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Homeotropic orientation behavior of nematic liquid crystals induced by copper ions

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ABSTRACT

A homeotropic ordering film of nematic liquid crystal (LC) induced by copper ions (Cu^{2+}) had been developed. The $Cu(ClO_4)_2$ was directly spin-coated on the glass substrate without any other chemical modification. A homeotropic orientation of LC thin-film was generated by the interfacial chemical interaction between nitrile-containing LC and copper ions on the surface. Results showed that an appropriate density of Cu^{2+} could shorten the response time of orientation, but a shelf-time was prolonged. The LC film fabrication not only offered a simple process, but also presented a great repeatability to detect organophosphonates (DMMP). This study provided guidance for the design of LC films responding to organic molecules as a biosensor.

1. Introduction

Nematic liquid crystal (LC) possesses a series of excellent properties such as fluidity, which is similar to the isotropic liquid, and unique orientational ordering of optical anisotropy (birefringence). The orientation of LC provided on the surfaces of solid substrates can be greatly changed when a slight change of topography or chemical composition occurs on these surfaces of solid substrates. Furthermore, this orientation transition can be rapidly propagated to 100 μm away in LC bulks within tens of milliseconds. With the development of LC study [1], the special material began to be used in chemical and biological areas—biosensors. The key issue to design a biosensor [2–4] was to obtain an uniform and stable orientation film. In the LC biosensor production, the orientation of LC [5] molecular determines the sensitivity and the stability index of the sensor. Therefore, in the application of LC biosensor, researchers [6,7] use physical and chemical method of surface treatment to obtain a vertical or horizontal orientation on the substrate. Recently, Abbott [8] had presented a chemical sensor regarding the orientational transition of LC. The sensing response to the present sensor transduced chemical binding events occurring on the surface into an amplified orientation transition of LC. This sensing method is extremely suitable to field monitoring because it can provide rapid, label-free and highly sensitive detection results. Furthermore, the results can be observed directly through naked eyes without any expensive and sophisticated instruments. In the past decades, LC-based chemical sensors have been exploited to detect a variety of toxic organic matters including glutaraldehyde [9], organicamine [10], thiol [11], and organophosphonate [12–16].

In the LC-based chemical sensors for organophosphonate detection, the LC thin-film modified by chemical molecules (called as orientation molecules) presented an original homeotropic orientation through intermolecular forces between chemical molecules and LC molecules [17]. In the presence of target analyte on the surfaces of glass slides, the binding events between the orientation molecules and the analyte can disturb the original homeotropic orientation, and result in the orientation transition of the LC thin-film. This difference can easily be observed by the cross-polarlized lens. Therefore, in order to obtain a uniform homeotropic orientation, the chemical modification of the surface of the glass slides is the crucial process. Recently, several strategies of surface treatments to orient LC perpendicularly had been proposed [18]. Although the resultant sensors adopting these surface treatments possess numerous advantages including selectivity, sensitivity and repeatability, there are still some shortcomings and limitations on preparing sensors. Yang [19] reported that DMOAP could successfully induced LC molecular to a uniform orientation, however, it was a complicated and difficult process. The Abbott group [20] proposed that copper ions (Cu^{2+}) coordinated with LC on the modified glass of self-assembled monolayers. The results indicated that the film had more advantages in orientation effect and stability, while

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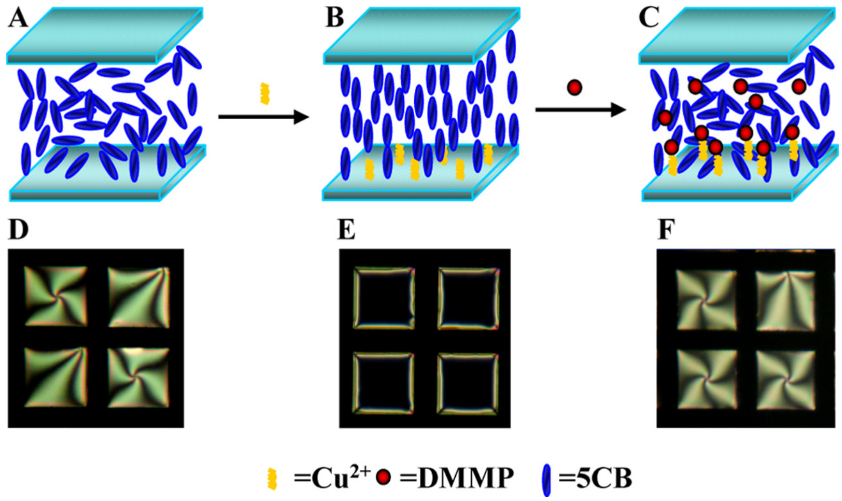

