ABSTRACT: Carbon dots (CDs) exhibit chemical stability and low toxicity, so they are promising for biomedical and imaging applications. The quantum yield of the photoluminescence is typically 10−20%, which limits practical applications. We fabricate carbon dot-gold nanoparticle photonic crystals (CD-GNP PCs) and demonstrate enhanced photoluminescence intensity from the carbon dots using the photonic and plasmonic double-resonant effects. A severalfold enhancement was obtained compared to the neat CD. The method developed in this study provides a universal scheme to enhance light-emitting materials, which is promising for the development of ultrahigh molecular sensing and bioimaging techniques.

INTRODUCTION
Carbon dots (CDs) fabricated by hydrothermal\textsuperscript{1,2} and laser ablation\textsuperscript{3,4} methods have been widely used as light-emitting elements because of their tunable and broad-band characteristics.\textsuperscript{5−7} The photoluminescence (PL) quantum yield of CDs is typically a few tens of a percent\textsuperscript{8} and has improved up to 60%, very recently.\textsuperscript{9,10} Since the CDs show high chemical stability and low toxicity to biomolecules,\textsuperscript{11} in a similar fashion to gold, the enhancement of the PL intensity is highly demanding for molecular sensing, bioimaging, and imaging applications.\textsuperscript{12} Plasmons excited in gold nanoparticles (GNPs)\textsuperscript{13−15} and photonic crystals (PCs)\textsuperscript{16−18} are compatible with biological applications and promising for the amplification of light–matter interactions. Plasmons spatially confine and consequently amplify optical fields.\textsuperscript{13,19,20} Plasmonic optical fields have been applied to enhance PL from various chromophores.\textsuperscript{21,22} The PL can be enhanced in both excitation and radiation processes.\textsuperscript{21,22} GNP show a plasmon resonance of longer than 500 nm, while most chromophores can be excited by ultraviolet (UV) light.\textsuperscript{23} Hence, the plasmon excited in the GNP cannot be utilized to enhance the PL of the CDs in the excitation process. The light confinement capability of the PCs is ideal for this purpose because the resonance is tunable for the UV region by adjusting the size and periodicity of the PCs with various substances.\textsuperscript{17,18,26,27} To enhance the PL in both excitation and radiation processes, in this letter, we propose to utilize the resonance effect of the PCs and plasmon for the incident and radiation processes, respectively. This double-resonant scheme is ideal for excitation of the PL from the chromophores since most chromophores show absorption in the UV region. In this study, we fabricated the CD PCs and CD-GNP PCs by nanosphere lithography and an electron-beam-induced chemical reaction to amplify the PL from the CDs.

EXPERIMENTAL SECTION
The CD PCs and CD-GNP PCs were prepared by nanosphere lithography and electron-beam-induced chemical reactions. Schematic fabrication schemes in the cross-sectional view are depicted in Figure 1a,b. In Figure 1a, polystyrene (PS) nanospheres (diameter 372 and 500 nm) are self-assembled on a glass substrate. Then, the substrate is spin-coated with a poly(vinyl alcohol) (PVA) solution, and the PS nanospheres are dissolved using toluene to form honeycomb PVA PCs. As shown in Figure 1b, the CDs are prepared by irradiating the electron beam (acceleration voltage 15 kV; probe current <1 nA; electron dose 10 mC/cm\textsuperscript{2}) onto the PVA PCs using a scanning electron microscope (SEM, S-3400N; Hitachi). Then, the GNPs are prepared by depositing gold vapor on the CDs to form CD-GNP PCs. Figure 1c shows the top views of the fabricated PVA PCs in Figure 1a and CD-GNP PCs in Figure 1b. The formation of the CDs is identified by transmission electron microscopy (TEM), absorption spectroscopy, and Raman scattering spectroscopy, as previously reported.\textsuperscript{28} The morphology of the fabricated samples was examined by an SEM and an atomic force microscope. Scattering and PL

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properties of the samples were evaluated by dark-field optical microscopy (Ti-U; Nikon) and confocal optical microscopy, respectively. In the dark-field optical microscopy, the sample was illuminated through a dark-field condenser (NA = 0.8–0.95), and the scattered light was collected beneath the sample substrate by an objective lens (NA = 0.43). In the confocal microscopy, the sample was illuminated through an objective lens (NA = 0.85 or 1.3), and the PL from the sample was collected by the same objective. To excite the PL, a continuous wave (CW) laser (λ = 375 nm) was used. The PL was detected by either an avalanche photodiode (SPD-050-CTE; Micro Photon Devices) for the single-channel measurement or a charge-coupled device detector (CCD, DU-420-OE; Andor) equipped with a monochromator for the spectral measurement.

