Electronic Supplementary Material (ESI) for Nanoscale Advances.

Zn-assisted modification of the chemical structure of N-doped carbon dots and their enhanced quantum yield and photostability

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N-doped carbon dot (N-CD)

The morphology of the **N-CD** was investigated using a TEM equipment (H-7650 Hitachi, Japan) installed in the Center for University-wide Research Facilities (CURF) at the Jeonbuk National University. The average particle size was calculated by measuring the diameters of 200 particles in the TEM images (Figure S1).

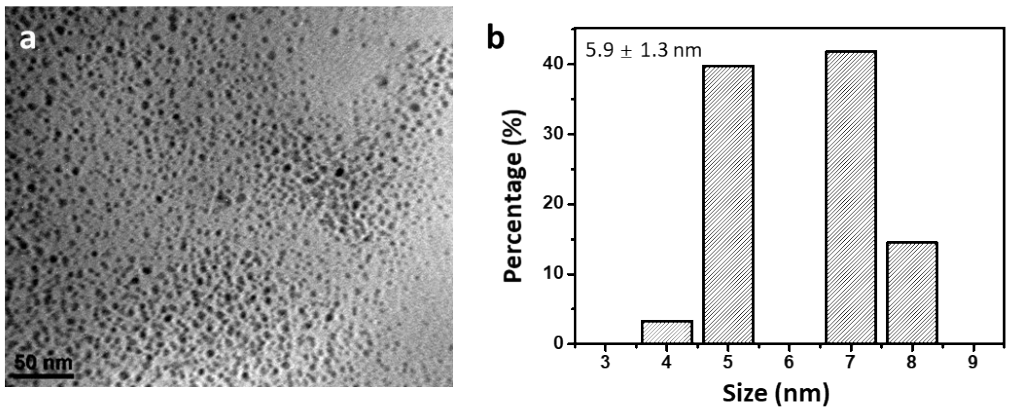

Figure S1. TEM image of **N-CD** and the corresponding particle size distribution histogram.

The crystalline structure of **N-CD** was analyzed by -ray diffraction (XRD, SmartLab, Rigaku, Japan). The XRD pattern N-CD exhibits a broad diffraction peak centered at ~19.58° (Figure S2), which is attributed to the (002) lattice spacing of a typical carbon-based material (JCPDS # 26-1076).

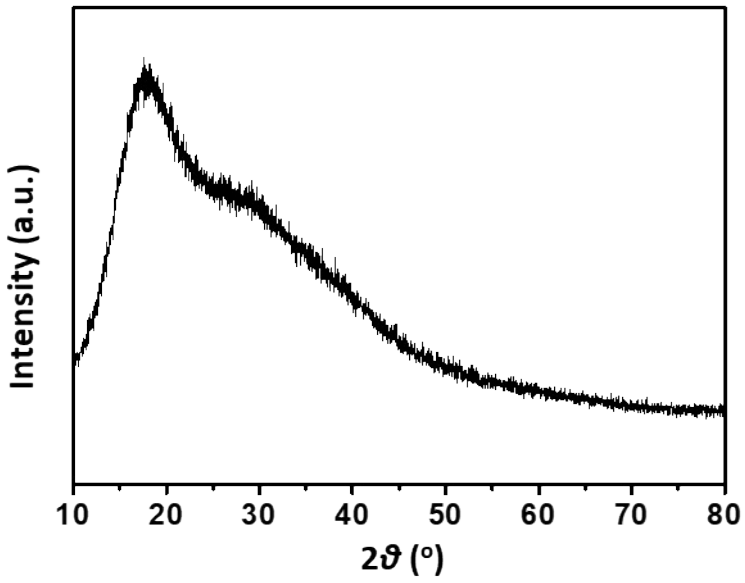

Figure S2. XRD pattern of **N-CD**.

Excitation-dependent emission of Zn:N-CDs

Fluorescence spectra of the **Zn:N-CD**s were recorded on a fluorescence spectrometer (QM-400, HORIBA) by varying the excitation wavelength from 310 to 390 nm.

