[Article]

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ZIF-8 对向列相液晶电-光性能的提升

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摘要: ZIF-8 (沸石咪唑酯骨架结构材料)是一种金属有机物骨架结构材料, 因其极高的比表面积、出色的热稳定性而被广泛应用于各种性质研究中。ZIF-8通过传统的水热法在甲醇溶液中合成, 其颗粒尺寸约为250 nm, 形貌为菱形十二面体。研究发现, 合成的ZIF-8材料具有良好的热稳定性及相当大的比表面积。将其掺杂进液晶中会增强液晶的电-光性能, 增强效果与掺杂浓度有关。在向列相液晶4-氰基-4'-戊基联苯(5CB)中, ZIF-8可以吸附杂质离子, 抑制屏蔽效应, 最终使液晶驱动电压降低, 响应加快。在掺杂浓度为0.05% (w, 质量分数)时, 液晶体系的电-光性能改善最明显, 阈值电压(V_{th})最小达到0.92 V, 饱和电压(V_{sat})达到1.31 V, 响应时间仅为10.04 ms。而当掺杂浓度大于0.05% (w)时, ZIF-8在液晶盒中发生团聚, 影响液晶分子的有序排布, 同时吸附杂质离子减少, 不利于液晶电-光性能的改善。

关键词: ZIF-8; 向列相液晶; 电-光性能; 阈值电压; 响应时间; 屏蔽效应
中图分类号: O643

Improvement of the Electro-Optical Properties of Nematic Liquid Crystals by Doping with ZIF-8 Materials

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Abstract: ZIF-8 (zeolitic imidazolate framework-8), a kind of metal-organic framework material, is one of the most important energy materials and widely used in various fields because of its high specific surface area and excellent thermal stability. In this research, we synthesized ZIF-8 by the traditional hydrothermal synthesis method in a purely methanol system. The obtained particles were ~250 nm in diameter with a rhombic dodecahedron morphology. Moreover, the prepared ZIF-8 materials exhibited good thermal stability and a large surface area. We also found that the rhombic dodecahedral ZIF-8 enhanced the electro-optical (E-O) properties of nematic liquid crystal (N-LC) depending on the ZIF-8 doping concentrations. ZIF-8 in N-LC cells adsorbs ionic impurities and suppresses the screen effect, leading to a lower driving voltage and faster response time. At a ZIF-8 doping concentration of 0.05% (w, mass fraction), the N-LC cells showed the best E-O properties, including the lowest threshold voltage (V_{th}) of 0.92 V, the lowest saturation voltage (V_{sat}) of 1.31 V, and a short response time of 10.04 ms. However, above a doping concentration of 0.05% (w) ZIF-8 aggregated in N-LC cells, affecting the arrangement of the LC molecules and trapping less impurity ions, which deteriorated the E-O properties of N-LC.

Key Words: ZIF-8; Nematic liquid crystal; Electro-optical property; Threshold voltage; Response time; Screen effect

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1 Introduction

Liquid crystal (LC) is a fascinating stage of matter and has an exceptionally big impact on electronic displays. However, the ever-growing market of liquid crystal display (LCD) requires high quality liquid crystal materials. Recent years, researchers found that nanoparticles (NPs) were one kind of the best and the most efficient additives in liquid crystals because of their excellent properties, such as the small size effect and large surface area^{1–4}. Metal NPs^{5–11}, metal oxide NPs^{12–14}, carbon nanotube (CNT)^{15,16}, and ferroelectric NPs¹⁷ have been dispersed into LC to improve the electro-optical (E-O) characteristics, such as lowering V_{th} ^{5,9,12,17–19}, increasing contrast ratio¹³, expedited response^{6,13,14,19}, modulating frequency response^{7,8}, strengthen memory effect^{15,16}, and other properties^{10,11,20,21}.

ZIF-8, a subfamily of metal-organic frameworks (MOFs), has high stability^{22–25} and large specific surface area²⁶. Since Yaghi *et al.*²⁷ synthesized the ZIFs in 2006, ZIFs has become a promising material and been widely used in gas adsorption and separation^{24,28}, energy storage²⁹ as well as catalysis fields^{30,31}. However, no study has demonstrated the effects of ZIF-8 on E-O properties of liquid crystal.

