

Fast Response of Liquid Crystal Devices Doped with Poly(cyclodextrin)-Stabilized ZrO₂/Ag Hybrid Nanoparticles

Yukihide SHIRAISHI*, Takahito KANZAKI*, Hiroya SAWAI*, Hitoshi ASANO*, Yukou DU** and Naoki TOSHIMA***

Abstract: Poly (β-cyclodextrin)-stabilized zirconia/silver (PβCyD-ZrO₂/Ag) nanoparticles were prepared from colloidal dispersions of PβCyD-ZrO₂ nanoparticles. Particles of PβCyD-ZrO₂/Ag (molar ratio of ZrO₂/Ag = 0.8/0.2) nanoparticles have an average diameter of 4.5 nm. The nanoparticles were dispersed in 4'-pentyl-4-cyanobiphenyl to construct liquid crystal displays. The response time of this display in the presence of PβCyD-ZrO₂/Ag nanoparticles was faster than that in the absence of nanoparticles.

Key words: Liquid crystal display, Nanoparticles, Silver, Zirconia, Poly(cyclodextrin)

1. Introduction

Liquid crystal molecules have been studied 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 displays (LCDs), however, have a disadvantage of slow response compared with electroluminescence displays. Thus, it will be a big impact to design LCDs with fast response, if liquid crystal sol containing nanomaterials 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 nanomaterials or nanotechnology in a wide sense into self-assembled systems such as LCDs may attract the attention of researchers who are interested in inaugurating a new kind of combination of different fields.¹⁾ In fact, the number of papers, especially patents on a liquid crystal display concerning with nanomaterials increases rapidly these years. The nanomaterials reported as a dispersed phase in LCDs involves fullerene,²⁾ carbon nanotubes,³⁾ diamond powders,⁴⁾ and metal nanoparticles,^{5,6)} 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.

Nanoparticles have attracted a great interest in scientific research and industrial applications, owing to their unique large surface-to-volume ratios and quantum-size effects.⁷⁾ From both the scientific and technological point of view, bimetallic nanoparticles composed of two different metal elements are more promising than monometallic nanoparticles, because synergistic effect is expected.⁸⁾ Bimetallic nanoparticles have shown novel catalytic behaviors based

on the effect of second metal element added. This effect of second metal element can be often explained in terms of an ensemble and/or a ligand effect. The synthesis of bimetallic nanoparticles is mainly divided into two methods, that is, the chemical and physical methods, or the “bottom-up” and “top-down” methods. The chemical method involves simultaneous or coreduction, successive or two-step reduction of two kinds of metal ions, and “self-organization” of bimetallic nanoparticles by physically mixing two kinds of already-prepared monometallic nanoparticles with or without after treatments. Previously, we reported 4'-pentyl-4-cyanobiphenyl (5CB)-stabilized Ag/Pd bimetallic nanoparticles by the light irradiation of the tetrahydrofuran solution of silver(I) perchlorate and palladium(II) acetate in the presence of a liquid crystal molecule.⁹⁾ Infrared spectra of carbon monoxide adsorbed on the bimetallic nanoparticles suggested that bimetallic nanoparticles had a random alloy structure.¹⁰⁾ To the best of our knowledge, there is no reports on electro-optic properties of liquid-crystal display doped by oxide/metal hybrid nanoparticles.

Recently, we obtained poly (cyclodextrin)-stabilized zirconia (PCyD-ZrO₂) nanoparticles by ultrasonic and microwave reaction of zirconium(IV) ethoxide in tetraethylene glycol.¹¹⁾ This study is aimed to develop novel functional PβCyD-ZrO₂/Ag hybrid nanoparticles having high dispersibility into liquid crystal matrices. Colloidal dispersions of ZrO₂/Ag hybrid nanoparticles were applied to the electro-optic properties of LCDs.

2. Experimental

PβCyD-ZrO₂ nanoparticles were prepared by using a microwave

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*Department of Applied Chemistry, Tokyo University of Science Yamaguchi, Daigakudori, SanyoOnoda, Yamaguchi 756-0884, Japan.

