Electronic Supplementary Information (ESI)

Adding ethanol can effectively enhance the graphene concentration in water/surfactant solutions

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S1 Experimental details

The natural graphite flakes was purchased from Alfa Aesar Co., Ltd. (-325 mesh, 99.8%). Ethanol and acetone were purchased from Fuguang Chemical reagent Co., Ltd. Sodium Deoxycholate (SDOC) and other surfactants were purchased from Sinopharm Chemical Reagent Co., Ltd. The purified water was purchased from Beijing Kebai'ao Biotech. Co., Ltd. All the materials employed in the experiments were used without further preparation. The ethanol-water solution was pre-prepared. The mixing procedure was simple and the solution was directly used.

When using SDOC as the surfactant, graphite dispersion was prepared by adding 1g graphite powder to 200 ml SDOC-water-ethanol mixture in 300 ml capped round-bottomed flask.[1] The mixture was pre-prepared by adding different quantities of SDOC into ethanol-water solution, by which we can get SDOC solutions of different concentrations, i.e. 0.025 mg/ml, 0.05 mg/ml, 0.1 mg/ml, 0.25 mg/ml, 0.5 mg/ml, 1mg/ml and 2.5 mg/ml. It is worth noting that the dissolution of SDOC in water is not so well as the concentration of SDOC rise, so ultrasonication about 1 minute is needed to accelerate the dissolution. The SDOC solution mixed with graphite was transferred into six same-sized reagent bottles (30 ml). The graphite solution was then ultrasonicated by 100 W ultrasonic bath machine (KX-1730T Shenzhen Kexi Chemical Co., Ltd) for exactly 8 hours. In order to remove the massive graphite sediment, the bottles would stew overnight. After those procedures, the supernatant liquor was taken out into 10ml test tube for centrifugation (Xiang Yi L600; 1500 rpm, 30 min). Then the centrifuged liquor was extracted for the measurement of absorption by a UV-visible light spectrophotometer (TV-1900 Beijing Purkinje General Instrument Co., Ltd.; 660 nm wave length), through which we can detect the concentration of graphene dispersed in the solution. According to the Lambert-Beer Law, $A=\alpha_{660nm}C_G l$，C_G can be obtained from absorption with the coefficient of $\alpha_{660nm}=1390$ mLmg^{-1}m^{-1}. Different from powder-like SDOC, Tween 80 is sticky liquids, so that magnetic stirring for 10h was need before graphite was added to the solution.

Transmission electron microscope (TEM) and high resolution TEM (HRTEM)

images were performed by a JEOL JEM-2010FEF operated at 200 kV. AFM images were purchased by a Multimode 8 microscope (Bruker Corporation) equipped with a ScanAsyst-Air probe in ScanAsyst mode. Raman spectroscopy was performed on a Renishaw inVia Raman microscope with a 532 nm He–Ne laser. TEM samples were prepared by pipetting a few micro liters onto holey carbon mesh grid without diluting. For AFM sample preparation, we first diluted the centrifuged superficial clear solution by acetone (1:1000), and then ultrasonicated the solution for about 1minute. One drop of solution was dripped onto the mica plate. The prepared sample was placed into a dry case until acetone was evaporated entirely. In case that Tween 80 has poor compatibility with organic solvents, their solution with Tween 80 was diluted by deionized water. Raman samples were obtained by filtering graphene dispersion on an organic membrane filter, followed by drying in ambient conditions.
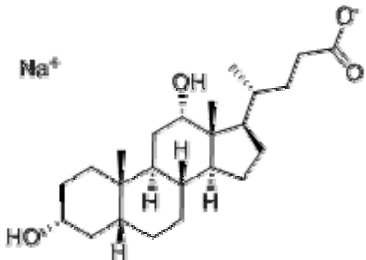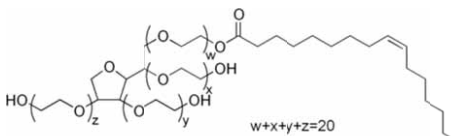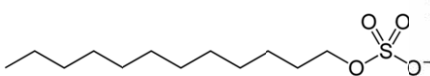
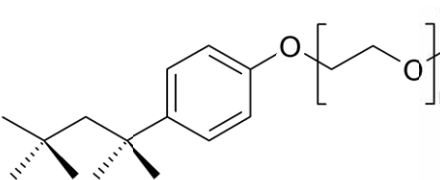## S2 Surfactants used in this experiment

