift (Fig.3a), and the PL intensity of TA-CDs increased linearly ranging from 0.2% to 70% (Fig.3b), giving a linear fit of  $I=1.54\times 10^3 c+92.0$  with  $r^2=0.992$ , wherein  $I$  and  $c$  represent for PL intensity and content of THF in percentage of volume, respectively. Different from the blue shift of PL wavelength, the characteristic absorption band displays red shift with the increase of THF contents (Fig.3c).

The aggregation of TA-CDs in the presence of THF can be identified by observing the TEM images. It can be seen that the spherical TA-CDs with average size about 4.5 nm become into amorphous messes with the size of several hundreds of nanometers with the increase of THF (Fig. 3d, e and f and Fig.S12 a, b, c, d and e, ESI†). With the occurrence of aggregations in 80% THF solution, the lifetime of TA-CDs decreased from 1.85 ns to 1.21 ns (Table 1), while the quantum yields (QY) which indicate the PL efficiency get increased from 7.16% in water to 42.65%.

Owing to the change of QY and lifetime, the radiative rate constants raised from  $38.7\times 10^6\text{ s}^{-1}$  to  $352.5\times 10^6\text{ s}^{-1}$  and the non-radiative rate get decreased from  $5.02\times 10^8\text{ s}^{-1}$  to  $4.74\times 10^8\text{ s}^{-1}$  (Table 1, Table S3 and Fig.S13, ESI†). The increase of radiative rate and the decrease of non-radiative rate obviously make the enhancement of PL efficiency according to following equation<sup>7</sup>:

$$k_r = \frac{\phi}{\tau} \quad (2)$$

$$k_{nr} = \frac{1-\phi}{\tau} \quad (3)$$

Wherein  $k_r$  and  $k_{nr}$  refer to radiative and non-radiative rate constant, while  $\phi$  and  $\tau$  refers to the PL QY and lifetime, respectively.

The aggregation of TA-CDs in organic solvents with low permittivity makes the surface groups on TA-CDs, including aromatic rings and phenolic hydroxyl groups, as have been identified by (FTIR) (Fig.S6, ESI†), hampered, greatly enhanced the extent of  $\pi$ -conjugation and thus making the AIEE occurred. This process could be further identified by measuring the enhanced emission of TA-CDs in a medium containing glycerol (Fig. S14, ESI†), which makes the medium highly viscous. The greatly enhanced emissions of TA-CDs in viscous medium indicates that the rotation hindering of the surface groups on TA-CDs reduces the non-radiative decay,

and thus greatly improving photoluminescence efficiency. That is to say, AIEE of TA-CDs, just like fluorescent OSMS,<sup>21-23</sup> has really occurred because non-radiative decay is reduced during the aggregation of TA-CDs, and thus greatly enhancing photoluminescence (Scheme S1).

In summary, we have reported a simple and green route to synthesize water-soluble polymer-like CDs with a uniform size of 4.57 nm on a large scale through hydrothermal treatment of tannic acid in water, which shows AIEE effect owing to the rotation hindering of aromatic rings and phenolic hydroxyl groups on their surface. The mechanism of CDs-AIEE might be attributed to the reduction of non-radiative decay. This finding of organic solvents induced aggregation emission enhancement of carbon dots related to permittivity sensing is interesting and shows potential applications in the developments of designing new sensing devices.

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