Holographic polymer-dispersed liquid crystals (HPDLCs) have great promise for the facile fabrication of large-area electrically responsive optical elements. Through careful selection and design of the components, the liquid crystal, monomer, initiator, and various organic additives, the switching speed and other optical properties can be optimized for a given application. There are a number of limitations, however, to an all-organic system. For example, the refractive-index contrast between a typical liquid crystal and the polymer constituents of a PDLC is generally small. To circumvent this difficulty, it may be desirable to add inorganic materials that can span a much-larger range of refractive indices to tailor the periodic refractive-index profile. One of the simplest methodologies of introducing an inorganic material into HPDLC systems is through the controlled addition of nanoparticles. Nanoparticles of many materials can be synthesized in sizes small enough to avoid the addition of deleterious light scattering, and numerous surface-functionalization techniques are available to control the chemical interaction of the nanoparticles with the HPDLC system. Previous research has demonstrated that under holographic exposure of liquid-crystal-free systems containing monomers and nanoparticles, the nanoparticles tend to counter-diffuse away from the polymerizing regions, and are sequestered into the low-intensity regions. This has been demonstrated for Au, ZnO, SiO2, and TiO2 nanoparticles. In the case of oxide particles, sequestration in this domain is consistent with the presence of charged surface hydroxyls, causing the particles to be organophobic. However, for holographic photopolymerization to be of use as a generic manufacturing technique for holographic optical elements, it is necessary to be able to select and control where the majority of the nanoparticles will reside within the periodic structure. In particular, it is very important that the nanoparticles not be sequestered into the liquid-crystal phase, as they generally negatively impact the switching behavior. Here, we demonstrate the incorporation of high volume fractions of chemically functionalized silica nanoparticles into electrically switchable HPDLCs with sub-micrometer lattice constants, and show the importance of the nature of the chemical functionalization. SiO2 nanoparticles were selected primarily as a model system. Because the refractive index and low-frequency dielectric constant of silica is similar to the polymer matrix, we do not expect dramatic changes in switching behavior or optical properties due to the fundamental optical constants of the nanoparticles; we do, however, find that they change the phase-separation behavior and morphology of the phase-separated droplets, which does have a strong effect on the optical behavior. The general approach utilized here is illustrated schematically in Figure 1.

When unfunctionalized silica is added to a holographic system, it is expected the particles, in a manner analogous to previous works, will counter-diffuse away from the polymerizing regions. As represented in Figure 1b, upon macroscopic phase separation of the liquid crystal and polymer, the particles will coalesce with the liquid crystal in the low-intensity regions of the holographic pattern. In Figure 1c, the nanoparticles are functionalized with pentyltriethoxysilane (PTES). The presence of the alkyl chains render the nanoparticles hydrophobic, which should result in the particles being sequestered within the polymeric domain. However, we observe that the particles aggregate, probably because nanoparticle–polymer interactions are unfavorable with respect to polymer–polymer interactions. The entropy of mixing of polymeric and nanoparticle interactions is generally quite small, and thus even small unfavorable polymer–nanoparticle interactions can lead to nanoparticle aggregation into structures large enough to scatter light. In Figure 1d, the nanoparticles are functionalized with methacryloxypropyl-trimethoxysilane (MPTMS), which will covalently copolymerize with the acrylate monomer as the monomer
undergoes a photoinitiated free-radical polymerization. The nanoparticles then become covalently trapped in the polymer matrix and do not aggregate.

To test the efficacy of the model system, 20 nm SiO$_2$ nanoparticles created via a Stöber process with the previously discussed functionalizations are used. Both PTES and MPTMS covalent functionalizations were verified using $^{29}$Si NMR (Supporting Information, Sec. 1). The nanoparticles were added to holographic syrups containing an acrylate monomer, and then used to create reflection Bragg gratings. The resultant grating’s optical- and electrical-switching properties were characterized before microtoming sample cross-sections for transmission electron microscopy (TEM) analysis. A control syrup without nanoparticles was created as a baseline for comparison purposes. A cross-sectional TEM image of a grating without particles is shown in Figure 2a. The morphology displayed in the image is typical of acrylate-based HPDLC gratings, with irregularly shaped liquid-crystal droplets arranged in a periodic linear array.[$^{10}$] The remaining syrups were identical in composition to the control syrup, with the exception of 10 wt% of the monomer being replaced by an equal weight of the respective nanoparticles. Despite the presence of 10 wt% unfunctionalized nanoparticles in the starting syrup, the sample shown in Figure 2b appears to have few nanoparticles present, with the exception of an occasional small agglomeration of particles in the polymer-rich domain, as shown in the inset. This lack of particles is strongly indicative of the particles residing in the liquid-crystal domains of the sample. The sample containing PTES-functionalized nanoparticles (Fig. 2c) displays a significantly larger fraction of particles in the polymer-rich domain, but the nanoparticles are agglomerated. As seen in the TEM image, this undesirable agglomeration appears to significantly disrupt the periodic structure of the grating in areas localized around the particle agglomerations. For the gratings containing the MPTMS-functionalized nanoparticles, the cross-section shown in Figure 2d exhibits particles that are well dispersed throughout the polymer domain. Overall, when looking at the progression of liquid-crystal droplet morphology in the images in Figure 2, the presence of particles in the samples changes the structure from an irregular droplet structure to a more continuous lamellar structure resembling that observed in a different nanoparticle-free HPDLC system.[11] Evaluating the optical- and electrical-switching characteristics of these samples, as shown in Figure 3, yields an indication of the overall effect of adding high loadings of nanoparticles on the optical response of the HPDLC to an applied field. In Figure 3a, it can be seen that the diffraction efficiency of the control sample, as measured by the depth of the reflection notch, is 81%. The diffraction efficiency of the other films displayed in the figure, except for the film containing the PTES-functionalized nanoparticles, is the same within observed experimental variation, as expected because of
the similarity between the refractive index of the silica and the polymer. An optical refractometer was used to check the refractive index of the homogeneous holographic syrups, and the addition of nanoparticles only caused a change in refractive index of 0.005, confirming that there should be little change in diffraction efficiency due to the enhancement of index contrast. However, the film containing PTES-functionalized nanoparticles exhibited markedly degraded diffraction efficiency, indicating that observed distortion of the periodic structure is a macroscopic effect across the sample. It should be additionally noted that the background scattering is not significantly changed from the control sample to the samples containing the functionalized nanoparticles. The background falloff in the blue region of the sample is attributed to scattering from the liquid crystal and is present in all samples. Therefore, the addition of dispersed SiO$_2$ nanoparticles into the HPDLC system has little to no measurable effect on optical scattering, which is not surprising, given the small refractive-index difference between the nanoparticles and the polymer matrix.