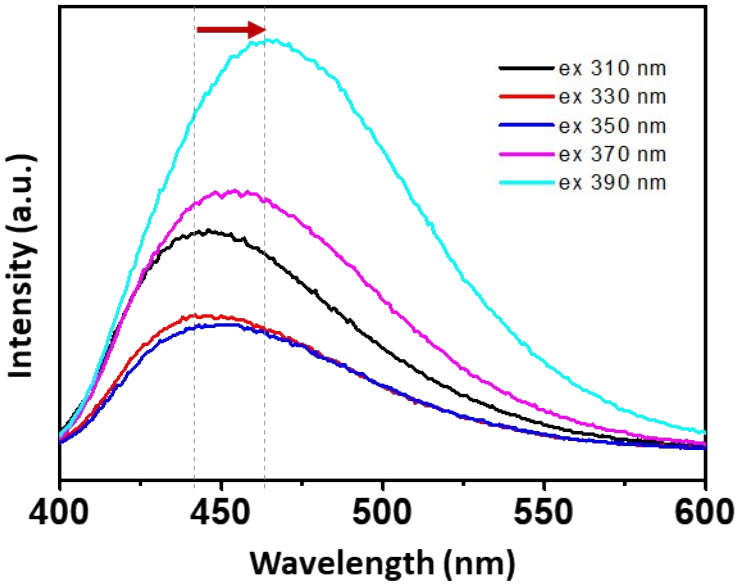

Figure S3. Excitation-dependent photoluminescence spectra of the **Zn:N-CD** sample.

Fluorescent comparison of Zn:N-CDs and N-CD

The brightness difference of **Zn:N-CD**s and **N-CD** solutions are clearly displayed in diluted conditions (0.08 mg·mL^{-1}; Figure S4). The emission spectra of the suspensions in the same concentration clearly exhibited a brightness variation (Figure S5).

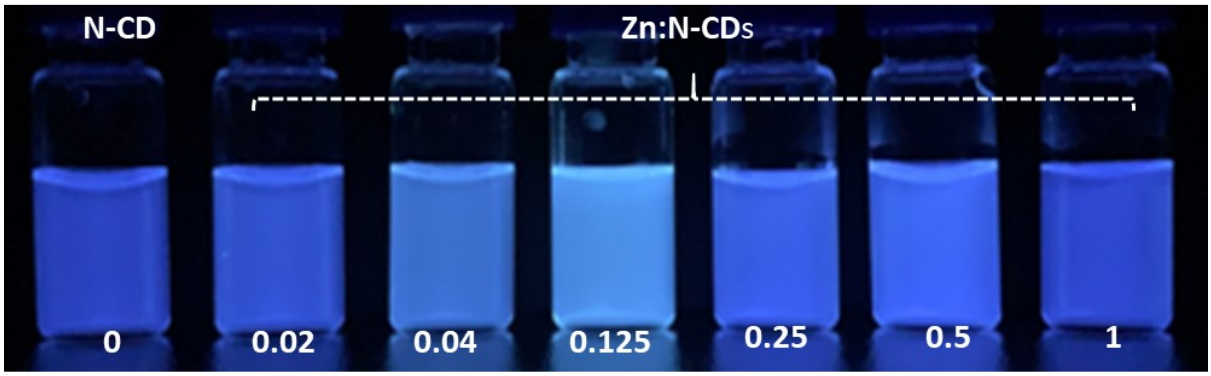

Figure S4. Photograph of the suspensions of the Zn:N-CDs and N-CD (Conc.: 0.08 mg·mL^{-1}) placed on top of a UV lamp (365 nm).

