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Kwang-Sup Lee^a, Moon-Soo Kim^a, Hyun-Kwan Yang^a,
Bong-Keun Soo^a, Hong-Bo Sun^b, Satoshi Kawata^b
& Paul Fleitz^c

^a Department of Polymer and Engineering, Hannam University, Daejeon, Korea

^b Department of Applied Physics, Osaka University, Suita, Osaka, Japan

^c Materials and Manufacturing Directorate, US Air Force Research Laboratory, OH, USA

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LITHOGRAPHIC MICROFABRICATION BY USING TWO-PHOTON ABSORBING PHENYLENEVINYLENE DERIVATIVE

*Kwang-Sup Lee, Moon-Soo Kim, Hyun-Kwan Yang,
and Bong-Keun Soo*

*Department of Polymer and Engineering, Hannam University,
Daejeon 306-791, Korea*

Hong-Bo Sun and Satoshi Kawata

*Department of Applied Physics, Osaka University, Suita,
Osaka 565-0871, Japan*

Paul Fleitz

*Materials and Manufacturing Directorate, US Air Force Research
Laboratory, OH 45433-7707, USA*

The phenylenevinylene-based two-photon absorbing chromophore (EA4BPA-VB) with a triphenyl amine as an electron donor was synthesized. The two-photon absorption (TPA) cross-section values of EA4BPA-VB measured by two-photon-induced fluorescence method with 80 fs-pulse laser were found to be $\sigma_2 = 4.7 \times 10^{-48} \text{ cm}^4\text{s/photon}$. By adding this chromophore into photo-reactive SCR resin, we have successfully fabricated 3-D micro-structure (a larva) with high spatial resolution at low laser power with less than 5 mW. To improve the resolution of 3-D patternings, we also investigated a voxel size and shape depending on laser exposure time and concentration of TPA chromophore in SCR resin at near-threshold exposure condition.

Keywords: lithographic microfabrication; photopolymerization, two-photon absorption

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Address correspondence to Kwang-Sup Lee, Department of Macromolecular Science, Hannam University, 133 Ojunt-Domg Daejeon 306-791, Korea. Tel.: +82-42-629-7394, Fax: +82-42-626-8841, E-mail: kslee@mail.hannam.ac.kr

INTRODUCTION

Two-photon photopolymerization has been recognized as a promising tool for the lithographic microfabrication because two-photon light can deeply penetrate into the medium which result in high spatial resolution [1–3]. Actually by employing this method, a wide variety of 2-D and 3-D photonic and micromechanical devices with a near 100-nm lateral spatial resolution have been successfully developed [4–6]. Such success means that it is possible to accomplish the manufacturing that is otherwise not accessible, and can develop new scientific and technological possibility in nano research.

To improve the resolution of micro-patterns obtained by photopolymerization, the adjustment of the irradiation laser power and the control of the laser exposure time is required. In addition to these, the current research effort is focused to the development of highly efficient TPA chromophores. The large TPA cross-section of chromophores would open a large dynamic power range for tailoring microstructure dimensions by laser power control. In this paper we report the preparation of new TPA active chromophore and the dependence of voxel size by changing the exposure time.

EXPERIMENTAL

Synthesis of TPA Chromophore

To a solution of 4-[(4-bromo-phenyl)phenylamino]benzaldehyde **1** (1 g, 1.58 mmol) and [4-(diethoxyphorylmethyl)-2,5-bis(2-ethylhexyloxy)benzyl]phosphonic acid diethyl ester **2** (1.1 g, 3.15 mmol) in THF (20 mL), sodium *t*-butoxide (0.39 g, 3.15 mmol) was added. The mixture was stirred at room temperature for 4 h. Then the reaction mixture poured into water. After washing, the organic layer was concentrated by rotary evaporator under reduced atmosphere. The product was recrystallized by ethanol and collected by filtration as green solid (1.49 g, 92% yield). ¹H-NMR (CDCl₃, ppm) : δ = 7.68 (2H, d, Ar-CH); 7.65 (2H, d, Ar-CH); 7.57 (2H, s, Ar-CH); 7.54 (4H, t, Ar-CH); 7.47 (2H, d, Ar-CH); 7.44 (2H, d, C=C); 7.42–7.25 (12H, m, Ar-CH); 7.37 (2H, d, Ar-CH); 7.31 (2H, d, Ar-CH); 7.29 (2H, d, C=C); 1.98 (4H, d, -OCH₂-); 1.07–0.64 (18H, m, -CH₂-); 0.63–0.41 (12H, m, -CH₃).

