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Electric field-assisted migration of dye molecules into organic-inorganic hybrid film by Capillary Electrophoresis Doping technique

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A new doping method of functional molecules or ions into the optical film of organic-inorganic hybrid materials is demonstrated for the fabrication of optical devices. Capillary Electrophoresis Doping (CED) technique uses the transportation of molecules based on the electrophoresis phenomena in liquid under the electric field. One of the most luminescent dyes, rhodamine 6G (R6G), is incorporated into the hybrid film synthesized from silicon and titanium alkoxides, 3-methacryloyloxypropyltrimethoxysilane (MAPTMS), tetramethoxysilane (TMOS) and titaniumtetraisopropoxide (TTIP), by the sol–gel process. In order to clarify the migration of R6G molecules into the hybrid materials, pre-bake treatment is applied to the hybrid film before CED treatment. R6G content in the doped region shows complex dependence on the pre-bake time. Structural changes caused by the pre-bake treatment induce different migration phenomena of R6G molecules in hybrid films; elimination of solvents, thermal curing between –C= C– bonds in organic groups.

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Key-words : Capillary electrophoresis doping, Organic-inorganic hybrid materials, Rhodamine6G, Pre-bake

1. Introduction

Chemically designed organic-inorganic hybrid materials were proposed in 1980s and have been fabricated for various kinds of optical devices such as optical fibers, amplifiers, lasers, and detectors. Moreover, integration of small-sized optical components with various functions is essential for meeting practical requirements, where several kinds of materials are placed with the desired dimensions and concentration to realize their functionalities and higher integration on the one-tip circuits is required with increasing speed.

Combination of inorganic and organic components is expected to extend the potential beyond the limits of the individual application. Organic molecule is one of the best candidates to demonstrate new functionalities in certain host materials. Organic-inorganic hybrid materials are suitable platform (host) materials due to their good affinity to the functional organic molecules as shown in previous studies. Their flexibility of the design of organic groups is quite fascinating to fix incorporate organic molecules inside the matrix. In order to fabricate multifunctional optical devices on the same platform, we need certain reliable and convenient methods to dope the desired amount of organic molecules into the appropriate position of the host matrix.

A new doping method of functional molecules or ions into the optical waveguide and/or film of organic-inorganic hybrid materials have been demonstrated for the fabrication of optical devices. Capillary Electrophoresis Doping (CED) technique which has been developed based on the transportation phenomena in liquid inside the capillary delivers the functional molecules into the hybrid films or waveguides. The electric field applied between the electrode on the other end of capillary and the electrode beneath the hybrid materials enables the migration of molecules inside the materials. This enables to fabricate various functional devices on the same circuit; we can introduce various molecules after the fabrication of a plain structure like the optical circuit (e.g., waveguide) and to fix them in the desired parts of the circuit (“post-doping”). However, the migration mechanisms of the molecules via CED technique are not well known. It is indispensable to know how the molecules are transported and have interaction with the host materials because the stability of the doped molecules is quite important for the realization of high and lasting functionalities.

In this paper, we investigate the migration behavior of the functional molecules into organic-inorganic hybrid materials. Rhoamine6G (R6G), one of the most luminescent dyes, is doped into fabricated organic-inorganic hybrid films by the CED method. Pre-bake treatment is applied to the hybrid films before CED treatment in order to clarify the relationship between the migration of R6G molecules and the structure of the hybrid materials.

2. Experimental

2.1 Fabrication of organic-inorganic hybrid films

Organic-inorganic hybrid films were prepared using the sol-gel process and dip-coating method. Figure 1 shows the synthesis flow of hybrid sol for the film on a glass substrate. 3-methacryloyloxypropyltrimethoxysilane (MAPTMS, LS-3380, Shin-Etsu Chemical Co., Ltd.), tetramethoxysilane (TMOS, T0588, TCI), and titaniumtetraisopropoxide (TTIP, Soekawa Chemical Co., Ltd.) were used as the starting materials for the film components, and their molar ratio was MAPTMS: TMOS: TTIP = 70:20:10. First, MAPTMS was hydrolyzed with aqueous HCl.
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(pH2) at room temperature (RT) for 2 h where MAPTMS: H2O = 1:1.5. TMOS was also hydrolyzed in another solution with the molar ratio, TMOS: H2O = 1:2, using HCl catalysis at RT for 1 h, mixed with MAPTMS sol, and stirred for 24 h. TTIP in i-PrOH was added to the above mixed solution and stirred at RT for 1 h.

