

## Supporting Information

### Stable Graphene Oxide Hydrophobic Photonic Liquids

Yi-Tao Xu,<sup>a</sup> Joyce Li,<sup>a</sup> and Mark J. MacLachlan<sup>\*,a,b,c,d</sup>

<sup>a</sup>Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia V6T 1Z1, Canada

<sup>b</sup>Stewart Blusson Quantum Matter Institute, University of British Columbia, 2355 East Mall, Vancouver, British Columbia V6T 1Z1, Canada

<sup>c</sup>WPI Nano Life Science Institute, Kanazawa University, Kanazawa 920-1192, Japan

<sup>d</sup>Bioproducts Institute, University of British Columbia, 2360 East Mall, Vancouver, British Columbia V6T 1Z3, Canada

\* mmaclach@chem.ubc.ca

#### 1. Experimental Procedures

**General:** Powder X-ray diffraction (PXRD) measurements were taken using a Bruker D8-Advance X-ray diffractometer. The morphology and structures of the samples were examined with a Hitachi S4700 field-emission scanning electron microscope and a FEI Tecnai G2 Twin TEM transmission electron microscope. Polarized optical microscopy (POM) images were collected using an Olympus BX41 microscope equipped with a complementary metal oxide semiconductor camera. Infrared spectra of GO nanosheets were collected on a PerkinElmer Frontier Fourier Transform Infrared (FT-IR) spectrometer.

Reflectance spectra were obtained with an Ocean Optics setup. The UV-vis and NIR reflectance measurements were taken using a FLAME-S-XR1 spectrometer (Ocean Optics Inc., USA) and a NIRQUEST 512 SWIR spectrometer, respectively. A tungsten halogen light source was used to generate incident light (DH2000-BAL, Ocean Optics Inc., USA). The spectrometer and light source were connected to the sample probe using a bifurcated optical fiber. 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. For thermal stability tests, samples were placed in an oven at a pre-set temperature for the desired time. After heating, the samples were cooled down for 30 mins, and homogenized by a sonicator (or by a vortex mixer) since aggregation might occur during heating. An Ocean Optics setup was then used to record the reflection wavelength.

To reveal the photonic structure of the GO suspensions, we made GO-cellulose nanocrystal (GO-CNC) aerogels according to our previous work.<sup>1</sup> CNCs were used to induce the gelation to lock the GO-CNC hybrid suspensions via a solvent exchange process. In a typical procedure, aqueous GO-CNC hybrid suspension (2 mL, the concentrations of GO and CNC are 10 mg/mL) was kept in the fridge for at least 48 h (<10 °C). Next, ethanol was carefully added on the top of the hybrid suspension. A two-phase system could be observed after the addition: the top layer was the ethanol and the bottom layer was the hybrid suspension composed of GO and CNCs. The water in the lower phase was slowly exchanged with ethanol at room temperature. The upper organic phase was replaced with fresh ethanol 2-3 times each day until the lower GO-CNC phase formed a stable alcogel (needs ~ 1 week). The resulting alcogel was converted into an aerogel with a Tousimis Autosamdri 815B critical point dryer.

**Hydrophobization of SiO<sub>2</sub> nanoparticles:** In a typical procedure, 8 mL tetrahydrofuran (THF) was first added into 1 mL aqueous SiO<sub>2</sub> nanoparticle suspension (LUDOX<sup>®</sup> TMA, W.R. Grace & Co.-Conn., 340 mg/mL). The clear suspension became turbid after introducing THF. Next, 0.1 mL dichlorodimethylsilane was added into the mixture. After leaving the suspension overnight, it became clear again, indicating the successful hydrophobization of the nanoparticles. Ethyl acetate (3 mL) was added into the mixture to induce phase separation for extracting the SiO<sub>2</sub> and THF. The upper SiO<sub>2</sub>-THF-ethyl acetate phase was separated from the mixtures using a separatory funnel and dried with molecular sieves. Although THF can be removed through rotary evaporation, it was not necessary to remove THF here since GO photonic liquids are compatible with THF as shown in Fig. 5. The obtained hydrophobic SiO<sub>2</sub> nanoparticles have a diameter of ~25 nm (Fig. S11, S12, S13).

**Preparation of aqueous graphene oxide photonic suspensions:** Graphene oxide (GO) was prepared according to previous reports.<sup>1-3</sup> 6 g of graphite, 3 g of NaNO<sub>3</sub>, and 138 mL of H<sub>2</sub>SO<sub>4</sub> were mixed together by stirring (220 rpm). A cold water bath was used to keep the temperature below 10 °C. 24 g of KMnO<sub>4</sub>

was then added to the mixture (4 g/60 mins). Afterwards, the mixture was stirred for 18-20 hours. Next, 20 mL of H<sub>2</sub>O was added every 30 minutes until a total of 100 mL of H<sub>2</sub>O was added. The mixture was then transferred to a water bath heated to 50 °C where it was allowed to stir for 30 minutes. Following this, an additional 300 mL of H<sub>2</sub>O was added, and the entire mixture was stirred for another 5 minutes. Finally, 9 mL of 30% H<sub>2</sub>O<sub>2</sub> was added slowly, turning the mixture mustard yellow. The obtained product was washed repeatedly with deionized water by centrifugation (14 000 rpm, 2 h each time, 11 times). The GO slurry was obtained at the bottom of centrifuge tube. The GO slurry was diluted with deionized water to obtain the GO aqueous suspensions with desired concentrations. The suspensions could display different colors that depended on the GO concentration (Fig. S3).

