DOI: 10.1002/masy.201100066

Fast Electro-Optic Switching of Twisted Nematic LCD Doped with Cyclodextrin Capped Silica Nanoparticles

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Summary: We prepared cyclodextrin (CyD)-capped silica (CyD-SiO_2) nanoparticles and poly(cyclodextrin) (PCyD)-capped silica (PCyD-SiO_2) nanoparticles. The average diameter of SiO_2 nanoparticles capped by αCyD, βCyD, γCyD and PγCyD are 9.4, 8.4, 10.6, and 6.4 nm, respectively. The nanoparticles were dispersed in liquid crystal; 4′-pentyl-4-cyanobiphenyl to construct novel twisted nematic liquid crystal device (TN-LCD). The response time of this TN-LCD in the presence of PγCyD-SiO_2 nanoparticles was faster than that in the absence.

Keywords: cyclodextrin; electro-optic properties; nanoparticles; nanotechnology; twisted nematic liquid crystal device

Introduction

Nanoparticles capped by organic molecules are now creating a new class of materials different from either conventional bulk materials or atoms, giving one of the smallest building blocks of matter.[1–3] Metal nanoparticles are stabilized by citrate ion,[4] surfactants,[5] polymers,[6] and organic ligands.[7] For example, palladium nanoparticles, obtained by refluxing an alcohol–water solution of palladium ions in the presence of poly(*N*-vinyl-2-pyrrolidone) (PVP), are capped by PVP and used as an active catalyst for selective hydrogenation of dienes to monoenes.[8] Surfactant micelle-capped palladium and platinum nanoparticles can be obtained by irradiation with visible light in the presence of the surfactant and work as active catalysts for hydrogenation of unsaturated fatty acids with high regioselectivity.[9] Poly(acrylic acid)-capped silver nanoparticles had much higher activity than PVP-capped ones on oxidation of ethylene.[10] Thus, stabilizers play important roles for not only protecting nanoparticles but also controlling catalytic properties.

On the other hand, liquid crystal molecules themselves have been investigated as raw materials for an electronic display device for more than three decades due to its electro-optic properties, and now constructs main parts of information industries. The liquid crystal display (LCD), however, has a disadvantage of slow response compared with electroluminescence displays. Thus, it will be a big impact to design a liquid crystal display with fast response, if liquid crystal sol containing nanoparticles may have novel dynamic properties different from the original liquid crystal medium by giving a perturbation to a self-assemble property of liquid crystal. The merging of metal nanoparticles or nanotechnology in a wide sense into self-assembled systems such as LCD may attract the attention of researchers who are interested in inaugurating a new kind of combination of different fields.[11] In fact, the number of documents, especially patents on a liquid crystal display concerning with nanoparticles increases rapidly these years. The nanoparticles reported as a dispersed phase in LCDs involves fullerene,[12] carbon nanotubes,[13] diamond powders,[14] noble metal nanoparticles,[15] and semiconductor

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nanoparticles,[16] etc. When used as a dopant for LCDs they were expected to improve the contrast, decrease the driving voltage, capture ions, and shorten the response time. To the best of our knowledge there is no reports on electro-optic properties of liquid-crystal display doped by cyclodextrin-capped silica nanoparticles.

This study is aimed to develop novel functional SiO_2 nanoscopic materials having high dispersibility into liquid crystal matrices. We obtained cyclodextrin-capped SiO_2 (CyD-SiO_2) nanoparticles and poly(cyclodextrin)-capped SiO_2 (PCyD-SiO_2) nanoparticles by ultrasonic and microwave reaction of silicon tetrachloride. Colloidal dispersions of SiO_2 nanoparticles were applied to the electro-optic properties of LCD.

Experimental Part

Syntheses and Characterization

CyD-SiO_2 nanoparticles were prepared by using a microwave reactor equipped with ultrasonic nozzle mixing in a tetraethylene glycol solution of silicon tetrachloride in the presence of cyclodextrin. Contaminants like ions in the dispersions were removed by washing the dispersions three times with ethanol by using an ultrafiltration. Complete removal of the solvent and volatile byproducts by vacuum evaporation gave CyD-capped SiO_2 nanoparticles.

UV-Vis (ultraviolet and visible light) absorption spectra were measured with a Shimadzu UV-2500PC recording spectrophotometer using a quartz cell with 10 mm of optical path length. Transmission electron microscopy (TEM) images were observed with a JEOL TEM 1230 at accelerated voltage of 80 kV. An average diameter and standard deviation were calculated by counting the diameters of 200 particles on the enlarged TEM photographs.

