Supporting Information

Temperature and electric field-responsive flexible smart film with full broadband optical modulation

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Experimental Methods

Materials. Unless specified, the chemicals were purchased from Sigma-Aldrich (St. Louis, MO). Methacryloxypropyl-trimethoxysilane (MPTMS) and Irgacure 651 were obtained from TCI Co., Ltd. Hydroxypropyl methacrylate (HPMA) and dodecyl methacrylate (LMA) were purchased from Tokyo Chemical Industry Co., Ltd. Polyethylene glycol diacrylate (PEGDA600) was provided by Sartomer Co., Ltd. S811, the used chiral dopant was purchased from Merck Co., Ltd. C6M, 4'-octyl[1,1'-biphenyl]-4-carbonitrile (8CB, SmA-LCs), and the N*-LCs were synthesized according to the methods suggested by Broer et al.[1] and Gray et al..[2] The LCs with the SmA-N* phase transition is prepared by mixing 8CB (SmA-LCs) and N*-LCs, and the SmA-LCs concentration related SmA-N* phase transition temperature was investigated as shown in **Figure S7**. The chemical structures and physical properties of some chemicals used were listed in **Scheme S1.**

Synthesis of ITO NCs. The ITO NCs were synthesized according to literature[3] with modified procedures. Typically, 300 mg of indium acetylacetonate (In(acac)$_3$), 30 mg of tin bis(acetylacetonate)dichloride, (Sn(acac)$_2$Cl$_2$) and 17 mL of 1-octadecene were added in a four-neck flask with a distillation setup. This mixture was heated to 250 ^{o}C (10 ^{o}C/min) under N$_2$ flow with continuous stirring for 30 minutes. After that, 1 mL of oleic acid was injected, and the mixture was heated to 270 ^{o}C for 1 h. Then, 3 mL of oleylamine was added, and the mixture was heated to 290 ^{o}C for 1 h. After the above mixture was cooled to room temperature, 30 mL of isopropyl alcohol was added to flocculate the NCs. The product was separated by centrifugation, and the precipitated NCs were redispersed in 20ml of hexane with a slight amount of oleylamine (0.2 mL) and oleic acid (0.2 mL). Subsequently, 20 mL of ethanol was added to precipitate the NCs and followed by centrifugation for separation. This process was repeated once. Finally, the ITO NCs were dispersed in 20 mL hexane for further use. In the synthesis, the Sn composition in ITO NCs was regulated by varying the feeding dosage of Sn precursors.

Synthesis of silica-encapsulated ITO NCs. The ITO NCs were encapsulated by silica according to a reverse microemulsion method described by Nann *et al.*.[4] Briefly, 20 mL of cyclohexane as a solvent and 2.4 g of IGEPAL CO-520 as a surfactant were mixed at room temperature. 100 mg of ITO NCs dispersed in 0.6 mL of toluene were introduced into the above mixture, and then 0.4 mL of TEOS was added and stirred continuously. After 20 minutes, the reaction was initiated by dropwise adding 0.6 mL of ammonium solution (20 wt%) , and the condensation was allowed to proceed for 24 h. After that, the ITO/SiO_2 NCs were separated from the microemulsion by adding 3 mL of ethanol, followed by centrifugation at 2000 rpm for 5 minutes. The final product, ITO/SiO_2 NCs were repeatedly rinsed with ethanol and dispersed in 20 mL ethanol for further use.

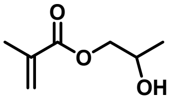
Surface modification of ITO/SiO_2 NCs. Briefly, 20 mL of ITO/SiO_2 NCs ethanol solution was mixed with 0.2 mL of ammonium solution (20 wt%) to adjust the pH to 9. 0.2 mL MPTMS was added into the above solution and stirred under room temperature for 24 h. The resultant functionalized NCs were cleaned four times *via* dialysis exchange in ethanol.