Electromagnetic simulations using the finite integration technique (FIT) and the finite element method (FEM) were carried out to reveal the optical properties of the sample and the plasmonic and PC resonant effects.29

RESULTS AND DISCUSSION

Characterizations of the CDs fabricated from the PVA film using electron-beam reactions are provided in the Supporting Information (Figure S1), and the important features are briefly described here. Size of the CDs is determined from TEM observation and is typically a few nm. A high-resolution TEM image shows lattice patterns ascribable to diffraction due to the graphene crystal. The absorption spectrum of the CDs shows a peak near 270 nm and the absorption extends to 400 nm. The peak is attributable to π−π* transition of the phenyl ring, and the tail observed in the long-wavelength side is ascribable to extension of π conjugation. The Raman spectrum of the CDs shows two vibrational bands near 1340 and 1590 cm⁻¹ assignable to D and G bands for carbon materials, respectively, and are typical observations for the CDs. PL quantum yield of the CD is about 6%.

Figure 2a,b shows the top and cross-sectional SEM images of the fabricated CD PCs using the PS nanosphere (diameter 372 nm). The images show that the holes are hexagonally ordered with a given distance and form periodic structures. The diameter of the hole is 275 ± 10 nm, the interhole distance is 50 nm, and the height is 210 nm. The hole diameter is smaller than that of the PS used in the fabrication. This result can be explained as follows. The thickness of the PVA polymer film (~210 nm) is less than the diameter of the PS sphere. The PS spheres are partly embedded in the PVA polymer film. Hence, the effective hole diameter is smaller than that of the PS sphere. The observed spatial pattern in Figure 2a is consistent with that in Figure 1c. This fact also supports the aforementioned formation mechanism of the hole. We similarly fabricated CDs from the PS spheres with a 500 nm diameter. In this case, the diameter of the hole, the interhole distance, and the height are 350, 60, and 360 nm, respectively. The fabricated PC region is larger than 3600 μm², as shown in the Supporting information (Figure S2).

We examined the optical properties of the fabricated CD PCs. Figure 3a shows the scattering spectra of the CD PCs with two different hole diameters. The diameters of black and red lines are 275 and 350 nm, respectively. The black line shows a resonant peak near 360 nm, and the red line shows a peak near 370 nm and a resonant-like shoulder near 470 nm. The size dependency of the scattering spectrum indicates that the resonance wavelength red-shifts with the increase in the hole diameter. To reveal the physical origin of the observed
spectral features in Figure 3a, we carried out the spectral simulation using the FEM method.

Figure 3b shows the simulated scattering spectra of the CD PCs with various hole diameters \((d = 275, 350, \text{and} 450 \text{nm})\). The scattering spectrum for the smallest hole \((d = 275 \text{nm})\) shows a sharp peak near 370 nm, while those for the larger holes \((350, 450 \text{nm})\) show a sharp peak and a broad peak on the blue side. We found from the simulation that these peaks shifted toward red with the increase in the hole diameter. To reveal the physical origin of the sharp peak, we visualized the optical field distribution near the hole \((d = 275 \text{nm})\), as shown in Figure 3b. The optical field is effectively confined inside the hole and amplified several times, which implies that the resonance can be assigned to the lowest photonic mode. The observed peak near 370 nm and a broad resonant-like feature near 470 nm in Figure 3a can both be assigned to the lowest mode. Compared to the simulated spectra, the observed peaks are significantly broadened. The simulation reveals that the broadening originates from the size distribution of the holes, as shown in the Supporting Information (Figure S3).

