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**Microwave assisted one-step green synthesis of cell-permeable multicolor photoluminescent carbon dots without surface passivation reagents†**Xiaohui Wang,<sup>ab</sup> Konggang Qu,<sup>ab</sup> Bailu Xu,<sup>ab</sup> Jinsong Ren<sup>a</sup> and Xiaogang Qu<sup>\*a</sup>

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**A facile, economic and green one-step microwave synthesis route towards photoluminescent carbon dots is proposed. The preparation requires a carbohydrate (glycerol, glycol, glucose, sucrose, etc.) and a tiny amount of an inorganic ion, and can finish in just a few minutes, no surface passivation reagent is needed. The carbon dots are biologically compatible and show favorable optical properties and have potential applications in biolabeling and bioimaging.**

Photoluminescent carbon dots have attracted growing interest in recent years due to their great potential in biological labeling, bioimaging, drug delivery and optoelectronic device applications.<sup>1–8</sup> Compared to luminescent semiconductor quantum dots, which have known toxicity and are potentially environmentally hazardous due to the contained heavy metals and chalcogens, carbon based photoluminescent nanomaterials are environmentally and biologically compatible.<sup>6–9</sup>

Currently, intensive research has been concentrated on the synthesis of these benign photoluminescent materials. Common routes in preparing fluorescent carbon nanoparticles include the high-energy ion beam radiation based creation of point defects in nanodiamond particles;<sup>1,6</sup> the covalent modification of nanodiamond particles with octadecylamine;<sup>10</sup> the oxidation of carbon nanotubes<sup>11</sup> or candle soot<sup>7,12</sup> with nitric acid; collecting nanoparticles in water from non-sooting regions of ethylene/air laminar flames;<sup>13</sup> the electrooxidation of carbon nanotubes<sup>14</sup> or graphite;<sup>9,15,16</sup> the laser ablation of graphite;<sup>3,4,8,17</sup> high temperature treatment of resols tethered on silica nanospheres;<sup>5</sup> the dehydration of carbohydrates by concentrated sulfuric acid to form carbonaceous materials;<sup>18</sup> the thermal oxidation of citrate acid and sodium 11-amino-undecanoate molecular precursors at 300 °C in air;<sup>19</sup> the microwave pyrolysis of glucose solution in PEG<sub>200N</sub> solution<sup>20</sup> and the laser irradiation of