Film formation was carried out by the dip coating method. Drawing speed of the substrate from the sol was 300 mm/min under nitrogen atmosphere. The ITO (Indium tin oxide)-coated slide glasses were used as the substrate of the hybrid film. The hybrid films were formed on the ITO-coated side. These substrates were pre-baked at 60 °C for 0.5–24 h under nitrogen atmosphere. The thickness of the as-prepared films was 10 μm.

Isothermal gravimetry (TG) and differential thermal analysis (DTA) of the hybrid sol was carried out at 60 °C in air (Thermo Plus TG–DTA 8120; Rigaku Co.).

2.2 Capillary Electrophoresis Doping of rhodamine 6G

Figure 2 shows the schematic illustration of the Capillary Electrophoresis Doping (CED) technique. CED of R6G molecules was carried out using the silica-glass capillary with the outer diameter (O.D.) = 660 μm and the inner diameter (I.D.) = 530 μm. Details about CED have already been reported in our previous paper.4 R6G is one of laser dyes with the highest quantum efficiency among organic ones. R6G was dissolved into EtOH and/or the mixture of n-hexanol (HexOH) and EtOH (90:10 in volume%). The R6G concentration was 1 × 10^{-3} M. CED treatments were carried out under the condition of the applied voltage 1000 DCV for 2 min. The current through the electric circuit was recorded. A fluorescence microscope was used to measure the size of the R6G doped area.

In order to evaluate the polymerization of –C = C– bonds in MAPTMS molecules in the hybrid materials, the infrared absorption spectra were recorded on the pre-baked films by the KBr pellet method using FT–IR spectrometer (IR Prestige–21, Shimadzu Co.). Spectral resolution was 4 cm^{-1}, and the accumulation number was 80.

3. Results

3.1 Thermal reactions in hybrid films during pre-bake treatment

Figure 3 shows the isothermal TG and DTA traces of the prepared hybrid film during baking at 60°C. TG trace shows an immediate decrease of the film weight for the first 2 h. This can be attributed to the evaporation of solvent contained in the as-prepared film. After 10 h pre-baking, the decreases of the film weight became slow and finally reached a constant value of 38%. On the contrary, DTA trace shows continuous exothermic peaks after the reduction of TG trace ceased; especially between 8–20 h pre-bake treatments.

Figure 4 shows the examples of the infrared absorption spectra of –C = C– bonds of MAPTMS in the films, and the plots of the peak intensity ratio of –C = C– bond to that of –C = O bond against the pre-bake time. The increasing pre-bake time reduces the absorption of –C = C– bonds, indicating that the curing between organic groups in MAPTMSs proceeds during pre-bake treatment at 60°C and the cross linking of hybrid network starts via the polymerization process between –C = C– bonds after the elimination of solvents.

3.2 Electric current during CED treatment

Figure 5 shows the examples of the electric currents for 2 min during CED treatment on the hybrid films baked for 3, 9, 14, and 24 h. The current curve of 3 h-film shows the typical trace found in the films pre-baked for a short period of time of several hours.
After showing a quick projection at around 7 s, the current decreases steeply to sub-μA order. The CED treatment on 9 h-film shows a gradual increase after a small projection followed by a plateau at around 30 s. After 30 s, the current decreases to about a half of the maximum current, but about the twice of that of 3 h-film. The 14 h-film, on the other hand, shows a sudden current decrease after a quick projection around the first few seconds. After having a minimum around 15 s, the current gradually increases and reaches a constant value. The 24 h-film has no projection and keeps a constant current during CED treatment.

