



Article High-Efficiency Responsive Smart Windows Fabricated by Carbon Nanotubes Modified by Liquid Crystalline Polymers

Yuan Deng, Shi-Qin Li, Qian Yang, Zhi-Wang Luo and He-Lou Xie *

Key Lab of Environment-friendly Chemistry and Application in Ministry of Education, and Key Laboratory of Advanced Functional Polymer Materials of Colleges, Universities of Hunan Province and College of Chemistry, Xiangtan University, Xiangtan 411105, Hunan, China; 201821531564@smail.xtu.edu.cn (Y.D.); 202021001821@smail.xtu.edu.cn (S.-Q.L.); 201921001575@smail.xtu.edu.cn (Q.Y.); 202031000166@smail.xtu.edu.cn (Z.-W.L.)

* Correspondence: He-lou@xtu.edu.cn

Abstract: Smart windows can dynamically and adaptively adjust the light transmittance in nonenergy or low-energy ways to maintain a comfortable ambient temperature, which are conducive to efficient use of energy. This work proposes a liquid crystal (LC) smart window with highly efficient near-infrared (NIR) response using carbon nanotubes grafted by biphenyl LC polymer brush (CNT-PDB) as the orientation layer. The resultant CNT-PDB polymer brush can provide the vertical orientation of LC molecules to maintain the initial transparency. At the same time, the smart window shows a rapid response to NIR light, which can quickly adjust the light transmittance to prevent sunlight from entering the room. Different from common doping systems, this method avoids the problem of poor compatibility between the LC host and photothermal conversion materials, which is beneficial for improving the durability of the device.

Keywords: smart window; NIR response; liquid crystal; orientation layer; photothermal

1. Introduction

Due to increasingly serious global warming, constructing comfortable living environments with a cozy somatosensory temperature for humans has become a high-attention issue requiring continuous improvements [1–4]. At present, ventilation and air conditioning systems with high energy consumption are still the main method used to adjust temperature and humidity, which contribute to energy shortages and global warming [5,6]. Compared with such approaches, smart windows that can dynamically and adaptively adjust solar radiation transmittance in low- or non-energy manners show widespread applications in building energy conservation, privacy protection, roofs, skylights and greenhouse windows, etc. [7–10].

Generally, active and passive modes are the main options for the modulation of smart windows. The typical active smart windows using liquid crystal (LC) [11–16] and electrochromic materials [17–21] are realized by applying electricity to modulate the color or transparency of the window. The passive-mode smart windows with energy-saving efficiency function by external environmental stimuli, such as temperature and light, etc. Thermal-responsive smart windows fabricated by hydrogels [22–25] and LC [26,27] are generally colorless or transparent at low temperature and dark or opaque at high temperature. Compared with electrically active smart windows, the thermal-responsive passive mode can automatically adjust the light transmittance without external energy input through the variation in the external environmental temperature [28–31]. Therefore, this kind of smart window demonstrates ideal energy-saving and sun-shading efficiency.

Near-infrared (NIR) light with 700–2500 nm wavelength accounts for 50% of total solar radiation, which is an important energy source used for some chemical reactions and driving devices [9,32]. The multi-responsive smart window, with high transmittance



Citation: Deng, Y.; Li, S.-Q.; Yang, Q.; Luo, Z.-W.; Xie, H.-L. High-Efficiency Responsive Smart Windows Fabricated by Carbon Nanotubes Modified by Liquid Crystalline Polymers. *Crystals* **2021**, *11*, 440. https://doi.org/10.3390/cryst11040440

Academic Editors: Vladimir Chigrinov, Qi Guo, Jiatong Sun and Ying Ma

Received: 14 March 2021 Accepted: 13 April 2021 Published: 18 April 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and NIR light-responsive ability, has been successfully constructed with photothermal conversion materials such as inorganic materials and nanomaterials [33-35]. For example, the LC smart window doped with inorganic nanoparticles (e.g., ITO, Cs_xWO₃, and VO₂) can realize color regulation under NIR irradiation [36-39]. The adaptive smart window with mesogen-functionalized graphene (MFG) can modulate the light transmittance by switching from the initial transparency to the high-scattering state when illuminated by NIR light [40]. However, most LC smart windows with NIR shielding properties are realized by doping with photothermal conversion materials. Thus, their durability is seriously affected during long-term use because the incompatible behavior of the LC and photothermal conversion materials are required to induce the vertical alignment of LC molecules [41,42], which also reduces durability.

The spatial orientation control of LC molecules plays a significant role in the construction of LC polymer devices [43,44]. Previously, we successfully fabricated a responsive smart window with azobenzene LC polymer brush as photothermal and orientation materials, but this smart window only showed ultraviolet (UV)-responsive behavior, which limits their further application [45]. Consequently, we attempted to construct a type of smart window with NIR-responsive behavior using LC polymer brush. As is well-known, carbon nanotubes (CNTs) show excellent NIR photothermal effects. Moreover, the surface of CNTs can be modified by other functional materials or polymers [46]. Herein, we construct high-efficiency smart windows using CNTs grafted by LC polymer brush (CNT-PDB). The chemical structure is shown in Scheme 1. The resultant CNTs grafted by LC polymer brush provide both the vertical orientation of LC molecules and NIR photothermal effects. Moreover, this kind of CNTs can be dissolved in common organic solvents, then spin-coated on the substrate as the orientation and photothermal layer, which avoids disturbing the performance of LC hosts. Thus, the smart windows are expected to quickly adjust the light transmission with excellent durability upon exposure to NIR irradiation.