Fig. 1. Schematic illustration of copper-induced LC thin-film for DMMP detection: (A) random arrangement of 5CB supported on clean glass slides, (B) homeotropic orientation of 5CB supported on glass slides coated with Cu^{2+}, (C) DMMP disrupted orientation of 5CB, (D–F) photograph under polarized light microscope.

the drawback was the cost. Therefore, a simple method of generating LC molecules homeotropic alignment with great stability has become the direction of our research.

The study represents a simple and useful design of the homeotropic alignment film regarding $Cu(ClO_4)_2$ directly spin-coated on the glass substrate without any chemical modification, which enables surface-induced orientations of 5CB. The proposed film is applied successfully on DMMP detection. As shown in Fig. 1B, when the 5CB thin-film deposited on the glass substrate with Cu^{2+} spin-coating, LCs adopted a homeotropic orientation as a consequence of weak coordination interactions between Cu^{2+} and nitrile group (—CN) in 5CB molecule, and the resultant optical appearance appeared black under the crossed polarizer (Fig. 1E). Upon exposure to dimethyl methyl phosphonate (DMMP) vapor, the original homeotropic orientations of 5CB thin-film were disrupted because of the stronger binding ability between DMMP and Cu^{2+}, and the 5CB was displaced from the Cu^{2+}. This event occurring on the surface resulted in 5CB assuming planar or tilted orientation (Fig. 1C) and the resultant optical appearance appears bright (Fig. 1F).

2. Materials and methods

2.1. Reagents and materials

The copper perchlorate hexahydrate ($Cu(ClO_4)_2{\cdot}6H_2O$) and DMMP were purchased from Sigma-Aldrich (St. Louis, USA). LC 4-cyano-4′-pentylbiphenyl (5CB) was obtained from Huajing Scientific and Technological Development Co., Ltd. (Hebei, China). Copper grid was obtained from Zhongjingkeyi Technology Co., Ltd (Beijing, China). Glass slides were provided by Xinhua Laboratory Glassware Company (Haimen, China). All the reagents were used as received without further purification.

2.2. Preparation process of film

2.2.1. Cleaning of glass substrates

The glass slides were first cut into size of 2 cm × 2 cm square, and then immersed in freshly prepared piranha solution (70% H_2SO_4, 30% H_2O_2) at 80 °C for about 2 h. The slides were rinsed sequentially in copious amount of deionized water, ethanol, and acetone. Finally, the slides were dried under a stream of Nitrogen (N_2), and then, heated at 110 °C at least 3 h.

2.2.2. Deposition of Cu^{2+}

$Cu(ClO_4)_2{\cdot}6H_2O$ was first dissolved in ethanol and prepared to different concentrations. Two coating methods were described as follows.

Dip coating, clean glass slides were immersed in copper solution for hours, these slides were then heated in a drying oven at 110 °C for 90 min and stored at room temperature.

Spin coating, the copper solution was deposited on clean glass slides using a spin coater (Chemat Limited Company, model CE 100). Copper solution was dispensed from a pipette on the substrate with 20 s at 200 rpm. After that, turning spin rate to 800 rpm for another 45 s' coating. The prepared slides were finally heated in a drying oven at 110 °C for 90 min and stored at room temperature.

