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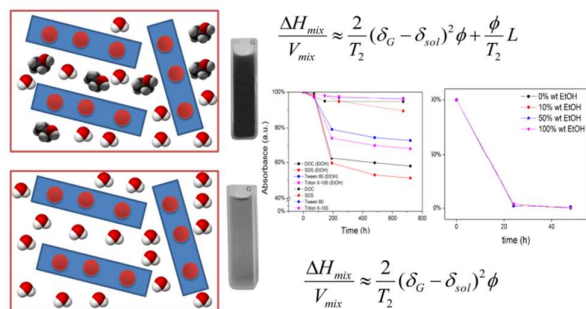


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Adding proper ethanol into the water/surfactant dispersion can enhance the graphene concentration up to 3 times. The combination of water and ethanol can decrease the exfoliation energy while the surfactant act as a stabilizer preventing graphene sheets from agglomeration.

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## COMMUNICATION

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

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We demonstrate that in water/surfactant solutions, adding ethanol can achieve graphene dispersions of high concentration (~0.46 mg/mL). For both ionic and non-ionic surfactants, ~10 wt% addition of ethanol is found to enhance the exfoliation efficiency and thus the graphene concentration up to three times. This enhancement is attributed to the combination of decreasing mixing enthalpy by ethanol addition and enhancing stability by surfactants. This method opens a whole new vista for preparing high-concentration graphene dispersions.

## Introduction

Graphene has attracted great interests due to its unique two dimensional structure since it was first discovered in 2004.<sup>1,2</sup> At present, graphene-based large-scale applications are hindered by the lack of high yield, high throughput and inexpensive methodologies for the production of this material.<sup>3-6</sup> As for liquid-phase exfoliation route, water/surfactant solutions were proved to be excellent media for exfoliating and dispersing graphene.<sup>7,8</sup> However, the same issues, i.e. low yield and low throughput, remain to be solved. In previous works, Lotya et al. used sodium cholate as the surfactant and relied on extremely long-time sonication (up to 400 h) to achieve high graphene concentration ( $C_G$ ) of 0.3 mg/mL.<sup>7,8</sup> Guardia et al. optimized the surfactant type and adopted an extremely high initial concentration of graphite (~100 mg/mL).<sup>9</sup> Notley et al. used an extremely high initial graphite concentration (~50 mg/mL) and high surfactant concentration, achieved high  $C_G$  of about 5 mg/mL by continuous surfactant addition.<sup>10</sup> Niu et al.<sup>11</sup> used NaCl or CuCl<sub>2</sub> ( $C_{\text{RCl}}=20$  mg/mL;  $C_{\text{SDBS}}=20$  mg/mL) and Du et al.<sup>12</sup> used organic salts to assist exfoliation, in order to achieve concentrated graphene dispersions. Obviously, these works mainly rely on extremely long sonication time, extremely high initial graphite concentration, continuous surfactant addition, or new ions to enhance  $C_G$ . Hence, it is still highly recommended to develop a method which can overcome the above disadvantages.

On the other hand, organic solvent with proper surface tension can reduce the threshold force for exfoliation.<sup>6</sup> For surfactant assisted exfoliation, surfactant molecules can prevent graphene sheets from aggregating.<sup>13</sup> Within these two distinct routes, organic solvents may show advantages predominately in reducing exfoliation energy, while surfactants may predominately serve as stabilizer once exfoliation happens. It is nature to envision that

