

Electronic Supplementary Information

The effect of surfactants and their concentration on the liquid-exfoliation of graphene

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S1. Characterization method

S2. Determination of the coefficient α in Beer-Lambert Law

S3. t_{sonic} and CF rate as functions of C_G

S4. XPS analysis of graphene

References

S1. Characterization method

TEM and high-resolution TEM (HRTEM) images were performed by a JEOL JEM-2010FEF operated at 200 kV. Atomic force microscope (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. X-ray diffraction (XRD) spectra were collected by Rigaku D/max 2200 X-ray diffractometer at 40kV and 40mA. X-ray photoelectron spectroscopy (XPS) spectra were obtained by ThermoFisher Scientific's ESCALAB, with a 150 W monochromated Al K α X-ray source.

TEM samples were prepared by pipetting a few micro liters of the dispersion onto holey carbon mesh grid. For AFM sample preparation, we first diluted the centrifuged supernatant clear solution by acetone (1:1000), and then ultrasonicated the solution for about 1 minute. One drop of solution was dripped onto the mica substrate. The prepared sample was dried in ambient temperature. Since Tween 80 and Triton X-100 have poor compatibility with organic solvents, the 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. The Raman, XRD and XPS samples were prepared by filtering graphene dispersion onto the organic filter membrane.

S2. Determination of the coefficient α in Beer-Lambert Law

C_G was determined through absorption, and calculated by Beer-Lambert law [1].

Water/surfactant/graphene dispersion spectrum in the range from 300 nm to 900 nm shows that 660 nm is a decent wavelength for characterization. According to Lambert-Beer Law, absorption of the dispersion equals to a factor $\alpha_{660\text{nm}}$ multiplies $C_G l$. As $\alpha_{660\text{nm}}$ was valued differently by different groups [1-3], a uniform value of $\alpha_{660\text{nm}}$ must be determined. We first prepared graphene dispersion through liquid-phase exfoliation, and measured the absorption of the dispersion with the wavelength of 660 nm. The dispersion (volume V) was then filtrated by a pre-weighted membrane (m_1). The membrane was then dried in vacuum and weighted (m_2). C_G is determined by the formula $C_G=(m_1-m_2)/V$.

S3. t_{sonic} and CF rate as functions of C_G

t_{sonic} , which may likely affect C_G . The C_G -T curve of the six surfactants was depicted in Fig. 3a. C_{G_i} is uniformly 0.1 mg/mL. From the curves, we can find that absorption approximately linearly increased as time passes. The input energy increases with t_{sonic} , and so does the exfoliation degree. It is worth noting that after 8 hours sonication, the increase of absorption slows down. After long time sonication (8 h), most of the surfactants were adhered to the graphene sheets. The decrease of C_{sur} may occur after this process, and the increase of C_G may retard. In order to minimize the influence of t_{sonic} on C_G , for the following experiments, t_{sonic} was all fixed at 8 h.

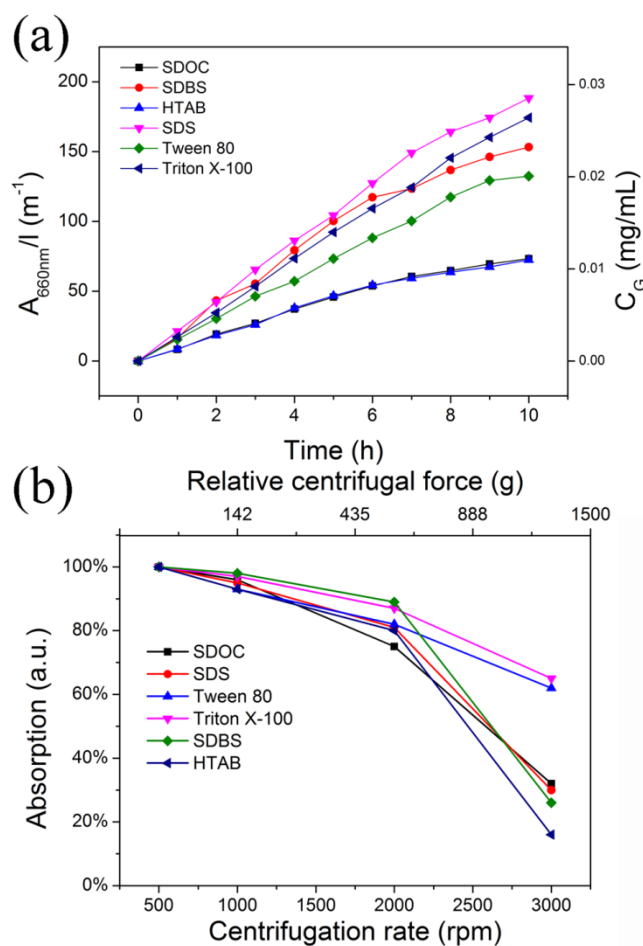


Fig.S1 (a) Absorption per unit length of graphene dispersion, $A_{660\text{nm}}/l$, as a function of time with six kinds of surfactants. (b) Relative absorption as a function of centrifugal

force, which was converted from CF rate.

