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Polymer-Metal Nanoparticle Complexes for Improving the Performance of Liquid Crystal Displays

Naoki Toshima

Summary: Here we applied metal nanoparticles as a dopant of liquid crystals. Since liquid crystal molecules are self-assembled, it is not so easy to disperse metal nanoparticles in liquid crystal media. We first prepared metal nanoparticles protected by liquid crystal molecules by reduction of metal ions in the presence of liquid crystal molecules. This liquid crystal molecule-protected metal nanoparticles can be easily dispersed in liquid crystal media to fabricate liquid crystal sol containing metal nanoparticles. A simple liquid crystal molecule, 4′-pentylbiphenyl-4-carbonitrile (abbreviated as 5CB) was used in the present experiments at first. 5CB sol containing metal nanoparticles could construct novel twisted nematic liquid crystal devices (TN-LCDs), which revealed the electrooptic properties depending on the kind of metal of nanoparticles. During the experiments we discovered that 5CB-protected metal nanoparticles could move in liquid crystal media by applying the voltage. This phenomenon is inconvenient for liquid crystal displays, especially those driven by a matrix of thin-film transistors (TFTs). In order to avoid this phenomenon, we prepared polymer-protected metal nanoparticles and applied them to liquid crystal devices, which provided good performance as the devices, i.e., low driving voltage, rapid response at low temperature, and so on.

Keywords: 5CB; liquid crystal; metal nanoparticle; poly(N-vinyl-2-pyrrolidon); PVP; response time; STN-LCD; TN-LCD; twisted nematic

Introduction

Metal nanoparticles have been receiving much attention for a decade because of their characteristic location in size between metal ions or atoms and bulk metal as well as their novel properties, which are expected to be applied to the various fields.[1,2] We discovered the formation of metal nanoparticles by accident in 1976 when the mixtures of Rh^{3+} ions and poly(L-glutamic acid) were refluxed in ethanol-water aiming to prepare poly(L-glutamic acid)-Rh^{3+} complexes as a model of artificial enzymes.[3] In fact, this treatment provided a colloidal dispersion of poly(L-glutamic acid)-protected Rh nanoparticles, where ethanol worked as a reductant of Rh^{3+} ions. The reaction process can be written as shown in Scheme 1.

This alcohol reduction method can be used to prepare various colloidal dispersions of not only precious metal[4] but also late transition metal nanoparticles by using high boiling point alcohols like glycol.[5] The produced metal nanoparticles can be applied to various fields such as catalysts and electrocatalysts,[1,6–8] sensors and biosensors,[9–11] nanomagnets,[12–14] pharmaceutical or medical applications.[15–17] In fact, the number of publications collected by SciFinder Scholar® increases rapidly especially after 2000, as shown in Figure 1.

Merging of this metal nanoparticles with liquid crystal displays (LCDs) occurred at Tokyo University of Science Yamaguchi, a small university in Japan. This small scale is

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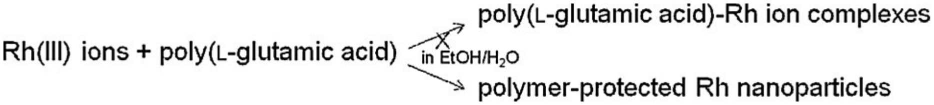
Department of Applied Chemistry, Tokyo University of Science Yamaguchi, SanyoOnoda-shi, Yamaguchi 756-0884, Japan
E-mail: toshima@ed.yama.tus.ac.jp



Scheme 1.
Accidental formation of polymer-protected Rh nanoparticles during the experimental trial to prepare polymer-Rh ion complexes as an artificial enzyme.

an advantage for merging of the completely different fields to create a new interdisciplinary field.[18] Here, the application of metal nanoparticles to LCDs is focused to improve the performance of LCDs, e.g., shortening the response time at low temperature.

