Supplemental Materials

Two- and Three-Dimensional Self-Folding of Free-Standing Graphene by Liquid Evaporation

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S1. Evaporation-driven self-folding of a single suspended graphene sheet

S 1.1 Rectangular/Square graphene

For a rectangular/square graphene (Fig. S1a), the folding line could be the symmetric axis of the rectangle/square (Fig.S1), or the diagonal of the square (Fig.S2a), and either of them will form an axial symmetric folding. In addition, the square graphene could be folded in central symmetric pattern (Fig.S2b).

S 1.1.1 Folding along the symmetric axis

Fig.S1a shows a planar rectangular graphene with length l and width w. Assume the deformation is unidirectional along its long symmetric axis. Given a bending angle θ_b after deformation (Fig.S1b), the bending radius is

$$r_b = \frac{l}{2\theta_b} \tag{S 1.1}$$

The coordinate of the point marked by green is $(0, -w/2, 0)$ and the coordinate of the point marked by yellow is $(d, 0, h)$, where $d = r_b \sin\theta_b$ and $h = r_b(1 - cos\theta_b)$. Based on the full contact assumption between solid and liquid, these two points should be also on the surface of liquid. Then the profile of liquid can be estimated via

$$x^2 + y^2 + (z - c)^2 = r_c^2 \tag{S 1.2}$$

With $(0, -w/2, 0)$ and $(d, 0, h)$, one can have

$$c = \left(d^2 + h^2 - w^2/4\right)/2h \tag{S 1.3}$$

and

$$r_c = \sqrt{w^2/4 + c^2} \tag{S 1.4}$$

Due to the minimization of the system energy and the surface energy of liquid, the overall configuration of the liquid surface may not be a sphere. Only the molecules in the $x - z$ and $y - z$ planes satisfy Eq. (S1.2). In order to get the overall profile of liquid surface, the total height of graphene and liquid along the y axis needs to be determined and it is

$$h_{lg} = \sqrt{r_c^2 - y^2} + c, y \in [-w/2, w/2] \tag{S 1.5}$$

Take the height of graphene $h_g = h$, independent of y, the height of liquid is $h_l = h_{lg} - h_g$ (Figs. S1c-e). Assume the profile of liquid is an arc, it can be determined by the points $(0,y,h_{lg})$, (d,y,h) and $(-d,y,h)$, and could be represented by the radius of curvature, r_{ly} and half central angle of the profile of liquid, θ_{ly} (Figs. S1c-e). With these analyses, the profile of liquid can be determined in each plane parallel to the $x-z$ plane in the range of $-w/2 \le y \le w/2$. So the surface area of liquid exposed to the vacuum is

$$A_l = 2\left(\int_0^{w/2} 2r_{ly}\theta_{ly}dy + A_{cap}\right) \quad \text{(S 1.6)}$$

where $A_{cap} = \varepsilon(r_c - w/2)2\pi r_{cap}(r_c - w/2)$ is the surface area of the spherical cap of liquid at $|y| > w/2$. $\varepsilon(r_c - w/2)$ is the Heaviside step function and $r_{cap} = \left(r_b^2 + (r_c - w/2)^2\right)/2(r_c - w/2)$ is the bottom radius of the spherical cap. Similarly, the volume of liquid can be obtained via

$$V_l = 2\left(\int_0^{w/2} [r_{ly}^2(\theta_{ly} - sin\theta_{ly}cos\theta_{ly}) + r_b^2(\theta_b - sin\theta_b cos\theta_b)]dy + V_{cap}\right) \quad \text{(S 1.7)}$$

where $V_{cap} = \varepsilon(r_c - w/2)\pi(r - w/2)^2(r_{cap} - (r - w/2)/3)$ is the volume of the spherical cap of the liquid.

It needs to be mentioned that the expression of A_l and V_l are derived based on the condition $h_{lg}^{|y| = w/2} > h$, and when $h_{lg}^{|y| = w/2} \le h$, the point $(0, -w/2, 0)$ and $(d,0,h)$ are no longer on the surface of same sphere, a new point $(d, -w/2, h)$ will replace $(d,0,h)$ to generate a new r_c and c, respectively. The spherical cap will also diminish and $A_{cap} = \pi r_b^2$, $V_{cap} = 0$. The surface area and volume of liquid can still be calculated based on Eqs. (S 1.6) and (S 1.7).

Once A_l is obtained, the total energy can be calculated via Eq. (2) in the main text. Further, if the deformation is along its short symmetric axis, the total energy can also be calculated by swapping l and w in the related equations.

S 1.1.2 Folding along the diagonal axis

As shown in Fig. S2a, when the folding line is the diagonal of the square, given a bending angle θ_b, the bending radius is

$$r_b = \frac{\sqrt{2}l}{2\theta_b} \tag{S 1.8}$$

The coordinate of the tip of deformed graphene is $(d,0,h)$, where $d = r_b \sin(\theta_b)$ and $h = r_b(1 - cos\theta_b)$. Plug in $(d,0,h)$ and $\left(0, -\frac{\sqrt{2}}{2}l, 0\right)$ into Eq. (S 1.2), one will have

$$c = \frac{d^2 + h^2 - l^2/2}{2h} \tag{S 1.9}$$

and

$$r_c = \sqrt{\frac{l^2}{2} + c^2} \tag{S 1.10}$$

After the geometric relationship between solid and liquid are determined, the total energy during folding can be calculated by following **S1.2.1** and is shown in Fig. S7a.

S 1.1.3 Folding along the central symmetric axis

As shown in Fig. S2b, when the folding occurs along the central symmetric pattern with four folding lines, given a bending angle θ_b, the bending radius is

$$r_b = \frac{\sqrt{2}l}{4\theta_b} \tag{S 1.11}$$

The tip coordinate of deformed graphene is $(d,0,h)$, where $d = r_b \sin(\alpha + \theta_b)$ and $h = r_b(\cos(\alpha) - cos(\alpha + \theta_b))$. $\alpha = \arcsin(\theta_b)$ is the angle formed between the z axis and the line connecting the bending center and middle point of the folding line of graphene. Plug in $(d,0,h)$ and $\left(\frac{\sqrt{2}}{4}l, -\frac{\sqrt{2}}{4}l, 0\right)$ into Eq. (S 1.2), one will have

$$c = \frac{d^2 + h^2 - l^2/4}{2h} \quad \text{(S 1.12)}$$

and

$$r_c = \sqrt{\frac{l^2}{4} + c^2} \quad \text{(S 1.13)}$$

After the geometric relationship between solid and liquid are determined, the total energy during folding can be calculated by following **S 1.3.2** and is shown in Fig. S7a.

