Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Organic dispersions of graphene oxide with arbitrary concentrations and improved chemical stability

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Experimental details.

Dispersion of GO. Graphite oxide was synthesized from natural graphite powder (12,000 mesh, Qingdao Huatai Lubricant Sealing S & T Co. Ltd.) by a modified Hummers method.[S1,S2] As-prepared graphite oxide was soaked in 1:10 (by volume) HCl (36%-38%, Beijing Chemical Reagent Co., China) aqueous solution for 12 h and then centrifuged (10,000 r.p.m. for 10 min) to remove HCl aqueous solution. Repeated this procedure for five times to extensively remove residual metal ions, and then the graphite oxide sample was washed with anhydrous alcohol (Beijing Chemical Reagent Co., China) in the same way for another five times to remove residual HCl aqueous solution. This ethanol washed graphite oxide was air dried for about 3 hours to evaporate superfluous ethanol. Successively, the ethanol-wetted graphite oxide containing about 30 wt% ethanol was put into deionized water or an organic solvent to form a stable dispersion by stirring or mild sonication. The organic solvents include PC (⩾99%, Alfa－Aesar), DMSO (Analytical grade, Beijing Chemical Reagent Co., China), EG (spectrum pure, ⩾99%, Aladdin) and DMF (Analytical grade, Beijing Chemical Reagent Co., China).

Stability testes of GO in PC and H_2O. 100 mg freshly prepared ethanol-wetted graphite oxide was dispersed in 10 mL PC or H_2O to form a 10 mg mL^{-1} GO dispersion. Both dispersions were stored at room temperature for certain period. Then ethanol (10 mL) was first added into each of the dispersions and mixed by shaking. Successively, 10 mL 1:10 HCl aqueous solution was added to induce the aggregation of GO sheets. The aggregated GO particles were collected by centrifugation (10,000 r.p.m. for 10 min) and washed with anhydrous alcohol. Finally, the two purified samples were vacuum dried at 40 °C for XPS, FTIR and NMR spectroscopy characterizations. For UV-Vis spectra analysis, two copies of the purified graphite oxide (0.6 mg of each) were added into PC (30 mL) and H_2O (30 mL) independently, forming GO dispersions of 0.02 mg mL^{-1}. UV-Vis spectra data were recorded at the stated time.

Characterizations. AFM images were taken out by using a SPM-9600 atomic force microscope (Shimadzu). The samples were prepared by dropping diluted GO dispersions with ethanol (0.03 mg mL^{-1}) on mica sheets. XPS spectra were recorded on an ESCALAB 250 photoelectron spectrometer (ThermoFisher Scientific) with Al Kα (1486.6 eV) as the X-ray source set at 150 W and a pass energy of 30 eV for high resolution scan. UV–visible spectra were taken out by the use of a U-3010 UV–visible spectrometer (Hitachi, Japan). Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) spectra were recorded on a Fourier transform infrared spectrometer (Bruker Vertex V70). Solid state ^{13}C magic-angle spinning (MAS) NMR spectra were acquired on a Bruker advance III 400 spectrometer (100.38 MHz ^{13}C).

Supplementary Tables

Table S1. Composition comparison of the GO purified by repeated washing with ethanol (GO1) with that of the GO purified by dialysis (GO2); the values listed in this table are the atomic percentages of the elements.

GO	C	O	S	Cl	Mn	Ref.
GO1	73.56	25.53	0.59	0.19	0.13	This work
GO2	68.42	31.04	0.31	0.23	Undetectable	S3

Table S2. Dielectric constants of different solvents at 20 $^{o}C^{S4, S5}$.

Solvent	Dielectric constant
DMSO	46.7
PC	62.9
DMF	37.1
NMP	32.6
THF	7.47
Acetone	21.4
H_2O	80.4
EG	38.7
IPA	18.6
Ethanol	25.0

Supplementary Figures

Figure S1. Insolubilization of graphite oxide in ethanol.

The photograph shows the phase separation of graphite oxide in ethanol, implying graphite oxide is insoluble in ethanol.

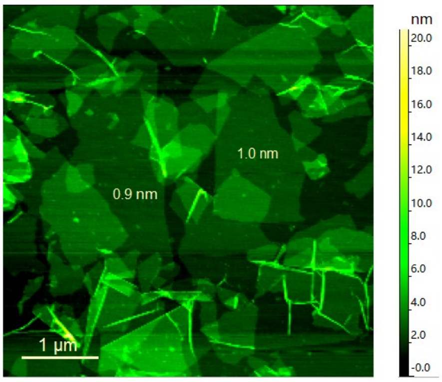

Figure S2. AFM image of GO sheets from GO (PC) dispersion.

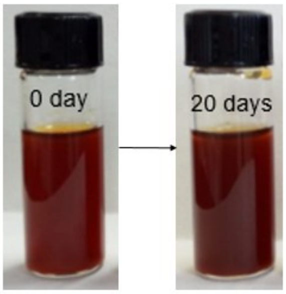

Figure S3. Stability test of concentrated GO (PC) dispersion.

