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Supporting Information

Kinetics of nitrogen-doped carbon dot formation via hydrothermal synthesis

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SI-1. Experimental apparatus

This apparatus is designed in such a way that sampling tube mounted on reactor withdraws the liquid samples by the internal pressure expeditiously.

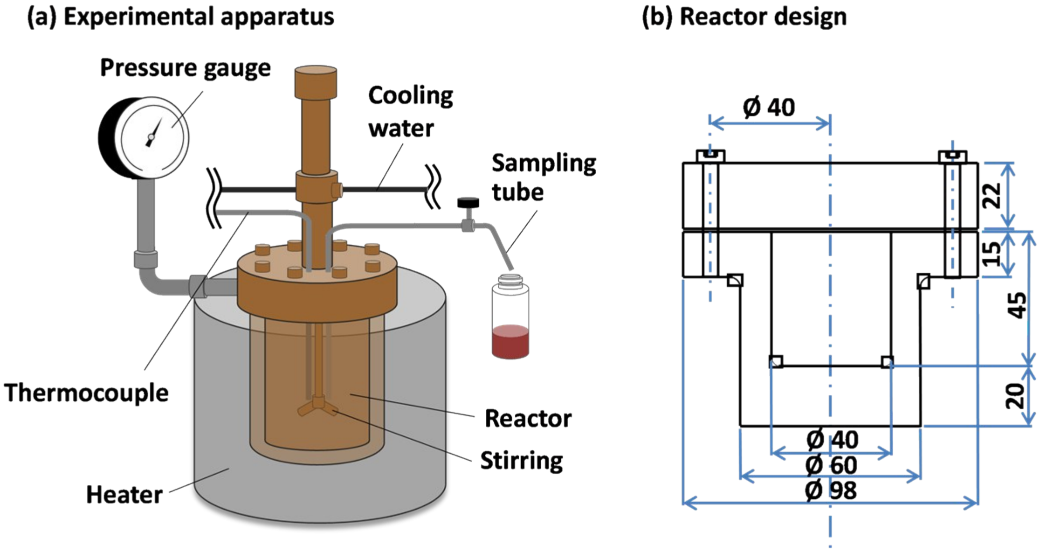

Fig. S1 Developed experimental apparatus for hydrothermal reaction. (a) Experimental apparatus, (b) Reactor design. A PTFE liner was used inside autoclave reactor.

SI-2. Effect of precursor concentrations on the optical properties of N-CDs

Seve N-CDs samples were prepared using different precursor concentrations of 0.0254, 0.0508, 0.0763, 0.127, 0.254, 0.763, and 1.27 mol/L with the same composition ratio of citric acid and urea (Table SI2-1). The time course of the reaction at each initial concentration was monitored by PL and PLE, as displayed in Fig. SI2-1. After 60 min of reaction, the emission intensity increases with the initial concentration (Fig. SI2-1 (a)). This is because the nucleation of luminescent species (CDs) was promoted at high precursor concentration. After reaction for 90 min (Fig. SI2-1 (c)), emission intensities of all samples were much higher than those of the corresponding samples reacted for 60 min. In addition, higher initial concentration gave increased emission intensities except for the sample with a precursor concentration of 1.27 mol L^{-1}. After 90 min, citric acid and urea reacted to generate many nanocrystalline N-CDs species in the solution, causing emission intensity to increase. The decrease in emission intensity observed for the highest precursor concentration of 1.27 mol L^{-1} was attributed to the generation of large N-CDs; that is, condensation of citric acid amide to form nanoparticles. A decrease in N-CDs concentration for this sample is also confirmed from the peak position and shape of PL and PLE spectra. The emission peak position of the sample prepared with a precursor concentration of 1.27 mol L^{-1} is shifted to higher wavelength and the shape of its excitation spectrum changed drastically compared with that of the other samples. This phenomenon is explained below. After 120 min of reaction (Fig. SI2-1 (e)), the emission intensities of samples prepared using precursor concentrations of 0.0763 and 0.127 mol L^{-1} increased and those of samples prepared using precursor concentrations of 0.763 and 1.27 mol L^{-1} decreased compared with the corresponding samples reacted for 90 min.