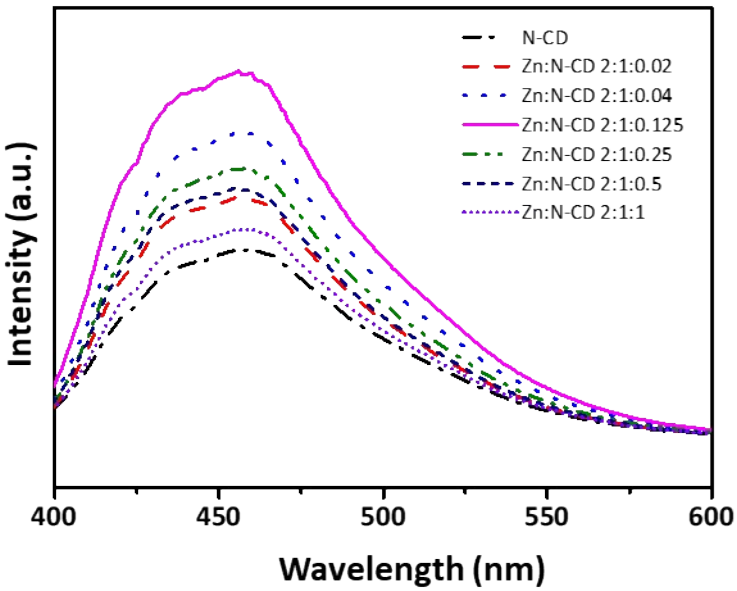

Figure S5. Emission spectra of the **Zn:N-CD**s and **N-CD.**

Quantum yield (QY) and photostability of various N-CDs and Zn-CDs

N-CDs and **Zn:N-CD**s were prepared according to a previously reported method with some modifications. In a typical synthesis, CA (10 μmol), and EDA (5 μmol) were dissolved in deionized water (15 mL). Each control reagent (0.250 μmol) is further added, and the resulting mixture was hydrothermally treated in a Teflon-lined stainless steel autoclave at 200 °C. After one hour of the reaction, the mixture was cooled to room temperature, and the residue was purified by column chromatography (CombiFlash NextGen100, Teledyne ISCO) to obtain brown **N-CD** and **Zn:N-CD** samples. QY of each sample is obtained following the method described in the experimental section of the main text (Figure S6). For the comparison of photostability, aqueous suspensions containing **N-CD**s (0.1 $mg \cdot mL^{-1}$) were exposed to daylight for 48 h, and their fluorescence intensity at 450 nm (λ_{ex}: 350 nm) was measured using a fluorometer (Figure S7).

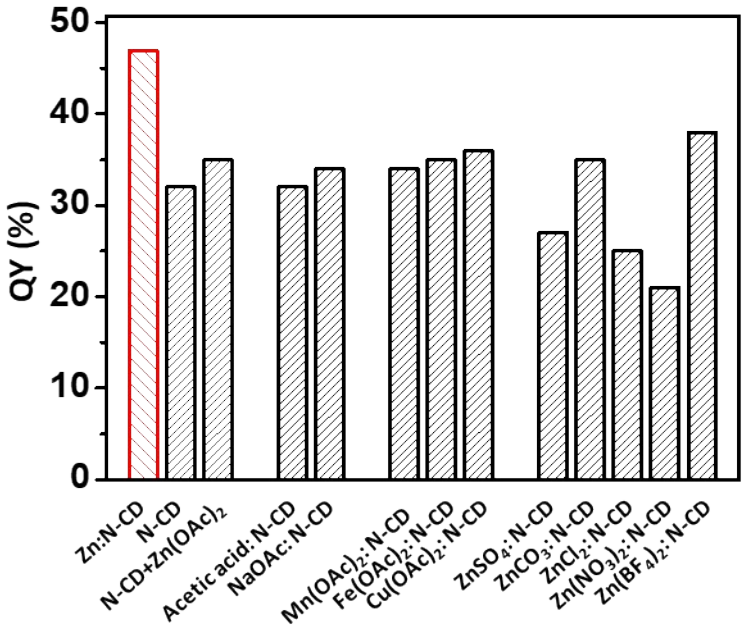

Figure S6. Relative QYs of **Zn:N-CD** and **N-CD** samples after post-reaction with $Zn(OAc)_2$, and **N-CD** samples synthesized using acetic acid, NaOAc, metal$(OAc)_2$, and various Zn salts.

