Electronic Supplementary Material (ESI) for Soft Matter

Supplementary Information for:

Highly stable, concentrated dispersions of graphene oxide sheets and their electro-responsive characteristics

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1. Experimental Section

Materials: Graphite (flake, <20 μm, synthetic) was purchased from Sigma–Aldrich. Other reagents including $KMnO_4$, HCl, H_2SO_4, H_2O_2 and ethanol were also obtained from Aldrich Chemical Co. All regents were used as received. Distilled water was used in all experimental processes. For electrorheological (ER) fluid application, silicone oil (Aldrich, poly(methylphenylsiloxane), viscosity = 100 cSt) was used as a dispersing medium.

Fabrication of graphene oxide (GO) sheets: GO was synthesized from graphite using a modified Hummers method. Typically, graphite (1.0 g) was added to 70 mL of H_2SO_4 in an ice bath, which was followed by the addition of $KMnO_4$ (3.0 g) and $NaNO_3$ (0.5 g). After stirring for 4 h, 70mL of distilled water was slowly added and maintained at that temperature for 30 min. Subsequently, H_2O_2 solution was added to the solution until the color turned a brilliant brown indicating fully oxidizing state. The as-prepared graphite oxide slurry was exfoliated to generate GO nanosheets by sonication using an ultrasonic generator (42 kHz, 100W, Branson 3510, Branson Cleaning Equipment Co., Shelton, CT, USA) for 3 h. Finally, the mixture was separated by centrifugation, washed repeatedly with 5% HCl and distilled water, and dried in a vacuum oven at 40 ºC for 24 h.

Preparation of mechanically grinded and solvent exchanged GO sheets: The dried GO was ground into uniform powder using a milling machine (Analytical Mill. A11, IKA Works). The

solvent exchanged GO sheets were prepared using the difference of density between silicone oil and ethanol medium. First, 2.0 g of graphite oxide slurry (filter cake) in 20 mL of ethanol was sonicated for 2 h, and centrifuged at 500 rpm for 30 min to remove large particles. The supernatant of graphene in ethanol was decanted and further sonicated for several minutes to give the required homogeneous GO sheets dispersion in ethanol. Second, the 10 mL of GO sheets dispersed in ethanol was poured into 10 mL of silicone oil. The mixture was centrifuged at 10000 rpm for 30 min to settle down into silicone oil phase. After centrifugation, the supernatant was decanted and further dried. The loosely flocculated GO sheets were redispersed in silicone oil under sonication at room temperature, resulting a homogeneous black suspension. The repeated settling steps yield a stable dispersion of graphene in silicone oil containing up to 5.0 wt%.

Investigation of electrorheological properties: The ER properties of the GO-based ER fluids were examined via rheometer (AR 2000 Advanced Rheometer, TA Instruments) with a concentric cylinder conical geometry of 15 mm cup radius with a gap distance of 1.00 mm, a high-voltage generator (Trek 677B), and a temperature controller. To start a run, an ER fluid is placed between cup and rotor, and DC voltage is applied. An electric field was applied for 3 min to obtain an equilibrium chain-like or columnar structure before applying shear. All measurements were made at a room temperature. Under our experimental condition, the yield stress values for the prepared ER fluids were mainly obtained from a flow curve, which was

measured by a controlled shear rate (CSR) mode experiment. The stress value of the transition point at which shear viscosity abruptly decreased was regarded as the dynamic yield stress.

2. XPS C1s Spectra of GO Sheets

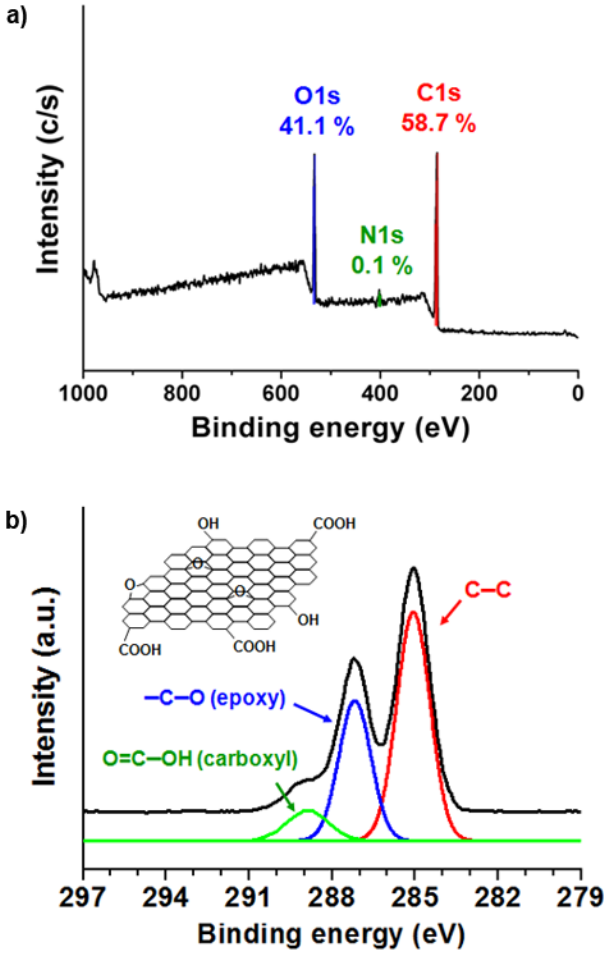

Fig. S1. a) XPS Survey of GO sheets oxidized graphene discs and b) XPS C1s spectra of GO sheets.