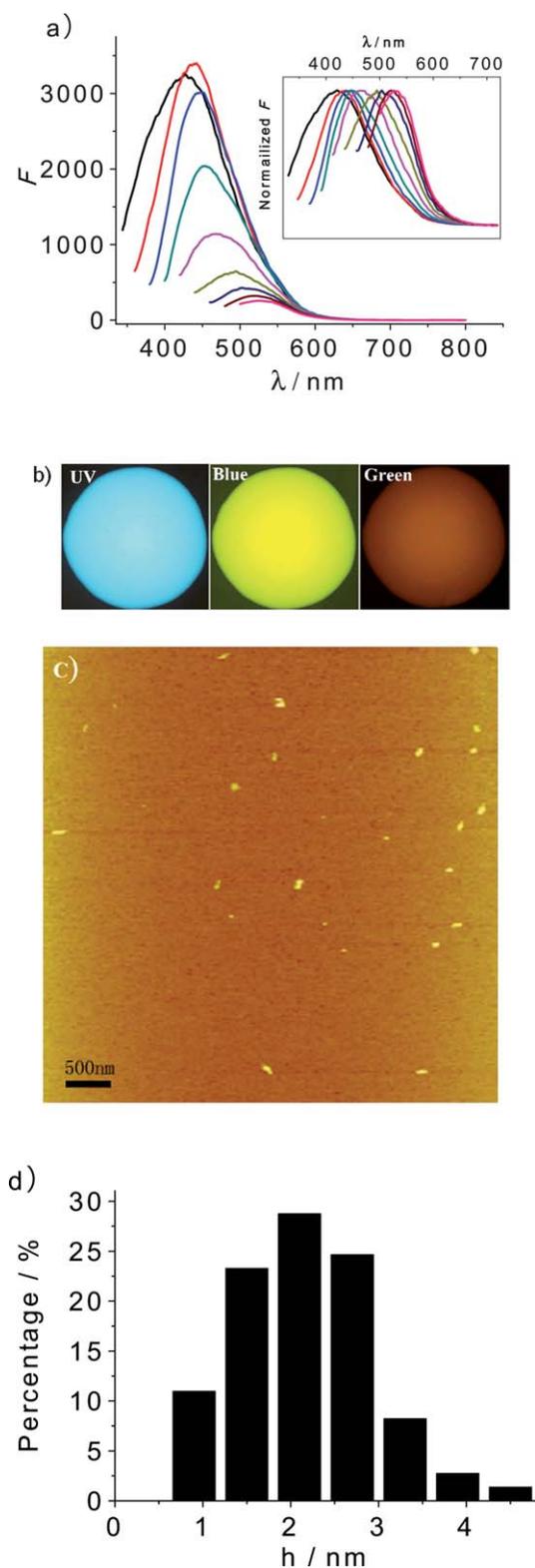
a suspension of graphite powders in PEG<sub>200N</sub> solvent.<sup>21</sup> Most of these methods require surface passivation reagents,<sup>3–5,8,17–21</sup> and the reported quantum yields for carbon nanoparticles without surface passivation are relatively low (~1%).<sup>7,9,11,12</sup> Additionally, these methods usually involve tedious processes,<sup>3–5,7,8,10,12,17,18</sup> expensive starting materials,<sup>1,6,10,11,14</sup> or harsh synthetic conditions,<sup>1,5,6,13,19</sup> which severely limit the availability of large quantities of the luminescent carbon nanomaterials for practical applications. Thus, the development of simple, cost-effective and environmentally friendly method for large scale synthesis of fluorescent carbon dots still remains challenging. Herein, we report a facile, economic and green one-step microwave synthesis route towards photoluminescent carbon dots. Our preparation requires a carbohydrate (glycerol, glycol, glucose, sucrose, etc.) and a tiny amount of an inorganic ion and can finish in just a few minutes. A characteristic feature of this method is that no surface passivation reagent is needed. Additionally, the photoluminescence intensity of the as-synthesized carbon dots do not change at the physiological and pathological pH range of 4.5–9.5 and show no photobleaching. Furthermore, these carbon dots enter into cells and can be used for photoluminescence-based cell-imaging applications.

Carbohydrates have been widely used to produce carbon materials owing to their sustainability,<sup>18,20,22–28</sup> but few of these materials show strong photoluminescence.<sup>18,20</sup> Glycerol (70% (v/v)) was mixed with 7.1 mM phosphate solution (pH 7.4) and heated in a domestic microwave oven (750 W) for 14 min. As shown in Fig. 1a, the emission spectra of the as prepared carbon dots were broad, ranging from ~430 (blue) to ~525 nm (yellow), with a dependence on the excitation wavelengths; the carbon dots exhibited blue, yellow and red photoluminescence under ultraviolet (330–385 nm), blue (450–480 nm) and green (510–550 nm) light excitation (Fig. 1b). AFM was used to observe the formed carbon dots and showed the carbon dots have height around  $2.1 \pm 0.76$  nm (Fig. 1c and 1d). It should be noted that pure glycerol solution after being treated with 20 min microwave remained clear and no apparent photoluminescence was observed. Since neither glycerol nor phosphate is emissive in the visible and near-UV range, the bright and colorful photoluminescence emission must therefore be attributed to the formed carbon dots. A typical luminescence lifetime ( $\tau$ ) was also measured (Figure S1, ESI†), where a value of  $8.00 \pm 0.07$  ns was obtained. FT-IR spectra (Fig. 2a) were used to identify the functional groups present on carbon dots. New bands at 1743 and 1597  $\text{cm}^{-1}$  were attributed to carboxyl groups and aromatic C=C vibrations,

<sup>a</sup>Laboratory of Chemical Biology, Division of Biological Inorganic Chemistry, State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin, 130022, China. E-mail: xqu@ciac.jl.cn; Fax: +86-431-85226266

<sup>b</sup>Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences, Changchun, Jilin, 130022, China

