CO₂ phonon mode renormalization using phonon-assisted energy up-conversion

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Molecular dissociation under incident light whose energy is lower than the bond dissociation energy has been achieved through multi step excitation using a coupled state of a photon, electron, and multimode-coherent phonon as known as the dressed photon phonon (DPP). Here, we have investigated the effects of the DPP on CO₂, a very stable molecule with high absorption and dissociation energies, by introducing ZnO nanorods to generate the DPP. Then, the changes in CO₂ absorption bands were evaluated using light with a wavelength longer than the absorption wavelength, which confirmed the DPP-assisted energy up-conversion. To evaluate the specific CO₂ modes related to this process, we measured the CO₂ vibration-rotation spectra in the near-infrared region. Detailed analysis of the 3ν₃ vibrational band when a DPP source is present showed that DPP causes a significant increase in the intensity of certain absorption bands, especially those that require higher energies to activate.

Carbon dioxide, one of the major greenhouse gases, has been widely studied as an important molecule in Earth’s atmosphere and interstellar media. With a view to mitigating the effects of global warming, different approaches to the photoreduction of CO₂ have been investigated. The bond dissociation energy $E_{\text{diss}}$ of one CO₂ molecule has been reported to be more than 7 eV, equivalent to the energy of incident light wavelength of 174 nm ($\lambda_{\text{diss}}$). Such a high energy requirement has inspired scientists to investigate photocatalytic reduction of CO₂ in dissolved liquids. Photocatalytic conversion of CO₂ to hydrocarbon fuels has been experimented widely and implemented using wide band gap oxides, such as TiO₂ and ZnO. However, the high energy requirements of this process, its multielectron transfer, and the complex design of the catalysts have limited the efficiency of the photo-electrocatalytic approach. Dissociation of CO₂ molecules using radio-frequency discharge with maximum energy efficiency of 3% has also been introduced. There have been many reports on the dissociation dynamics of CO₂ in the gas phase, most of them focusing on two main dissociation paths: a dissociation process $\text{CO}_2 + h\nu \rightarrow \text{CO}(\Sigma_g^+) + \text{O}(\text{D})$ with incident light of wavelength 157 nm (red curve in Fig. 4(a)) and a predissociation process $\text{CO}_2 + h\nu \rightarrow \text{CO}(\Sigma_g^+) + \text{O}(\text{P})$ with deep UV light (174–195 nm, blue curve in Fig. 4(a)). Photodissociation of CO₂ gas molecules following these two paths with incident light with wavelengths longer than $\lambda_{\text{diss}}$ could enable photoreduction of CO₂ using the solar spectrum from the UV to visible light region, although no report on this process has been published yet. In this research, we performed phonon-assisted energy up-conversion to dissociate CO₂ molecules by introducing ZnO nanorods. This process has been implemented previously for dissociating gas phase diethylzinc molecules using an optical near field generated around the nanostructure to stimulate multistep excitation via molecular vibrational modes under incident light with an energy less than the bond dissociation energy.

The physics of these nanoscale optical effects has been developed under the assumption of a conventional multipolar quantum electrodynamic Hamiltonian in a Coulomb gauge and of single-particle states in a finite nanosystem. In such a system, fluctuations in the electromagnetic field (e.g., zero-point fluctuations of the vacuum) cause nanomaterials to emit or absorb virtual photons, i.e., the optical near-fields continuously present around illuminated materials. These so-called virtual absorption and emission processes violate the energy conservation law but are consistent with the Heisenberg uncertainty principle, and to take these processes into account, nanomaterial can be considered to be covered with a cloud of virtual photons. Within this framework, a virtual photon can be described as a coupled state of the electron and a real photon (i.e., a free photon). The quasiparticle representing this coupled state has been called a dressed photon (DP), which has a greater amount of energy than a free photon because of energy contributed by the coupled electron. To take advantage of the nanoscale optics, a thorough understanding of the nanoscale material is required. Such nanoscale materials are...
composed of a crystal lattice, and after a DP is generated at the surface of an illuminated nanoscale particle, its energy can be exchanged with this crystal lattice. Through this exchange, vibrational modes can be coherently excited in the crystal lattice, creating multiple modes of coherent phonon states. Consequently, the DP and a coherent phonon form a coupled state. This state (the dressed photon and phonon, DPP) constitutes a quasi-particle that is generated only when the particle size is sufficiently small that the crystal lattice vibration is excited coherently. In contrast, vibrational modes cannot be excited coherently in bulk materials, and energy is instead dissipated as heat throughout the material, which is heated as a result. Therefore, the DPP has a higher energy than the DP or the incident free photon. Numerous experiments have been reported for which the results were explained by DPP theory, including experiments on photochemical vapour deposition, photolithography, visible-light water splitting, photovoltaic devices, energy up-conversion devices, and Si lasers. In addition, since the DPP is excited only in nanoscale structures, it can be utilized to realize selective etching of nanoscale bumps to achieve atomically flattened substrates. This DPP energy, when absorbed by a molecule adjacent to the nanostucture, allows the molecule to absorb multimode coherent phonons to become excited to a vibrational mode of higher energy. This intermediate excitation of molecules is the key to energy upconversion processes, allowing dissociation with less energy.