CF rate also determines the graphene dispersion in both concentration and quality aspects. The same samples (SDBS, $t_{\text{sonic}}=8$ h, $C_{\text{Gi}}=5$ mg/mL) were processed with different CF rate and time, and the results were shown in Fig. 3b. Higher CF rate leads to higher quality graphene dispersions, and vice versa. Long time CF can also decrease C_{G} . For CF higher than 2000 rpm, much of the graphene sheets and graphite flakes will precipitate. Based on above discussions, 1500 rpm CF is suggested. To sum up, 8 h sonication, 1500 rpm CF may have a decent effect on producing graphene dispersion; meanwhile the interaction between C_{sur} and C_{Gi} should be considered.

S4. XPS analysis of graphene

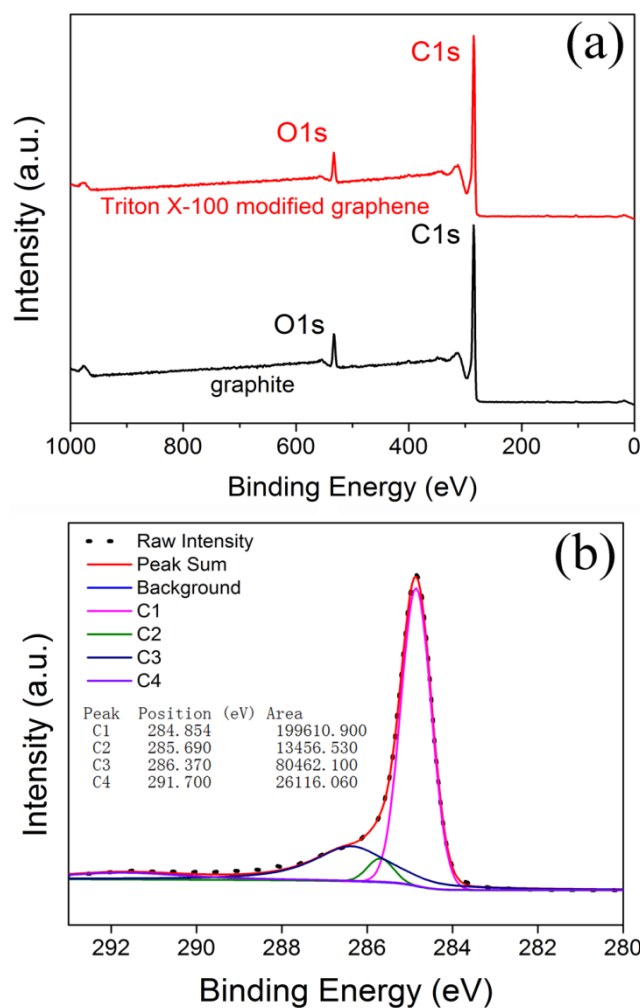


Fig. S2 XPS survey of graphite flakes and graphene from surfactant assisted exfoliation. (b) XPS narrow scan of graphene in C1s range.

In Fig. S2 (a), XPS spectrum of graphene presents similarity to that of graphite., which means that, the Structure of carbon atoms and oxygen atoms didn't changed. In Fig. S2 (b), considering the structure of Triton X-100, we fit the C1s peak with binding energies at ~ 284.80 eV (sp² C, C1), ~ 285.69 eV (sp³ C, C2), ~ 286.37 eV (C in C-O-C, C3), and 291.7 eV (C in π - π bond, C4) as shown in Fig. S2 (b). C1 is related to the graphene structure, while C2, C3 and C4 are related to Triton X-100's structure. The areas under C2 and C4 curve have the ratio of 1:2, which is consistent with the structure of Triton X-100. C3, which represents the C atoms consisted in the

C-O-R chain in Triton X-100 also suits well. The non-sp² C atoms are in consistence with Triton X-100 structure, so C atoms in graphene are mainly sp² hybridized. Non chemical modified clues were found through XPS characterization.

References

1. Hernandez Y, Nicolosi V, Lotya M, Blighe F M, Sun Z, De S, Mcgovern I T, Holland B, Byrne M, Gun'ko Y K, Boland J J, Niraj P, Duesberg G, Krishnamurthy S, Goodhue R, Hutchison J, Scardaci V, Ferrari A C, Coleman J N (2008) High-yield production of graphene by liquid-phase exfoliation of graphite *Nature nanotechnology* 3:563-568
2. Lotya M, Hernandez Y, King P J, Smith R J, Nicolosi V, Karlsson L S, Blighe F M, De S, Wang Z, Mcgovern I T, Duesberg G S, Coleman J N (2009) Liquid phase production of graphene by exfoliation of graphite in surfactant/water solutions *Journal of the American Chemical Society* 131:3611-3620
3. Lotya M, King P J, Khan U, De S, Coleman J N (2010) High-concentration, surfactant-stabilized graphene dispersions *ACS nano* 4:3155-3162