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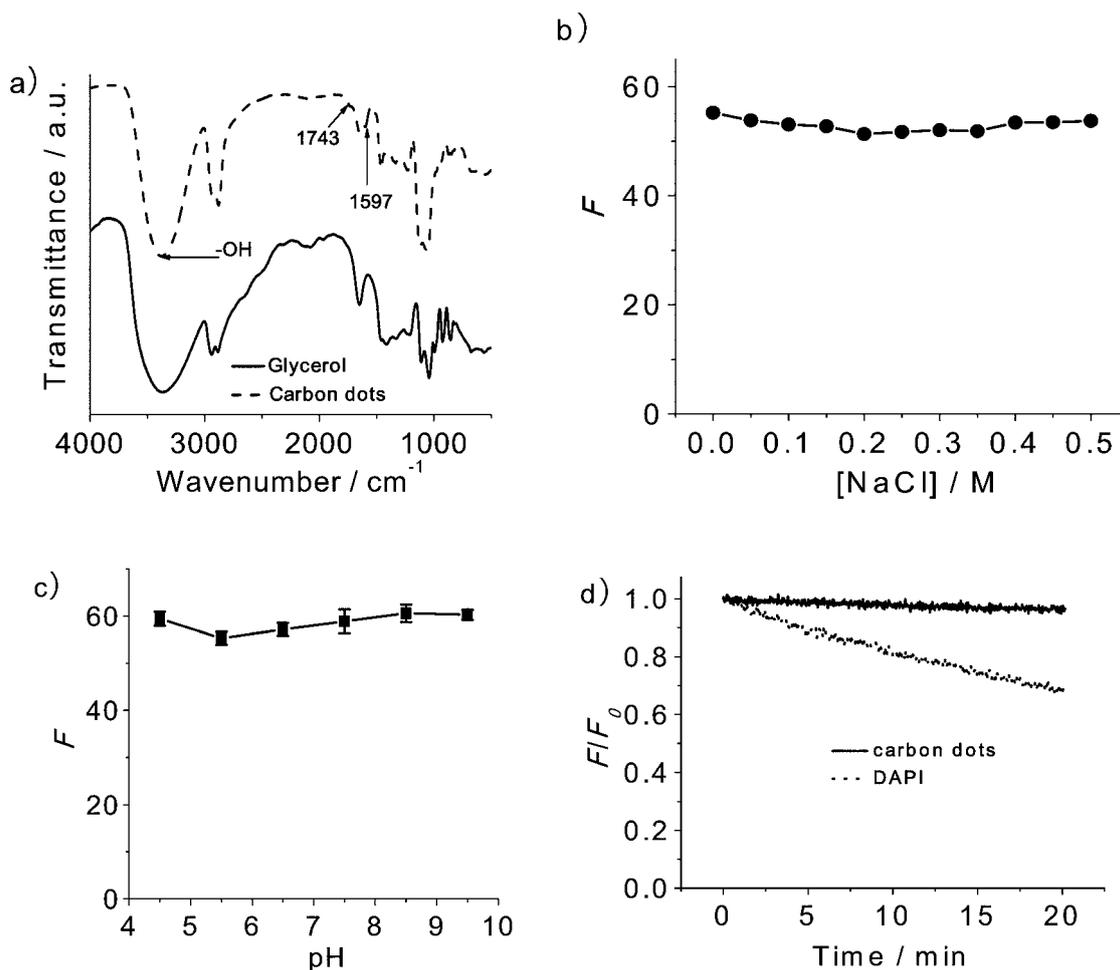


**Fig. 1** (a) Photoluminescence emission spectra (with progressively longer excitation wavelengths from 320 nm to 480 nm in 20 nm increments) of carbon dots (microwave pyrolysis condition: 70% glycerol, 7.1 mM phosphate, 14 min). In the inset, the emission spectral intensities are normalized. (b) Photoluminescence photographs of carbon dots in water under ultraviolet (330–385 nm), blue (450–480 nm) and green (510–550 nm) light excitation; the picture was taken by an Olympus BX-51