Here, we studied the effect of the DPP on CO2 molecules. To induce the DPP, we fabricated ZnO nanorod structures with average diameters of 30–50 nm. As the light source for photo-activation of the CO2 molecules, we used a YAG laser of λ = 213 nm, which is longer than the maximum absorption wavelength of CO2 λabs = 200 nm. To observe the change in concentration of CO2 gas as well as the vibrational excitation of the CO2 molecules, we performed infrared spectroscopy. In particular, we measured the absorption spectrum of CO2 in the near-infrared region (1430–1452 nm) while irradiating a substrate consisting of ZnO nanorods inside a chamber filled with CO2 gas. The infrared absorption in this region mainly consists of two different transition bands. We analysed the changes in the vibration-rotation spectra due to UV irradiation and the excitation of DPPs. We confirmed that energy was transferred between the two bands (the traditional ‘cold’ band and accompanying ‘hot’ band) at room temperature under UV irradiation, and this was proved to be a reversible process, as the molecules returned to their initial state after a certain time. However, because of the DPP excitation, significant and irreversible energy transfer occurs, causing the absorption at higher energy ‘hot’ bands to increase. We explained this result using the fact that DPP excitation allows molecules to absorb multimode coherent phonons, resulting in an average population increase in the high energy bands, in other word, phonon mode renormalization. The result also supports the assumption that DPP excitation permits CO2 molecules to absorb light with wavelengths longer than the absorption wavelength (λ = 213 nm > λabs = 200 nm).

Results

Measurement of CO2 absorption spectrum. The absorption spectrum of CO2 was measured using infrared spectrometer and a halogen lamp as a light source. To determine the CO2 concentration, first, the intensity of transmitted light (Io) was measured without CO2 gas in the chamber. Later, CO2 was added to the chamber and the intensity of transmitted light was measured (I). The total absorption by CO2 was calculated using the equation for the absorbance A = \log(Io/I). A typical measured spectrum is shown in Fig. 1(a).

The absorption was measured in the wavelength region from 1430 nm to 1452 nm, where the absorption spectrum peaks originate from the asymmetric stretching of CO2 molecules. We confirmed that this spectrum is similar to the one recorded in the HITRAN (High-Resolution Transmission Molecular Absorption) 2004 database. The spectrum in this region is dominated by the 3ν3 overtone 00001 → 00031, the accompanying hot band 01101 → 01131, and another hot band 10002 → 10032. The details of these three bands obtained from calculations are listed briefly in Table 1. The 00001 → 00031 band has a band centre at 1434.19 nm, the accompanying hot band 01101 → 01131 has a band centre at 1441.94 nm, and another hot band 10002 → 10032 has a centre at 1447.79 nm. The line strength of the 01101 → 01131 hot band is about 1.25 × 10^{-2} cm^{-1} molecule^{-1} cm^{-1}, which is 10 times smaller than that of the main band (1.45 × 10^{-2} cm^{-1} molecule^{-1} cm^{-1}). The line strength of the 00002 → 10032 hot band is about 2.69 × 10^{-2} cm^{-1} molecule^{-1} cm^{-1}, which is 1000 times smaller than that of the main band. The corresponding energy band diagram of these three transition bands is illustrated in Fig. 1(b).

