2.2.2. Procedure 2. Manufacturing of a hydrogel with Procedure 1 is tenable because the concentration of used CNCs (2−2.2 wt %) yields a suitably viscous sol that maintains an object's shape and director alignment during and after printing and before cross-linking. However, when printing with CNC concentrations less than 2.0 wt %, low viscosities diminish both an object's well-defined orientational ordering and its geometric stability as its precursor slowly collapses and flows under surface-tension and gravitational forces. Procedure 2 addresses these concerns by tuning the viscosity to an appropriate range (1−20 Pa s) before cross-linking so that precursors with CNC concentrations less than 2.0 wt % can be easily printed. While Procedure 1 limits GNRs and CNCs to co-axial alignment, Procedure 2 enables the tuning of guest−host alignment. As CNC concentrations increase up to 2.0 wt %, the following alignment regimes in hydrogels become practicable: (1) isotropic CNC and GNR organization, (2) nematic CNC and isotropic GNR organization, and (3) nematic CNC and GNR organization. We found that a gel precursor with a final CNC concentration of 0.76 wt % yielded a gel with the properties of (1) and, after evaporation over tens of minutes, the properties of (2). Condition (3) was realized at 1.0 wt % CNCs, though the critical concentration for differentiating (2) and (3) has not been determined (see the Supporting Information for optical characterization of these regimes).

To implement Procedure 2, the precursor is oligomerized before printing. Aqueous colloidal dispersions of CNCs and GNRs were mixed with AAm, Irgacure-2959, and TEMED and then were exposed to UV radiation to tune the sol's viscosity. The viscous sol with added cross-linker MBAA was printed, as depicted in Figure 2b. Subsequent cross-linking of PAM oligomers within the printed object occurred with UV exposure, as illustrated in Figure 2c. Because polymer chains

maintains the solid network's structural alignment and optical anisotropy present in both its hydrogel and alcogel states.

4. CONCLUSIONS

We have developed a plasmonic metamaterial whose guest–host optical interactions cause polarization-dependent extinction of incident light. Capitalizing on 3D printing, we have programmed spatially complex optical extinction behavior across the lateral extent of each printed layer. Moreover, we have shown that the direct-ink-writing 3D printing method enables macroscopic physical scaling in the lateral spatial extent and of the number of layers. Selective alignment and layering permit the formulator to tune the optical properties of the gel. By converting the printed hydrogel into an aerogel, the plasmonic resonances blueshift while the aerogel's selective extinction of polarized radiation suggests polarization-sensitive and ultralight material applications.[41] Our work propounds the usage of these composite gels as hosts for upconverting plasmonic nanoparticles, nanoantennas, or both. Mechanically and electrically coupled via elastic assembly, such novel guest particles could enhance both optical absorption by intrinsic plasmonic resonances and the resultant luminescence of higher-energy photonic signals.[42] We hypothesize that an additional possibility to extend this work would be to actuate the gels photomechanically by inclusion of azobenzene-surface-func-

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