The PLE spectra of samples prepared by reaction for 60, 90, and 120 min are presented in Fig. SI2-1 (b,d,f), respectively. The changes of PLE intensities show almost the same trend as that of the PL spectra. However, it should be noted that the shape of PLE spectra obviously changed with reaction time (compare spectra in Fig. SI2-1 (d) and (f)). Comparing spectra obtained for samples reacted for 90 and 120 min, peak shapes are clearly changed from a single peak to double peaks over precursor concentrations of 0.763 and 0.127 mol L^{-1}, respectively. This change of PLE spectra corresponds to the change of molecular structure of CDs in the solutions. Interestingly, this change of PLE spectrum is obviously correlated with the PL intensity. When the double peaks appeared, PL intensity decreased markedly, indicating that a luminescent species (molecular structure) responsible for high emission intensity exists until double peaks appear in the PLE spectra.

Table SI2-1 Precursor concentrations of the synthesized samples.

Concentration [mol/L]	**Urea [g]**	**Citric acid [g]**	**UPW [ml]**
0.0254	**0.150**	**0.008**	**100**
0.0508	**0.300**	**0.016**	**100**
0.0763	**0.451**	**0.024**	**100**
0.127	**0.751**	**0.041**	**100**
0.254	**1.502**	**0.081**	**100**
0.763	**4.505**	**0.243**	**100**
1.27	**7.508**	**0.405**	**100**

