Supporting Information

Magnetic Field-responsive Graphene Oxide Photonic Liquids

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1. Experimental Procedures

General: All chemicals and solvents were purchased from Sigma Aldrich unless otherwise indicated. Cellulose nanocrystal (CNC) suspensions (6 wt%, pH ~6.6) in water were obtained from CelluForce. The morphology and structure of the samples were examined with a Hitachi S4700 field emission scanning electron microscope, a Zeiss CrossBeam 350 CryoFIB scanning electron microscope and a Hitachi H7600 transmission electron microscope. Samples were sputter-coated with 7 nm Pt. Reflectance spectra were obtained with an Ocean Optics setup with the following parts: spectrometer (FLAME-S-XR1, Ocean Optics Inc., USA), tungsten halogen light source (DH2000-BAL, Ocean Optics Inc., USA) and reflection probe (R400-7-UV-VIS, Ocean Optics Inc., USA). OceanView software (1.6.7, Ocean Optics Inc., USA) was used for collecting and exporting the data. Samples were homogenized with a Thermo Scientific LP Vortex Mixer or a Durasonix 3 Litre Ultrasonic Cleaner (120 W, 40 kHz). Zeta potential measurements were conducted at room temperature on a NanoBrook Omni (Brookhaven Instruments). Magnetization measurements were performed with a Quantum Design Physical Property Measurement System (PPMS) equipped with a Vibrating Sample Magnetometer (VSM) option. The EDX mapping results were obtained using a Zeiss CrossBeam 350 CryoFIB scanning electron microscope. This microscope is equipped with an Oxford XMAX 170mm EDX detector, which was used for the EDX experiments.

Preparation of graphene oxide hydrophobic photonic liquids: Graphene oxide photonic liquids in water were prepared according to previous works.^{1,2} Poly(APMS-co-DMS) copolymer [(2-3% aminopropylmethylsiloxane)–dimethylsiloxane, transparent liquid, 4500-6000 g/mol, Gelest Inc.] was used as phase transfer additive to direct GO from water to organic solvents. The copolymer (2.24 g) was

dissolved in 400 mL of diethyl ether, then a GO aqueous suspension (320 mL, 1 mg/mL) was added. After gently stirring the mixture for 48 h, the upper organic phase appeared reddish brown, indicating successful extraction of GO from water into diethyl ether. The upper organic layer was then separated from the mixture, washed with deionized water (3 x 15 mL) and dried over molecular sieves. Diethyl ether could be replaced with other organic solvents through rotary evaporation. For instance, to make a 5 mL GO suspension in butyl acetate, 5 mL of dry butyl acetate was added to 5 mL of GO suspension in diethyl ether. The diethyl ether was then removed by rotary evaporation. Additional butyl acetate and rotary evaporation may be needed to ensure the diethyl ether was removed, and to ensure the final volume of the suspensions is 5 mL. In this study, a mixture of butyl acetate and poly(APMS-co-DMS) with a 1:1 volume ratio was used to minimize liquid evaporation. Structural colors were observed by illuminating the liquids with white light.

Preparation of Fe₃**O**₄ **magnetic nanoparticles:** Fe₃O₄ nanoparticles were prepared based on previous work with some modifications.³ Polyacrylic acid (PAA) powder (0.8 g; 1800 g/mol) was dissolved in 100 mL deionized water by stirring in a 250 mL three-necked flask. The mixture was deoxygenated by sparging the solution with nitrogen for 30 mins and the temperature was raised to 85 °C. Meanwhile, FeCl₃·6H₂O (0.29 g, 1.1 mmol), FeSO₄·7H₂O (0.16 g, 0.58 mmol), HCl solution (4 mL, 1 M) and deionized water (6 mL) were mixed together and this solution was injected into the PAA solution. The resulting mixture was sparged with N₂ for 10 mins, followed by slow addition of ammonium hydroxide (30 mL, 28%). The solution turned black during the addition of ammonium hydroxide. After heating the solution at reflux for 40 mins, the system was allowed to cool down to room temperature. Impurities were removed by dialysis (molecular weight cut-off = 14,000) against deionized water for 12 d.

*Phase transfer of Fe*₃*O*₄ *nanoparticles from water into organic liquid media:* Organic suspensions of Fe₃O₄ *nanoparticles were prepared by a phase transfer method according to previous work.*⁴ The poly(APMS-co-DMS) copolymer (4500-6000 g/mol, Gelest Inc.) was used as a phase transfer additive and was dissolved in diethyl ether by stirring for 5 min (1 g in 15 mL), followed by addition of 1 mL of 0.01 M HCl aqueous solution. The Fe₃O₄ aqueous suspension was then added to the organic phase (10 mL, 4 mg/mL) and the stirring was continued for 48 h. The color of the upper organic phase turned to reddish

brown after stirring, similar to the change observed in the phase transfer process of graphene oxide. Next, the Fe₃O₄-ether phase was separated from the mixture, washed with deionized water (3 x 15 mL) and dried over molecular sieves. The diethyl ether was then removed by rotary evaporation, leaving the suspension of Fe₃O₄ nanoparticles in poly(APMS-co-DMS) copolymer.