***Preparation of graphene oxide hydrophobic photonic liquids in diethyl ether:*** GO nanosheets can be directed into the diethyl ether in the presence of the poly(APMS-co-DMS) copolymers [(2-3% aminopropylmethylsiloxane)-dimethylsiloxane, molecular weight: 4500-6000, product code: AMS-132, Gelest Inc.]. The diethyl ether can then be replaced by other liquid media to give other GO photonic liquids. In a typical procedure, the poly(APMS-co-DMS) copolymers (2 g) were dissolved in 400 mL of diethyl ether by stirring for 5 minutes. Next, 320 mL of aqueous GO suspension (1 mg/mL) was added to the organic phase. After stirring for 18-24 h, the GO concentration in the aqueous phase was ~0.17 mg/mL, indicating ~83% of GO nanosheets went into the organic phase. Afterwards, the upper organic layer was separated from the mixture and washed with water (~15 mL). The GO-ether phase was dried with molecular sieves. GO suspensions with a concentration of ~60 mg/mL were obtained by rotary evaporation of most of the diethyl ether. To obtain GO suspensions with desired concentrations, prescribed amounts of diethyl ether were added to the suspensions. Different structural colors either from first order or second order reflectance in the visible range related to the GO concentrations could be observed by illuminating the liquids with white light.

***Preparation of graphene oxide hydrophobic photonic liquids in other liquid media:*** To prepare other GO photonic liquids discussed in the main text, diethyl ether was replaced by a series of liquid media through rotary evaporation. For instance, to make a GO suspension in butyl acetate with green color, 6 mL of dry butyl acetate was added to 6 mL of 5 mg/mL GO suspension in diethyl ether. The diethyl ether

was then removed by rotary evaporation. Additional butyl acetate (or other solvents, since some solvents like THF may be evaporated as well during the rotary evaporations) and rotary evaporation may be needed to ensure the diethyl ether was removed, and to ensure the final volume of the suspensions is 6 mL. The final products were homogenized using a Thermo Scientific LP Vortex Mixer or by sonication to give a homogeneous GO photonic suspension in butyl acetate.

For the preparation of GO photonic suspensions in dichloromethane (DCM), extra precautions were needed since the boiling point of DCM is very close to that of diethyl ether. Two approaches could be used: In one method, 5 mL of the GO in diethyl ether was dried completely by passive evaporation, which required 2 days at room temperature. The dried GO was then soaked in 3.5 mL of DCM for one or two days before applying sonication and agitation to resuspend the GO completely. In the second method, we first concentrated 6 mL of the GO suspension in diethyl ether to ~3 mL using rotary evaporation. Afterwards, 10 mL of DCM was added to the concentrated GO suspension. Diethyl ether was removed using rotary evaporation. After the volume of the suspension was noticeably decreased, another 10 mL of DCM was added. This process was repeated for several times to ensure the nearly complete removal of diethyl ether. The GO suspensions in DCM from both methods may need to be concentrated again by rotary evaporation to generate structural colors.

***Preparation of GO-SiO<sub>2</sub> hybrid hydrophobic photonic liquids:*** The hybrid hydrophobic photonic liquids were prepared by mixing GO with SiO<sub>2</sub> in a suitable ratio. For instance, to make a suspension that reflected yellow light, 86 µL (35 mg/mL) of SiO<sub>2</sub> suspension in THF/ethyl acetate (3:1) or pure ethyl acetate was added to 1.6 mL of 3 mg/mL GO suspension in ethyl acetate. GO and SiO<sub>2</sub> were mixed homogeneously using a Thermo Scientific LP Vortex Mixer or by sonication. The reflected yellow color was observed by illuminating the suspension with white light.

## 2. Estimation of periodicity of photonic liquids, based on the Bragg reflection

$$n\lambda = n_r 2d \sin \theta$$

$n$ , reflection order

$\lambda$ , reflection wavelength

$n_r$ , refractive index

$d$ , interlayer separation (periodicity)

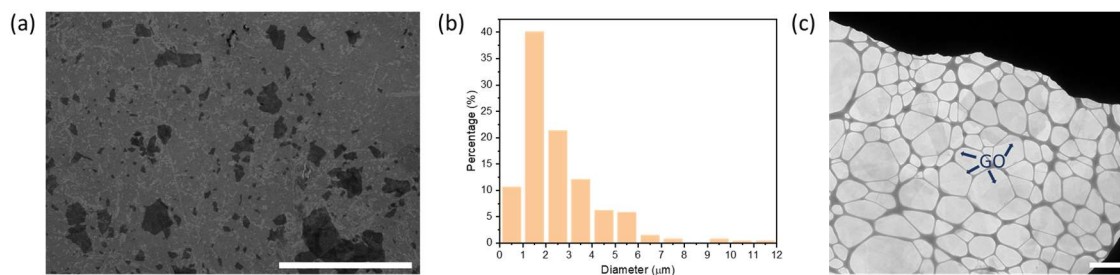
$\theta$ , angle of incident light with respect to the container surface

### 3. Supporting tables and figures

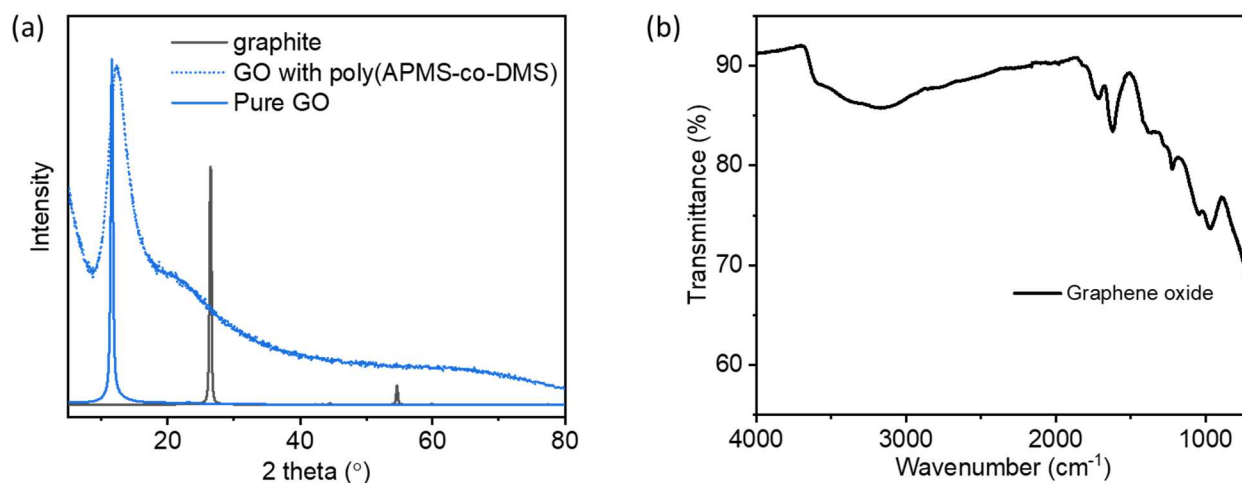
Table S1. Hildebrand and Hansen solubility parameters, and dielectric constants of the liquid media