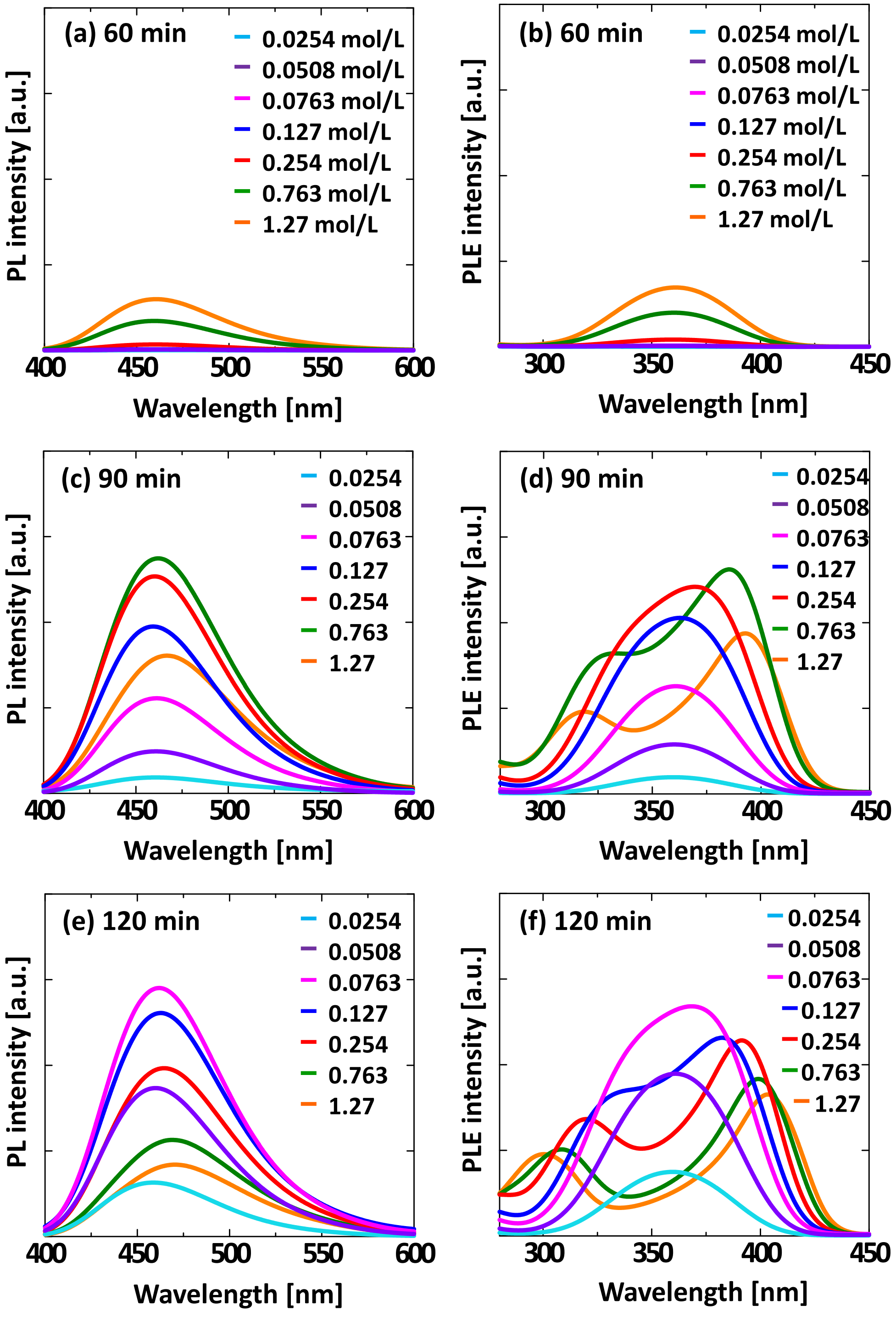

Fig. SI2-1 Effect of initial concentration of the precursor solution on the PL and PLE spectra of N-CDs; (a)(c)(e) PL spectra under excitation at 365 nm, (b)(d)(f) PLE spectra under excitation at 460 nm. Heating rate, 1.6 °C min^{-1}.

Fig. SI2-2 (a) plots the time courses of emission intensity and solution temperature as functions of precursor concentration. The emission intensity increased rapidly as the reaction time lengthened until it reached the maximum PL intensity, after which the peak intensity decreased for all precursor concentrations. The solution temperature at which maximum emission intensity was attained ranged from 146 to 166°C. This result reveals that there is an optimal reaction time and temperature to produce highly fluorescent N-CDs even if the precursor concentration is changed.