respectively. The presence of carboxyl groups offers various surface modifications for potential applications in drug delivery and biomedical imaging. The broad and intense peak centered at  $3370\text{ cm}^{-1}$ , and the bands in the range of  $1000\text{--}1300\text{ cm}^{-1}$  which include the C–OH stretching and –OH bending vibrations imply the existence of large numbers of residual hydroxyl groups. These functional groups improve the hydrophilicity and stability of the carbon dots in aqueous systems. As shown in Fig. 2b, the photoluminescence intensity of carbon dots did not change with ion strength, indicating that the carbon dot aqueous solution was stable. Unlike the carbon dots reported by Liu *et al.*<sup>12</sup> and Zhao *et al.*,<sup>9</sup> the photoluminescence intensity of the carbon dots synthesized here is pH independent at the physiological and pathological pH range of 4.5–9.5 (Fig. 2c). Additionally, the carbon dots show excellent photostability, as the photoluminescence intensity did not change even after continuous excitation with a 150 W Xe lamp (Fig. 2d). Moreover, the inhomogeneity of the photoluminescence of the carbon dots can be exploited for optical labeling to allow the selection of different emission colors with different excitation wavelengths.<sup>17</sup> All these features make carbon dots good candidates for biological labeling, bioimaging or other biomedical applications. Photoluminescence microscopic observation (Figure S2, ESI<sup>†</sup>) showed that the carbon dots could readily enter into *E. coli* and 293T cells and be used for biolabeling and bioimaging.

To elucidate the factors influencing carbon dots formation, the effect of microwave time was firstly investigated. As shown in Figure S3a (ESI<sup>†</sup>) with the increase in microwave treatment time, the glycerol solution turned brown and the UV-visible absorption peak at around 260 nm of the resulting carbon dots shifted to shorter wavelengths (4 min, 265.5 nm → 14 min, 253.5 nm). AFM analysis showed the mean height of carbon dots synthesized after 7 min and 14 min microwave treatment was  $1.1 \pm 0.42\text{ nm}$  (Figure S4, ESI<sup>†</sup>) and  $2.1 \pm 0.76\text{ nm}$  (Fig. 1c and Figure 1d), respectively. As indicated in Figure S3b (ESI<sup>†</sup>) the photoluminescence of the glycerol solution increased with reaction time, but the normalized photoluminescence emission spectra could be almost superposed and no apparent quantum confinement effect was observed. These results indicate that the photoluminescence is most likely to result from the dot surface, where emissive energy trap sites are located.<sup>5,17,20,21</sup> In contrast to previous reported methods,<sup>3–5,8,17–21</sup> no surface passivation agents and passivation steps are incorporated in this green microwave synthesis route. Through microwave pyrolysis, the carbohydrate is carbonized which results in the formation of carbon dots; meanwhile, their surfaces have oligosaccharide and aliphatic chains due to the partial dehydration and condensation of the carbohydrate.<sup>25,29</sup> These functional groups stabilize the surface energy traps and make them emissive. As shown in Figure S5 (ESI<sup>†</sup>) in contrast to photoluminescence intensity, which monotonically increased with microwave time, the relative quantum yield of carbon dots firstly increased with increasing of reaction time and then significantly decreased. This result indicated that the carbon dots have strong photoluminescence only when they are small enough, which is consistent with previous studies.<sup>7,12,17</sup>