Equipments

For the micro-fabrication, we have employed a laser system of mode-locked Ti-sapphire laser of 780-nm wavelength, 80-fs plusewidth and 82-MHz repetition rate, which was focused by a high numerical aperture (~1.4)

objective lens into the resin [8]. ^1H -NMR spectra were recorded on a Varian NMR (300 MHz). The UV/vis spectra were obtained by using a Perkin-Elmer Lambda14 spectrophotometer. The PL spectrum was obtained using a Fluoro Max-2 fluorescence spectrophotometer.

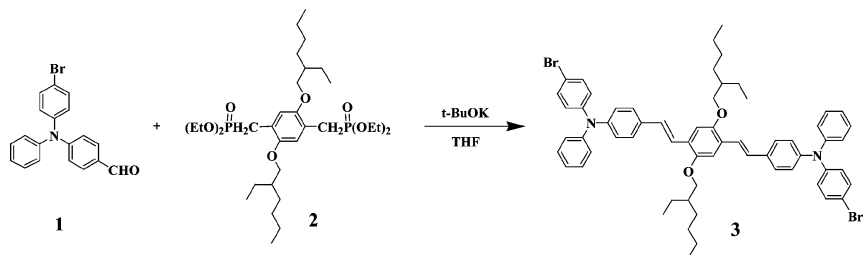
RESULTS AND DISCUSSION

As shown in Scheme 1, TPA chromophore, [1,4-bis(2-ethylhexyloxy)-2,5-bis(2-(4-(bis(4-bromophenyl)amino))vinyl)benzene] (EA4BPA-VB) **3**, was prepared by the Honor reaction of 4-[(4-bromo-phenyl)phenylamino] benzaldehyde **1** and [4-(diethoxyphorylmethyl)-2,5-bis(2-ethylhexyloxy) benzyl]phosphonic acid diethyl ester **2** [9]. The absorption maximum and emission maximum of EA4BPA-VB were observed at 424 nm and 507 nm, respectively (Fig. 1).

The TPA cross-section value (σ) of EA4BPA-VB was determined from two-photon-induced fluorescence method with the following Eq. (1),

$$\sigma_s = \frac{S_s \eta_r \Phi_r C_r}{S_r \eta_s \Phi_s C_s} \sigma_r \quad (1)$$

where the subscripts s and r refer to the sample and reference molecules, respectively. The intensity of signal collected by a PMT detector was denoted as S . The η and Φ are the overall fluorescence collection efficiency and the fluorescence quantum yield, respectively. The number density of the molecules in solution is denoted as C . σ_r is the TPA cross-section value of the reference (fluorescein). To get the experimental σ values, a mode-locked Ti:Sapphire laser pumped by an argon ion laser, whose oscillating pulse duration of 80 fs and repetition rate of 82 MHz was employed as the excitation source. The experimental σ value of EA4BPA-VB was found to be $4.7 \times 10^{-48} \text{ cm}^4/\text{s/photon}$ at 780 nm.



SCHEME 1 Synthetic route for EA4BPA-VB.

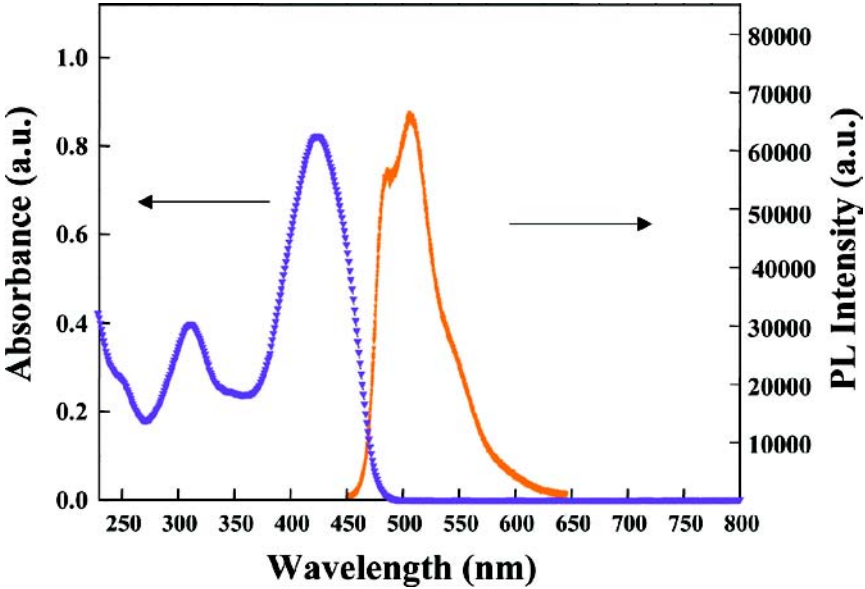


FIGURE 1 Absorption and Fluorescence emission spectra of EA4BPA-VB.