According to Table 1, the 00001 → 00031 band ranges in wavelength from 1430.89 nm to 1468.65 nm and consists of numerous spectral lines resulting from the vibrational and rotational motion. The vibration-rotation spectra of CO2 for the 00001 → 00031 transition have been studied in detail previously. Table 2 shows the line positions taken from the work of C. Miller. The lines are mostly divided into two branches, the P branch and R branch. The R branch results from a vibrational transition accompanied by an increase in the rotational quantum number (+1), and the P branch results from a vibrational transition accompanied by a decrease in the rotational quantum number (−1). The concept behind the P branch and R branch is illustrated in Fig. 1 (c). The line positions in the spectrum measured in our experiment are summarized in Table 2, along with the reported values k values for comparison, and they are found to coincide within an average deviation of 0.06 cm⁻¹.

Other than the spectral lines originating from the 00001 → 00031 transition, we also found some weak and irregular lines from the hot band transition, the details of which are summarized in Table 3. We also compare our measured line positions with the values reported for the 01101 → 01131 hot transition. Because the line strength of the other hot transitions, 10002 → 10032, was too weak compared to that of the cold band, it was not detectable by our experimental setup.

Vibrational energy transfer. Next we used a YAG laser of wavelength λ = 213 nm and observed the change in the CO2 absorption spectrum at P = 40 kPa and T = 295 K. All of the absorption peaks mentioned in Tables 2 and 3 were considered. The experimental results indicate that the absorption peaks change periodically with time and have a strong correlation with each other. For example, in Fig. 2(a), we see that the R(30) peak from the 00001 → 00031 transition and the R(27e) peak from the 01101 → 01131 transition oscillate with opposite phases and have a correlation coefficient of −0.83. Peak R(27e) has its maximum absorption at time t = 1840 s and minimum absorption at t = 9000 s. We have plotted all the R branch and P branch peaks of the 00001 → 00031 transition band with respect to the branch number in Figs. 2(b) and 2(c). In addition, the 01101 → 01131 hot branch peaks are also plotted in Fig. 2(d). The symmetric nature of the graph suggests that all of the absorption peaks oscillate in the same way, with extreme values at t = 1840 s and t = 9000 s. This periodic nature of the absorption change indicates that population inversion in the ground states of the transition bands occurs after a certain period of time, which is almost 1000 s in our experimental results.

We consider this change in the spectrum to result from the intramolecular vibrational energy transfer due to collisions between CO2 molecules. When sufficient heat is supplied, molecules at lower energy levels can be excited to upper levels, but the oscillating change in the absorption peaks indicates that the energy transfer should be reversible. If the population in the upper energy level becomes
sufficiently high, some of the molecules will relax, causing the population to eventually decrease. Furthermore, excitation and relaxation from different energy levels can be considered. Vibrational energy transfer between the ground energy levels of the cold band (00001\( \rightarrow \) 00031) and the accompanying hot bands (01101\( \rightarrow \) 01131 and 10002\( \rightarrow \) 10032) is a well-known phenomenon\(^1\), equivalent to the 00001\( \rightarrow \) 01101 bending vibrational transition, which requires an energy of 73 meV (667.4 cm\(^{-1}\)). Figure 2(d) shows that the hot bands at wavelengths of 1435.63 nm, 1437.28 nm,

Table 1 | Details of the 3\( \nu_3 \) overtone vibrational transition bands

| Band center (nm) | Vibrational band | Min. position (nm) | Max. position (nm) | Vibrational band strength (cm\(^{-1}\)/mol. cm\(^{-2}\)) | Range of rotational lines |
|------------------|------------------|--------------------|--------------------|---------------------------------|--------------------------|
| 1434.19          | 00001 \( \rightarrow \) 00031 | 1468.65            | 1430.89            | 1.45 \( \times \) 10\(^{-21}\) | P(98) \( \rightarrow \) P(98) |
| 1441.93          | 01101 \( \rightarrow \) 01131 | 1471.79            | 1438.56            | 1.25 \( \times \) 10\(^{-22}\) | P(89) \( \rightarrow \) P(89) |
| 1447.78          | 10002 \( \rightarrow \) 10032 | 1472.14            | 1444.30            | 2.69 \( \times \) 10\(^{-24}\) | P(78) \( \rightarrow \) P(78) |
Table 2 | Line positions of the 00001 → 00031 band

