Research article

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Wide-field photothermal reflectance spectroscopy for single nanoparticle absorption spectrum analysis

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Abstract: Photothermal imaging is useful for detecting individual nanoparticles and obtaining the absorption spectra. This study presents a wide-field photothermal reflectance spectroscopy technique achieved by incorporating a pump beam, a probe beam, and a charge-coupled device (CCD) camera into a commercial microscopic setup. The presented design does not require precise alignment between the pump and the probe beams and enables the observation of numerous individual nanoparticles during image acquisition. Despite the use of a simple imaging processing method, i.e., a four-bucket method using a CCD camera, sufficient sensitivity for the spectral imaging of a single gold nanorod (20 nm diameter and 84 nm length) is demonstrated. Numerous individual nanoparticles within a wide field of view ($240\ \mu\text{m} \times 180\ \mu\text{m}$) are detected in an image captures at an imaging measurement speed of $0.02\ \text{mm}^2\ \text{min}^{-1}$. Furthermore, the proposed photothermal reflectance spectroscopy technique can detect the variation in the absorption peak of the measured spectra depending on the aspect ratio of individual nanoparticles within a spectral resolution of 1 nm.

Keywords: four-bucket method; gold nanorod; photothermal; photothermal reflectance imaging; single nanoparticle spectroscopy.

1 Introduction

Single nanoparticle spectroscopy is an indispensable technology with biological, medical, and material science applications [1–7]. In particular, in the field of biomedicine, it is utilized in photothermal therapy, during which the necrosis of cancer cells is induced using the heat generated from the metal nanoparticles with laser illumination. For photothermal cancer therapy, while it is necessary to apply a sufficient laser intensity to the nanoparticles to ensure that the operating temperature is sufficiently high to destroy the cancer cells, damage to healthy cells should be prevented as much as possible [8]. Therefore, it is important to accurately distinguish the surface plasmon resonance peaks of differently sized and shaped nanoparticles to produce sufficient heat with a low laser intensity [9, 10].

Thus far, although research on absorption spectra has been implemented at the level of individual nanoparticles, most studies have focused on nanoparticles with spherical structures and equal aspect ratios. Therefore, a spectroscopy technique capable of measuring the absorption spectrum for an individual nanoparticle of unknown size and shape is essential [2, 11–14]. This would not only provide important insights into the unique properties of the individual particles but would also overcome the limitations due to various sources of inhomogeneity present in the measurement of ensembles or aggregates.

For particles with a diameter of less than 40 nm, the optical absorption of metal particles by an excitation source dominates over scattering [15]. This absorption is released as heat, which causes a change in the temperature of the surrounding medium of the particles, resulting in a localized refractive index variation [16]. Photothermal microscopy enables the detection of metal nanoparticles by monitoring the refractive index variations and is an important tool for implementing single nanoparticle absorption spectroscopy [15, 17–22]. Various photothermal microscopy methods have been studied [15, 17, 18]. Boyer et al. [15] developed the

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photothermal interference contrast method, which involves the detection of the refractive index changes around the absorbing particle (>2.4 nm diameter) from the change in the magnitude of the interference signal of the probe beam using a Wollaston prism. Berciaud et al. [17] developed the photothermal heterodyne imaging method, which involves the detection of changes in the refractive index around the nanoparticles (>1.4 nm diameter) generated by a time-modulated pump beam from the change in the frequency-shifted signal magnitude of a modulated probe beam. Dijk et al. [18] developed the interferometry photothermal microscopy method, whereby pump-induced changes in the nanoparticles (>10 nm diameter) are monitored using a delay (10 ps) between the pump pulse and the reference-probe pair separated by a calcite crystal. The sensitivity and signal-to-noise ratio (SNR) of photothermal microscopy has gradually advanced. However, the sensitivity is significantly dependent on the optical axis alignment between the pump and the probe beams [15, 17, 18]. Moreover, image acquisition is time-consuming because the imaging module configuration is based on single-point illumination and sample scanning.

