

OPTICAL NEAR-FIELD INDUCED CHEMICAL PARTIAL HYDROPHOBIC/ HYDROPHILIC MODIFICATION WITH SUB-DIFFRACTION LIMIT RESOLUTION

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ABSTRACT

This study reports a novel partial hydrophobic/hydrophilic modification using the optical near-field (ONF) induced photocatalytic reaction. Herein the achievement of sub-diffraction limit resolution by photo-induced method opens a new platform towards extended-nano (100nm~1000nm) fluidic devices, in which the partial surface modification is indispensable to exploit functional applications, yet difficult to realize due to the diffraction limit nature of light. It is also worthy to note that the simple experimental setup and feasible protocol in our method promise critical impacts on surface modification and the development of extended-nano devices.

KEYWORDS

Optical near-field, partial surface modification, sub-diffraction limit resolution, nano/ extended-nano fluidics

INTRODUCTION

Recent researches have targeted to extended-nano (100nm~1000nm) fluidic system to explore new science and technology in the space that bridges the gap of single molecule and condensed phase. We have previously clarified specific properties of liquid confined in extended-nano spaces such as enhanced proton mobility, high viscosity, and utilizing them in novel separation, single cell analysis devices, integrated fuel cell, etc... [1]. However, one of the most challenging issues in realizing functional nano/extended-nano fluidic devices is the partial surface modification. With state-of-the-art lithography such as dip-pen lithography, the modified pattern has been reached several hundreds nm resolution [2], yet its direct writing (contact) protocol is not suitable for closed spaces like channels. Photo-induced methods are dominant technology in microfluidic, for they operate in non-contact mode; however the diffraction limit nature of light poses critical challenges in scaling down patterns to extended-nano scale. The emerging development of deep UV sources or superlenses technique have attracted much attention in electronic fields to scale down the spatial resolution of photolithography, however the complicated protocol and expensive setup limit its practical application as surface modification in nano/extended-nano fluidics [3]. In this study we have developed a novel photo-induced modification method with sub-diffraction limit resolution, using the optical near-field (ONF) induced photocatalytic reaction on nanostructure TiO_2 . In previous works, we have reported the excitation of TiO_2 with light energy lower than its bandgap (~380nm, equivalent to UV light) by using the ONF generated on nanostructures. For example, we have observed more than 2 orders of magnitude enhancement of visible response photocatalytic activity of nanorod TiO_2 as compared to that of flat film and we attributed it to the ONF-induced excitation of TiO_2 [4,5]. The large difference in visible response photocatalytic activity of nanostructure and flat TiO_2 has inspired us a novel modification of surface by photo chemical reaction using visible light.

PRINCIPLE

Fig.1 shows the concept of ONF-induced selective decomposition of Octa Decyl Silyl (ODS) monolayer (hydrophobic) at nanostructure TiO_2 (hydrophilic). For the generation of ONF, patterns (nanopillars or nanogaps) with the size of 100nm~500nm are fabricated on fused-silica, followed by the deposition of TiO_2 , and the surface is then modified with ODS. As the whole substrate is irradiated with visible propagating light (488nm), ONF is generated at the nanopatterns only and it allows the excitation of TiO_2 , followed by the decomposition of ODS even though the light energy is lower than its bandgap (~380nm). The usage of visible light here in leads to the selective removal of ODS at ONF-generated sites only. Since on the remaining areas, 488nm could not excite TiO_2 , consequently no decomposition reaction occurs. To analyze the spatial resolution of decomposition, we introduce the selective photo-deposition of Pt onto the ODS-removed area by exploiting the photocatalytic activity of exposed TiO_2 , and observed the spatial resolution by scanning electron microscopy (SEM).