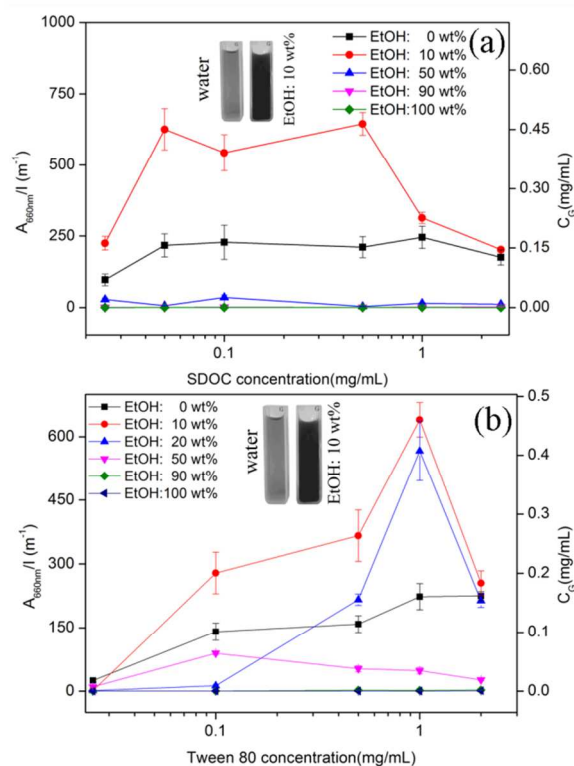
the combination of organic solvents and surfactant may perform much better. To the best of our knowledge, no literatures have reported the combination of their merits to enhance the exfoliation efficiency and thus  $C_G$ .

With the above points in mind, in this communication we for the first time add ethanol into the water/surfactant/graphite mixture to assist the liquid-phase exfoliation process. This simple route has a higher exfoliation efficiency when compared with previous modified methods (ESI†, S7). Both for ionic and non-ionic surfactant, ethanol was found to improve the exfoliation efficiency and  $C_G$  up to three times. It can be anticipated that the strategy of surfactant/water solutions with addition of organic solvents could advance the surfactant-assisted production for graphene.

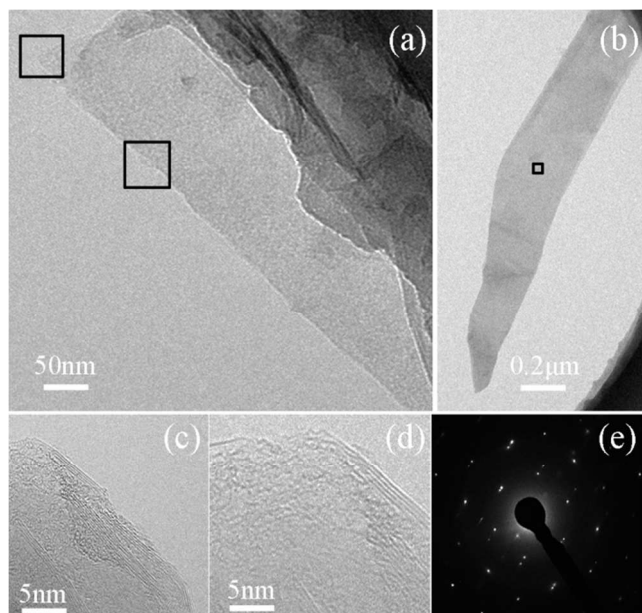
## Results and discussion

Four typical surfactants, i.e. Tween 80, Triton X-100 as non-ionic surfactants and sodium deoxycholate (SDOC), sodium dodecyl sulfate (SDS) as ionic surfactants, were chosen to be blended with water to form surfactant/water solutions for preparing graphene (Fig. S1, ESI†). By adding ethanol into these solutions and measuring the concentration of as-prepared graphene dispersions, we can obtain the dependence of  $C_G$  on the surfactant concentration and ethanol/water ratio. The graphite powder was first dispersed into water/ethanol/surfactant dispersion and sonicated for 8 h, then stayed overnight. After centrifuge for 30 min, the supernatant liquor was taken and the absorption of the dispersion was measured (S1, ESI†).

The inset of Fig. 1a shows photographs of the graphene dispersions in different ethanol/water/SDOC mixtures. Clearly, at an appropriate ethanol/water ratio, much darker graphene dispersions can be obtained. This means that adding a certain amount of ethanol can enhance  $C_G$ . The curves in Fig. 1a also quantitatively show that the concentration of graphene is strongly dependent on the mass fraction of ethanol. Solutions with 10 wt% ethanol performed much better than the water/SDOC mixture. By adding 10 wt% ethanol into the water/SDOC solutions,  $C_G$  can increase up to three times, from 0.15 mg/mL in water/SDOC mixture to 0.46 mg/mL in ethanol/water/SDOC mixture when the SDOC concentration is 0.5 mg/mL. However, adding ethanol with loading higher than 10 wt% could lead to inferior performance. When using the typical non-ionic surfactant Tween80, we also find the similar variation trend regardless of its



**Fig. 1** Optical absorbance ( $A_{600\text{nm}}$ ) and  $C_G$  as a function of (a) SDOC and (b) Tween 80 concentration in ethanol/water/surfactant solutions with different ethanol loading. Insets, photographs of graphene dispersions (diluted by two times, SDOC and Tween 80 concentration is 0.5 mg/mL) in solutions with and without ethanol addition.



