博士論文（要約）

Development of Optical Methodology

for Extended-nano Fluidic Device Engineering

（拡張ナノ流体デバイス工学に向けた光学手法の開発）

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1. Introduction

Over the past decades, microfluidics has contributed various functional devices for analysis, synthesis, bio and related sciences and technologies. Recently, the downscaling of micro space to 10^1-10^2 nm space, which is referred to as extended-nano space, has opened new perspectives for integrated chemical systems. As the dimensions of channels decrease to extended-nano scale, unique fluidic and transport behaviors, which are negligible or absent in micro scale, play increasingly significant roles. For example, the liquid confined in 10^1-10^2 nm space was reported to have higher proton mobility, higher viscosity, and low dielectric constant, compared to those in bulk.[1] Various novel analytical devices have also been developed to exploit new functionality. Especially, the 10^1 nm space, whose scale is comparable to the characteristic length scales such as electric double layer (EDL), proton transfer layer, or the size of biomolecules promises many novel properties and devices, however the lack of fundamental methodology has limited the studies in this region of extended-nano fluidics.

Optical methodologies have been widely applied in detection, surface chemical modification, or fluidic control in microfluidics and extended-nano fluidics in 10^2 nm space. For example, the differential interference contrast thermal lens microscopy (DIC-TLM) is one of the ultra-sensitive optical detections applicable to nonfluorescent molecules in 10^2 nm space.[2] However, the introduction of optical methodologies into 10^1 nm space is quite challenging, as the channel size is one order smaller than the wavelength of light, and the confocal length (~μm) that determines the detection area or the diffraction limit (~10^2 nm) that determines the spatial resolution of photochemical reactions. In such cases, conventional methods employing far-field light are not applicable. I focused on the optical near-field (ONF). ONF is generated on nanostructures whose sizes are much smaller than the wavelength. ONF can confine light in ~10^1 nm spaces and it has an apparent energy higher than incident photon.[3] Therefore, the introduction of ONF into 10^1 nm space is expected to solve the problems of far-field light and bring new functionality. In this study, novel optical methodologies were developed for extended-nano fluidics in 10^1 nm space by device engineering and the integration of ONF. This doctoral thesis consists of five chapters.

Chapter 1: Introduction
Chapter 2: DIC-TLM detection in 10^1 nm space
Chapter 3: ONF-assisted DIC-TLM detection of UV-absorbing biomolecules by visible light
Chapter 4: ONF-assisted photochemical reactions for fabrication
Chapter 5: Concluding remarks

2. DIC-TLM detection in 10^1 nm space

2. 1. New channel structure for compensation of signal cancellation in DIC-TLM detection

The principle of DIC-TLM detection is based on the change of temperature (dT), as the target molecules absorbs the excitation light, following by the change of refractive index (dn) in the medium. Signals are detected as the phase shift of light due to the change of refractive index, thus they are very sensitive to thermo-optical coefficient dn/dT of materials. When the channel size becomes 10^1 nm scale, most of generated thermal diffuses to the substrates. In conventional fluidic devices, SiO_2 is usually used as substrate material. The dn/dT of SiO_2 is positive ($dn/dT = +9.8 \times 10^{-6}$ K^{-1}), while those of value in solvents are negative. Consequently, the signal induced by solvents is cancelled out by that of SiO_2 (figure 1(a)). Here, I proposed the compensation

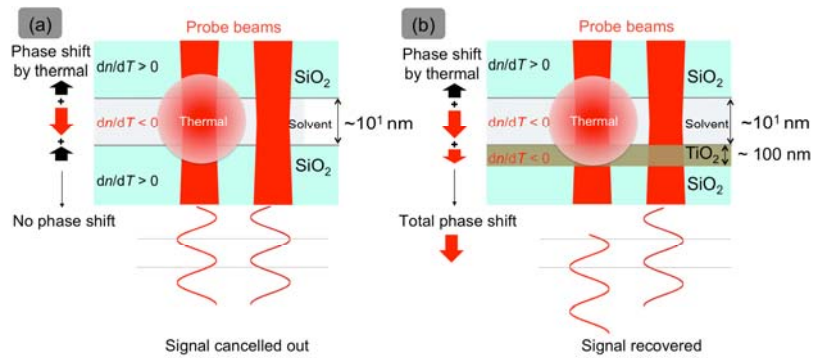Figure 1. (a) Signal cancellation in 10^1 nm SiO_2-channel and (b) TiO_2-channel structure for compensating of signal cancellation

of cancellation by a new channel structure using negative dn/dT material - TiO_2 ($dn/dT = -3.0 \sim 1.8 \times 10^{-4}$ K^{-1}), as shown in figure 1(b). The phase shift induced in the lower TiO_2 substrate will compensate the phase shift in the upper SiO_2 substrate, consequently the signals are recovered. The required thickness of TiO_2 was determined to be 100 nm according to the calculation of thermal diffusion length in TiO_2 material.