Preparation of Metal Nanoparticles Protected by Liquid Crystal Molecules

The conventional polymer-protected metal nanoparticles prepared by alcohol reduction are usually dispersed in water or alcohol, and thus, are difficult to dispersed in hydrophobic organic media, especially in liquid crystal media. Thus, we have developed a new method to prepare metal nanoparticles by reduction of the corresponding metal ions in the presence of liquid crystal molecules.[19] The reduction should be carried out under the conditions which could minimize the contaminations byproduced with the reduction reaction. Photoirradiation and alcohol reduction, shown in Scheme 2 as equation (1) and (2), respectively, for $PdCl_2$, are examples matching with the requirements.

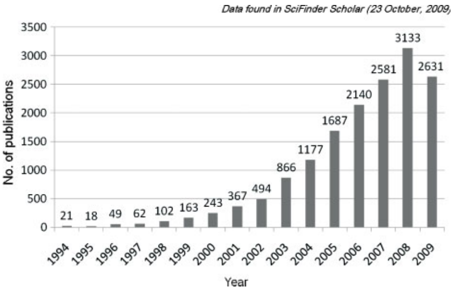


Figure 1.
Increase of publications on "application of nanoparticles" based on the data in SciFinder Scholar® (23 October, 2009).

After removal of byproducts and solvents, metal nanoparticles protected by liquid crystal molecules can be dispersed in liquid crystal media. For example, if the liquid crystal molecule is 4′-pentylbiphenyl-4-carbonitril (abbreviated as 5CB), the cyano group of 5CB can interact with Pd nanoparticles by coordination bonds[19] as shown in Figure 2.

Other metals like Ag, Rh, Pt and Au can also produce the similar nanoparticles from the corresponding metal salts. Even bimetallic nanoparticles, for example Ag/Pd bimetallic nanoparticles can be produced by reduction of $Pd(OAc)_2$ (OAc = acetate) and $AgClO_3$ in the presence of 5CB.[20]

Improvement of the Performance of Liquid Crystal Displays by Doping with Metal Nanoparticles Protected by Liquid Crystal Molecules

Liquid crystals can be utilized to switch on and off the passing light by changing the alignment of liquid crystal molecules according to the applied voltage. For example, 5CB molecules can be used as the medium for twisted nematic mode liquid crystal displays (TN-LCDs). When no voltage is applied to a TN-LCD cell, composed of 5CB molecules with a large positive dielectric anisotropy, between two conducting glass plates in parallel, the 5CB molecules near vertical and horizontal ridges etched on two glass electrodes, which

$$PdCl_2 \xrightarrow[\text{in EtOH}]{h\nu} Pd^0 + Cl_2 \quad (1)$$

$$PdCl_2 + CH_3CH_2OH \xrightarrow[\text{in EtOH}]{} Pd^0 + 2\,HCl + CH_3CHO \quad (2)$$

Scheme 2.
Photoreduction (eq. 1) and alcohol reduction (eq. 2) of $PdCl_2$ in ethanol.

are placed in perpendicular alignment to each other as designed, do align in the same direction as the vertical or horizontal ridges on the electrodes.[21] Thus, the 5CB molecules placed between the two electrode films are continuously varied from 90° to 0° against the directions of the incident light (so-called ''twist'') as shown in Figure 3a. The polarized films placed outside the incident electrode can polarize the incident light, and the light passing through the incident polarized film is twisted by the twisted molecular alignment. So, the light passing through the TN liquid crystal medium is polarized and can pass the polarized film outside the other glass electrode. Thus, the light can pass through the LCD cell, providing the white display. When a dc (direct current) or ac (alternating current) voltage larger than the threshold voltage is applied to a 5CB liquid crystal medium between the two electrodes, in contrast, all the 5CB molecules align perpendicular to the both electrodes in spite of the directions of the ridges (Figure 3b). Then the incident light passing through the incident polarized film keeps the polarization in the same direction as the incident direction in the liquid crystal medium and can be blocked by the polarized film placed outside the electrode on the other side of the device, providing the black display. Thus, it must be emphasized that the movement of liquid crystal molecules depending on the applied voltage is essential for the on-off switching of LCDs. This is quite different from other flat panel displays like organic electroluminescent displays or plasma displays, and results in a weak point that the response time of