Scheme 1. Chemical structure of CNT-PDB.

2. Experimental Section

2.1. Preparation of CNT-PDB

The NIR photothermal polymer brush CNT-PDB was synthesized according to our previous work [47]. The detailed information is provided in the Supporting Information.

2.1.1. Preparation of Phase-Transition Chiral LC Mixtures

Scheme 2a illustrates the chemical structures and contents of the compositions in chiral liquid crystalline (ChLC) mixtures. These components (4-cyano-4'-pentylbiphenyl (5CB) (10.1 wt %), 4-cyano-4'-heptylbiphenyl (7CB) (5.1 wt %), 4-cyano-4'-octylbiphenyl (8CB) (35 wt %), 4-cyano-4'-octanoylbiphenyl (8OCB) (3.2 wt %), 4-cyano-4'-decylbiphenyl (10CB) (25 wt %), 4-cyano-4'-dodecylbiphenyl (12CB) (10 wt %), and 4-cyano-4'-pentylparaterphenyl (5TB) (1.6 wt %)), photoinitiator Irgacure-651 (0.3 wt %), commercially available chiral dopant S811 (7 wt %), and photopolymerizable monomer C6M (4 wt %) were dissolved in dichloromethane solution and sonicated for about 30 min. Then, dichloromethane was slowly evaporated off before the samples were placed in a vacuum system for 48 h at 35 °C. The obtained ChLCs were used for further experiments.



Scheme 2. (a) Chemical structures and contents of the compositions in ChLC mixtures; (b) the fabrication process of the PSLC cell.

2.1.2. Preparation of Photothermal Smart Windows

The preparation of the photothermal smart window is illustrated in Scheme 2b. First, the bare glass substrate was treated with piranha solution to form a hydrophilic surface. Then, CNT-PDB was dispersed in chlorobenzene to form a solution with a concentration gradient of 0.01–2 wt %. The polymer solution was spin-coated on the surface of the treated glass at a 3000 rpm for 30 s and then annealed at 130 °C. A photothermal polymer brush that could induce the vertical alignment of LC molecules was formed on the substrate. Two glasses with spin-coated CNT-PDB were assembled into a cell with a spacer of 20 µm. The ChLCs were heated to their isotropic phase and capillary-filled into the cells. Finally, the LC cell was cross-linked by irradiation with UV light (8 mW·cm⁻², λ = 365 nm). The polymer stabilized LC (PSLC) photothermal smart window was successfully fabricated.

3. Results and Discussion

3.1. Synthesis and Characterization of CNT-PDB Polymer Brush and ChLCs

The NIR photothermal polymer brush CNT-PDB was synthesized according to our previously reported work, and detailed information about the synthetic process is shown in the Supporting Information. Firstly, nuclear magnetic resonance (¹HNMR) and Fourier transform infrared spectroscopy (FTIR) were used to identify the structure of CNT-PDB. As shown in Figure S1 (in Supplementary Material), the baseline of the CNT-PDB becomes very rough and the peak shapes become broadened compared with the ¹HNMR spectrum of the HO-PDB, which is attributed to the interference effect of carbon nanotubes on the magnetic field of the instrument. Figure S2 shows the FTIR spectra of HO-PDB, CNT-Br, and CNT-PDB. The characteristic absorption peaks of MWNT-Br and homopolymerized

HO-PDB appeared in the FTIR spectrum of CNT-PDB. The absorption peak of the carbonyl group at 1724 cm⁻¹ was much stronger than that of the initiator CNT-Br, and the position showed a distinct shift, which implied that the CNT-PDB was successfully synthesized. Figure S3 shows the thermal weight loss (TGA) curve of CNT-COOH, CNT-Br, and CNT-PDB in a nitrogen atmosphere. The weight loss ratios of CNT-COOH, CNT-Br, and CNT-PDB at 480 °C are 14%, 13%, and 83%, respectively. The thermal weight loss gradually increased, especially for CNT-PDB, which indicated that LC polymer was successfully grafted. Based on the result, the content of the grafted biphenyl LC polymer was calculated to be 83%. The resultant CNT-PDB showed uniform dispersion in chlorobenzene solvent rather than deposition on the bottom of the bottle for CNT (Figure 1a), which further proved that PDB was successfully grafted onto the CNT surface. Subsequently, the highresolution transmission electron microscope (TEM) experiment was further carried out to investigate the morphology of the CNT-PDB. As shown in Figure 1b, the monodispersed CNT-PDB was clearly observed, and the polymer shell was wrapped on the outer wall of the carbon nanotubes, similar to the core-shell structure, which also confirmed that LC polymer was successfully grafted onto the CNT surface.



Figure 1. (a) Dispersion image: A is CNT-COOH and B is CNT-PDB in chlorobenzene solution; (b) TEM image of CNT-PDB.