Wide-field photothermal microscopy is based on wide-field illumination and a charge-coupled device (CCD) camera [19, 20, 22]. Atlan et al. [20] employed wide-field heterodyne holographic photothermal microscopy with the sensitivity required to detect gold nanoparticles smaller than 50 nm, which allowed for a large observation area (up to 100 μm^2) and rapid photothermal imaging. Choi et al. [22] combined the photothermal imaging techniques with a CCD-based thermoreflectance microscope to detect single gold nanorods (GNRs) with a 25 nm diameter and 102 nm length. The SNR of the detected GNRs was expressed as a histogram to confirm the detection of single GNRs. Although wide-field photothermal microscopy methods may alleviate the above-mentioned problems of scanning-based photothermal microscopy, the sensitivity of each method is insufficient.

In this study, we developed a new photothermal spectroscopy method that combines a tunable continuous-wave pump laser with a wide-field photothermal reflectance microscope. The proposed system has a simple configuration, which reduces the dependence on the optical axis alignment, and allows the detection of multiple nanoparticles during image acquisition. It can also record the spectra of individual nanoparticles with a sufficient sensitivity (20 nm diameter and 84 nm length GNRs) despite the simple imaging processing used, i.e., the four-bucket method. Furthermore, a dark-field microscopy system was used to directly distinguish nanoparticles from

pollutants in the region of interest (ROI) of the sample before performing the photothermal experiment.

2 Experimental method

Figure 1 illustrates the experimental setup of the photothermal reflectance spectroscopy system developed in this study. The system was constructed on a commercial inverted microscope (Eclipse Ti-U, Nikon). The pump beam used for the photothermal excitation of the nanoparticles was a continuous-wave Ti:sapphire laser (Solstis, M Squared) with the following specifications: 700–1000 nm tunable wavelength, <5 MHz linewidth, and 3 W laser power. In this system, the intensity of the pump beam is modulated at a frequency of 1 Hz using a modulation set composed of an electro-optic amplitude modulator (EOM; EO-AM-NR-C1, Thorlabs) controlled using a high-voltage power amplifier (2205, Trek Inc.) and two calcite polarizers (GL5B, Thorlabs). Subsequently, two reflective collimators (RC; RC02SMA-P01, RC04SMA-P01, Thorlabs) transfer and expand the pump beam through a multimode fiber. Then, the expanded beam finally reaches the nanoparticle sample by reflection through a dichroic mirror (DM1). A probe beam with a wavelength of 635 nm, produced by a xenon arc lamp (LB-LS/17, Sutter Instrument Co.), is collimated across lens 1 (L1) with a bandpass filter (BF1; FLH635-10, Thorlabs). Then, it is reflected by a beam splitter (BS) and is focused on the sample through a microscope objective (40 $\times$, NA = 0.75, CFI Plan Fluor, Nikon) to detect the temperature variations with time. The center of the modulation pump beam area ($1/e^2 = 2.0$ mm with a Gaussian intensity distribution) irradiated to the sample was designed to coincide with the center of the probing area (focused probe beam diameter = 0.6 mm). The intensity of the reflected probe beam changes according to the temperature variation arising in the local area around the nanoparticles owing to the pump beam. The beam is passed and reflected by BS and DM2, respectively. Then it passes through BF2 and L2, and finally reaches the monochrome CCD camera (14 bit, 1600 $\times$ 1200 pixels, pco 1600, PCO AG.). BF2 prevents the pump beam from reaching the CCD camera.

For dark-field microscopy, the illumination reaches the nanoparticle sample by passing through a dark-field condenser and DM1. At this time, the scattered light from the nanoparticles passes through the objective lens and the BS and reaches the monochrome and color (12 bit, 2560 $\times$ 1920 pixels, DS-Fi1c, Nikon) CCD cameras via DM2 and the mirror (M), respectively. Dark-field images can be observed only with the illumination on.