2.2.3. Fabrication of LC cells

A clean copper grid (20 μm) was placed on the prepared substrate, the grid was filled with LC using a microcapillary tube as described in other reports [21]. After that, a clean glass was carefully covered on it to form an LC layer of 20 μm in thickness.

2.3. Data acquisition

2.3.1. Measurements of the surface density of Cu^{2+}

To measure the surface density of Cu^{2+}, first, we dissolved the copper perchlorate salt on the surfaces into 2% nitric acid, and then the mixture was vortexed to extract salt. The concentration of Cu^{2+} was measured using ICP-ES. The surface density of copper ions was calculated with ICP-ES data.

2.3.2. Imaging of the optical appearance of LC

Optical appearance of LC was examined using a XP-201POL microscope (Shanghai Changfang Optical instrument Co., Ltd.) equipped with a Power Shot A640 Canon digital camera. The whole process was performed using a crossed polarizer in transmission mode. The average grey value of images was evaluated using MATLAB.

3. Results and discussion

3.1. Effects of copper ions on LC orientation

Past research [15] demonstrated that copper ions induced vertical orientation of 5CB with SAM molecules modified through Cu^{2+}–carboxy interaction. We then considered how this

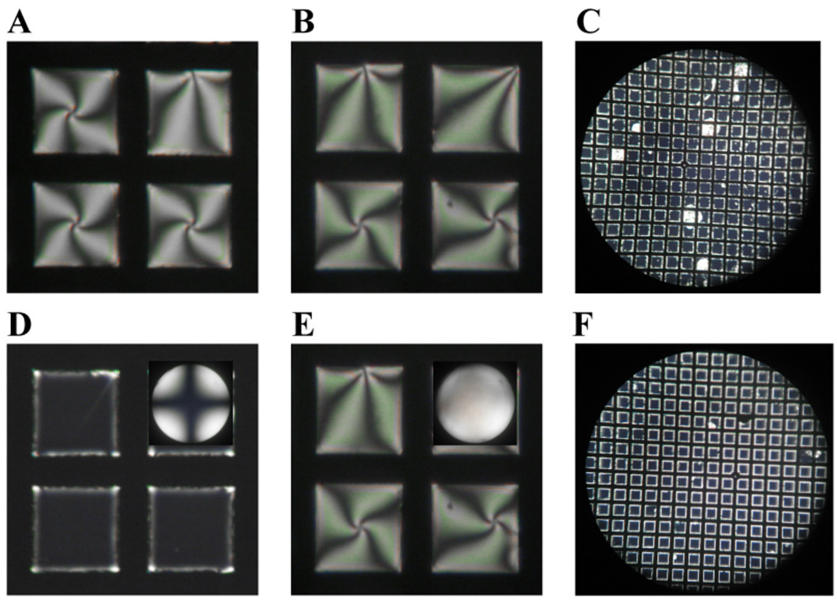

Fig. 2. Optical appearances of LC cells under crossed polarizers with freshly prepared (A)10 mmol/L $Cu(ClO_4)_2$ and (D) after16 min, (B) control group and (E) after 24 h, copper ions were (C) dip coating and (F) spin coating after 16 min.

mechanism might be applied without SAM modification. To test this idea, we established two groups, one group with 10 mmol/L $Cu(ClO_4)_2$, while the other group without, both of them were made into LC cells and observed through polarizing microscope. As described in the picture (Fig. 2), under orthoscopic light mode, there were significant Schlieren texture in the two polarized images (Fig. 2A and B), which suggested that 5CB assume non-homeotropic orientation. In contrast, after 16 min, a uniform dark region appeared, the brightness of the birefringent domains spots decreased in short periods, the process continued for 16 min to a uniform dark ground in Fig. 2D and a black cross existed under conoscopic light mode (the upper right in Fig. 2D), which indicated that the LC molecular was presented in a homeotropic orientation. As to the control group, the phenomena did not happen after 24 h in room temperature (Fig. 2E). The brightness of birefringent changed little, what's more, the cross did not appear in conoscopic mode (the upper right in Fig. 2E), which reflected that the LCs were presented in a random arrangement. Since the copper ions coordinated with LC molecule on the surface of substrate, the reaction between Cu^{2+} and —CN listed the LCs order [14,20]. The ClO_4^{2-} was used because copper was a weakly coordinating ion, and perchlorate counterion allowed the LCs and organophosphonates to coordinate with copper ions. Previous experimental study [22] has revealed that the intermolecular interactions of LC molecules induced its orientation within 100 μm thick and remained stable. In this study, the thickness of copper grid was 20 μm, the LC molecular layers would be presented in vertical arrangement. The process was characterized by the optical images of LC cells changed from birefringent to dark with a cross appeared in conoscopic mode. These results strongly indicated that the process of SAM in fabrication of LC cells is not essential for homeotropic orientation of LCs thin-film.