Due to the existence of abundant LC polymer brush covalently grafted onto the CNT surface, we speculated that this kind of CNT complex could present LC behavior. Subsequently, Differential scanning calorimetry (DSC) experiments were carried out to investigate phase transitions of CNT-PDB. To eliminate the thermal history, the sample CNT-PDB was first heated to 240 °C at the rate of 20 °C/min followed by isothermal annealing for 10 min. Then, the first cooling trace and the second heating trace were recorded at 10 °C/min. In Figure 2a, two clear phase transitions can be observed. According to the thermal behavior of the LC polymers CNT-PDB, we deduced that the transition located at around 126 °C could be ascribed to the transition of two different LC phases, and another one located at around 157 °C was attributed to the transition of the LC phase to isotropic (Iso) phase. The polarized optical microscopy (POM) results revealed that the distinct birefringence could be developed (Figure 2a, inset image) and the texture almost did not show any change until isotropic temperature at 157 °C, which meant that CNT-PDB could form a stable LC phase under isotropic temperature. To explore the detailed LC phase structure, an X-ray scattering experiment was carried out. As shown in Figure 2b, two obvious diffraction peaks were located at 0.2 and 0.4 \AA^{-1} in the low-angle region and a peak was located at 1.35 Å⁻¹ in the high-angle region at 30 and 90 °C. The *q*-ratio of the low-angle peaks was 1:2, which implied that smectic B was formed. Further increasing temperature, the peaks in low-angle regions almost remained unchanged, but the peak transferred into a halo in high-angle regions, meaning the smectic B phase turned into a lower-order smectic A structure. When the temperature reached 180 °C, all peaks in both low- and high-angle regions disappeared, implying isotropic phase was achieved. This result is in good agreement with the DSC result.



Figure 2. (a) The DSC curve of the polymer CNT-PDB. Inset image: POM image of the polymer CNT-PDB at 140 °C. (b) X-ray scattering profiles of the polymer CNT-PDB recorded at various temperatures upon heating and cooling.

3.2. Orientation Behavior of the CNT-PDB Polymer Brush

In this work, ChLC mixtures were used as the main materials for PSLC smart windows, and suitable compositions were further chosen to regulate the phase transition temperature close to daily life. The DSC and POM results revealed that this transition temperatures of chiral smectic A(SmA*)~chiral nematic(N*) and N*~Iso for ChLC mixtures were 31 and 44.5 °C, respectively (Figures S4 and S5). Since the smart window depended on the orientation transformation of the LC molecules to adjust the light transmittance, the alignment effect of the LC molecules greatly affected the optical performance of the smart window. Therefore, the orientation behavior of the CNT-PDB polymer film for PSLC was investigated. CNT-PDB showed good dispersibility in organic solvents such as chloroform and chlorobenzene, and the sample was dissolved in the chlorobenzene to prepare polymer solutions with different concentrations of 0.01, 0.05, 0.1, 0.5, 1, and 2 wt %. Then, the resultant solution was spin-coated on the surface of the hydrophilic substrate to prepare the substrate with the orientation layer. Furthermore, the obtained glasses with CNT-PDB as substrate were prepared into LC cells. When the PSLC was placed into the LC cell with the substrate prepared from 0.01 wt % CNT-PDB solution, obvious birefringence was observed at room temperature under orthoscopic POM, indicating that these LC cells presented the inability to induce the vertical alignment of the PSLC. However, when the PSLC was placed into the LC cell with the substrate prepared from more than 0.05 wt %CNT-PDB solution, a dark field under orthoscopic POM and obvious black crosses under the conoscopic POM were observed (Figure 3a–e), which implied that the LC cells could induce the homeotropic orientation of the PSLC. Therefore, the orientation of PSLCs depended on the substrate of LC cells prepared in the solution concentration.

In our previous work, we demonstrated the orientation behavior that was dependent on the solution concentration originated from the thickness of the polymer brush film, which could be controlled by changing the concentration of the spin-coating solution. The low concentration resulted in thin film, which could not cover the glass substrate completely. Only the concentration with a critical value could produce the prepared film with appropriate thickness, which could cover the glass substrate completely. Consequently, the film with sufficient thickness could induce the vertical LC arrangement. Herein, the coverage of CNT-PDB on the substrate was further evaluated through the water contact angle (θ_w) experiment. The θ_w on the bare silicon substrate was 15°. For the glass substrate coated with 0.01 wt % CNT-PDB, the value of θ_w was 83°. For the substrate coated with 0.05 wt % CNT-PDB, the value of θ_w increased to 88°. Increasing the concentration of CNT-PDB further led to the values entirely exceeding 90° (Table 1). This phenomenon is consistent with previous experiment results. When the solution with a diluted concentration was used for preparing the substrate, the resultant thin film of CNT-PDB could not completely cover the substrate. Thus, the PSLC molecules in the LC cells were randomly arranged, which exhibited the typical birefringence phenomenon under orthoscopic POM. On the contrary, as the concentration of the spin-coating solution increased, the resulting thicker film covered the entire substrate, which could induce the vertical alignment of the PSLC due to the anchoring effect of the LC brush. The surface morphology of the substrates was further investigated by atomic force microscopy (AFM). Our previous work demonstrated that the surface of the bare glass substrate was fairly smooth. As shown in Figure 4, the substrate coated with 0.05 wt % CNT-PDB exhibited a continuous protrusion layer in each domain, and the surface roughness of the film was about 0.982 nm, which indicates that the substrate spin-coated by 0.05 wt % CNT-PDB was relatively uniform. Other samples with different CNT-PDB concentrations showed similar results and the root mean-square (RMS) values remained almost unchanged, which implied that increasing concentrations hardly influenced the roughness of the CNT-PDB-coated surface. Evidently, this result also further demonstrated that the vertical orientation was from the driven force of the anchoring energy, which was different from the LC vertical arrangement by the small island due to the increase in the surface roughness.