Liquid media	$\delta_{HI}$	$\delta_d$	$\delta_p$	$\delta_h$	dielectric constants ( $\epsilon$ )
poly(dimethylsiloxane)	14.9	15.9	0.1	4.7	
diethyl ether	15.4	14.5	2.9	5.1	4.0 (40 °C)
cyclohexane	16.8	16.8	0	0.2	2
ethyl acrylate	17.6	15.5	7.1	5.5	6.1 (30 °C)
n-butyl Acetate	17.7	15.8	3.7	6.3	5.0
toluene	18.2	18.0	1.4	2.0	2.4
ethyl acetate	18.4	15.8	5.3	7.2	6.4
3-pentanone	18.4	15.8	7.6	4.7	17.0
tetrahydrofuran	19	16.8	5.7	8.0	11.0
dichloromethane	20.2	18.2	6.3	6.1	9.1
tetraethylorthosilicate		13.9	4.3	0.6	4.1
2-octanone		15.8	4.9	3.5	10.3
cyclohexanone	20.2	17.8	6.3	5.1	18.2
1,4-dioxane	20.5	19.0	1.8	7.4	2.2
N-methyl-2-pyrrolidone	22.8	18.0	12.3	7.2	32 (25 °C)
N,N-dimethylformamide	24.0	17.4	13.7	11.3	36.71 (25 °C)
ethanol	26.0	15.8	8.8	19.4	24.3 (25 °C)
water	47.9	15.5	16	42.3	80.4

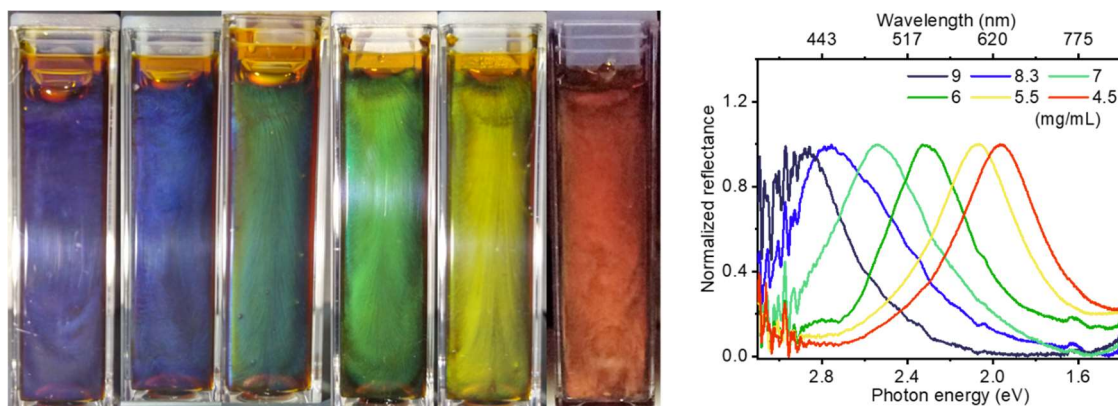
Note: Solubility parameter value is at 25 °C.  $\delta_{HI}$  is the Hildebrand solubility parameter.  $\delta_d$  is the Hansen solubility parameter that related to the energy from dispersion forces between molecules.  $\delta_p$  is the Hansen solubility parameter that is related to the energy from dipolar intermolecular force between molecules.  $\delta_h$  is the Hansen solubility parameter that is related to the energy from hydrogen bonds between molecules. The unit for solubility parameter is MPa<sup>1/2</sup>. Dielectric constant value is at 20 °C unless otherwise specified.<sup>[4-9]</sup>



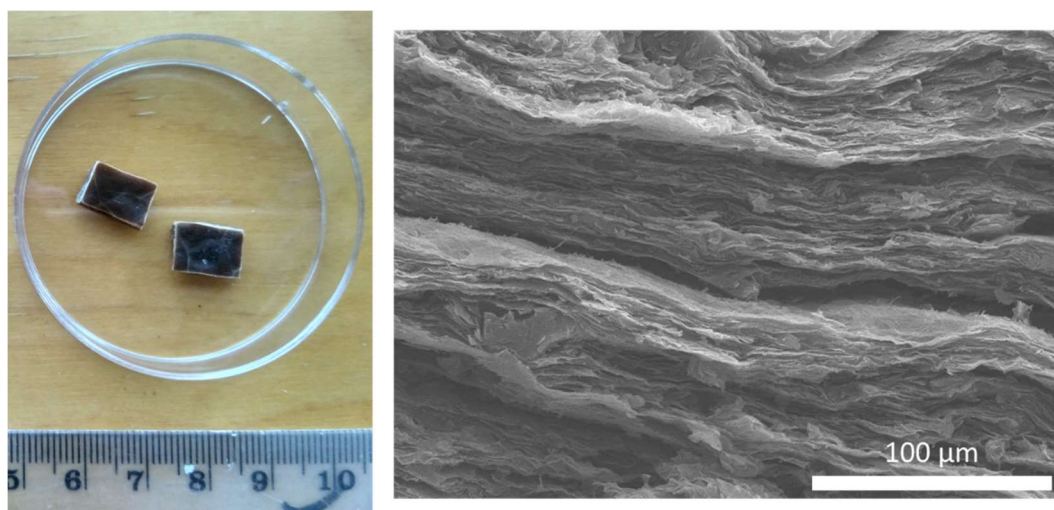
**Fig. S1** (a) SEM image of GO nanosheets. (b) Lateral size distribution of GO nanosheets (272 nanosheets were analyzed). The lateral size was estimated by averaging the lengths of the longest side and shortest side of each particle. (c) TEM image of GO nanosheets. Scale bar is 30 and 2  $\mu\text{m}$  for (a) and (c), respectively.