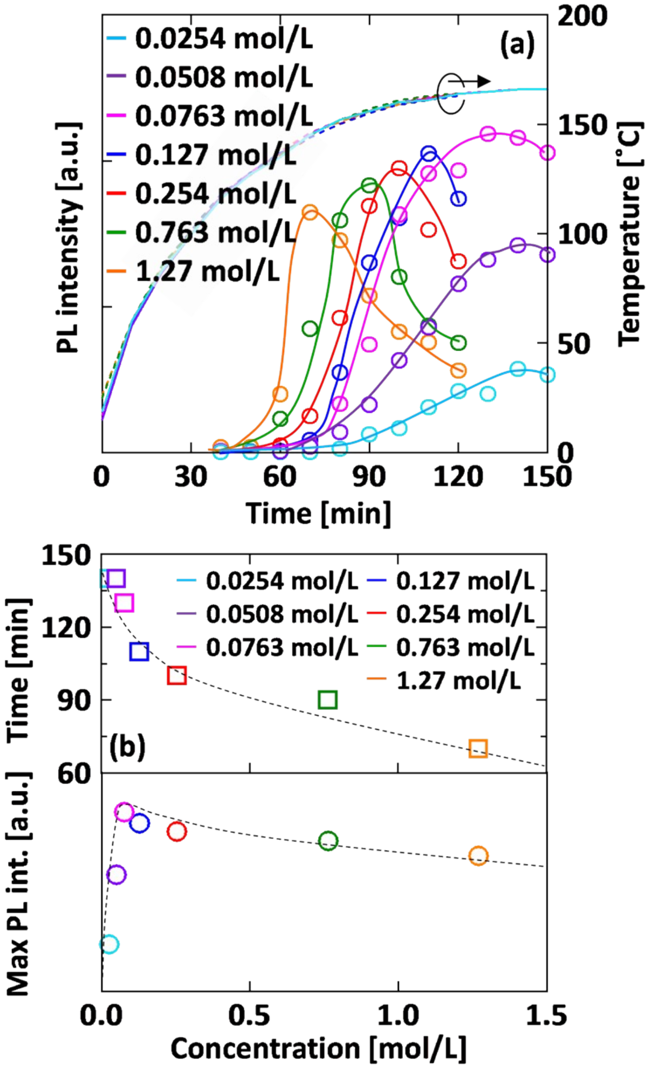

Fig. SI2-2 Time courses of emission properties as functions of reaction time and precursor concentration; (a) PL intensity, (b) maximum PL intensity and reaction time to obtain maximum PL intensity. Heating rate, 1.6 °C min^{-1}.

Fig. SI2-2 (b) shows the correlations between the precursor concentration and maximum PL intensity and the required reaction time to obtain highest PL intensity. The reaction time needed to achieve maximum PL intensity is longer at lower precursor concentration, and the highest PL intensity was obtained for the sample prepared using a precursor concentration of 0.0763 mol L^{-1}. This is because the reaction rate of citric acid and urea is quite slow when their initial concentrations are low (0.0508 and 0.0254 mol L^{-1}). As result, the maximum PL intensities are lower because of the lack of the luminescent species (N-CDs).

Table SI2-2 shows the QYs and absorption ratios of the samples with the highest PL intensity for each precursor concentration. The maximum QY of 39.7% was obtained for the N-CD sample prepared using a precursor concentration of 0.0763 mol L^{-1}. This is a 7% increase compared with that of the sample reported in our previous paper (*RSC Adv.*, 2014, 4, 55709.).

Table SI2-2 QYs and absorption ratios of samples prepared using different precursor concentrations

Concentration [mol/L]	**QY [%]**	**Abs. [%]**
0.0254	**39.4**	**87.5**
0.0508	**38.4**	**95.9**
0.0763	**39.7**	**96.2**
0.127	**33.8**	**96.2**
0.254	**32.6**	**96.8**
0.763	**29.9**	**97.2**
1.27	**30.7**	**97.6**

SI-3 Kinetics analysis for N-CDs generation (5.0˚C min^{-1} of heating rate)

The reaction of N-CDs generation is first order reaction, so the following equations were used.

$$t = C_{CA0}\int_{0}^{x_{CA}} \frac{dx_{CA}}{-r(x_{CA})} = -\frac{1}{k}\ln\left(1 - x_{CA}\right) \qquad (ES1)$$

Here, *t* is the reaction time [min], *k* is the reaction rate constant [min^{-1}] and x_{CA} is the reaction rate of citric acid [-]. The reaction rates from 130 to 160°C were used in the calculation, and x_{CA} = 1−(0.2/4) = 0.95 from Table 2. In the case of a heating rate of 2.0 °C min^{-1}, *t* = −1/0.095ln(1−0.95) = 31.5 min = 0.525 h. Therefore, the required reactor volume is 0.525 m^3 (=525 L).

In addition, *k* for a reaction rate of 5.0 °C min^{-1} was calculated by the same procedure using the following equations.

$$t = -0.0003T^2 + 0.24T - 2.5 \qquad (ES2)$$

$$r = -\frac{dC_{CA}}{dt} = -\frac{dC_{CA}}{(-0.0006T + 0.24)dT} = kC_{CA} \qquad (ES3)$$

$$lnC_{CA} = -k\left\{-0.0003\left(T^2 - T_0^2\right) + 0.24\left(T - T_0\right)\right\} + lnC_{CA0} \quad (ES4)$$

Here, *k* was calculated as the gradient of a slope obtained by plotting the values of lnC_{CA} and {−0.0003(T^2−T_0^2)+0.24(T−T_0)} in equation (ES4). Table SI3 shows the concentration of citric acid and the calculated values for each solution temperature. Fig. SI3 depicts the plots, in which X' indicates {−0.0003(T^2−T_0^2)+0.24(T−T_0)} of equation (ES4). The graph was a straight line, confirming that N-CDs generation was a first-order reaction. The gradient of the graph revealed that *k* was 0.634 min^{-1}. In the case of a heating rate of 5.0 °C min^{-1}, *t* = −1/0.634ln(1−0.95) = 4.72 min = 0.079 h. Therefore, the required reactor volume is 0.079 m^3 (=79 L).