| Line  | λ (nm)   | k (cm⁻¹) | k’ (cm⁻¹) |
|-------|----------|----------|-----------|
| R(36) | 1430.92  | 6988.501 | 6988.501  |
| R(30) | 1431.08  | 6987.754 | 6987.604  |
| R(28) | 1431.2   | 6987.129 | 6987.247  |
| R(24) | 1431.38  | 6986.255 | 6986.084  |
| R(22) | 1431.56  | 6985.382 | 6985.428  |
| R(20) | 1431.77  | 6984.386 | 6984.7    |
| R(18) | 1431.94  | 6983.513 | 6983.896  |
| R(14) | 1432.2   | 6982.27  | 6982.068  |
| R(12) | 1432.43  | 6981.154 | 6981.043  |
| R(10) | 1432.68  | 6979.911 | 6979.943  |
| R(8)  | 1432.96  | 6978.542 | 6978.77   |
| R(6)  | 1433.27  | 6977.057 | 6977.523  |
| R(4)  | 1433.55  | 6975.69  | 6976.202  |
| R(2)  | 1433.7   | 6974.96  | 6974.808  |
| R(0)  | 1433.96  | 6973.71  | 6973.339  |
| P(2)  | 1434.36  | 6971.731 | 6970.998  |
| P(4)  | 1434.72  | 6970.001 | 6969.345  |
| P(6)  | 1435.1   | 6968.151 | 6967.618  |

| Line  | λ (nm)   | k (cm⁻¹) | k’ (cm⁻¹) |
|-------|----------|----------|-----------|
| P(8)  | 1435.48  | 6966.301 | 6965.817  |
| P(10) | 1435.89  | 6964.331 | 6963.943  |
| P(12) | 1436.29  | 6962.363 | 6961.995  |
| P(14) | 1436.75  | 6960.148 | 6959.973  |
| P(16) | 1437.18  | 6958.066 | 6957.878  |
| P(18) | 1437.66  | 6955.738 | 6955.709  |
| P(20) | 1438.12  | 6953.532 | 6953.467  |
| P(22) | 1438.62  | 6951.087 | 6951.151  |
| P(24) | 1439.13  | 6948.647 | 6948.762  |
| P(26) | 1439.66  | 6946.089 | 6946.299  |
| P(28) | 1440.19  | 6943.533 | 6943.763  |
| P(30) | 1440.79  | 6940.617 | 6941.153  |
| P(32) | 1441.02  | 6939.524 | 6938.469  |
| P(34) | 1441.93  | 6935.164 | 6935.713  |
| P(36) | 1442.43  | 6932.745 | 6932.884  |
| P(40) | 1445.14  | 6919.745 | 6920.832  |
| P(46) | 1445.37  | 6918.668 | 6917.636  |
| P(60) | 1450.13  | 6893.576 | 6893.221  |

1438.95 nm, and 1450.13 nm particularly active, which is evidence of this vibrational energy transfer phenomenon. Moreover, we also observed certain branches of the cold band to be active like the hot bands, such as R(18), P(32), P(36), P(44), P(46), and P(60). This suggests that energy transfer between different P and R branches of the 00001 → 00031 cold band can also be considered.

To analyse the periodic population inversion in the ground states of the transition bands, we also performed rate equation analysis. A simple model with three energy levels is suggested, under the assumption that the excitation and relaxation occur spontaneously. The energy levels are noted as l, 2, and 3 and their corresponding populations are n₁, n₂, and n₃. The rate equations are given below as

\[
\frac{dn_1}{dt} = -r_{12} n_1(n_1 - n_2) - r_{23} n_1(n_1 - n_3) + r_{13} n_1(n_1 - n_2) + r_{12} n_2(n_2 - n_1) + r_{23} n_3(n_2 - n_1)
\]

(1)

\[
\frac{dn_2}{dt} = -r_{23} n_2(n_2 - n_3) - r_{12} n_2(n_1 - n_2) + r_{13} n_2(n_2 - n_3) + r_{23} n_3(n_3 - n_2) + r_{13} n_3(n_3 - n_1)
\]

(2)

\[
\frac{dn_3}{dt} = r_{13} n_3(n_1 - n_3) + r_{23} n_3(n_2 - n_3) - r_{23} n_3(n_1 - n_2)
\]

(3)

where r_{ij} is the transition rate from energy level j to energy level i and I is the light intensity.