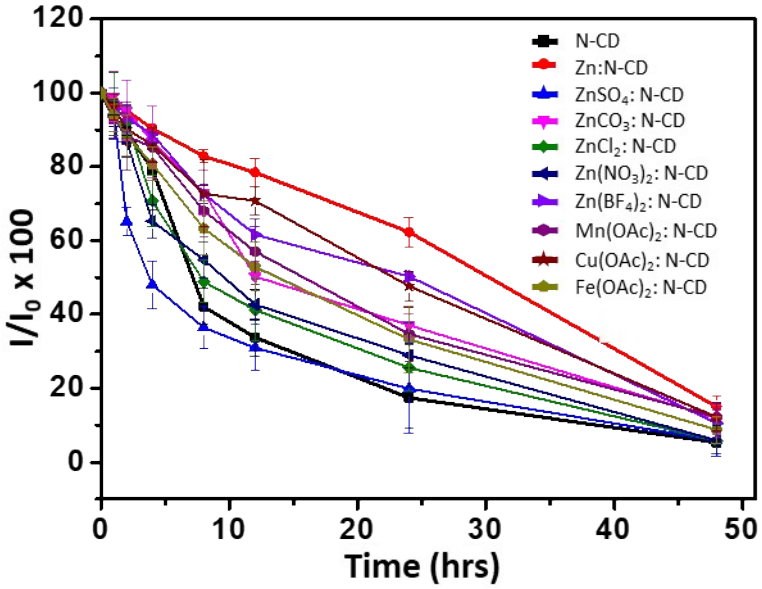

Figure S7. Time-dependent fluorescence intensities of **N-CD**s under exposure to daylight (λ_{ex}: 350 nm, λ_{em}: 450 nm).

Analysis of the Zn ion content in Zn:N-CDs using inductively coupled plasma–mass spectrometry (ICP–MS)

The amounts of Zn ions in three batches of **Zn:N-CD**s were analyzed using ICP–MS (NEXION-350X, PerkinElmer, USA), and the results are shown in Table S1.

Table S1. Amount of Zn ions in **Zn:N-CD**s

Ratio of citric acid: ethylenediamine: $Zn(OAc)_2$	**Weight of Zn:N-CDs (mg)**	**Amount of Zn^{2+} (mg)**	**Wt% of Zn in Zn:N-CDs**	**at% of Zn in Zn:N-CDs**
2:1:0.02	10.2	1.47×10^{-5}	1.45×10^{-4}	2.65×10^{-5}
2:1:0.04	10.2	0.70×10^{-5}	0.69×10^{-4}	1.26×10^{-5}
2:1:0.125	10.5	3.59×10^{-5}	3.41×10^{-4}	6.28×10^{-5}
2:1:0.25	10.3	3.91×10^{-5}	3.80×10^{-4}	6.97×10^{-5}
2:1:0.5	10.4	0.18×10^{-5}	0.17×10^{-4}	3.18×10^{-5}
2:1:1	10.3	10.40×10^{-5}	10.13×10^{-4}	18.53×10^{-5}

Comparison of the infrared (IR) spectra of N-CDs and Zn:N-CDs

The Fourier-transform IR spectra of **Zn:N-CD**s and **N-CD**s were obtained using a Nicolet 6700 (ThermoFisher Scientific, Waltham, USA). The **Zn:N-CD** and **N-CD** samples consist of similar functional groups. However, a peak at 895 cm^{-1} corresponding to the C-O-C groups in the glycosidic structure is absent in the IR spectrum of the **Zn:N-CD**, in comparison with the spectrum of the **N-CD** (red dotted line). In addition, a new peak at 1039 cm^{-1}, originating from the C-O bonds in polysaccharide, is observed in the IR spectrum of the **Zn:N-CD** (blue dotted line).

