Liquid Crystalline Nanocolloids for the Storage of Electro-Optic **Responsive Images**

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Supporting Information

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ABSTRACT: Liquid crystalline nanocolloids (LCNCs), which are nanostructured composites comprising nanoparticles (NPs) and a liquid crystal (LC) host, have attracted a great deal of attention because of their promising new fundamental physical behaviors and functional properties. Yet, it still remains a big challenge to pattern LCNCs into mesoscale-ordered structures due to the limited NP loading in the LC host. Here, we demonstrate LCNCs in the nematic phase with a high NP loading (~42 wt %) by in situ cofunctionalizing the NP with alkyl and mesogenic ligands. The LCNCs can be assembled into ordered structures through holographic photopolymerization-induced phase separation,



giving rise to holographic polymer-dispersed nematic nanocolloids (HPDNNC). Interestingly, high diffraction efficiency, low light-scattering loss, and unique electric-switchable capability are realized in the HPDNNC. In addition, high-quality switchable and unclonable colored images are reconstructed, promising a host of advanced applications (e.g., anticounterfeiting). Our findings pave a way to advance the fundamental understanding of nanostructured LCs and their practical utility in enabling a new breed of inorganic-organic composite materials.

KEYWORDS: holography, nanocolloid, liquid crystal, self-assembly, confinement

1. INTRODUCTION

Dispersion of colloidal particles in a nematic liquid crystal (LC) host has led to rich fundamental physical observations, such as elasticity-mediated multipolar colloidal interactions, templating,² and stabilization of particle-induced topological defects.³ Nematic nanocolloids (NNCs), formed by dispersing nanoparticles (NPs) in a nematic LC host, offer a useful platform for harnessing the synergistic interplay of anisotropic LCs with nanomaterials. $^{4-13}$ Thus, they promise advancing the fundamental LC nanoscience and technological applications. For example, triclinic colloidal assemblies with the lowest symmetry,⁴ three-dimensional (3D) knotted topological solitons,⁵ fluid colloidal ferromagnets,⁶ electrically tunable anisotropic luminescence, and polarization-dependent surface plasmonic resonance have been reported.⁷⁻¹⁰ However, it still remains a big challenge to form stable NNCs with high inorganic NP loading due to the poor miscibility. This challenge further hinders efforts to pattern NNCs into mesoscale-ordered structures. In the regime of several nanometer colloidal particles within the nematic host, mesogenic functionalization of NPs represents an effective way to reduce the mismatch of solubility parameters between NPs and an LC host.¹³⁻¹⁹ Yet, 100% mesogen functionalization fails to enable stable NNCs with a high NP loading. Usually, only 3 wt % NP loading can be achieved on the basis of 100% mesogenic functionalization.¹⁹ Mehl and co-workers have found that the Au NPs co-functionalized with both mesogen and hexylthiol groups are completely miscible with the corresponding mesogen.²⁰ Herein, we demonstrate a robust protocol to form concentrated (~42 wt %) but stable NNCs by in situ co-functionalizing the NPs with mesogenic and alkyl ligands. Although the co-functionalization approach has been identified as a promising route toward stable NNCs theoretically and experimentally,^{21–23} these NNCs with such a

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Scheme 1. Synthesis Route for 8OCBSH



high NP loading are rarely reported. Such in situ cofunctionalization enables a nematic phase in colloidal NPs and the solubility match between the inorganic NPs and organic LC host. Notably, neither sole alkyl functionalization nor pure mesogenic functionalization leads to the formation of a nematic LC phase in NPs. Stable NNCs are then controllably assembled into ordered structures through laser holography, yielding a new type of optical functional materials with alternating polymer-rich and NNC-rich phases, e.g., holographic polymer-dispersed nematic nanocolloids (HPDNNC).

Holography²⁴ is a powerful top-down technique capable of aligning LCs or NPs into ordered structures. One typical approach is holographic photopolymerization-induced phase separation, where photoreactive monomers polymerize in the bright (constructive interference) regions, whereas photoinert parts (LCs or NPs) are squeezed into the dark (destructive interference) regions. Because of the well-designed periodic structures with alternative refractive indices, high diffraction efficiency holograms can be readily realized for colored 3D image storage,^{25–27} rainbow display,²⁸ and other applications. Holograms with LCs exhibit unique electro-optic responses and high diffraction efficiency. Typical examples are holographic polymer-dispersed LCs (HPDLCs) and polymer LC polymer slices (POLICRYPS).^{29–34} Nevertheless, these holograms usually suffer from a significant light-scattering loss due to the formation of relatively large LC droplets. On the other hand, high-performance polymer-based holograms are also readily achieved with high-refractive-index NPs (e.g., ZnS, TiO₂).^{27,35} Nevertheless, these holograms with NPs only typically lack electro-optic response capability. Incorporation of inorganic NPs into HPDLCs represents a promising way to "break through the bottleneck",^{36–38} where partial replacement of the LC by high-refractive-index NPs within the destructive regions is critical. Yet, bare inorganic NPs are found to primarily aggregate in the destructive (LC-rich) regions, hindering realization of facile responses to electric fields and other external stimuli. On the other hand, traditional organic functionalized NPs tend to stay in the constructive regions rather than the predesigned destructive regions.^{37,38} This set of circumstances pose a challenge of developing holograms with facile electro-optic response capabilities and low lightscattering losses.