For the micro-fabrication, we used a mixture of SCR-500 resin (99.9 wt.%) and TPA chromophore (0.1 wt.%). The photo-active resin is polymerized by focused laser beam, controlling three-dimensional directions by using

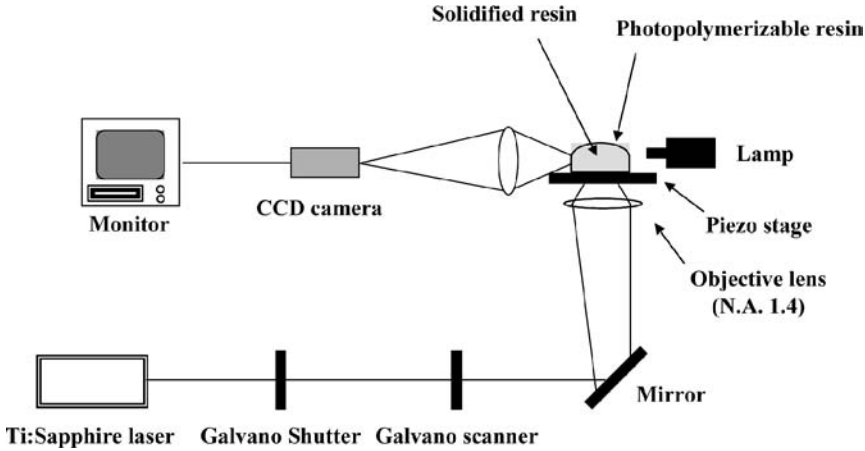


FIGURE 2 Laser Set-up for the 3-D micro-fabrication by TPA photo-polymerization.

galvano scanner and piezo stage. The exposure time of laser beam was controlled by a galvano shutter (Fig. 2). After the solidification of SCR resin by TPA-induced photo-polymerization, the unpolymerized resin was removed with ethanol. In this process, TPA chromophore act as a sensitizer of polymerization and intense near-IR light beam was converged into a focus to photopolymerizable resin, leading to two-photon fluorescence that induces two-photon polymerization. By employing this TPA patterning technique, we have successfully fabricated 3-D micro-structure (a larva) with high spatial resolution, which is smaller than the human red blood cell at low laser power with less than 5 mW. The size of 3-D pattern with a larva structure was $9.3 \text{ (width)} \times 11.9 \text{ (length)} \times 7.0 \mu\text{m}$ (height) (Fig. 3).

To improve the quality of patterns, we also investigated voxel shape turning dependence on laser power, exposure time and chromophore concentration of TPA sensitizer (EA4BPA-VB). Figure 4(a) shows SEM images of voxels formed at definite incident laser power of 5.0 mW and moderate exposure time. Figure 4(b) represents a variation of voxel size depending on laser exposure time, uniformly fixing exposure energy of 5 mW. As shown in this figure, vertical and lateral size of voxel increased with increasing exposure. Here, the increasing rate of vertical size is much more significant than that of lateral size.

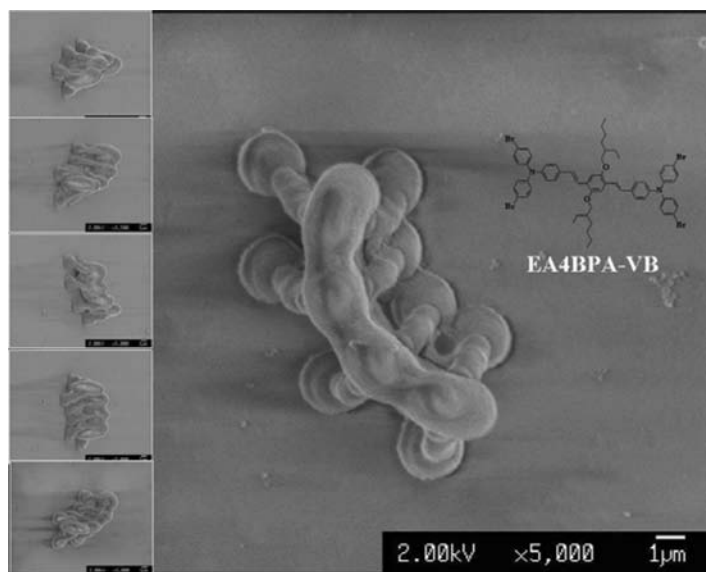


FIGURE 3 SEM image of 3-D pattern fabricated by using TPA chromophore (EA4BPA-VB).