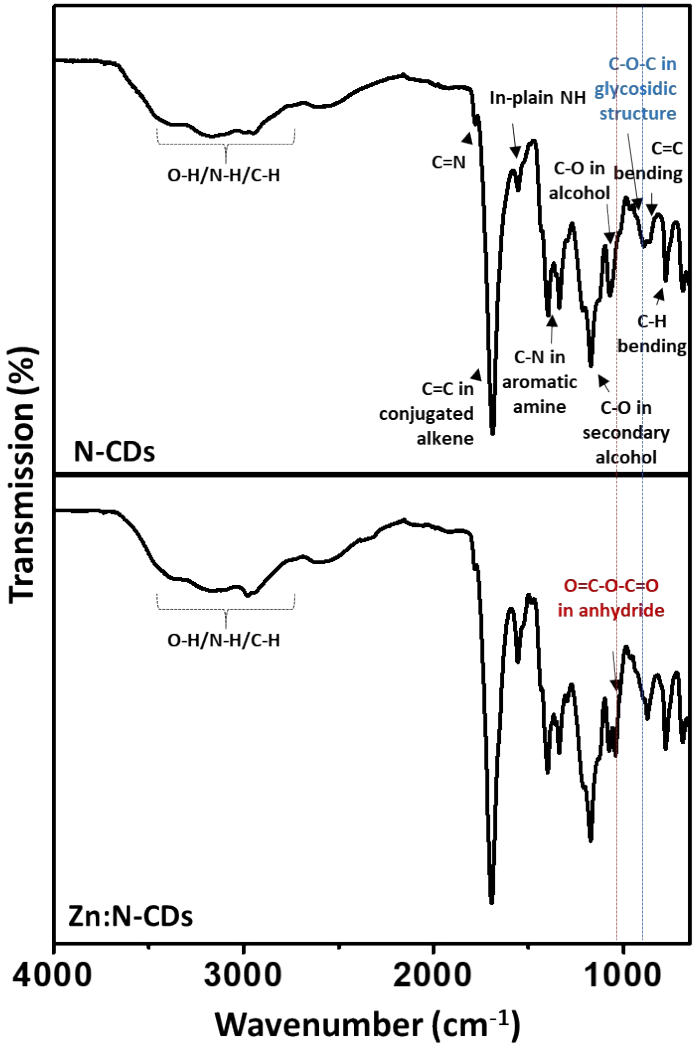

Figure S8. Comparison of the IR spectra of the **N-CD** and **Zn:N-CD** samples**.**

Zeta potential of the Zn:N-CD and **N-CD**

The **Zn:N-CD** and **N-CD** possesse a net negative charge owing to the rich –COOH groups from citric acid.

Table S2. ζ-potential of the **Zn:N-CD** and **N-CD**

pH	#1	#2	#3	#4	#5	Average (eV)
Zn:N-CD	−8.572	−7.773	−9.819	−9.773	−7.16	−8.6194
N-CD	−27.02	−26.90	−22.02	−19.44	−25.87	−24.25

Comparison of the relative atomic compositions of the Zn:N-CD and N-CD samples through X-ray photoelectron spectrometry (XPS)

The chemical compositions of the **Zn:N-CD** and **N-CD** samples were investigated through XPS (K-Alpha+, ThermoFisher Scientific, USA). The relative contents of the atoms and chemical bonds were quantified by measuring the peak area of each atom in the survey scan spectra and high-resolution spectra shown in Figure 5.