Here, we design and synthesize the rhombic dodecahedron ZIF-8 in an anhydrous methanol system. ZIF-8 is dispersed into nematic liquid crystal (N-LC) with different concentrations to explore the effect of ZIF-8 on the E-O properties of N-LC. The ZIF-8 doping concentrations are from 0% to 0.10% (w, mass fraction). The results show that the ZIF-8 enhances the E-O properties of N-LC depending on the doping concentration. The 0.05% (w) doping ZIF-8 has the most excellent E-O properties, such as the lowest V_{th} and V_{sat} , fastest response, and highest contrast (C_{on}) among all ZIF-8/N-LC composites. The optimum doping concentration, 0.05% (w), is contributed to trapper of impurity ions in the LC cells and suppression of the screen effect, leading to the improved E-O properties.

2 Experimental

2.1 Materials

All of the chemicals were analytical grade reagents and used without further purification.

Polyvinyl alcohol (PVA) and Hmim ($C_4H_6N_2$, 97%) were purchased from Alfa Aesar. Anhydrous methanol (99.7%), ethylene glycol (96%), and ethanol (99.7%) were purchased from Beijing Chemical Works. $ZnAc \cdot 2H_2O$ (99%) was purchased from Aladdin. 4-Cyano-4'-pentylbiphenyl (5CB, the clearing temperature, T_c , is 308.5 K; the melting temperature, T_m , is 297.0 K) was gotten from Shijiazhuang Chengzhi Yonghua Display Material Co. Ltd.

2.2 Synthesis of ZIF-8

First, $ZnAc \cdot 2H_2O$ and Hmim, respectively, were dissolved in anhydrous methanol at room temperature and the two solutions were heated to 35 °C. Then, the two clear solutions were combined with the molar ratios of 0.01 and stirred for 1 h in a 35 °C water bath. Subsequently, the samples were washed with methanol

several times. At last, the ZIF-8 with rhombic dodecahedron structure and 250 nm in mean particles size were obtained by centrifugation. A small part of the samples were re-dispersed in alcohol to prepare samples for scanning electron microscopy (SEM), and another part of products were dried at 65 °C overnight in a drying oven for other characterization studies.

2.3 Preparation of ZIF-8/5CB composites

ZIF-8 was dispersed into 5CB at mass fractions of 0%, 0.01%, 0.03%, 0.05%, 0.07%, and 0.10%, respectively to get the N-LC mixtures.

2.4 Liquid crystal sample cell fabrication

The twisted nematic (TN) LC cells were made using 2.0 cm × 3.0 cm glass substrates coated with the indium tin oxide (ITO). The glass plates were coated with PVA using a spin coater. These coated substrates were prebaked at 80 °C for 30 min in an oven. The baked, PVA-coated substrates were rubbed with velvet to get uniform grooves on PVA. Then, the TN cells were prepared with a cell gap of about 12 μm to measure the E-O characteristics. The N-LC mixtures were injected into the each cell by capillary action at room temperature, respectively.

2.5 Characterization

Sample morphologies were examined by SEM (HitachiS-4800 FE, Japan). To investigate the crystallinity of the samples, the powders were further analyzed with X-ray diffraction (XRD, Rigaku, Dmax2200 with $Cu-K_{\alpha}$ radiation ($\lambda = 0.1542$ nm), Japan). The surface areas and porous volume were examined by the Brunauer Emmett Teller nitrogen adsorption-desorption workstation (BET, NOVA 2200e, USA). The thermal gravimetric (TG) curve was obtained by the thermal gravimetric analyzer (NETZSCH STA449F3, German). The E-O measurements were carried out using the LCT-5066C LCD integrated parametric tester (North LCD Engineering Research and Development Center, China). The optical textures of composites were observed by a polarizing optical microscope (Olympus BX51, Japan).