Fabrication and Electro-Optic Properties of TN-LCD Containing SiO_2 Nanoparticles

SiO_2 nanoparticles were mixed with 4′-pentyl-4-cyanobiphenyl (5CB) at room temperature resulting in a liquid crystal sol of 5CB containing 0.075 wt% of total metal (sum of SiO_2). The sols were injected into an empty cell for a TN mode with a cell gap of 5 μm, supplied by Nippo Denki Co. Ltd. The electro-optic properties, especially applied voltage vs. optical transmittance (V-T) curves of TN-LCD cells were measured by applying the 100 Hz square wave alternating current at 25 °C with a LCD evaluation system (Photal Ohtsuka Electronics, Ltd., model LC-5200).

Results and Discussion

Preparation and Characterization of SiO_2 nanoparticle

Colloidal dispersions of silica nanoparticles, capped by CyD were prepared by an ultrasonic and microwave reaction of the mixed solution of silicon tetrachloride and CyD in tetraethylene glycol, having a dark brown color and being stable for months at room temperature. Figure 1 shows UV-Vis absorption spectra of the dispersions of CyD-SiO_2 nanoparticles. The dispersions of CyD-SiO_2 nanoparticles obtained after ultrasonic and microwave reaction show broad absorption spectra without structure from the visible region to the near UV. The absorption peak due to silicon tetrachloride completely disappeared on reaction, showing the formation of CyD-SiO_2 nanoparticles.

Figure 2 shows transmission electron micrographs and size distributions histo-

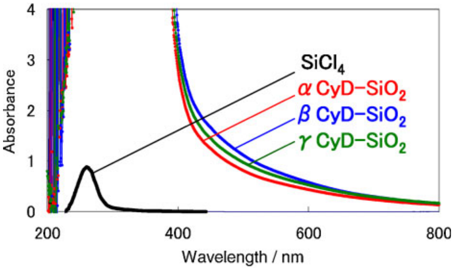

Figure 1.
UV-Vis absorption spectra of an tetraethylene glycol solution of silicon tetrachloride and colloidal dispersions of CyDSiO_2 nanoparticles.

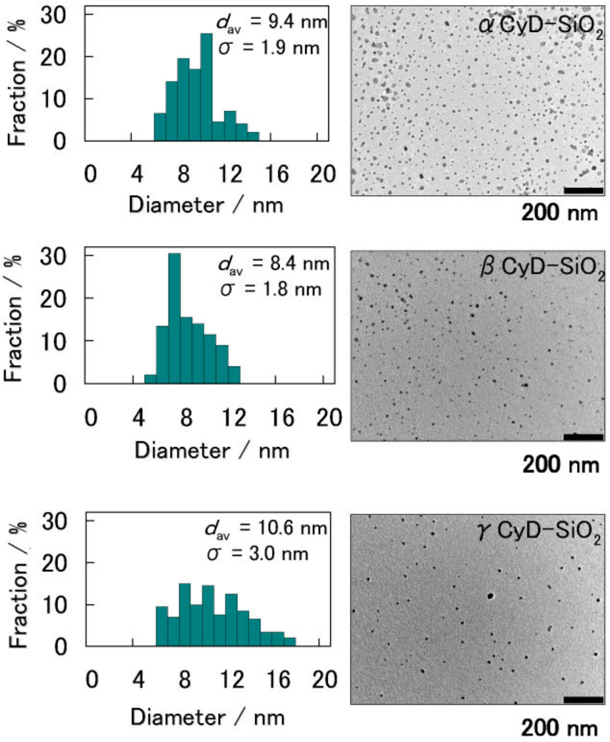

Figure 2.

Transmission electron micrographs and particle size distribution histograms of CyD-SiO_2 nanoparticles. d_{av} = average diameter, σ = standard deviation.

gram of the obtained nanoparticles. The most CyD-SiO_2 nanoparticles at mole ratio of CyD to silica of 0.1 were distributed in the range of 5–16 nm, suggesting that the size of CyD-SiO_2 is homogeneous. The results reveal that βCyD-SiO_2 nanoparticles examined here have the average diameter of 8.4 nm and relatively small standard deviation. The average diameters of αCyD-SiO_2 and γCyD-SiO_2 nanoparticles are 9.4, and 10.6 nm, respectively, as shown in Figure 2. The size distribution of γCyD-SiO_2 nanoparticles (3.0 nm) is wider than that of αCyD-SiO_2 (1.9 nm) and βCyD-SiO_2 (1.8 nm) nanoparticles. Komiyama *et al.* reported the syntheses of CyD-capped rhodium nanoparticles by refluxing in the presence of ethanol.[17] They described that the protecteng abilities of CyD are in the following other:

βCyD > αCyD >> γCyD.

This weak protecteng ability of γCyD is consistent with the wide size distribution of γCyD-SiO_2 nanoparticles.