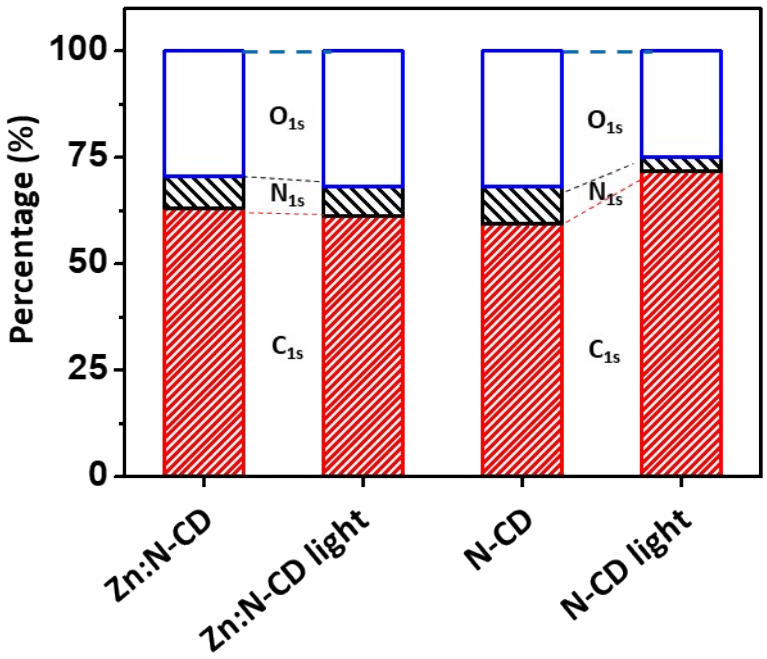

Figure S9. Ratios of the atomic components of the **Zn:N-CD** and **N-CD** samples, based on the XPS peak areas, before and after exposure to light.

Fluorescent variation of Zn:N-CD and N-CD under continuous UV irradiation

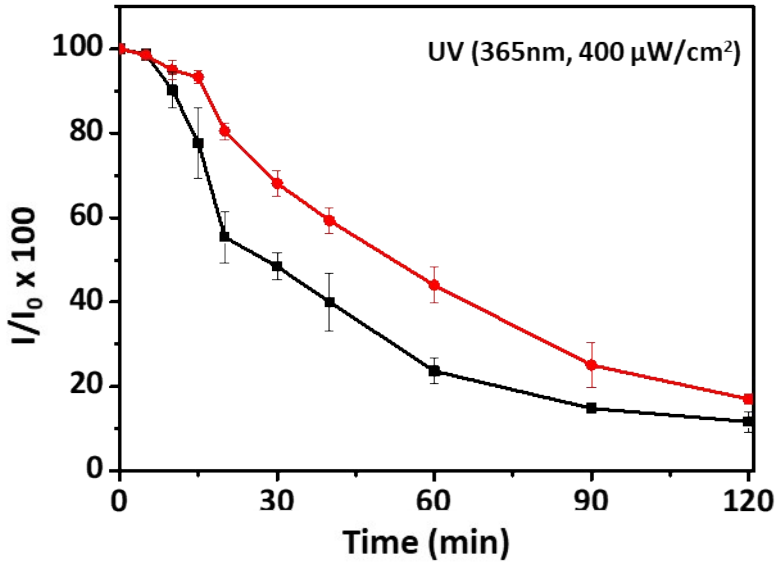

Figure S10. Time-dependent fluorescence intensities of **Zn:N-CD** and **N-CD** under continuous exposure to UV light.

