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Fabrication of Multi-Functional Optical Waveguides by Capillary-Electrophoresis Doping Technique

Tetsuji Yano*, Jun Taguchi, Hiroyo Segawa and Shuichi Shibata

Department of Chemistry and Materials Science, Tokyo Institute of Technology, 2-12-1-S7-4
Ookayama, Meguro-ku, Tokyo, 152-8550 JAPAN

ABSTRACT

Capillary Electrophoresis Doping (CED) technique is proposed for the new doping technique of the functional molecules into the hybrid materials. Organic-inorganic hybrid films or waveguides are fabricated on the cathode and the capillary tube bridge is made between the hybrid materials and the anode solution bath. The capillary and the anode bath are filled with the solution of the functional molecules and DC voltage is applied between cathode electrode and the anode one. The functional molecules (ions) move along the electric field, and their doping into the hybrid materials can be attained by the control of the capillary position and the electric current through the circuit. In this study, siloxane based hybrid films and waveguides are prepared, and the doping of organic laser dyes, Rhodamine6G and Cresyl violet are demonstrated using SiO_2 glass capillaries. It is shown that CED technique has a great potential to fabricate the multifunctional optical devices in which various different functional chemicals are contained.

Keywords: Capillary electrophoresis doping, organic-inorganic hybrid materials, film, waveguide, organic dye

1. INTRODUCTION

The telecommunication network has continued to expand globally and the bandwidth of the information traffics has also been increasing. DWDM (optical dense wavelength division multiplexing) is a key technology to enable these expansions, where the network is outgrowing the performance of electronics devices. The development of the optical links using the optical fiber is one of the important issues and various materials and process technology have been proposed.

Integrated optical circuit (IOC) is one of the ideal forms of the optical links. Various types of the optical devices have been proposed; tunable filters, variable optical attenuators (VOAs), amplifiers, tunable optical add/drop multiplexers (OADMs), photonic crystal superprism waveguide, digital optical switches (DOSs), etc. The choice of the platform on which some of these devices are constructed is important, because it has to satisfy rapid processibility, cost-effectiveness, high yield, high performance and compactness. Among various materials, organic-inorganic hybrid materials (hereafter this is simply called as hybrid material) is considered to be promising materials for the IOC platform.

As proposed first by Najafi's group[1-4] the addition of UV-patternability to hybrid materials explores their potential uses for the optical devices. This "direct lithographic patterning" enables us to give high precision structures to hybrid materials, and 3D complex circuits can also be prepared. [5-7] Photosensitive unsaturated organic groups are introduced into the raw materials, and their photopolymerization by irradiation of light induces the differences of solubility(development) to the developer solution. To initiate the polymerization, the photoiniciator is usually added, and exposed to the light with suitable wavelength to the absorption of the photoinitiator (normally in UV region). Choices of materials and fabrication parameters enable us to form complex waveguide structure.

The combination of organic and inorganic is advantageous in the incorporation of complex material functionalities. High affinity of organic molecules with hybrid materials is important to disperse uniformly them in matrix media. [8] For instance, the incorporation of non-linear optical function can be realized by doping of NLO organic chromophores Electro-optic device has been widely investigated using hybrid materials.[6,9-11] In order to attain high EO coefficient and its long term stability, the organic chromophore molecules with high $\mu\beta$ (μ: chromophore dipole moment, β:molecular first hyperpolarizability) should be incorporated and orientated by the poling treatment. These chromophores are usually incorporated into hybrid solution before the formation of film on the substrate, and subjected to the following baking,

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UV irradiation, development in photolithography etc. As pointed out previously,[12-14] the UV irradiation causes photobleaching of azo-type chromophores(decomposition of -N=N- and $-NO_2$ groups) to loose the NLO functionality. Zhang *et al.*[10] used a longer wavelength laser light (λ=405 nm) for pattern writing although sacrificing the spatial resolution of lithography. This is one of many cases in which the photolithography process is not consistent with the incorporation of highly functional dopants into hybrid materials. Therefore it is necessary to separate doping process from the patterning process of IOC fabrication using hybrid materials.

