# Decreasing the Residual DC Voltage by Neutralizing the Charged Mobile Ions in Liquid Crystals

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**Abstract:** The decrease of the residual direct current (DC) voltage ($V_{rdc}$) of the anti-parallel liquid crystal (LC) cell using silver (Ag)-doped Polyimide (Ag-d-PI) alignment layers is presented in this manuscript. A series of Ag/PI composite thin layers are prepared by spurting or doping PI thin layers with Ag nano-particles, and Ag/PI composite thin layers are highly transparent and resistive. LC are homogeneously aligned between 2.0 mg/mL Ag-d-PI alignment layers, and the $V_{rdc}$ of the cell that assembled with Ag-d-PI alignment layers decreases about 82%. The decrease of $V_{rdc}$ is attributed to the trapping and neutralizing of mobile ions by Ag nano-particles. Regardless of the effect of Ag nano-particles on the conductivity of Ag-d-PI alignment layers, the voltage holding ratio (VHR) of the cells is maintained surprisingly. The experiment results reveal a simple design for a low $V_{rdc}$ LC cell.

**Keywords:** liquid crystal; alignment layer; residual DC; Ag nano-particles doping

## 1. Introduction

Liquid crystals (LC) are widely used in electro-optic devices because of their unique electro-optic anisotropy; however, the mobile ions in LC cause a lot of problems relating to LC switching. The moving of mobile ions driven by electric forces towards alignment layers results in their accumulation on alignment layers, which finally generates residual direct current (DC) voltage ($V_{rdc}$) inside LC cells and adversely affects LC' switching [1–6]. During the last several decades, a series of researches focused on distinguishing, detecting mobiles ions, and revealing the influences of mobile ions shifting on LC switching were conducted, and nowadays a lot of explorations are carried out to reduce mobile ions' adverse functions on LC [7–12]

A lot of attempts have been adopted to prevent the influences of mobile ions on LC electro-optical performances, such as designing special LC molecules, purifying LC, doping LC [13,14], replacing the polyimide (PI) alignment layers with conductive materials [15–18], and photo-aligning LC [19–21], etc. Compared with other methods, doping is much easier; however, doping LC with nano-materials brings new issues, for instance, the doped nano-materials are too poor to be dispersed, and the aggregation of these nano-materials makes LC insensitively respond to external voltage. The aggregation of nano-materials is partially prevented by tightly limiting the amount of doped nano-materials; however,

because of the electric field, the doped nano-materials in LC move towards alignment layers and are accumulated on alignment layers, which enhances $V_{rdc}$ generation. Replacing PI alignment layers with conductive alignment layers significantly reduces $V_{rdc}$ on cells; however, the conductive alignment layers in the cells raise the issue of a voltage holding ratio (VHR) decrease [22,23].

Micro silver (Ag) particles are highly transparent and conductive and have been adopted to accelerate LC optical switching and trap the ionic charges. In this manuscript, Ag-spurted PI (Ag-s-PI) alignment layers and Ag nano-particles-doped PI (Ag-d-PI) alignment layers are prepared and used to trap the mobile ions in LC, and the residual DC of the cell assembled with Ag-d-PI alignment layers decreases obviously. As shown in Figure 1, the displacement polarization occurs in Ag nano-particles, when the external voltage is applied on the cell that assembled with Ag-d-PI composite alignment layers. The Ag nano-particles are immobilized by PI molecules, which restricts their shift to the LC medium. The mobile ions driven by electric forces move towards and gather near Ag-d-PI composite alignment layers, and the positive and negative charges carried by mobile ions are trapped and neutralized by Ag nano-particles. In this case, the $V_{rdc}$ caused by the accumulation of mobile ions is prohibited. Because the amount of doped Ag nano-particles is limited up to 2 mg/mL ($m_{Ag}/V_{PI}$), the electrical conductivity change of Ag-d-PI composite alignment layers could be ignored, and the decrease of voltage holding ratio on the cell is prevented.
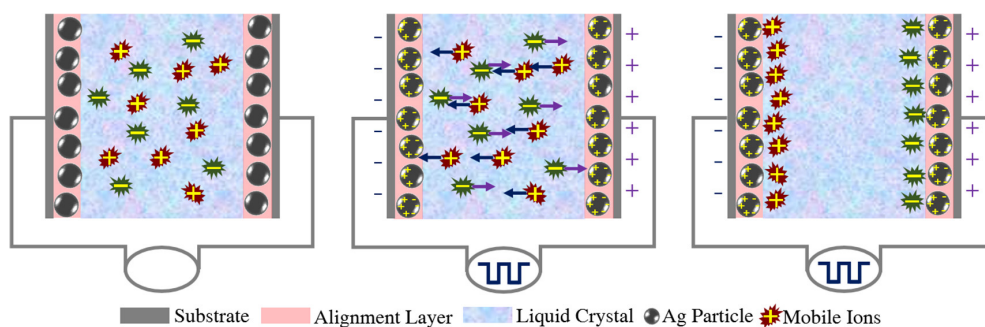