S1.2 Circular graphene

For a circular graphene, the folding may along the axis of symmetry of the circle (Fig. S3). These will form an axial symmetric folding. It could also be folded in the central symmetry pattern with three folding lines (Fig. S4a) or four folding lines (Fig. S4b).

S 1.2.1 Folding along the symmetric diameter axis

Fig.S3a shows a planar circular graphene with length l. Assume the deformation is unidirectional along its symmetric axis. Given a bending angle θ_b after deformation (Fig.S3b), the bending radius is

$$r_b = \frac{l}{2\theta_b} \quad \text{(S 1.14)}$$

The coordinate of the point marked by green is (0, $-l/2$,0) and the coordinate of the tip of folded graphene (marked by yellow) is $(d,0,h)$, where $d = r_b \sin(\theta_b)$ and $h = r_b(1 - \cos(\theta_b))$. Based on the full contact assumption between solid and liquid, these two points should be also on the surface of liquid. Then plug in $(d,0,h)$ and $(0,-l/2,0)$ into Eq. (S 1.2), one can get

$$c = \frac{d^2 + h^2 - l^2/4}{2h} \quad \text{(S 1.15)}$$

and

$$r_c = \sqrt{\frac{l^2}{4} + c^2} \tag{S 1.16}$$

Due to the minimization of the system energy and the surface energy of liquid, the overall configuration of the liquid surface may not be a sphere. Only the molecules in the $x-z$ and $y-z$ plane satisfy Eq. (S1.2). In order to get the overall profile of liquid surface, the total height of graphene and liquid along the direction of y axis needs to be determined and it is

$$h_{lg} = \sqrt{r_c^2 - y^2} + c, y \in [-l/2, l/2] \tag{S 1.17}$$

The bending angle of graphene at the plane parallel to the $x-z$ plane is

$$\theta_{by} = \frac{\sqrt{l^2/4 - y^2}}{r_b} \tag{S 1.18}$$

And the height of graphene is

$$h_g = r_b(1 - \cos\theta_{by}) \tag{S 1.19}$$

The height of liquid is $h_l = h_{lg} - h_g$, and the distance of tip of graphene to the $y-z$ plane is

$$d_g = r_b \sin\theta_{by} \tag{S 1.20}$$

Assume the profile of liquid is also an arc, it can be determined by the points $(0, y, h_{lg})$, (d_g, y, h_g) and $(-d_g, y, h_g)$, and could be represented by the radius of curvature, r_{ly}, and half central angle of the arc, θ_{ly} (Figs. S3c-e). With these analysis, the profile of liquid can be determined in each plane parallel to the $x-z$ plane in the range of $-l/2 \le y \le l/2$. The surface area of liquid exposed to the vacuum is

$$A_l = 2\left(\int_0^{l/2} 2r_{ly}\theta_{ly}dy + A_{cap}\right) \tag{S 1.21}$$

where $A_{cap} = \varepsilon\left(r_c - \frac{l}{2}\right)2\pi r_{cap}(r_c - l/2)$ is the surface area of spherical cap of the liquid surface when $|y| > l/2$. $\varepsilon(r_c - l/2)$ is the Heaviside step function and $r_{cap} = \sqrt{r_c^2 - l^2/4} + c$ is the bottom radius of the spherical cap. Similarly, the volume of liquid can be obtained via

$$V_l = 2\left(\int_0^{l/2} \left[r_{ly}^2(\theta_{ly} - sin\theta_{ly}cos\theta_{ly}) + r_b^2(\theta_{by} - sin\theta_{by}cos\theta_{by})\right]dy + V_{cap}\right) \tag{S 1.22}$$

where $V_{cap} = \varepsilon(r_c - l/2)\pi(r_c - l/2)^2\left(r_{cap} - (r_c - l/2)/3\right)$ is the volume of spherical cap of the liquid.

Once A_l is obtained, the total energy can be calculated by following the type of Eq. (2) in the main text.

S 1.2.2 Central symmetric folding with three folding lines

When the circular graphene folds in the central symmetric pattern with three folding lines, as illustrated in Fig. S4a, given a bending angle θ_b, the bending radius is

$$r_b = \frac{l}{4\theta_b} \tag{S 1.23}$$

The coordinate of the tip of deformed graphene is $(d,0,h)$, where $d = r_b \sin\left(\alpha + \theta_b\right)$ and $h = r_b\left(\cos(\alpha) - cos(\alpha + \theta_b)\right)$. $\alpha = \text{asin}\left(\theta_b\right)$ is the angle formed between the z axis and the line connecting the bending center and middle point of the folding axis of graphene. Plug in $(d,0,h)$ and $\left(\frac{1}{4}l, -\frac{\sqrt{3}}{4}l, 0\right)$ into Eq. (S1.2), one will have

$$c = \frac{d^2 + h^2 - l^2/4}{2h} \tag{S 1.24}$$

and

$$r_c = \sqrt{\frac{l^2}{4} + c^2} \tag{S 1.25}$$

After the geometric relationship between solid and liquid are determined, the total energy during folding can be calculated by following **S1.3.2** and is shown in Fig. S7b.

S 1.2.3 Central symmetric folding with four folding lines

When the circular graphene folds in the central symmetric pattern with four folding lines, as illustrated in Fig. S4b, given a bending angle θ_b, the bending radius can be determined, which is

$$r_b = \frac{(2-\sqrt{2})l}{4\theta_b} \quad \text{(S 1.26)}$$

The coordinate of tip of the deformed graphene is $(d,0,h)$, where $d = r_b \sin(\alpha + \theta_b)$ and $h = r_b(\cos(\alpha) - cos(\alpha + \theta_b))$. $\alpha = \text{asin}\left(\frac{\sqrt{2}}{2-\sqrt{2}}\theta_b\right)$ is the angle formed between the z axis and the line connecting the bending center and middle point of the folding axis of graphene. Plug in $(d,0,h)$ and $\left(\frac{1}{4}l, -\frac{\sqrt{3}}{4}l, 0\right)$ into Eq. (S 1.2), one will have

$$c = \frac{d^2 + h^2 - l^2/4}{2h} \quad \text{(S 1.27)}$$

and

$$r_c = \sqrt{\frac{l^2}{4} + c^2} \quad \text{(S 1.28)}$$

After the geometric relationship between solid and liquid are determined, the total energy during folding can be calculated by following **S1.3.2** and is shown in Fig. S7b.

S1.3 Triangular graphene

For a triangular graphene, the folding line could be the axis of symmetry of the triangle (Fig. S5). This will form axial symmetric folding. It could also be folded in the central symmetric pattern with three folding lines (Fig. S6).