**Fig. S2** (a) PXRD data for graphite, GO, and GO with poly(APMS-co-DMS). (b) FTIR spectrum of GO.

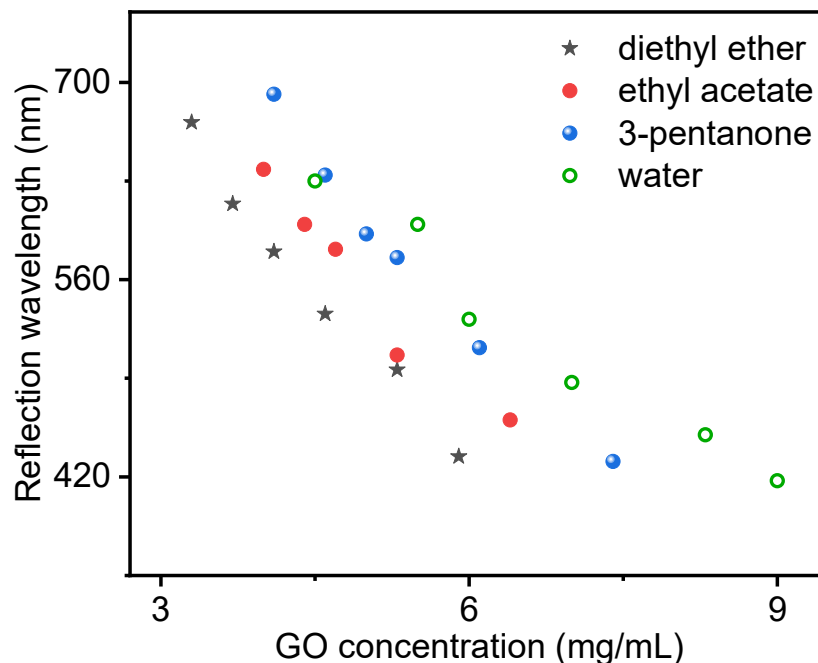


**Fig. S3** Photographs of aqueous photonic GO suspensions at different concentrations (left), along with the corresponding reflectance spectra of the GO photonic suspensions (right). The concentrations of GO in the suspensions were 9, 8.3, 7, 6, 5.5, 4.5 mg/mL from left to right (in deionized water).