Our group has focused on capillary electrophoresis behavior as a tool for doping of functional molecules, ions, etc. into IOC of hybrid materials. As used in the analysis area[15] of organic molecules including biomolecules, DNA and so on, the transportation of these molecules using the external electric field is convenient for doping of molecules into hybrid films or waveguides. In this work, we propose a new doping method, Capillary Electrophoresis Doping (CED), and demonstrate the doping of organic molecules into hybrid films or waveguides. Fluorescent dye molecules of Rhodamine 6G(R6G) and Cresyl Violet (CV) are chosen as examples. We do not need to incorporate dopants and to take care of their bleaching in the fabrication process of film or waveguide. Since they are incorporated after the patterning of device structures, we incorporate multi-functions into the same waveguides by doping various functional molecules.

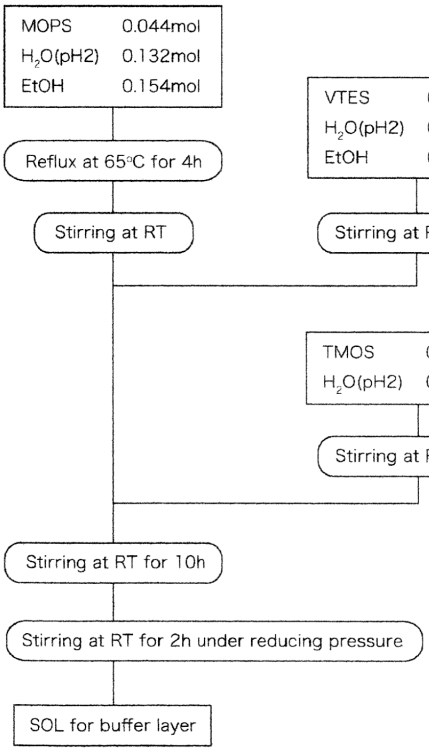

Figure 1. Flow chart of the synthesis of the sol for buffer layer.

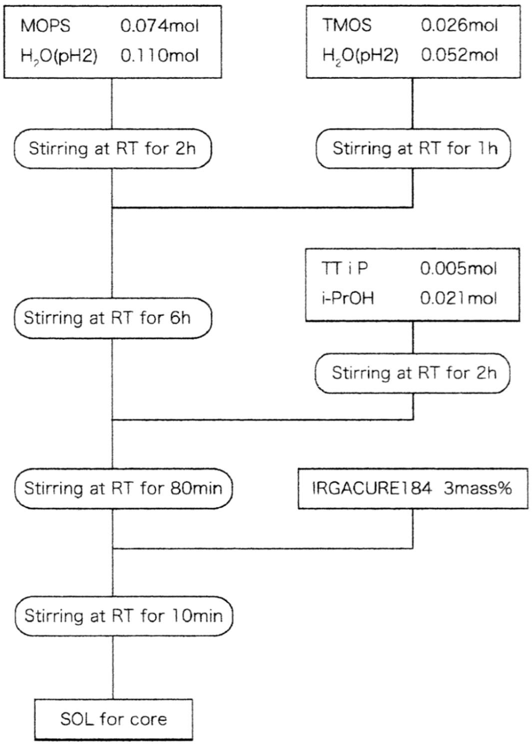

Figure 2. Flow chart of the synthesis of the sol for the core of waveguide.