In this report, through affording a nematic phase in NPs via in situ co-functionalization, we enable concentrated NNCs and employ the HPDNNC strategy to reduce the light-scattering losses while enabling facile electro-optic responses of holo-

grams. The nematic inorganic NPs act as nucleation centers allowing one to reduce the LC droplet size. Owing to the strong interaction between nematic NPs and an LC host within the NNCs, the nematic inorganic NPs are found uniformly distributed within the destructive regions of HPDNNC. The high diffraction efficiency of holograms requires maintaining a high refractive index contrast between the constructive and destructive regions, which we achieve using nematic zinc sulfide (namely, LC-ZnS) NPs to boost the effective refractive index of the NNCs. ZnS NPs are selected as the nematicforming NPs because of their high refractive index,^{39,40} good transparency in the visible region, low cost of raw precursors, and ease of scalable synthesis.^{27,39} The demonstrated HPDNNC affords ~67% lower light-scattering loss than HPDLCs while maintaining a high diffraction efficiency of 90% along with the electro-optic response capability, which may enable a host of advanced applications (e.g., anticounterfeiting).

2. EXPERIMENTAL SECTION

2.1. Materials. 4'-Hydroxybiphenyl-4-carbonitrile, 1,8-dibromooctane, potassium carbonate, thiourea, hexylthiol, zinc acetate dihydrate, glacial acetic acid, petroleum ether, *N*,*N*-dimethylformamide (DMF), ethanol, and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd., China. *N*,*N*-Dimethylacrylamide (DMAA) was purchased from J&K Scientific. Hyperbranched acrylate monomer 6361-100 was donated by Eternal Chemical Co., Ltd., China. 3,3'-Carbonylbis(7-diethylaminocoumarin) (KCD) and *N*-phenylglycine (NPG) were received from Aldrich and Aladdin, respectively. The room-temperature nematic LC in the brand of P0616A [$n_{e(589 nm, 20 °C)} = 1.72$, $n_{o(589 nm, 20 °C)} = 1.52$] was obtained from Shijiazhuang Chengzhi Yonghua Display Material Co., Ltd., China.

2.2. Synthesis of the LC Ligand 4'-(8-Mercaptooctyloxy)biphenyl-4-carbonitrile (80CBSH). 80CBSH was synthesized in three steps (Scheme 1).^{22,41,42} The procedure to prepare the compound 1 was as follows: 4'-Hydroxybiphenyl-4-carbonitrile (0.39 g, 2.00 mmol), 1,8-dibromooctane (4.35 g, 16.00 mmol), and K_2CO_3 (2.15 g, 15.60 mmol) were placed in a three-neck roundbottom flask fitted with a condenser. After purging argon gas for 30 min, 28 mL of dry acetone was added through a cannula. The resulting suspension was stirred at 60 °C for 21 h and then filtered when hot. The filtrate was concentrated by rotary evaporation. Finally, warm petroleum ether was added to the concentrated residue to wash the product. The resulting precipitate after washing was separated by filtration and purified via recrystallization from hot ethanol (yield: 50%).

Synthesis of the compound 2: A solution of the compound 1 (0.385 g, 1 mmol) and thiourea (0.175 g, 2.3 mmol) was refluxed in 16 mL of ethanol under the protection of nitrogen gas at 80 $^{\circ}$ C for 21

Scheme 2. One-Pot Synthesis Route for the LC-ZnS (8OCBSH/C₆H₁₃SH@ZnS) NPs



h. Subsequently, the solution was cooled down to room temperature. The generated solids were separated by filtration and recrystallization from hot ethanol. The resulting salts were used for the next step reaction without further purification.

Synthesis of the compound 3 (i.e., 80CBSH): The compound 2 (0.450 g, 1.00 mmol) and KOH (0.073 g, 1.30 mmol) were dissolved in about 27 mL of an ethanol/water (1:3 in volume) solvent. The mixture was stirred at 80 °C for 7 h under the protection of nitrogen gas. The resulting mixture was cooled down to room temperature and then acidified with glacial acetic acid (pH = 4). After removing the solvent under vacuum, the residue was dissolved in deionized water and extracted with chloroform $(3 \times 100 \text{ mL})$. The chloroform phase was separated, dried by CaCl₂, and concentrated under reduced pressure. The resulting white powder was chromatographed using a silica-gel column. Dichloromethane/hexane (1:1 by volume) was used as the eluent. The separated solution with the product was concentrated, giving rise to white crystals (yield: 40%). The chemical structure of 8OCBSH was characterized by nuclear magnetic resonance (NMR), Fourier transform infrared (FT-IR), and Raman spectroscopies.

2.3. Density Measurement. The density was determined by the Excellence XP/XS analytical balance (XS105DU, Mettler-Toledo). The chemical was weighed in air and then in water. The density was calculated from the two measured values as follows

$$\rho = \frac{A}{A-B}(\rho_{\rm w} - \rho_{\rm a}) + \rho_{\rm a} \tag{1}$$

where A and B are the weights of the sample measured in air and water, respectively. $\rho_{\rm w}$ and $\rho_{\rm a}$ are the densities of water and air, respectively.

2.4. Synthesis of LC-ZnS NPs. The LC-ZnS NPs (i.e., 8OCBSH/C₆H₁₃SH@ZnS) were synthesized using a one-pot procedure (Scheme 2). Zinc acetate dihydrate (16.1 g, 0.073 mol), thiourea (4.7 g, 0.062 mol), hexylthiol (3.0 g, 0.025 mol), and 8OCBSH (4.0 g, 0.012 mol) were added into a three-neck roundbottom flask equipped with a condenser. The mixture was then refluxed at 155 °C in 150 mL of DMF for 5 h. A continuous nitrogen gas purge was exerted to protect the reaction. The resulting suspension was concentrated under reduced pressure. Subsequently, the LC-ZnS NPs were obtained by precipitating in 300 mL of ethanol. The LC-ZnS NPs were further isolated by centrifugation (5000 rpm, 5 min) using a common centrifuge (Hunan Xiangyi Laboratory Instrument Development Co. Ltd., China. Rotor radius: ~6 cm). Purification was implemented by precipitating the product in ethanol (thrice), methanol (twice), and *n*-hexane/dichloromethane mixture (twice). After each precipitation, the solid was concentrated by centrifugation (5000 rpm, 5 min). The final product was dried under vacuum at 40 °C for 24 h and then kept at room temperature (yield: 10.8 g).