2. 2. Verification of compensation of cancellation and DIC-TLM detection in 10^1 nm channel

The microchip using TiO_2 was successfully fabricated. The DIC-TLM measurements in TiO_2-channels with various channel depth d ranging in $10^1 - 10^2$ nm were investigated, using Sunset Yellow dye as analyte and ethanol as solvent. The result in figure 2(a) clearly shows that sensitivity in SiO_2-channel is proportional to $(depth)^3$, while in TiO_2-channel,
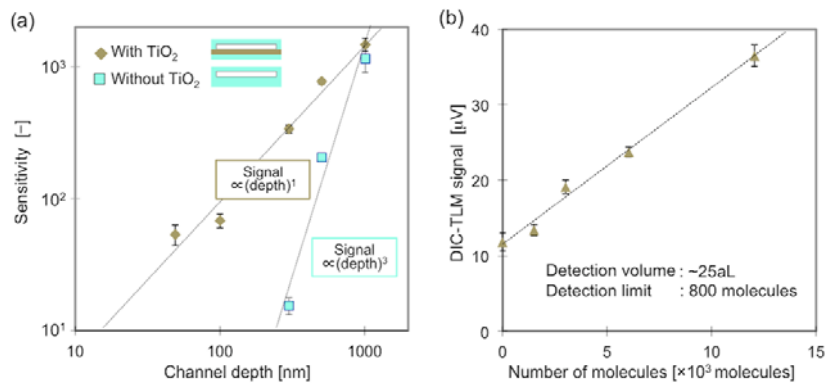

Figure 2(a) Dependency of sensitivity on depth in TiO_2 and SiO_2-channel and (b) calibration curve of Sunset Yellow in TiO_2-channel (depth = 50nm)

sensitivity is proportional to $(depth)^1$. It indicated that the signal cancellation was successfully compensated in TiO_2-channel, because without cancellation, the sensitivity should be proportional to $(depth)^1$ or the detection volume. The DIC-TLM detection was also successfully demonstrated in 50 nm-deep TiO_2-channel. The limit of detection (LOD) reached to zeptomole in a detection volume of 25 aL (figure 2(b)).

3. ONF-assisted DIC-TLM detection of UV-absorbing biomolecules by visible light

4. ONF-assisted photochemical reactions for fabrication

4. 1 Partial surface modification by ONF

Photochemical surface modification is an important technique in functionalization of devices such as patterning of biomolecules for molecular capture, hydrophobic/hydrophilic patterning for fluidic control, etc. However, in 10^1 nm space, as the channel size is much smaller than the wavelength, the conventional far-field techniques are not applicable due to the diffraction limit of light. Here, new concept of partial surface modification by ONF on nanostructures was proposed as described in figure 3(a). As TiO_2 nanostructures were irradiated with visible (488 nm) light, ONF was generated and enhanced at the edges of nanostructures. This ONF allows the excitation of TiO_2, leading to the photocatalytic decomposition of modifying chemicals (e.g. hydrophobic octadecylsilane (ODS)) at the edges

Figure 3.(a) Principle of partial surface modification by ONF (b) (c) ODS decomposed at edges on $10^1 – 10^2$ nm scale verified

of nanostructures, even though the light energy (visible) is lower than the bandgap of TiO_2 (~380 nm). SEM images in figure 3(b), (c) verified the ODS decomposition at the edges or nanostructures while the centers remained untreated. At minimum, 40 nm ODS-decomposed (hydrophillic) patterns were achieved (figure 3(c)). Importantly, the pattern size could be easily controlled on $10^1 – 10^2$ nm scale by 488-nm irradiation intensity.[4]
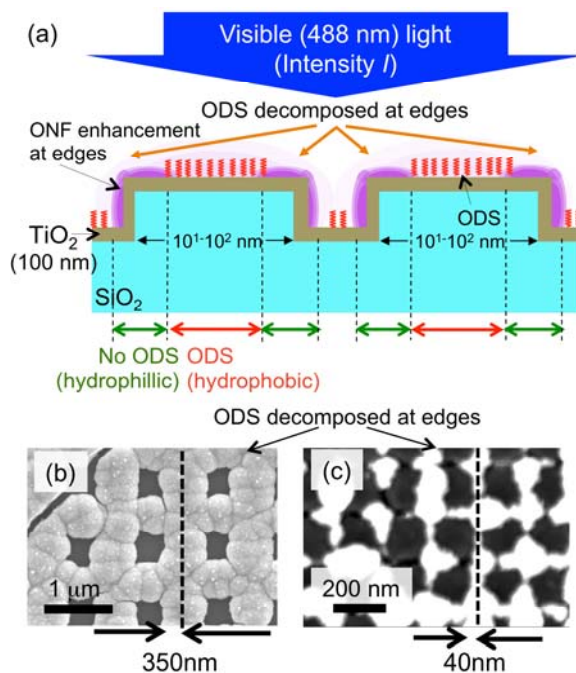
<u>4. 2 Visible response photocatalytic water splitting by ONF</u>

The ONF-assisted photochemical reaction was also applied to the photocatalytic water splitting by visible light. The result showed a two orders enhancement in visible response of water splitting in nanostructures TiO_2 compared to TiO_2 flat film without nanostructure. The enhancement was attributed to the ONF generated on nanostructures TiO_2 and ONF-assisted excitation of TiO_2 by visible light. The reaction is promising for fuel (hydrogen) generation in integrated energy devices.[5]

5. Concluding remarks

In summary, novel optical methodologies such as DIC-TLM detection, surface modification, etc. were successfully introduced to extended-nano fluidics in 10^1 nm space by device engineering and the integration of ONF. This study has contributed fundamental tools that may accelerate the studies on fluidic behavior, or properties of liquid confined in 10^1 nm space, as well as the development of functional devices employing those unique properties. The combination of nanophotonics and extended-nano fluidics also promises many novel spectroscopies in extremely small spaces.

6. References

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