S 1.3.1 Axial symmetric folding

Fig.S5 shows a planar triangular graphene with an equilateral edge length l, given a bending angle θ_b, the bending radius is

$$r_b = \frac{l}{2\theta_b} \quad \text{(S 1.29)}$$

The coordinate of the tip of deformed graphene is $(d,0,h)$, where $d = r_b \sin(\theta_b)$ and $h = r_b(1 - cos(\theta_b))$. Plug in $(d,0,h)$ and $\left(0, \frac{\sqrt{3}}{2}l, 0\right)$ into Eq. (S 1.2), one will have

$$c = \frac{d^2 + h^2 - 3l^2/4}{2h} \quad \text{(S 1.30)}$$

and

$$r_c = \sqrt{\frac{3l^2}{4} + c^2} \quad \text{(S 1.31)}$$

After the geometric relationship between solid and liquid are determined, the total energy during folding can be calculated by following **S1.2.1** and is shown in Fig. S7c.

S 1.3.2 Central symmetric folding

Fig. S6a shows a planar triangular graphene with length l. Assume the deformation is in the central symmetric pattern with three folding lines. Given a bending angle θ_b after deformation, the bending radius is

$$r_b = \frac{\sqrt{3}l}{4\theta_b} \quad \text{(S 1.32)}$$

The coordinate of the point marked by green is $\left(\frac{\sqrt{3}}{12}l, -\frac{1}{4}l, 0\right)$ and coordinate of tip of the deformed graphene is $(d,0,h)$ (marked by yellow), where $d = r_b \sin(\alpha + \theta_b)$ and $h = r_b(\cos(\alpha) - cos(\alpha + \theta_b))$. $\alpha = \text{asin}(\theta_b/3)$ is the angle formed between the z axis and the line connecting the bending center and middle point of the folding line of graphene (when the graphene is folded into a closed form, $\alpha + \theta_b = \pi$, and it could be derived that the maximum value of θ_b is 0.72π). Plug in $(d,0,h)$ and $\left(\frac{\sqrt{3}}{12}l, -\frac{1}{4}l, 0\right)$ into Eq. (S 1.2), one will have

$$c = \frac{d^2 + h^2 - l^2/12}{2h} \quad \text{(S 1.33)}$$

and

$$r_c = \sqrt{l^2/12 + c^2} \quad \text{(S 1.34)}$$

Due to the minimization of the system energy and the surface energy of liquid, the overall configuration of the liquid surface may not be a sphere and needs to be analyzed along the z

axis. Consider the geometry of triangle, the total angle formed by graphene and liquid (Figs.S6c-e) is

$$\theta_{lg} = \theta_{lz} + \theta_{gz} = \pi/3 \tag{S 1.35}$$

the radius of curvature of liquid in the plane parallel to the $x-y$ plane is

$$r_{lz} = \sqrt{r_c^2 - (z-c)^2}, z \in [0, r_c + c] \tag{S 1.36}$$

and the width of deformed graphene is

$$w_{gz} = -\frac{2}{3}\sqrt{3} r_b \left[\text{acos}\left[cos\alpha - \frac{z}{r_b}\right] - \alpha\right] + l/2 \tag{S 1.37}$$

Thus, the angle formed by graphene is

$$\theta_{gz} = \text{asin}\left(\frac{w_{gz}}{2r_{lz}}\right) \tag{S 1.38}$$

The surface area of liquid can be determined via

$$A_l = 3\int_0^h 2\theta_{lz} r_{lz} dz + A_{cap} \tag{S 1.39}$$

where $A_{cap} = 2\pi r_{cap}(r_c + c - h)$ is the surface area of the spherical cap of liquid and $r_{cap} = \sqrt{r_c^2 - (h-c)^2}$ is the bottom radius of the spherical cap. Similarly, the volume of liquid can be obtained via

$$V_l = 3\int_0^h (w_{gz} r_{lz} cos\theta_{gz}/2 + \theta_{lz} r_{lz}^2) dz + V_{cap} \tag{S 1.40}$$

where $V_{cap} = \pi(r_c + c - h)^2\left(r_{cap} - (r_c + c - h)/3\right)$ is the volume of spherical cap of the liquid.

After A_l is calculated, the total energy can be obtained by following the type of Eq. (2) in the main text.

S2. Determination of elastocapillary length

S2.1 Rectangular graphene

Eq. (2) in the main text gives the total energy during folding

$$E_{tot} = \frac{2B\theta_b^2}{\eta} + A_l\gamma_l + lw\gamma_s + lw\gamma_i \tag{S 2.1}$$

where $E_{def} = 2B\theta_b^2/\eta$ is the deformation energy, $E_{surf}^{\ l} = A_l\gamma_l$ is the surface energy of liquid, $E_{surf}^{\ g} = lw\gamma_s$ is the surface energy of solid and $E_{inter} = lw\gamma_i$ is the interfacial energy between solid and liquid. To determine the elastocapillary length, assume the solid has been folded to a whole circle very closely ($\theta_b + \Delta\theta_b = \pi, \Delta\theta_b > 0 \ and \ \Delta\theta_b \to 0$), the surface area of liquid can be estimated by

$$A_l = 2\pi\left(\frac{l}{2\theta_b}\right)^2 + \left(2\pi\left(\frac{l}{2\theta_b}\right) - l\right)w \tag{S 2.2}$$

Suppose there is no detaching happens, $\Delta E_g = \Delta E_i = 0$, and the energy competition only involves ΔE_{def} and $\Delta E_{surf}^{\ l}$. Consider a critical condition,

$$\Delta E_{def} = \left|\Delta E_{surf}^{\ l}\right| \tag{S 2.3}$$

which yields

$$\frac{2B\pi^2}{\eta}-\frac{2B(\pi-\Delta\theta_b)^2}{\eta} = \gamma_l\left[2\pi\left(\frac{l}{2(\pi-\Delta\theta_b)}\right)^2-2\pi\left(\frac{l}{2\pi}\right)^2+\left(2\pi\left(\frac{l}{2(\pi-\Delta\theta_b)}\right)-l\right)w-\left(2\pi\left(\frac{l}{2\pi}\right)-l\right)w\right] \quad \text{(S 2.4)}$$

left side of Eq. (S 2.4) leads to

$$\frac{2B\pi^2}{\eta}-\frac{2B(\pi-\Delta\theta_b)^2}{\eta}=\frac{2B}{\eta}\left(2\pi\Delta\theta_b-\Delta\theta_b^2\right) \quad \text{(S 2.5)}$$

and right side of Eq. (S 2.4) leads to

$$\gamma_l\left[2\pi\left(\frac{l}{2(\pi-\Delta\theta_b)}\right)^2-2\pi\left(\frac{l}{2\pi}\right)^2+\left(2\pi\left(\frac{l}{2(\pi-\Delta\theta_b)}\right)-l\right)w-\left(2\pi\left(\frac{l}{2\pi}\right)-l\right)w\right] = \gamma_l l^2\left[\frac{(2\pi\eta+2\pi^2)\Delta\theta_b-(2\pi+\eta)\Delta\theta_b^2}{2\pi\eta(\pi-\Delta\theta_b)^2}\right] \quad \text{(S 2.6)}$$