Based on these results, a comparison of two normal coating techniques—dip coating (Fig. 2C) and spin coating (Fig. 2F), had been conducted. The thicknesses and density of the copper layers were measured by spectroscopic ellipsometer and elemental analysis. Results showed that in the same concentration, spin coating had a better uniformity than dip coating method. Although there was not a great deal of difference between the two methods, some irregularly domains could be observed in part of the image (Fig. 2C), which would affect the result. Results showed that a better uniformity of a homeotropic orientation LCs supported on the spin coating surfaces than the other, which may owe to the coverage uniformity of Cu^{2+}. Thus, we chose spin coating method to avoid interference.

3.2. Measurements of the saturated solubility of copper ions in LC

Previous study [21] has reported that the surface-induced ordering of nitrile-containing LC molecules at interfaces presenting metal salts could coordinate with the nitrile group of the LC molecules. Metal salts dissolved in 5CB were greatly affected the orientation of 5CB as to the formation of electric double layer between LC bulk and the surface. To determine the solubility of copper ions in the LC, the $Cu(ClO_4)_2$ were added to 200 μL of 5CB in a eppendorf tube and store for days. The solubility of samples was measured by atomic absorption spectrometer, which was shown in Table 1. Result showed that the solubility of Cu^{2+} increased as the aging time, while this phenomenon stopped after 16 days at a concentration of 0.68 mmol/L. This was lower than another transition metal ion, aluminum, which saturated solubility was 1.7 mmol/L. From the point of view of results, the copper ions dissolved were very slowly, it would take about half month to finish this process. Therefore, the amount of Cu^{2+} might be one of the factors to influence the storage and sensitivity of the film.

Table 1
The solubility of $Cu(ClO_4)_2$ in 5CB measured by Hitachi 180-80 type of atomic absorption spectrometer.

Store days	Cu^{2+} concentration in dilutions (mg/L)	Cu^{2+} concentration in LC (mg/L)/(mmol/L)
2	0.102	10.2/0.16
4	0.128	12.8/0.20
10	0.180	18.0/0.28
12	0.201	20.1/0.32
13	0.227	22.7/0.36
15	0.405	40.5/0.64
16	0.429	42.9/0.68
17	0.433	43.3/0.68
18	0.434	43.4/0.68

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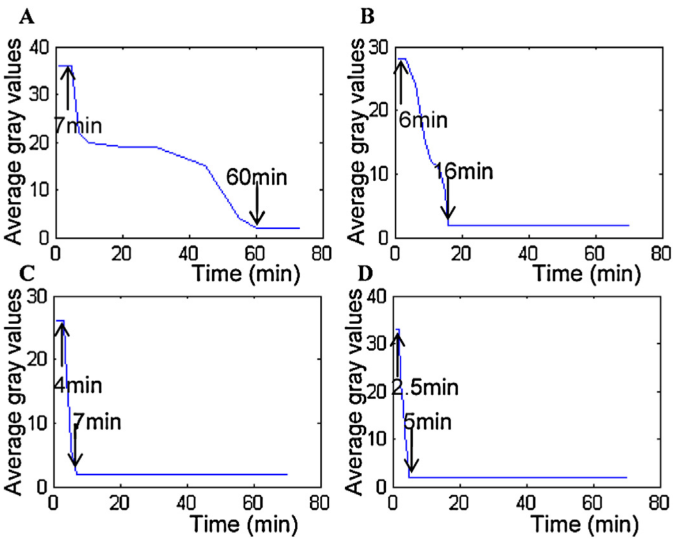

Fig. 3. The average gray values of birefringent domains changed with time on the surfaces with different surface density of Cu^{2+} (A) 0.16 ng/mm^2, (B) 0.71 ng/mm^2, (C) 1.12 ng/mm^2, (D) 2.58 ng/mm^2.