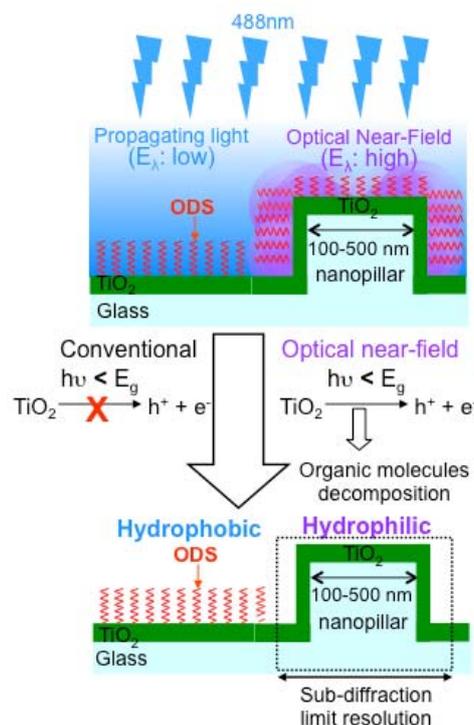


Figure 1. Concept of ONF-induced decomposition of ODS on TiO_2 nanopillars

EXPERIMENT

The experiment was conducted using an open flat substrate to confirm the principle and spatial resolution before applying into fluidic application, according to the scheme shown in Fig. 2. Patterns with extended-nano size (100nm~500nm) were fabricated onto fused-silica substrate by electron beam lithography and dry etching. The fabricated substrate was deposited with 30nm-thick and 120nm-thick layers of ITO (for conductive purpose in SEM observation) and TiO₂ (for photocatalytic reaction) respectively. The whole film was then modified with ODS monolayer (hydrophobic) by silane coupling reaction on TiO₂ surface. The hydrophobic film was irradiated with visible light (488nm) spot in 5 hours at certain power density to decompose the ODS at nanopattern area only, as there is no ONF generated at the flat area. The decomposition of ODS was confirmed by staining the non-decomposed ODS with fluorescent dye (Rhodamine B) and observed under florescent microscope. However, this optical method is impossible to analyze the spatial resolution of decomposition. The analysis of spatial resolution was conducted by selectively depositing Pt onto the exposed TiO₂ by wet protocol. The whole film was dipped into H₂PtCl₆ 2.0mM; 10% ethanol and irradiated from the backside under 5mWcm⁻²; 365nm light by a Hg lamp equipped with 365nm band pass filter, in 30 min. The platinization reaction is expected to strongly enhance at exposed TiO₂ surface by the assistance of photocatalytic activity of TiO₂. As a result, Pt is deposited merely onto the exposure of TiO₂, while the ODS-modified area is remained untreated.

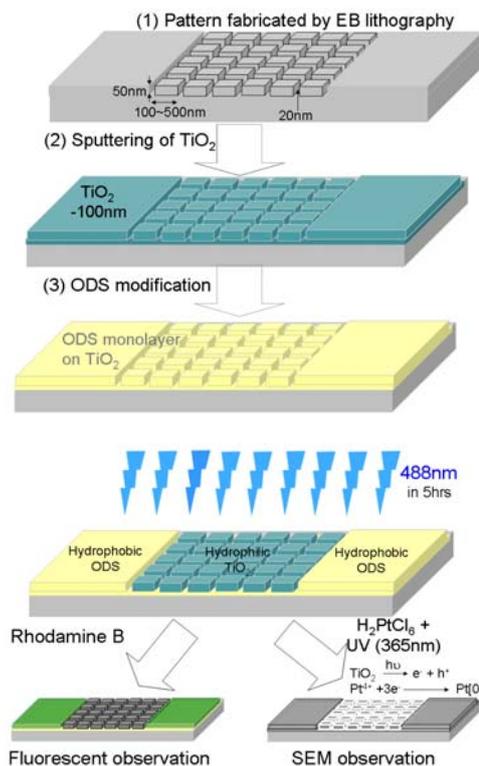


Figure 2. The schematic diagram of the whole protocol: fabrication, modification and observation on open flat substrate to verify the concept