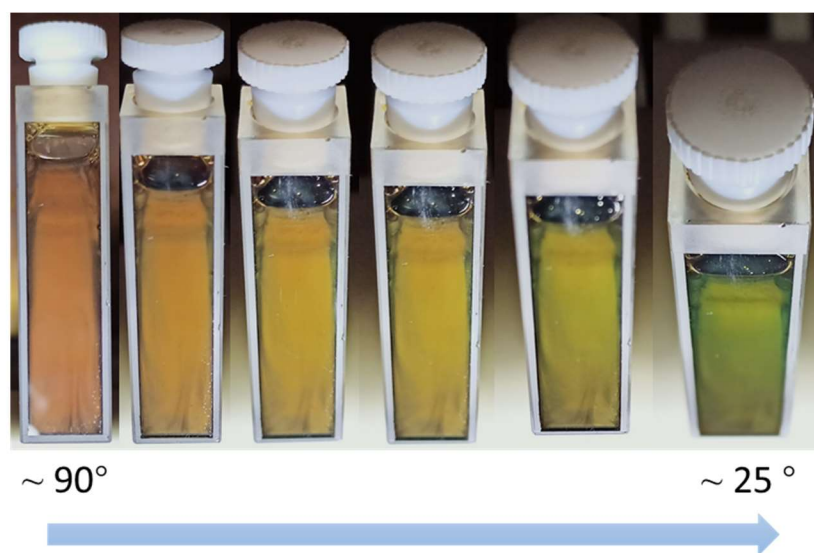


**Fig. S4** Photograph of the GO-CNC aerogels (left) and the corresponding cross-section SEM image (Right).

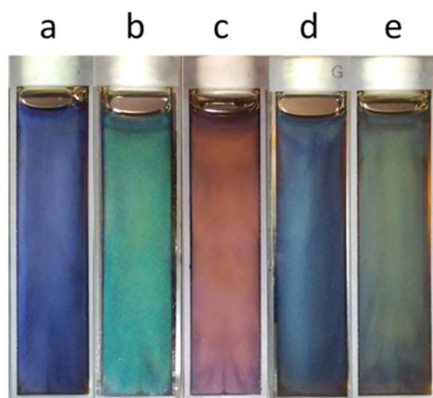




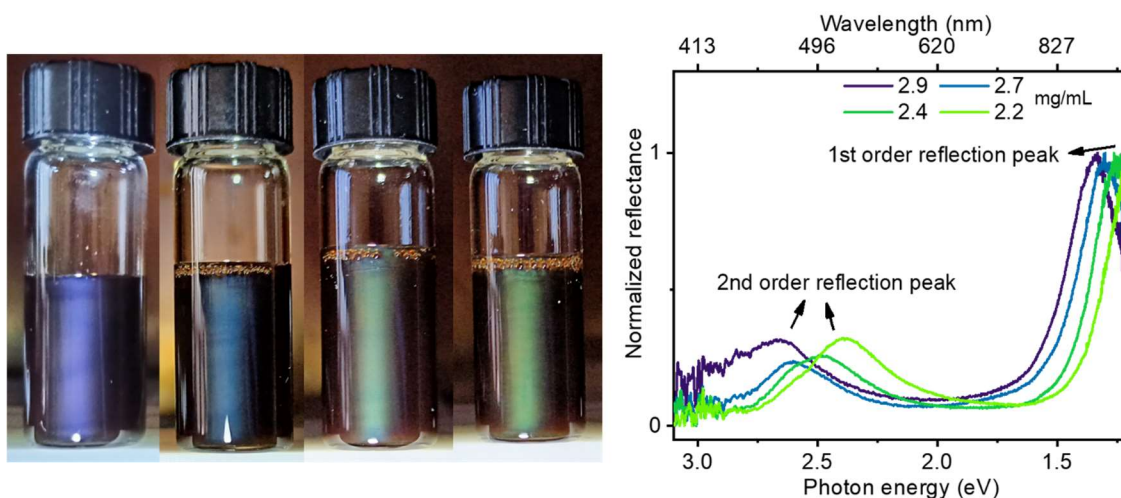
**Fig. S5** Reflection wavelength as a function of concentration of GO in diethyl ether, ethyl acetate, 3-pentanone, and water.



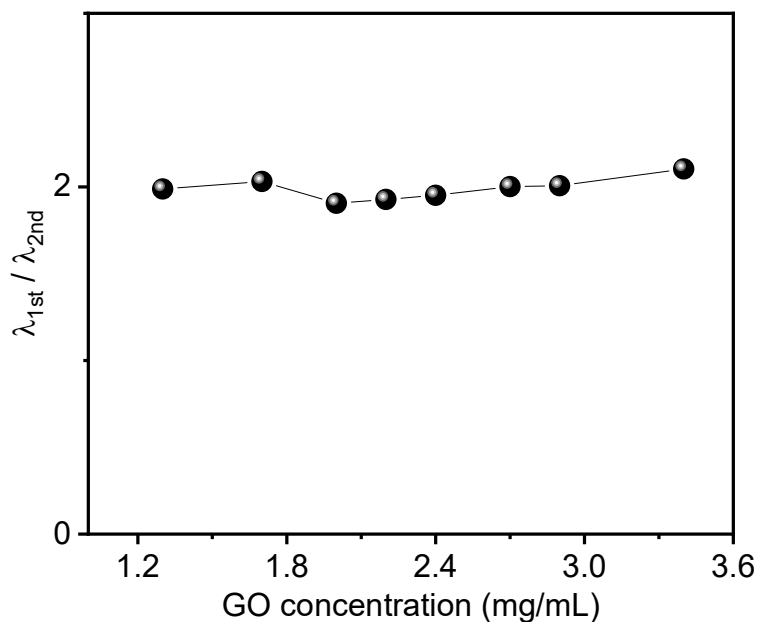
**Fig. S6** Viewing the GO hydrophobic photonic liquids in ethyl acetate at different angles reveals the angle-dependent coloration. The viewing angle decreases from  $\sim 90^\circ$  to  $\sim 25^\circ$  for sample from left to right. The viewing angle here is the angle between the viewing direction and the surface of cuvette. The concentration of the GO is  $\sim 4$  mg/mL.



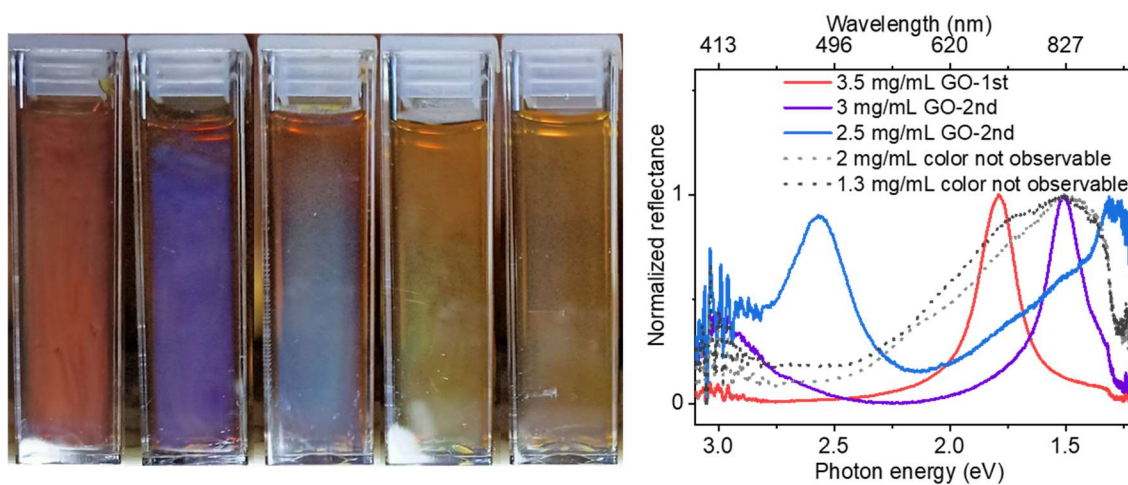
**Fig. S7** (a, b, c, d, e) GO photonic suspensions in ethyl acetate showing tunable structural colors. From (a) to (e), the samples were continuously diluted. Diluting the red sample (c) generated GO photonic liquids with blue (d) and green color (e) again, indicating the emergence of second order Bragg reflection in the visible range.