Fig. S1a depicts a survey scan of oxidized graphene sheets with the relative atomic percentages. Oxidized graphene consisted of carbon (58.7 %), oxygen (41.1 %), nitrogen (0.1 %), respectively. The C/O composition ratio of GO sheets (1.43) has good agreement with previous XPS studies of GO. The deconvoluted C1s XPS spectrums of GO sheets is also

presented (**Fig. S1b**). Generally, the C1s signal of GO sheets mainly consists of three components, which are C=C/C−C in aromatic rings (285.0 eV), C−O (286.5 eV) and O=C−OH (288.5 eV) peaks. While the C−O component comes from epoxy and hydroxyl groups, the O=C−OH bond originates from carboxyl groups ($I_{C-O}/I_{C-C} \approx 0.61$). The XPS spectrum result indicated that oxygen-containing groups are introduced on graphene surface during the oxidation step.

3. Comparison of Sediment Velocity of GO Sheets in Silicone Oil

Table S1. Physical parameters and sedimentation velocity of GO sheets in silicone oil

	Solvent exchanged GO sheets	Mechanically grinded GO sheets
Particle size [a]	*ca.* 20 μm	*ca.* 300 μm
Particle density [b]	1.14 g/cm^3	2.17 g/cm^3
Fluid density [c]	0.97 g/cm^3	0.97 g/cm^3
Fluid viscosity [c]	0.097 Pa·s	0.097 Pa·s
Sedimentation velocity [d]	0.00000038 m/s	0.00060680 m/s

[a] The average particle size was determined by SEM (50 particles counted), [b] Particle density was obtained using density hydrometer at a standard temperature of 20 ºC, [c] Silicone oil [poly(methylphenylsiloxane), viscosity = 100 cSt] was used as a dispersing medium, [d] The calculation method used was Stoke's settling equation. Particle Reynolds number less than 0.2.

The physical parameters and sedimentation velocity of two different types of GO sheets are summarized in **Table S1**. the sedimentation velocity (V_g) was estimated using the Stoke's settling equation and was found to be 3.8×10^{-7} and 6.1×10^{-4} m s^{-1} for solvent exchanged GO sheets and mechanically grinded GO sheets, respectively. It is noteworthy that the V_g value of solvent exchanged GO sheets is *ca.* 1600 times slower than that of mechanically grinded GO sheets.

4. Shear stress for GO sheet-based ER fluids under electric field strength.

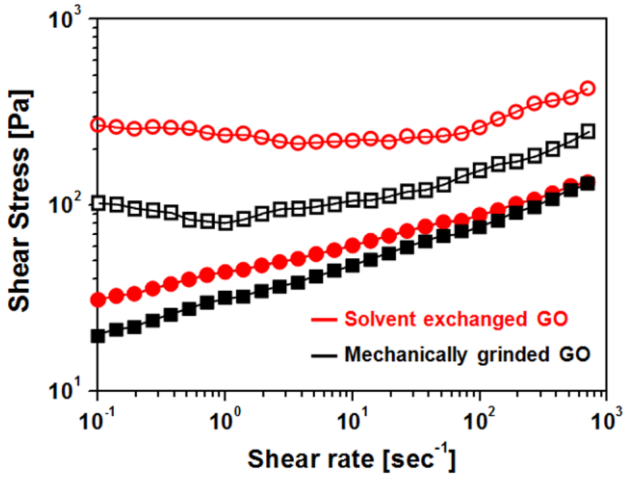

Fig. S2. Shear stress for the 5 wt% of GO sheet-based ER fluids under electric field strength (5 kV/mm). Open and closed symbols indicate with and without electric field strengths, respectively.

5. Off-field viscosity of GO sheet-base ER fluids

The off-field viscosity of dispersion increases with increasing intermolecular forces between dispersing materials. In dispersion state, well-dispersed isolated GO sheets produce larger particle-particle interaction between GO sheets than flocculated or agglomerated GO sheets at equal GO concentration (Fig. S3). Therefore, the solvent exchanged GO sheet-based ER fluid has a relatively high off-field viscosity. The off-field viscosity value of solvent exchanged GO sheets is *ca.* 0.513 Pa·s, which is 2.1 times that of mechanically grinded GO sheets (Table S2).

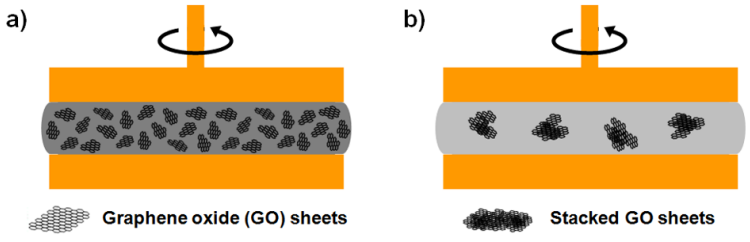

Fig. S3 Schematic illustration for the dispersing state of (a) solvent exchanged GO sheets and (b) mechanically grinded GO sheets.

Table S2. Off-field viscosity of GO sheets in silicone oil

	Silicone oil [a]	Mechanically grinded GO sheets	Solvent exchanged GO sheets
Off-field viscosity [b]	0.097 Pa·s	0.245 Pa·s	0.513 Pa·s

[a] The silicone oil (Aldrich, poly(methylphenylsiloxane), viscosity = 100 cSt) was used as a dispersing medium. [b] These values were obtained using rheometer (AR 2000 Advanced Rheometer, TA Instruments) at a standard temperature of 20 ºC.