Figure 6 plots the total electric charge conducting CED circuit during 2 min treatment on the hybrid films pre-baked for various time periods.

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Figure 6 plots the total electric charge conducting CED circuit during 2 min treatment on the hybrid films pre-baked for various time periods.

3.3 Fluorescence from R6G molecules doped into the hybrid films

Figure 7 shows the fluorescence microscope images of the R6G–doped regions of the hybrid films baked for various periods of time; (a) 1 h, (b) 3 h, (c) 6 h, (d) 9 h, (e) 12 h, (f) 14 h and (g) 16 h. These samples were subjected to CED treatment for 2 min. Figure 7 clearly shows that the doped pattern of R6G is strongly dependent on the pre-bake time. When the pre-bake time was shorter than 10 h, the doped patterns have a deep-red circle with the same size as the capillary O.D., accompanying with the yellow outer region. The deep-red circle indicates that R6G molecules are doped with quite a high concentration. A large overlap of the fluorescence and absorption of R6G allows only fluorescence of the longer wavelength region than that from the yellow region. Figure 8 shows the fluorescence image of the cross-section of R6G-doped hybrid film baked for 9 h.
shown in Fig. 7(d). The doped R6G molecules are found to reach to the glass substrate at the red region, and certain concentration gradients towards the outer side is confirmed between the red region and yellow one. For baking more than 10 h, the central red circle disappeared and the size of the yellow circular region started to spread while the intensity of the yellow emission decreased. Figure 9 shows the relation between the pre-bake time and the diameters of the doped area. The sizes of the central red circular region and the outer yellow one are almost constant before 10 h. After 12 h pre-bake treatment, the yellow circular region steeply spreads accompanied with decreasing the fluorescence intensity (Fig. 7). The fluorescence was finally undetected from the doping treated region of the film baked for 24 h. This means that the migration of R6G molecules does not proceed into the film baked for a long period of time. Figure 7(h) is the image of the CED treated film which was prepared as a reference sample using the solution with a photopolymerization initiator, Irgacure184 (Ciba Special Chemicals Co., Ltd.). This film was irradiated by UV light (30 mW/cm² at 365 nm) for 2 min after 9 h pre-bake treatment and subjected to CED treatment. Fluorescence of R6G was not detected at all. Figure 10 shows the infrared absorption spectra of \(-\mathrm{C} = \mathrm{C}–\) bonds of MAPTMS in the as-prepared film and in the film after the UV irradiation. It was confirmed that the UV irradiation reduced the absorption of \(-\mathrm{C} = \mathrm{C}–\) bonds by photopolymerization.

4. Discussion

Heat treatment of the as-prepared gel is an important procedure to promote i) elimination of residual solvent and ii) finishing the residual chemical reactions like polymerization of silanol groups. High packing (densification), increasing hardness and a chemically durable surface can be achieved during heat treatment. The weight decrease found in the isothermal TG trace for the first 7 h (Fig. 3) clearly shows the elimination of residual solvent and liquid in the prepared film. This means that the space held between skeletons of the hybrid network shrinks and decreases in their amount. Doping and migration of organic molecules into the film require a certain amount of available spaces, which would define the mobility of molecules and the maximum amount of doped molecules inside the hybrid matrix. 38% weight loss was completed at the first 12 h, which can be attributed to the evaporation of methanol, isopropanol and water, which come from the solvent and/or the by-products of the hydration reactions of metal alkoxides, and dehydration between \(-\mathrm{OH}\) groups. The incorporation of alkyl-groups and \(-\mathrm{SiC}=\) bonds introduces chain- or sheet like network flames into 3 dimensional rigid networks, and then induces certain structural flexibility into the matrix. Pore-free and densely packed structure of hybrid materials is considered to be due to this kind of characteristic feature of the matrix network. The release of the solvents means that the as-prepared films possess certain amount of space among networks, and the incorporated R6G molecules are able to use them for the migration into the films well under the electric field gradient. Red circular patterns in Fig. 6 reveal that there are large amount of space available to be occupied by a large amounts of R6G molecules even in the film baked for 9 h.

