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Inorganic gel and liquid crystal based smart window using silica sol-gel process

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ABSTRACT

A controllable transparent device using an inorganic glass gel-dispersed liquid crystal (GDLC) was fabricated using the sol-gel method to overcome the limitations of conventional polymer-dispersed liquid crystals, such as haziness and yellowing. In this study, silica gel and titanium dioxide acted as a matrix holding the liquid crystal droplets, and the optical properties of the proposed GDLC were then studied in a silica solution by mixing tetra ethyl ortho-silicate, methyltriethoxysilane, isopropyl alcohol, and nitric acid in an aqueous solution. A titanium solution with titanium isopropoxide and acetylacetone was also mixed with the silica solution, with the further addition of a nematic liquid crystal. A parameter study was carried out by varying the concentration to obtain the best sample, with fast response times of ~0.5 and 3 ms, respectively for the on and off processes, high contrast, and low haziness when compared with previously reported results. The GDLC samples exhibited low scattering, a clear colorless state, and a low driving voltage, which are all very important advantages for applications. For demonstration, our glass-based smart window was also applied as a rear-view mirror in a vehicle for anti-dazzling purposes at night, which has not been reported by others.

1. Introduction

Smart windows have attracted a significant amount of attention in an effort to achieve energy-savings in eco-friendly buildings and transportation systems. Polymer-dispersed liquid crystal (PDLC) windows are the type of smart windows that has been commercialized the most to date [1–3]. PDLC is composed of droplets of liquid crystal and a polymer matrix, and in general, the size of an LC droplet is in the range from 1 to 20 µm. In the droplets, the nematic liquid crystal (LC) molecules at the interface with the polymer are oriented parallel to the surface, and due to the isotropic orientation, the PDLC scatters incident beam and becomes opaque, which is referred to as the 'off-state'. When a uniform electric field is applied to the PDLC, the LC molecules are aligned along the electric field line, and in this state, the PDLC becomes transparent, referred to as the 'on state'. The on/off ratio of the transmittance can be estimated from the matching and mismatching of the refractive indexes between the LC droplets and the polymer matrix. The polymer matrix holds LC droplets and provides an anchoring interaction, determining the LC orientation. Also, the size and surface area of the droplets influences the anchoring force of the LC. However, the PDLC has limitations in that it requires a high driving voltage and has a milky haziness in the off-state, which is a serious impediment to satisfy commercial demands. The haziness of PDLC is related with large scattering angle due to the large size of the LC droplets. Furthermore, the yellowing effect due to UV aging is an additional drawback of the PDLC.

Many attempts have been made to replace the polymer matrix with a glass matrix in order to overcome the limitations of conventional PDLC [4–6]. One possible alternative is to use glass gel as the matrix instead of the organic polymer [7–10], and the sol-gel method has also been used to synthesize a glass gel-based LC [11]. The LC can be dispersed in glass gel while silica alkoxide is dried in ambient air, which results in a xerogel [12]. Although a thin film of xerogel can form with no damage [13,14], bulk xerogel cracks or breaks during the gelation or drying process due to the capillary force of the remaining solvent. Nevertheless, the solvent can be substituted with a liquid crystal during the drying process to obtain a xerogel matrix with no cracks, and this process is used to fabricate the glass-gel disposed LC (GDLC). The LC droplet and gel matrix have different refractive indexes, so the incident beam is scattered and the GDLC becomes opaque with no electric field.

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When an electric field is applied to the GDLC, the LC is aligned along the electric field, and the LC droplet thus obtains the same refractive index as the glass. As a result, the GDLC becomes transparent in the on-state, and the glass is in fact clearer than polymer and is also thermally more stable. In other words, the GDLC exhibits high quality electro-optical behavior.

Two different refractive indexes, n_o and n_e, can be observed as a result of the birefringence of the LC. When the LC molecules are confined in a porous matrix, the molecules are randomly-oriented, anchored parallel to the surface of the pore, as shown in Fig. 1. The mean refractive index of the randomly-oriented LC molecules is given by $< n > = (n_e+2n_o)/3$ [1], and the index mismatch between the LC and the matrix (n_m) causes the parallel beam to refract at the interface, rendering it opaque (off-state). When an alternating electric field is applied, the LC molecules are oriented along the electric field direction. If the ordinary refractive index of the LC (n_o) is equal to that of the matrix (n_m) for the incident beam parallel to the electric field, it becomes transparent (on-state). In contrast, an index mismatch between the LC and the matrix causes the incident beam to refract at the interface, rendering the GDLC opaque in the off-state..

The sol-gel process was first studied in the mid-1800s during Ebelman and Graham's work on silica gel [15], and it has gained widespread use since then to synthesize fabrics, coating layers and nano-structures. The sol-gel is a method that synthesizes a certain material starting from sol to gel through gelation including hydrolysis, condensation, molding, and drying. In general, the gel solution contains a metal compound that synthesizes the metal oxide, water for hydrolysis, solvent to dissolve them uniformly, acid or base as a catalyst, and other additives. Timusk et al. studied the optical properties of a liquid crystal-xerogel composite film [7]. The liquid crystal droplets were encapsulated in a titanium-mixed silica xerogel matrix that was prepared via sol-gel and phase separation. In particular, titanium alkoxide, in addition to silicon alkoxide, was used as a precursor for synthesis. The resulting increase in the refractive index of the matrix produced high-performance films that exhibited a 75.9% change in transmittance in response to changes in the electric field. However, further measurements of the optical properties, like the response time and haziness, had to be studied in detail in addition to optimization for low-voltage driving.