Let

$$\frac{2B}{\eta}\left(2\pi\Delta\theta_b-\Delta\theta_b^2\right)=\gamma_l l^2\left[\frac{(2\pi\eta+2\pi^2)\Delta\theta_b-(2\pi+\eta)\Delta\theta_b^2}{2\pi\eta(\pi-\Delta\theta_b)^2}\right]$$

$$\rightarrow l=\sqrt{\frac{B}{\eta\gamma_l}}\sqrt{\frac{2\pi\eta\left(8\pi^3-10\pi^2\Delta\theta+4\pi\Delta\theta^2-\frac{\Delta\theta^3}{2}\right)}{-2\pi\Delta\theta-\eta\Delta\theta+4\pi\eta+4\pi^2}} \quad \text{(S 2.7)}$$

Plug in $\Delta\theta_b=0$, we can get

$$l_{ec}=\sqrt{\frac{4\pi^3}{\eta+\pi}}\sqrt{\frac{B}{\gamma_l}} \quad \text{(S 2.8)}$$

S2.2 Circular graphene

As has been proved in S1.2 (Fig. S7b), the axial symmetric folding pertains the lowest energy when the volume of water is small enough and the elastocapillary length will be derived based on the axial symmetry folding pattern. Given the bending stiffness of graphene B=2.31 $\times 10^{-19}$ J[1] and the surface tension of water γ_l=0.0613 $J/m^2$2, by varying the length of the graphene, the critical length l_{ec}^{g} can be obtained via

$$\left|\frac{\Delta E_{def}}{\Delta E_{surf}^{l}}\right|_{\theta_b=\pi}=1 \tag{S 2.9}$$

$l_{ec}^{g}=12.27$nm and the geometric factor can be calculated via $s=l_{ec}^{g}/\sqrt{B/\gamma_l}$. This geometric factor is a constant for a circular graphene and is independent of the dimension of liquid and graphene. Therefore, the elastocapillary length is

$$l_{ec}=6.32\sqrt{\frac{B}{\gamma_l}} \tag{S 2.10}$$

S2.3 Triangular graphene

As has been proved in S1.3 (Fig. S7c), the central symmetric folding always pertains the lowest energy and the elastocapillary length will be derived based on the central symmetric folding pattern. Given the bending stiffness of graphene B=2.31 × 10^{-19} J[1] and the surface tension of water γ_l=0.0613 $J/m^2$2, by varying the length of the graphene, the critical length can be obtained via

$$\left|\frac{\Delta E_{def}}{\Delta E_{surf}^{l}}\right|_{\theta_b=0.72\pi}=1 \tag{S 2.11}$$

$l_{ec}^{g}=6.70$ nm and the geometric factor can be calculated via $s=l_{ec}^{g}/\sqrt{B/\gamma_l}$. This geometric factor is a constant for a triangular graphene and is independent of the dimension of liquid and graphene. Therefore, the elastocapillary length is

$$l_{ec}=3.45\sqrt{\frac{B}{\gamma_l}} \tag{S 2.12}$$

Note that in comparison with rectangular graphene, the geometric factors in Eqs. (S 2.10) and (S 2.12) are given as a specific value for both circular and triangular graphene because the explicit geometric relationship at their critical folding condition cannot be formulated and numerical iterative approaches were used to solve Eqs. (S 2.9) and (S 2.11).

S3. Determination of wet-capillary length when considering surface wettability of solid

S 3.1 Rectangular and Circular graphene

Based on Eq. (7) in the main manuscript, define

$$\gamma_d = -\frac{B\theta_b^2}{2l^2} + \gamma_l(1 + cos\theta_c) \tag{S 3.1}$$

$\gamma_d = 0$ yields

$$l = \theta_{b,c}^{r/c} \sqrt{\frac{B}{2\gamma_l(1 + cos\theta_c)}} \tag{S 3.2}$$

where $\theta_{b,c}^{r/c}$ is the ultimate bending angle for rectangular and circular graphene, and $\theta_{b,c}^{r/c} = \pi$, and thus we have

$$l_{wc} = \pi \sqrt{\frac{B}{2\gamma_l(1 + cos\theta_c)}} \tag{S 3.3}$$

S 3.2 Triangular graphene

Based on the geometric analysis, replace l by $\sqrt{3}l/4$ in Eq. (S 3.1), we can get

$$\gamma_d = -\frac{8B\theta_b^2}{3l^2} + \gamma_l(1 + cos\theta_c) \tag{S 3.4}$$

$\gamma_d = 0$ yields

$$l = \theta_{b,c}^{t} \sqrt{\frac{8B}{3\gamma_l(1 + cos\theta_c)}} \tag{S 3.5}$$

where $\theta_{b,c}^{t}$ is the ultimate bending angle for triangle and $\theta_{b,c}^{t} = 0.72\pi$, and thus we have

$$l_{wc} = \frac{2.9\pi}{\sqrt{3}} \sqrt{\frac{B}{2\gamma_l(1 + cos\theta_c)}} \tag{S 3.6}$$

S4. Energy competition at the vdW energy-driven self-folding

S 4.1 Rectangular graphene

When the graphene is self-folded into a "racket-like" pattern, the total energy is

$$E_{tot} = \frac{Bl_b w}{2r_b^2} + \gamma_b l_o w + \gamma_s(2lw - 2l_o w) \tag{S 4.1}$$

Further, consider

$$r_b = \frac{l}{2\pi} - \frac{l_o}{\pi} \tag{S 4.2}$$

the total energy becomes a function of overlapping length, which is

$$E_{tot} = \frac{2\pi^2 Bw}{l - 2l_o} + \gamma_b l_o w + \gamma_s w(2l - 2l_o) \tag{S 4.3}$$

And the energy ratio is

$$\frac{\Delta E_{def}}{\Delta\left(E_{vdW} + E_{surf}^{g}\right)} = 4\pi^2 B \frac{1}{(\gamma_b - 2\gamma_s)[(l - 2l_o)[l - 2(l_o + \Delta l_o)]]} \tag{S 4.4}$$

Let $l_o = 0$

$$\frac{\Delta E_{def}}{\Delta\left(E_{vdW} + E_{surf}^{s}\right)} = \frac{4\pi^2 B}{(\gamma_b - 2\gamma_s)\left(l^2 - 2l\Delta l_o\right)} \tag{S 4.5}$$

