Supporting Information for
Plasmonic Metamaterial Gels with Spatially Patterned Orientational Order via 3D Printing

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1. Preparation of Gold Nanorods (GNRs)

We synthesized the GNRs using a seed-mediated method. To prepare the seed solution, 0.1 mL of an aqueous 0.025 M solution of chloroauric acid (HAuCl₄·3H₂O, Sigma-Aldrich) was added to 10 mL of a 0.10 M cetyl trimethyl ammonium bromide (CTAB, Sigma-Aldrich) solution in a conical flask. The solution changed its color from clear to brown-yellow, indicating the formation of gold seeds, when 0.6 mL of an aqueous 0.01 M ice-cold sodium borohydride (Sigma-Aldrich) solution was added by vigorous stirring. Separately, the growth solution was prepared by mixing 5 mL of deionized (DI) water, 5 mL of 0.20 M CTAB, 0.200 mL of 0.025 M HAuCl₄·3H₂O, and 0.040 mL of 0.016 M silver nitrate solutions in a conical flask. Then 0.090 mL of 0.08 M ascorbic acid was added to the growth solution. Finally, 0.012 mL of seed solution was added to the growth solution. The combined solution was undisturbed at 27 °C for at least 10 h. Subsequently, it was centrifuged at 7.8 kRCF for 30 min. twice and re-dispersed in DI water to remove excess CTAB. Next, the GNRs were surface-functionalized by thiol-terminated methoxy-poly(ethylene glycol) (mPEG-SH, JemKem Technology) to minimize aggregations of the GNRs within aqueous lyotropic dispersions of CNCs in a sol-phase material. For this, 1 mL of aqueous solution with 30 mg of 5 kDa mPEG-SH was added to 50 mL of a diluted GNR dispersion with an optical density of 4. After standing for 24 h, this dispersion was purified via centrifugation to remove the excess mPEG-SH. The GNRs were then washed three times via centrifugation at 7.8 kRCF for 20 min. and redispersed into DI water for further usage.

2. Preparation of Cellulose Nanocrystals (CNCs)

Cellulose nanocrystals were synthesized via sulfuric-acid catalyzed hydrolysis of cotton balls as described elsewhere, albeit with slight modifications. Briefly, cellulose (Swisspers brand cotton balls) was reacted as-is with sulfuric acid (H₂SO₄, ACS Plus, Fisher chemical) at a ratio of
1 g of cellulose to 5 mL of sulfuric acid to 5 mL of DI water in a reaction flask placed inside a sonicator (Branson 3800), whose bath temperature was held at 46-48°C. The reaction was mechanically stirred; the stirring speed (~700-1200 rpm) was adjusted every 15 min. to be as fast as possible while minimizing splashing on the vessel walls. The reaction proceeded for 2 h under continuous sonication and was subsequently quenched by threefold dilution with DI water while in an ice bath. The reaction fluid was then repeatedly washed via centrifugation at 10-11 kRCF until a turbid solution was obtained, typically after 4-5 wash cycles. Afterward, any gelatinous subnatant was discarded and the turbid supernatant was dialyzed against a cellulose membrane with 12,000-14,000 molecular weight cutoff. The dialysis water bath was changed every few hours until its pH remained at 7 for at least 6 h. Then the aqueous CNCs were collected, bath sonicated for 5 min., and then centrifuged one last time at 5 kRCF for 5 min., to remove any remaining dehydrated cellulose. The supernatant was filtered against a cellulose nitrate membrane with an average pore size of 5μm to obtain purified aqueous CNCs with a concentration < 1 wt%. Finally, the CNCs were concentrated in a loosely covered glass dish on a hotplate with a surface temperature of 30°C with moderate stirring until the desired concentration was obtained. The CNCs were then stored in sealed glass jars in a 4-°C refrigerator until needed.