Preparation of smart films incorporated with 0-5 wt% ITO/SiO_2 NCs. A polymeric syrup, consisting of a homemade LCs with a SmA-N* phase transition, NAMs, HPMA, LMA, ethoxylate dimethacrylate (Bis-EMA15), PLCs, C6M, photo-initiator, Irgacure 651, 0-5 wt% of functionalized ITO/SiO_2 NCs was prepared and mixed homogeneously. An additional 0.5 wt% of 20 μm, nonreactive glass bead spacers were added to adjust the thickness of the films. Prior to use, the NCs ethanol solution was added to the acrylate monomers followed by ultra-sonicating for 30 minutes to ensure well dispersion of the NCs. Then the mixture was distilled with a rotary evaporator to remove the ethanol. The smart films were prepared according to **Scheme 1**. In details, the syrup was sandwiched between the two pieces of transparent plastic substrates. Then, the cell was irradiated under UV light (PS135, UV Flood, Stockholm Sweden, 365nm) with an intensity of 0.5 mw/cm^2 for 90 seconds at room temperature. After that, a voltage (square wave, 50 Hz, 150V) was applied to the cell to homeotropically oriented the LCs, then cured by UV light with an intensity of 0.5 mw/cm^2 for an additional 5 minutes with the voltage applied at room temperature to complete the polymerization.

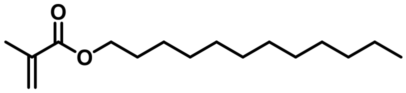
Measurements. XRD patterns were acquired on a Bruker AXS D8-Advanced diffractometer with Cu Kα radiation (λ=1.5418 Å). TEM and HRTEM images were obtained on a Tecnai G2 F20 microscope operating at 200 kV. FT-IR spectra were obtained on a BrukerVector-22 FT-IR spectrophotometer using a KBr pellet over a range of 4000-600 cm^{-1}. DLS analysis was carried out using a Zetasizer Nano ZS (Malvern Ltd.) at a copolymer concentration of 0.25 mg/mL. The measurements were based on 12~14 runs, 10-second sub-runs. The syrup containing 5 wt% of ITO/SiO_2 NCs was analyzed at 273.15 K with a scattering angle of 173^o and a 633 nm HeNe laser. The refractive index (RI) and viscosity of the syrup were 1.503 and 6.63 x 10^{-3} Pa·s, respectively. The morphologies of the polymer network were characterized by scanning electron microscopy (SEM, HITACHI S-4800). To observe the polymer network, all films were dipped in hexane (AR) for about 15 days at room temperature to fully extract the LC molecules from films, then dried in vacuum for about 24 h. Finally, the thin gold layers were coated onto the films to eliminate any electric charge problem. The Vis-NIR spectra and the thermo-optical transmittance were obtained by a UV/vis/NIR spectrophotometer (JASCO V-570) equipped with a hot stage (Linkam

LK-600PM) calibrated to an accuracy of ±0.1 K. The optical textures of the LCs were observed by polarizing optical microscopy (POM, Carl Zeiss Axio Vision SE64) equipped with a hot stage (Linkam LK-600PM) calibrated to an accuracy of ±0.1 K (**Figure S8**). Electro-optical properties of the smart films at 306 K were measured by a LC device parameters tester (LCT-5016C, Changchun Liancheng Instrument Co. Ltd., China) equipped with a hot stage (Linkam LK-600PM). A halogen tungsten lamp (560 nm) was used as an incident light source. The transmittance of the smart films was recorded by a photodiode whose response, and monitored by a digital storage oscilloscope. The distance between the detector and the films was approximately 300 mm, and an electric field (square wave, 50Hz) was applied during the measurement. The shearing strength was measured by universal tensile testing machine (LETRY) at the rate of 10 mm min^{-1} and the size of the tested films was 43 mm × 31 mm. Exposure time dependence of temperature of the films with and without NCs were investigated by irradiating the films containing 5% and no ITO/SiO_2 NCs with a solar simulator (Oriel Newport, 91195A-1000) on the same strength for 180 seconds at 288 K, 293 K and 298 K, respectively. The temperature variations of the films during the irradiation were tracked using a thermographic camera (FLIR SC7000).