3 Results and discussion

3.1 Characterization of ZIF-8

Fig.1 shows XRD patterns and SEM images of ZIF-8 samples. The XRD patterns in Fig.1a demonstrated that the products were pure-phase ZIF-8 material with perfect nanocrystals. Fig.1b shows that the synthesized ZIF-8 has a rhombic dodecahedron shape and the average diameter is ~250 nm.

The thermal stability of ZIF-8 was measured by TG. A gradual weight-loss step of 4% up to 65 °C was observed on TG curve in Fig.S1 (Supporting Information), corresponding to the removal of methanol molecules from the cavities. Then, a long plateau was shown in the temperature range of 65–350 °C, indicating high thermal stability of the sample. The second weight-loss step of 67% above 350 °C is due to the collapse of the ZIF-8 frameworks above 350 °C. This result indicates that ZIF-8 is rather stable below 350 °C.

The surface areas and the porosity were examined by N_2 sorption analysis. Fig.S2a (Supporting Information) shows a type

Fig.1 XRD patterns (a) and SEM image (b) of ZIF-8 samples

I isotherm. It reveals that ZIF-8 behaves microporous structure. The microporous volume was about $0.60 \text{ cm}^3 \cdot \text{g}^{-1}$ and the Langmuir surface area was $1730 \text{ m}^2 \cdot \text{g}^{-1}$, respectively. As shown in the Fig.S2b (Supporting Information), the density functional theory (DFT) was used to calculate the Brunauer-Emmett-Teller (BET) cumulative surface area and porous volume of ZIF-8. The aperture was about 1.6–2.1 nm on samples. Above result demonstrates that ZIF-8 has an excellent adsorptive ability.

3.2 Characterization of the prepared ZIF-8/5CB composites

The textures of the N-LC cells dispersed with various concentrations of ZIF-8 were investigated as shown in Fig.2. Fig.2(a–d) shows the textures of N-LC cells with the concentration of ZIF-8 of 0 to 0.05% (w), exhibiting uniformly homogeneous alignment. However, when the ZIF-8 doping concentrations were up to 0.07% (w), even 0.10% (w), aggregations were observed as shown in Fig.2(e, f). This result indicates that 0.05% (w) doping is the optimum concentration and ZIF-8 is not well dispersed

within the N-LC above 0.05% (w).

The characteristics of transmittance–voltage ($T-V$) are shown in Fig.3a under applied voltages from 0 to 5.0 V at room temperature. Before the electric field was applied, the original transmittance was to the maximum value. When the applied voltage increased, the light transmittance decreased. The V_{th} and V_{sat} were defined as the applied voltage for the light transmittance of 90% and 10% in on-stage. C_{on} is the ratio of the maximum and minimum light transmittance. T_{on} is defined as the time of the light transmittance from 90% to 10% of TN LCD cells in on-stage. Oppositely, T_{off} is the time of the light transmittance from 10% to 90% in off-stage. In our E-O experiment, the values of V_{th} , V_{sat} , C_{on} , and response time of pure 5CB were 1.08 V, 1.63 V, 22.38, and 23.34 ms, respectively. Here, the response time was the sum of T_{on} and T_{off} . The $T-V$ curve demonstrates that V_{th} and V_{sat} decrease when doping ZIF-8. From 0.01 to 0.05% (w) ZIF-8 doping, the V_{th} and V_{sat} are decreased. However, the V_{th} and V_{sat} increase from 0.07 to 0.10% (w). Fig.3b shows the C_{on} characteristics of the TN cells.

Fig.2 Photomicroscope images of N-LC cell doped with different ZIF-8 doping concentrations (a) 0% (w), (b) 0.01% (w), (c) 0.03% (w), (d) 0.05% (w), (e) 0.07% (w), (f) 0.10% (w); A: analyzer, P: polarizer

Fig.3 E-O properties of 5CB/ZIF-8 composites

(a) The transmittance–voltage (T – V) curves for pure 5CB and compositions LC cells dependent on the concentration of ZIF-8 and the insets show the variation of V_{th} and V_{sat} of composites. (b) Variation of C_{on} with mass ratio of ZIF-8. The response time curves for the composites dependent on the mass ratio of ZIF-8. (c, d) T_{on} and (e, f) T_{off} . The mass fraction (w) varied from 0% to 0.10%.