To understand the population inversion between the cold band and the hot bands, let us consider energy level n₁ as the ground state 00001, n₂ as the excited state 01101, and n₃ as the other excited state 10002. Vibrational energy transfer between all three states occurs according to the following reactions:

\[
CO_2(00001)\leftrightarrow CO_2(01101) + E = 73 \text{ meV}
\]

(4)

\[
CO_2(01101)\leftrightarrow CO_2(10002) + E = 67 \text{ meV}
\]

(5)

\[
CO_2(00001)\leftrightarrow CO_2(10002) + E = 140 \text{ meV}
\]

(6)

CO₂(00001) + CO₂(10002) ↔ 2CO₂(01101) + E = 6 meV

(7)

By performing a simulation using the differential rate equations, we solved for the energy level populations n₁, n₂, and n₃. The initial population values were set as n₁ = 1.0, n₂ = 0.0, and n₃ = 0.0, since the molecules exist in the ground state initially. As shown in Fig. 2(e) we find that the populations of all three energy levels oscillate with time, n₁ (00001) and n₂ (01102) with the same phase and n₃ (01101) with the opposite phase. The correlation coefficient between n₁ (00001) and n₂ (01101) is -0.85, which is almost the same as the experimental correlation coefficient between the absorption changes at R(30) (from 00001) and R(27e) (from 01101), -0.83. Therefore, this three-level system can explain the oscillations observed in absorption peaks under UV irradiation without any nanostucture, supporting the vibrational energy transfer mechanism.

**Phonon-assisted vibrational energy transfer.** To understand the effect of the DPP, we irradiated ZnO nanorods with λ = 213 nm light and observed the changes in the CO₂ spectrum. The nanostructures were found to induce significant changes in some absorption peaks. Figure 3(a) shows the absorption changes at R(30) peak from the 00001 → 00031 transition and at the R(27e) peak from the 01101 → 01131 transition, which have a correlation coefficient of -0.97. Instead of the oscillating nature of the absorption change observed under UV irradiation without nanorods, we see the absorption at the R(27e) peak increasing and that at the R(27e) peak decreasing continuously with time, and both saturate after about t = 6000 s. The R and P branches of the 00001 → 00031
transition band are plotted as a function of the branch number in Figs. 3(b) and 3(c), and the 01101 \textsuperscript{R} 01131 hot band peaks are plotted in Fig. 3(d). The changes in absorption without nanorods at time \( t = 1840 \text{s} \) are also plotted in Figs. 3(b), 3(c), and 3(d) so that the nature of the absorption changes can be compared. As was the case for irradiation without nanorods, the peaks that are particularly active are R(18), P(32), P(36), P(44), P(46), and P(60) from the 00001 \textsuperscript{R} 00031 transition and the hot bands at wavelengths of 1435.63, 1437.28, 1438.95, and 1450.13 nm. For irradiation with nanorods, however, the population increases at these particular branches are significantly higher than those at the other energy bands. While the populations at the different P and R branches were quite uniform during irradiation without nanostructures, irradiation of the nanostructure results in irregular population increases in these particular branches. Because the R(18), P(32), P(36), P(44), P(46), and P(60) branches require high energies to get excited, the excitation of the DPP must be responsible for excitation of these particular branches.

**Discussion**
Oscillation of the absorption peaks is observed regardless of the location of the UV irradiation in the chamber. Moreover, the absorption spectrum is measured for all gas molecules inside the chamber (total number of molecules, \( N = 8.4 \times 10^{21} \)). Although the collisional
energy transfer between two molecules is very quick, with a lifetime on the order of microseconds, it can be said that energy transfer in the whole system of \( N = 8.4 \times 10^{21} \) molecules takes a much longer time, causing the population inversion occurring after almost \( t = 1000 \) s.

To further support our assumption that intermolecular energy transfer is responsible for the observed absorption changes, we considered other possible mechanisms as well. Because the absorption wavelength of the CO\(_2\) molecules has been reported to be smaller than 200 nm, it is impossible for the molecules to reach the excited state by absorbing radiation at \( \lambda = 213 \) nm (Fig. 4(a)). Therefore, only vibrational energy transfer at the electronic ground state needs to be considered. Moreover, neither of the product molecules of CO\(_2\) dissociation reaction, CO and O\(_2\), would show infrared absorption in the 1430–1452 nm range: CO absorbs at wavelengths less than 1200 nm and at 1570 nm, while O\(_2\) absorbs at wavelengths less than 1300 nm and greater than 1560 nm. Therefore, molecular dissociation can also be excluded in this system.