Response Time of TN-LCD Containing SiO_2 Nanoparticle

The CyD-SiO_2 nanoparticles prepared in the present experiments were easily mixed with liquid crystal molecule 5CB at room temperature to form liquid crystal sol for twisted nematic liquid crystal device (TN-LCD). The phase transition temperature between nematic and isotropic (*N-I*) phase of LCDs were observed on polarizing microscope images taken with an OLYMPUS BH-2 polarizing microscope equipped with a METTLER Toledo FP82HT hot stage. The *N-I* transition temperature of 5CB without and with αCyD-SiO_2, βCyD-SiO_2, and γCyD-SiO_2 nanoparticles were 34.2, 34.2, 34.1, and 34.1 °C, respectively. These results suggest that ionic impurities

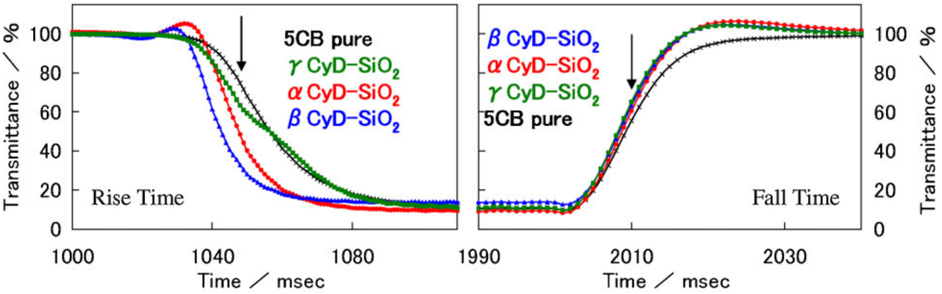

Figure 3.
Relationship between response time and transmittance of TN-LCD fabricated by 5CB sol in the absence and the presence of CyD-SiO_2 nanoparticles.

which may be contaminated in the nanoparticles have been completely wased out by the ultrafiltration. The TN-LCD fabricated by injecting the liquid crystal sol containing nanoparticles into empty cells were supplied to measure the electro-optic properties.

Figure 3 shows the relationship between response time and transmittance of TN-LCD fabricated by 5CB sol in the presence of CyD-SiO_2 nanoparticles. The response times (τ_{on}; the rise time from 90% transmittance to 10%, and τ_{off}; the fall time from 10% transmittance to 90%) of TN-LCD fabricated by 5CB sol in the presence of CyD-SiO_2 nanoparticles are summarized in Table 1. The response times of TN-LCD fabricated by 5CB sol are 96.2, 76.7, 71.5, and 90.7 msec for 5CB pure, αCyD-SiO_2-doped 5CB, βCyD-SiO_2-doped 5CB, γCyD-SiO_2-doped 5CB, respectively. Cyclodextrin exhibits remarkable catalytic activities owing to the following effects: (1) the solubilization of insoluble compounds, (2) the protection of intermediates, (3) the conformation effect, (4) the microscopic-solvent effect, and (5) the control of molecular size.[18] According to (1) the solubilization of insoluble compounds, CyD plays an important role in this TN-LCD fabricated by 5CB sol. The solubility of silica in 5CB is poor. Therefore, bare silica may be little dispersed in 5CB sol. When silica is capped with CyD, it can be disperse in 5CB sol and worked for the TN-LCD. The promotion of response time by βCyD-SiO_2 is probably attributable to inclusion complex formation. 5CB has a framework of biphenyl. The formation constant (2100 M^{-1}) of the βCyD–biphenyl complex was exceedingly lager than that (24 M^{-1}) of the αCyD–biphenyl complex.[19] The association between γCyD and biphenyl has not been observed, according to the literature.[19] Thus, the response time of this LCD in the presence of βCyD-SiO_2 nanoparticles is faster than that in the presence of αCyD-SiO_2 and γCyD-SiO_2 nanoparticles, suggesting an inclusion complex formation of βCyD-SiO_2 with 5CB as the host liquid crystal. A biphenyl molecule was axially included in the cavity of βCyD, according to the literature.[20] Previously, we have reported the conformation of inclusion complex between βCyD and 4-biphenylcarboxylic acid on the aqueous alkaline solution by measurements of ^{1}H-NMR chemical shifts of βCyD and the rotating frame Overhauser enhancement spectroscopy.[21] The 4-biphenylcarboxylate was axially included in the cavity of βCyD with an orientation which located the carboxylate group at the primary hydroxyl side of

Table 1.
Response time of TN-LCD fabricated by 5CB sol in the absence and the presence of CyD-SiO_2 nanoparticles.

	Time/msec			
	5CB pure	αCyD-SiO_2	βCyD-SiO_2	γCyD-SiO_2
τ_{on}	76.0	61.9	56.3	76.6
τ_{off}	20.2	14.8	15.2	14.1
Total	96.2	76.7	71.5	90.7

βCyD and the 4′-position of 4-biphenylcarboxylate at the secondary hydroxyl side of βCyD. The 5CB molecule having a electron-withdrawing substituent is also found to have an orientation as well as βCyD-4-biphenylcarboxylate inclusion complex.