Substrate    Alignment Layer    Liquid Crystal    Ag Particle    Mobile Ions

**Figure 1.** The schematic of mobile ions accumulating on Ag-d-PI composite alignment layers.

## 2. Materials and Methods

Ag-doped PI solutions were prepared by doping Ag nano-particles (particle size < 100 nm, Sigma-Aldrich) into homogeneous PI solutions (SE7792, Nissan Chemical Corporation) with their concentrations maintained at 0.2 mg/mL, 0.5 mg/mL, 1.0 mg/mL, and 2.0 mg/mL, respectively, and Ag/PI solution was sonicated at room temperature for 30 min to disperse Ag nano-particles uniformly. Ag-d-PI thin layers were prepared by spin-coating the prepared Ag/PI solutions on ITO substrates, and Ag nano-particles spurted PI thin layers were prepared by spurting Ag nano-particle solutions (Ag/acetone, 0.2 mg/mL, 0.5 mg/mL, 1.0 mg/mL, and 2.0 mg/mL) onto spin-coated PI alignment layers. Considering that the rubbing process is necessary to align LC, and during the rubbing process Ag nano-particles may be partially removed, two Ag nano-particles-spurted PI alignment layers were prepared. One is spurting Ag nano-particles on the PI alignment layers and then followed with the rubbing process (Ag-s-PI), and the other is spurting Ag nano-particles on the rubbed PI alignment layers (Ag-s-rPI). The transmittance spectra of Ag/PI thin layers on glass slides were characterized by using a double-beam UV-Vis spectrophotometer (UV-2101, Shimadzu, Japan) and a 3-D laser-beam profiler system.

Anti-parallel cells with the cell gaps of 60 and 5 μm were assembled, and the commercial LC ($n_e$ = 1.5702, $n_0$ = 1.4756, and $\Delta\varepsilon$ = 10.7; from Merck) was injected into the fabricated cells. Alignment of LC between Ag/PI composite alignment layers was characterized by a polarized optical microscopy (POM, BXP 51, Olympus); the anchoring energy of LC on Ag/PI composite alignment layers, the $V_{rdc}$ and the capacitance of the cells were evaluated by means of a capacitance-voltage (C-V) hysteresis method (LCR meter, Agilent 4284A) with the maximum bias voltage of 10 V and a step bias voltage of 0.1 V.

## 3. Results and Discussion

As shown in Figure 2, the prepared Ag/PI alignment layers are transparent and have a transmittance above 82%; no obvious transmittance difference is observed between Ag-s-rPI, Ag-s-PI and Ag-d-PI alignment layers. Besides the transmittance decrease, the aggregation of Ag nano-particles may cause more serious issues, for instance, the aggregated Ag nano-particles block light and result in the non-uniform transparency of thin layers. The blocking performance of Ag/PI composite thin layers was characterized by using a 3D profiler as shown in Figure 3, and no significant difference is observed between the light source and the laser crossing Ag/PI composite thin layers in distribution and intensity, which reveals the potential application of Ag/PI composite thin layers for real LC devices.
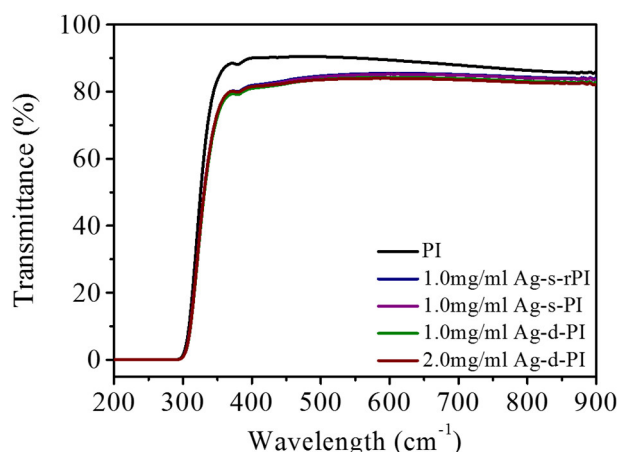