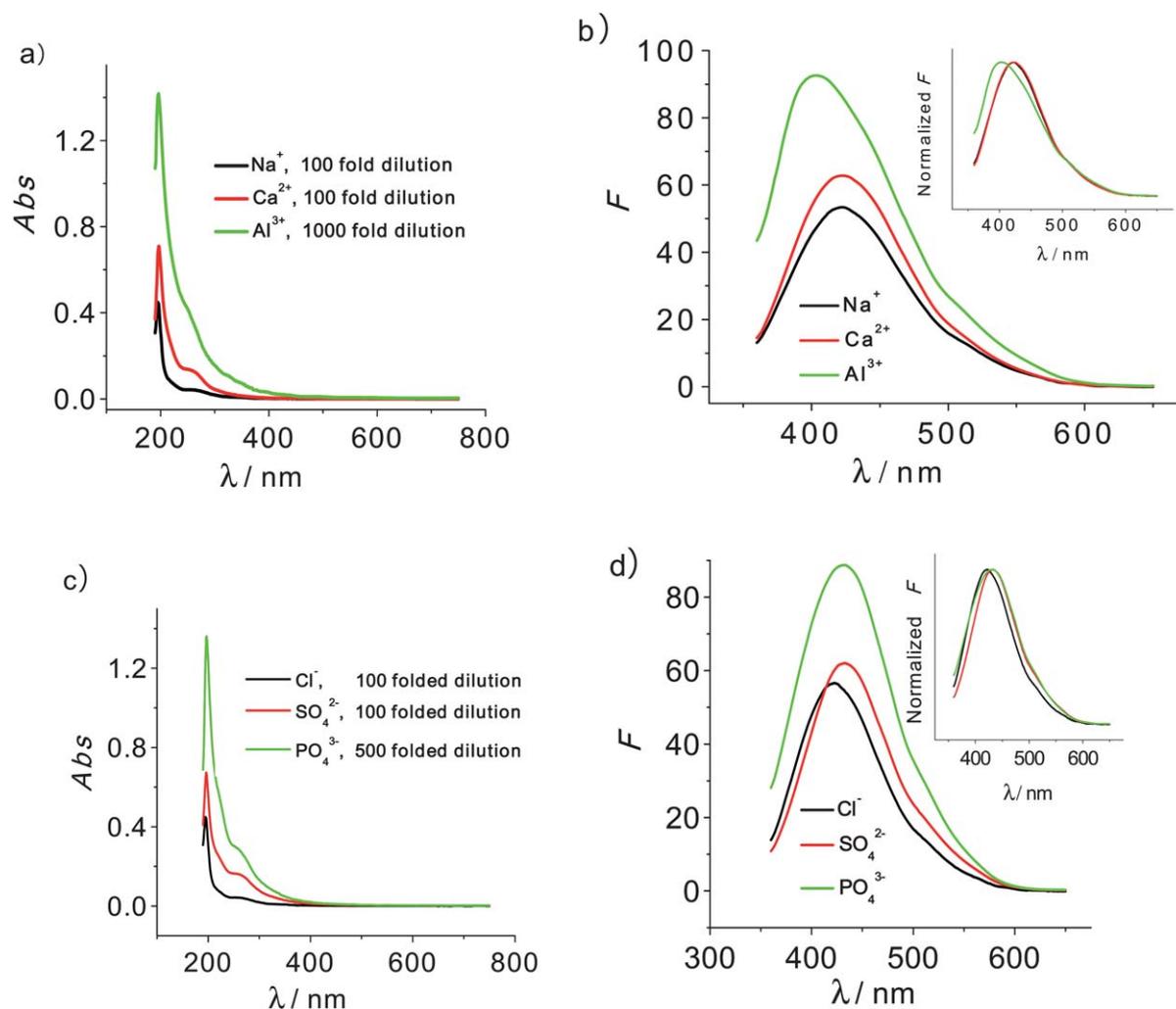
optical system microscope (Tokyo, Japan). (c, d) AFM characterization of the as prepared carbon dots.



**Fig. 2** (a) FT-IR spectra of glycerol and carbon dots. (b) Effect of salt concentration on the photoluminescence intensity at 450 nm ( $\lambda_{\text{ex}} = 360$  nm) of the carbon dots. (c) Effect of pH on the photoluminescence intensity at 450 nm ( $\lambda_{\text{ex}} = 360$  nm) of carbon dots. At pH 4.5, 5.5 and 6.5, the 10 mM phosphate buffer was used while at pH 7.5, 8.5 and 9.5, 10 mM Tris buffer was chosen. All the values are the average of triplicate measurements. (d) The time-dependence of photoluminescence intensity at 450 nm ( $\lambda_{\text{ex}} = 360$  nm) of carbon dots and a commercial dye 4',6-diamidino-2-phenylindole (DAPI).