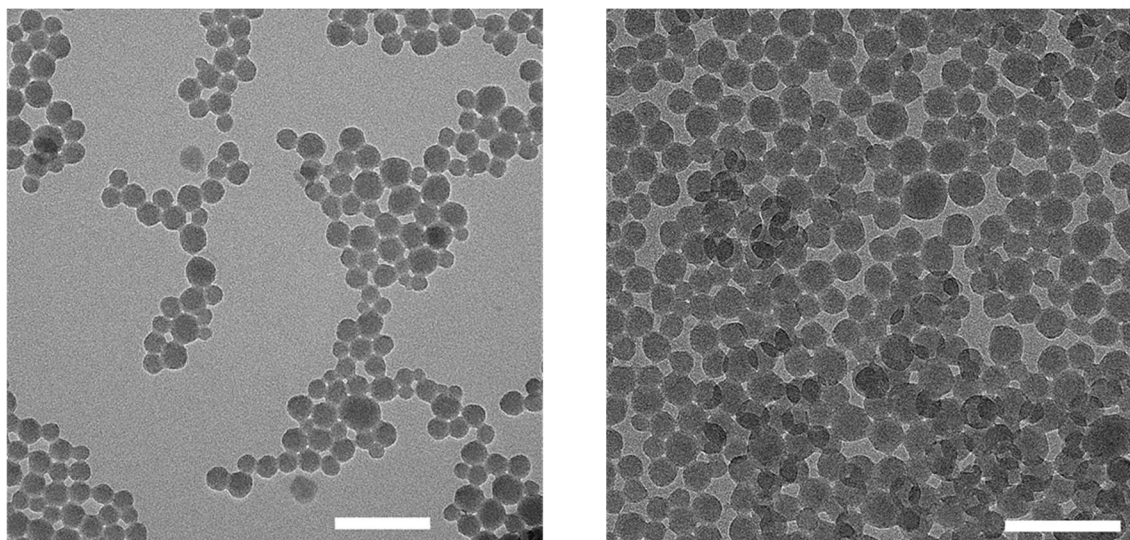
**Fig. S8** Dilute GO hydrophobic liquids (in 3-pentanone) showing first order and second order reflectance at the same time. The concentrations for the samples were  $\sim 2.2$  to  $2.9$  mg/mL.



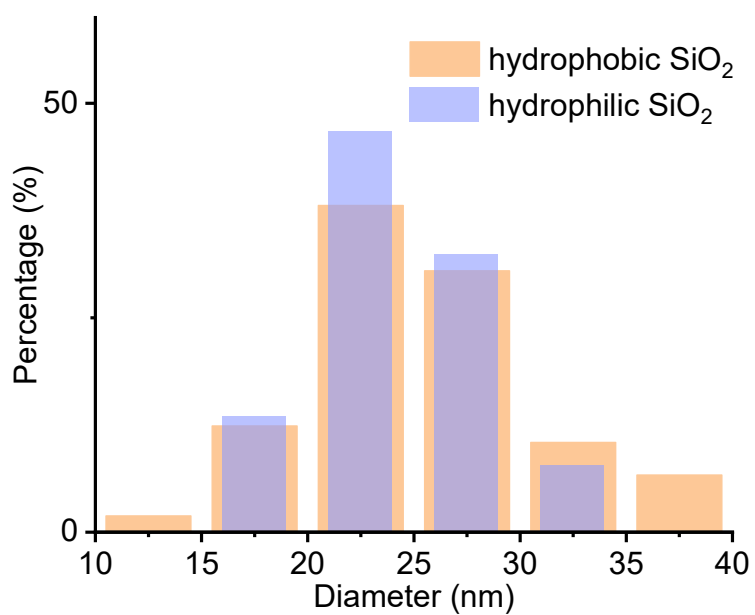
**Fig. S9** The ratio between 1st order reflection and 2nd order reflection wavelength ( $\lambda_{1st}/\lambda_{2nd}$ ).



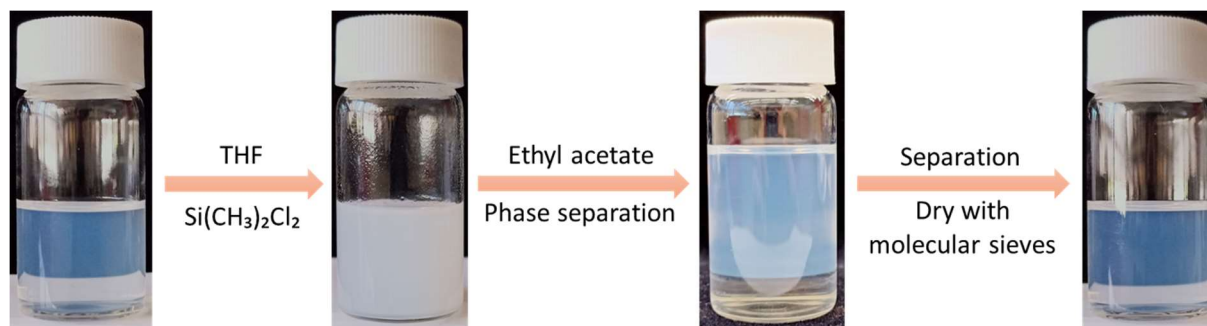
**Fig. S10** Diluting a GO aqueous suspension that shows a red reflection color caused by first order reflection produced GO suspensions with blue color caused by second order reflection. Further dilution did not generate other reflection colors, indicating it is difficult for GO nanosheets to arrange themselves into a highly ordered structure with large periodicity in water.