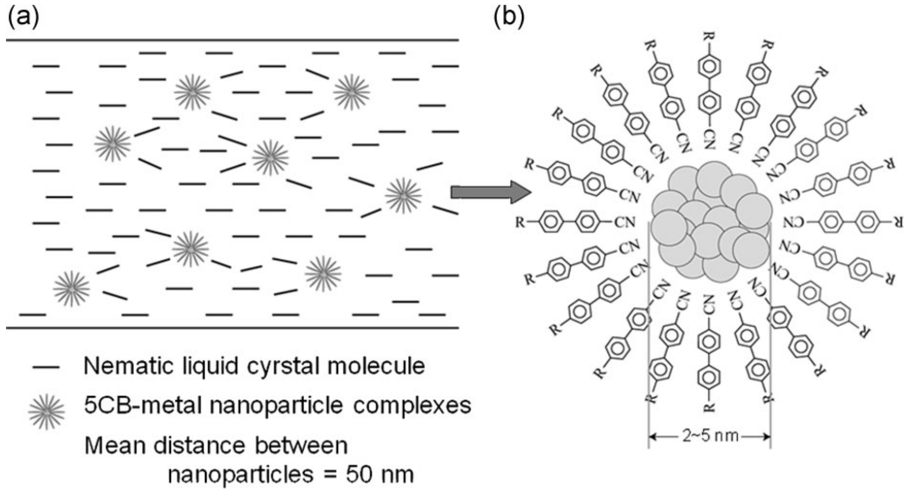


Figure 2.
Schematic illustration of 5CB-protected metal nanoparticls (b) and their dispersion in a nematic liquid crystal medium (a).

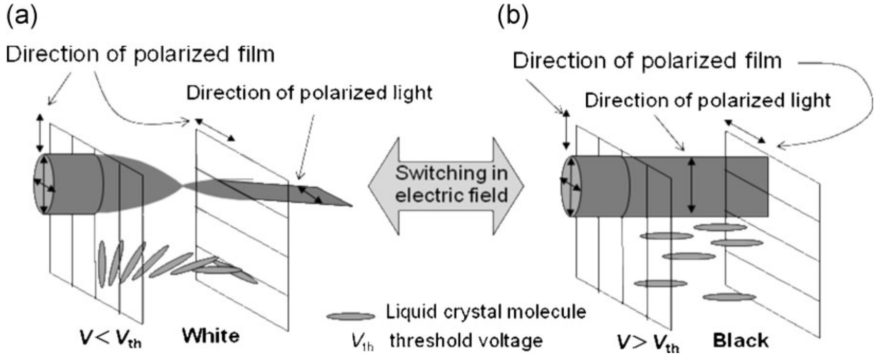


Figure 3.
Schematic illustration of on-off switching of twisted nematic LCD.

on-off switching of LCDs is longer than other flat panel displays.

Addition of metal nanoparticles into liquid crystal media could partially disturb the alignment of liquid crystal molecules, which may result in the change of the movement of liquid crystal molecules. This change may improve the performance of LCDs. In fact we have succeeded in shortening the response time of practical super-twisted nematic (STN) LCDs, especially at low temperature, e.g., at –20 °C and –30 °C. The results are shown in Table 1.[22] The response times (the sum of rising time τ_{on} and falling time τ_{off}) of the practical STN-LCD containing nanoparticles are about half to one third of that without nanoparticles, especially at low temperature. In this case we used Ag-Pd bimetallic nanoparticles because the Ag-Pd bimetallic nanoparticles revealed the better performance than Pd nanoparticles, and in addition had the long term stability compared with Ag nanoparticles.[20] The better stability could be easily observed in the 5CB cells as shown in Figure 4.[20] Although the LCD containing Ag nanoparticles had several defects after heat treatment at 80° for 28 days, no defects were observed for the LCD with Ag-Pd bimetallic nanoparticles after the same treatment. Practical improvement in response time at –15 °C could be demonstrated in photograph of the practical STN-LCD.[23] In fact, for the LCD with nanoparticles, the quick response have provided a clear picture, while, without nanoparticles, the response is not enough quick, which results in afterimages.