3. Preparation of Hydrogels: Procedure 1

Approximately 5 wt% acrylamide monomers (AAm, Acros Organics) were added to an aqueous CNC dispersion whose initial concentration was 28.2 wt%. The CNC dispersion comprised ~76 wt% of the final sol before printing. The solution was vigorously stirred and bath sonicated to thoroughly mix the AAm. Next, while vigorously stirring, the solution’s pH was adjusted to neutral or basic by the dropwise addition of an aqueous sodium hydroxide (Fisher Chemical)
solution. An aqueous GNR colloidal dispersion was added to bring the GNR’s final concentration to ~0.023 wt%. The AAm-CNC-GNR dispersion was mixed thoroughly using a vortex mixer. Approximately 0.1 wt% of the photo-initiator 1-[4-(2-Hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one (Irgacure-2959, Sigma Aldrich) and ~0.06 wt% of base catalyst N,N,N',N'-tetramethylethane-1,2-diamine (TEMED, Acros Organics) were directly added to the dispersion. Both the Irgacure-2959 and TEMED were vigorously mixed into the AAm-CNC-GNR dispersion by a vortex mixer. Finally, N,N'-methylenebis(acrylamide) (MBAA, Acros Organics), which was used as a cross-linker, was separately dissolved in DI water. An aliquot was taken and mixed by vortexing with the dispersion to bring the MBAA’s final concentration to ~0.04 wt%. DI water was added to bring the total to 100%. Immediately after the AAm-CNC-GNR sol was prepared, it was stored in a 4-˚C refrigerator for up to two days prior to printing.

4. Preparation of Hydrogels: Procedure 2

Approximately 20 wt% or ~9 wt% AAm were added to a ~63 wt% or ~73 wt% aqueous CNC dispersion whose initial CNC concentration was ~1 wt% or ~14 wt% for a total CNC concentration of ~0.8 wt% or ~10 wt% of the final sol, respectively. The solution was vigorously stirred and bath sonicated to thoroughly mix the AAm. Next, while vigorously stirring, the solution’s pH was adjusted to neutral or basic by the dropwise addition of aqueous sodium hydroxide solution. An aqueous GNR colloidal dispersion was added to bring the GNR’s final concentration to ~0.023 wt%. The AAm-CNC-GNR dispersion was mixed thoroughly using a vortex mixer. Approximately 0.1 wt% of the photo-initiator Irgacure-2959 and ~0.06 wt% of the base-catalyst TEMED were directly added to the dispersion. Both the Irgacure-2959 and TEMED were vigorously mixed into the AAm-CNC-GNR dispersion by a vortex mixer. The
dispersion, while inside a 20-mL glass scintillation vial, was exposed to UV light (~2 mW cm\(^{-2}\) at ~275 nm) for ~50 min. (~0.8 wt% CNCs) or ~40 min. (~10 wt% CNCs) while slowly stirred for 3 min. and rested for 3 min. repeatedly.

The UV-exposure time was adjusted to yield a sol with a viscosity within the ideal working range for our direct-ink-writing (DIW) printer. A qualitative viscosity test was developed to determine a suitable range of viscosities for printed sols. The sol’s scintillation vial was rotated upside-down and observed for ~1 min. If negligible flow was visibly detected and if, upon insertion into the gel and subsequent retraction of a spatula, the spatula drew a bead of material similar in elasticity and texture to saliva, then the sol would be printed. Otherwise, the UV-exposure duration was increased and implemented in the described manner above.

Next, MBAA was separately dissolved in DI water. An aliquot was taken and mixed by vortexing with the oligomerized, viscous dispersion to bring the MBAA’s final concentration to ~0.04 wt%. DI water was added to bring the total to 100%. Immediately after the PAM-CNC-GNR sol was prepared, it was stored in a 4-°C refrigerator for up to two days prior to printing.

5. 3D Printing Equipment Design

A fused-filament-fabrication (FFF) 3D printer (Aleph Objects, Inc. Lulzbot Mini v1) was retooled in-house to print as a DIW printer. Briefly, a syringe (5-60 mL, Figure S1(a) item i) was inserted into a syringe pump (Figure S1(a) item ii, Yale Apparatus Multi-Phaser Model YA-12). A length of flexible vinyl tubing (Figure S1(a) item iii) was installed between (i) and another syringe with its plunger cut off (Figure S1(a) item iv) so that (iv) was actuated hydraulically from the rear. The closed volume defined by (i), (iii), and (iv) was completely filled with water. Sol was then introduced through (iv)’s orifice and extruded through a separate length of stiff tubing in place of a needle (Figure S1(a) item v). The syringe and tube assembly (Figure S1(b)
item iv and v) guided sol to the printer’s extrusion nozzle (Figure S1(b) item vi, Lulzbot Mini Tool Head v2) and replaced the plastic filament typically used for this printer. The entire assembly is presented in Figure S1(c) with a schematic representation in Figure S1(d). Sol was extruded from (vi) onto the printing substrate (Figure S1(c) or (d) item vii). In our case, we printed directly on microscope slide glass, shown in Figure S1(c) affixed atop item (vii), instead of atop the reddish stock printer substrate (vii). 3D motion was achieved along the coordinate axes shown (Figure S1(d)) by translating the print head (Figure S2(b)) along x and z and separately translating the printing substrate (vii) along y.