Table SI3. The concentration of citric acid (C_{CA}) and values of X' ({$-0.0003(T^2-T_0^2)+0.24(T-T_0)$}) at various solution temperatures.

Temp. **[˚C]**	**C_{CA}** **[mol/m^3]**	**lnC_{CA}** **[mol/m^3]**	**X'** **[-]**
130	**40**	**3.69**	**0.00**
140	**15**	**2.71**	**1.56**
150	**7.0**	**1.95**	**3.13**
160	**2.0**	**0.693**	**4.61**

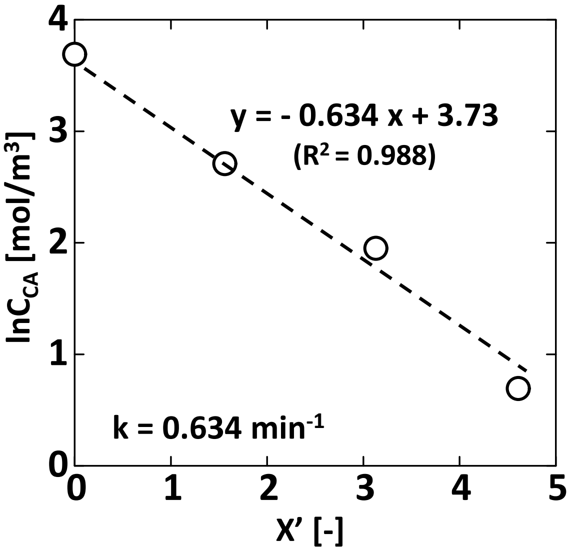

Fig. SI3. The plot results in case of 5.0˚C min^{-1} for the calculation of the reaction rate constant of N-CDs production reaction.

SI-4 Effects of solution temperature and reaction time on the N-CDs generation.

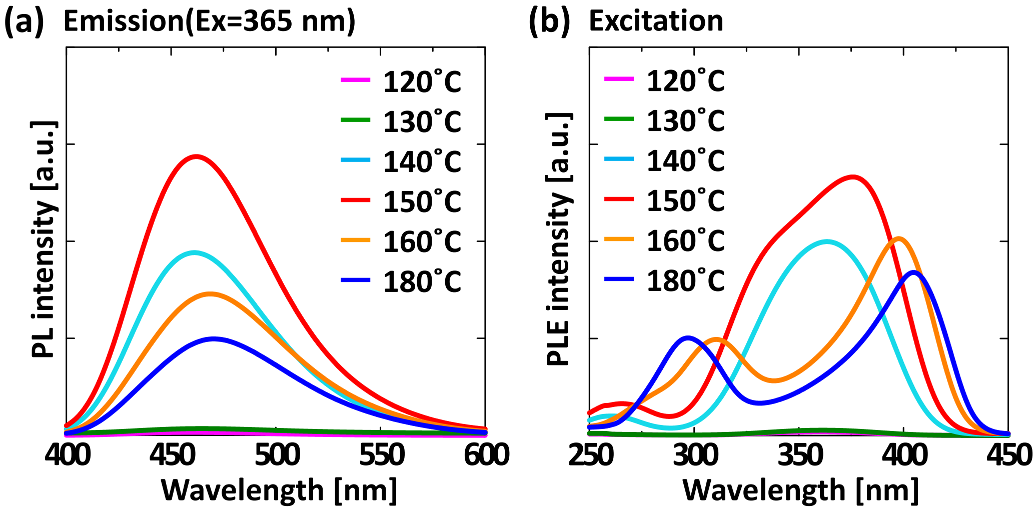

Fig. SI4 Effect of solution temperature on the emission properties of CDs; (a) PL spectra under excitation at 365 nm, (b) PLE spectra.