Ionic Type	Surfactant Name	Molecular Image	CMC (w/v)	HLB	Molecular Weight
Anion	Sodium deoxycholate (SDOC)		1.66	15	415
Non-ionic	Tween 80		0.0157	15.0	1310
Anion	Sodium Dodecyl Sulfonate (SDS)		2.3		288
Non-ionic	Triton X-100		0.3438	13.5	625

Fig. S1 Details about the used surfactants

S3 Experimental results of SDS and Triton X-100 Optical absorbance (A660nm) and graphene concentration (CG) as a function of SDS
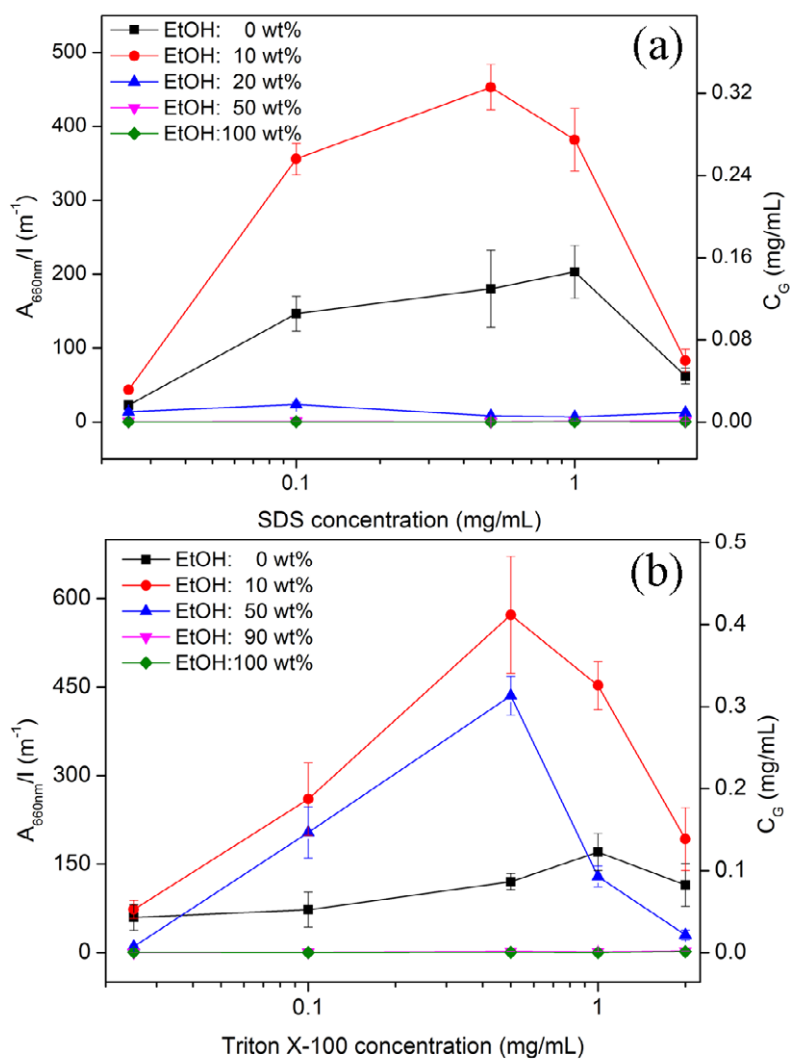
Fig. S2 Optical absorbance (A_{660nm}) and graphene concentration (C_G) as a function of concentration of (a) SDS and (b) Triton X-100.

S4 Surface tension of water-ethanol mixture as the function of temperature and mass ratio

In our experiment, the temperature of the dispersion was controlled between 20 ℃ and 40 ℃, the data was collected from Vazquez et al.'s article.[2]

Table S1 Surface tension of water/EtOH mixtures

mass ratio of EtOH/wt%	$\sigma/(mN \cdot m^{-1})$ at t/℃		
	20	30	40
0	72.75	71.21	69.52
10	48.14	46.88	45.58
20	38.56	37.38	36.28
50	28.51	27.53	26.64
90	23.23	22.32	21.53
100	22.31	21.41	20.62