Inorganic ions have been demonstrated to effectively accelerate the carbonization of carbohydrates.<sup>24,30</sup> Therefore, we subsequently examined the role of inorganic ions in carbon dots formation. As shown in Figure S6 (ESI†) with the increase of phosphate salt, the absorption band at around 260 nm of the carbon dots' bathochromic shift decreases (7.1 mM, 262 nm  $\rightarrow$  35.7 mM, 254 nm). Meanwhile, as indicated in Figure S7 (ESI†) the photoluminescence intensity and quantum yield of the produced carbon dots increased with reaction time, but the photoluminescence emission peaks only slightly red shifted (7.1 mM, 440 nm  $\rightarrow$  35.7 mM, 450 nm). By selecting quinine sulfate as the standard, the photoluminescence quantum yield for the carbon dots synthesized by 70% glycerol in the presence of 35.7 mM phosphate salt with 12 min of microwave treatment was measured and calculated to be 3.2%. The results indicate that the phosphate salt catalyzes the carbon dots formation. Though the amount of phosphate salt affects the formation rate and quantum yield of carbon dots, it does not significantly affect the photoluminescence characteristic of the carbon dots.

We also systematically investigated the effect of different valence cations and anions on the carbon dots formation. As shown in Fig. 3, both the formation rate and quantum yield of carbon dots increased with the increasing valence of the cation or anion. Compared to monovalent ions, divalent and trivalent ions show much greater ability to catalyze carbohydrate carbonization and carbon dot formation. The photoluminescence emission peak of the carbon dots blue shifts with the increase in valence of the cation, while it slightly red shifts with the increasing of valence of anions. As expected, we found that carbon dots catalyzed by both divalent cation and divalent anion ( $\text{CuSO}_4$ ) catalysts show very strong fluorescence (Figure S8, ESI†) and the quantum yield was calculated to be 9.5%, which is much higher than that of reported carbon dots without surface passivation,<sup>7,9,11,12</sup> and is comparable to that of previous reported ligand protected carbon dots.<sup>5,17-21</sup> It has been known that  $\text{H}^+$  catalyzes carbohydrate carbonization.<sup>24,31</sup> As shown in Figure S9 (ESI†)  $\text{H}^+$  can also catalyze carbohydrate to form carbon dots, and a dose and time dependence was observed (Figure S10, ESI†).



**Fig. 3** Absorption spectra (a, c) and photoluminescence emission spectra excited at 340 nm (b, d) of carbon dots synthesized from 70% glycerol in the presence of 10 mM different valence cations (a, b) or anions (c, d) with 15 min microwave pyrolysis. The samples are diluted with water and recorded on a spectrometer or fluorescence spectrometer. It should be noted that photoluminescence emission spectra (b, d) have been normalized to the absorbance at 340 nm. The insets show the normalized photoluminescence emission spectra.

