We report on the photoluminescent (PL) properties of carbon nanodots (CNDs) doped with nitrogen and sulfur obtained by the pyrolytic carbonization of amino acids as precursors. Prepared CNDs exhibit stable PL emission under a wide variety of aqueous conditions. The results also provided the way to tune a PL intensity of CNDs by varying the amount of heteroatoms in precursors with a binary mixture of amino acids. The PL quantum yields of the obtained CNDs were determined to be from 0.079 to 0.571.

**Keywords** Carbon nanodots, photoluminescence, carbonization, amino acids

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**Introduction**

Recently, photoluminescent nanocarbons, including carbon nanotubes, detonation diamonds1 and graphene quantum dots (GQDs),2 have received intensive attention concerning applications to analytical and biochemical research.3 As an alternative to organic fluorophores4 and toxic semiconductor quantum dots,5 luminescent nanocarbons are superior in terms of chemical inertness, environmental suitability and stable photoluminescence (PL). Among them, carbon nanodots (CNDs), which are generally obtained by relatively mild synthetic conditions and simple procedures, possess practical dispersibility in water owing to oxygenated functional groups on the surface. Utilizing the affinity between functional groups on the CNDs surface and analyte molecules or ions, CNDs-based PL sensing systems were reported for pH,6,7 ions8,9 and biological substances.10,11 In general, above-mentioned systems mainly depend on the change in the PL intensity of CNDs upon interaction with the target analyte. On the basis of photochemical processes, conventional response mechanisms, including electrochemiluminescence,12 fluorescence resonance energy transfer13,14 and inner filter effect,15 are also employed for CNDs-based sensing systems. Regardless of the response mechanisms, the PL intensity of CNDs is an influencing factor for improving the efficiencies and sensitivities of luminescence-based detection and determination. Therefore, it is highly desired to prepare CNDs with high PL intensity, i.e., PL quantum yield (QY), for developing effective sensing systems.

The PL properties of CNDs have been investigated since luminescent CNDs were first discovered during the purification of carbon nanotubes.16 CNDs have been mainly prepared by oxidative procedures for the treatment of various carbon sources, such as graphite,17 candle soot,18 and organic compounds.19 Several synthetic approaches20 were applied to tune the PL properties of CNDs by a post-treatment, such as chemical reduction,21 organosilane-functionalization,22 and electrochemical agitation.23 Among them, hydrothermal24 and microwave-assisted25 treatments of organic precursors, natural products26 and raw materials27 have been widely used to prepare CNDs. Although CNDs have become attractive as PL probes, the QY values of as-prepared CNDs are not very high (often less than 0.2; see Table S1, Supporting Information) in many cases. To overcome these difficulties, heteroatom-doping has been actively investigated, since it is considered to be the most promising candidate to dope nitrogen and sulfur into CNDs, resulting in improvements of the QY values.28,29

In this report, we focus on the effect of the elemental composition of nitrogen and sulfur in precursors on the PL properties and QY values of obtained CNDs. We used several amino acids as precursors for the preparation of CNDs doped with nitrogen and sulfur. Since the elemental composition of these amino acids is clearly defined, we expect that they and their mixtures our suitable precursors for preparing CNDs with a series of different doping levels of hetero atoms. Pyrolytic carbonization in an electronic furnace was employed as a low-cost and efficient method for the preparation of CNDs. Three kinds of amino acids—glycine, cysteine and glutamic acid—were used for precursors in this study. The PL properties of obtained CNDs were first confirmed regarding the linear relationship between the absorbance at the excitation maximum and the PL intensity at the emission maximum; then, QY values were determined. The PL emission stabilities of obtained CNDs were also examined concerning the effect of the pH, ionic strength and excitation wavelength in aqueous solutions.

**Experimental**

**Reagents**

Glycine (Sigma Aldrich, ≥99%), l-glutamic acid (Sigma Aldrich, ≥99.0%), and l-cysteine (Sigma Aldrich, 97.0%) were used as received. 2-Morpholinoethanesulfonic acid monohydrate...
The crude product was cooled to room temperature and then heated in an electric furnace at 250 °C for 2 h. After heating, the crude product was cooled to room temperature and then filtered. Suction filtration and centrifugal filtration were applied to the solution, and CND stock solutions were obtained. Hereafter, CNDs obtained from glycine, cysteine and glutamic acid were abbreviated as G-CND, C-CND and E-CND, respectively.

Apparatus
A Horiba Model D-54 pH meter equipped with a combination glass electrode (Horiba, 9611-10D), calibrated by standard buffer solutions (pH 12.45, 9.18, 6.86, 4.01, and 1.68 at 25°C), was used to determine the pH value. The UV-vis absorption and photoluminescence spectra were measured by a UV-vis spectrophotometer (JASCO, V-650) and a fluorescence spectrophotometer (JASCO, FP-8300), respectively, using 1.00 cm quartz cuvettes.

Pyrolytic synthesis of CNDs
The general procedure for the synthesis of CND was conducted as follows. Briefly, the precursor was dissolved in water and heated in an electric furnace at 250°C for 2 h. After heating, the crude product was cooled to room temperature and then dispersed in water. Suction filtration and centrifugal filtration were applied to the solution, and CND stock solutions were obtained. Hereafter, CNDs obtained from glycine, cysteine and glutamic acid were abbreviated as G-CND, C-CND and E-CND, respectively.