Figure 3. POM photographs of PSLC alignment in CNT-PDB brush-coated hybrid cells at different spin-coating concentrations: (a) 2, (b) 1, (c) 0.5, (d) 0.1, (e) 0.05, and (f) 0.01 wt%.

Table 1. Water contact angle (θ	w) on the	e CNT-PDB b	rush surface.
--	-----------	-------------	---------------

Concentration (wt %)	0.01	0.05	0.1	0.5	1	2
Contact angle $\theta_{\rm w}$ (degrees)	83	88	91	94	95	96



Figure 4. The 3D topographic AFM image (**a**) and corresponding height profiles (**b**) of the 0.05 wt % of the CNT-PDB film on the silicon substrate.

3.3. Optical Performance of PSLC in the LC Cells Using the CNT-PDB Polymer Brush as Substrate

Since the substrate coated by CNT-PDB could induce PSLC orientation, the transmittance of the prepared PSLC cells with different concentrations of the CNT-PDB polymer brush from 0.01 to 2 wt % was further investigated to explore the influence of polymer brush concentration on the optical performance of LC cells. Because the experiment was carried out at room temperature, all PSLC cells remained in the normal SmA* phase. Figure 5 shows that the PSLC LC cells with 0.01 wt % CNT-PDB concentration presented a serious light scattering state and the light transmittance was as low as 13.4%. This result was ascribed to the extremely low polymer brush concentration, which led to incomplete coverage of the substrate and could not induce the vertical orientation of the PSLC. Consequently, the unvertical orientation of the PSLC resulted in serious light scattering and low light transmittance. As the concentration of the polymer brush increased, the PSLC orientation effect improved, which led to the increase in light transmittance of the smart window. The PSLC cell gradually showed a transparent state. The smart window with a polymer brush concentration of 2 wt % showed the highest transparency, whose transmittance value achieved 77.2%. Evidently, the optical performance of the PSLC smart windows is affected by the concentration of the polymer brush.



Concentration(wt%)

Figure 5. Images of the proposed PSLC cells with different CNT-PDB polymer brush concentrations and their corresponding POM images. Upper right corner: transmittance value at 550 nm.

3.4. Photothermal Effect of CNT-PDB Polymer Brush

The photothermal effect of the CNT-PDB was investigated using a thermal imager under NIR irradiation. Figure 6a describes the temperature variation in the substrate coated

with 2 wt % CNT-PDB polymer brush upon the NIR irradiation. The temperature of the substrate coated with the CNT-PDB polymer brush rose to 55.3 °C within 3 s, which indicated excellent NIR photothermal-responsive behavior. This temperature exceeded the SmA~N* phase transition of the prepared ChLC mixtures, which evidently satisfied the requirement for the NIR photothermal LC smart window. Furthermore, the temperature variations in the substrate with different concentrations of the polymer brush under different NIR irradiation intensities were investigated, as shown in Figure 6b. As the concentration of the CNT-PDB solutions increased, the maximum temperature of the polymer brush film showed a slight increase. However, the maximum temperature rise was closely related to the intensity of the NIR irradiation. When the intensity of the NIR irradiation increased to 5 W, the maximum temperature of the polymer brush rose sharply, which almost exceeded 90 °C. As is well-known, the stability of the NIR photothermal properties has a strong influence on the performance of responsive smart windows. Thus, a repetitive experiment was carried out with NIR light irradiation, and the results showed that the temperature variation remained the same after many repeated irradiations (Figure 6c). No attenuation or enhancement phenomena were observed in this repeated experiment, which indicated that the photothermal effect was very stable. Therefore, we speculated that the CNT-PDB substrate is suitable for the preparation of photothermal-responsive smart windows.



Figure 6. (a) IR images of the substrate coated with CNT-PDB polymer brush recorded at different NIR light irradiation times. (b) The maximum heating curves of polymer brushes with different concentrations under different NIR irradiation intensities. (c) The temperature of CNT-PDB polymer brush under cyclic NIR light radiation.