To elucidate the effect of the photonic mode on the optical properties of the CDs, we examined the CD film and CD PCs of various hole sizes with excitation of 375 nm. Figure 3d shows the PL spectra for the CD thin film (thickness: 100 nm) and CD PCs \((d = 275 \text{nm})\). The PL intensity is proportional to the number density of the CDs and the thickness of the sample. We prepared the CDs for each film under identical conditions, and thus the concentrations of the CD are the same. In the figure, the PL intensity is normalized by the optical densities of the CDs, considering the geometrical difference between the samples. Both spectra show a broad PL centered at 520 nm. Note that the PL intensity of the CD PC is nearly 3 times higher than that of the film. We also found that PL intensity is the most intense for the CD PCs \((d = 275 \text{nm})\). This indicates that excitation probability of the PL is resonantly enhanced by the resonance of the PC. We also examined the PL from the same samples with the 532 nm excitation and found no enhancement in this case. The results support that the observed PL enhancement in Figure 3d originates from the resonant effect of the PC in the excitation process.

To enhance the PL in the excitation and radiation processes, we fabricated GNPs on the CD PCs. First, we examined the scattering properties of the fabricated CD-GNP PCs. Figure 4a shows the observed scattering spectrum of the sample with the simulated one. The observed scattering spectrum shows peaks near 370 and 470 nm, and an intense band in the long-wavelength region. The peak near 370 nm is attributed to the lowest PC mode. The intense band observed near 650 nm is attributed to a plasmon resonance excited in GNPs, as discussed below. Figure 4b shows a calculated optical field distribution near the hole illuminated with 650 nm radiation. In this sample, the top and bottom edges of the hole are covered with the nanometer-scale gold, which are called top and bottom GNPs hereafter, respectively. The optical field near the top GNP is more intense than at any other location and is responsible for the intense scattering in this spectral range. The maximum enhancement near the top GNP is more than 10 times that of the incident light, whereas the bottom GNP shows less enhancement. Figure 4c shows the PL spectra of the CD PCs and CD-GNP PCs. Both spectra show a broad PL band center near 500 nm, while the peak for the CD-GNP PCs is slightly red-shifted compared with that for the CD PCs. In addition, the PL intensity for the CD-GNP PCs is 1.6 times stronger than that for the CD PCs. The number density of the CDs for these samples is identical, so the intense PL for the CD-GNP PCs originates from the presence of the GNPs. As previously discussed, the plasmon enhances the PL from the chromophore in the excitation and radiation process. In Figure 4c, PL is excited with 375 nm, and the plasmon is not excited in the GNPs at the excitation wavelength but is excited by the radiative wavelength, which enhances the PL quantum yield. In this case, the spectral profile of the PL is modulated by the resonant profile of the plasmon excited by the radiative photons. The red-shifted PL is also consistent with this enhanced mechanism. The spectral modulation can be directly obtained by dividing the PL spectrum of the CD-GNP PCs with that of the CDs and the simulated scattering spectrum of the GNPs inside the hole (dotted curve).

![Figure 4.](https://dx.doi.org/10.1021/acsomega.0c03588)
quantum yield is estimated from the radiative enhancement factor to be nearly 10%.

We examined the PL from the Cd-metal nanoparticle nanocomposites excited at 375 nm and found that the plasmonic enhancement due to the GNP's is effective in the radiation process, and the enhancement is nearly two times. In this study, the PL is enhanced by both photonic and plasmonic effects in the excitation and radiation processes, and the enhancement increases to several times, which overcomes the limitations for practical use of CdS as the light-emitting elements. The double-resonant enhancement scheme developed in this study is not limited to the present samples but extends to other chromophores. Thus, it opens the way for developing ultrahigh molecular sensing and bioimaging techniques.

**CONCLUSIONS**

We fabricated the Cd PCs and Cd-GNP PCs using the nanoparticle lithography and electron-beam-induced chemical reactions. The Cd PCs showed the photonic band that depends on the hole size and the interhole distance. The PL from the Cd can be enhanced 3 times by the resonant excitation of the lowest photonic mode. The fabricated Cd-GNP PCs showed the photonic band near the UV region and the plasmonic band near 650 nm. The PL from the Cd-GNP PCs was enhanced in both excitation and radiation processes by the photonic and plasmonic resonances, respectively. A severalfold enhancement was obtained compared to the neat Cd. The method developed in this study provides a universal scheme to enhance light-emitting materials, which is promising for developing Cd PCs for Bright and Colorful Photoluminescence. J. Am. Chem. Soc. 2006, 128, 7756–7757.

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