The photothermal reflectance image was obtained by applying the four-bucket method with a CCD camera (see Section 3 of the Supplementary material for details) [23]. Dark-field microscopy was used to determine the location of the nanoparticles to be measured in the sample before performing the photothermal experiment. Because scattered color appears differently according to the size and shape of the nanoparticles, the target particles can be selected accordingly [24]. In particular, in the case of nanorods with different aspect ratios, the wavelength band of the absorption and scattered light are red-shifted as the aspect ratio increases [24, 25]. Furthermore, the dark-field microscopy image was compared with a scanning electron microscopy (SEM) image to confirm the presence of the individual, evenly spaced nanoparticles within the sample (Figure S1). Therefore, compared with the photothermal microscopy mentioned in the introduction, which

Figure 1: Schematic of the wide-field photothermal reflectance spectroscopy system used in this study. The inset shows the simple configuration of the wide-field photothermal reflectance spectroscopy system, which incorporates a pump beam, a probe beam (Xenon arc lamp), and charge-coupled device (CCD) cameras into a commercial microscope setup.

detects nanoparticles while scanning a random region, this method can quickly find the area of individual target nanoparticles.

3 Results and discussion

In the reflected sample image, individual GNRs with a size of 100 nm or less cannot be observed owing to the low SNR/background ratio (Figure 2a). Therefore, it is necessary to locate the individual GNR on the dark-field image (Figure 2b) before performing the photothermal reflectance imaging experiment. The intensity of the pump beam was modulated at a 1 Hz frequency and irradiated on the location of the dispersed GNRs. The refractive index of the surrounding medium changed due to the heat generated from the GNRs, and the reflected probe beam was collected by the CCD camera. This variation in reflectance is shown in Figure 2c as a photothermal reflectance image. It was

confirmed that the photothermal reflectance signals were detected at the same locations as the GNRs observed in the dark-field image. The photothermal reflectance image is a zoomed-in image of the actual measurement area ($240\ \mu\text{m} \times 180\ \mu\text{m}$). Hundreds of GNRs can be measured in the one detection process. However, a sufficient SNR must be ensured to distinguish the GNRs detected in a large area. An SNR is related to the change in the amplitude of the probe beam reflected on the sample, owing to the heat generated by the GNRs. A sample was prepared by enclosing GNRs using polydimethylsiloxane (PDMS) (Figure S2, see Supplementary material for details), which has a low thermal conductivity ($0.15\ \text{W/m K}$), to confine the heat in a local area. Furthermore, PDMS has a large and linear thermo-optic coefficient ($-4.5 \times 10^{-4}/^\circ\text{C}$) compared to other materials [26, 27]. The relative reflectivity change of the surface of the PDMS layer was measured as the PDMS temperature was increased (Figure S4, see Supplementary

material for details). The thermorefectance coefficient was $-1.23 \times 10^{-3}/\text{K}$ with a $20\times$, 0.4 NA objective lens, and a 635 nm wavelength probe beam. The PDMS layer is transparent at visible and near-infrared (NIR) wavelengths, which minimizes the loss of intensity when the pump beam reaches a GNR [28]. The SNR in images of 147 GNRs obtained with and without PDMS was found to be 5.84 ± 0.73 and 2.77 ± 0.55 , respectively (Figure 2d). Therefore, the SNR increased 2.1-fold times when PDMS was used.

Before the spectral analysis, a test was conducted to verify whether the photothermal reflectance signal of the GNRs changed according to the variation in the wavelength of the pump beam. The average aspect ratio of the GNRs used was measured to be 3.8 ± 0.6 (Figure S5). The wavelength of the pump beam was increased from 750 to 870 nm in steps of 10 nm, and the variation in the photothermal reflectance signal was observed (Figure S6). Using an optical

attenuator, the intensity of the pump beam was maintained at a constant value as the wavelength changed. The SNR decreased gradually as it moved away from the 810 nm wavelength to both sides (Figure S6), which proves that the photothermal reflectance signal responds well to the variation in the wavelength. The photothermal reflectance signal was measured 10 times for each wavelength, and the peak position of the absorption spectrum was determined through Lorentzian fitting [29]. The transverse plasmon resonance of the GNRs was not considered owing to the limitation of the tunable wavelength range (700 – 1000 nm) of the pump beam.

Figure 3 illustrates the absorption spectra of five GNRs, which were selected using the collected photothermal reflectance signals for each wavelength. It can be seen that as the wavelength approaches 810 nm from both ends, the standard deviation of the absorption increases gradually.

Figure 2: Photothermal microscopy for single nanoparticle detection.