Preparation of GO-Fe₃O₄ photonic liquids: The hybrid hydrophobic photonic liquids were prepared by mixing GO with Fe₃O₄ in different ratios. For instance, to make a suspension that reflected green light, 175 μ L of Fe₃O₄ suspension (20 mg/mL) in poly(APMS-co-DMS) was added to 1 mL of 3.5 mg/mL GO suspension in the solvent mixture of butyl acetate and poly(APMS-co-DMS) (volume ratio, ~1:1). GO and Fe₃O₄ were mixed homogeneously using a Thermo Scientific LP Vortex Mixer or by sonication. The reflected green color was observed by illuminating the suspension with white light. The GO-Fe₃O₄ aqueous photonic liquids can be prepared with similar procedures, except that the aqueous GO and Fe₃O₄ suspensions are used instead.

Preparation of GO-SiO₂-Fe₃O₄ and GO-CNC-Fe₃O₄ aerogels for SEM analysis: To attempt to reveal the orientation of GO in the presence of magnetic field, we made GO-SiO₂-Fe₃O₄ and GO-CNC-Fe₃O₄ aerogels for SEM analysis. In a typical procedure for making GO-SiO₂-Fe₃O₄ aerogels, a GO-Fe₃O₄ suspension in water (3 mL; 4 mg/mL for GO and 2.3 mg/mL for Fe₃O₄) was mixed with tetramethyl orthosilicate (0.3 mL) and stirred for 1 h. After stirring, a magnet (~4500 G) was placed below the mixture, and the mixture became a wet gel after 2 d. The water in the wet gel was replaced with ethanol by solvent exchange to produce GO-SiO₂-Fe₃O₄ alcogel according to our previous studies.⁵ The resulting alcogel was converted into an aerogel with a Tousimis Autosamdri 815B critical point dryer.

In a typical procedure for making GO-CNC-Fe₃O₄ aerogels, aqueous GO-CNC-Fe₃O₄ suspension (3 mg/mL for GO, 15 mg/mL for CNCs and 2.3 mg/mL for Fe₃O₄) was kept in the fridge for at least 6 h. The cold mixture was then placed above a magnet (~4500 G), and ethanol was carefully added on the top of the mixture to initiate the solvent exchange process. The upper ethanol phase was replaced with fresh ethanol 2-3 times each day until the lower GO-CNC-Fe₃O₄ phase formed an alcogel.^{1, 2, 5} The resulting alcogel was converted into an aerogel with a Tousimis Autosamdri 815B critical point dryer.

2. Supporting Figures



Fig. S1 (a) SEM image of GO nanosheets. (b) Lateral size distribution of GO nanosheets (146 nanosheets were analyzed). The lateral size was estimated by averaging the lengths of the longest side and shortest side of each particle. (c) TEM image of Fe₃O₄ nanoparticles. (d) Diameter distribution of Fe₃O₄ nanoparticles (123 nanoparticles were analyzed). The size distribution was analyzed using ImageJ software. (e) Magnetization versus applied field (M–H) curve for Fe₃O₄ nanoparticles measured at 2 K. (d) M–H curve for Fe₃O₄ nanoparticles measured at 300 K. (f) Magnetization versus temperature for Fe₃O₄ nanoparticles measured in an applied field of 1.0 mT. The results for zero-field cooling and field-cooling curves are shown.



Fig. S2 Photographs showing the phase transfer of Fe_3O_4 from water (bottom layer) into diethyl ether (top) upon addition of the phase transfer agent. A similar visual change occurs to suspensions of GO that are transferred from water to diethyl ether.



Fig. S3 (a) Photographs of GO aqueous photonic liquids showing visible colors from red to blue (~4 to 8 mg/mL). The vials shown have a diameter of ~24 mm. (b) Photographs of 10 mm cuvettes containing GO hydrophobic photonic liquids in butyl acetate showing visible colors from blue to red (~3.5 to 7 mg/mL). (c) No reflection colors were observed from Fe_3O_4 suspensions alone in the presence or absence of a magnetic field (the brown color seen in the photo arises from absorption) (left: without a magnetic field; right: with a magnetic field).



Fig. S4 (a) Photographs of GO hydrophobic photonic liquids in butyl acetate demonstrating that they were stable for more than 1 month. (b) Photographs of GO aqueous photonic suspensions show that they lost their reflection colors after 7 days. Samples shown in (a) and (b) were vortexed before being photographed.