**Fig. 2** (a), (b) Typical TEM images of graphene flakes and graphene ribbon after sonication and centrifugation. (c), (d) HRTEM images of rectangle region in (a). (e) SAED pattern corresponding to the square region in (b).

non-ionic property, as shown in Fig. 1b. The optimal ratio of ethanol is also 10 wt%, which is consistent with the previous result in the case of SDOC. The highest concentration occurs

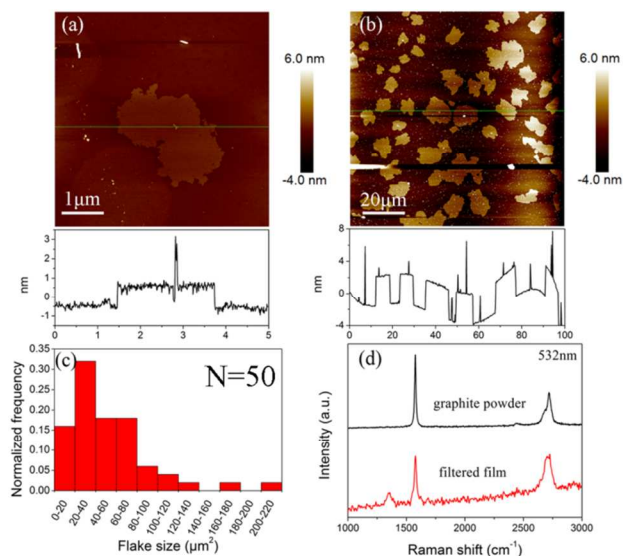
when the concentration of Tween 80 approaches 1 mg/mL. It is worth noting that though graphene can hardly be dispersed in pure ethanol, adding a small amount of ethanol (~10 wt%) into the surfactant/water solutions can significantly enhance the exfoliation efficiency and thus  $C_G$ . However, the strategy of adding ethanol does not work for solutions with too high or too low surfactant concentration. The experiments by using SDS and Triton X-100 have similar results (Fig. S2, ESI†). The highest yield reaches 9.4% which is fascinating if we compare these results to previous works (Table S2, ESI†). The exfoliation efficiency here is much higher than that of others except Notley, who achieved a little higher efficiency. However, in his work, continuously adding surfactant needs complicated equipment and the flow velocity should be controlled accurately.<sup>10</sup>

The graphene flakes prepared by the ethanol addition strategy are characterized by transmission electron microscope (TEM), atomic force microscope (AFM), and Raman spectrum to examine their quality. Fig. 2 shows the TEM images of the exfoliated graphene flakes. The edge TEM image in Fig. 2a is a few-layer graphene with the layer number lower than five. The selected area electron diffraction (SAED) pattern corresponding to the square region in Fig. 2b shows the typical six-fold symmetry which is indicative of graphene structure.<sup>14,15</sup> Graphene flakes have also been verified by AFM. Fig. 3a shows one graphene flake with the thickness of ~1 nm. As shown in Fig. 3b, large numbers of graphene sheets could be seen, with the average area of 52.12  $\mu\text{m}^2$  (Fig. 3c) and thickness of ~1 to 3 nm. The white dots on the graphene flakes or the mica substrate could be the agglomeration surfactant molecules after water and ethanol are vaporized away. Apart from TEM and AFM images, Raman spectra of the graphite powder and the filtered film prepared from graphene dispersions are presented in Fig. 3d. Seeing that in the filtered film the D band is relatively weak and the G band is not broadened, the graphene flakes may mainly suffer from edge defects rather than basal-plane disorder defects<sup>7</sup>, because disorder defects in basal plane often induce much higher D band and largely broadened G band as commonly found in graphene oxide or chemical reduced graphene.<sup>16</sup> The shape of the 2D band in the filtered film is intrinsically different from that in graphite, indicating the nature of few-layer graphene.<sup>17</sup> Meanwhile, the relatively high intensity with respect to G band ( $I_{2D}/I_G$ ), also give a strong evidence of the existence of graphene flakes.<sup>18</sup>