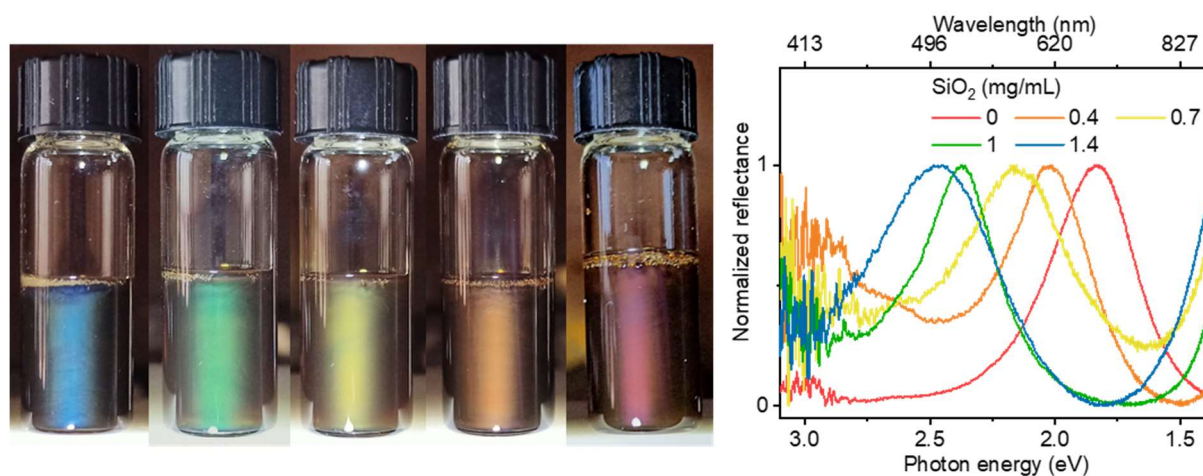
**Fig. S11** TEM images of SiO<sub>2</sub> nanoparticles before (left) and after (right) hydrophobization. Scale bar: 100 nm



**Fig. S12** Diameter distribution of hydrophilic and hydrophobic SiO<sub>2</sub> nanoparticles. 105 nanoparticles for each species of SiO<sub>2</sub> nanoparticles were analyzed. The mean size for hydrophilic and hydrophobic SiO<sub>2</sub> nanoparticles is  $24 \pm 3.8$  nm and  $25 \pm 5.4$  nm, respectively.

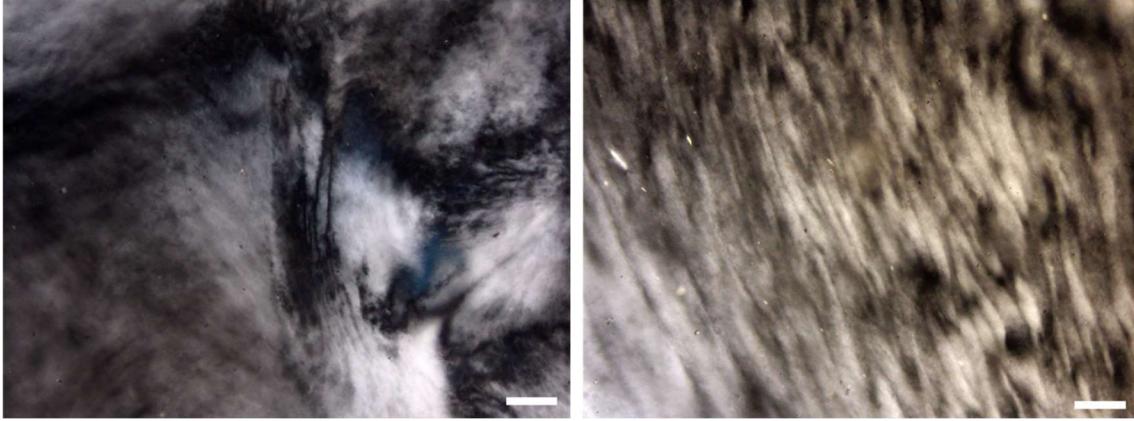


**Fig. S13** Photographs of the suspensions during the hydrophobization of SiO<sub>2</sub> nanoparticles. (Detailed procedures are in the experimental section). The light blue color from the suspensions is due to the Rayleigh scattering of SiO<sub>2</sub> particles, which have sizes that are much smaller than the light wavelength.