When $\Delta l_o = 0$, the critical length can be obtained, and it is

$$l_{cr} = 2\pi\sqrt{\frac{B}{|\gamma_b - 2\gamma_s|}} \tag{S 4.6}$$

S 4.2 Circular graphene

The total energy during self-folding of a circular shaped graphene is

$$E_{tot} = \frac{BA_b}{2r_b^2} + \gamma_b A_o + \gamma_s(2A - 2A_o) \tag{S 4.7}$$

where A_b is the area of deformed part, A_o is the area of overlapped part and $2A - 2A_o$ is the area exposing to the air/vacuum. Define $h = r_s - l_o$, where r_s is the radius of graphene and l_o is the overlap length, one can find $\alpha = \operatorname{acos}(h/r_s)$, and

$$A_o = \text{acos}\left(\frac{r_s - l_o}{r_s}\right) r_s^2 - (r_s - l_o)\sqrt{2r_s l_o - l_o^2} \tag{S 4.8}$$

and

$$A_b = \pi r_s^2 - 2\text{acos}\left(\frac{r_s - l_o}{r_s}\right) r_s^2 - 2(r_s - l_o)\sqrt{2r_s l_o - l_o^2} \tag{S 4.9}$$

So

$$E_{def} = \frac{B\pi^2\left[\pi r_s^2 - 2\text{acos}\left(\frac{r_s - l_o}{r_s}\right) r_s^2 + 2(r_s - l_o)\sqrt{2r_s l_o - l_o^2}\right]}{2(r - l_o)^2} \tag{S 4.10}$$

$$E_{vdW} = \gamma_b\left[\text{acos}\left(\frac{r_s - l_o}{r_s}\right) r_s^2 - (r_s - l_o)\sqrt{2r_s l_o - l_o^2}\right] \tag{S 4.11}$$

and

$$E_{surf}^{\ g} = \gamma_s\left[2\pi r_s^2 - 2\text{acos}\left(\frac{r_s - l_o}{r_s}\right) r_s^2 + 2(r_s - l_o)\sqrt{2r_s l_o - l_o^2}\right] \tag{S 4.12}$$

the total energy is

$$E_{tot} = \frac{B\pi^2\left[\pi r_s^2 - 2\text{acos}\left(\frac{r_s - l_o}{r_s}\right) r_s^2 + 2(r_s - l_o)\sqrt{2r_s l_o - l_o^2}\right]}{2(r - l_o)^2} + \gamma_b\left[\text{acos}\left(\frac{r_s - l_o}{r_s}\right) r_s^2 - (r_s \\ + \gamma_s\left[2\pi r_s^2 - 2\text{acos}\left(\frac{r_s - l_o}{r_s}\right) r_s^2 + 2(r_s - l_o)\sqrt{2r_s l_o - l_o^2}\right] \tag{S 4.13}$$

Energy competition can be calculated based on Eq. (12) in the main manuscript and the critical length for self-folding can be evaluated by

$$\left|\frac{\Delta E_{def}}{\Delta E_{surf}^{\ g} + \Delta E_{vdW}}\right|_{l_o = 0} = 1 \tag{S 4.14}$$

Given the bending stiffness of graphene B=2.31 × 10 − 19 J [1] and the surface energy density of graphene γ_s=0.047 $J/m^2$2 and the binding energy density of graphene γ_b =− 0.232$J/m^2$2, by varying the length of the graphene, the critical length can be obtained by solving Eq. (S 4.14)

and we get $l_{cr}^{g} = 9.87$ nm and the geometric factor can be obtained via $k = l_{cr}^{g}/\sqrt{B/|\gamma_b - 2\gamma_s|}$=11.72. This geometric factor is a constant for the "racket-like" pattern of the circular graphene and is independent of the dimension of graphene. Therefore, the critical self-folding length is

$$l_{cr} = 11.72\sqrt{\frac{B}{|\gamma_b - 2\gamma_s|}} \qquad \text{(S 4.15)}$$

S 4.3 Triangular graphene

After the first stage of evaporation, one of the tips of triangle unfolds into a flat pattern while the other two tips keep folding and finally a "Cone-like" pattern will be obtained (Fig.1c). This is a three-dimensional pattern and the geometric feature of this pattern needs to be discussed.

As shown in Fig. S9a, suppose the two lower tips of the triangle will be folded while the top tip of the triangle will not. Further, suppose the folding line of the left lower tip is parallel to the right boundary of triangle and the folding line of the right lower tip is parallel to the left boundary of triangle. The overlap length l_o is defined as the distance of the tip of triangle to the folding line. So, if l_o increase, the folding line will propagate inside the triangle. The absolute values of slope of the folding lines are the same and is $k = \sqrt{3}$ for the right bundles and $k = -\sqrt{3}$ for the left bundles.

Consider the symmetry of the folding lines, we will analyze the right bundles. For a given length l and the overlap length l_o, the function of folding line is

$$y = \sqrt{3}x - \frac{\sqrt{3}}{2}l + 2l_o \qquad \text{(S 4.16)}$$

The coordinate of the interception points between the folding line and the axis of symmetry of the triangle is

$$\left(0, -\frac{\sqrt{3}}{2}l + 2l_o\right), \left(0 \le l_o \le \frac{\sqrt{3}}{4}l\right) \qquad \text{(S 4.17)}$$

and the coordinate of the interception points between the folding line and bottom boundary of

triangle is

$$\left(\frac{l}{2}-\frac{2\sqrt{3}}{3}l_o,0\right),\left(0\le l_o\le\frac{\sqrt{3}}{4}l\right) \tag{S 4.18}$$

Further, suppose an arc centered at $\left(0,-\frac{\sqrt{3}}{2}l+2l_o\right)$ with a radius of r_{arc}, if the arc has an interception point with the triangle, the radius should satisfy

$$\frac{\sqrt{3}}{2}l-2l_o\le r_{arc}\le\sqrt{3}l-2l_o \tag{S 4.19}$$

And the equation of arc satifies

$$x^2+\left(y+\frac{\sqrt{3}}{2}l-2l_o\right)^2=r_{arc}^2\left(\frac{\sqrt{3}}{2}l-2l_o\le r_{arc}\le\sqrt{3}l-2l_o\right) \tag{S 4.20}$$

During the self-folding of "Cone-like" pattern, averaged radius of curvature of the atoms on the same arc is a function of r_{arc}, which is discussed below.