The photograph demonstrates that the GO (PC) dispersion is stable without serious aggregation after a long-term storage of 20 days; GO concentration = 10 mg mL^{-1}.

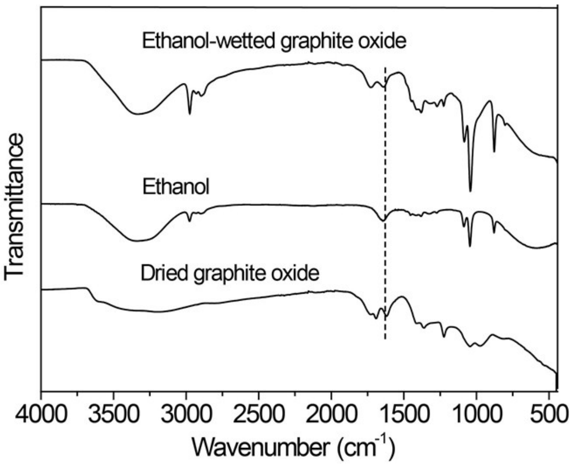

Figure S4. FT-IR spectra of ethanol-wetted graphite oxide, ethanol and dried graphite oxide.

The near 1619 cm^{-1} (denoted by the dotted line) absorption band is assigned to the bending modes of water molecules.[S6] The intensity of the water peak in ethanol-wetted graphite oxide is almost equivalent to that of dried graphite oxide, implying the negligible water content in the ethanol-wetted graphite oxide.

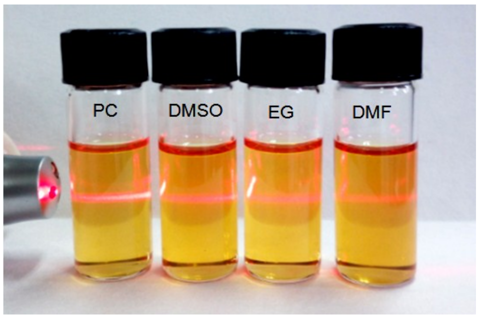

Figure S5. Colloidal nature of GO dispersions in PC and other organic media.
The photographs show the Tyndall effect of GO dispersions with different organic solvents; GO concentration = 0.5 mg mL^{-1}.

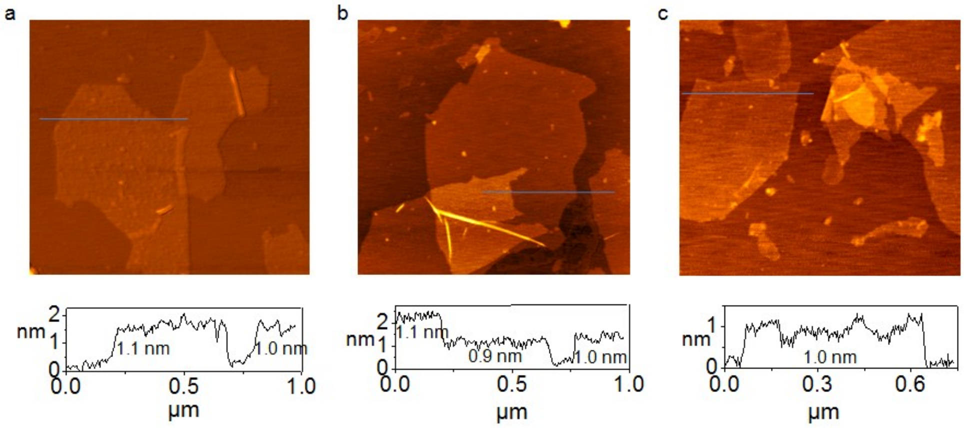

Figure S6. AFM images of GO sheets with thickness profiles; (a) GO (DMSO), (b) GO (EG), and (c) GO (DMF).

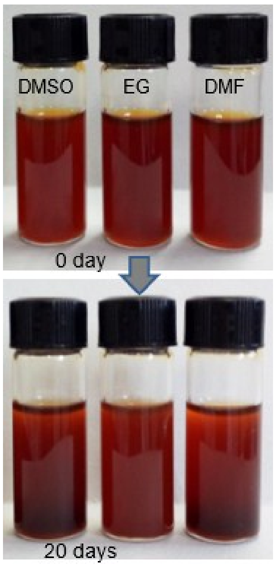

Figure S7. Stability of concentrated GO dispersions in DMSO, EG and DMF respectively.

The photographs demonstrate that the organic dispersions of GO are also stable without serious aggregation after a long-term storage of 20 days; GO concentration = 10 mg mL^{-1}.

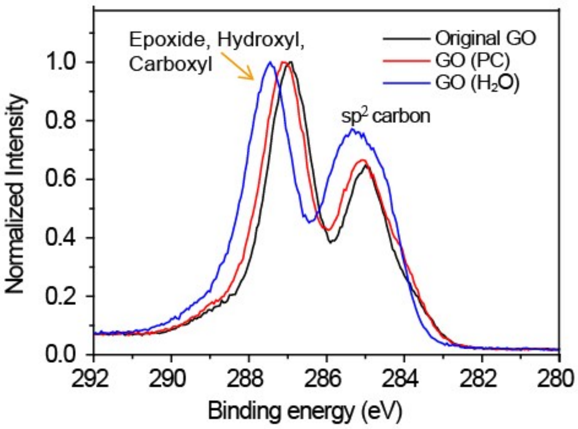

Figure S8. C1s XPS spectra of as-prepared GO sheets and those collected from the GO (PC) or GO (H_2O) dispersion after storing under ambient environment for two weeks.