S5 Calculation of enthalpy of Mixing of water/ethanol/surfactant dispersion
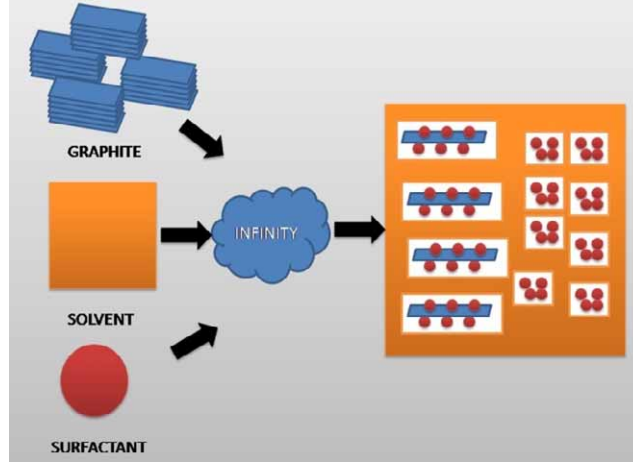
Fig. S3 schematic diagram of exfoliation process

For water/ethanol/surfactant medium, the calculation of enthalpy of mixing is analogous comparing with Coleman's work on water/solvent medium.[3] We first separated graphene sheets, solvent molecules, surfactant molecules to infinity, and the energy required by this step is denoted E_1. Then the separated molecules or sheets were resembled in particular order, the energy retrieved by this step is denoted E_2. We assume that the graphene sheets were first assembled with surfactant molecules, and the sandwich-like membrane structures filled the void in the solvent space ($E_2^{G-sa2} + E_2^{sa2-sol}$). The residual surfactant molecule directly filled the void in the solvent space ($E_2^{sa1-sol}$). By using the same procedure, we can obtain the enthalpy of mixing by

$$\Delta H_{mix} = E_1^G + E_1^{sol} + E_1^{sa} - (E_2^G + E_2^{Sol} + E_2^{sa1} + E_2^{G-sa2} + E_2^{sa2-sol} + E_2^{sa1-sol})$$

Eq S1

in which

$$E_1^{sa} = V_{sa} E_{coh}^{sol} - A_1^{sa} E_{sur}^{sa}$$

$$E_2^{Sol} = V_{sol} E_{coh}^{sol} - A_2^{sol} E_{sur}^{sol} - A_{inter}^{G-sol} E_{sur}^{sol} - A_{inter}^{sol-sa} E_{sur}^{sol}$$

$$E_2^{sa1} = V_{sa1} E_{coh}^{sol}$$

$$E_2^{G-sa2} = 2N_2 2A_2 E_{inter}^{G-sa}$$

$$E_2^{sa2-sol} = 2N_2 2A_2 E_{inter}^{sol-sa}$$

$$E_2^{sa1-sol} = A_{inter}^{sol-sa} E_{inter}^{sol-sa}$$

$$V_{sa} = V_{sa1} + V_{sa2}$$

The subscript *inter* represents interface. The superscript *G* stands for graphene sheets, *sol* stands for solvent, *sa* stands for surfactant, *sa1* stands for the part of surfactant molecules which self-agglomerate, *sa2* stands for the part of surfactant molecules which adhere to the graphene sheets, *G-sol* stands for the interface of graphene sheets and solvent molecules, *mix* stands for *mixture*.

Putting all the equations to Eq1, and using Coleman's two approximations ($A_2^{sol} \approx A_1^{sol}, T_1 \gg T_2$), we can get

$$\frac{\Delta H_{mix}}{V_{mix}} \approx \frac{2}{T_2}(\delta_G - \delta_{sol})^2 \emptyset + \frac{V_{sa2}}{V_{mix}} E_{coh}^{sol} - \frac{A_{inter}^{sol-sa}}{V_{mix}} E_{inter}^{sol-sa} + \frac{\emptyset}{T_2}(E_{inter}^{G-sol} - E_{inter}^{G-sa}$$

$$- E_{inter}^{sol-sa})$$

In our experiment, the volume of surfactant is about one tenth of graphite's, so the volume of surfactant molecules whose self-agglomeration is much less than the volume of the mixture (V_{mix}). Hence, we have $V_{mix} \gg V_{sa2}; V_{mix} \gg A_{inter}^{sol-sa} \cdot 1$. $E_{inter}^{G-sol}, E_{inter}^{G-sa}$ and E_{inter}^{sol-sa} are fixed values. Then we can get

$$\frac{\Delta H_{mix}}{V_{mix}} \approx \frac{2}{T_2}(\delta_G - \delta_{sol})^2 \varphi + \frac{\varphi}{T_2} L \qquad \text{Eq S2}$$