RESULTS AND DISCUSSION

The contact angle of TiO₂ flat film before and after modification of ODS has been measured to be (24.3° ± 5.6°) and (81.5° ± 2.9°) and respectively. The Fig. 3(a) shows the decomposition of ODS or the exposure of TiO₂ (hydrophilic) in the irradiated spot, confirmed by fluorescent (FL) microscope and SEM. The ODS decomposition ratio is estimated as below:

$$\text{Decomposition ratio(\%)} = \frac{\text{FL intensity (non-irradiated)} - \text{FL intensity (irradiated)}}{\text{FL intensity (non-irradiated)}} \times 100\%$$

The Fig. 3(b) shows the dependence of decomposition ratio on irradiation intensity in both nanopatterns-fabricated and flat films. The enhancement of up to 6-fold at lower power density and 4-fold at higher power density in nanopattern fabricated films as compared to those of flat ones has been confirmed. This result indicates that the ODS decomposition is strongly enhanced by ONF generated at nanopatterns. The slight decomposition on flat film can be attributed to the absorption of TiO₂'s vacancies that is equivalent to the energy of 488nm. It also suggests that the principle can be applied to obtain a spatial resolution equivalent to that of EB lithography at suitable irradiation intensity.

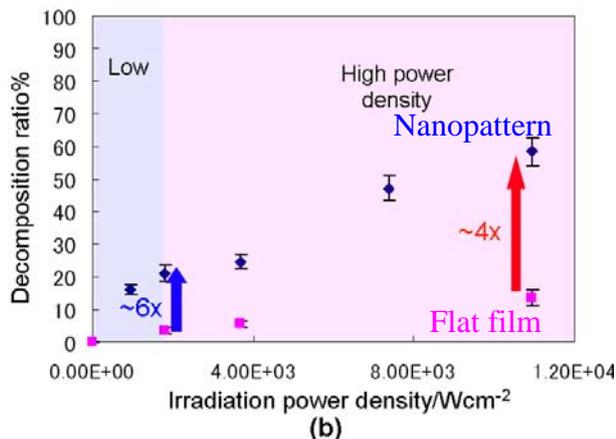
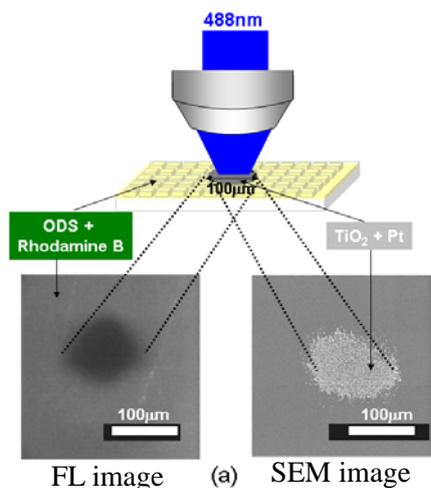


Figure 3.(a) The FL image of irradiation spot after stained by Rhodamine B and SEM image after the photo deposition of Pt (b) The decomposition ratio estimated by FL intensity on both nanopattern fabricated and flat film

The modification on different nanopatterns has been demonstrated and shown in Fig. 4 and Fig. 5. It is obviously

shown that Pt is only deposited on nanopatterns area as bright patterns in SEM. The higher the ODS decomposition ratio is, the more uniform and thicker Pt layer has been formed, with the same Pt deposition condition. To further confirm the existence of Pt, the Energy dispersive X-ray spectrometry (EDS) analysis has been introduced and the mapping result clearly shows that the bright patterns in Fig. 4 and 5 are Pt atom. At the lower ODS removal ratio (~21.0%) as in Fig.4, a non-uniform and incomplete Pt distribution indicates that the ODS removal is insufficient. Meanwhile at the higher ODS removal ratio (~58.3%) as in Fig.5, it is clearly observed that ODS is completely decomposed and Pt is distributed uniformly onto the nanopatterns. The originally fabricated pattern which is ~400nm in width ~600nm in pitch is shown in Fig. 5(b). After treatment, the spatial resolution of this sample shown in EDS line analysis is calculated to be ~550nm in width and ~450nm in pitch. The broadening of ~150nm (~75nm to each edge of nanopatterns) compared to original patterns has been confirmed and it indicates the achievement of sub-diffraction limit resolution of our method. We believe that the broadening is dependent on the 488nm irradiation intensity used and the optimization under investigation.