**Figure 2.** The transmittance of Ag/PI composite alignment layers (Coated on glass substrate).
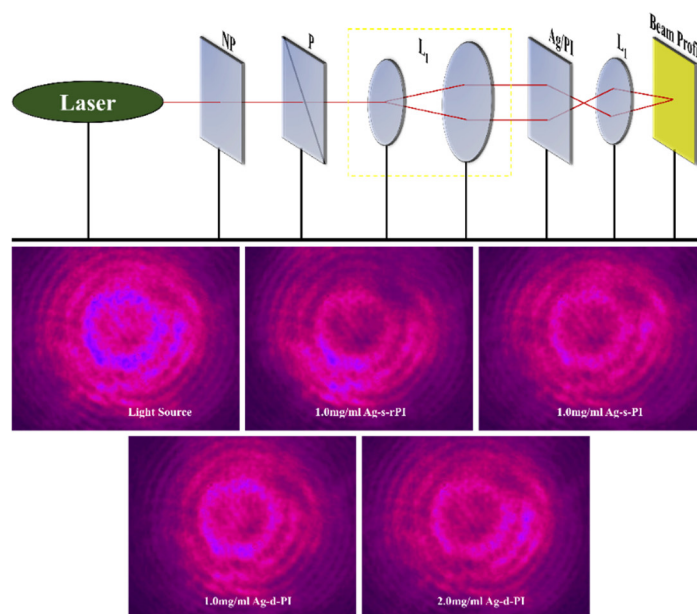


**Figure 3.** The schematic diagram of 3-D profiler and the captured images of laser-crossed Ag/PI alignment layers.

The alignment of LC between Ag/PI composite alignment layers was confirmed by using POM as shown in Figure 4. Obvious light leakages are observed from the cell assembled with Ag-s-rPI alignment layers, and due to the Ag nano-particles aggregation effect, the light leakages become more serious while increasing the amount of spurted Ag nano-particles. The alignment of LC sandwiched between Ag-s-PI alignment layers is more uniform compared with the mentioned Ag-s-rPI alignment

layers, which indicates that the aggregated Ag nano-particles have been removed during the rubbing process. Even the concentrated Ag nano-particles, as high as 2.0 mg/mL, are doped into PI solutions; LC are homogeneously aligned between Ag-d-PI alignment layers and no obvious light leakages are observed.
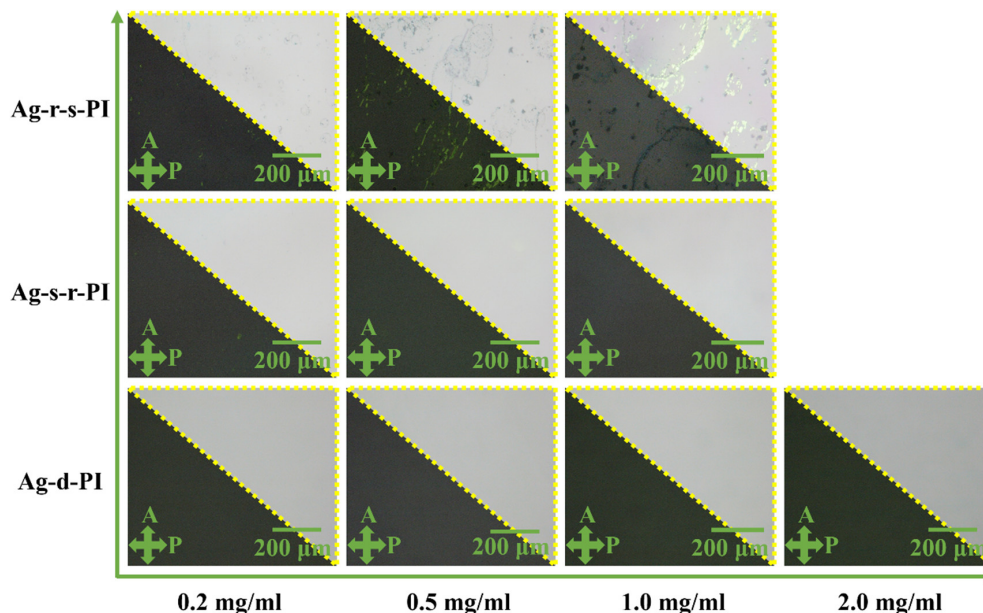