2.5. Transmission Electron Microscopy (TEM) Characterization of LC-ZnS NPs. To prepare the sample for TEM investigation, LC-ZnS NPs were homogeneously dispersed in DMF and then dropped on a copper grid. Subsequently, they were dried by near-infrared heating. High-resolution TEM characterization was implemented on a 300 kV Titan probe-corrected transmission electron microscope.

2.6. Refractive Index of the LC-ZnS NPs. The refractive index was measured using an ME-L ellipsometer (Wuhan Eoptics Technology Co., China). For characterization, a series of optical films were formulated by loading these LC-ZnS NPs uniformly in the cross-linked poly(acrylate-*co*-acrylamide). Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) was used as the photo-initiator when preparing the optical films.

2.7. Polarized Optical Microscopy (POM). To characterize the LC textures, a polarized optical microscope (Zeiss AX10) with a heating plate was employed. Before measurement, the LC-ZnS NPs were precipitated from DMF by methanol and then deposited on a glass slide. Pictures were taken after removing the solvent.

2.8. Preparation of NNCs Composed of LC-ZnS NPs and P0616A. The NNCs were formed by dispersing LC-ZnS NPs in an LC host (e.g., P0616A). In detail, LC-ZnS NPs were added into P0616A and then ultrasonicated at room temperature for about 1 h. No co-solvent was required to promote the dispersion. Since we assumed the primary location of LC-ZnS NPs in the destructive (LC-rich) regions within the holographic gratings, the total loading of LC-ZnS NPs and P0616A was considered to be 33 wt % according to our previous optimization.^{26,43,44} Subsequently, the weight ratios of LC-ZnS NPs to P0616A were controlled to be 0/33, 3/30, 6/27, 9/24, and 12/21.

2.9. Preparation of Mixtures for Holography. To prepare the mixtures for holography, the NNCs (LC-ZnS NPs/P0616A) with varied mass ratios were added into the monomer mixtures (DMAA/ 6361-100) in capped brown vials (Table 1 and Scheme 3).

Table 1. Chemical Components for Holography (by Weight Percentage)^a

entry	LC-ZnS	P0616A	DMAA	6361-100
1	0.0	33.0	44.7	22.3
2	3.0	30.0	44.7	22.3
3	6.0	27.0	44.7	22.3
4	9.0	24.0	44.7	22.3
5	12.0	21.0	44.7	22.3

^aThe KCD and NPG concentrations were set as 0.6 and 1.3 wt % of the total mass of monomers (DMAA and 6361-100), LC (P0616A), and LC-ZnS NPs, respectively.

Subsequently, common bulk ultrasonication was conducted at 30 °C for 30 min to obtain homogeneous mixtures. Potential ligand decomposition⁴⁵ or ligand exchange reactions^{20,22,46} were avoided under such relatively mild conditions. Then, 0.6 wt % KCD and 1.3 wt % NPG were added into the aforementioned mixtures, followed by another 10 min of bulk ultrasonication in dark.

2.10. Viscosity Measurement. Viscosities of holographic mixtures were characterized using a rheometer (MCR 302, Anton-Paar). The holographic mixtures were injected into two parallel

Scheme 3. Chemical Structures of P0616A, DMAA, and 6361-100



Figure 1. (a) Schematic illustration of the chemical structure of LC-ZnS NPs, i.e., $8OCBSH/C_6H_{13}SH@ZnS$. (b) TEM image of the as-synthesized LC-ZnS NPs (indicated by dashed yellow circles). The size of the inorganic crystalline core is 3-5 nm. The measured lattice spacing of 0.31 nm is ascribed to the (111) lattice plane of cubic ZnS. (c) Electron diffraction patterns of the LC-ZnS NPs, suggesting the characteristic (111), (220), and (311) lattice planes of cubic ZnS.

circular plates with a diameter of 25 mm. The gap between the two plates was set as 0.2 mm, and the shear rate was set from 0 to 100 s^{-1} .

2.11. Photopolymerization Kinetics. A photodifferential scanning calorimeter (P-DSC, Q2000, TA Instruments) was used to investigate the photopolymerization kinetics. Approximately, 10 mg of holographic mixtures were added using a micropipette into an aluminum pan, and then, the pan was placed onto the DSC sample holder. Another empty pan was placed onto the reference holder. After being purged by nitrogen gas at a rate of 50 mL/min and kept isothermal at 30 °C for 5 min, the two aluminum pans were simultaneously irradiated from the top by two independent monochromatic 442 nm light beams. The irradiation was exerted isothermally for 20 min. The light intensities were varied from 1.0 to 5.0 mW/cm² for each beam. The exothermal heat flow during photoreaction as a function of irradiation time was recorded during characterization, which was used to calculate the photopolymerization rate (R_p) and double-bond conversion (α), as previously reported.

2.12. Photorheology. The rotational rheometer (MCR 302, Anton-Paar) was used to measure the photorheology behavior of holographic mixtures upon flood exposures. The rheometer was equipped with two parallel circular plates (diameter: 25 mm), wherein the bottom plate was a transparent polyester allowing light transmission. During measurement, the temperature, strain amplitude, angular frequency, and gap between the two plates were optimized to be 25 °C, 15%, 10 rad/s, and 0.1 mm, respectively. Samples were sheared for 1 min prior to reaction and then isothermally exposed to a monochromatic 442 nm light with intensities ranging from 1.0 to 5.0 mW/cm². The measurement was implemented under the protection of purged nitrogen gas at a rate of 50 mL/min. The storage and loss moduli were simultaneously recorded, and their crossover was considered as the gelation point.^{26,47,48}

2.13. Holographic Recording. To fabricate holographic transmission gratings, glass cells with a gap of 12 μ m were constructed using two indium-tin-oxide (ITO)-coated glass plates. Holographic mixtures were introduced into glass cells by capillary action. To exert a holographic recording, a splitter was used to divide the incident 460 nm laser beam into two separate beams with an equal intensity (from 1.0 to 5.0 mW/cm² for each beam). These two equal-intensity light beams simultaneously irradiated the samples to reconstruct holographic gratings. For recording nonslanted transmission gratings, the angle bisector of these two beams was controlled to be normal to the cell surface. Finally, the generated holograms were solidified upon flood exposure to UV irradiation for 5 min.