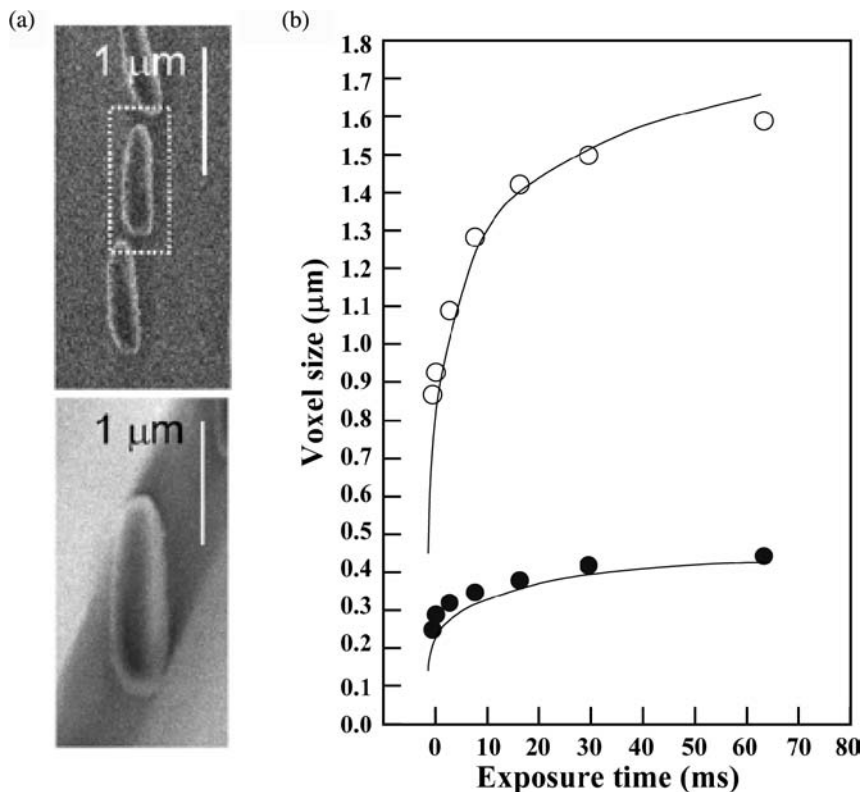


FIGURE 4 Exposure time dependent voxels. (a) SEM images of voxels produced with varied exposure time (5 mW, 0-64 ms) and (b) corresponding time dependence. Symbols denoting vertical (O) and lateral (●) sizes are from experiments. All scale bars are 1 μm.

Also, we observed a correlation between concentration of TPA initiator and voxel size, maintaining incident energy to 10.5 mW. Under certain condition of incident light intensity, the voxel size increased with the rise of the concentration of TPA chromophore in photopolymerizable resin (Fig. 5). These results indicate that TPA sensitizer have an influence on the threshold for polymerization as well as spatial resolution. This is a meaningful result for the future work related with nano-fabrication.

CONCLUSIONS

We have synthesized TPA material having high TPA cross-section value (σ) for the application of micro-fabrication. Voxel shape scaling performed on

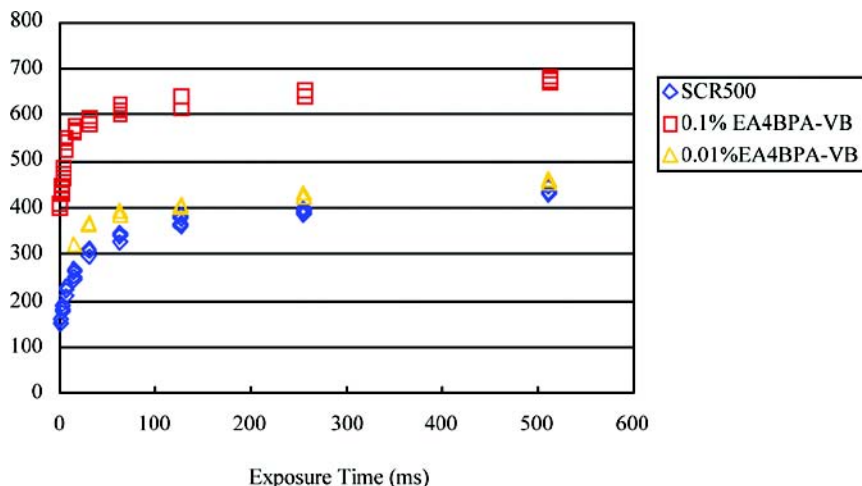


FIGURE 5 Voxel size dependence on the exposure time and TPA chromophore concentration turning.

various conditions turning such as a incident power, exposure time and concentration. The results could be useful for further advanced two-photon photopolymerization as a 3-D nano-fabrication technology.

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