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Absorption spectra of localized surface plasmon resonance observed in an inline/picoliter spectrometer cell fabricated by a near ultraviolet femtosecond laser

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ABSTRACT

Absorption spectra based on localized surface plasmon resonance (LSPR) were obtained with an inline/picoliter spectrometer cell. The spectrometer cell was fabricated into an optical glass fiber by focusing a near UV (NUV) femtosecond laser pulses at a wavelength of 400 nm with an energy of 30 μJ. The laser beam was focused from two directions opposite to each other to fabricate a through-hole spectrometer cell. A diameter of the cell was approximately 3 μm, and the length was approximately 62.5 μm, which was nearly equal to the core diameter of the optical fiber. Liquid solution of gold nanoparticles (GNPs) with a diameter of 5–10 nm was injected into the spectrometer cell with its volume of 0.4 pL. The absorption peak centered at 518 nm was observed. An increase of absorption associated with the increase of the number of nanoparticles was in agreement with the numerical calculation based on the Lambert–Beer law.

1. Introduction

Metal nanoparticles have a potential to solve advanced problems in the various fields such as bio-measurements [1–3]. The plasmon in the metal nanoparticles is induced by propagating the incident light through the nanoparticles. A specific wavelength of the light is then absorbed by the plasmon, which is specifically called as localized surface plasmon resonance (LSPR). A wide availability of stable gold nanoparticles (GNPs) with various diameters has been utilized with different resonance wavelengths in the visible spectral region. The resonance peak of the plasmon is tunable by selecting the size, shape and composition of nanoparticles. The peak wavelength is also sensitive with the refractive index of the external condition surrounding nanoparticles. For example, biomolecules were immobilized onto the target surface with GNPs. The biomolecules attached to the target with GNPs induced the change of the surrounding condition of nanoparticles, leading to the shift of the plasmon resonance spectra [4,5].

The LSPR is also induced by using unique designs of optical fibers. A U-bent optical fiber was suitable for obtaining spectra of LSPR [6–8]. A cladding layer of a fiber was removed and the core layer was exposed. The exposed core region was then bent with flame. An evanescent wave of the propagating light was generated effectively because of the bending structure. In order to stabilize the GNPs onto the sensing region, an aminosilane solution was used to form a self-assembled monolayer (SAM). The GNPs were stabilized onto the sensing area, whereupon biomolecules were modified on the surface of the nanoparticles. For instance, by selecting glucose oxidase for sensing material, blood glucose was detected [9]. A tip-shaped fiber optic was also utilized for bio-sensing [10]. The end-face of the fiber optic was used for a sensing element. The surface of the sensing element was aminosilanized and the GNPs were stabilized onto the surface. The interaction between propagating light and GNPs was recorded in the reflected light. After bio-modification on the surface of GNPs, antibody–antigen reaction such as interferon-gamma was detected [11].

On the other hand, femtosecond laser processing has advantage for removing materials with minimized heat effects. In the femtosecond temporal regime, laser irradiation onto the materials such as metals [12], semiconductors [13], and dielectrics [14] completed before the noticeable deformation of processed regions due to a thermal effect. Nonlinear optical phenomena such as multiphoton ionization are also induced in the materials because of the high peak power of the

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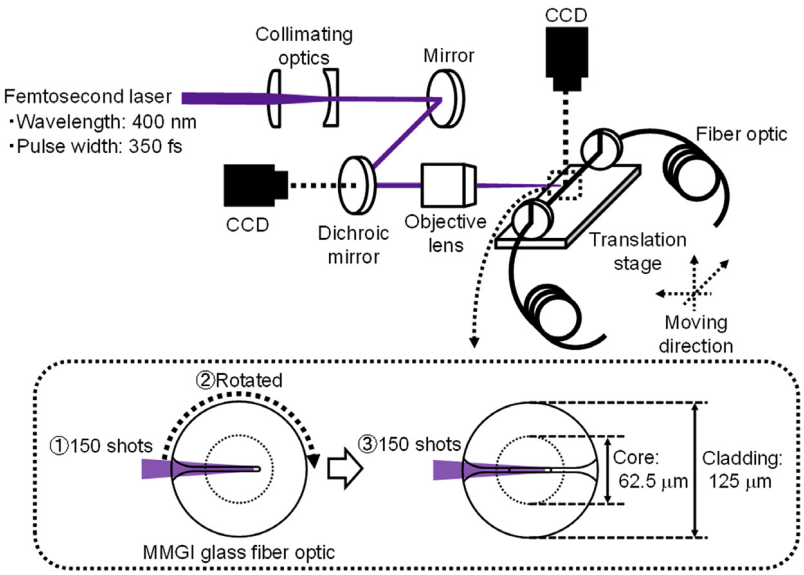

Fig. 1. The experimental apparatus of the laser system to fabricate an inline/picoliter spectrometer cell. Inset represents a schematic diagram of two-directional irradiation to make a through-hole for the spectrometer cell.

femtosecond laser pulses. Femtosecond laser drilling was also applied to even transparent materials. A microhole in the middle of a glass optical fiber was fabricated by using femtosecond laser pulses at the wavelength of 400 nm [15,16]. The microhole in the optical fiber worked as a spectrometer cell, and it had capability of measuring the refractive index of liquid samples in the picoliter volume. The GNPs were also introduced into the inline/picoliter spectrometer cell. The spectroscopy of liquid with a small volume of the cell meets the conditions of inducing LSPR.