2. EXPERIMENTAL

2.1. Synthesis of hybrid film and ridge waveguides

Organic-inorganic hybrid films for buffer layer were prepared using the combination of sol-gel process and dip-coating method. This is aimed for the isolation of the core waveguide from the high-index substrate glass. Figure 1 shows the synthesis flow of the hybrid sol for the buffer films on the glass substrate. 3-Methacryloxypropyl-trimethoxysilane (MAPTMS, Shinetsu Chemical Co., Ltd., LS-3380), vinyltriethoxysilane (VTES, Shin-etsu Chemical Co., Ltd., LS-2300) and tetramethoxysilane(TMOS, TCI, T0588) were used as the starting chemicals for the film components, and their molar ratio was MAPTMS:VTES:TMOS=35:35:30. First, MAPTMS was hydrolyzed with aqueous HCl (pH2) in EtOH solution using a reflux treatment at 65 °C for 4 h and then cooled to the room temperature(RT), where MAPTMS:H_2O:EtOH=1:3:3.5 (MAPTMS-sol). VTES was also hydrolyzed in the another solution with the molar ratio VTES:H_2O:EtOH=1:3:3.5 using HCl catalysis at RT for 2 h, and mixed with MAPTMS-sol. After the mixing with the partially hydrolyzed TMOS with TMOS:H_2O=1:2, the solution was stirred for 10h to improve the polymerization between various silicon units followed by the condensation treatment under the reducing pressure. Elimination of EtOH from buffer is aimed to change the viscosity and the film thickness by dip coating. The elimination condition was optimized to obtain the appropriate viscosity with which the crack-free thick film (about 5 μm) can be prepared by dip-coating method on the glass substrate.

Core of the ridge waveguide was prepared using sol-gel process, dip-coating method and photolithography technique. Sol for the core which has to have higher refractive index than that of buffer layer, is consisted from MAPTMS, VTES, TMOS and titaniumtetraisopropoxide (TTiP, Soekawa Chemical Co. Ltd.) with the composition MAPTMS:TMOS:TTiP=70:25:5 in molar ratio. The synthesis flow of this core-sol is shown in Figure 2. Partially hydrolyzed solutions of MPATMS:H_2O=1:1.5 and TMOS:H_2O=1:2 were prepared using HCl catalysis and mixed at RT for 24h. TTiP i-PrOH-solution is added to the former mixed solution and stirred at RT for 80 min. In order to initiate the photopolymerization between methacryl groups in MAPTMS, the UV-light induced photoinitiator, IRGACURE 184 (Ciba Chemical Co. Ltd.) was added with 3 mass%.

All of the film preparation procedures were carried out by dip coating. Drawing speed of the substrate from the sol was fixed at 300mm/min. The slide glass(soda-lime glass) were used as the substrate of the hybrid film and the waveguide. 10nm Au film was coated on the slide glass by sputtering, and a monolayer of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (APTMS) was formed by dip coating in air in order to increase the affinity with the hybrid solution. Dip coating of the buffer sol was conducted in dry N_2 atmosphere and baked at 100°C for 1h in air. The thickness of the buffer layer after baking was 4 μm.

Another hybrid film for core of waveguide was formed on the baked buffer layer by dip coating. Both of drawing and drying atmosphere were dry N_2 gas, because titanium component was very reactive with the moisture in the atmosphere. The prepared film was pre-baked at 60 °C for 15 min in a dry N_2 atmosphere. After this process, this film loses the sensitivity to the moisture and can be dealt in air. The waveguides were patterned in this photosensitive hybrid film by UV photolithography technique. The light of g-line (385 nm) was used for the initiation of photopolymerization. The width of the ridge waveguide was 160μm, which was a little larger than the O.D. of the thin capillary tube. After the exposure of light through the photomask, the pattern was developed by dipping the film into 2-PrOH to dissolve away the unexposed (uncured) part, and dried at RT. Post-baking treatment was performed after the capillary electrophoresis doping (CED).

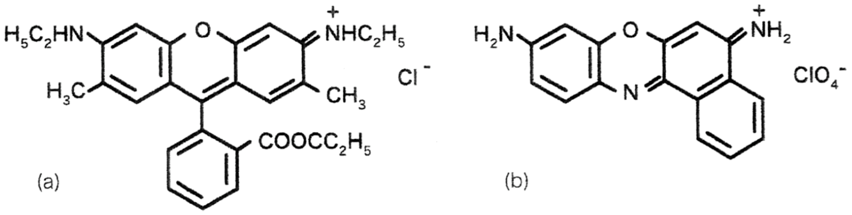

Figure 3. Doped laser dyes of (a)Rhodamin 6G (o-(6-ethylamino-3-ethylimino-2,7-dimethyl-3H-xanthen-9-yl)benzonic acid ethylester) and (b)Cresyl Violet (5,9-diaminobenzo(a)phenoxazonium perchloirate).