Many exothermic peaks on the isothermal DTA trace from 8 to 20 h is important because they are observed after the weight loss of the film is completed as shown in TG. MAPTMS is a quite useful component because its high photo-curability due to the methacryl group.\(^{10}\) It is also known that the incorporation of MAPTMS oligomers is thermally curable. Zhang et al. reported the thermal reaction of the TEOS/MAPTMS system.\(^{11}\) Thermal curing of methacryl groups started at about 100°C and showed a maximum exothermic peak around 150°C. It also accompanied with the weight loss of the materials. In our isothermal DTA trace, although it was at a lower constant temperature, 60°C, the exothermic peaks between 8–20 h are clearly observed just after the weight loss of about 38% of the film, which means that the intermolecular distance between the MAPTMS (methacryl groups) is shortened due to the elimination of solvent in the film. It enables thermal curing of \(-\mathrm{C} = \mathrm{C}–\) bonds to link between organic parts, MAPTMSs. Changes in the IR spectra (Fig. 4) clearly prove this structural reaction during pre-bake treatment. Thus, available spaces for R6G molecules lessen and the molecules could migrate using a limited amount of the retained space. Disappearance of the red region in Fig. 7(d) is consistent with the isothermal TG–DTA results. In other words, eliminating solvent molecules have occupied the space around methacryl groups, and R6G molecules are suggested to utilize the same space to migrate inside the hybrid films.

According to Fig. 7(h) and Fig. 10, doping of R6G is found to be suppressed well by the photo-curing of \(-\mathrm{C} = \mathrm{C}–\) bonds. Cross-linking of organic groups surely terminate the migration.
pathway of R6G molecules in film. Figure 11 illustrates the relation between hybrid structure and the migration of R6G molecules in the pre-baked film. Inorganic chains consisting of Si–O–Si, Ti–O–Ti and/or Si–O–Ti bonds are formed in sol and as-prepared film, where MAPTMSs were also contained as members to form a network flame. Baking improves polymerization of retained –OH groups, eliminates the solvents in the film, and shrinks the network. A long organic chain in MAPTMS is considered to suppress the polymerization of Si–OH groups due to steric hindrance, and their high affinity to the organic molecules provides the space for the organic solvents to occupy inside the films. Before the formation of cross-linking between MAPTMSs, R6Gs utilize enough space to migrate inside the film. However, more than 12 h baking limits the available space for R6G molecules, and restricts the amount of R6G molecules to be doped into the hybrid film, due to the thermal curing of –C = C– bonds.

4.1 Transportation of R6G molecules in hybrid film under the electric field

In the CED process, the driving force of the migration of R6G molecules is the electric force applied to the R6G solution and the hybrid film between the electrodes. Here we have to consider several transportation mechanisms in hybrid films under the electric field, because the pre-bake treatment drastically changed the behavior of the CED phenomena. 38% weight loss means that the as-prepared film contains 48 vol% spaces for the solvents among the hybrid networks. They are eliminated mostly for the first few hours at 60°C. In such films, the migration of R6G molecules is not necessary to be under the restriction of available volume. As found in gel electrophoresis process,12,13 the electric field might induce electroosmotic flow inside pores of film and transport R6G molecules with a positive charge towards cathode (ITO underneath the film). A sudden current increase for the first 5 s of 3 h-film represents this kind of transportation of R6G into the hybrid film.