Response Time of Practical TN-LCD Containing SiO_2 Nanoparticle

Now, the result obtained by collaboration with industries is shown. Since a joint research enterprise requested the fast response speed, especially the rapid improvement of fall time, we can select γCyD as the stabilizer of SiO_2 nanoparticles. We demonstrate the fast responce speed of SiO_2 nanoparticles doped TN dot matrix LCD by showing a photographic image of TN-LCD (Figure 4).[22] The practical liquid crystal M03 from Merck, Ltd. were used as the host liquid crystal. On the other hand, the traial panel as shown in Figure 4 is asked the long-term stability of nanoparticles. We have recently reported that the poly(γ-cyclodextrin) (PγCyD) molecule coordinated to palladium nanoparticles at multiple sites, being stable for months at room temperature.[23] Even though each coordination bond is weak, the multi-coordination would result in the strong chemical adsorption of polymer molecule on the SiO_2 nanoparticle surface. Thus, PγCyD as the stabilizer was selected from the viewpoint of the improvement of fall time and long-term stability. The average diameter of SiO_2 nanoparticles capped by PγCyD was 6.4 nm.

Figure 4.
Photograph of a TN-LCD doped with PγCyD-SiO_2 nanoparticles.

Figure 5 shows the response behaviors at 24 °C of practical M03 and that doped with PγCyD-SiO_2 nanoparticles. The rise times of TN-LCD fabricated by M03 sol are 0.54 and 0.42 msec for pure M03, and PγCyD-SiO_2-doped M03, respectively. The rise time of TN-LCD in the presence of PγCyD-SiO_2 nanoparticles is faster than that in the absence. The rise time is given by

$$\tau_{\mathrm{on}} = (\gamma_1 d^2)/\varepsilon_0 \Delta\varepsilon (V_{\mathrm{on}}^2 - V_{\mathrm{th}}^2)$$

where γ_1, d, ε, and V_{th} are rotational viscosity, a thickness of host LCD, dielectric constant, and threshhold voltage, respectively. On the other hand, the fall times of TN-LCD fabricated by M03 sol are 2.00 and 1.93 msec for pure M03, and PγCyD-SiO_2-doped M03, respectively. The fall time is given by

$$\tau_{\mathrm{off}} = (\gamma_1 d^2)/(\pi^2 K_{\mathrm{eff}})$$

where γ_1, d, and K_{eff} are rotational viscosity, a thickness of host LCD, and Ossen-Frank elastic constants, respectively. Yasuda *et al.* reported cyclodextrin derivatives reduced the viscosity of liquid crystal.[24] This result suggests that the presence of PγCyD-SiO_2 nanoparticles in liquid crystal makes it easy for liquid crystal molecules to change the viscosity probably due to the inclusion effect of PγCyD upon intermolecular interactions among liquid crystal molecules. Further studies related to this preliminary successful result to the evaluation of physical properties

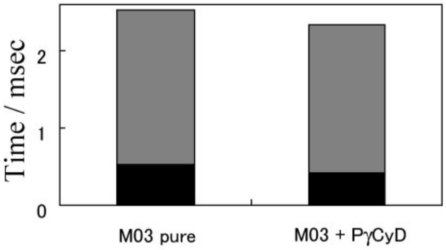

Figure 5.
Response time of TN-LCD fabricated by practical M03 doped with PγCyD-SiO_2 nanoparticles. The rise time is deep color and the fall time is faint color.

as rotational viscosity, and Ossen-Frank elastic constants are in progress.

Conclusion

When SiO_2 nanoparticles capped with various CyD were added into 5CB, the response time of this LCD in the presence of βCyD-SiO_2 nanoparticles is faster than that in αCyD-SiO_2 and γCyD-SiO_2. This result suggests an inclusion complex formation of βCyD-SiO_2 with 5CB molecule as the host liquid crystal. The response time of LCD of practical liquid crystal (M03) was reduced by addition of PγCyD-SiO_2 nanoparticles. Addition of capped nanoparticles to liquid crystal media as a dopant can improve the response time of the LCD. The capped nanoparticles may work as a disturbant to the ordered liquid crystal media, resulting in easy movement of liquid crystal molecules. Fast response speed achieved by our present research may give a great impact to LCD industries such as LC-TVs automobile displays, and mobile phones.

Acknowledgements: This work was partially supported by Konica Minolta Imaging Science Foundation and the Shinsei Foundation to Y.S. and a Grant-in-Aid for Scientific Research (C) (No. 20510109, 24510158 to Y.S.) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan.

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