Supporting Information

## Tuning the Photonic Properties of Graphene Oxide Suspensions with Nanostructured Additives

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## Experimental

General: The morphology and structures of the samples were examined with a Hitachi S4700 field-emission scanning electron microscope and a Hitachi H7600 transmission electron microscope. Samples for SEM and TEM were prepared by drop-casting a 0.002 wt.% GO aqueous suspension onto carbon-coated copper grids and silicon wafers, respectively. The samples were sonicated (< 2 mins) before being cast. Reflectance spectra were obtained with an Ocean Optics setup. This setup contained a Flame series spectrometer (FLAME-S-XR1, Ocean Optics Inc., USA), a tungsten halogen light source (DH2000-BAL, Ocean Optics Inc., USA), and OceanView software (1.6.7, Ocean Optics Inc., USA). The light source, spectrometer, and sample probe were connected by a bifurcated optical fiber (R-400-UV-Vis, Ocean Optics Inc., USA). Polarized optical microscopy (POM) images were collected using an Olympus BX41 microscope equipped with a complementary metal oxide semiconductor camera. X-ray scattering measurements were performed on a Ganesha 300XL+ instrument. Suspensions of GO with a GO concentration of 0.5 and 2 mg/mL were used for dynamic light scattering (DLS) and zeta potential measurements, respectively. Additive concentrations were adjusted according to the ratios between GO and additives. GO and additives were mixed using a Thermo Scientific LP Vortex Mixer. DLS and zeta potential measurements were conducted at room temperature on a NanoBrook Omni (Brookhaven Instruments). X-ray diffraction patterns were collected using a Bruker D8 Advance X-ray diffractometer. A Durasonix 3 Litre Ultrasonic Cleaner (Power of 120 W, Frequency of 40 kHz) and a Thermo Scientific LP Vortex Mixer were used for homogenization treatment. Hermans order parameters were calculated according to previous work using the following equations<sup>1</sup>:

$$S = \frac{3(\cos^2 \gamma) - 1}{2}$$
Eq. 1
$$(\cos^2 \gamma) = 1 - 2(\cos^2 \emptyset)$$
Eq.2

2

$$\langle \cos^2 \phi \rangle = \frac{\int_0^{\pi} I(\phi) \cos^2 \phi \sin \phi \, d\phi}{\int_0^{\pi} I(\phi) \sin \phi \, d\phi}$$
 Eq. 3

To reveal the liquid crystalline structure in suspension by electron microscopy, we made GO-CNC aerogels according to our previous work.<sup>2</sup> The GO-CNC aerogels were prepared through the supercritical drying of the corresponding alcogels. Typically, 2 mL of the GO-CNC hybrid suspension (the concentrations of GO and CNC are 10 mg/mL) was kept in the fridge for 48 h (about 5 to 7 °C). Next, 16 mL of ethanol was carefully added on the top of the hybrid suspension. After the addition, a two-phase system could be observed: the top layer was the ethanol and the bottom layer was the GO-CNC hybrid suspension. The water in the lower phase was slowly exchanged with ethanol at room temperature. The upper organic phase was removed and exchanged with fresh ethanol 1–2 times each day until the lower GO-CNC phase formed a stable alcogel (needs about one week). The resulting alcogel was converted into an aerogel with a critical point dryer, where the solvent was exchanged with liquid CO<sub>2</sub>, followed by supercritical drying.

**Preparation of graphene oxide photonic suspensions:** Graphene oxide was prepared according to previous reports.<sup>3,4</sup> The GO nanosheets used here have a lateral size of ~ 0.8-8  $\mu$ m as shown in Fig. S1. The successful expansion of graphite was proven by XRD as shown in Figure S22. In a typical procedure, graphite powder (4 g), sodium nitrate (2 g), and concentrated sulfuric acid (120 mL) were mixed by stirring for 1 h. Potassium permanganate (16 g) was then added to the mixture (4 g/30 mins, a cold water bath was used to provide a temperature of < 8 °C). After 16 h, 120 mL of water was added to the reaction mixture (30 mL / 10 mins). The temperature was raised to about 80 °C and the stirring was continued for another 30 mins. Finally, 120 mL of water was added to mixture, followed by addition of hydrogen peroxide (6 mL). This changed the reaction color to ochre yellow. The obtained

product was washed repeatedly by centrifugation (14 000 rpm, 2 h each time, 11 times) using distilled water. The gel-like GO was obtained at the bottom of centrifuge tube. The GO gel was diluted with a prescribed amount of deionized water to obtain the GO aqueous suspensions with desired concentrations. The suspensions could display different colors, depending on the GO concentrations.