Figure S8 shows the C 1s X-ray photoelectron (XPS) spectra of fresh GO sheets and those collected from the aqueous or PC dispersion (10 mg mL^{-1}) after storing for two weeks; the latter samples are called GO (H_2O) or GO (PC). The spectrum of GO (H_2O) shows a sp^2-carbon related peak much stronger than that of fresh GO. In comparison, the intensity difference between the sp^2-carbon related peaks in the spectra of GO (PC) and fresh GO is negligible, reflecting the chemical structure of GO sheets in PC kept nearly intact after a long-time storage.

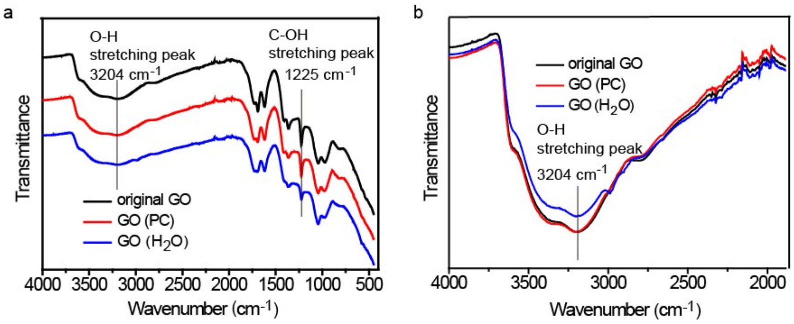

Figure S9. (a) FT-IR spectra of as-prepared GO sheets, and the GO sheets collected from GO (PC) or GO (H_2O) dispersions after storing under ambient environments for two weeks, and (b) corresponding detailed FT-IR spectra between 4000–2000 cm^{-1} of as-prepared GO sheets, GO (PC) and GO (H_2O). The three spectra are normalized with respect to the 1723 cm^{-1}.

The spectrum of GO (PC) after storing for two weeks is nearly identical to that of original GO. However, the spectrum of GO (H_2O) after storing for two weeks exhibits obvious difference from that of original GO, especially at 1225 cm^{-1} (C−OH stretching peak) and 3204 cm^{-1} (O-H stretching peak). The intensity of C−OH and O-H peaks in GO (H_2O) is weakened, implying the decrease in its content of OH groups. This is consistent with the reaction mechanism of GO in H_2O.[S7] These results indicate that the organic solvent greatly improved the structural stability of GO sheets.

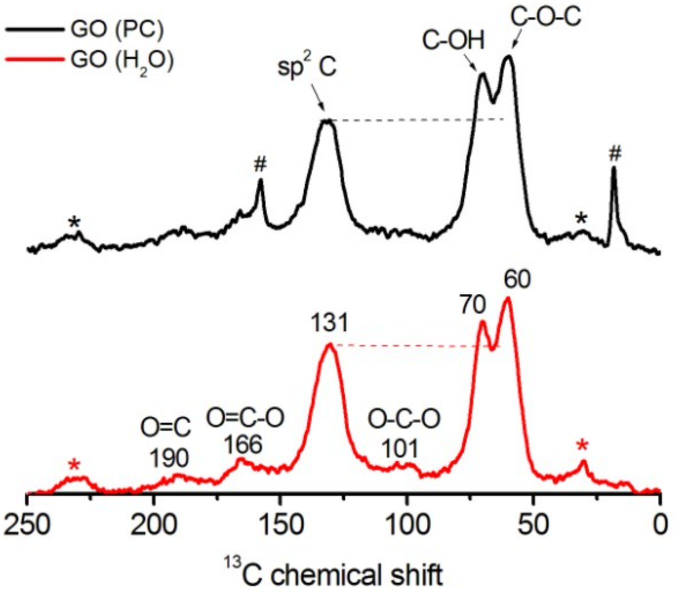

Figure S10. Solid-state ^{13}C NMR spectra of the GO sheets collected from GO (H_2O) and GO (PC) after storing under ambient environment for 28 days. Direct ^{13}C pulse spectra obtained with 10.0 kHz MAS. The spectra are normalized with respect to the height of the signal at 60 ppm. Asterisks (*) denote spinning sidebands. The weak signals indicated by pound sign (#) in the GO (PC) spectrum result from residual PC.

The spectra of both GO samples show the presence of C-O-C (60 ppm), C-OH (70 ppm), O-C-O (101 ppm), sp^2 C (131 ppm), O=C-O (166 ppm) and O=C (190 ppm) groups.[S8] The main difference between the spectra of GO (PC) and GO (H_2O) is that the sp^2 C signal of GO (H_2O) at 131 ppm is stronger than that of GO (PC), indicating that the GO sheets in water are structurally more unstable than those in PC.

Supplementary References

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