2.14. Electro-Optic Response Characterization. Gratings were nondestructively probed at the Bragg angle for measuring the diffraction efficiency. The probed beam was a 2 W p-polarized 633 nm laser with high collimation (Thorlabs). The diffraction efficiency was defined as the ratio of the first-order diffraction intensity to the total intensities of the diffraction and transmission beams at the Bragg angle. Electro-optic properties of the holographic gratings were measured by an LCT-S016C display parameter tester (North LC Engineering Research and Development Center, China). A square wave alternative current (AC) voltage with a peak-to-peak amplitude of 240 V (frequency: 1 kHz) was applied to switch the gratings. Five independent samples were characterized to give the average value and standard deviation.

2.15. Morphology Characterization of Holographic Gratings. The glass cells with gratings were soaked in *n*-hexane for more than 48 h to fully remove the LC from the gratings. After being dried in air, the surface topology of transmission gratings was investigated by atomic force microscopy (AFM, Shimadzu SPM-9700) in the tapping mode with a resonant frequency of 300 kHz.



Figure 2. (a) Powder XRD pattern of the as-prepared LC-ZnS NPs, indicating the cubic crystal structure of ZnS NPs (measured by Smart Lab-SE XRD). (b) UV-vis absorption spectrum of the LC-ZnS NPs dispersed in DMF, indicating that the NPs will display no side effect on the photon absorption of sensitizers during the fabrication of holographic gratings using visible lasers.



Figure 3. TGA curves of the (a) LC-ZnS NPs (i.e., $8OCBSH/C_6H_{13}SH@ZnS$), (b) 8OCBSH@ZnS, and (c) $C_6H_{13}SH@ZnS$. 66%, 83%, and 66% in the figures indicate the weight fractions of inorganic ZnS core. Measurements were implemented on PerkinElmer TGA 400 at a ramp rate of 20 °C/min.

3. RESULTS AND DISCUSSION

3.1. Morphology, Crystal Structure, and Visible Transparency of LC-ZnS NPs. NNCs are formed by homogeneously dispersing NPs in a nematic LC host. To generate nematic-forming ZnS NPs (e.g., LC-ZnS NPs, Figure 1a), we first synthesized a mesogenic ligand 80CBSH Scheme 1 in the Experimental Section, Figures S1-S4 in the Supporting Information (SI)]. LC-ZnS NPs were then prepared through a one-pot facile reaction (Scheme 2 in the Experimental Section).^{39,40} Organic ligands of 8OCBSH and hexylthiol (C₆H₁₃SH) were employed to in situ co-functionalize the ZnS NPs (Figure S5 in the SI), enhancing the formation of the nematic phase of NPs.^{20,46,49,50} Highresolution TEM images clearly demonstrate the successful synthesis of crystalline LC-ZnS NPs (diameter: 3-5 nm, Figure 1b). A lattice spacing of 0.31 nm is clear in the TEM image, corresponding to the (111) lattice plane of cubic ZnS. Electron diffraction patterns are clear for these LC-ZnS NPs under TEM investigation (Figure 1c), suggesting the characteristic (111), (220), and (311) lattice planes of cubic ZnS.^{40,51}

The powder X-ray diffraction (XRD) pattern displays four dominant peaks at 2θ values of 2.7, 28.5, 47.7, and 56.4° (Figure 2a). The last three wide-angle diffraction peaks are attributed to the characteristic (111), (220), and (311) crystal planes of the cubic ZnS with lattice spacings of 0.31, 0.19 and 0.16 nm, respectively.^{27,39} These diffraction peaks are in good agreement with the standard pattern of JCPDS card no. 05-0566 and with the diffraction peak at a 2θ value of 2.7° is attributed to the characteristic separation between NPs,⁴⁰ which implies a diameter of 3.3 nm for the LC-ZnS nanocrystallite. This small-angle diffraction peak is also observed in the non-LC ligand-coated NPs.⁴⁰ The measured nanocrystallite size is in good agreement with that determined by TEM investigation (Figure 1b). In addition, nanocrystallite size, $D_{\rm NP}$, is estimated to be 4 nm according to the Debye–Scherrer formula⁴⁰

$$D_{\rm NP} = 4/3L = 4/3 \times 0.9\lambda/(B\cos\theta) \tag{2}$$

where *L* is the coherent length, λ is the irradiated wavelength of the probed X-ray (~1.54 Å), *B* represents the full width at half-maximum of the XRD peak (unit: rad), and θ is the Bragg angle of diffraction. Slight variations are common when measuring the nanocrystallite size with different methods.⁴⁰ Because of the tiny size (e.g., much smaller than the visible wavelength), light scattering is suppressed for the LC-ZnS NPs when dispersed in a good medium. The UV–vis absorption of LC-ZnS NPs is dominant in the wavelength ranges smaller than 350 nm (Figure 2b), which is good agreement with Sarma's work⁴⁰ and Cheng's work⁵¹ and will show no side effect on the visible laser holography.