**Figure S1.** (a) The hydraulic system enabling extrusion of gelatinous sol from the 3D printer. (b) The modified print head with a syringe and tube (item iv and v) conveying sol to the extrusion nozzle (item vi). (c) The completely assembled 3D printer. (d) A schematic representation of the 3D printing system shown in (c).
6. 3D Printing Procedures and Parameters

Sol material was warmed to room temperature and introduced through the second syringe’s orifice (Figure S1(a) item iv and v) by running the syringe pump in reverse. Typically, a total volume of ~3 mL of sol would be used for each printing batch. The second syringe replaced the tool head’s original sprocket assembly. A new short length of stiff yet flexible tubing connected the second syringe’s orifice to the tool head’s hot-end filament heater and extrusion nozzle by inserting the stiff tubing in place of typical FFF filament (Figure S1(b)).

Printed objects were designed with Python code formatted according to the g-code commands used by the printer’s controlling and slicing software (Matter Control v.1.7.). The g-code file contained the starting and ending sequences as well as the code for the printed object. Care was taken to modify the starting sequence to operate the printer’s extrusion nozzle and printing surface at room temperature, to override the printer’s low-temperature extrusion exception, and to account for the modified starting height due to the printing substrate.

The extrusion nozzle was primed with the sol by briefly running the syringe pump at an elevated rate of ~0.6 mL min\(^{-1}\). Once the sol was visibly detected at the tip of the nozzle, the syringe pump was stopped. Excess sol was wiped away. Next, the printer’s starting sequence was activated. Tens of seconds before the printer’s starting sequence was completed, the syringe pump was re-started at the extrusion rate. The sol filament was printed on a microscope-slide-glass substrate. A pump rate of ~0.06 mL min\(^{-1}\), a tool-head and print-surface raster speed of 95 mm min\(^{-1}\), and a nozzle height of ~0.35 mm from the substrate for a 0.5-mm-diameter nozzle enabled the printing of uniform, contiguous, and aesthetically appealing shapes. Immediately after printing, the sample was exposed to UV radiation for cross-linking. For Irgacure-2959’s peak extinction at ~275 nm, the sol was exposed to an intensity of ~2 mW cm\(^{-2}\) for 5 – 12 min.
atop a black light (ADJ UV Panel HP with four bulbs LL-UVP40) or to an intensity of ~82 mW cm\(^{-2}\) for up to 1 min. from a UV-curing lamp (Omnicure Series 2000, Lumen Dynamics). The hydrogel was placed in a Petri dish with a few water drops to prevent the hydrogel’s dehydration during storage. The Petri dish was then sealed immediately after curing.

7. Preparation of Aerogels

To convert a hydrogel into an aerogel, the hydrogel was first converted into the intermediary alcogel state by three times immersion in 20 mL of absolute ethanol for at least 12 h each rinse. Alcogels were then converted to aerogels via carbon dioxide critical point dryer (CPD) (Automegasamdrì 915B or Samdri-780A, Tousimìs, Inc.). Before the alcogel was inserted into the CPD chamber, the chamber was filled approximately half full with ethanol. The alcogel and its attached glass microscope slide were then placed in the chamber. Liquid carbon dioxide used for solvent exchanges was pressurized at ~5.5 MPa and purged from the chamber until all ethanol was removed. Next, the chamber was heated beyond carbon dioxide’s critical point to ~40 °C and ~8.3 MPa. After the critical point was reached, it was held for ~15 min. to allow any fluid trapped within the gel to become supercritical. Finally, while maintaining the temperature at 40 °C, the pressure was bled off at a maximum rate of ~0.34 MPa min\(^{-1}\) until the chamber pressure reached 1.7 MPa, after which the carbon dioxide gas was exhausted as quickly as possible. After the aerogel was removed from the chamber, it was sealed and stored at a relative humidity of ~20% at room temperature.