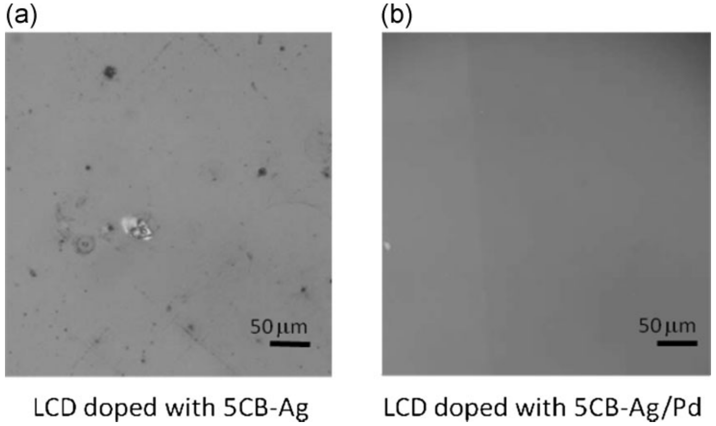
Size Effect of 5CB-Pd Nanoparticles upon the Performance of LCDs

In the previous section, we demonstrate the quick response of the practical STN-LCD doped with a small amount of

Table 1.
Response time τ of STN-LCD with and without Ag/Pd bimetallic nanoparticles

Temp.	Presence of nanoparticles	τ_{on}/ms*	τ_{off}/ms	($\tau_{on} + \tau_{off}$) ms
–30 °C	No	14000	17000	31000
	Yes	5300	4400	9700
–20 °C	No	8600	1700	10200
	Yes	2400	1800	4100
0 °C	No	820	230	1050
	Yes	730	230	960
25°C	No	580	320	900
	Yes	290	68	360

τ_{on}: response time when voltage is applied. τ_{off}: response time when voltage is cut off.



LCD doped with 5CB-Ag

LCD doped with 5CB-Ag/Pd

Figure 4.
Thermal stability of 5CB LCD doped with 5CB-Ag/Pd bimetallic nanoparticles (b), compared with that with 5CB-Ag nanoparticles (a).

metal nanoparticles. This STN-LCD was addressed by a passive matrix.[24,25] Recently, however, an active-matrix addressing drive with thin-film transistors (TFTs) is rather common for the LCD used for TV sets and personal computers because the active-matrix address has advantages such as clear representation and wide viewing angle. This active-matrix address requires the liquid crystal materials a high voltage-holding ratio since the applied voltage should be kept for a while after switching-off. Thus, the voltage-holding ratio of TN-LCDs constructed by practical liquid crystal materials with and without 5CB-Pd nanoparticles was evaluated. The results are shown in Figure 5. Without addition of Pd nanoparticles, the initial applied voltage ($V_1 = 5.00\,\text{V}$) is almost kept constant ($V_2 = 4.99\,\text{V}$) after 0.017 sec, while, with Pd nanoparticles, the voltage goes down rapidly ($V_2 = 0.07\,\text{V}$). This result suggests the possibility that 5CB-Pd nanoparticles may move in a liquid crystal medium and work as a carrier of electric charge. In order to prove the above possibility, we have prepared