3.2. Ligand Density on the NP Surface. To determine the ligand density on the NP surface, thermogravimetric analysis (TGA) was conducted. The LC-ZnS NPs (i.e., $8OCBSH/C_6H_{13}SH@ZnS$) are stable upon heating up to 230 °C (Figure 3a) and give rise to 66 wt % residue when heated to 424 °C. Thus, the organic ligand content is calculated to be 34 wt %. Combined with the elemental analysis (see the SI), the ligand density on the surface of LC-ZnS NPs is calculated to be approximately 2.0 ligands/nm² for

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8OCBSH and 1.4 ligands/nm² for C₆H₁₃SH (see the SI), regardless of their precursors' ratio. The ligand mole ratio of 1.4 is in good agreement with those in previous reports (ligand ratio: 1.0-1.3) when co-functionalizing gold NPs with mesogenic and alkylthiol ligands.^{15,20,50} In contrast, distinct 1.0 and 7.3 ligands/nm² are calculated for the pure 8OCBSH and pure C₆H₁₃SH, respectively, on the basis of the organic ligand contents of 17 and 34 wt % (Figure 3b,c). In general, ligand densities ranging from ~1 to 6.3 ligands/nm² have been reported.^{18,50} Thus, all calculated ligand densities in our study are reasonable considering the steric effect.

3.3. Refractive Index of LC-ZnS NPs. The refractive index of LC-ZnS NPs is experimentally predicted to be 1.77 (Figure 4), according to the linear relation between the



Figure 4. Refractive index of the optical polymer nanocomposites vs LC-ZnS NP content. The pristine polymer was the cross-linked copolymer of acrylamide (DMAA) and acrylate (6361-100). In practice, because of the limitation due to the maximum packing fraction for hard spheres, the volume fraction of ZnS cannot go to 100% in a bulk solid.

refractive index and volume fraction of NPs within a uniform polymer nanocomposite film.³⁹ Theoretically, the refractive index (n) of the LC-ZnS NPs can be estimated using the following equation²⁷

$$n = \sum n_i V_i \tag{3}$$

where V_i and n_i are the volume fraction and refractive index for each component *i*, respectively. The volume fractions of pure cubic ZnS NPs, 80CBSH, and hexylthiol in one LC-ZnS NP are calculated to be 29.2, 56.2, and 14.6%, respectively, according to their weight fractions and densities. The densities of ZnS, 80CBSH, and hexylthiol are 4.10,²⁷ 0.88, and 0.84 g/ cm³, respectively. The refractive index of the pure cubic ZnS NPs is reported to be 2.40,^{27,39} which is much higher than those of 80CBSH (1.57) and hexylthiol (1.45).⁵² Thus, the refractive index of LC-ZnS NPs is theoretically calculated to be 1.79. It is clear that the experimentally determined refractive index (1.77) is in quantitative agreement with the theoretical value.

3.4. Nematic Phase of LC-ZnS NPs. The LC-ZnS NPs exhibit a biphasic region with orientational LC ordering. The nematic LC phase is evidenced by polarizing optical micrographs with Maltese crosses, formed by dark and bright textural brushes (Figure 5), owing to the defects and birefringence of the NPs self-assembled into the mesophase material. In addition, the nematic phase is weakened when maintained at 170 °C for 1 h (Figure 6). The remaining dark tactoidal region



Figure 5. (a) POM image of the LC-ZnS NPs. The micrograph with asymmetric Maltese crosses and dark tactoidal disordered regions indicates that the material is in a biphasic state with nematiclike ordering. (b) Schematic illustration of the self-assembled LC-ZnS NPs that exhibit a nematiclike organization (not to scale).

upon heating indicates the biphasic characteristic. However, the nematic-isotropic phase-transition peak is not well pronounced in DSC (Figure S6 in the SI), which might be due to the biphasic nature and hybrid composition of the LC-ZnS NPs with strong nanoscale confinement of mesogenic moieties between NPs.

3.5. Formulation of Stable NNCs. Concentrated but stable NNCs are formed by dispersing the LC-ZnS NPs in the nematic LC host (e.g., P0616A), with a high loading of ~42 wt % (Figure S7 in the SI). This is realized due to the co-functionalization of NPs with both 80CBSH and $C_6H_{13}SH$ ligands. Mehl and co-workers have found that the mesogenand hexylthiol-co-functionalized Au NPs are highly miscible with the corresponding mesogen,²⁰ supporting our rational design on the concentrated NNCs with a high refractive index.

Interestingly, a severe precipitation is clear for the 100% 80CBSH- or hexylthiol-functionalized NPs (e.g., 80CBSH@ ZnS and C₆H₁₃SH@ZnS, respectively, Figure 7). Compared with the solubility parameters of 80CBSH@ZnS (21.7 J^{1/2}. cm^{-3/2}) and C₆H₁₃SH@ZnS (17.5 J^{1/2}·cm^{-3/2}),⁵² the LC-ZnS NPs with co-functionalized ligands (20.8 J^{1/2}·cm^{-3/2}) demonstrate good miscibility with the LC host (P0616A, 20.5 J^{1/2}. cm^{-3/2}). More pronounced precipitation is observed for 80CBSH@ZnS compared with that for C₆H₁₃SH@ZnS, presumably because of the lower content of organic ligands for the former (Figure 3). Interestingly, the LC-ZnS NPs show good miscibility with the monomer DMAA, whereas they are immiscible with *n*-hexane. The good miscibility of LC-ZnS NPs with both DMAA and P0616A is expected to afford homogeneous mixtures for holography.

3.6. Phase Behaviors of NNCs. NNCs (Figure 8a) with varied NP loadings show distinct textures. POM provides insights into the spatial variation of a director field in unaligned samples. Schlieren textures are clear at different volume fractions of NPs relative to that of a nematic host. Dark brushes reveal regions where the director is parallel to a crossed polarizer or analyzer. Since the optical anisotropy of the nanostructured nematic LC is positive, cyan-blue indicates the parallel alignment, whereas yellow shows perpendicular



Figure 6. POM images of the LC-ZnS NPs at (a) 25 °C and (b) 170 °C. The nematic phase is clear at low temperature. A high temperature of 170 °C for 1 h gives rise to an isotropic phase. The phase-transition process is reversible but quite slow because of the limited molecular mobility by the rigid ZnS core. The remaining dark tactoidal region upon heating indicates the biphasic characteristic.