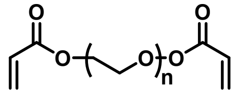
(1) Non-liquid crystalline acrylate monomers (NAMs):



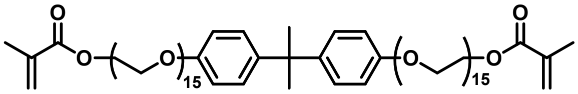
HPMA



LMA

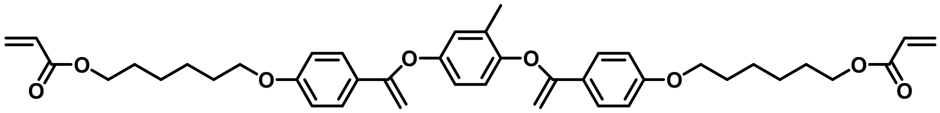


PEGDA600



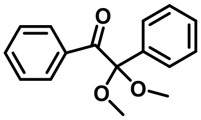
Bis-EMA15

(2) Photo-polymerizable LCs (PLCs):



C6M

(3) Initiator:



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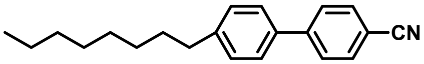
(4) LCs with a SmA~N* phase transition:

SmA-LCs:



N*-LCs (Lab synthesized): Cr 254.6 K N* 354.2 K I

Scheme S1. Chemicals structures and physical properties of the materials used in the reactive syrup.

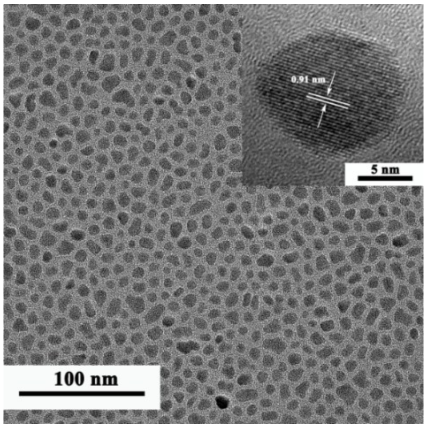


Figure S1. TEM image of the original ITO NCs in hexane. Inset: HRTEM image of a single ITO NC.

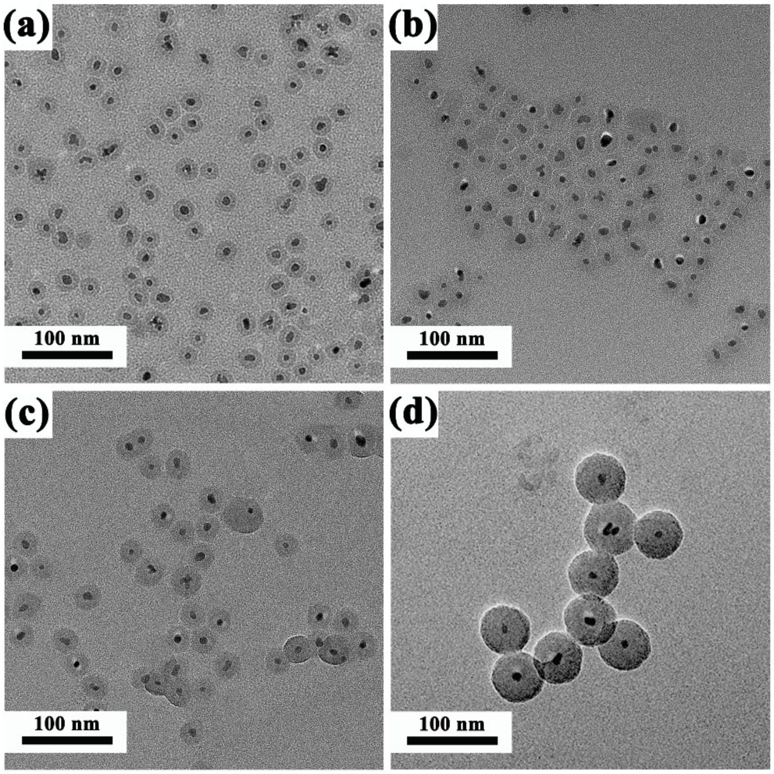


Figure S2. TEM images of ITO/SiO_2 NCs with various thickness of silica shells. (a) 6, (b) 9, (c) 16 and (d) 25 nm.