PERSPECTIVE & CONCLUSION

Although there is still a broadening of ~75nm to each edge as compared to original patterns fabricated by EB lithography, in this study we have successfully realized a novel photo-induced method of partial surface modification with sub-diffraction limit resolution. The advantage of non-contact protocol in our method raises various feasible applications for surface modification of extended-nano channels such as two-phase flow, local control and handling of fluidic by Laplace valve, etc.... Moreover, the photocatalytic activity of TiO₂ can be further used to selectively modify the surface with functional groups for separation or single cell analysis, etc... Our result also has initially realized the local driving of photochemical reaction in restricted volume, which enables to fulfill the demand of mesoscopic engineering. This method is expected to have a wide range of applications and facilitate the development of new functional nano/extended-nano fluidic devices.

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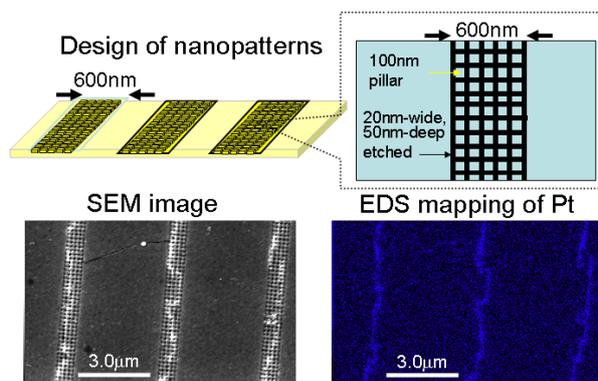


Figure 4. The SEM images and EDS mapping of Pt of the samples with ODS removal ratio of 21.0% clearly shows the exist of Pt on nanopatterns only

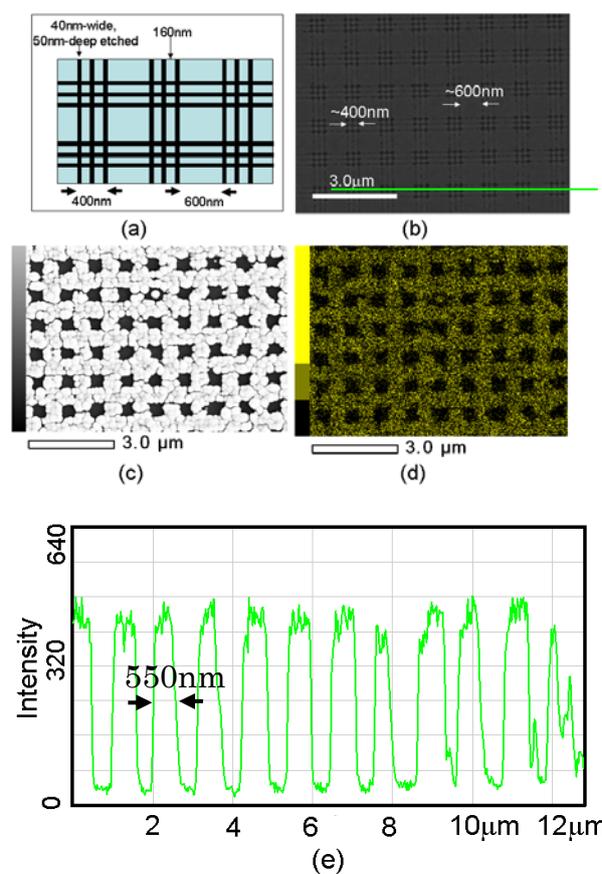


Figure 5.(a) The design of nanopatterns (b) SEM images of origin patterns before treatment (c) The SEM images the samples with ODS decomposition ratio calculated to be 58.3% (d) EDS mapping of Pt atom and (e) EDS line analysis of Pt atom for the same sample. The results shows the broadening of 100nm~150nm compared to original patterns