3.5. NIR Responsive Behavior of Photothermal Smart Windows

The above experiments proved that the CNT-PDB polymer brush not only showed an excellent NIR photothermal effect, but also induced the vertical orientation of PSLC when the concentration was more than 0.05 wt %. The results showed that the CNT-PDB polymer brush sufficiently satisfied the requirements of the PSLC smart window. Therefore, the PSLC smart windows modified by the CNT-PDB polymer brush with varying concentrations were constructed and their NIR-responsive transitions were investigated. Figure 7a displays the images of the PSLC smart windows fabricated with 2 wt % CNT-PDB polymer brush, the optical performance of which can be transformed between the homeotropic SmA* (transparency), focal conic N* (opacity), and isotropic (transparency) state upon thermal stimulus [48]. PSLC smart windows prepared with CNTs modified by polymer brushes at a 2 wt % concentration showed a transparent state and very clear view of the text in the background at room temperature (27 °C) because the maximum light transmittance was from the perpendicular arrangement of the LC molecules in the substrate. When irradiated by NIR light, the ambient temperature quickly reached the phase transition temperature of the PSLC due to the strong NIR photothermal effect of the CNT-PDB polymer brush. The PSLC smart windows presented an opaque state and the view of the text in the background became invisible, because the PSLC in the smart windows underwent a SmA*~N* transition. The LC molecules in the N* phase generating a mismatched refractive index between the LC domains and the polymer network resulted in strong light scattering under the irradiation of NIR light (Figure S6). As shown in Figure 7b, other PSLC smart windows prepared with CNTs modified by polymer brushes at a concentration of 0.05 to 2 wt % showed a similar phenomenon. We observed that increasing the spin-coating concentration of CNT-PDB from 0.05 to 2 wt% enhanced the modulation contrast to some extent. The transmittance value of the as-made smart window fabricated with 2 wt % CNT-PDB dropped to 7.2%, whose initial value was 77.2%, exhibiting more flexible light control ability in response to both temperature and NIR light compared with low concentration samples (T_{0.05wt%} decreased from 60.9 to 12.1%). Thus, this result indicated that the smart window could adjust to the ambient temperature adaptively under the irradiation of NIR light. The Vis-NIR transmittance spectrum of the as-made smart window modified with 2 wt % CNT-PDB polymer brush as an example was measured at different environmental temperatures. As shown in Figure S7, a conspicuous change in NIR transmittance was observed at different temperatures. The transmittance of the opaque state (40 °C) was lower than that of the transparent state (20 °C). Specifically, during the heating process from 20 to 40 °C, the NIR light transmittance at 1150 nm significantly decreased from 86.6 to 39.8% for the as-prepared smart window, presenting a high-efficiency thermally controllable NIR light property (Figure S8).

Interestingly, the NIR-responsive rate of the PSLC smart window was proportional to the concentration of the polymer brush. The higher concentration of the polymer brush showed a faster response speed (Figure 8a). The smart windows with a polymer brush concentration of 2 wt % demonstrated the best NIR-responsive behavior with a response time of only 1.2 s. In addition, the response time of the smart window was dependent on the NIR radiation intensity. As the intensity of NIR light increased, the smart window responded more quickly. As described in Figure 8b, when the NIR irradiation intensity increased from 2 to 6 W, the phase transition of the PSLC smart window decreased to 0.88 s. Similarly, different NIR light intensities produced different maximum temperatures in the different PSLC smart windows with different polymer brush concentrations. As shown in Figure 8c, when a low-concentration polymer brush was used to prepare photothermal smart windows, the PSLC could not reach the phase transition temperature of N*~Iso (44.5 °C) due to its weak photothermal effect under low NIR light intensity. Therefore, no transition from opaque state to transparent state was observed because of overheating. Based on the above experiment results, we determined that the substrate coated with 0.1 wt % polymer brush is the most appropriate choice for the construction of photothermal PSLC smart windows, as it showed a phase transition temperature closest to human

somatosensory temperature from the photothermal property. It is expected that controlling the photothermal smart window to not change to an isotropic state by adjusting the concentration of the polymer brush is more in line with energy-saving requirements.



Figure 7. (a) The images of the fabricated PSLC cell in the SmA*, N*, and Iso phases. (b) Images of the fabricated PSLC cells with different polymer brush concentrations before and under NIR irradiation (27 °C, the incident height: 3 cm). Upper right corner: transmittance value at 550 nm after NIR irradiation.



Figure 8. (a) The relationship between response time and polymer brush concentration (b) The relationship between response time and NIR radiation intensity. (c) Maximum temperature rise of PSLC cells with different polymer brush concentrations under different light intensities.

4. Conclusions

In summary, we used the carbon nanotubes modified with biphenyl LC polymer (CNT-PDB) as a polymer brush to construct a high-efficiency responsive smart window. This polymer brush induced the vertical alignment of PSLC, which produced a smart window with high transparency at normal temperature. Moreover, it possesses excellent photothermal performance, endowing smart windows with remarkable NIR responsive-

ness. The optical performance of smart windows can be adjusted by NIR irradiation. This NIR photothermal polymer brush can be used to fabricate highly efficient responsive PSLC smart windows without additional orientation materials and avoid interference with the LC host, which improves the durability of the device. This as-prepared smart window presents a high-efficiency thermally controllable NIR light property. Unfortunately, this kind of smart window fabricated with this CNT-PDB polymer brush as the substrate cannot be driven by environmental light, and gaps remain to be filled before this system can be applied in reality. Improving the responsiveness of LC smart windows to natural light may become a future research direction in this field.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/cryst11040440/s1, Scheme S1. Synthetic route to CNT-PDB; Figure S1: ¹H NMR spectra of polymer HO-PDB and CNT-PDB;Figure S2:FTIR spectra of HO-PDB, CNT-Br and the polymer brush CNT-PDB; Figure S3: TGA curves of CNT-Br, CNT-COOH and CNT-PDB; Figure S4: The DSC curve of chiral LC mixture(ChLC); Figure S5: The optical textures of unaligned chiral LC mixture under crossed polarizers at different temperatures; Figure S6: The optical textures of polymer stabilized chiral liquid crystalline thin film (0.5 wt%, 20 um thick cell with homeotroic alignment) under crossed polarizers upon cooling from the isotropic phase at a rate of 1 °C /min;Figure S7: The Vis-NIR transmittance spectra from 400 nm to 2000 nm for the as-made smart window modified with 2 wt% CNT-PDB polymer brush at different environmental temperatures;Figure S8: NIR light transmittance at 1150 nm of the as-made smart window modified with 2 wt% CNT-PDB polymer brush during the heating process from 20 to 40 °C (heating rate: 5 °C/min).