Irradiation of nanorods with incident light at a wavelength of \( \lambda = 213 \) nm causes (1) irreversible vibrational energy transfer from the cold bands to the hot bands (Fig. 4(a)) and (2) a significant population increase at specific high-energy transition bands. The DP is known to be able to excite multimode coherent phonons inside the nanostructure, which can be absorbed by molecules around the nanostructure (Fig. 4(a)). The coherent phonon absorption due to the continuous irradiation with UV light causes the rate of excitation of the molecules to the upper energy level to be significantly higher than the relaxation rate. While absorption of phonons from heat energy produces a uniform population distribution as shown in Fig. 2(c), the non-uniform population distribution observed in this experiment as shown in Fig. 3(c) can only be explained by the absorption of coherent phonons. This phonon-assisted energy up-conversion process can be explained as CO\(_2\) phonon mode renormalization (Fig. 4(b))\(^{19}\). The heat absorption results in a broad density distribution of phonon energy states (dashed black curve in Fig. 4(b)), while absorption of multimode coherent phonons by CO\(_2\) molecules created by DPP excitation leads to a change in the density distribution of phonon energy states to form peaks (red solid curve in Fig. 4(b)). This hypothesis is supported by comparing Figs. 2(c) and 3(c), in which the absorptions of the absorption changes are uniform and non-uniform, respectively. In particular, the absorption change at the P(32) peak in Fig. 3(c) was 7 times greater than that in Fig. 2(c), indicating that the phonon energy states were renormalized. This process can also be used to induce absorption and dissociation of CO\(_2\) with wavelengths longer than the absorption and
Figure 5 | SEM images: (a) ZnO nanorods with average diameters of 50 nm were grown by MOCVD with a growth temperature of 450 °C for 30 min. (b) ZnO nanorods with smaller average diameters of 20 nm were grown with a growth temperature of 450 °C for 30 min and at 750 °C for 10 min.

Methods

Fabrication of nanostructures. ZnO nanorods are grown on a sapphire substrate using a catalyst-free metal-organic vapour phase epitaxy (MOVPE) system. Diethylzinc (DEZn) and oxygen are used as the reactants, with argon as the carrier gas. The pressure inside the reactant chamber is maintained at 5 Torr. The substrate temperature is controlled using a thermocouple and a radio-frequency-heated carbon susceptor. The temperature of the system can be adjusted to control the growth rate and structure of the nanorods. We used a two-temperature growth method, with lower-temperature growth of vertically aligned thick ZnO nanorods and subsequent higher-temperature growth of vertically aligned ultrathin ZnO nanorods. In the first step, vertically aligned thick nanorods are grown at 450 °C for 30 min. In the second step, ultrathin nanorods are grown at 750 °C for 10 min at the tips of the preformed thick nanorods. The average diameters of the nanorods are 20–50 nm. Scanning electron microscopic (SEM) images of the fabricated ZnO nanorods are shown in Fig. 5.

UV irradiation. We used a 30 cm long glass chamber and filled it with CO₂ gas at a pressure of 40 kPa, then irradiated the gas with UV light (see Fig. 6). To determine the effect of the phonon-assisted process, we put a substrate with ZnO nanorods inside...
Figure 6 | ZnO nanorods were irradiated inside a chamber filled with CO₂ gas at pressure \( P = 40 \) kPa, temperature \( T = 295 \) K, and the infrared absorption spectrum of CO₂ was measured simultaneously.

de the chamber filled with CO₂ and irradiated the nanorods with UV light. The absorption spectrum was measured simultaneously. The spectra were recorded continuously in 1000 shots, where each shot had an exposure time of 10 s.

To interpret these results, let us assume that the intensity of transmitted light at time \( t = 0 \) is \( I_1 \) and that at time \( t = 1 \). The concentration of CO₂ at \( t = 0 \) is \( N \) and that at \( t = N + \Delta N \), where \( \Delta N \) is the change in concentration over \( t \). According to the Beer-Lambert law, \( I_1 = I_0 e^{\alpha N} \) and \( I_2 = I_0 e^{-\alpha(N+\Delta N)} \). From these two equations, we can determine \( \Delta N \).

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Author contributions
T.Y. planned the project. N.T. performed experiments. T.K. was responsible for providing guidance for the experiments. All authors discussed the results. N.T. and T.Y. wrote the manuscript and edited the final manuscript. All authors reviewed the manuscript.

Additional information
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