8. Optical Imaging and Spectroscopy

Optical micrographs were obtained using an Olympus BX-51 microscope with 2× and 4× magnification. Transmission-mode brightfield microscopy and polarizing optical microscopy (POM) with and without a 530 nm full-wave retardation plate were used to qualitatively
determine the gels’ director and thickness variation. Optical micrographs were captured with Diagnostic Instruments, Inc. Spot Insight 14.2 Color Mosaic CCD camera. Other optical images were captured with a Nikon D300 Digital Camera with a Nikon AF-S Nikkor 18 – 200 mm lens. Spectra were obtained in transmission mode from the microscope’s sample plane and with a fiber-optic adapter affixed in place of the microscope’s camera. The sample’s extinction spectra were recorded via an Ocean Optics USB2000-FLG spectrometer.

9. Degree of Order of Plasmonic Inclusions, Spectral Data Collection, and Analysis

Methodology

From previous results, which used static methods to co-align GNRs and CNCs,[S3] we were motivated to understand the attainable degree of alignment for GNRs through DIW 3D printing methods. The extent of anisotropic GNRs’ average angular fluctuations away from a uniform director field $N$ can be quantified with a scalar order parameter $S$, where $S = 0$ represents no orientational ordering and $S = 1$ indicates perfect orientational alignment along $N$. Measured longitudinal surface plasmon resonance (LSPR) and transverse surface plasmon resonance (TSPR) extinction spectra were used to calculate the GNRs’ scalar order parameters in Procedure 1 and Procedure 2, where $S_1 = 0.45 \pm 0.13$ and $S_2 = 0.34 \pm 0.07$, respectively. Representative TSPR and LSPR extinction spectra for PAM-CNC-GNR gels with 21.5 wt% CNCs, prepared according to Procedure 1, and for gels with 10.2 wt% CNCs, prepared according to Procedure 2, are shown in Figure S2(a). For gels with 0.76 wt% CNCs, prepared according to Procedure 2, no observable polarization-dependent extinction peak was evident, thereby indicating isotropic alignment of GNRs with $S = 0$. A representative extinction spectrum taken with unpolarized incident light is shown in Figure S2(b). In this case, rather than the emergence of two distinct TSPR and LSPR extinction peaks, instead a single, broadened extinction peak is observed. The
existence of such an extinction profile is likely indicative of complex, coupled configurations of GNRs within the PAM-CNC-GNR gel.\[S4\] A possible alignment of CNCs and GNRs in the 21.5-wt% and 10.2-wt% gels is depicted in Figure S2(a)’s inset while an isotropic organization of the 0.76-wt%-PAM-CNC-GNR gel is represented by the inset in Figure S2(b).

Figure S2. Spectral characterization of PAM-CNC-GNR hydrogel LSPR ($N \parallel P$) and TSPR ($N \perp P$) extinction modes with insets demonstrating possible alignment of CNCs and GNRs. Cross-link symbols are omitted for clarity. (a) Spectral comparisons between representative extinction curves from hydrogels printed according to Procedure 1 (21.5 wt% CNCs) and Procedure 2 (10.2 wt% CNCs). Orientational co-alignment of GNRs and CNCs, indicated by director $N$ with the double headed arrow, (inset) is crucial for polarization selective metamaterials. (b) A representative polarization-independent extinction spectrum from a hydrogel (0.76 wt% CNCs) with isotropic GNR and CNC organization (inset) prepared with Procedure 2.

The extinction spectra corresponding to the 10.2-wt%-CNC data shown in Figure S2(a) were chosen from a larger set, which is displayed in Figure S3(a). The 21.5-wt%-CNC data shown as well in Figure S2(a) originate from the set shown in Figure S3(b). For the data in Figure S3(a) and (b), two spectra corresponding to each sample’s LSPR ($N \parallel P$) and TSPR ($N \perp P$) were collected for each manufactured sample. The LSPR spectra are shown in black while those for the TSPRs are displayed in grey. All spectra were normalized to zero at 900 nm. Next, the LSPR extinction spectra were scaled by a scaling coefficient to unity at their extinction peaks.
For each pair of LSPR and TSPR spectra, the TSPR spectrum in a pair was scaled by the corresponding LSPR scaling coefficient. This scaling approach was used because of sample thickness and illumination intensity differences among the collected spectral data. To determine the GNRs’ scalar order parameter $S_{\text{GNR}}$, the extinction formula was used:

$$S_{\text{GNR}} = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}},$$

where $A_{\parallel}$ and $A_{\perp}$ represent the magnitudes of the longitudinal extinction peaks for $P_{\parallel} \parallel N$ and $P_{\perp} \perp N$, respectively.\(^{[S3]}\) For the first method used to determine $S_{\text{GNR}}$, the scalar order parameter was calculated for each spectral pair without scaling. Next, the mean and standard deviation of the scalar order parameters were calculated to estimate total uncertainty. As the second method, the means and standard deviations for both $A_{\parallel}$ and $A_{\perp}$ were calculated from the populations shown in Figure S3(a) and (b). A standard combined uncertainty calculation yielded

$$\delta S_{\text{GNR}} = \frac{3}{(\delta A_{\parallel} + 2\delta A_{\perp})^2} \sqrt{\delta A_{\parallel}^2 + (A_{\parallel} \delta A_{\perp})^2}.$$ 

Of the two methods, the larger values are presented above.

Calculation of the dichroic ratios for both Procedure 1 and 2 used the normalized curves shown in Figure S3(a) and (b). The means and standard deviations for both $A_{\parallel}$ and $A_{\perp}$ were used to calculate the mean dichroic ratio $R = \frac{A_{\parallel}}{A_{\perp}}$ and the standard combined uncertainty $\delta R_{\text{GNR}} = \sqrt{\left(\frac{\delta A_{\parallel}}{A_{\perp}}\right)^2 + \left(\frac{A_{\parallel} \delta A_{\perp}}{A_{\perp}^2}\right)^2}$. The dichroic ratios for Procedure 1 and 2 were found to be $R_1 = 3.2 \pm 1.2$ and $R_2 = 2.6 \pm 0.46$.

Finally, the representative spectrum from those in Figure S3(c) is shown in Figure S2(b). Because the GNRs are isotropic, $S_{\text{GNR}} = 0$. Thus, unpolarized incident light was used to collect the spectra shown in Figure S3(c). Each curve has been normalized to zero at 900 nm and scaled to unity at the extinction peak near 650 nm. One spectrum per sample was taken.
Figure S3. (a, b) LSPR (black) and TSPR (grey) spectra used to determine the GNRs’ order parameter within hydrogels containing 10.2 wt% CNCs (a) and 21.5 wt% CNCs (b). (c) Polarization-independent extinction spectra of GNRs within hydrogels containing 0.76 wt% CNCs.

10. Electron Microscopy

Transmission electron microscopy (TEM) micrographs of gold nanorods (GNRs) were obtained with a FEI Tecnai T12 Spirit at 100 kV accelerating voltage and at $13000 - 68000 \times$ magnification. Micrographs of aqueous GNRs were obtained by dropcasting and subsequently drying $\sim 0.00028$ wt% GNRs on Cu Formvar Square 300 Mesh grids. Focused ion beam and scanning electron microscopy (FIB-SEM) cross-section imaging was performed using a FEI Nova 600 nanolab dualbeam. The aerogel sample was mounted on a regular SEM stub. For Figure 1(d), the sample was placed carefully inside the microscope, with the top of the sample tilted by $52^\circ$ to face directly the FIB. After protecting with a band of Pt, a trench $\sim 5 \mu m$ wide by $3 \mu m$ long by $\sim 1 \mu m$ deep was milled using the ion beam at 30 kV and 93 pA. After milling the sample, a thin layer of Pt was deposited in situ on the fresh surface. SEM images were taken at 5 kV accelerating voltage, $15000 \times$ magnification, and 5.1 mm WD using the through-the-lens detector (TLD) with secondary-electron detection. To ensure no astigmatism in the image, circular features of the gel were imaged with different sources and detectors. No astigmatism was detected for the electron source with the secondary-electron TLD. For Figure 1(e), the sample was tilted by $52^\circ$ to face directly the FIB. After protecting with a band of Pt, a trench $\sim 5$
µm wide by 3 µm long by 1.7 µm deep was milled using the ion beam at 30 kV and 93 pA. After milling the sample, a thin layer of Pt was deposited *in situ* on the fresh cross-section. SEM images were taken at 5 kV accelerating voltage, 25000× magnification, and 5.1 mm WD using the TLD with secondary-electron detection.

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