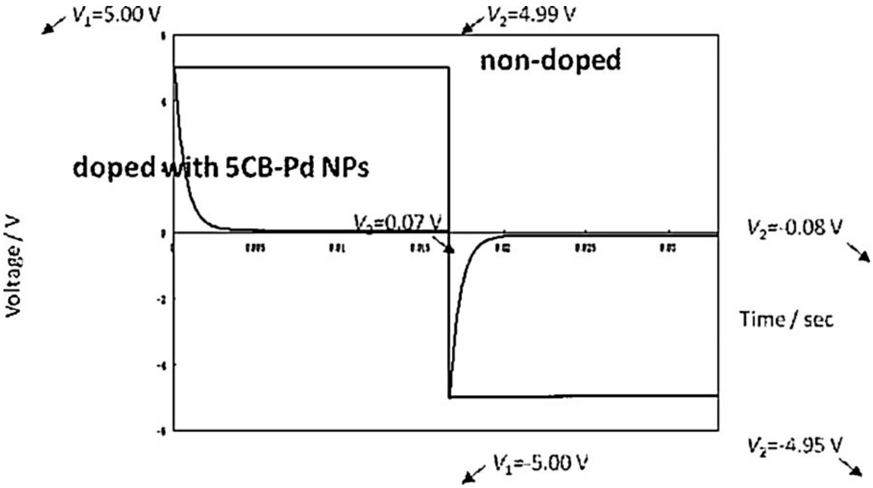


Figure 5.
Measurement of voltage-holding ratio of TN-LCDs composed of doped and non-doped practical LC.

Table 2.
Preparation of 5CB-Pd nanoparticles with various sizes by photoreduction in THF/2-propanol

	Preparation conditions		Pd nanoparticle
Metal conc./mM	5CB/Pd ratio/–	2-Propanol ratio/vol%	Mean diameter/nm
0.13	40	0	0.8 ± 03
0.66	40	0	2.0 ± 0.8
1.98	5	20	3.5 ± 1.4
3.30	5	40	6.7 ± 2.1

various sizes of 5CB-protected Pd (5CB-Pd) nanoparticles and evaluated the properties of LCDs composed of liquid crystal materials doped with 5CB-Pd nanoparticles having various sizes. The preparation conditions of 5CB-Pd nanoparticles with various mean diameters are shown in Table 2. The particles having mean diameters from 0.8 nm to 6.7 nm were successfully prepared by varying the reaction conditions.

Conductivities of TN-LCD cells composed of 5CB with various sizes of 5CB-Pd nanoparticles were measured under application of an ac (alternating current) voltage of 0.2 V at 1 kHz. Interestingly the conductivity increases gradually with decreasing the particle size as shown in Table 3.[26] This result could be reasonably explained by the hypothesis that the 5CB-Pd nanoparticles move in the liquid crystal medium and work as a carrier of electric charge.

Figure 6 shows the temperature dependence of conductivity of the LC cell composed of 5CB with and without 5CB-Pd nanoparticles. In the case of pure 5CB without nanoparticles, the conductivity is very small and does not vary depending on temperature. In other words, the conductivity is independent from the alignment of liquid crystal molecules, i.e., a nematic and an isotropic phase. In addition the conductivity does not depend on the direction of liquid crystal molecules. The conductivity depends on neither the molecular direction parallel to that of the electric field, which can be achieved by application of voltage higher than threshold voltage V_{th}, nor that perpendicular to the electric field, which can be achieved without application of voltage or with application of voltage lower than V_{th}.

In the case of LC cells composed of 5CB doped with a small amount of 5CB-Pd nanoparticles, in contrast, the conductivity depends on temperature. Even in the isotropic phase, the conductivity increases linearly with increasing temperature. This suggests that Pd nanoparticles move by application of voltage in the isotropic phase, and that the increment in conductivity by increasing temperature comes from decrease in viscosity depending on the temperature. In the nematic phase, the conductivity in the direction parallel to the electric field ($\sigma_{//}$) is always larger than that perpendicular to the electric field ($\sigma_{\perp}$), which suggests also that the movement of nanoparticles can be depressed by the 5CB

Table 3.
Conductivity and threshold voltage (V_{th}) of TN-LCD of 5CB doped with 5CB-Pd nanoparticles with various mean diameters (0.1 wt%)

Dopant (d_{av}/nm)	Conductivity of TN-LCD cell (mS/cm)	V_{th} of TN-LCD cell at 100 Hz (V)
None	1.34	0.6
5CB-Pd (6.7)	8.4	1.0
5CB-Pd (3.5)	12.6	1.2
5CB-Pd (2.4)	26.6	1.2
5CB-Pd (2.0)	15.8	1.4
5CB-Pd (0.9)	29.9	1.6

