Electric Conductivity of Conductive Polymer 3D Micro-structures Fabricated by Multi-photon Sensitized Polymerization

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1. Introduction

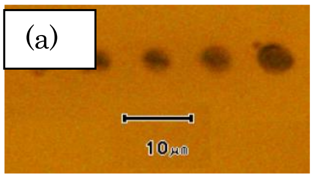
We have already reported that multi-photon excitation of tris(2,2'-bipyridyl)ruthenium complex [$Ru(bpy)_3^{2+}$] by femtosecond pulse laser with near infrared wavelength as the light sources, the 3D printing system of conductive polymers. [1-3] The proposed printing system enabled to form 2D and 3D patterns with fine process resolution. In the reaction system, spatially localized oxidation power was generated by two-photon absorption of $Ru(bpy)_3^{2+}$ as the sensitizer and the successive photo-induced electron transfer between the exited state of the $Ru(bpy)_3^{2+}$ and methylviologen [MV^{2+}] as the electron acceptor. This 3D printing system has already achieved the sub-micron process resolution which was better than the diffraction limit (864 nm) for the employed optical system. [4] As the result in the electric conductivity evaluation of the obtained 3D PPy micro-structures by a two-probe method, relatively higher values of a few hundred Scm^{-1} were obtained at the full doped state. Influences of the illumination conditions on the electric conductivity of the obtained PPy depositions were studied in this work.

2. Experimental section

An aqueous solution was used as the polymerization solution that contained 0.1 M of sodium p-toluenesulfonate, 0.22 M of pyrrole, 1 mM MV^{2+} and $Ru(bpy)_3^{2+}$. A 10 mm x 10 mm piece of Nafion 212 sheet (thickness: 50 µm) was used as the deposition support of PPy. The Nafion sheet was immersed in the polymerization solution, and then illuminated to form the 3D micro-structures of PPy. Multi-photon excitation of $Ru(bpy)_3^{2+}$ was induced by a mode-locked Ti/sapphire laser (λ = 850 nm). The original laser pulse with the repetition rate of 80 MHz was reduced from 8 MHz to 10 kHz by a pulse selector with an acousto-optic modulator. The laser beam was tightly focused by the water immersion objective lens (N.A.=1.20). The focus was scanned under PC-control by shuttering the beam and driving the Nafion sheet using XYZ stage.

3. Results and discussion

In order to evaluate the electric conductivity of the obtained PPy deposition from this system, the Z axis scanning of the laser focus was carried out to penetrate the Nafion sheet. After the photofabrication, the product sheet was processed with a micro knife to expose the cross section of the sheet. Figure 1 shows the surface (a) and cross section (b) views of the product sheet. Five line shape depositions of PPy were found from the fig.1. These PPy depositions penetrated completely the Nafion sheet. Figure 2 shows the relationships between the incident laser power and the line width of the PPy depositions.



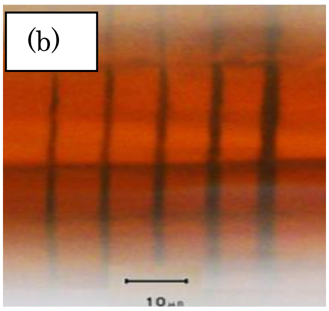


Figure 1 Surface (a) and cross section (b) micrographs of the product sheet.

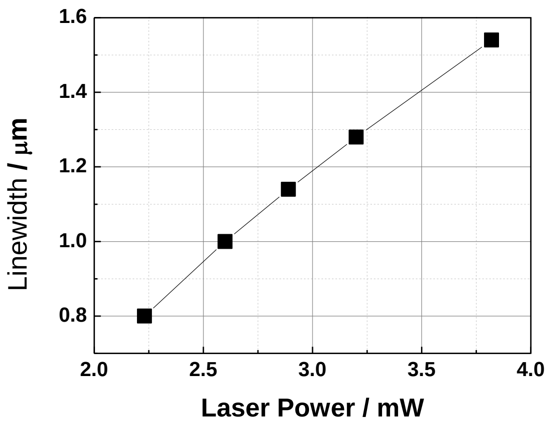


Figure 2 Relationship between incident laser power and line width.

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