**Figure 4.** POM images of LC sandwiched between Ag-s-rPI thin layers, Ag-s-PI thin layers and Ag-d-PI thin layers, respectively.

The polar anchoring energy of LC sandwiched between Ag/PI composite alignment layers varies a lot as shown in Figure 5. LC sandwiched between Ag-s-PI alignment layers and Ag-s-rPI alignment layers have similar polar anchoring energies, however, the polar anchoring energy of LC sandwiched between Ag-d-PI composite alignment layers decreases a lot in comparison. The surfaces of Ag nano-particles-spurted PI alignment layers are almost covered with Ag nano-particles, and the surfaces of Ag-d-PI alignment layers are almost PI molecules conversely. Thus, the difference between polar anchoring energies is due to the surface composition alterations by spurting or doping Ag nano-particles, which tunes the interactions between LC and Ag/PI composite thin layers.
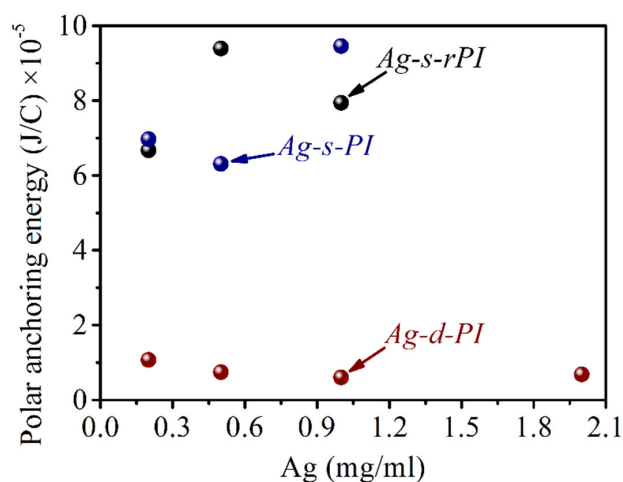


**Figure 5.** The polar anchoring energy of LC sandwiched between Ag-s-rPI alignment layers, Ag-s-PI alignment layers and Ag-d-PI thin layers, respectively.

When the external voltage is applied on the cell, the mobile ions in LC are driven to shift towards alignment layers and trapped in the localized defect regions, and in this case, $V_{rdc}$ is generated. The fractional coverage of the alignment layer surface, which indicates alignment layers ability to trap mobile ions, is determined as $\varphi_s$, and

$$\varphi_s = \frac{\delta}{\delta_s},$$

here, $\delta$ and $\delta_s$ are the surface density of the adsorption sites occupied by ions and the surface density of all adsorption sites on the alignment layer surface, respectively. After the displacement polarizing of Ag nano-particles, the Ag nano-particles in PI layers trap and neutralize the mobile ions, and thus the $\varphi_s$ of Ag/PI composite alignment layers get much lower compared with that of the conventional PI alignment layers.