2.2. Capillary electrophoresis doping of functional molecules

Capillary electrophoresis doping (CED) of functional molecules was carried out using two kinds of SiO_2-glass capillary with O.D.=370 μm and I.D.=75 μm or O.D.=125 μm and I.D.=50 μm. Fluorescent organic molecules, Rhodamine6G (R6G) and Cresyl violet (CV) shown in Figure 3 were doped into hybrid materials using CED technique. R6G is one of the laser dyes with the highest quantum efficiency in organic dyes. The excitation of the visible blue region shows the strong luminescence between 550-700 nm (peak at 590 nm). CV perchlorate is a synthetic dye that is widely utilized to stain neuronal tissues. The excitation at 595 nm gives the luminescence peak at 623 nm in ethanol.

R6G and CV were dissolved in EtOH and the mixture of n-hexanol(HexOH) and EtOH (90:10 in volume%, hereafter simply called as HexOH solution). Their concentrations were ranged from 1×10^{-6} to 0.1 M, and the typical concentration of the doping experiments was 1×10^{-3} M. These molecules are electrolytic-dissociated in these solvents, and their solutions have ionic conduction against the application of the DC electric field. In advance, the capillary tube was filled with the respective solution, and its ionic transportation behavior (ionic conductivity and transport number) was analyzed. Figure 4 shows the capillary end filled with the solution and the electric circuit. The capillary and the sample substrate were held on the fixed holder and high-precision XYZ stage, respectively, and the meniscus at the capillary end was controlled manually using the injection cylinder. Under the appropriate electric field application, the current through the electric circuit was recorded and the amount of the functional molecules doped into the hybrid materials from the capillary tube was calculated referring to the calibration data.

2.3. Characterization of doped hybrid films and waveguides

Dye-doped hybrid films were irradiated by UV light (Hg lamp), and the luminescence images emitted from the doped dyes were captured using the optical microscope equipped with the sharp-cut filter and the CCD camera. For the ridge waveguide, Ar^+ laser light (λ=514.5 nm) was introduced into the waveguide, and the luminescence from the doped regions were captured and analyzed by CCD camera and spectrometer, respectively.

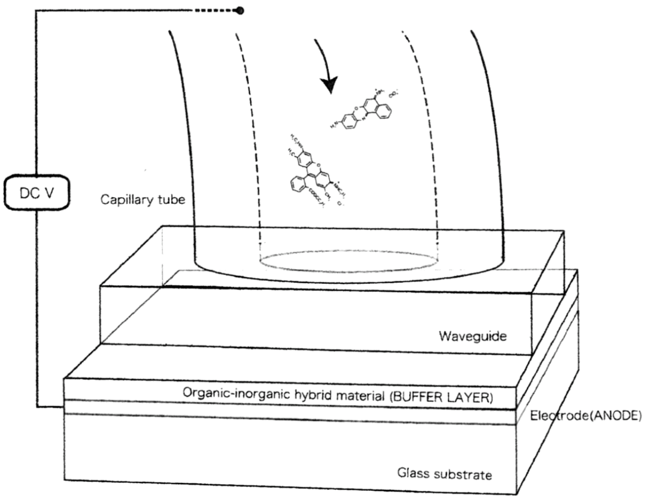

Figure 4. Schematic illustration of Capillary Electrophoresis Doping (CED) technique to dope the functional chemical species into the hybrid materials.