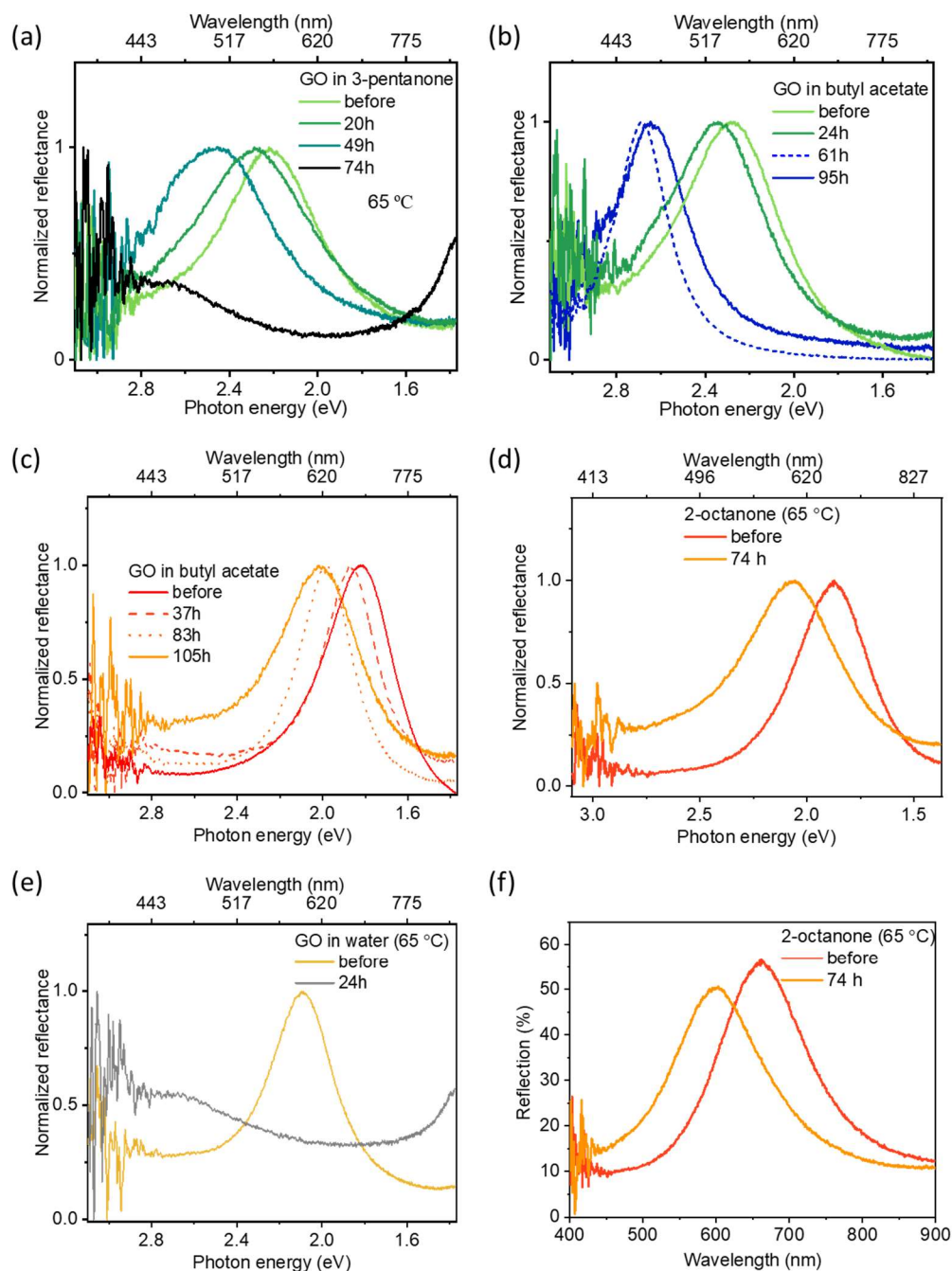


**Fig. S14** Dilute GO-SiO<sub>2</sub> suspensions in ethyl acetate showing second-order reflections in the visible range. The concentration of GO is 1.6 mg/mL.

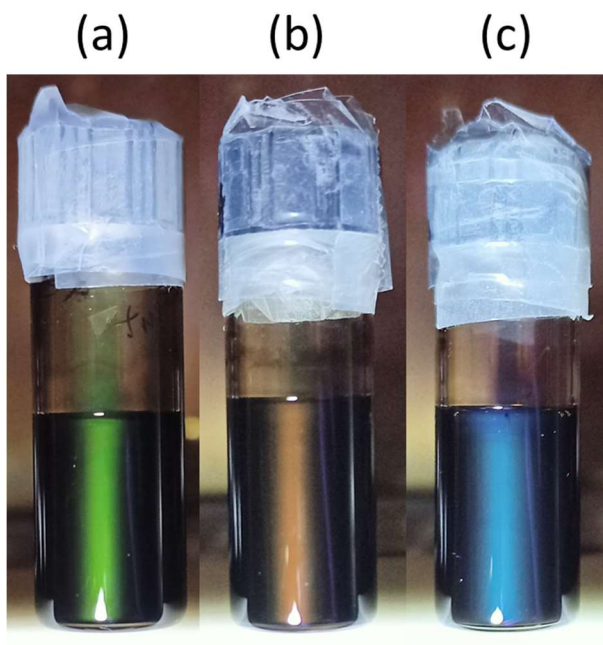




**Fig. S15** POM image of GO suspension in cyclohexane (left) and toluene (right). The concentration of GO is 5.1 mg/mL. Scale bar: 100  $\mu\text{m}$



**Fig. S16** Reflectance spectra of (a) GO in 3-pentanone, (b,c) GO in butyl acetate, (d) GO in 2-octanone, (e) GO in water during heating shown in Fig. 6. (f) Reflectance spectra without normalization for GO in 2-octanone during heating shown in Fig. 6d. The concentration is 5.4, 4.9, 3.4, 4.1 and 5.5 mg/mL for (a), (b), (c), (d) and (e), respectively. For (a,d,e), the temperature and heating time were 65 °C for 74 h for (a,d), and 24 h for (e). For (b,c), the temperatures and heating time were 75 °C for 24 h, then 80 °C for 37 h, then 90 °C for 34 h for (b), and 75 °C for 37 h, then 80 °C for 46 h, then 90 °C for 22 h for (c).

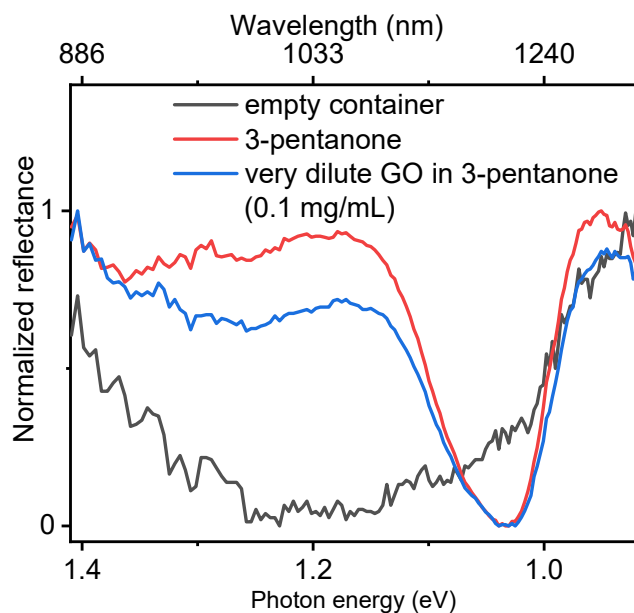


**Fig. S17** (a) A green GO hydrophobic liquid obtained after heating at 80 °C for 60 h. (b) Dilution of the sample shown in (a) gave a red GO hydrophobic liquid. (c) Adding high concentration GO suspension to (a) to increase the total GO concentration gave a blue GO hydrophobic liquid. The liquid medium was butyl acetate.



**Fig. S18** GO photonic suspensions in pure poly(APMS-co-DMS) copolymer liquids were injected into a plastic mold to make an “UBC” pattern with different reflection colors. Scale bar: 1 cm.





**Fig. S19** NIR spectrum for empty container, container with 3-pentanone, and very dilute GO suspensions in 3-pentanone.

#### Reference for supporting information

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