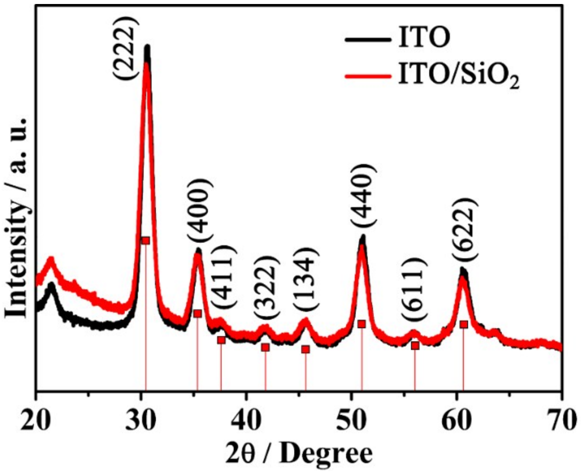


Figure S3. XRD of ITO (black) and ITO/SiO$_2$ NCs (red

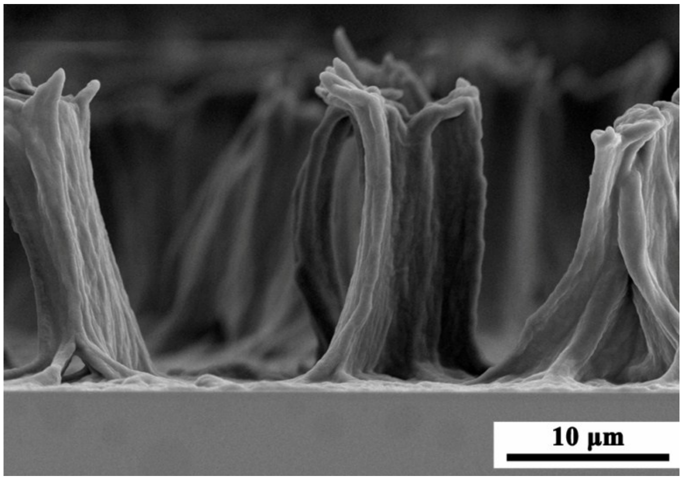


Figure S4. SEM image of the polymer network within the PSLC film

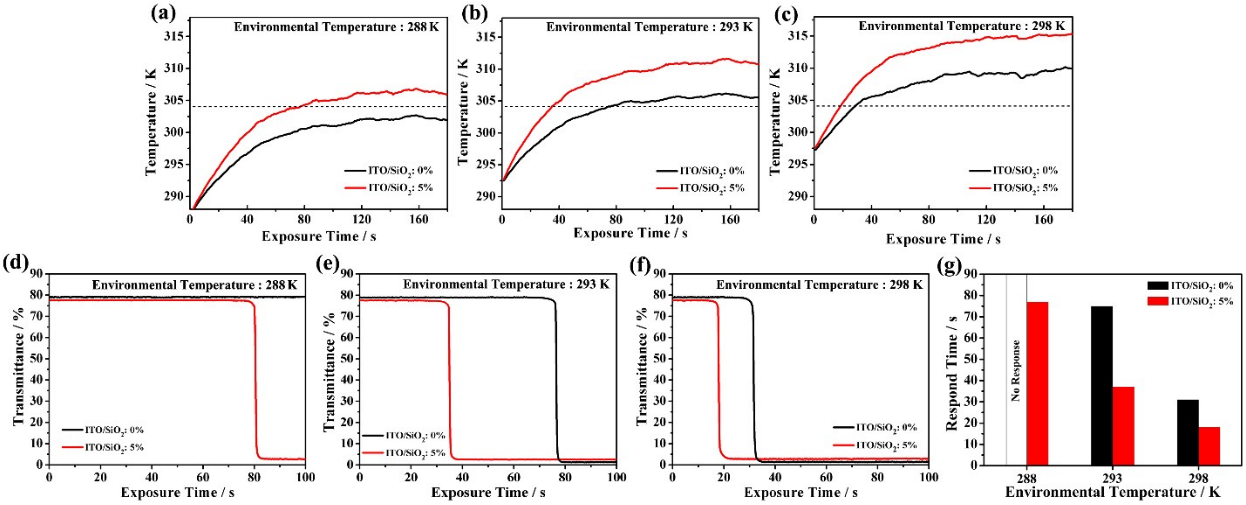


Figure S5. Temperature variations of the films with 5% (red line) and without (black line) ITO/SiO_2 NCs during the exposure at the environmental temperature of (a) 288 K, (b) 293 K and (c) 298 K, respectively. Transmittances of the films at 550 nm with 5% (red line) and without (black line) ITO/SiO_2 NCs during the exposure at the environmental temperature of (d) 288 K, (e) 293 K and (f) 298 K, respectively. (g) Summarized response time of the films during the exposure at the environmental temperature of 288 K, 293 K and 298 K, respectively. Here, the response time is defined as the time required for the film to turn from transparent to opaque states.