During the rubbing process or driven by external electric filed, partial Ag nano-particles spurted on PI alignment layers are detached and dive into LC. A small amount of detached Ag nano-particles in LC trap and neutralize the charged mobile ions and decrease $V_{rdc}$. However, if the amount of detached Ag nano-particles is large, the Ag nano-particles shift towards the alignment layers and contribute to the generation of $V_{rdc}$. By doping and immobilizing Ag nano-particles in PI alignment layers, the $V_{rdc}$ generated by detached Ag nano-particles is prevented. As shown in Table 1 and Figure 6, the $V_{rdc}$ of the cell assembled with Ag-d-PI alignment layers is as low as 0.1132 V when the concentration of doped Ag nano-particles in PI alignment layers is increased to 2.0 mg/mL.

**Table 1.** $V_{rdc}$ of cells assembled with Ag/PI composite alignment layers.

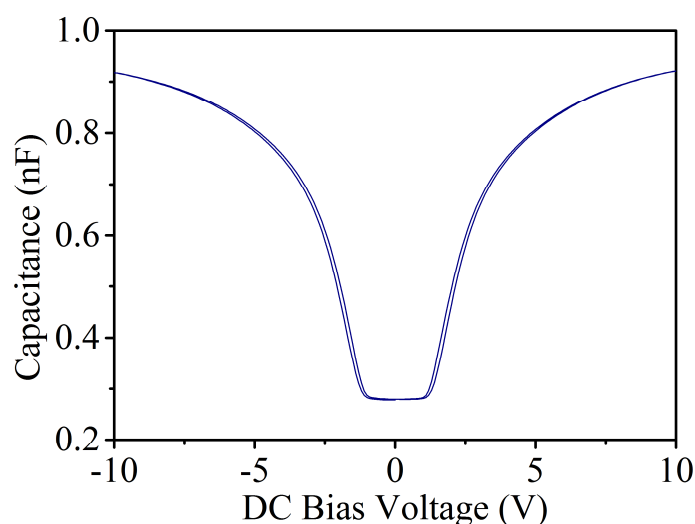|  | Ag-s-PI | | | Ag-s-rPI | | | Ag-d-PI | | |
|---|---|---|---|---|---|---|---|---|---|
|  | $V_{rdc}^{+}$ | $V_{rdc}^{-}$ | $V_{rdc}$ | $V_{rdc}^{+}$ | $V_{rdc}^{-}$ | $V_{rdc}$ | $V_{rdc}^{+}$ | $V_{rdc}^{-}$ | $V_{rdc}$ |
| 0.2 | 0.6735 | 0.5899 | 0.6317 | 0.7455 | 0.8417 | 0.7936 | 0.4915 | 0.5107 | 0.5011 |
| 0.5 | 0.6371 | 0.6685 | 0.6528 | 0.8900 | 0.8608 | 0.8754 | 0.3234 | 0.3518 | 0.3376 |
| 1.0 | - | - | - | - | - | - | 0.2121 | 0.2049 | 0.2085 |
| 2.0 | - | - | - | - | - | - | 0.1091 | 0.1173 | 0.1132 |



**Figure 6.** Voltage-dependence capacitance hysteresis characteristic of the cell fabricated from 2.0 mg/mL Ag-d-PI thin layers.

Trapping and neutralizing the charged mobile ions in LC by the displacement polarization in Ag nano-particles may cause the undesired screening effect and the decrease of VHR, and the capacitance of the cells assembled with Ag-d-PI alignment layers is characterized and shown in Figure 7. The capacitance of the cells assembled with Ag-d-PI alignment layers is found slightly decreased with