Author Contributions: Conceptualization, Y.D.; methodology, Y.D.; software, Q.Y.; validation, Y.D. and S.-Q.L.; formal analysis, Y.D.; investigation, Y.D.; resources, Y.D.; data curation, Z.-W.L.; writing—original draft preparation, Y.D.; writing—review and editing, Y.D.; visualization, Y.D. and S.-Q.L.; supervision, H.-L.X.; project administration, H.-L.X.; funding acquisition, H.-L.X. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by National Natural Science Foundation of China (NNSFC 21975215 and 21674088), Scientific Research Foundation of Hunan Provincial Education Department (19A486), and the Hunan 2011 Collaborative Innovation Center of Chemical Engineering & Technology with Environmental Benignity and Effective Resource Utilization.

Data Availability Statement: The data presented in this study are available within the article.

Acknowledgments: This work was financially supported by the National Natural Science Foundation of China (NNSFC 21975215 and 21674088), Scientific Research Foundation of Hunan Provincial Education Department (19A486), and the Hunan 2011 Collaborative Innovation Center of Chemical Engineering & Technology with Environmental Benignity and Effective Resource Utilization.

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

References

- Allouhi, A.; El Fouih, Y.; Kousksou, T.; Jamil, A.; Zeraouli, Y.; Mourad, Y. Energy Consumption and Efficiency in Buildings: Current Status and Future Trends. J. Clean. Prod. 2015, 109, 118–130. [CrossRef]
- 2. Bell, L.E. Cooling, Heating, Generating Power, and Recovering Waste Heat with Thermoelectric Systems. *Science* 2008, 321, 1457–1461. [CrossRef]
- 3. Berardi, U. A Cross-Country Comparison of the Building Energy Consumptions and Their Trends. *Resour. Conserve. Recy.* 2017, 123, 230–241. [CrossRef]
- Cao, X.; Dai, X.; Liu, J. Building Energy-Consumption Status Worldwide and the State-Of-The-Art Technologies for Zero-Energy Buildings During the Past Decade. *Energy Build*. 2016, 128, 198–213. [CrossRef]
- 5. Omer, A.M. Energy, Environment and Sustainable Development. Renew. Sust. Energy. Rev. 2008, 12, 2265–2300. [CrossRef]
- 6. Pérez-Lombard, L.; Ortiz, J.; Pout, C. A Review on Buildings Energy Consumption Information. *Energy Build*. **2008**, *40*, 394–398. [CrossRef]
- Llordés, A.; Wang, Y.; Fernandez-Martinez, A.; Xiao, P.; Lee, T.; Poulain, A.; Zandi, O.; Saez Cabezas, C.A.; Henkelman, G.; Milliron, D.J. Linear Topology in Amorphous Metal Oxide Electrochromic Networks Obtained via Low-Temperature Solution Processing. *Nat. Mater.* 2016, 15, 1267–1273. [CrossRef] [PubMed]
- 8. Ke, Y.; Zhou, C.; Zhou, Y.; Wang, S.; Chan, S.H.; Long, Y. Emerging Thermal-Responsive Materials and Integrated Techniques Targeting the Energy-Efficient Smart Window Application. *Adv. Funct. Mater.* **2018**, *28*, 1800113. [CrossRef]