The intersection point between the arc and the right boundary of triangle can be determined by

$$\begin{cases} y=-\sqrt{3}x+\frac{\sqrt{3}}{2}l,\left(0\le x\le\frac{l}{2}\right) \\ x^2+\left(y+\frac{\sqrt{3}}{2}l-2l_o\right)^2=r_{arc}^2,\left(\frac{\sqrt{3}}{2}l-2l_o\le r_{arc}\le\sqrt{3}l-2l_o\right) \end{cases} \tag{S 4.21}$$

and the intersection point between the arc and the bottom boundary of triangle can be determined by

$$\begin{cases} y=0,\left(0\le x\le\frac{l}{2}\right) \\ x^2+\left(y+\frac{\sqrt{3}}{2}l-2l_o\right)^2=r_{arc}^2,\left(\frac{\sqrt{3}}{2}l-2l_o\le r_{arc}\le\sqrt{3}l-2l_o\right) \end{cases} \tag{S 4.22}$$

After we get the intersection points, we may have three conditions:

(I) The arc only has two symmetric intersection points with the bottom boundary of triangle (Fig. S9b(I)), and in this case, the length of arc is

$$l_{arc}=2r_{arc}\alpha_b \tag{S 4.23}$$

where

$$\alpha_b = \arcsin\left(\frac{x_b}{r_{arc}}\right) \quad \text{(S 4.24)}$$

x_b is the x coordinate of the intersection point. Further, the length of the central part of the arc is

$$l_{arc}^{c} = \frac{\pi}{3} r_{arc}, \left(l_{arc} > l_{arc}^{c}\right) \quad \text{(S 4.25)}$$

Therefore, the average radius of curvature of the folded triangle is

$$r_{ave} = \frac{l_{arc}^{c}}{2\pi} \quad \text{(S 4.26)}$$

(II) The arc has two intersection points with the left and right boundary of triangle respectively and two symmetric intersection points with the bottom boundary of triangle (Fig. S9b(II)), and in this case, the length of arc is

$$l_{arc} = 2r_{arc}(\alpha_{rl} + \alpha_b - \alpha_{rr}) \quad \text{(S 4.27)}$$

where

$$\alpha_{rl} = \arcsin\left(\frac{x_{rl}}{r_{arc}}\right), \alpha_b = \arcsin\left(\frac{x_b}{r_{arc}}\right), \alpha_{rr} = \arcsin\left(\frac{x_{rr}}{r_{arc}}\right) \quad \text{(S 4.28)}$$

and the length of the central part of the arc is

$$l_{arc}^{c} = \frac{\pi}{3} r_{arc}, \left(l_{arc} > l_{arc}^{c}\right) \quad \text{(S 4.29)}$$

Therefore, the averaged radius of curvature of the folded triangle is

$$r_{ave} = \frac{l_{arc}^{c}}{2\pi} \quad \text{(S 4.30)}$$

(III) The arc only has one intersection point with the left and right boundary of triangle respectively (Fig. S9c(III)), and in this case, the length of arc is

$$l_{arc} = 2r_{arc}\alpha_r \quad \text{(S 4.31)}$$

where

$$\alpha_r = \arcsin\left(\frac{x_r}{r_{arc}}\right) \quad \text{(S 4.32)}$$

And the length of the central part of the arc is

$$l_{arc}^{c} = \frac{\pi}{3} r_{arc}, \left(l_{arc} < l_{arc}^{c}\right) \tag{S 4.33}$$

Therefore, the average radius of curvature of the folded triangle is

$$r_{ave} = \frac{l_{arc}^{c}}{2\pi} \tag{S 4.34}$$

After the length of arc and average radius of curvature are determined, the energy of the folded "Cone-like" pattern can be calculated. Given the equilibrium distance t between the overlapped part of graphene, the deformation energy is

$$E_{def} = \frac{B\pi}{t} \int_{\frac{\sqrt{3}}{2}l - 2l_o}^{\sqrt{3}l - 2l_o} \ln\left(\frac{r_e}{r_i}\right) dr_{arc} \tag{S 4.35}$$

where

$$r_i = \frac{l_{arc} - \pi t N^2}{2\pi N} \tag{S 4.36}$$

and

$$r_e = r_i + Nt \tag{S 4.37}$$

$N = l_{arc}/2\pi r_{ave}$ is the number of folded rings.

The binding energy is

$$E_{vdW} = \gamma_b \int_{\frac{\sqrt{3}}{2}l - 2l_o}^{\sqrt{3}l - 2l_o} \frac{2l_{arc} - (2\pi r_i + \pi t^2) - \left(2\pi r_e - \pi t^2\right)}{2} dr_{arc} \tag{S 4.38}$$

and the surface energy is

$$E_{surf}^{g} = 2\pi\gamma_s \int_{\frac{\sqrt{3}}{2}l - 2l_o}^{\sqrt{3}l - 2l_o} \left(r_i + r_e\right) dr_{arc} \tag{S 4.39}$$

Energy competition can be calculated with Eq. (12) in the main manuscript and the critical

length for self-folding can be evaluated by

$$\left|\frac{\Delta E_{def}}{\Delta E_{surf}^{s}+\Delta E_{vdW}}\right|_{l_o=0}=1 \tag{S 4.40}$$

Given the bending stiffness of graphene B=2.31 $\times 10^{-19} J$ [1], the surface energy density of graphene γ_s=0.047 $J/m^2$2 and the binding energy density of graphene γ_b =− 0.232$J/m^2$2, by varying the length of the graphene, the critical length can be obtained by solving Eq. (S 4.40) and we get $l_{cr}^{g}=11.42$ nm and the geometric factor can be obtained via $k=l_{cr}^{g}/\sqrt{B/|\gamma_b-2\gamma_s|}$=13.57. This geometric factor is a constant for the "cone-like" pattern of the triangular graphene and is independent of the dimension of graphene. Therefore, the critical self-folding length is

$$l_{cr}=13.57\sqrt{\frac{B}{|\gamma_b-2\gamma_s|}} \tag{S 4.41}$$

Similar to the determination of elastocapillary length in section 2.2 and section 2.3, the geometric factors in Eqs. (S4.15) and (S4.41) are given with a specific value for both circular and triangular graphene because the explicit geometric relationship at their critical folding condition cannot be formulated and numerical iterative approaches were used to solve Eqs. (S 4.14) and (S 4.40).

