Self-Alignment of Plasmonic Gold Nanorods in Reconfigurable Anisotropic Fluids for Tunable Bulk Metamaterial Applications

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ABSTRACT We demonstrate the bulk self-alignment of dispersed gold nanorods imposed by the intrinsic cylindrical micelle self-assembly in nematic and hexagonal liquid crystalline phases of anisotropic fluids. External magnetic field and shearing allow for alignment and realignment of the liquid crystal matrix with the ensuing long-range orientational order of w278278.395(of3he)-278.4(liquid)-2738

phases of the CTAB/benzyl alcohol/water ternary system with well-established phase diagram.[16,17] Typically, the LC in the hexagonal phase was prepared using a composition of 25% CTAB, 5% benzyl alcohol (both from Aldrich, used as supplied) and 70% of aqueous suspension of GNRs stabilized by CTAB with GNRs at about 10^{-8} M. This was followed by centrifugation at 3000 rpm for 10 min and ultrasonication for 30 min at room temperature. The samples exhibited no visible aggregates, indicating that GNRs are well-dispersed in the hexagonal H1 phase. The lyotropic LC in the nematic phase was prepared as above but consisted of 25% CTAB and 75% of aqueous GNRs dispersion.[17] The LC phases of studied nanocomposites were further changed by adjusting the surfactant concentration. The hexagonal phase is composed of cylindrical surfactant micelles exhibiting long-range orientational and hexagonal 2D positional ordering while the nematic phase exhibits only long-range orientational ordering.[16,17] Dispersing nanoparticles (especially in anisotropic fluids) is a technical challenge and often requires surfactant stabilization of GNRs.[18,19] The used lyotropic LC is composed of the same surfactant molecules that stabilize GNRs during the synthesis procedures, yielding

angle with respect to the LC director. Optical imaging and spectroscopy show no evidence of nanoparticle aggregation

the solvent's refractive index from that of water 1.33 to ~1.4 as more and more CTAB is added to form nematic or columnar hexagonal phases (in agreement with computer simulations shown in the inset of Figure 3b). The longitudinal SPR band of GNRs in the LC is polarized (Figure 3c,d and Figure S1a in Supporting Information) and its peak slightly shifts when changing the angle between **n** and polarizer (Figure 3c and Figures S1 and S2 in Supporting Information). Using the experimental spectra, one can estimate the three-dimensional order parameter of GNRs in the uniaxial LC matrix defined as $_{3D} = (3\langle\cos^2 \theta_{3D}\rangle - 1)/2$, where θ_{3D} is an angle between **n** and GNRs. The order parameter of GNRs

be both attractive and repulsive, depending on the orientation of the interparticle separation vector with respect to **n**. Since the size of nanorods is smaller than the surface anchoring extrapolation length $/ \sim 10^{-7}$, the maximum elasticity- and surface anchoring-mediated binding energy for GNRs aligned along **n** can be estimated as $2 \; {}^{2} \leq$ and is comparable to or smaller than the thermal energy, where $\sim 10^{-5} / \; {}^{2}$ is the typical surface anchoring strength at the solid−LC interface.[25] The above estimates show that the elasticity-mediated interactions of GNRs with the surrounding nematic matrix are strong enough to induce uniform long-range alignment of rods but the ensuing interparticle interactions are weak and comparable in strength to thermal energy, so that they are not causing aggregation. This explains why the long-term stability of the studied GNR dispersion in nematic LCs is comparable to that in water at similar concentrations: the CTAB surfactant layer effectively stabilizes GNRs against aggregation due to the van der Waals and other interparticle forces present in both LC and water while the weak elasticity-mediated anisotropic forces (present only in the LC hosts) are comparable in strength to thermal fluctuations and do not cause colloidal aggregation. In

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based on these data is rather high ($_{3D} \approx 0.88$), and its value is consistent with the 2D order parameter measured in the columnar hexagonal LC using FFTEM images in different fracture planes for slightly shorter GNRs (Figure 2). Polarized light scattering of individual GNRs resolved by imaging the scattered light in a darkfield mode reveals that all rods within the field of view orient along **n** (Figure 5) and such alignment is, in principle, achievable on the scales of meters and larger.

In conclusion, we have demonstrated aggregation-free elastic self-alignment of nanorods dispersed in LCs and their realignment by shearing and magnetic fields. The unidirectional self-ordering of gold nanorods with high 3D order parameter values approaching 0.9 gives rise to the strong polarization sensitivity of surface plasmon resonance effects, showing the potential for LC-mediated oriented self-assembly of bulk optical metamaterials with tunable and switchable properties. Our method of device-scale large-volume bulk alignment of nanorods extends the capabilities provided by other alignment methods[8–13,23,24,26–29] and can be used for a broad range of rodlike particles with different length-to-diameter aspect ratios and chemical compositions. Furthermore, the observed strong orientation dependence of SPR spectra may allow for novel orientation sensors[30] and plasmonic versions of 3D label-free imaging of director structures in liquid crystals.[31]

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REFERENCES AND NOTES

(1) Yao, J.; Liu, Z.; Liu, Y.; Wang, Y.; Sun, C.; Bartal, G.; Stacy, A. M.; Zhang, X.

SUPPORTING INFORMATION:

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1. Synthesis of gold nanorods.

the medium and issues 2-4 above result in angular dependence of SPR peak wavelength, Figure S2b (not expected for perfectly-aligned nanorods in isotropic media) and modify

SUPPLEMENTARY REFERENCES

S1. Tavlove, A. Computational Electrodynamics: The Finite-Difference Time-Domain Method, *Artech House*, Norwood, 1995.

S2. Moharam, M. G. & Gaylord, T. K. *J. Opt. Soc. Am. A* **1986**, 3, 1780.

SUPPLEMENTARY

FIGURES

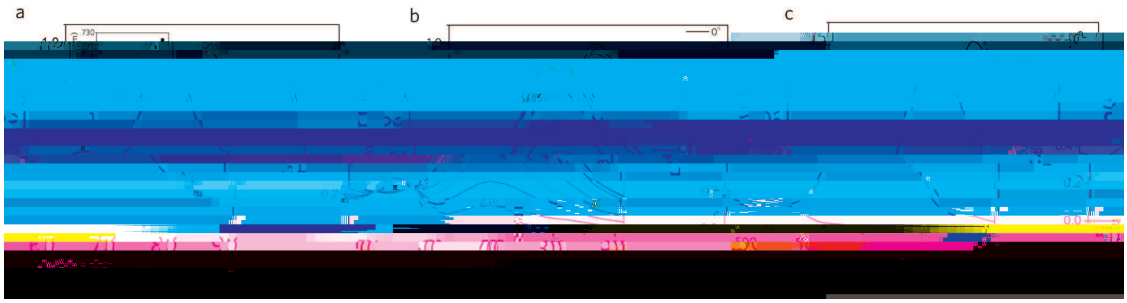

Figure S1. Computer-simulated spectra obtained using the RCWA method[S2] with the spectra on (a), (b), and (c) corresponding to FDTD-simulated spectra in Figures 3b, 3d, and 4b, respectively. Compared to the spectra obtained using the FDTD method, the RCWA-calculated spectra have broader bands and display small bumps/shoulders, which stem from solving the full vectorial Maxwell's equations in the Fourier domain and accounting for nanorod size polydispersity using the distributions similar to the one shown in the inset of Figure 2a.