**College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China

***Advanced Materials Institute, Tokyo University of Science Yamaguchi, Daigakudori, SanyoOnoda, Yamaguchi 756-0884, Japan

Corresponding author. Tel: +81 836 88 4580, fax: +81 836 88 3844

Email address: shiraishi@rs.tusy.ac.jp (Y. Shiraishi)

reactor equipped with ultrasonic nozzle. P β CyD (0.017 mmol in monomeric units, 0.1 times the total amount of zirconyl chloride octahydrate) and zirconyl chloride octahydrate (0.17 mmol) were mixed in mixture of water/tetraethylene glycol(1/16, v/v) to form a 250 cm³ solution. The mixed solutions was filled with pure nitrogen (99.999%) and then exposed to the microwave (2450 MHz) and ultrasonic waves (150 W, 20 kHz) at the same time. 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 P β CyD- ZrO_2 nanoparticles. The P β CyD- ZrO_2 nanoparticles prepared were used as core seeds for ZrO_2 -core/Ag-shell nanoparticles. The seed P β CyD- ZrO_2 nanoparticles were dispersed into tetraethylene glycol in a two-necked 100-mL flask equipped with a dropping funnel, which was charged with a degassed aqueous solution (50 mL) of silver(I) perchlorate (0.033 mmol). The silver(I) perchlorate solution was added into the reaction mixture dropwise over about 1 h period. P β CyD- ZrO_2/Ag (molar ratio of ZrO_2/Ag = 0.5/0.5, 0.67/0.33, 0.75/0.25, and 0.8/0.2) nanoparticles thus produced were collected on an ultrafilter, washed with ethanol, and dried under vacuum at 40 °C. P β CyD- ZrO_2/Ag were prepared by the similar method.

Ultraviolet and visible light (UV-Vis) 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 JEM 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. P β CyD- ZrO_2/Ag nanoparticles were mixed with the liquid crystal 5CB at room temperature resulting in a liquid crystal sol of 5CB containing 0.075 wt% of ZrO_2/Ag . The sols were injected into an empty cell for a twisted nematic mode with a cell gap of 5 μm , supplied by Sun Trading Co. Ltd. The electro-optic properties, especially applied voltage versus optical transmittance (V - T) curves of twisted nematic liquid crystal displays (TN-LCDs) were measured by applying the 100 Hz square wave alternating current at 25 °C with a LCD evaluation system (Photol Ohtsuka Electronics, Ltd., model LC-5200).

3. Results and Discussion

Colloidal dispersions of P β CyD- ZrO_2/Ag nanoparticles were prepared by this method, having a yellow color and being stable for months at room temperature. No aggregates or sediments were observed in P β CyD- ZrO_2/Ag nanoparticles thus prepared. Figure 1 shows UV-Vis absorption spectra of the dispersions of P β CyD- ZrO_2/Ag nanoparticles at various ZrO_2/Ag ratios. When a colloidal dispersion of P β CyD- ZrO_2 nanoparticles was mixed with silver(I) perchlorate, the absorption at 320 nm of ZrO_2 nanoparticles disappeared completely after 1 h. On the other hand, the absorption peak at 423 nm can be attributed to the surface plasmon of Ag nanoparticles.¹²⁾ This phenomenon suggests that the ZrO_2 nanoparticles is covered by the Ag nanoparticles. The surface plasmon absorption of

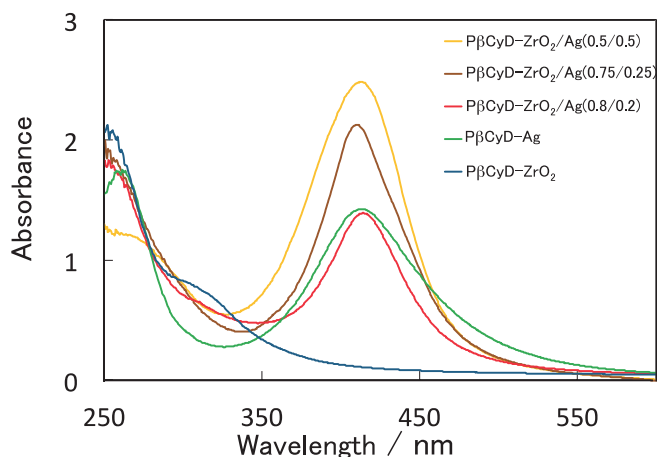


Fig. 1. UV-Vis absorption spectra of colloidal dispersions of P β CyD- ZrO_2/Ag nanoparticles.