Reference:

1. Y. Wei, B. Wang, J. Wu, R. Yang and M. L. Dunn, *Nano letters*, 2013, **13**, 26-30.

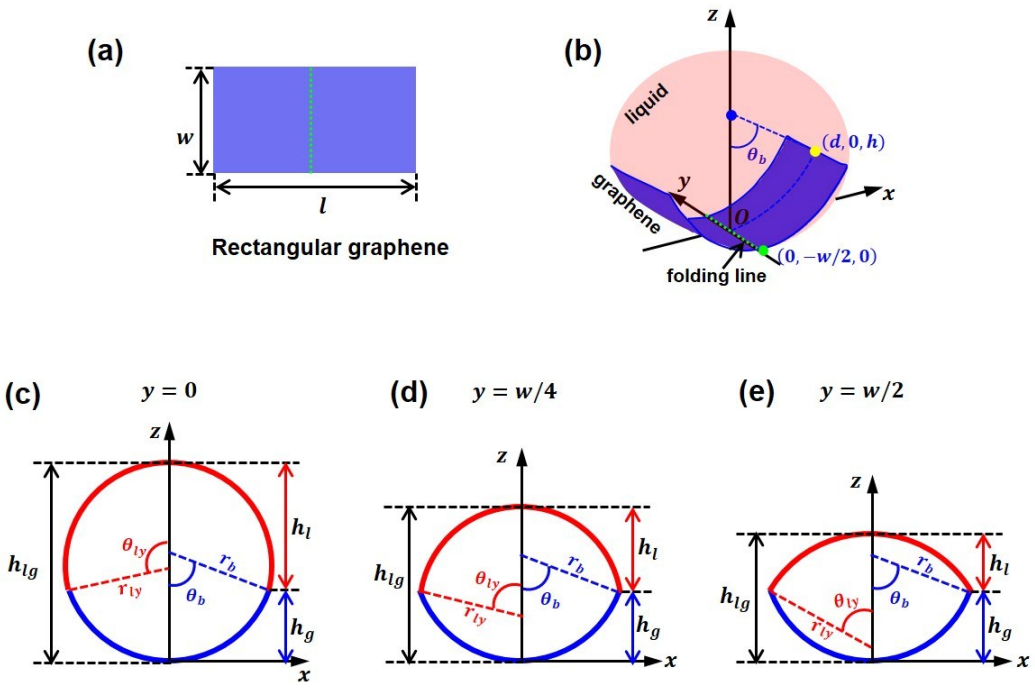

Figure S1. Evaporation-driven self-folding of a single suspended rectangular graphene sheet. Schematics of (a) planar rectangular graphene, and (b) suspended in liquid. (c) The variation of profile of graphene and liquid along the y direction at (c) $y = 0$, (d) $y = w/4$ and (e) $y = w/2$.

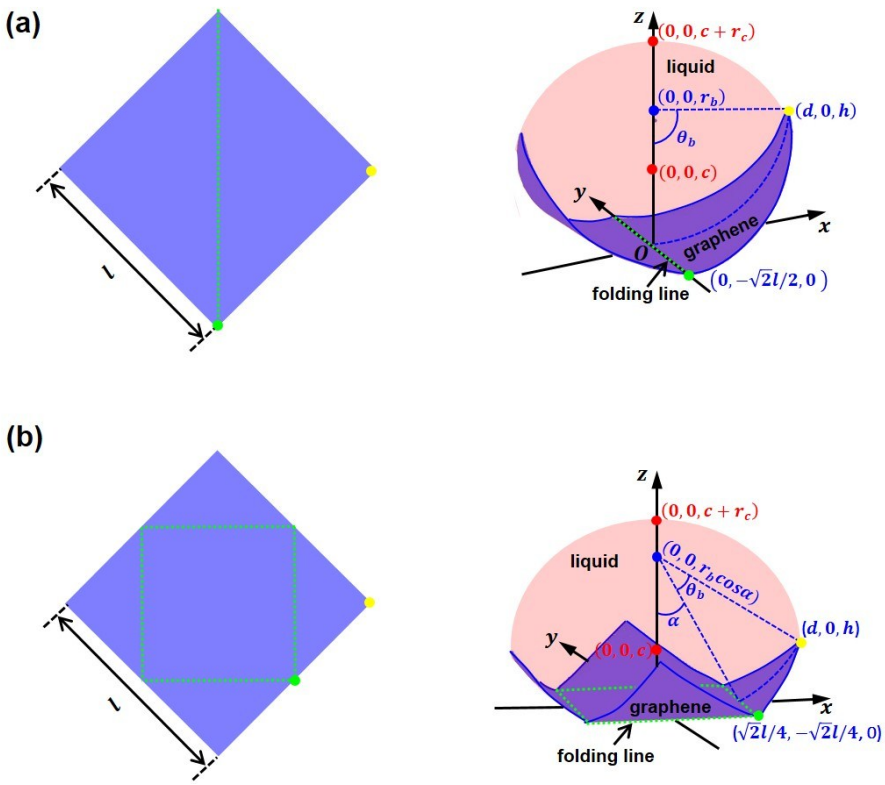

Figure S2. Schematic figures of the square graphene folded in different patterns. (a) Schematics of planar square graphene, and after suspended in liquid. (b) Schematics of planar square graphene, and after suspended in liquid. The green dotted line shows the folding line of the graphene.

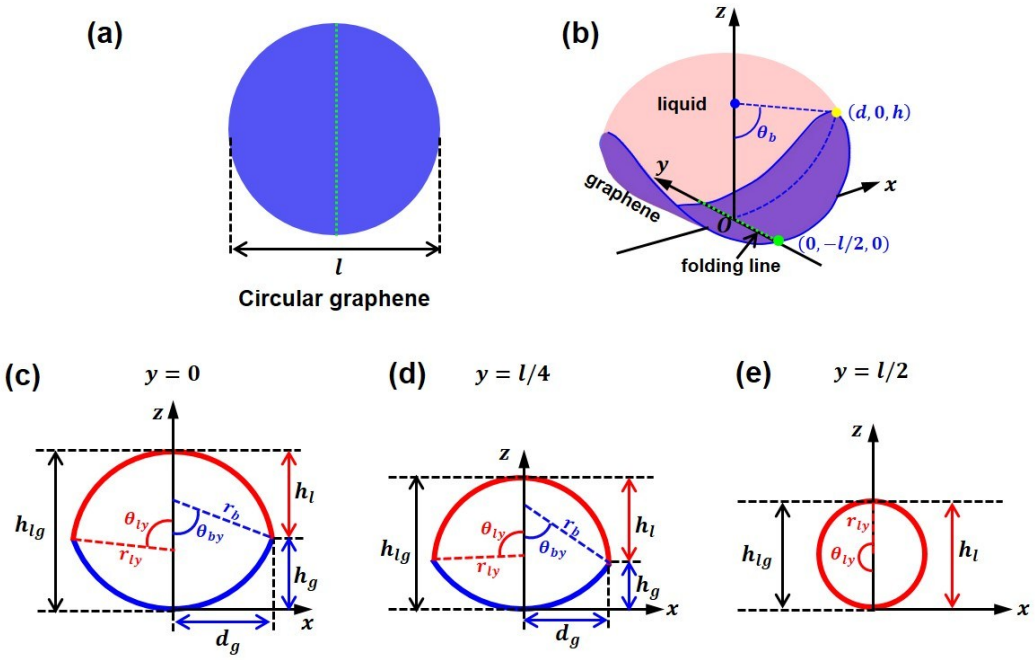

Figure S3. Evaporation-driven self-folding of a single suspended circular graphene sheet. Schematics of (a) planar circular graphene, and (b) suspended in liquid. (c) The variation of profile of graphene and liquid along the y direction at (c) $y = 0$, (d) $y = l/4$ and (e) $y = l/2$.