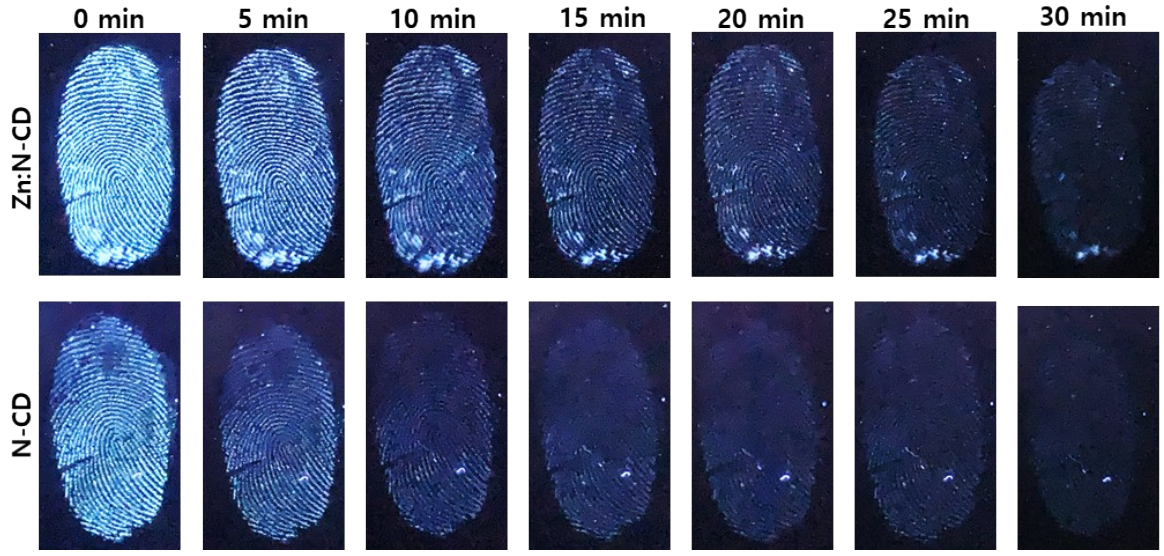

Figure S11. Images of the fingerprints visualized using **Zn:N-CDs** and **N-CDs** at different time points under continuous UV irradiation.

Toxicity assay of the Zn:N-CD

The biocompatibility of the **Zn:N-CD** sample was evaluated using human lung cancer cells (A549) via a 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay. Cells (2×10^5 cells per well) were cultured overnight in a 96-well microtiter plate in a 5% CO_2 atmosphere at 37 °C. The wells were filled with a cell medium containing the **Zn:N-CD**s or **N-CD**s (12.5, 25, 50, 75, 100, 250, and 500 μg mL^{-1}) and incubated for 24 h. Then, 10 μL of the MTT solution was added to each well (final concentration: 0.5 mg mL^{-1}). After the incubation of the cells with the MTT solution for 4 h, the formazan crystals, which were formed as a result of NAD(P)H-dependent oxidoreductase in living cells, were dissolved by adding the solubilization solution from the kit. The dissolved formazan was quantified by measuring the absorbance of the solution at 550 nm using a microplate reader (SpectraMax M2e, Molecular Devices, LLC, San Jose, USA).

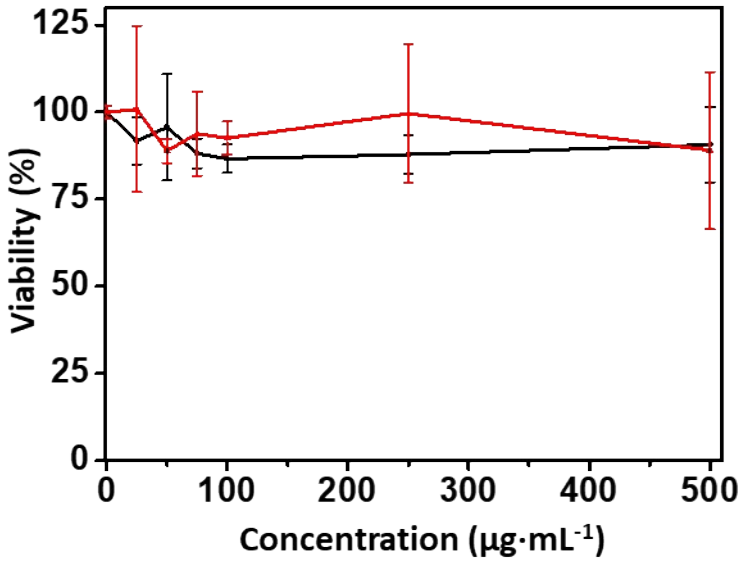

Figure S12. Viability test of the **N-CD** and **Zn:N-CD** samples. The viability of A549 cells was examined using an MTT assay, in which the cells were treated with a cell medium containing **N-CD**s or **Zn:N-CD**s for 24 h.