3. RESULTS AND DISCUSSION

3.1. Calibration of CED equipment and control of the transportation of fluorescent dopants

Capillary electrophoresis behavior has been utilized to separate the chemical species solved in the solution like metal ions, inorganic anions, organic molecules, biomolecules etc. DC electric field forms the electroosmosis flow (EOF) in the capillary. When SiO_2 glass capillary is used, $Si\text{-}O^-$ on its inner surface plays a role to transport the charged species in the electric double layer formed on the inner surface towards the cathode side. This is the reason why EOF is formed in the capillary tube. As a result, the positively charged species move fast and the negative ones also move slowly towards the same direction. On the other hand, the solvent used for dyes (R6G and CV) does not show the electrolytic dissociation, and the electric double layer is not necessarily formed on the inner surface. Figure 5 plots the examples of the capillary calibration results of DC voltage versus current (V-I) relations. Figure 5(a) shows the results of R6G EtOH solution in the capillary (125 μm O.D., 50 μm I.D., 20 cmL). Simple linear relations were obtained. The resistance of the solution in this thin capillary of the unit length was a function of R6G concentration. Since R6G free EtOH in the capillary has an undetectably large resistance, the observed current for R6G EtOH solution is considered to be due to the ionic conduction of R6G molecular ions. In Figure 5(b), the effects of the solvent on the V-I relations are shown. HexOH solution shows smaller current than EtOH solution even when R6G concentration is same. Elecrtolytic dissociation data on R6G in these solutions are not available, but the viscosity of HexOH is 4.9 times larger than that of EtOH. The differences of the resistance of these solution are in the same order as the difference of viscosities, and viscosity term would cause the difference of the ionic conduction through Stoke-Einstein relation.

Figure 5(c) compares the V-I relations between R6G and CV in EtOH. Electrolyte dissociates in solution, and both the formed cation and anion have contribution to the ionic conduction under the electric field application. Lower current of CV solution than that of R6G is considered to be due to the differences of three factors; dissociation degree, molecular size and anions. In order to estimate the transport number of R6G (R6G cation and Cl-anion), the capillary bridge was constructed between the cathode bath and the anode one, and 0.1 M R6G EtOH-solution was injected into the capillary and the cathode bath while the anode bath was filled with R6G-free EtOH, and DC voltage applied between the bathes. From the absorption spectra of the solution in the anode bath, the amount of the transported R6G