Ag can be observed for the colloidal dispersions of ZrO_2/Ag nanoparticles at a ZrO_2/Ag molar ratio of 0.8/0.2. When the amount of Ag was larger than 0.2, a strong plasmon absorption was remarkably observed. In the absence of ZrO_2 nanoparticles, the Ag ions were not reduced in this reaction condition.

Colloidal dispersions of P β CyD- ZrO_2/Ag nanoparticles were prepared by covering ZrO_2 -core nanoparticles with Ag atoms successively produced by adsorbed on the ZrO_2 nanoparticles. Figure 2 depicts transmission electron micrographs and the corresponding histograms indicating the particle size distributions of nanoparticles. The P β CyD- ZrO_2/Ag (0.8/0.2) nanoparticles have an average diameter of 4.5 nm, while the P β CyD- ZrO_2 nanoparticles have 2.2 nm. The size distribution of the P β CyD- ZrO_2/Ag nanoparticles exhibits Gaussian distribution. These results suggest that the P β CyD- ZrO_2/Ag nanoparticles are not mixtures of ZrO_2 and Ag nanoparticles but consist of single particle having homogeneous structure. The same tendency was observed in the case of PVP-stabilized core/shell-structured Pd/Ag bimetallic nanoparticles.¹³⁾ This observation suggests that Ag atoms, produced by reduction of Ag ions on the surface of the ZrO_2 seed, cover the ZrO_2 seeds completely to form an Ag shell.

The P β CyD- ZrO_2/Ag nanoparticles prepared in the present experiments were easily mixed with liquid crystal molecule 5CB at room temperature to form liquid crystal sol for TN-LCDs. The TN-LCDs fabricated by injecting the liquid crystal sol containing nanoparticles into empty cells were supplied to measure the electro-optic properties. Electro-optic properties of TN-LCDs fabricated by 5CB with and without P β CyD- ZrO_2/Ag nanoparticles were measured by applying voltage in alternating current at 25 °C. Figure 3 shows the time evolution of transmittance of TN-LCDs fabricated by 5CB sol in the absence and presence of P β CyD- ZrO_2/Ag (0.8/0.2) nanoparticles and P γ CyD- ZrO_2/Ag (0.8/0.2) nanoparticles. The response times (τ_{on} ; the rise time from V_{on} -time to transmittance-10% time, and τ_{off} ; the fall time from V_{off} -time to transmittance-90 % time) of TN-LCDs fabricated by 5CB sol in the presence of nanoparticles are summarized in Table 1. The fast response time was observed in the presence of P β CyD- ZrO_2/Ag nanoparticles with the τ_{on} of 48.8 ms and the τ_{off} of 13.7 ms, while

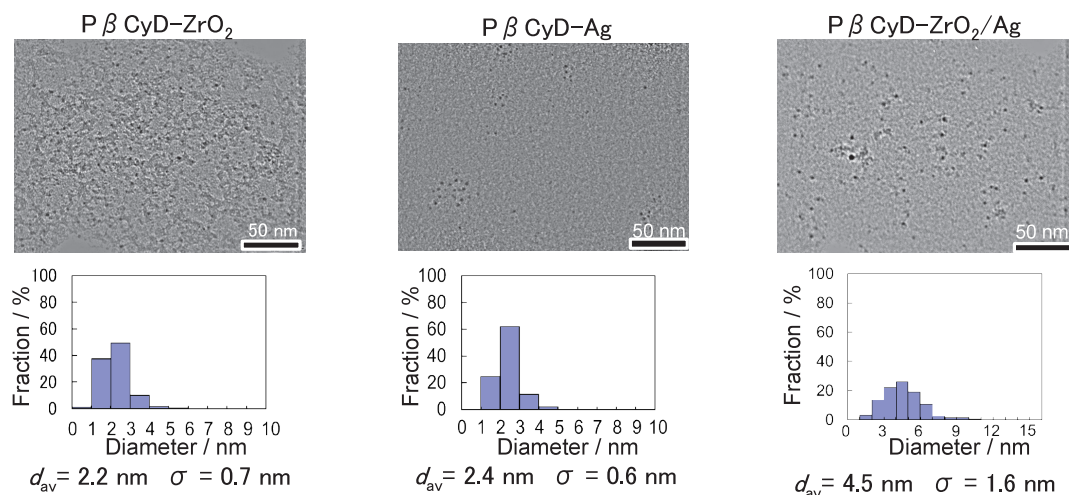


Fig. 2. Transmission electron micrographs and particle size histograms of ZrO_2 , Ag and ZrO_2/Ag nanoparticles. d_{av} = average diameter, σ = standard deviation.