Figure 7. Compatibility of NPs with the LC, monomer, and *n*-hexane. (a) LC-ZnS NPs (i.e., 80CBSH/ C_6H_{13} SH@ZnS NPs) in *n*-hexane; (b) LC-ZnS NPs in DMAA; (c) LC-ZnS NPs in P0616A; (d) 80CBSH@ZnS NPs in P0616A; and (e) C_6H_{13} SH@ZnS NPs in P0616A. Pictures were captured after sonicating the samples at 70 °C for 5 min. Results show that the co-functionalization of ZnS NPs with 80CBSH and C_6H_{13} SH facilitates the dispersion of ZnS NPs in the nematic host P0616A. However, the LC-ZnS NPs are incompatible with the solvent *n*-hexane.

alignment with respect to the slow axis of the microscope's phase retardation plate (inserted among crossed polarizers).⁵³ For the pristine nematic LCs, schlieren textures with fourarmed brushes are commonly observed (Figure 8b). The introduction of LC-ZnS NPs tends to manifest itself in the changes of appearance of textural defects and in slowed-down relaxation of the textures with defects and Maltese crosses (Figure 8c), resulting in considerably smaller textural grain dimensions. Nematic marbled textures are preserved when further increasing the mass ratio to 9/27 and 12/21 (Figure 8d). Generally, the introduction of LC-ZnS NPs results in the reduction of LC textural domain sizes, which might be due to the changes of elastic constants and viscosity associated with the NP content variations within the nematic host.

NNCs with varied NP loadings exhibit distinct phasetransition behaviors, in comparison with the pristine nematic host. With the increase of the LC-ZnS content in the nematic host P0616A, no significant change of the isotropic–nematic phase-transition temperature is observed (Figure S8 in the SI). However, the enthalpy of phase transition dramatically decreases to 1.36 J·g⁻¹ by 72.5% in comparison with that of the pristine host when the weight ratio of LC-ZnS NPs to P0616A increases from 0/33 to 12/21. The results indicate a strong confinement on the LC ordering by LC-ZnS NPs.

3.7. Holographic Patterning of NNCs. Stable NNCs allow for a holographic recording through photopolymerization-induced phase separation, giving rise to HPDNNC. To do this, the NNCs consisting of LC-ZnS NPs and P0616A were further mixed with photoreactive monomers. The photo-



Figure 8. (a) Schematic illustration of NNCs composed of LC-ZnS NPs and a nematic host. POM images of the (b) nematic host P0616A and NNCs with varied weight ratios of LC-ZnS NPs to P0616A: (c) 3/30, (d) 12/21 (i.e., 36 wt % LC-ZnS in the NNCs). Clearly, (b) four-armed brushes, (c) branches with nodes, and (d) marbled textures consecutively appear when increasing the LC-ZnS content.

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Figure 9. (a) Viscosities of holographic mixtures when varying the weight ratio of LC-ZnS NPs to the nematic host (P0616A). (b) Polymerization rate (R_p) as a function of double-bond conversion (α) upon exposure to a 442 nm light with an intensity of 3.0 mW·cm⁻². (c) Gelation time during photopolymerization upon exposure to a 442 nm light with an intensity of 3.0 mW·cm⁻². (d) Diffraction efficiency (η) of holographic gratings. These gratings were formed under the interference of two coherent laser beams in 460 nm with an intensity of 3.0 mW·cm⁻² for each beam. The recording time was 30 s. Diffraction efficiency was defined as the ratio of diffracted light intensity to the sum of diffracted and transmitted light intensities when characterized at the Bragg angle.

initibitor composed of 3,3'-carbonylbis(7-diethylaminocoumarin) (KCD) and N-phenylglycine (NPG) was employed to exert better control on the phase separation spatially and temporally due to the simultaneous initiation and inhibition functions.^{26,43} For the purpose of maintaining a high diffraction efficiency and facile electro-optic response capability while decreasing the light-scattering loss, it is critical to partially replace the LC by the high-refractive-index LC-ZnS NPs. Since we assume that the NNCs are primarily located in the destructive regions whereas the constructive regions are primarily formed by the polymer, we changed the mass ratio of LC-ZnS NPs to P0616A from 0/33 to 12/21 while fixing the monomer weight percentage at a constant value (Table 1). Such an experimental design is consistent with the NNC formulation change. The addition of NPs usually leads to an increase of fluidic viscosity.^{27,38}

As displayed in Figure 9a, a clear increase in viscosity is noted from 6.2 to 9.6 mPa·s when raising the weight ratio from 0/33 to 12/21. Higher viscosity is expected to result in slower component diffusion. As a consequence, the photopolymerization, which is implemented through the molecular collision between active radicals and monomers, is expected to be slowed down. Figure 9b shows that the maximum polymerization rate and overall double-bond conversion decrease by 22.0% (i.e., from 5.0×10^{-3} to 3.9×10^{-3} s⁻¹) and 32% (i.e., from 71 to 48%), respectively, in comparison with those of the pristine with an increase of the LC-ZnS content. The depressed photopolymerization gives rise to prolonged gelation by 47.6% (i.e., from 63 to 93 s) (Figure 9c). Nevertheless, the diffraction efficiency, η , which is defined as the ratio of diffraction intensity to the sum of diffraction and transmission intensities when probed at the Bragg angle, is maintained to be ~91% when the weight ratio is less than 6/27, whereas decreasing to 73 and 63% when further raising the LC-ZnS content (Figure 9d). Since prolonged gelation during photopolymerization usually leads to enhanced phase separation and improved grating diffraction efficiency (Figure S9 in the SI),^{25–27,38,43} such a diffraction efficiency decay at a relatively high loading concentration of LC-ZnS NPs might be primarily caused by the trapping of NPs in the growing polymer domains. It is worth mentioning that although the delayed gelation here is at the expense of lower conversions, flood cure is exerted after holographic recording to further consume the unreacted monomers, which ensures the practical stability of holograms.