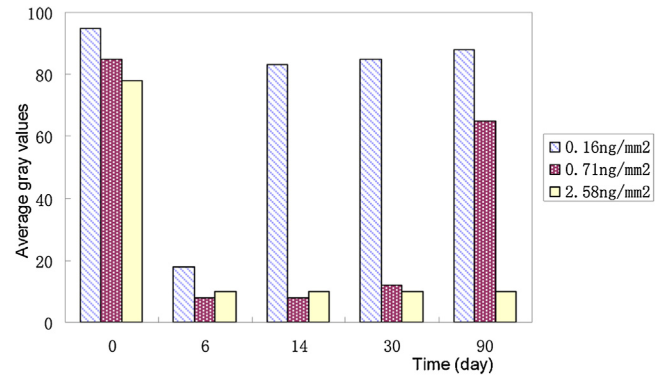

Fig. 4. Shelf-time under different density of Cu^{2+} (0.16 ng/mm^2, 0.71 ng/mm^2, 2.58 ng/mm^2), from freshly prepared (0 day) to three month (90 days).

3.3. Optical responses and stability of LC to copper ions

Copper ions samples were prepared with different concentrations of $Cu(ClO_4)_2$, and the response time of LC orientation with different concentrations of Cu^{2+} was observed through crossed polarizer microscope. The copper ions could induce arrangement of LCs was confirmed by the results. Moreover, higher concentrations of copper ions had more effect on the inducing ability of LC alignment, the perfectly ordered LC was formed in a few seconds. This was obviously due to the copper ions on the surface of substrates, the reaction between Cu^{2+} and —CN listed the LCs order. The formation of Cu–CN complex became faster as the copper concentration increased, that produced more intermolecular interactions, and shorter response time. Images captured were analyzed by MATLAB, the average gray values represented the brightness of birefringent domains (Fig. 3). Result showed that the average gray values deceased with time went by (7, 6, 4, 2.5 min) with Cu^{2+} concentrations of 0.16, 0.71, 1.12 and 2.58 ng/mm^2, after longer time (60, 16, 7, 5 min), a complete black ground was observed. High Cu^{2+} concentration on the surface were sufficient for the bond of Cu^{2+}–CN, moreover, a higher Cu^{2+} concentration was more likely dissolved in 5CB bulks faster, which accelerated the formation of electric double layer to assume a homeotropic orientation.

The shelf-time of the sensors (LC cell) is essential for commercial applications. To test the stability of the homeotropic ordering LCs on copper ions decorated surface, we observed these groups of LC cells for 90 days. Result showed that almost all the groups presented few dissolved spots as time went by, after a month's storage, this phenomenon developed into a bright domain. The images were analyzed by MATLAB, changes of different concentrations were illustrated in a histogram. As shown in Fig. 4, lower surface density 0.16 ng/mm^2 could stay in homeotropic orientation for 6 days, while the highest surface density 2.58 ng/mm^2 maintain a dark ground until the ninetieth day. A middle concentration of 0.71 ng/mm^2 kept a homeotropic orientation for a month but disappear with longer time. These results might associate with the dissolution of copper ions in LC. Lower density of Cu^{2+}, shorter shelf-time. The concentration of 0.16 ng/mm^2 was fully dissolved in 20 μm thick film of 5CB which result in the disappearance of homeotropic orientation after a period of time. However, with a higher density of 0.71 ng/mm^2 or 2.58 ng/mm^2, which showed a surplus of metal ions could maintain a longer time. This result