Spectral measurements of CNDs
Sample solutions for spectral measurements were prepared by diluting stock solutions of CNDs with water or appropriate buffer solutions. The concentrations of CNDs in the measurement samples were defined by the absorbance at the excitation maximum (λex, xxx denotes the excitation wavelength, which depends on the type of CNDs). Unless otherwise stated, λex were less than 0.05 for PL spectra measurements. The quantum yield of the CNDs were determined using quinine sulfate (Φ = 0.546 in 0.5 M H2SO4) as a standard. The effect of the sample conditions on the PL intensity were examined for pH values of from 2 to 11 or ionic strength up to 4.5 mol dm⁻³.

Results and Discussion

PL properties of CNDs from amino acids
The UV-vis absorption spectra of G-CND dispersed in water (Fig. 1, dotted lines) show absorption peaks (λabs) centered at 306 nm, which may be attributed to the n-π* transition of the C=O double bond. G-CNDs, also have emission (solid lines, λem) spectra, with symmetrical and featureless peaks, recognized at 390 nm. The linearity ranges between the absorbance at the excitation maximum and the PL intensity of the emission maximum is depicted in Fig. 1 inset. Under the optimum conditions, the PL intensity of CNDs (Supporting Information, Fig. S1 for C-CND, Fig. S2 for E-CND) exhibited linear relationships with the absorbance at the excitation maximum of at least A = 0.05.

Like most CNDs reported, the emission wavelength of the CNDs depends on the excitation wavelength, as shown in Fig. 2. Namely, with the increase of the excitation wavelength, the maximum emission band is shifted to longer wavelength and the peak intensity decreases. This kind of excitation-dependent PL behavior was frequently reported in the literature, and ascribed to the distribution of different emissive trap sites and the difference in the particle size of the CNDs.

The PL intensity of CNDs is strong and stable in a neutral pH range (Fig. S3) and in a wide range of ionic strengths (Fig. S4). In the acidic and basic pH region, both the excitation and emission intensity were altered, whereas the absorbance at the excitation wavelength remained essentially unchanged. The effect of the pH values can be presumptively understood in terms of the change in the surface charge owing to the protonation-deprotonation of surface functional groups.

Table 1 summarizes the elemental composition of precursor amino acids and the PL properties of obtained CNDs. Concerning the precursors, the absorption and PL wavelength of the CNDs were hardly affected; by contrast, the QY values were drastically varied. Heteroatom-doping on the CNDs has been actively pursued since they are considered to improve QY, owing to the synergistic effect of nitrogen-sulfur co-doping. Contrary to an expectation based on the effect of heteroatom-doping, C-CND with the highest N,S-content studied here showed the lowest QY value. The results described above indicate that the improvement in QY is not directly proportional on the N,S-content of the precursors.
CNDs, glycine-glutamic acid (abbreviated as G1–x-Ex system) may result in a negative synergistic effect, i.e., C-CND) may result in a negative synergistic effect, i.e., E-CND) effectively improves the QY values of the obtained CNDs. It was found that E-CND showed the highest QY with a series of molar fractions of glutamic acid (0 < x < 1) were used to synthesize CNDs. Figure 3 shows the QY values of the obtained CNDs and the molar fraction of glutamic acid in G1–x-Ex and C1–x-Ex systems. Increasing the molar fraction of glutamic acid up to approximately x = 0.5 resulted in an increase in the QY values of the G1–x-Ex system, but no further increase was observed up to x = 1.0, converging with the QY value of E-CND. As summarized in Tables S2 and S3, the molar fraction of glutamic acid increases, while the N-content of the G1–x-Ex system decreases. This dependency suggested that the enhancement in QY of nitrogen doping does not correlate to the amount of nitrogen; also ca. 10% of N-content is optimum for the G1–x-Ex system. A similar increase in the QY values was also observed for the C1–x-Ex system until x = 0.6, resulting in the QY value being at a maximum of 0.571, which exceeds that of E-CND. As a result, the maximum QY values in the C1–x-Ex system were found for both the N- and S-contents to be ca. 10% in the elemental composition of the precursors. Although the PL mechanisms and electronic properties of CNDs are not fully understood, it is frequently proposed that the PL of the CNDs can be attributed to the radiative recombination of electrons and holes trapped on the CDs surface. According to the literature, Dong et al. assumed an enhancement in the QY values of N,S-doped CNDs in two aspects. First, the doping of nitrogen to CNDs introduces new types of surface states, which are able to facilitate radiative recombinations, resulting in increases in the QY values. Second, the co-existence of sulfur together with nitrogen further enhances the effect of nitrogen atoms in doped CND through a cooperative effect. As shown in Fig. 3, the cooperative effect on QY is recognized for the C1–x-Ex system over the G1–x-Ex system.

Conclusions

In summary, nitrogen and sulfur co-doped CNDs have been prepared by the pyrolytic carbonization of amino acids and their binary mixtures as precursors. The obtained CNDs show stable and excitation-dependent PL emission with tunable PL QY depending on the elemental composition of precursors. Even though the exact mechanism and relationships are still unclear, it is reasonable to believe that the doping of nitrogen and sulfur can improve the QY values of CNDs, whose optimum content were revealed to be ca. 10% in precursors for the systems studied here. Further work on the extending synthetic scale and the direct elemental analysis of the prepared-CNDs in the present system is in progress in our laboratory to clarify the relationship between the elemental composition of the precursors and that of the resultant CNDs.

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Supporting Information

Detailed synthetic and treatment procedures for the preparation of CNDs, the method of quantum yield determination. Supplemental figures (Figs. S1 – S4) and tables (Tables S1 – S3). This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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