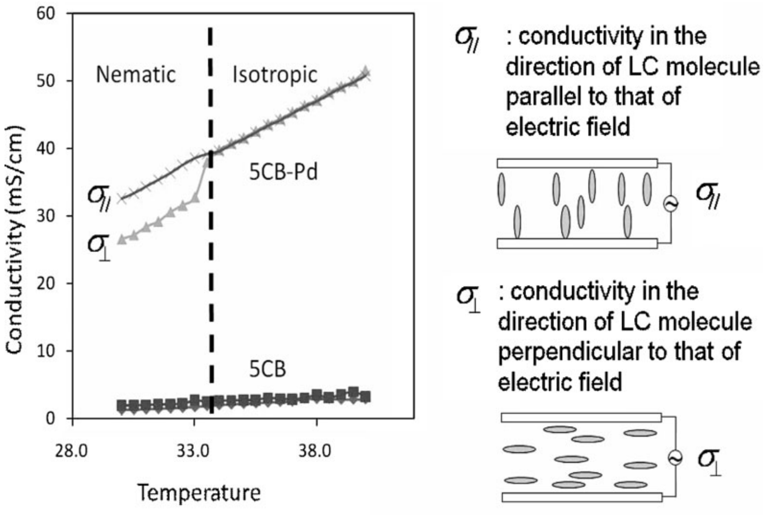


Figure 6.
Temperature dependence of conductivity of LC cell composed of 5CB with and without 5CB-Pd nanoparticles.

molecules aligned perpendicular to the direction of the movement, i.e., the electric field.

Thus, the 5CB-Pd nanoparticles can move in the LC media by the electric field, which results in disadvantage in voltage-holding ratio. In addition, the movement becomes slower in larger nanoparticles. This suggested the answer to the issue of the decrease in voltage-holding ratio by addition of nanoparticles.

Improvement of the Performance of Liquid Crystal Displays by Doping with Polymer-Protected Metal Nanoparticles

In the previous sections, we have found that the liquid crystal molecule-protected metal nanoparticles can improve the performance of LCDs, e.g., that of STN-LCDs which are addressed by a passive matrix. However, the doping of liquid crystal (LC) materials with liquid crystal molecule-protected Pd (LC-Pd) nanoparticles cannot be effective when the LCDs are driven by an active matrix, because LCDs doped with LC-Pd nanoparticles have very small voltage-holding ratio. This small voltage-holding ratio is attributed to the movement of LC-Pd nanoparticles in the LC media, and the movement can be depressed by enlargement of the particle size. These results suggest us to use polymer-protected metal nanoparticles as the dopant of LCs. The idea is illustrated in Figure 7. Since polymer is a large molecule, polymer can interest with many LC molecules, which can depress

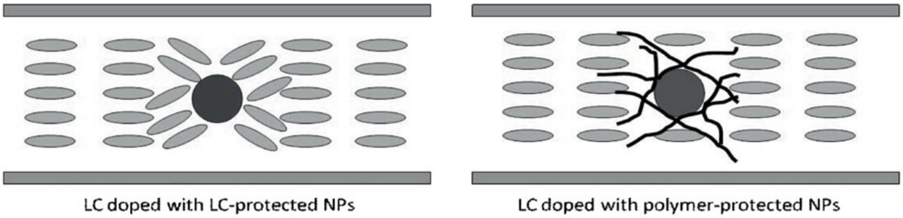


Figure 7.
Schematic illustration of LC- and polymer-protected nanoparticles dispersed in a LC medium.

the movement of polymer-protected nanoparticles in a LC medium.

Homopolymer and copolymer of *N*-vinyl-2-pyrrolidone were used as a protective polymer, and an alcohol reduction method is applied to prepare polymer-protected Pd nanoparticles from $Pd(OAc)_2$. Relatively monodispersed Pd nanoparticles were obtained. The TEM photograph and particles size distribution are shown in Figure 8.

Doping of 5CB with polymer-protected Pd nanoparticles resulted in only a little decrease in the threshold voltage by varying the frequency of applied voltage.[25] When the practical TN-LCD with an active-matrix drive was used with polymer-protected Pd nanoparticles, an excellent voltage-holding ratio was observed as shown in Table 4.