(a) Reflection image of gold nanorod (GNR) sample. The low signal-to-noise ratio (SNR) /background ratio prevent the observation of the GNRs on the sample. (b) Dark-field image of the GNR sample area is shown in (a). The positions of individual GNRs that could not be observed in the reflection image can be determined. (c) Photothermal reflectance image of the GNR sample area shown in (a) acquired using a pump beam at an 810 nm wavelength with a heating intensity of $1.5\ \text{kW cm}^{-2}$ and modulation frequency of $1\ \text{Hz}$. (d) Influence of the surrounding medium on the photothermal signal of individual GNRs. The mean SNR $\pm$ standard deviation values are 5.84 ± 0.73 and 2.77 ± 0.55 for 147 of single GNRs with and without the PDMS as surrounding medium, respectively.

This indicates that the photothermal reflectance signal responds sensitively as the absorption spectrum is closer to the peak position. As the intensity of the pump beam for each selected wavelength increases, the photothermal reflectance signal increases linearly (Figure S7). In addition, the relative variation in the photothermal reflectance signal of the five GNRs (inset of Figure 3) was measured in the wavelength range of 750–870 nm, and it was found to be within 15% on an average, which indicates good measurement reproducibility (Figure S8).

Figure 4 shows the results of the wide-field photothermal reflectance spectroscopy and the absorption spectrum (see the gray solid line) of the GNR ensemble measured using a UV–VIS/NIR spectrophotometer. To more accurately compare the GNR absorption spectra, the results from Figure 3 are normalized to the different lines. The full width at half maximum (FWHM) of the absorption spectrum is an indicator of how sensitively the GNRs respond to changes in the wavelength of the pump beam. The FWHMs of the absorption spectra of the individual GNRs are approximately 2.1 times narrower than that of the GNR ensemble acquired by conventional spectrophotometry, which cannot measure the absorption spectrum of the individual GNRs. These results demonstrate that the proposed method can precisely measure the absorption spectra of individual nanoparticles.

The difference in the refractive index of the surrounding medium affects the absorption peak position of nanoparticles. As the refractive index of the surrounding medium increases, the absorption peak of the nanoparticles is red-shifted [25, 30]. Here, the refractive indices

of the surrounding mediums used for the GNR ensemble and individual GNR samples are 1.33 (water) and 1.43 (PDMS), respectively. As shown in Figure 4, because the refractive index of PDMS is larger than that of water, the absorption peaks of the individual GNRs are red-shifted compared to that of the GNR ensemble.

The absorption peak wavelength is also affected by the aspect ratio of the GNRs; as this value increases, the absorption peak is red-shifted [25]. The absorption peak wavelengths are 806.8, 813.1, 808.1, 808.8, and 811.9 nm for GNR #1–#5, respectively. From the SEM images (right inset of Figure 4), the aspect ratios of GNR #1–#5 were found to be 3.91, 4.06, 3.96, 3.93, and 4.03, respectively (left inset of Figure 4). Theoretically, GNR #1 and #2, which have aspect ratios of 3.91 and 4.06, respectively, should be the most strongly blue- and red-shifted, respectively, among the five individual GNRs. From the left inset of Figure 4, where the absorption peak positions are clearly observed in the expanded plots of the spectra, it can be clearly seen that the absorption peaks of the individual GNRs are located in the order of their aspect ratios, which is consistent with the predictions.

To verify the measured absorption spectra, experimental results are compared with the theoretical calculations. For the theoretical calculation of the absorption spectra of the GNRs of different aspect ratios, the Mie-Gans theory is used (Figure S9, see Supplementary material for details) [31, 32]. The values of the peak wavelength difference between the experimental and calculated results are 5.9, 5.9, 4.9, 5.1, and 5.2 nm, respectively, in the order of the aspect ratio values. This difference seems to be an error

Figure 3: Absorption spectra of individual gold nanorods (GNRs) acquired by photothermal reflectance spectroscopy. The inset shows scanning electron microscopy (SEM) and photothermal reflectance images of individual GNRs. Each of the spectra corresponds to five individual GNRs; Lorentzian fits are shown as correspondingly colored lines. The standard deviation of the absorption intensity increases gradually as the wavelength approaches 810 nm owing to the sensitivity of the response of the photothermal reflectance signals to the pump beam. The length $\times$ diameter (aspect ratio) values of GNR #1–#5 are 86.9 nm $\times$ 22.2 nm (3.91), 86.8 nm $\times$ 21.4 nm (4.06), 85.6 nm $\times$ 21.6 nm (3.96), 88.5 nm $\times$ 22.5 nm (3.93), and 85.9 nm $\times$ 21.3 nm (4.03), respectively.