Incorporation of LC-ZnS NPs is able to decrease the LC host order and thus to reduce the polarization dependence of grating diffraction efficiency (η). The η of HPDNNC can be described using the Kogelnik coupled-wave theory⁴⁴

$$\eta = \sin^2 \left[\frac{2f(n_{\text{Des}} - n_{\text{Cons}})\sin(\beta\pi)L}{\lambda_{\text{probe}}\cos \theta_{\text{B}}} \right]$$
(4)

where *f* represents the volume fraction of NNCs in the destructive regions. n_{Des} and n_{Cons} are the refractive indices of destructive and constructive regions, respectively. In addition, β is defined as the ratio of destructive region width to the grating period, *L* is the grating thickness, λ_{probe} is the probing wavelength, and θ_{B} represents the grating Bragg angle. Clearly, the diffraction efficiency would decrease if some high-refractive-index LC-ZnS NPs are trapped in the constructive regions because both the *f* and refractive index contrast (n_{Des} –



Figure 10. (a) Electro-optic response and (b) light-scattering loss of HPDLCs and HPDNNC with varied weight ratios of LC-ZnS NPs to P0616A. HPDLCs here represent these gratings without NPs. A square wave AC voltage with a peak-to-peak amplitude of 240 V (frequency: 1 kHz) was applied to switch the holographic gratings.



Figure 11. Normalized diffraction efficiency (η) vs applied voltage for the holographic gratings: (a) HPDNNC with 3 wt % LC-ZnS NPs and HPDLCs without NPs wherein the P0616A content was set as 30 wt %. (b) HPDNNC with 6 wt % LC-ZnS NPs and HPDLCs without NPs wherein the P0616A content was set as 27 wt %. A square wave AC voltage with a peak-to-peak amplitude of 240 V (frequency: 1 kHz) was applied to switch the holographic gratings.

 n_{Cons}) decrease. Interestingly, a HPDNNC with high diffraction efficiency can be achieved when increasing the holographic exposure time (Figure S10 in the SI), primarily due to the enhanced phase separation. In addition, the dependence of diffraction on polarization is weakened in the HPDNNC compared with that in HPDLCs due to the less order of NNCs (Figure S11 in the SI).

3.8. Electro-Optic Response of HPDNNC. The formed NNCs are envisioned to confine the electro-optic response and light-scattering loss of the LC. Similar to HPDLCs, the HPDNNC holds the capability of switching light diffraction upon an external electric stimulus. In turn, the electro-optic response behavior is able to reflect the interaction of NPs with the LC within the HPDNNC. As displayed in Figure 10a, when increasing the ratio of LC-ZnS NPs to P0616A, the driving voltage of holographic gratings increases. The driving voltage of LC-based holographic gratings is generally proportional to the low-frequency conductivity of destructive regions whereas inversely proportional to that of constructive regions.^{33,38,44} Thus, a higher driving voltage is expected when the LC-ZnS NPs are located in the destructive regions. This is reasonable because ZnS holds a semiconductor characteristic. In addition, the strong interfacial confinement of the LC by the LC-ZnS NPs within the destructive regions is expected to hinder the LC rotation and thus to increase the driving voltage. Because of the confinement achieved through the incorporation of LC-ZnS NPs, smaller phase-separated LC domains are observed and thus the formed HPDNNC is

expected to show a smaller light-scattering loss in comparison with HPDLCs. To confirm this, the light-scattering loss was calculated from the total probe light intensity and the sum of transmission, diffraction, and reflection intensities. When the weight ratio of LC-ZnS NPs to nematic host approaches 6/27, the light-scattering loss is found to be decreased from 12.7 \pm 2.7 to 5.3 \pm 1.8%, in comparison with HPDLCs (Figure 10b). Increasing further the content of LC-ZnS NPs leads to a slight change of the light-scattering loss. For practical applications, the HPDNNC with a weight ratio of 6/27 for LC-ZnS/ P0616A is optimal because the increment in driving voltage is relatively modest, whereas the light-scattering loss is dramatically decreased. The increment of driving voltage here is one evidence to confirm the formation of NNCs in holograms, where NPs are located in the destructive regions rather than in previously reported constructive regions.³⁸ The slightly higher driving voltage of HPDNNC in comparison with that of HPDLCs with the same LC loading also indicates the spatial location of LC-ZnS NPs in the destructive regions within the grating (Figure 11 and Table S1). Furthermore, the difference in switching becomes less pronounced when decreasing the LC content. The driving voltage can be further lowered down by mitigating the interface action through the deployment of previously reported techniques, 54-56 which is beyond the scope of this work.

3.9. Morphology of HPDNNC. The HPDNNC microstructure can be inspected after the LC removal. Holographic gratings were soaked in *n*-hexane for 2 days to separate the



Figure 12. Schematic illustration showing (a) HPDLCs and (b) HPDNNC. AFM images for (c) HPDLCs and (d) HPDNNC (weight ratio: 6/27 for LC-ZnS NPs to P0616A). The grating pitches are (c) 730 ± 42 nm and (d) 860 ± 48 nm, and the grating depths are (c) 141 ± 33 nm and (d) 143 ± 19 nm, respectively. The HPDNNC shows a decreased light scattering because of the LC-ZnS NP confinement on the LC host. Larger grating pitch indicates a less volume shrinkage in the HPDNNC.

Scheme 4. Illustration of Colored Image Storage in the HPDNNC



NNCs from the solid polymer film. The resulting liquid after soaking was investigated, and the result clearly shows that some LC-ZnS NPs were removed from the HPDNNC (Figure S12 in the SI). The LC-ZnS NPs are not expected to be extracted from the holographic polymer composites by *n*hexane due to their poor miscibility (Figure 7). Therefore, the extracted LC-ZnS NPs from the HPDNNC confirm the formation of NNCs in the HPDNNC. Differences between HPDLCs and HPDNNC are clearly illustrated in Figure 12a,b.