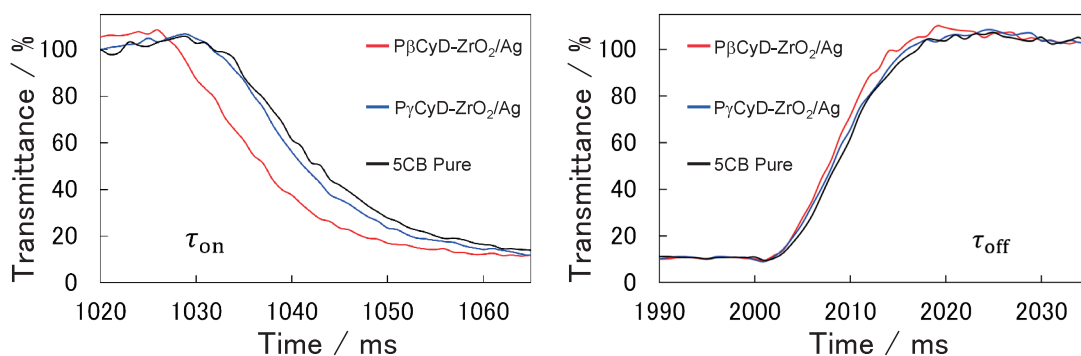


Fig. 3. The time evolution of transmittance of TN-LCDs fabricated by 5CB sol in the absence and presence of $\text{P}\beta\text{CyD-ZrO}_2/\text{Ag}$ nanoparticles and $\text{P}\gamma\text{CyD-ZrO}_2/\text{Ag}$ nanoparticles.

Table 1 Response times of TN-LCDs fabricated by 5CB sol in the absence of nanoparticles, in the presence of $\text{P}\beta\text{CyD-ZrO}_2/\text{Ag}$ and in the presence of $\text{P}\gamma\text{CyD-ZrO}_2/\text{Ag}$ nanoparticles.

	Response time / msec		
	5CB pure	5CB + $\text{P}\beta\text{CyD-ZrO}_2/\text{Ag}$	5CB + $\text{P}\gamma\text{CyD-ZrO}_2/\text{Ag}$
τ_{on}	55.7±0.4	48.8±1.0	54.2±1.9
τ_{off}	14.5±0.2	13.7±1.0	14.3±0.5
Total	70.2±0.5	62.5±1.9	68.5±2.4

The response times depict an average of 5 measured values and standard deviation.

the low response time was exhibited in the absence of them with the τ_{on} of 55.7 ms and the τ_{off} of 14.5 ms. The total response times of TN-LCDs were 62.5 and 68.5 ms for $\text{P}\beta\text{CyD-ZrO}_2/\text{Ag}$ nanoparticles and $\text{P}\gamma\text{CyD-ZrO}_2/\text{Ag}$ nanoparticles, respectively. Previously, we reported that the response time of 5CB in the presence of $\text{P}\beta\text{CyD-ZrO}_2$ nanoparticles was faster than that in the presence of $\text{P}\gamma\text{CyD-ZrO}_2$ nanoparticles.¹¹⁾ In this ZrO_2/Ag nanoparticles, the same tendency of response time was also observed on TN-LCDs doped with $\text{P}\beta\text{CyD-ZrO}_2/\text{Ag}$ nanoparticles.

The promotion of response time by $\text{P}\beta\text{CyD-ZrO}_2/\text{Ag}$ is probably attributable to inclusion complex formation. The 5CB molecule has a framework of biphenyl. Previously, we have reported the conformation of inclusion complex between βCyD and biphenyl derivative