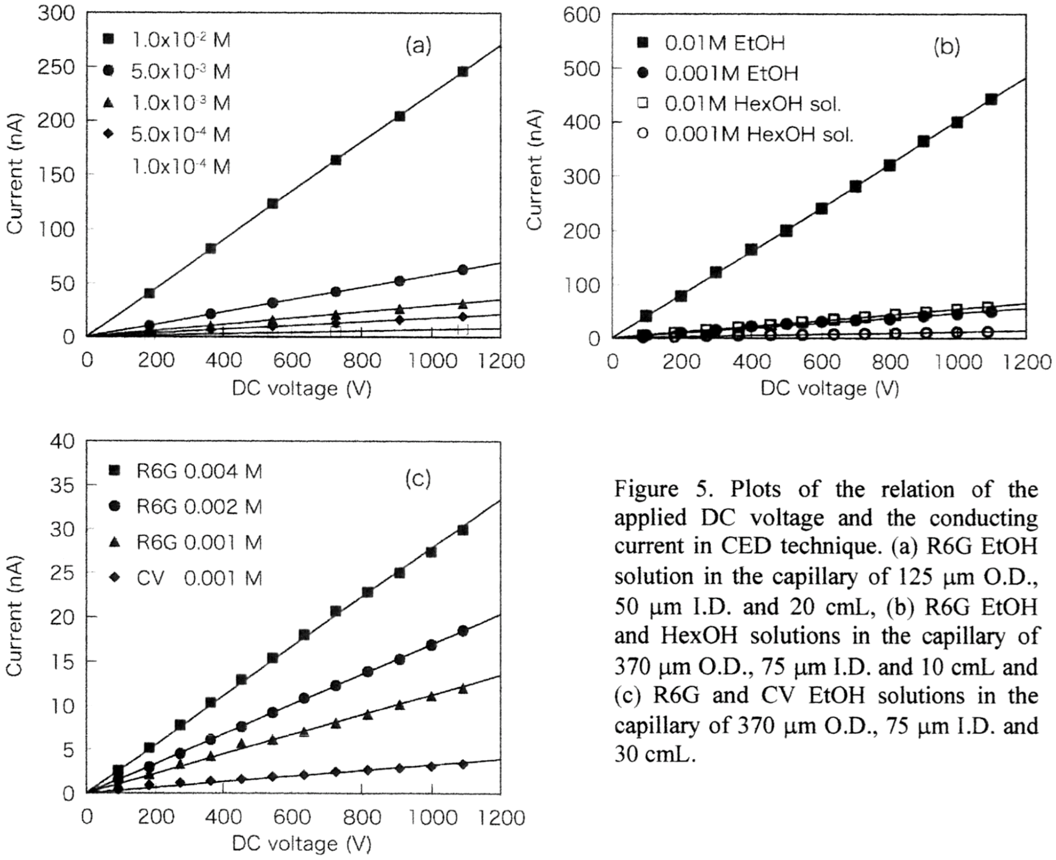

Figure 5. Plots of the relation of the applied DC voltage and the conducting current in CED technique. (a) R6G EtOH solution in the capillary of 125 μm O.D., 50 μm I.D. and 20 cmL, (b) R6G EtOH and HexOH solutions in the capillary of 370 μm O.D., 75 μm I.D. and 10 cmL and (c) R6G and CV EtOH solutions in the capillary of 370 μm O.D., 75 μm I.D. and 30 cmL.

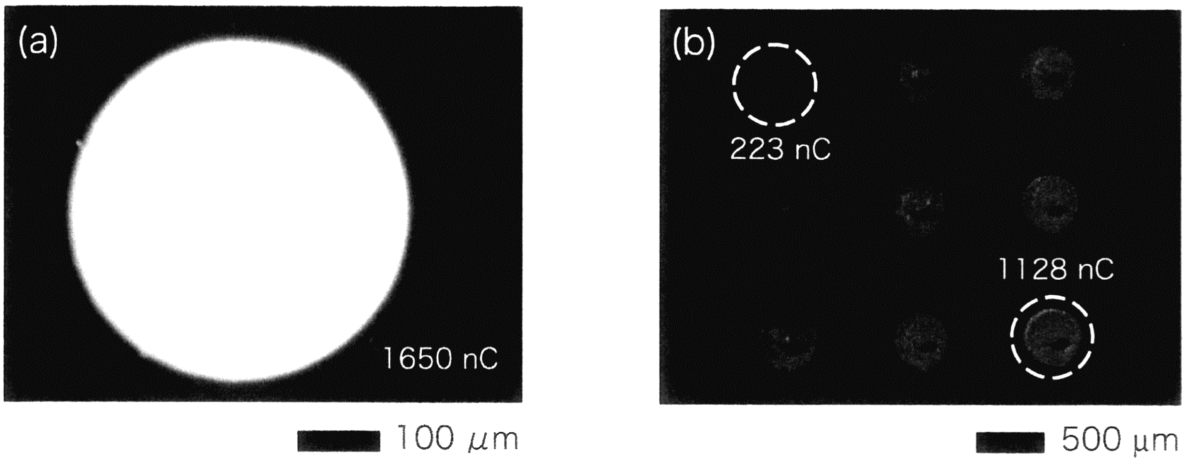

Figure 6. Fluorescence images from the dye-doped regions. (a) R6G-doped region using $1.0\text{x}10^{-3}$ M HexOH solution. (b) CV doped regions using $1.0\text{x}10^{-3}$ M HexOH solution. The total charge was changed by 5 steps from 223 nC (top and left) to 1128 nC (bottom and right).