Response performance was evaluated by using practical TN-LCDs with and without doping by Pd nanoparticles. The results are shown in Figure 9. An ac voltage (3 V, 100 Hz) was applied to the practical TN-LCDs at −10 °C. In the case of the TN-LCDs without dopants, when the voltage is applied at time = 1000 msec, the transmittance gradually decreases from 100% and reaches to ca. 15% at time = 2000 msec. In the case of TN-LCDs doped with polymer-protected Pd nanoparticles, on the other hand, the response curve goes down more rapidly and reaches to ca. 10% at time = ca. 1500 msec, which is similar to the case of TN-LCD doped with 5CB-Ag/Pd bimetallic nanoparticles. Since Ag/Pd bimetallic nanoparticles usually provides better performance than Pd monometallic nanoparticles, it is clearly demonstrated that polymer-protected nanoparticles are more effective than 5CB-protected ones.

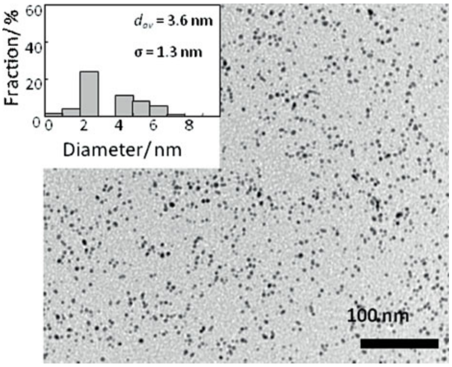


Figure 8.
TEM image and size distribution histogram of polymer-protected Pd nanoparticles.

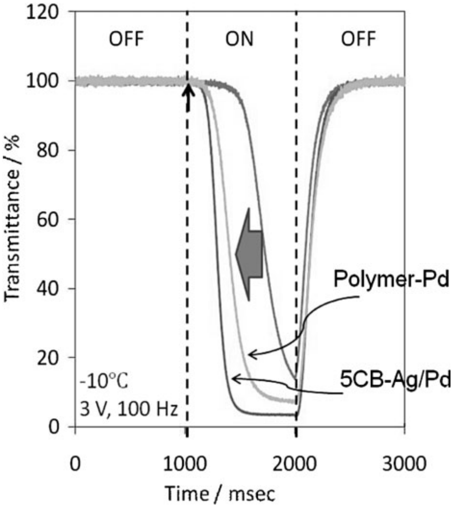


Figure 9.
Response curves of practical TN-LCDs with and without dopants at −10 °C. Dopant: Polymer-protected Pd and 5CB-protected Ag/Pd nanoparticles.

Table 4.
Voltage-holding ratio of practical TN-LCD for an active-matrix drive

Additive	VHR/%
None	98.1%
Polymer	98.0%
Polymer-Pd NP (*R* = 1, 1 wt%)	98.0%
Polymer-Pd NP (*R* = 0.5, 2 wt%)	98.0%

R = Polymer/Pd (mole ratio)

Conclusion

Merging of metal nanoparticles and liquid crystal displays is going to progress successfully at Tokyo University of Science Yamaguchi. Dispersion of metal nanoparticles in a liquid crystal medium successfully started in a system of a simple liquid crystal molecule 5CB and a 5CB-proteced Pd nanoparticle. In practical LCDs like STN-LCDs, the dispersion of Ag/Pd bimetallic nanoparticles could improve the performance of the LCDs. However, the LCDs doped by LC-protected metal nanoparticles had the issue of low voltage-holding ratio when driven by an active matrix, because LC-protected metal nanoparticles can move in the LC media by application of voltage. This problem could be solved by using polymer-protected metal nanoparticles instead of 5CB-protected ones, since large macromolecular ligands inhibit metal nanoparticles moving in LC media and working as electron carriers. By this way, the good performance, especially quick response at low temperature, of LCDs by doping with nanoparticles is going to be achieved step by step. Since there are various modes and driven systems in LCDs, the matching between nanoparticles and liquid crystal media is still in progress to achieve the improved performance of LCDs. In this research the concept of macromolecular complexes plays an important role, too.

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