In this experiment, tetra-ethyl-ortho-silicate (TEOS) and titanium isopropoxide were used as metal-alkoxides, M(OR)z with R as an alkyl group, and their concentration was optimized. Isopropyl alcohol (IPA) and nitric acid solutions in distilled ionized (DI) water were respectively used as solvent and catalyst. Methyltriethoxysilane (Me-TES) and acetylacetone were added to improve the optical properties of the material [4], and a black water-soluble dye was added to absorb visible light in the off-state. The optical properties were measured according to the density of the nitric acid aqueous solution and liquid crystal, and dry condition [16]. A metal-coated layer was inserted between the glasses to demonstrate its use in a smart mirror as a vehicle application.

2. Experimental details

The raw materials used in this study include TEOS, titanium isopropoxide, Me-TES, acetylacetone, and 70% HNO_3 (purchased from Sigma-Aldrich). A mixed nematic liquid crystal (4-pentylphenyl propylbenzoate (63 wt%) +4-*n*-Pentylbiphenyl (37 wt%)) with refractive indexes n_o=1.528 and n_e=1.732 (C7, Qingdao Intermodal Trading Ltd), a black water-soluble dye (WA dye, Water & Alcohol), IPA (Isopropyl alcohol), and DI (double-distilled) water were also used.

2.1. Preparation of sol

Solution A was prepared by mixing an alkoxide with TEOS and Me-TES, IPA, and solution A′ was then prepared by mixing solution A and HNO_3. Solution B contained titanium isopropoxide and acetylacetone. The sol was prepared by mixing solutions A and B. In solution A, the molar ratio was TEOS: Me-TES: IPA=0.55: 0.3: 0.4, and 15.7 M HNO_3 was mixed later. For solution B, titanium isopropoxide and acetylacetone were mixed with a molar ratio of 1:1 and were stirred for 15 min. After that, solutions A′ and B were mixed in the volume ratio of 3:1, and the mixture was stirred for 5 min

Finally, WA dye (final solution: WA dye=20: 1 in volume ratio) was added. Due to direct injection of a high concentration of HNO_3, a certain amount of silica gel was immediately precipitated, which was filtered out. The filtered liquid and LC were mixed at a volume ratio of 2:1 and were stirred for 30 min. All these processes were carried out at room temperature under ambient pressure, as shown in the diagram in Fig. 2. All substances used in the sol-gel process and their corresponding chemical formula and roles are summarized in Data in Brief Table S1..

2.2. Film deposition

The mixed sol was spin-coated onto an indium-tin oxide (ITO) coated glass at 1000 rpm for 15 s. The sheet resistance of the ITO was 150 Ω/sq, and the transmittance was 95%, excluding the effect of the

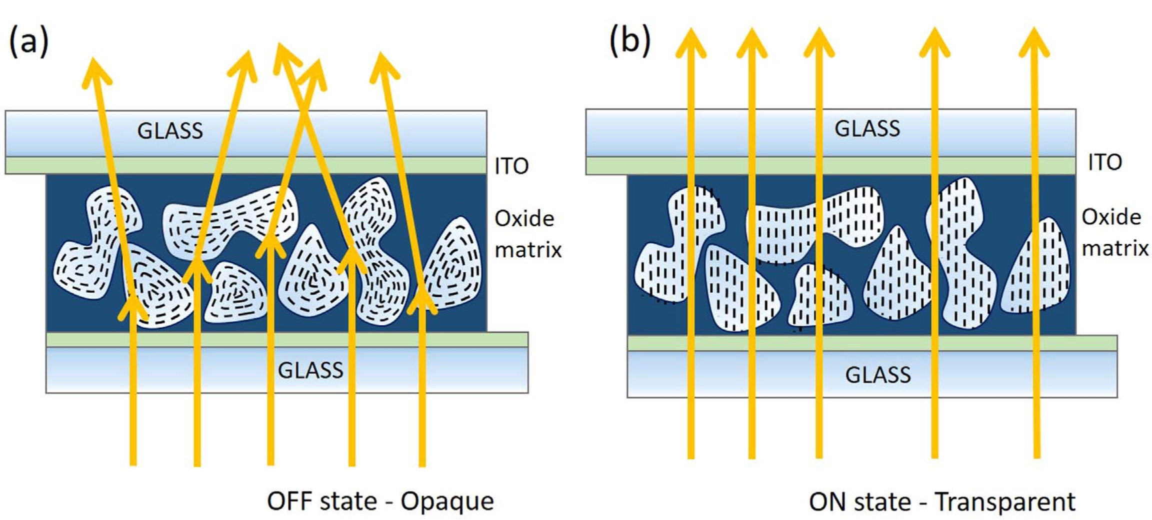

Fig. 1. Schematic diagram illustrating the basic principle of the GDLC. (a) LC molecules are randomly oriented, influenced by the geometry of the pores in matrix. (b) When an electric field is applied, the molecules are reoriented parallel to the field.