Increasing Fe₃O₄ concentration

Fig. S5 Photographs of cuvettes containing suspensions of GO as Fe_3O_4 NPs are added. (a) A red GO-only (4 mg/mL) aqueous photonic suspension. (b) Introducing Fe_3O_4 nanoparticles into the samples shown in (a) gave a green GO-Fe₃O₄ photonic suspension (Fe₃O₄, 1 mg/mL). (c) Further increasing the Fe₃O₄ concentration (to 1.3 mg/mL) produced a blue GO-Fe₃O₄ photonic suspension. The visible colors are related to the GO liquid crystalline domains, not from Fe₃O₄ nanoparticles.



Fig. S6 Photographs showing the front (a) and side (b) view of a red $GO-Fe_3O_4$ hydrophobic photonic liquid in the presence of a magnetic field with its the direction perpendicular to the front side of the cuvette. The magnetic field is ~4500 G.



Fig. S7 Photographs showing the disappearance of color of a GO/Fe₃O₄ aqueous suspension in response to a magnetic field over time (~4500 G). The mass ratio of GO:Fe₃O₄ is ~100:35 and the GO concentration is ~3 mg/mL. The magnet was placed behind the samples. The sample shown above the word "before" is the sample before the magnetic field was applied.



Fig. S8 (a) A green GO-Fe₃O₄ aqueous photonic liquid exhibited phase separation after being exposed to a magnetic field for 20 h. (b) A yellow GO-Fe₃O₄ hydrophobic photonic liquid in butyl acetate in the presence of a magnetic field did not show obvious phase separation after 20 h. The magnet (field strength ~4500 G) was placed at the right side of the photonic liquid.



Figure S9. (a,b) Low-magnification SEM images of the GO-CNC-Fe₃O₄ aerogels prepared in the presence of a magnetic field (~4500 G).



Fig. S10 (a-f) Cross-section SEM images of the GO-CNC-Fe₃O₄ aerogels prepared in the presence of a magnetic field (~4500 G). Note: we did not find obvious GO alignment since the cross-section of the aerogel was mostly covered by CNCs. However, the SEM images showed that the orientation of CNCs was nearly parallel to the magnetic field although they are nonmagnetic. We assume that this is likely a general phenomenon that can be extended to other nonmagnetic nanoparticles (e.g., CNCs here and GO in Figure S9). The alignments of CNCs shown here and the alignments of GO nanosheets shown in Figure S9 probably can support this assumption.







S11



Fig. S11 (a-d) Selected regions for EDX measurement of GO-SiO₂-Fe₃O₄ aerogel. The sample here is the same as the one shown in Fig. 1f. The selected regions for EDX measurements closely resemble those shown in Fig. 1h, 1j, and 1k. (e) EDX mapping results for the region shown in (b). (f) EDX mapping results for the region shown in (c). (g) EDX mapping results for the region shown in (d). The presence of Au and Pd signals is attributed to the Au/Pd sputter coating.



Fig. S12 (a-d) Cross-section SEM images of the GO-CNC-Fe₃O₄ aerogels prepared without magnetic fields.



Fig. S13 (a,b) A GO-only hydrophobic photonic liquid with amber color treated with magnetic field for ~0 h (a) and ~10 h (b). The magnet is positioned behind the sample. The magnetic field is ~4500 G.



Fig. S14 Spatial distribution of the magnetic field strength, measured using a Hall probe.



Fig. S15 Reflection spectra of the green hydrophobic GO-Fe₃O₄ photonic liquids shown in response to a magnetic field with increasing time. The magnetic field is ~ 2700 G for (a), ~1210 G for (b) and ~460 G for (c). The mass ratio of Fe₃O₄:GO is ~1:1 in each case.



Fig. S16 (a) Photograph showing the 10th off/on switching of the reflection color of a GO-Fe₃O₄ hydrophobic photonic liquid. The color restoration is achieved by adjusting the magnetic field direction. The process of switching off and on can be seen in Video S1 and Video S2. (b) Photograph showing the 1st off/on switching of the reflection color of GO-Fe₃O₄ hydrophobic photonic liquids. In this case, the color restoration is achieved by removing the external magnetic field. The process can be seen in Video S3 and Video S4. (c,d) Time-dependent reflection spectra of the green hydrophobic GO-Fe₃O₄ photonic liquids for the 10th color restoration in the presence of a magnetic field (c) and without a magnetic field (d). The concentration of GO is ~3.5 mg/mL in butyl acetate and the mass ratio of Fe₃O₄:GO is ~1:1. The magnetic field is ~4500 G. The word "before" in (a) and (b) means that no magnetic field was applied.

3. References for Supporting Information

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