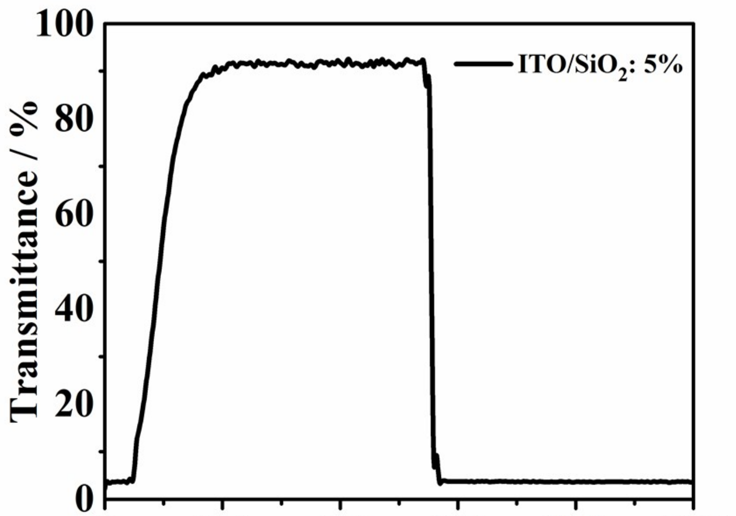


Figure S6. Electro-optical response of the smart film containing 5%wt ITO/SiO_2.

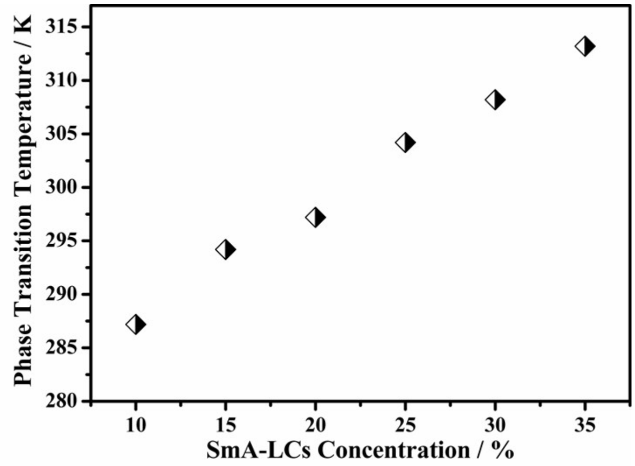


Figure S7. Phase transition temperature changes in LCs with a SmA~N* phase transition as a function of SmA-LCs concentration.

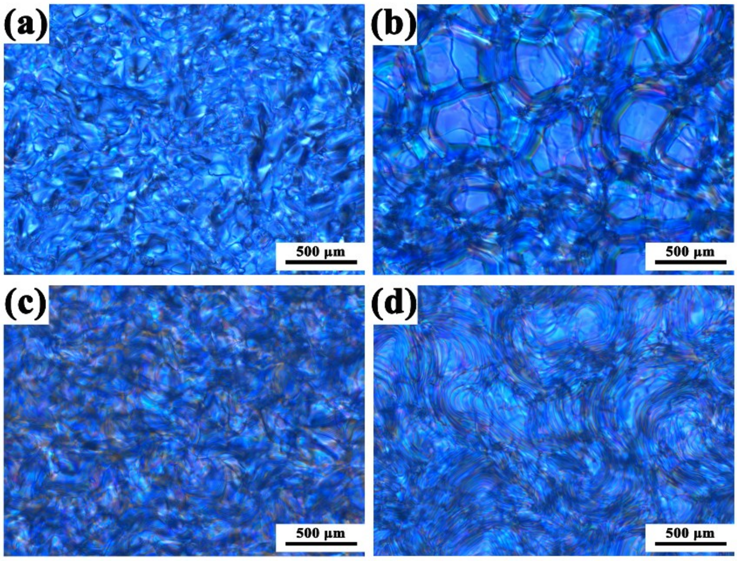


Figure S8. POM images of the textures of the LCs (a) in the SmA phase at 302 K, (b) in the N* phase at 308 K, (c) transition from SmA to N* phase during the heating process and (d) transition from N* to SmA phase during the cooling process.

References

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3 J. Lee, S. Lee, G. Li, M. A. Petruska, D. C. Paine and S. Sun, *J. Am. Chem. Soc.*, 2012, **134**, 13410-13414.

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