- 9. Khandelwal, H.; Schenning, A.P.H.J.; Debije, M.G. Infrared Regulating Smart Window Based on Organic Materials. *Adv. Energy Mat.* 2017, 7, 1602209. [CrossRef]
- Ke, Y.; Chen, J.; Lin, G.; Wang, S.; Zhou, Y.; Yin, J.; Lee, P.S.; Long, Y. Smart Windows: Electro-, Thermo-, Mechano-, Photochromics, and Beyond. Adv. Energy Mat. 2019, 9, 1902066. [CrossRef]
- Ghosh, A.; Norton, B.; Mallick, T.K. Influence of Atmospheric Clearness on PDLC Switchable Glazing Transmission. *Energy Build.* 2018, 172, 257–264. [CrossRef]
- 12. Ghosh, A.; Norton, B.; Mallick, T.K. Daylight Characteristics of a Polymer Dispersed Liquid Crystal Switchable Glazing. *Sol. Energy Mater. Sol. Cells* **2018**, 174, 572–576. [CrossRef]
- 13. Hu, X.; de Haan, L.T.; Khandelwal, H.; Schenning, A.P.H.J.; Nian, L.; Zhou, G. Cell Thickness Dependence of Electrically Tunable Infrared Reflectors Based on Polymer Stabilized Cholesteric Liquid Crystals. *Sci. China Mater.* **2018**, *61*, 745–751. [CrossRef]
- Kim, M.; Park, K.J.; Seok, S.; Ok, J.M.; Jung, H.T.; Choe, J.; Kim, D.H. Fabrication of Microcapsules for Dye-Doped Polymer-Dispersed Liquid Crystal-Based Smart Windows. ACS Appl. Mater. Interfaces 2015, 7, 17904–17909. [CrossRef]
- 15. Lee, K.M.; Tondiglia, V.P.; White, T.J. Bistable Switching of Polymer Stabilized Cholesteric Liquid Crystals Between Transparent and Scattering Modes. *MRS Commun.* 2015, *5*, 223–227. [CrossRef]
- Yoon, W.J.; Choi, Y.J.; Lim, S.I.; Koo, J.; Yang, S.; Jung, D.; Kang, S.W.; Jeong, K.U. A Single-Step Dual Stabilization of Smart Window by the Formation of Liquid Crystal Physical Gels and the Construction of Liquid Crystal Chambers. *Adv. Funct. Mater.* 2020, *30*, 1906780. [CrossRef]
- 17. Xie, S.; Chen, Y.; Bi, Z.; Jia, S.; Guo, X.; Gao, X.; Li, X. Energy Storage Smart Window with Transparent-To-Dark Electrochromic Behavior and Improved Pseudocapacitive Performance. *Chem. Eng. J.* **2019**, *370*, 1459–1466. [CrossRef]
- Cai, G.; Wang, J.; Lee, P.S. Next-Generation Multifunctional Electrochromic Devices. Acc. Chem. Res. 2016, 49, 1469–1476. [CrossRef] [PubMed]
- 19. Eh, A.L.S.; Tan, A.W.M.; Cheng, X.; Magdassi, S.; Lee, P.S. Recent Advances in Flexible Electrochromic Devices: Prerequisites, Challenges, and Prospects. *Energy Technol.* **2018**, *6*, 33–45. [CrossRef]
- 20. Yang, P.; Sun, P.; Mai, W. Electrochromic Energy Storage Devices. Mater. Today 2016, 19, 394–402. [CrossRef]
- Cai, G.; Eh, A.L.S.; Ji, L.; Lee, P.S. Recent Advances in Electrochromic Smart Fenestration. Adv. Sust. Syst. 2017, 1, 1700074. [CrossRef]
- 22. Zhou, Y.; Wang, S.; Peng, J.; Tan, Y.; Li, C.; Boey, F.Y.C.; Long, Y. Liquid Thermo-Responsive Smart Window Derived from Hydrogel. *Joule* 2020, *4*, 2458–2474. [CrossRef]
- 23. Zhou, Y.; Layani, M.; Wang, S.; Hu, P.; Ke, Y.; Magdassi, S.; Long, Y. Fully Printed Flexible Smart Hybrid Hydrogels. *Adv. Funct. Mater.* **2018**, *28*, 1705365. [CrossRef]
- 24. Zhou, Y.; Cai, Y.; Hu, X.; Long, Y. VO₂/hydrogel Hybrid Nanothermochromic Material with Ultra-High Solar Modulation and Luminous Transmission. *J. Mater. Chem. A* 2015, *3*, 1121–1126. [CrossRef]
- La, T.G.; Li, X.; Kumar, A.; Fu, Y.; Yang, S.; Chung, H.J. Highly Flexible, Multipixelated Thermosensitive Smart Windows Made of Tough Hydrogels. ACS Appl. Mater. Interfaces 2017, 9, 33100–33106. [CrossRef]
- Kakiuchida, H.; Tazawa, M.; Yoshimura, K.; Ogiwara, A. Thermal Control of Transmittance/Diffraction States of Holographic Structures Composed of Polymer and Liquid Crystal Phases. Sol. Energy Mater. Sol. Cells 2010, 94, 1747–1752. [CrossRef]
- Liang, X.; Chen, M.; Chen, G.; Li, C.; Han, C.; Zhang, J.; Zhang, J.; Zhang, L.; Yang, H. Effects of Polymer Micro-Structures on the Thermo-Optical Properties of a Flexible Soft-Mater Film Based on Liquid Crystals /Polymer Composite. *Polymer* 2018, 146, 161–168. [CrossRef]
- De Bastiani, M.; Saidaminov, M.I.; Dursun, I.; Sinatra, L.; Peng, W.; Buttner, U.; Mohammed, O.F.; Bakr, O.M. Thermochromic Perovskite Inks for Reversible Smart Window Applications. *Chem. Mater.* 2017, 29, 3367–3370. [CrossRef]
- Tang, Y.; Lin, G.; Yang, S.; Yi, Y.K.; Kamien, R.D.; Yin, J. Programmable Kiri-Kirigami Metamaterials. Adv. Mater. 2017, 29, 1604262. [CrossRef]
- Lee, H.Y.; Cai, Y.; Velioglu, S.; Mu, C.; Chang, C.J.; Chen, Y.L.; Song, Y.; Chew, J.W.; Hu, X.M. Thermochromic Ionogel: A New Class of Stimuli Responsive Materials with Super Cyclic Stability for Solar Modulation. *Chem. Mater.* 2017, 29, 6947–6955. [CrossRef]
- Ke, Y.; Wen, X.; Zhao, D.; Che, R.; Xiong, Q.; Long, Y. Controllable Fabrication of Two-Dimensional Patterned VO₂ Nanoparticle, Nanodome, and Nanonet Arrays with Tunable Temperature-Dependent Localized Surface Plasmon Resonance. ACS Nano 2017, 11, 7542–7551. [CrossRef]
- 32. Timmermans, G.H.; Hemming, S.; Baeza, E.; van Thoor, E.A.J.; Schenning, A.P.H.J.; Debije, M.G. Advanced Optical Materials for Sunlight Control in Greenhouses. *Adv. Opt. Mater.* 2020, *8*, 2000738. [CrossRef]
- 33. Wu, M.; Shi, Y.; Li, R.; Wang, P. Spectrally Selective Smart Window with High Near-Infrared Light Shielding and Controllable Visible Light Transmittance. *ACS Appl. Mater. Interfaces* **2018**, *10*, 39819–39827. [CrossRef]
- Hao, Q.; Li, W.; Xu, H.; Wang, J.; Yin, Y.; Wang, H.; Ma, L.; Ma, F.; Jiang, X.; Schmidt, O.G.; et al. VO₂/TiN Plasmonic Thermochromic Smart Coatings for Room-Temperature Applications. *Adv. Mater.* 2018, *30*, 1705421. [CrossRef] [PubMed]
- 35. Chou, H.T.; Chen, Y.C.; Lee, C.Y.; Chang, H.Y.; Tai, N.H. Switchable Transparency of Dual-Controlled Smart Glass Prepared with Hydrogel-Containing Graphene Oxide for Energy Efficiency. *Sol. Energy Mater. Sol. Cells* **2017**, *166*, 45–51. [CrossRef]
- 36. Liang, X.; Chen, M.; Guo, S.; Zhang, L.; Li, F.; Yang, H. Dual-Band Modulation of Visible and Near-Infrared Light Transmittance in an All-Solution-Processed Hybrid Micro–Nano Composite Film. *ACS Appl. Mater. Interfaces* **2017**, *9*, 40810–40819. [CrossRef]