the increase of the amount of doped Ag nano-particles; however, the maximum capacitance of each cell is almost maintained at about 2.4. By increasing the frequency of external voltage on the cells up to 10 khz, a slightly red shift of the capacitance is observed; however, no significant capacitance change in value is observed. The threshold voltage of the cells maintains at about 1.4 V regardless of the increase of the amount of doped Ag nano-particles or the frequency of external voltage, and the maintained capacitance and threshold voltage of cells is attributed to the fact that barely any electrical conductivity change is generated by the different amounts of Ag nano-particles doping.
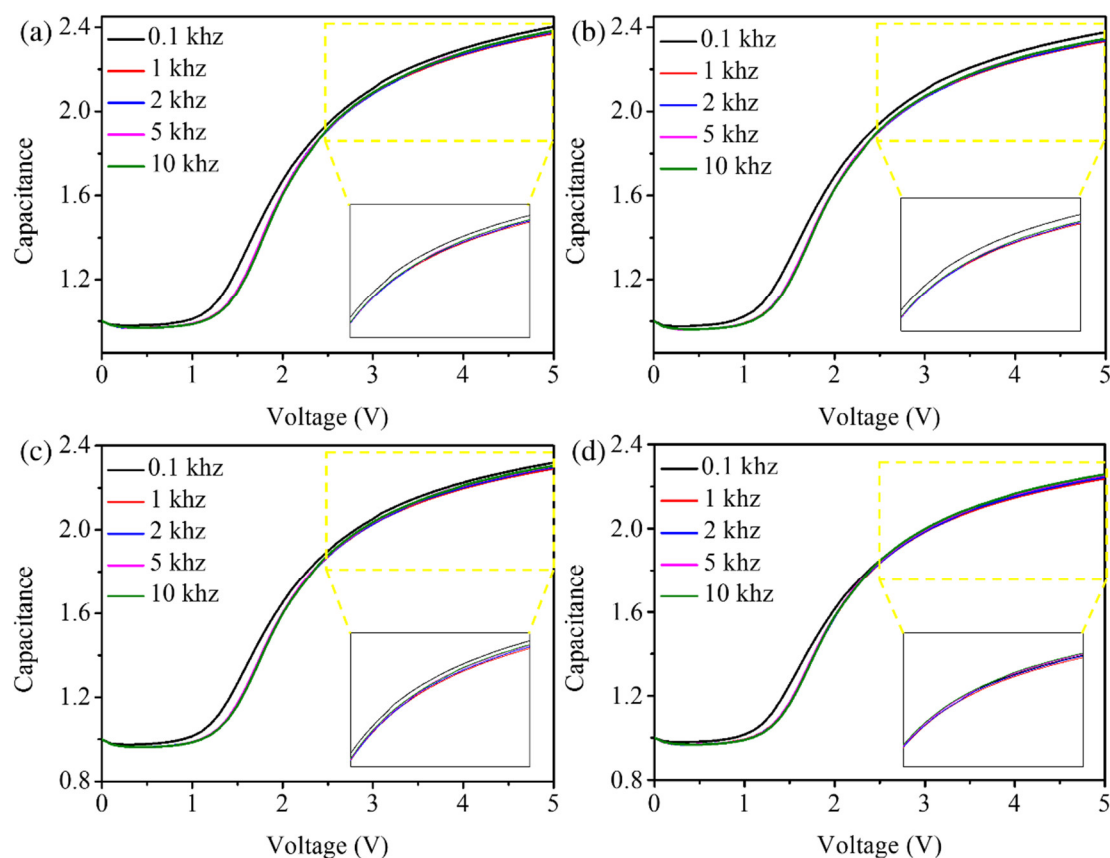


**Figure 7.** The capacitance-voltage curve of LC sandwiched between (**a**) 0.2 mg/mL, (**b**) 0.5 mg/mL, (**c**) 1.0 mg/mL, and (**d**) 2.0 mg/mL Ag-d-PI composite thin layers.

## 4. Conclusions

In conclusion, LC is homogenously aligned between Ag-d-PI alignment layers, and the mobile ions in LC are trapped and neutralized by Ag nano-particles due to their displacement polarization when the external voltage is on, which decreases the $V_{rdc}$ on cells effectively. Compared with the cells assembled with conductive alignment layer cells, the VHR of the cells assembled with Ag-d-PI composite alignment layers is maintained. The extremely simple design adopted to deduce the $V_{rdc}$ on the cells in this manuscript is worth more attentions.

**Author Contributions:** Y.L. and J.S. (Jiatong Sun) conceived the original idea and wrote the manuscript; Y.L., J.S. (Jiatong Sun), J.S. (Jingxin Sang), J.H.L. and H.-C.J. performed the experiments, H.L., H.X., S.Z. and D.-S.S. analyzed the data. Y.L. supervised and directed the research.

**Conflicts of Interest:** The authors declare no conflict of interest.

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