Figure 4: Normalized absorption spectra of individual gold nanorods (GNRs) and GNR ensemble. The gray solid line is the absorption spectrum of a GNR ensemble measured by UV-VIS/NIR spectrophotometry. The other lines are the absorption spectra of individual GNRs. The left inset shows expanded views of the absorption spectra of individual GNRs, which allows the comparison of the absorption peak positions. The overlaid numbers on the left inset indicate the aspect ratio of the individual GNRs. The right inset shows scanning electron microscopy (SEM) images of the individual GNRs, with their lengths and diameters given in the overlaid text.

caused by the difference in the dielectric constant value of the PDMS applied in the theoretical calculation from that of the experiment. It comes from an inevitable difference in the condition of the sample preparation process, such as curing temperature and time, the ratio of the PDMS base and curing agent, etc. [33]. Furthermore, as reported by Prescott et al. [34], the volume difference and the end-cap geometry of the GNRs used in the experiment can affect the absorption peak wavelength even if the aspect ratio is the same. The relationship between the experimental and calculated absorption peak wavelength and the aspect ratio of the GNRs is expressed as shown in Figure S10. The absorption peak wavelengths of both the results are linearly red-shifted as the aspect ratio of the GNRs increases. When the aspect ratio of the GNRs is changed from 3.91 to 4.06, the absorption peak wavelength variations of the experiment and the calculation are 6.3 and 7.0 nm, respectively. As a result, the measured absorption peak shift depending on the aspect ratio of the GNRs is in very good agreement with the theoretical calculation.

In the previous spectroscopic results (Figure 4), the measured peak absorption wavelength range for the GNRs was rather narrow (6.3 nm). To prove that wide-field photothermal reflectance spectroscopy as proposed in this paper is effective over a wider wavelength range, additional experiments were carried out using the same sample. As shown in Figure S11, the GNRs observed in the dark-field image Figure S11(a) were confirmed by the signals detected in the photothermal reflectance image Figure S11(b). Absorption spectra (Figure S12) were obtained by extracting

the photothermal reflectance signals of six GNRs in the ROI (white outlined box) defined in Figure S11(a) and S11(b) for each wavelength. The difference between the shortest and the longest peak absorption wavelengths for the measured GNRs was 53.9 nm. Thus, we have demonstrated by means of additional experiments that the proposed photothermal reflectance spectroscopy method is capable of measuring the absorption spectra of GNRs that have greater peak absorption wavelength differences.

4 Conclusions

We presented a method to measure the absorption spectra of single nanoparticles by applying a variable-wavelength pump beam to a wide-field photothermal reflectance microscope system for a simple composition. Compared to scanning-based photothermal microscopy, the proposed system can measure the absorption spectra of multiple individual nanoparticles quickly and easily by adding a few functions to a commercial microscope without the requirement of a precise optical axis alignment. In addition, by applying a dark-field imaging system, the target GNRs can be quickly selected, which reduces the measurement time, and the ROI is detected accurately. Furthermore, the measurement precision, which depends on the shape and size of the nanoparticles, is comparable to that obtained using conventional UV-VIS/NIR spectrophotometry. We recorded the absorption spectra information of a large number of individual nanoparticles by applying the one measurement

process. In future studies, it is expected that distinguishable absorption spectra can be obtained for mixed nanoparticles of different sizes and shapes, given the proven spectral resolution of the proposed technique.

Abbreviations

CCD	Charge-coupled device
SNR	Signal-to-noise ratio
GNR	Gold nanorod
ROI	Region of interest
EOM	Electro-optic amplitude modulator
RC	Reflective collimator
DM	Dichroic mirror
L	Lens
M	Mirror
LP	Linear polarizer
BF	Bandpass filter
BS	Beam splitter
PDMS	Polydimethylsiloxane
FWHM	Full width at half maximum

Author contributions: Jung-Dae Kim and Dong Uk Kim contributed equally. All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

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