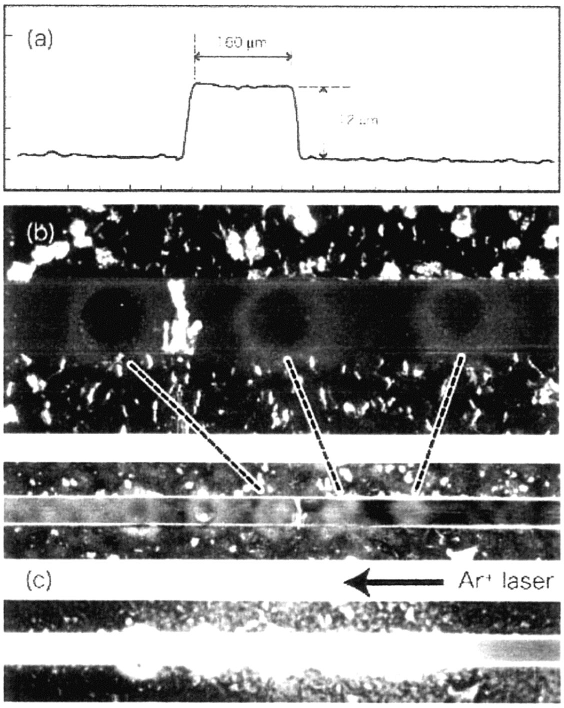

Figure 7. (a)Cross-section profile of the prepared ridge waveguide. (b)Optical microscope image of the typical R6G-doped regions using the capillary of 125 μm O.D. (c) Fluorescence image emitted from the doped dyes. The excitation was carried out by Ar^+ laser light (514.5nm) introduced into the waveguide from the right hand side. 514.5 nm light was cut by the holographic filter.

cations was measured. Transport number of R6G was calculated to be 0.025. This small value reveals that most of current was due to the conduction of anions. The differences found in V-I relation between R6G and CV might attribute to the size of anion Cl^- in R6G and ClO_4^- in CV. In the doping experiments, HexOH solution was used as the solvent, because EtOH has lower viscosity and larger vapor pressure than HexOH solution, and disables stable doping experiments.

3.2. Doping of dye molecules into hybrid films and waveguide

Figure 6 shows the optical microscope images of luminescence from dye molecules incorporated by CED (capillary: 370 μm O.D., 75 μm I.D., dye concentration $1x10^{-3}$ M). The shape and the size of the dye-doped regions correspond well with the capillary cross section. The outer diameter of the capillary determines the doped region in the hybrid materials. The increasing total charge increased the luminescence intensity as shown in Figure 6(b). The total charge of 1650 nC of Figure 6(a) is, for example, considered to correspond to the doping of $4x10^{-4}$ mol R6G into 380 μmϕ x 4 μm region of hybrid film. The observation of the cross section of the hybrid film by the confocal laser scanning microscopy showed that the dye molecules surely reached to the interface between the hybrid film and the electrode.

Figure 7 shows the R6G-doping results into the ridge waveguide prepared with the hybrid materials. The cross section profile of the waveguide is shown in Figure 7(a). The waveguide has a width of 160 μm and a height of 12 μm, and the thin capillary (125 μm O.D. and 50 μm I.D.) was used for doping experiment. From the optical microscope image(Figure 7(b)), the doped regions were also determined by the O.D. of capillary tube. The precise control of the capillary tip on the waveguide enabled the doping without leak to the side-wall of the waveguide. Figure 7(c) shows the fluorescence image from the R6G doped regions. The excitation light from Ar^+ laser (514.5 nm) was introduced into the waveguide (come from right hand side of the image). Strong excitation in the waveguide is clearly found. Figure 8 is the fluorescence spectrum from the doped region. The peak position and the spectral shape are almost the same as those in EtOH. This result clearly reveals that the functional materials can be incorporated into any position of the hybrid materials using CED method after the optical device structure is formed. Electric charge through the circuit would be used as a measure for the control of dopant concentration, and desired doped region about dopant, size and concentration can be fabricated. This is not only for the case of the ridge-type waveguide, but applicable to buried waveguide and covered ridge waveguide.