- Liang, X.; Chen, M.; Wang, Q.; Guo, S.; Zhang, L.; Yang, H. Active and Passive Modulation of Solar Light Transmittance in a Hybrid Thermochromic Soft-Matter System for Energy-Saving Smart Window Applications. J. Mater. Chem. C. 2018, 6, 7054–7062. [CrossRef]
- Liang, X.; Guo, C.; Chen, M.; Guo, S.; Zhang, L.; Li, F.; Guo, S.; Yang, H. A Roll-to-Roll Process for Multi-responsive Soft-Matter Composite Films Containing Cs_xWO₃ Nanorods for Energy-Efficient Smart Window Applications. *Nanoscale Horiz.* 2017, 2, 319–325. [CrossRef]
- 39. Liang, X.; Guo, S.; Chen, M.; Li, C.; Wang, Q.; Zou, C.; Zhang, C.; Zhang, L.; Guo, S.; Yang, H. A Temperature and Electric Field-Responsive Flexible Smart Film with Full Broadband Optical Modulation. *Mater. Horiz.* **2017**, *4*, 878–884. [CrossRef]
- Wang, L.; Bisoyi, H.K.; Zheng, Z.; Gutierrez-Cuevas, K.G.; Singh, G.; Kumar, S.; Bunning, T.J.; Li, Q. Stimuli-Directed Self-Organized Chiral Superstructures for Adaptive Windows Enabled by Mesogen-functionalized Graphene. *Mater. Today* 2017, 20, 230–237. [CrossRef]
- 41. Oh, S.W.; Kim, S.H.; Yoon, T.H. Control of Transmittance by Thermally Induced Phase Transition in Guest–Host Liquid Crystals. *Adv. Sustain. Syst.* **2018**, *2*, 1800066. [CrossRef]
- 42. Oh, S.W.; Kim, S.H.; Baek, J.M.; Yoon, T.H. Optical and Thermal Switching of Liquid Crystals for Self-Shading Windows. *Adv. Sustain. Syst.* 2018, 2, 1700164. [CrossRef]
- 43. Yin, K.; He, Z.; Wu, S.T. Reflective Polarization Volume Lens with Small f-Number and Large Diffraction *Angle. Adv. Opt. Mater.* **2020**, *8*, 2000170. [CrossRef]
- 44. He, Z.; Yin, K.; Wu, S.T. Passive Polymer-Dispersed Liquid Crystal Enabled Multi-Focal Plane Displays. *Opt. Express.* 2020, 28, 15294–15299. [CrossRef]
- 45. Kuang, Z.Y.; Deng, Y.; Hu, J.; Tao, L.; Wang, P.; Chen, J.; Xie, H.L. Responsive Smart Windows Enabled by the Azobenzene Copolymer Brush with Photothermal Effect. *ACS Appl. Mater. Interfaces* **2019**, *11*, 37026–37034. [CrossRef]
- 46. Qin, S.; Qin, D.; Ford, W.T.; Resasco, D.E.; Herrera, J.E. Polymer Brushes on Single-Walled Carbon Nanotubes by Atom Transfer Radical Polymerization of n-Butyl Methacrylate. *J. Am. Chem. Soc.* 2004, *126*, 170–176. [CrossRef]
- Hu, J.; Kuang, Z.Y.; Tao, L.; Huang, Y.F.; Wang, Q.; Xie, H.L.; Yin, J.R.; Chen, E.Q. Programmable 3D Shape-Change Liquid Crystalline Elastomer Based on a Vertically Aligned Monodomain with Cross-link Gradient. ACS Appl. Mater. Interfaces 2019, 11, 48393–48401. [CrossRef]
- 48. Seddon, J.M. Structural Studies of Liquid Crystals by X-ray Diffraction. In *Handbook of Liquid Crystals*; WILEY-VCH Verlag GmbH: Weinheim, Germany, 1998; Volume 1, pp. 635–679. [CrossRef]