in which

$$L = E_{inter}^{G-sol} - E_{inter}^{G-sa} - E_{inter}^{sol-sa}$$

$$\varphi = \frac{M_G}{\rho_G V_{mix}}$$

From Eq S2, we can find that, three factors influence the mixing enthalpy, i.e. the surface tension of the solvent δ_{sol}, the thickness of the later graphene sheets T_2 and the constant *L*. In our experiment, δ_{sol} represents the surface tension of water-ethanol solution without surfactant, the surface tension near δ_G can reduce the mixing enthalpy. T_2 represents the thickness of exfoliated graphene sheets; to obtain thinner sheets needs more energy. *L* is a fixed parameter related to the surfactant's property and has a fixed influence on the mixing enthalpy.

S6 Experimental results of the sedimentation curves of graphene/water/ethanol dispersion
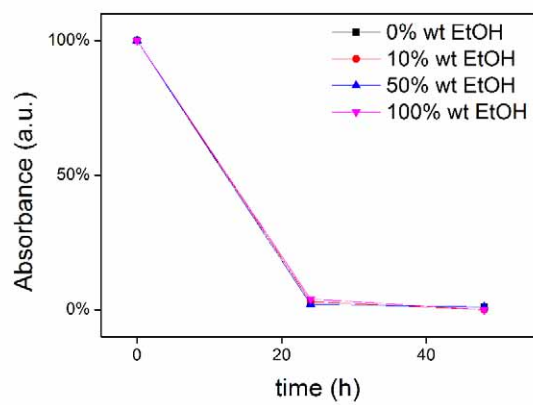
Fig. S4 Relative absorbance of graphene/water/ethanol dispersion as the function of time, with the differences in mass ratio of ethanol.

S7 Comparison of exfoliation efficiency between our results and others using surfactants as a stabilizer

In order to illuminate the efficiency of our method, we use a parameter $E = \dfrac{C_G}{C_{Gi} \times t}$ to calculate the exfoliation efficiency. C_G is the concentration of graphene after sonication and centrifugations. C_{Gi} is the pristine concentration of graphite. t is the sonication time. Hence, E can be a representative of exfoliation efficiency. E_0 represent the efficiency of our results and lower E/E_0 value shows preponderance of our results over others'.

Table S2 Comparison of exfoliation efficiency between our method and others.

C_{Gi} (mg/mL)	C_G (mg/mL)	t (h)	E	Surfactant	E/E_0	Reference
5	0.02236	0.5	0.00894	SDBS	76%	Nat. Nanotech.,2008,3,563
5	0.3	400	0.00015	SDOC	12%	ACS Nano,2010,4,3155
0.75	0.005	2.33333	0.00286	SC	24.3%	New J. Phys.,2010,12,125008
86	0.09	1	0.00105	SC	8.9%	Nano Lett.,2009,9,4031
100	1.5	5	0.003	P123	25.5%	Carbon,2011,49,1653
100	0.1	2	0.0005	SDOC	4.3%	Carbon,2011,49,1653
100	1	5	0.002	Tween 80	17%	Carbon,2011,49,1653
5	0.1	9	0.00222	PVP	18.9%	Small,2009,5,1841
5	0.02	0.5	0.008	Tween 80	68%	J. Am. Chem. Soc.,2009,131,3611
15	1.2	~6.66*	0.012	F108	102%	Langmuir,2012,28,14110
1	-	**	-	SDBS	-	Nanoscale,2013,5,7202
Not surfactant-assisted (10 mg/mL graphite in 20 mg/mL organic solvent)***						Chem. Phys. Lett.,2013,568,198
5	0.46	8	0.0115	SDOC	98%	Our results
5	0.47	8	0.01175	Tween 80	E_0	Our results

*Continuously addition of surfactant, hence the sonication time is not fixed. We use the average time.

**The group use thermal annealing method to help the exfoliation process and it is hard to make comparisons.

*** This method is more like an exfoliation process in organic solvent (introducing new ions). E/E_0 is about 150%.

References:

1. M. Lotya, P. J. King, U. Khan, S. De and J. N. Coleman, *ACS Nano.*, 2010, **4**, 3155-3162.

2. G. Vazquez, E. Alvarez and J. M. Navaza, *J. Chem. Eng. Data*, 1995, **40**, 611-614.

3. Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, T. McGovernI., B. Holland, M. Byrne, Y. K. Gun'Ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari and J. N. Coleman, *Nature Nanotech.*, 2008, **3**, 563-568.