Our HPDNNC gratings show one-dimensional periodical structure. The regular channels in AFM images are clear for the LC-rich or NNC-rich regions because of the removal of LCs or NNCs by *n*-hexane. The increased grating pitch for the HPDNNC was achieved compared to that for HPDLCs, i.e., from 730 ± 42 to 860 ± 48 nm, whereas the grating depth did not change (Figure 12c,d). Such a grating pitch increase is ascribed to the decreased volumetric shrinkage when loading

rigid NPs.²⁷ Further increase of LC-ZnS/P0616A to 9/12 and 12/21 results in decreased grating depths to about 45 ± 7 and 33 ± 4 nm, respectively (Figure S13 in the SI). Partial NPs' trapping by the growing polymer in the constructive regions is expected to be the reason for the grating depth decrease, agreeing with the decreased diffraction efficiency in Figure 9. Clearly, for boosting the holographic performance, more LC-ZnS NPs are required to be localized within the destructive regions rather than in the constructive (polymer-rich) regions.

3.10. Colored Image Storage in HPDNNC. The high diffraction efficiency and low scattering loss of the HPDNNC allow for the fabrication of high-quality colored images. Interestingly, colored images can be reconstructed directly from 3D real objects by taking advantage of one biconvex mirror (Scheme 4). Typically, one coherent laser was split into two beams: one (reference beam) directly illuminated the recording material, whereas another (object beam) irradiated a



Figure 13. Colored images directly reconstructed in the HPDNNC with 6 wt % LC-ZnS NPs from 3D real objects of (a) brooch and (b, c) wrist watch.



Figure 14. Colored images captured from the movie with HPDNNC viewed at different angles.

real object and then reflected to the recording material after passing through the biconvex mirror. During the image reconstruction, the light intensities of the reference and object beams were set as 0.5 and 0.2 mW/cm², respectively. The recording time was 200 s. Images were eventually consolidated by post-UV flood cure.

Clear multicolor images are easily identifiable to the naked eye under day-light illumination (Figure 13). In general, the image color comes from light diffraction.^{25,26} Images are clear when the incident angle (the angle between the incident beam and the normal of the image plane) is within $15-70^{\circ}$. Distinct images and colors are shown at varied viewing angles (Figure 14 and Movie S1). No image is displayed at the transmission state where the incident beam is normal to the image plane (Figure S14 in the SI). Because of the unique features, such images are impractical to be copied using scanning or printing. In addition, these colored images can be partially electrically switched (Movie S2). Thus, these unclonable and electricswitchable colored images are promising for anticounterfeiting and other applications (e.g., advanced advertisements).

4. CONCLUSIONS

Uniform LC-ZnS NPs, which spontaneously exhibited a nematic phase under ambient conditions, were synthesized and optimized to boost the effective refractive index. This was achieved through in situ co-functionalization with 80CBSH and hexylthiol. Not only the nematic phase in LC-ZnS NPs was enabled but also the match of solubility parameter between NPs and LC host was reached, giving rise to NNCs with high NP loading in conventional nematic hosts. The formulated NNCs were spatially aligned into ordered structures via holographic photopolymerization-induced phase separation, affording a new HPDNNC with high refractive index of ZnS allowed partial replacement of the LC

by LC-ZnS NPs without sacrificing the refractive index contrast and diffraction efficiency of holograms. Loading of LC-ZnS NPs facilitated the formation of small LC domains so that the optical performance of holograms was boosted by depressing the light-scattering loss. Naked-eye-identifiable colored images were reconstructed in the HPDNNC directly from 3D real objects through a simple one-step protocol. The recorded unclonable and electric-switchable colored images show great potential to be applied in advanced applications (e.g., anticounterfeiting and advanced advertising). The proposed protocol for forming highly concentrated NNCs paves the way for further advancing the nanostructured LC nanocomposites.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b22636.

Determination of ligand density on the NP surface; added figures, tables, and references. Chemical components for holography in the control experiments (Table S1); ¹H NMR spectrum of the LC 8OCBSH (Figure S1); Fourier transform infrared (FT-IR) spectrum of the LC 8OCBSH (Figure S2); DSC curves of the LC 80CBSH during the second scanning (Figure S3); POM images of the LC 8OCBSH (Figure S4); ¹H NMR spectrum of the LC-ZnS NPs (Figure S5); DSC curves of the LC-ZnS NPs (Figure S6); compatibility of NPs with the LC host P0616A at a loading content of 42 wt % (Figure S7); DSC curves for the nematic nanocolloids (NNCs) composed of LC-ZnS NPs and P0616A with varied mass ratios of ZnS to P0616A (Figure S8); influence of light intensity from 1 to 5 mW \cdot cm⁻² on the photopolymerization kinetics, gelation behavior, and diffraction efficiency for the system with LC-ZnS NPs/ P0616A nanocolloids in a weight ratio of 6/27 (Figure S9); diffraction efficiency, η , vs exposure time for the system with LC-ZnS NPs/P0616A nanocolloids in a weight ratio of 6/27 upon 460 nm laser exposures with an intensity of 3.0 mW·cm⁻² for each of the two coherent beams (Figure S10); incident-angle-dependent diffraction efficiency of (a) HPDLCs and (b) HPDNNC (Figure S11); TEM image to show the removed LC-ZnS NPs from the holographic gratings by *n*-hexane (Figure S12); AFM surface morphology for the HPDNNC with varied weight ratios of LC-ZnS NPs to P0616A (Figure S13); colored images viewed at the (a) diffraction state and (b) transmission state, indicating the viewing-angle-sensitive characteristic of the recorded images in the HPDNNC (Figure S14) (PDF)

Viewing angle dependent display (AVI) Electric switchable display (AVI)

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Notes

The authors declare no competing financial interest.

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