Preparation of GO-clay nanoplates and GO-CNC hybrid colloidal photonic suspensions: Clay nanoplates were obtained from Kunimine Industries Co. Ltd. Cellulose nanocrystals were obtained from FPinnovations. Clay nanoplates for this study have a lateral size that range from  $\sim$  0.1 to 1.2  $\mu$ m as shown in Fig. S2. CNCs are  $\sim$  100-500 nm in length and  $\sim$  20 nm in width as shown in Fig. S5. The hybrid colloidal photonic suspensions were prepared by mixing GO with clay nanoplates or CNCs in a proper ratio. For instance, to make a suspension that reflected green light, 8.4 mg of synthetic hectorite was added to 6 mL of 3 mg/mL GO suspension, or 2.4 mg of synthetic hectorite was added into 6 mL of 5 mg/mL GO suspension. As another choice for obtaining the photonic suspension with green color, 153 µL of CNC suspension (60 mg/mL) was added to 6 mL of GO suspension (3.1 mg/mL). The reflected green color was observed by illuminating the suspension with white light. GO and clay nanoplates (or CNCs or other additives) were mixed using a Thermo Scientific LP Vortex Mixer (or by sonication for 5 mins) and then kept at room temperature for 20 mins to give a homogeneous suspension. GO suspensions with polymeric and molecular additives listed in Table 1 were prepared by mixing the dried additives with GO suspensions using the vortex mixer (or by sonication). The ratios between GO and other additives were adjusted for comparision study. For variabletemperature (VT) experiments, hybrid suspensions with 2.5 mg/mL GO and 0.5 mg/mL colloidal additives (CNCs and clay nanoplates), and bare GO suspensions with a concentration of 4.5 mg/mL were prepared and placed in an oven set at a preset temperature for 35 mins. The samples were then cooled down for 30 mins before recording the reflection spectra with the Ocean Optics setup.

## Supplementary Table and Figure



**Scheme S1** Schematic for the arrangements of GO under different conditions. (a,b) Periodic structures (positional order) can be formed by (a) adding GO nanosheets or (b) colloidal additives like CNCs and clay nanoplates. (c) The positional order of GO is lost by adding anionic polymers or molecules while the orientational order might be maintained. (d) Nonionic polymers or molecules do not affect the positional order of GO.

Colloidal additives	Clay nanoplates (synthetic hectorite)		
	Cellulose nanocrystals (CNCs)	Tunable photonic phenomenon	
Macromolecular (polymeric) additives (non-ionic)	Polyethylene glycol (PEG) <sup>a</sup>	No effect	
	Hydroxypropyl cellulose (HPC) <sup>a</sup>	NO ENECL	
Macromolecular (polymeric) additives (anionic)	Sodium carboxymethyl cellulose (CMC-Na) <sup>a</sup>	Photonic properties destroyed	
	Sodium polyacrylate (PAA-Na) <sup>a</sup>	Filotofile properties destroyed	
Molecular additives (non-ionic)	Glucose	No effect	
Molecular additives (anionic)	Sodium dodecyl sulfate (SDS)	Photonic properties destroyed	
The molecular weights for REG. HPC. CMC-Na and RAA-Na are 20000, 20000, 25000, and			

<sup>a</sup> The molecular weights for PEG, HPC, CMC-Na and PAA-Na are 20000, 80000, 25000, and 5100 Da, respectively.



**Fig. S1** (a) SEM image of GO nanosheets. (b) Lateral size distribution of GO nanosheets (119 nanosheets were analyzed). The lateral size was estimated by averaging the lengths of the longest side and shortest side of each particle.



**Fig. S2** (a) SEM image of clay nanoplates. (b) Lateral size distribution of clay nanoplates (147 nanoplates were analyzed); (c) Photograph of clay nanoplate suspension (1 mg/mL) in a vial.