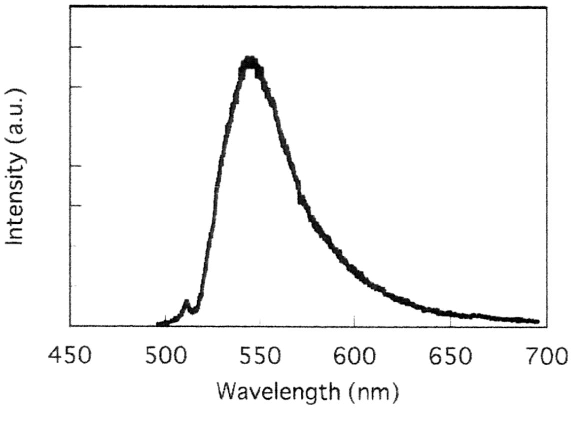

Figure 8. Fluorescence spectrum collected from the R6G-doped waveguide excited by Ar^+ laser (λ=514.5 nm).

3.3. Meniscus of the solution at the tip of capillary and the hybrid surface

The doping experiments clearly show that the doped region is determined by the capillary O.D. In order to clarify the contact of the solution in the capillary tube and the hybrid materials, the meniscus in the capillary tube was observed by the optical microscope, and its behavior was illustrated in Figure 9. DC voltage was already applied between the cathode electrode and the anode one lying under the hybrid materials, and the meniscus is controlled to be flat at the level of the capillary tip. When the capillary tip was approached to the hybrid film surface, the solution surface slightly drew out of the capillary end, and had a contact with the hybrid surface. After further approach of the tip to the film, the solution film was formed between the capillary tip and the hybrid surface. It was also found that the use of fluidic solution like EtOH tends to flow over the capillary outer diameter, and the size control becomes difficult. Wetting properties of the solution with the hybrid surface and also with the inner surface of the capillary tube should be paid much attention to control the meniscus in the capillary and the solution film between the capillary tip and the hybrid surface.

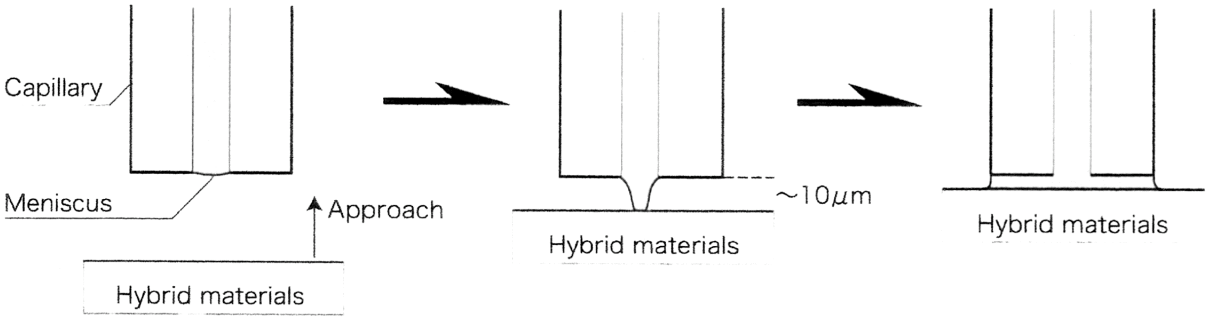

Figure 9. Schematic illustration of the observed movement of the meniscus at the capillary tip and the hybrid material surface.

4. CONCLUSION

Optically functional molecules of laser dyes were incorporated into the organic-inorganic hybrid films and waveguides by Capillary Electrophoresis Doping (CED) technique, and their luminescence from the materials were observed. The transportation of molecules from the capillary to the hybrid materials by the electric field application were succeeded and their amounts were known by monitoring the current conducting the circuit. The doped area was determined by the dimension of the cross section of the capillary tube and the control of the capillary tip position enables the selective doping to the desired region precisely. CED technique was shown to have great potential to fabricate multifunctional devices on the hybrid platforms after the patterning of the device structure, where dopants are not affected by the procedures of the lithography patterning like UV irradiation, baking etc.

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