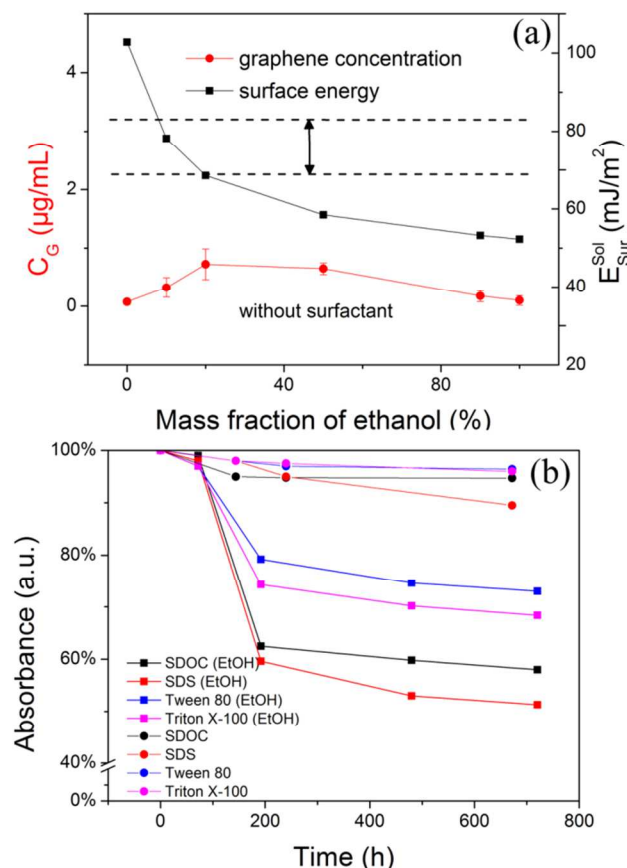
After obtaining enhanced concentration by ethanol addition and confirming the quality of the prepared graphene, another critical issue we must concern is that why adding ethanol into these surfactant solutions can enhance  $C_G$ . The mechanism of graphite exfoliation in organic solvents or water/surfactant medium was demonstrated by other researchers.<sup>6,13</sup> But for our experiment, both organic solvent (i.e. ethanol) and surfactant were used, so the interaction effect of both must be considered.

Firstly, we explore the effect of adding ethanol on the exfoliation energy. Following the idea of mixing enthalpy of organic solvent/graphite mixture proposed by Coleman et al.<sup>6</sup>, we assume that graphene sheets were covered by part of surfactant molecules on both side, and the surfactant-graphene-surfactant structures filled the voids in the solvent. Other isolated surfactant molecules filled other voids, as schematized in Fig. S3 (ESI†). Hence, we can get the expression (see S5 in ESI† for details):





**Fig. 3** (a), (b) Representative AFM images and the corresponding height profiles of the exfoliated graphene flakes in ethanol/water/SDOC solutions. (c) Histogram of graphene flake size in (b). (d) Raman spectra of the pristine graphite powder and the as-filtered film from graphene dispersions (ethanol/water/Tween 80; EtOH: 10 wt%; Tween 80: 1 mg/ml).



**Fig. 4** (a) C<sub>G</sub> in water-ethanol mixture without surfactant and the surface energy of water-ethanol mixture as the function of mass fraction of ethanol. The surface tension has been transformed into surface energy using a universal value for surface entropy of ~0.1 mJ/m<sup>2</sup>K. The vertical arrow shows the approximate range of the reported literature values for the surface energy of graphene. (b) Sedimentation curve of different graphene dispersion in water/ethanol/surfactant medium (square dots)

and in water/surfactant medium (circular dots).