Fig. S3 Reflectance spectrum of the GO suspensions with a concentration of 3 mg/mL.



**Fig. S4** Viewing the GO-(clay nanoplate) suspension at different angles reveals the angledependent coloration. The viewing angle is ~90° and around  $60^{-70°}$  for (a) and (b), respectively. The sample contains 3 mg/mL GO and 1.4 mg/mL clay nanoplates.



**Fig. S5** (a) TEM image of CNCs. (b) Length distribution of CNC rods (118 nanocrystals were analyzed). (c) Photograph of CNC suspension (1 mg/mL) in a vial.

(a)	(b)	(c)	(d)
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**Fig. S6** Photographs of the 6 mg/mL GO photonic suspension without additives (a,c) and with 0.9 mg/mL CNC-H (b) and 0.9 mg/mL CNC-Na (d).



**Fig. S7** (a) Photographs of photonic GO suspensions at different concentrations. The value under the cuvette corresponds to the concentration of GO (unit: mg/mL). (b) Corresponding reflectance spectra of the GO photonic suspensions.



**Fig. S8** Photograph of the GO-CNC aerogels (left, scale bar: 1 cm) and the coressponding crosssection SEM image (Right). Some CNC domains could be observed inside the GO-CNC mixtures, probably due to the demixing transitions between colloidal species caused by the depletion attraction between GO nanosheets.



**Fig. S9** Reflection wavelength as a function of the reciprocal volume fraction for GO, GO-clay nanoplates, and GO-CNC samples.



**Fig. S10** A GO suspension (6.6 mg/mL) with similar blue color as the GO-CNC samples shown in Figure 1b.



**Fig. S11** (a,b) Photographs of 5.5 mg/mL GO suspensions without additives (a) and with 2.3 mg/mL PEG (b). (c) Reflectance spectrum of GO suspensions with and without PEG additives.



**Fig. S12** (a,b) Photographs of 5.5 mg/mL GO suspensions without additives (a) and with 3.6 mg/mL HPC. (b). (c) Reflectance spectra of GO suspensions with HPC added.



**Fig. S13** (a,b) Photographs of 6 mg/mL GO suspensions without (a), with 0.7 (b) and 1.2 mg/mL glucose additives (c). (d) Reflectance spectra of GO suspensions with glucose additives.



**Fig. S14** (a,b) Photographs of 5.5 mg/mL GO suspensions without additives (a), with 0.7 (b) and 1.1 mg/mL CMC-Na (c). (d) Reflectance spectra of GO suspensions with CMC-Na added.



**Fig. S15** (a,b) Photographs of 5.5 mg/mL GO suspensions without additives (a) and with 1.8 mg/mL SDS (b). (c) Reflectance spectra of GO suspensions with SDS added.



**Fig. S16** (a) Reflectance spectra of photonic GO suspensions with different additives (samples with green visible light reflection were selected for comparison). (b) Corresponding  $\Delta\lambda/\lambda_{max}$  of (a) shows how the peak widths are affected by the additives. The numbers in (a) and (b) indicate the concentration of GO and additives



**Fig. S17** (a-c) 2D SAXS patterns of pure GO (3 mg/mL for a and 6 mg/mL for b) and GO-PEG suspensions (c), The values in the names for (a) and (b) indicate the concentration of GO and additives (unit: mg/mL).



**Fig. S18** (a) POM image of GO suspension. (b-d) POM images of GO suspension with CMC-Na (b), PAA-Na (c) and SDS (d). The GO concentration is 6 mg/mL and the anionic additives have a concentration of 2.4 mg/mL in each case. Scale bar:  $100 \mu m$ .



**Fig. S19** Zeta potential for GO suspensions with different additives. The initial GO concentration was 2 mg/mL



Fig. S20 Effective diameters of the GO-(PAA-Na) samples based on the DLS measurement



**Fig. S21** (a-c). Reflectance spectra of (a) GO-CNC, (b) GO-Clay nanoplates and (c) bare GO at different temperatures shown in Figure 4c. (d) Plots of  $\Delta\lambda/\lambda_{max}$  at different temperatures for hybrid colloidal suspensions and bare GO suspensions.



Fig. S22 XRD pattern of graphene oxide.

## References

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