The curve indicates that the C_{on} increases obviously after doping ZIF-8 in LC, and 0.05% (w) doping has the highest C_{on} value. Fig.3 (c, d) shows T_{on} of the TN cells with various doping concentrations of ZIF-8. Fig.3(e, f) shows T_{off} . We can see that 0.05% (w) doping is corresponding to the fastest response, T_{on} of 1.06 ms and T_{off} of 8.98 ms. These results revealed that E-O properties were related to the dispersion of ZIF-8 in N-LC, agreeing with the Fig.2. N-LC with 0.05% (w) ZIF-8 had the best dispersion and best E-O properties.

When doping concentration was below 0.05% (w), ZIF-8 was well dispersed in N-LC. When the voltage was applied to the LC cells, ZIF-8 trapped impurity ions because of the porous surface

structure in Fig.4(a, b). The screen effect was suppressed and the electric field around the ZIF-8 was strengthened, further decreasing the V_{th} and V_{sat} to 0.92 and 1.31 V, respectively. It is worth to mention here that impurity ions are inevitable in LC for following reasons. One hand, LCs itself, the alignment layers, the glue, the rubber process and the filling process may appear ionic impurities. On the other hand, the ZIF-8 may come with impurities such as Zn. However, when the concentration of ZIF-8 was over 0.05% (w), aggregation appeared consistent with the POM textures in Fig.2. ZIF-8 trapped less impurity ions in Fig.4c, leading to the increasing voltages. The weakened screen effect and aggregation also affect the C_{on} .

Fig.4 Schematic diagrams of the enhanced E-O properties of LC by doping ZIF-8

(a) On off-stage, impurity ions were located in the LC cells. (b) On on-stage, ZIF-8 trapped the impurity ions, weakening the screen effect. However, when the doping concentration was above 0.05% (w), ZIF-8 would aggregate and trap less impurity ions, decreasing the E-O properties in (c).

Decrease of response time of LC also results from the addition of ZIF-8. T_{on} is related to the switching rate of LC molecules¹¹. When the voltage was applied, the weakened screen effect and strengthened electric field made LC molecules easily and rapidly twist. This resulted in a faster T_{on} in the ZIF-8 concentration range of 0%–0.05% (w) on-stage. T_{off} is related to the interaction between impurity ions and ZIF-8. ZIF-8 could absorb the impurity ions from the alignment layer and LC molecule on-stage. Then, the interacting forces between LC and the alignment layer were increased, allowing the decreased T_{off} below 0.05% (w) concentration. However, the aggregation increased the resistance during the distortion above 0.05% (w) concentration, resulting in the increasing response times.

4 Conclusions

In this study, we prepared the rhombic dodecahedron ZIF-8 crystals with 250 nm in crystal size in methanol systems. ZIF-8 had large surface areas and enhanced the E-O properties of N-LC according to the various mass ratios. The N-LC/ZIF-8 composites had lower V_{th} and V_{sat} , higher C_{on} , and faster response time, especially at 0.05% (w). It may be contributed to the porous surface structure of ZIF-8, which could weaken the screen effect by adsorbing the impurity ions in the LC cells. And the weakened screen effect would make LC molecules quickly switch, resulting in lower driving voltage and faster response time. However, when doping concentrations were above 0.05% (w), ZIF-8 started aggregate because of the large surface area. The aggregation increased the resistance during the distortion, leading to a higher driving voltage and slower response than 0.05% (w) doping. The results showed that ZIF-8 doped into TN liquid crystal cells could improve the E-O characteristics of N-LC. We expect ZIF-8 could be used in future display fields.

Supporting Information: available free of charge *via* the internet at <http://www.whxb.pku.edu.cn>.

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ZIF-8 对向列相液晶电-光性能的提升

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Improvement of the Electro-Optical Properties of Nematic Liquid Crystals by Doping with ZIF-8 Materials

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Fig.S1 TG curve of ZIF-8

Fig.S2 (a) Nitrogen sorption isotherms of as-synthesized ZIF-8 at 77.3 K; (b) BET cumulative pore volume of ZIF-8