The elimination of solvents prohibits this process while another transport process might be brought about, because the large increase of the electric current was observed as in the 9 h-film. From the sol composition, the theoretical reduction of film weight by the completion of elimination of all solvents in the film is 44%. The difference between the calculated value and the observed one can be attributed to the residual silanol groups or water inside the films referred to the boiling point (vapor pressure) of solvent, by-product alcohols from alkoxides and water. Such circumstances of R6G inside the films would promote more electrolytic dissociation. It gives rise to a more efficient transportation of R6G by the electric field. The appearance of the concentrated red regions found even in the films pre-baked for 9 h indicates this kind of phenomenon.

On the other hand, thermal curing between 8–20 h increases cross-linking of the hybrid network as shown in Figs. 3 and 4. This would shrink the pass ways for the migration of R6G molecules in the hybrid materials. A lower electric current found in the 14 h-film clearly reveals this effect of the thermal curing of –C = C– bonds on the R6G doping than in the 9 h-one. The disappearance of the red circular region also shows the reduction of the amount of R6G molecules available to be doped into the film.

In solid, diffusion of charged species is required to hold charge neutrality; R6G is a positively charged organic ion (R6G⁺) and accompanied by anion of Cl⁻. The electric field forces the positively charged species to migrate towards the cathode electrode side, while negatively charged ones to the opposite direction towards the outside of the film. Probable charge carriers inside the film during CED treatment are R6G⁺, proton (or oxonium) and chloride ions. The first two ions are transported towards the cathode, and the last one is towards the anode side. The observed current in the CED circuit surely represents that these charged species are conducting in the film, although their transport numbers are not known (they might be different because their ionic radii are largely different from each other, and the positive charge of the incorporated R6G⁺ ions can be compensated by chloride ions to hold charge neutrality in the film). This means that the available amount of the incorporated R6G⁺ ions into the hybrid films are restricted not only by the available spaces in film to be occupied by R6G molecules but also the negatively charged species to compensate the charge of R6G⁺.

A long pre-bake treatment promotes further densification of the film. As found in Figs. 7 and 9, the size of the yellow region increases and its emission intensity decreases after the red region disappears. This behavior can be understood from the point of view of the changes of the hybrid film during baking. However, we also observed that the electric current keeps a constant value and the total charge conducting through the CED circuit also keeps at 250 μC after 14 h. This means that certain amount of the charged species migrate inside the films while much of the R6G cannot migrate into the film because of the lack of available space. Spreading of the yellow region should be governed by the electric field gradient from the capillary tip towards the cathode underneath the film even in the case of the film baked for 24 h, into which no R6G migration was observed. This transport phenomenon is quite similar to “electrowetting” behavior.14,15 The electric field induces the polarization of film; i.e., the negative charges appear on the top surface of the films. However, the film still contains mobile chlorine ions inside, and they would contribute to form the polarization of the film by moving to the film surface along the electric field. The spread of the R6G liquid compensates this charged surface by meeting R6G⁺ ions with the surface charge. Growth of the R6G liquid region would be an origin to keep the constant current during CED treatment. Therefore, the presence of the mobile charged species is an important key factor to control the doping behavior in the CED process.

As shown in the results of CED process on hybrid film by R6G molecules, the doping (migration in the film) and their
Rhodamine 6G (R6G) molecules were doped into organic-inorganic hybrid films baked for various time periods by the Capillary Electrophoresis Doping technique. Migration behavior of R6G molecules shows strong dependence on the baking time; elimination of solvents changes the transportation mechanism of R6G molecules from the electroosmotic flow into the ionic diffusion processes with an increasing baking time. The following thermal curing of –C=– bonds reduces the available space for R6G inside the film, and the R6G liquid spreads over the film by electrowetting.

5. Conclusion

Rhodamine 6G (R6G) molecules were doped into organic-inorganic hybrid films baked for various time periods by the Capillary Electrophoresis Doping technique. Migration behavior of R6G molecules shows strong dependence on the baking time; elimination of solvents changes the transportation mechanism of R6G molecules from the electroosmotic flow into the ionic diffusion processes with an increasing baking time. The following thermal curing of –C=– bonds reduces the available space for R6G inside the film, and the R6G liquid spreads over the film by electrowetting.