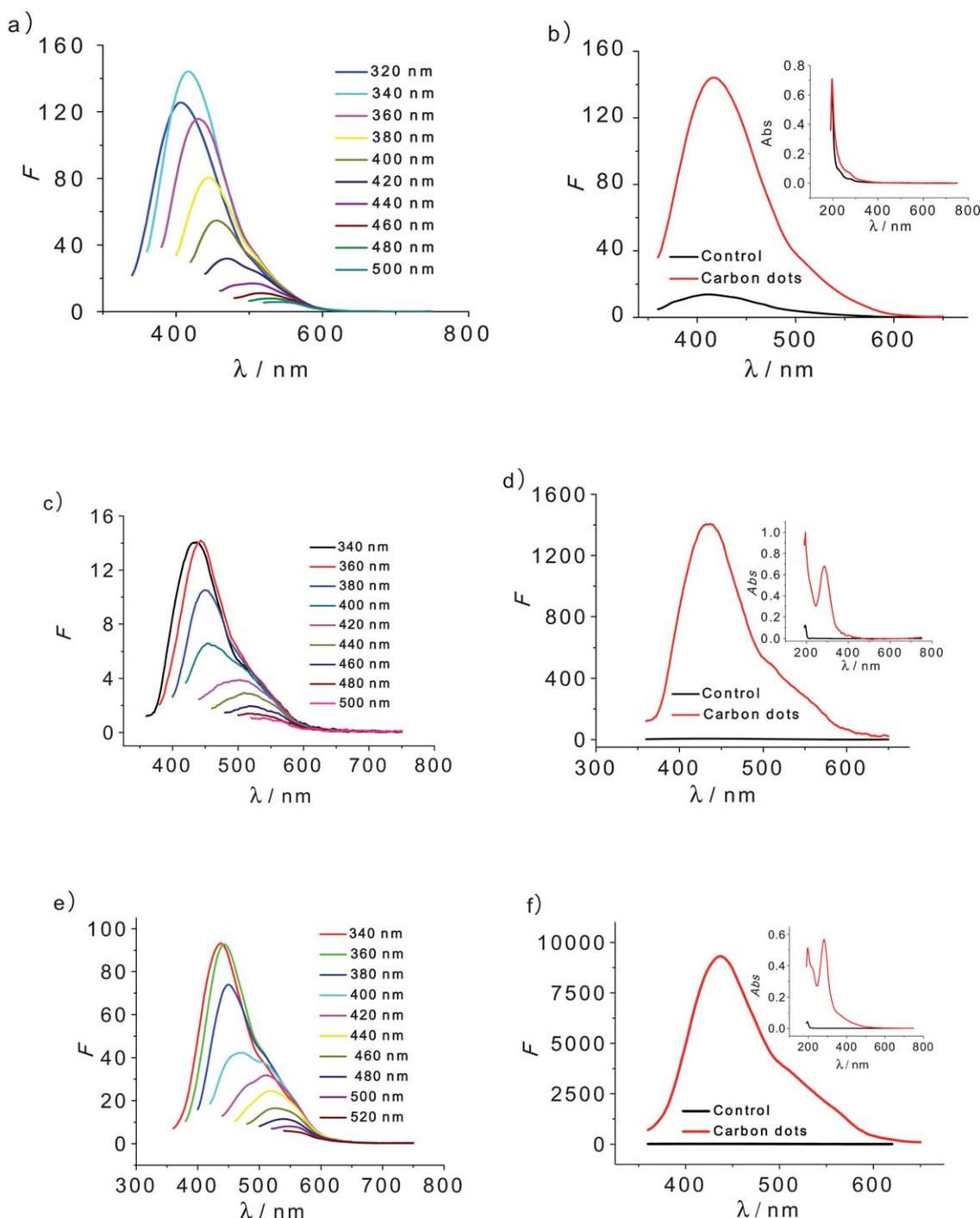
To investigate whether this microwave assisted photoluminescent dots synthesis can be applicable to other systems, we also used glycol, glucose and sucrose as the starting carbohydrate. As indicated in Fig. 4, similar to carbon dots synthesized from the glycerol, the carbon dots prepared from glycol, glucose or sucrose luminesce and their emissions depended on the excitation energy. The quantum yield for these carbon dots varied with the starting carbohydrate material and that for carbon dots synthesized from 70% glycol in the presence of 10 mM  $\text{AlCl}_3$  with 14 min microwave treatment was 5.8%. In parallel control experiments, where no inorganic ions were added, no apparent photoluminescence was observed. Together, these results demonstrate that this microwave assisted carbon dot synthesis method has generality. The influence of the starting materials on the luminescence characteristics of carbon dots was also investigated. The results in Figure S11 (ESI<sup>†</sup>) show that photoluminescence spectrum of carbon dots derived from glycol significantly blue shift compared to those of carbon dots derived from glucose, glycerol and sucrose and indicated that different starting materials resulted in the carbon dots with different photoluminescence. Thus, it is possible to tune the

luminescence from the carbon dots by changing the starting materials.

In summary, we have developed a general and simple microwave synthesis method to produce multicolor photoluminescent carbon dots. In comparison to the previous reported synthesis methods, three features become apparent: 1) our approach does not need surface passivation reagents; 2) the synthetic approach utilizes carbohydrate as the starting materials and is a green method; 3) the carbon dots synthesis is kitchen chemistry and does not involve special equipment and harsh synthesis conditions. As the synthesized carbon dots are biologically compatible and show favorable optical properties, they are promising imaging agents in biomedical and imaging applications.

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**Fig. 4** Photoluminescence emission spectra of carbon dots produced from different carbohydrate sources. Microwave pyrolysis conditions: (a, b) 70% glycol, 10 mM  $\text{AlCl}_3$ , 14 min; (c, d) 20% glucose, 10 mM phosphate, 4 min; (e, f) 20% sucrose, 10 mM phosphate, 4 min. Insets show the UV-visible absorption spectra of the corresponding carbon dots. Control represents the product of carbohydrate treated with the same procedure, but without the addition of salt.

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