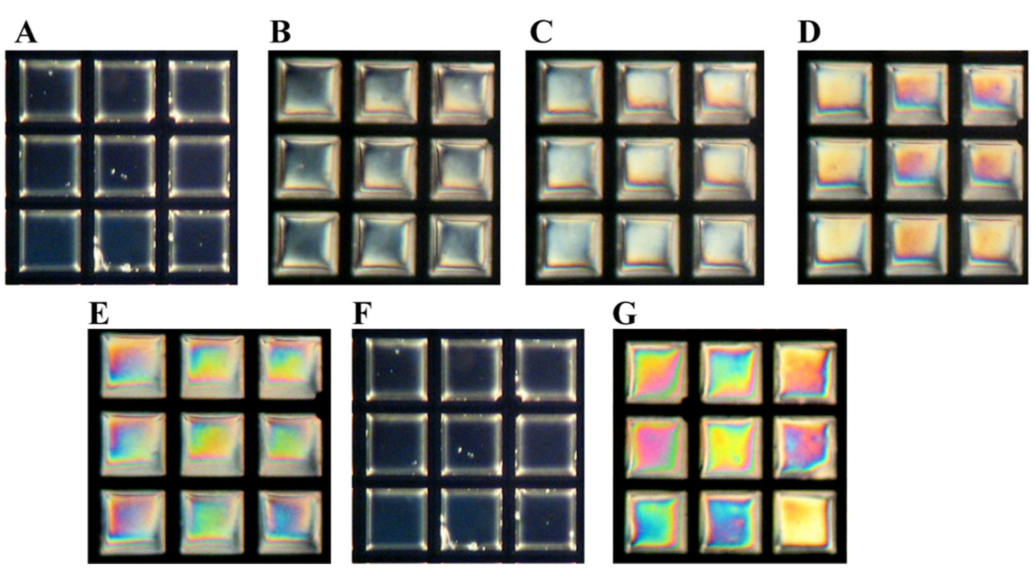

Fig. 5. Optical appearances of LCs-based chemical sensor to detect DMMP (A) before exposure to DMMP, upon exposure to 10 ppb DMMP with different time: (B) 25 s, (C) 30 s, (D) 50 s (E) 90 s, and fresh air was then inputted for (F) 120 s, and exposed to DMMP again (G) after 90 s.

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also established that without self-assemblement, copper ions could induce the homeotropic ordering of LC molecular, the stability exhibited in a certain concentration provided a basic condition in the following experiment.

3.4. Application

In this study, we used the proposed film to offer the basis of sensitive sensors for low molecular weight organic molecules, such as DMMP [23,24]. Previous study [25,26] revealed that the phosphoryl groups of DMMP binded Cu^{2+} with sufficient affinity that they could competitively displaced the —CN of LCs from coordinating with Cu^{2+}. This process reflected as an ordering transition in LCs that spread from the copper-coated surface across the LC film, with the brightness of LC images increased. Herein, it must be pointed out that this change started at 1 min after LCs exposed to a vapor of DMMP, the bright domain grew with time went by. The sensor could response DMMP with the concentration of 10 ppb, and the response time was about 30 s. The fresh air was then inputted when DMMP capacity attains saturation in 90 s. Images under polarized microscope were gradually restored to a uniform dark that LC reseted itself into original state. Lastly, DMMP was imported again, and same phenomenon observed as the first time that the dark ground turned bright gradually, which indicated that the response was reversible (Fig. 5). These results established the potential utility of copper-induced LC film as the basis of biosensors to detect DMMP.

4. Conclusion

The study reported in this paper developed a film decorated with copper ions that could induce the arrangement of 5CB. The capacity of LC could dissolve copper ions in certain level, which affected homeotropic orientation of 5CB. We used this film to fabricate a biosensor to detect DMMP, and results showed that this film worked well with good replicability. The manufacturing process of proposed film was much simple, less cost, which applied in organophosphonates assay. The results discussed here also provide a valuable insight into the fabrication of chemical sensors for commercial application.

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