While the MPTMS-functionalized nanoparticles are shown to be well dispersed in the polymer-rich domain in Figure 2d, the absence of the liquid crystal in the TEM image (it flows out of the cross section upon microtoming, leaving vacancies in the TEM cross-sections) prohibits the conclusion that the nanoparticles are sequestered in the polymer-rich domain. Closer examination of Figure 3b yields the interesting, and potentially technologically important, result that this sequestration drastically reduces the voltage necessary to switch the state of the grating, although further investigation is necessary to determine the precise mechanism by which this occurs.

A second unexplored area is the effect of nanoparticles on the morphology of the resultant holographic structures. A complete model will require the careful study of diffusion, gelation and polymerization kinetics as a function of nanoparticle volume fraction and surface coverage. We can, however, postulate that, in the case of MPTMS-functionalized particles, because the number of MPTMS molecules on a given nanoparticle is large, the probability of any given methacrylate group on the surface of the nanoparticle reacting with the polymerizing matrix is high, and that, given the large number of reactive sites per nanoparticle, the nanoparticles thus act as highly functional crosslinking agents. Previous works have shown an increasing degree of liquid-crystal phase separation when the degree of monomer functionality is increased.$^{[10,12]}$ It is speculated that in analogy to the previous cited works, the increase in crosslinking due to the reactive nanoparticles correspondingly increases the strength of the phase separation of the liquid crystal in the low-intensity region, resulting in a lamellar-like morphology. Careful examination of the liquid-crystal morphological changes in the TEM images in Figure 2 as a function of nanoparticle surface chemistry reveals that the liquid-crystal domains for the sample containing MPTMS-functionalized nanoparticles are significantly more distinct than for the other systems, supporting this conclusion. We can additionally posit that this lamellar morphology is responsible for the reduction in switching voltage for films containing MPTMS-functionalized nanoparticles sequestered in the polymer domain (Fig. 3). The lamellar morphology, as observed in Figure 2d, has a lower surface-to-volume ratio, thus reducing the field strength necessary to overcome effects such as liquid-crystal surface anchoring. While the PTES system also has a low switching voltage, the liquid-crystal domains are highly disordered, and the diffraction efficiency of this system is much lower than the control or MPTMS systems, thus a direct comparison to the MPTMS system is not appropriate.

The combination of the TEM image and the switching data strongly indicates that appropriate chemical functionalization enables control over where the nanoparticles reside within a HPDLC. The functionalized nanoparticles are sequestered in the polymer-rich domain, while the majority of the unfunctionalized nanoparticles are present in the liquid-crystal domain. Although these results are of a single system, they do suggest the feasibility of a more general scheme for directing the assembly of nanoparticles via externally applied optical fields. If the particle size approaches the periodicity of the holographic structure, particle alignment becomes possible (Supporting Information, Fig. S1). Although the work here only utilized a simple grating structure, the strength of this technique is that it can be used for arbitrarily complex 3D structures as long as the structure can be
created using holographic interferograms, and thus the technique can be generalized to a powerful tool for assembly of different types of particles into complex, designed structures on the sub-micrometer scale.

**Experimental**

Silica nanoparticles (20 nm diameter) were synthesized in ethanol using a modified Stober recipe [13]. All chemicals used to synthesize nanoparticles were used as received. In a 250 mL flask, 1.5 mL of deionized water and 3 mL of a 28% ammonium hydroxide solution (Alrich) were added to 120 mL of absolute ethanol and stirred vigorously for 30 min at room temperature using a magnetic stirring bar. 3 mL of tetraethoxysilane (TEOS, Gelasto) and 8.5 mL of H2O. A functionalizing agent, either 1 mL of methacryloxypropyl-trimethoxysilane (Gelasto) or 1.1 mL of pentyltriethoxy-silane (Gelasto), was added without modification to the unchanged basic monomer along with the stabilizer, ultrasonicated for 0.5 h to ensure adequate dispersion of the nanoparticles, then distilled with a rotary evaporator to remove the ethanol.

To create the holographic cell, the syrup was sandwiched between glass slides coated with a thin layer of indium tin oxide (ITO) and sealed at the edges with an epoxy adhesive. Bragg reflection gratings were created using a two-beam holographic system with the laser beams incident normal to the front and back cell surfaces. The laser used is a diode pumped solid-state Nd:YAG laser doubled to 532 nm (Coherent Verdi). For all experiments, the laser power was 50 mW at the sample. The samples were exposed for 60 s, followed by post-cures of 2 min each under a UV lamp and intense white light. After optical- and electrical-switching characterization, the samples were microtomed in 75 nm sections using a Leica ultramicrotome. TEM characterization was accomplished using a Philips CM200.

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