$$\frac{\Delta H_{mix}}{V_{mix}} \approx \frac{2}{T_2} (\delta_G - \delta_{sol})^2 \varphi + \frac{\varphi}{T_2} L \quad (\text{Eq1})$$

in which  $\Delta H_{mix}/V_{mix}$  is the mixing enthalpy per unit volume of the dispersion,  $T_2$  is the flake thickness,  $\delta = \sqrt{E_{sur}}$  is the square root of surface energy, which is related to surface tension  $\gamma$  ( $G$  denotes graphene and  $sol$  denotes solvent), and  $\varphi$  is the volume fraction of graphite. In Eq1,  $L$  is a relatively fixed parameter related to the binding energy between graphene, surfactant and solvent, indicating that the surfactant has a fixed influence on the mixing enthalpy. Adding ethanol into pure water will decrease the surface tension of water ( $\gamma_w$ ). When  $\gamma_w$  reaches ~50 mN/m, i.e., with 10 wt% ethanol addition,<sup>19</sup> the mixture becomes perfect for graphene exfoliation process. According to Eq1, adding surfactant into the mixture will not negatively affect the exfoliation circumstance. This is experimentally supported as follows. From Fig. 4a, the approximate range of the reported values for the surface energy of graphene falls into the vicinity of ~10 wt% ethanol/water mixture. The best proportion of ethanol must be 10 wt %, because under this condition, the mix enthalpy decreased the most.

Secondly, we explore the role of surfactant in terms of stability, since we have shown above that surfactant has a fixed influence on exfoliation energy. As a control experiment, we have exfoliated graphite in the ethanol/water dispersion without surfactant. As shown in Fig. 4a, the ethanol/water mixture with surface energy close to that of graphene can only achieve an extremely low concentration of 0.77 μg/mL. This indicates that without surfactant, even proper ethanol/water mixture has a weak performance, i.e., the surfactant plays an important role in the stabilizing process. We plot sedimentation curves to investigate the role of surfactant as a stabilizer. As shown in Fig. 4b, both the water/surfactant dispersion and water/surfactant/ethanol dispersion show good stability. About 55% graphene remained after 700 h for water/surfactant/ethanol mixture. While for water/ethanol dispersion without surfactant, graphene sheets rapidly reunited and were changed into sediment completely within 10 h (Fig. S4, ESI†). This proves that surfactant plays a critically important role in stabilizing the graphene dispersion even with the existence of ethanol. According to De Gennes<sup>20</sup>, it is the osmotic force that avoid two sheets aggregating which adhered by long non-polar groups. When the two sheets get closer, the osmotic repulsion force dominates van der Waals attraction force. Adding surfactant molecule can enhance the stability of the dispersion was verified by many experiments.<sup>7-11,21,22</sup> For our experiment, surfactant makes up the instability of graphene sheets in organic solvent, while maintain the advantage of water/ethanol dispersion which decrease the mixing enthalpy and exfoliation force.

Based on above discussions, it seems that ethanol and surfactant play two different roles. The major function of adding ethanol is to decrease the exfoliation energy, thus the threshold force for exfoliation process. The major function of surfactant is to serve as a stabilizer to prevent graphene sheets from aggregating. In our experiment, adding ethanol to the water/surfactant dispersion can cover the shortage of surfactant

by reducing the exfoliation energy, thus enhancing  $C_G$  while remain its excellent stability supported by surfactant molecules. Also as evidenced in Table S2 (ESI<sup>†</sup>), the efficiency of the strategy here by adding ethanol is obviously much higher than that in the literatures about the similar work without ethanol addition.

## Conclusions

In conclusion, based on liquid-phase exfoliation, we have reported a novel method to enhance  $C_G$  in water/surfactant solutions just by adding ethanol. In the case of both ionic and non-ionic surfactant, by ~10 wt% addition of ethanol, the exfoliation efficiency and thus  $C_G$  are enhanced up to 3 times, with a maximum concentration of ~0.46 mg/mL. The graphene flakes are 1-3 nm thick with average lateral size of ~50  $\mu\text{m}^2$  as examined by AFM. This novel method can achieve a higher yield of ~9.4%. The exfoliation efficiency was averagely enhanced ~5 times, when compared with previous works. Based on the model of mixing enthalpy and the control experiment, we find the different major functions of surfactant and ethanol, i.e. adding ethanol majorly decrease mixing enthalpy while surfactant can increase stability. It can be anticipated that the strategy of decreasing enthalpy and increase stability by surfactant/water solutions with addition of organic solvents could advance the surfactant-assisted production for graphene.

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## Notes and references

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- <sup>†</sup> Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/
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90