Various sensing targets can be detected by a colorimetric method using aggregation of GNPs in the inline/picoliter spectrometer cell [1–3]. It is, therefore, important for us to observe the absorption spectra in the solution of GNPs in the novel spectrometer cell. In addition to the advantage of the picoliter volume, the fabrication of the spectrometer cell inside an optical fiber is applicable and usable, since the spectrometer cell is directly connected with the optical devices. Moreover, GNPs need not be immobilized inside the spectrometer cell. Preparation of chemical thin layers to immobilize GNPs, therefore, may not be necessary in the optical fiber. The optical fiber sensor using LSPR should further make the measurement system inexpensive, since the system is simply fabricated and is miniaturized.

In this paper, we have observed the absorption spectra based on LSPR with the spectrometer cell with a volume on the order of picoliter. The spectrometer cell was fabricated in a commercially available multi-mode graded index (MMGI) glass optical fiber by focusing a near UV (NUV) femtosecond laser pulses at a wavelength of 400 nm with an energy of 30 μJ. The laser beam was focused from two directions opposite to each other to fabricate a through-hole spectrometer cell. A diameter of the cell was approximately 3 μm, and the length was approximately 62.5 μm, which was nearly equal to the core diameter of the optical fiber. Liquid solution of GNPs with a diameter of 5–10 nm was injected into the spectrometer cell with its volume of 0.4 pL. The absorption peak centered at 518 nm was observed. An increase of absorption associated with the increase of the number of nanoparticles was in agreement with the numerical calculation based on the Lambert–Beer law.

2. Experiment

2.1. Fabrication of inline/picoliter spectrometer cell

The experimental setup of fabricating the inline/picoliter spectrometer cell is shown in Fig. 1. The second-harmonic femtosecond pulses at 400 nm were irradiated from an infrared femtosecond Ti:Sapphire laser system (IFRIT, Cyber Laser Inc.). A pulse width, a typical pulse energy and a repetition rate were 350 fs (Gaussian), 30 μJ and 1 kHz, respectively. An original beam diameter of 6.0 mm was reduced to 2.8 mm to meet the size of the focusing optics by using a set of collimating lenses. The spectrometer cell was fabricated in the middle of a MMGI glass fiber, which had the core and cladding diameters of 62.5 and 125 μm, respectively. The optical fiber was mounted onto a three-dimensional translation stage with motorized rotating clamps. The laser pulses were focused at 50 μm in depth from the surface of the fiber by using an objective lens with a numerical aperture (NA) of 0.65. The focal area was determined with two CCD cameras, which were orthogonally placed to monitor the focus. The femtosecond pulses with 150 shots launched into the optical fiber to make a microhole [16]. After rotating the fiber 180°, the other pulses with 150 shots were focused into the fiber to make a micro through-hole, which was acted as a picoliter spectrometer cell.

Fig. 2 shows cross-sectional scanning electron microscope (SEM) photographs of the fabricated spectrometer cell. The white dotted circle in Fig. 2(a) indicates the boundary between the cladding and core layers. Note that small clacks observed around the through-hole was unintentionally produced by cleaving the fiber for the observation. It was confirmed that the through-hole spectrometer cell was fabricated in the glass optical fiber as shown in Fig. 2(b). The funnel shapes produced at the both exits indicated the focusing optical geometry. On the other hand, the through-hole was produced by self-channeling of the high-intensity laser irradiation, which was not affected by the focusing geometry [16]. In the core region, where the spectrometer cell was interacted with light irradiation though the fiber, a diameter of the spectrometer cell was approximately between 3 and 5 μm. Assuming that the diameter of the spectrometer cell was 3 μm, an active volume of the cell was approximately 0.4 pL.

2.2. Obtaining the absorption spectra

Fig. 3 shows a schematic diagram of the experimental setup for obtaining absorption spectra based on LSPR. A solution of GNPs was purchased from Tanaka Kikinzoku Kogyo Co., Ltd. The GNPs with a diameter between 5 and 10 nm were dispersed in pure water. Polyvinylpyrrolidone (PVP) covered the surfaces of GNPs to prevent conjugation each other.

A combination of a halogen white light source (HL-2000, Ocean Optics, Inc.) and a compact CCD spectrometer (CCS200/M, Thorlabs,