on alkaline solution by measurements of $^1\text{H-NMR}$ chemical shifts of βCyD and the rotating frame Overhauser enhancement spectroscopy.¹⁴⁾ The solubility of ZrO_2/Ag nanoparticles in 5CB is poor. Therefore, bare ZrO_2/Ag nanoparticles may be little dispersed in 5CB sol. When ZrO_2/Ag nanoparticles is stabilized with PCyD , it can be disperse in 5CB sol and worked for the TN-LCD. Besides, the formation constant ($2100 \text{ dm}^3 \text{ mol}^{-1}$) of the βCyD -biphenyl complex was exceedingly larger than that ($130 \text{ dm}^3 \text{ mol}^{-1}$) of the γCyD -biphenyl complex.¹⁵⁾ Thus, the response time of this LCD in the presence of $\text{P}\beta\text{CyD-ZrO}_2/\text{Ag}$ nanoparticles is faster than that in the presence of $\text{P}\gamma\text{CyD-ZrO}_2/\text{Ag}$ nanoparticles, suggesting an inclusion complex formation of $\text{P}\beta\text{CyD-ZrO}_2/\text{Ag}$ with 5CB as the host liquid crystal. In Figure 4, the ZrO_2 content of nanoparticles is plotted against the improvement rate of total response time of TN-LCDs fabricated by 5CB sol containing $\text{P}\beta\text{CyD-ZrO}_2/\text{Ag}$ nanoparticles from that of pure 5CB. No linear relationship was observed between the the improvement rate of total response time and ZrO_2 content. The improvement rate was larger for ZrO_2 -core/Ag-shell nanoparticle of $\text{ZrO}_2/\text{Ag} = 0.75/0.25$ and $0.8/0.2$. The fastest response was achieved by the ZrO_2/Ag ($0.8/0.2$) nanoparticles.

The rise time is given by

$$\tau_{\text{on}} = (\gamma_1 d^2) / \epsilon_0 \Delta \epsilon (V_{\text{on}}^2 - V_{\text{th}}^2)$$

where γ_1 , d , ϵ , and V_{th} are rotational viscosity, a thickness of host LCD, dielectric constant, and threshold voltage, respectively. The

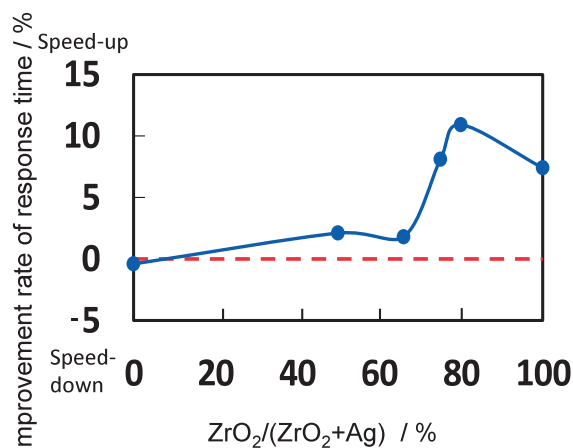


Fig. 4. Relationship between composition and improvement rate of total response time of TN-LCDs fabricated by 5CB sol in the presence of P β CyD-ZrO₂/Ag nanoparticles.

fall time is given by

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

where γ_1 , d , and K_{eff} are rotational viscosity, a thickness of host LCD, and Ossen-Frank elastic constants, respectively.¹⁶⁾ To consider this fast response, we measured the rotational viscosity. This measurement was done for an electrically controlled birefringence (ECB) mode cells by a Model 6254 (Toyo). The rotational viscosity obtained in this manner were 79.9, 68.7, and 75.7 mPa·s for LCDs in the absence of nanoparticles, in the presence of P β CyD-ZrO₂/Ag(0.8/0.2) and in the presence of P γ CyD-ZrO₂/Ag(0.8/0.2) nanoparticles, respectively, as shown in Table 2. This result suggests that the presence of P β CyD-ZrO₂/Ag nanoparticles in liquid crystal makes it easy for liquid crystal molecules to change the viscosity. Further studies will be described in detail elsewhere.

4. Summary

P β CyD-stabilized ZrO₂/Ag nanoparticles with ZrO₂-core/Ag-shell structure were prepared from P β CyD-ZrO₂ nanoparticles. The response time of TN-LCDs in the presence of P β CyD-ZrO₂/Ag(0.8/0.2) nanoparticles was faster than that in the absence of nanoparticles. The 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 automobile displays, digital signages, and smart phones. Since there are various modes and driving systems in LCDs, the matching between nanoparticles and liquid crystal media is still in progress to achieve the improved performance of LCDs.

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Table 2. Rotational viscosity of 5CB doped with P β CyD-ZrO₂/Ag and P γ CyD-ZrO₂/Ag nanoparticles

	γ_1 /mPa·s
5CB Pure	79.9
5CB+P β CyD-ZrO ₂ /Ag	68.7
5CB+P γ CyD-ZrO ₂ /Ag	75.7