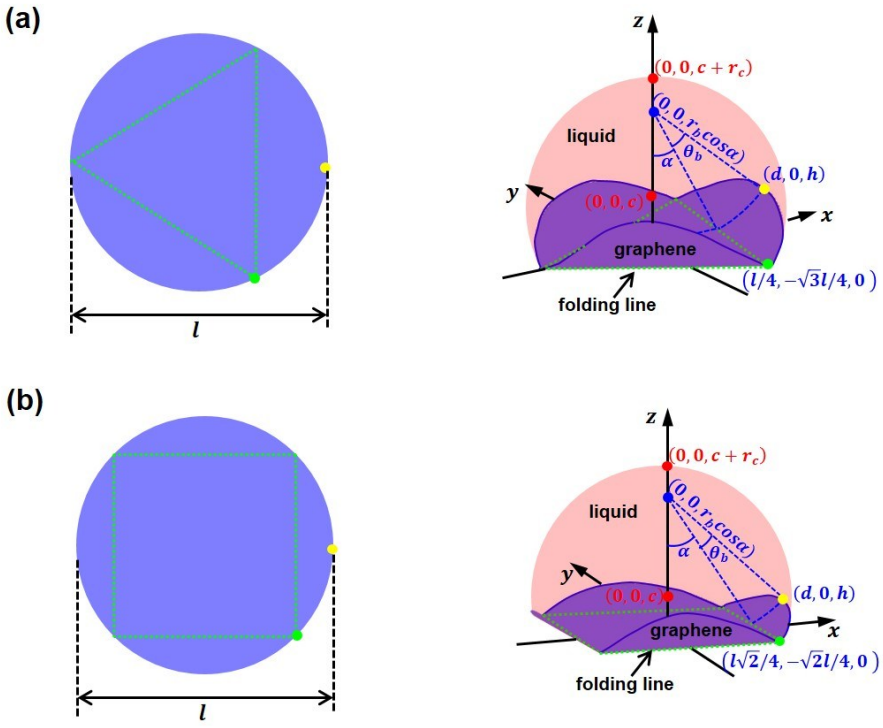

Figure S4. Schematic figures of the circular graphene folded in different patterns. (a) Schematics of planar circular graphene, and after suspended in liquid. (b) Schematics of planar circular graphene, and after suspended in liquid. The green dotted line shows the folding line of the graphene.

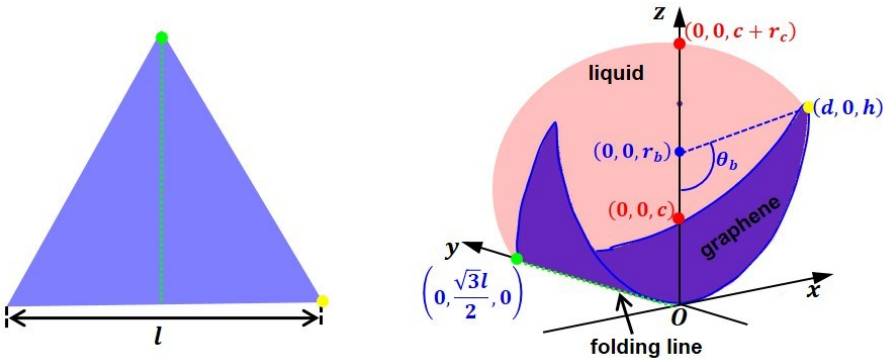

Figure S5. Schematics of planar triangular graphene, and after suspended in liquid. The green dotted line shows the folding line of the graphene.

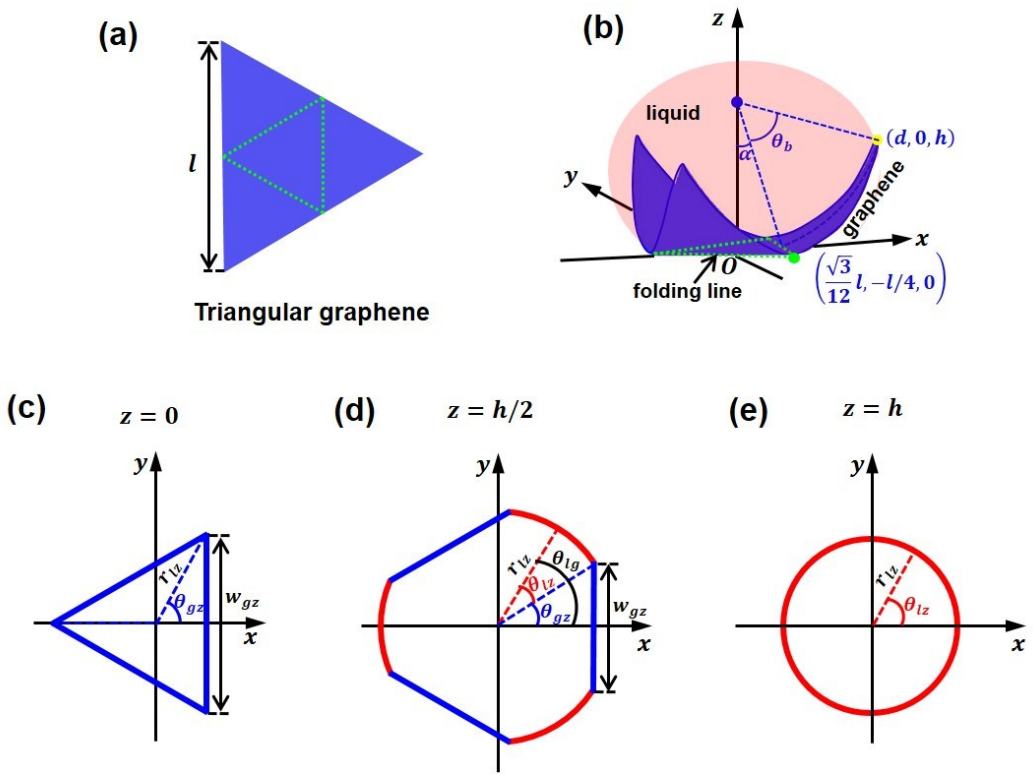

Figure S6. Evaporation-driven self-folding of a single suspended triangular graphene sheet. Schematics of (a) planar triangular graphene, and (b) suspended in liquid. (c) The variation of profile of graphene and liquid along the z direction at (c) $z = 0$, (d) $z = h/2$ and (e) $z = h$.

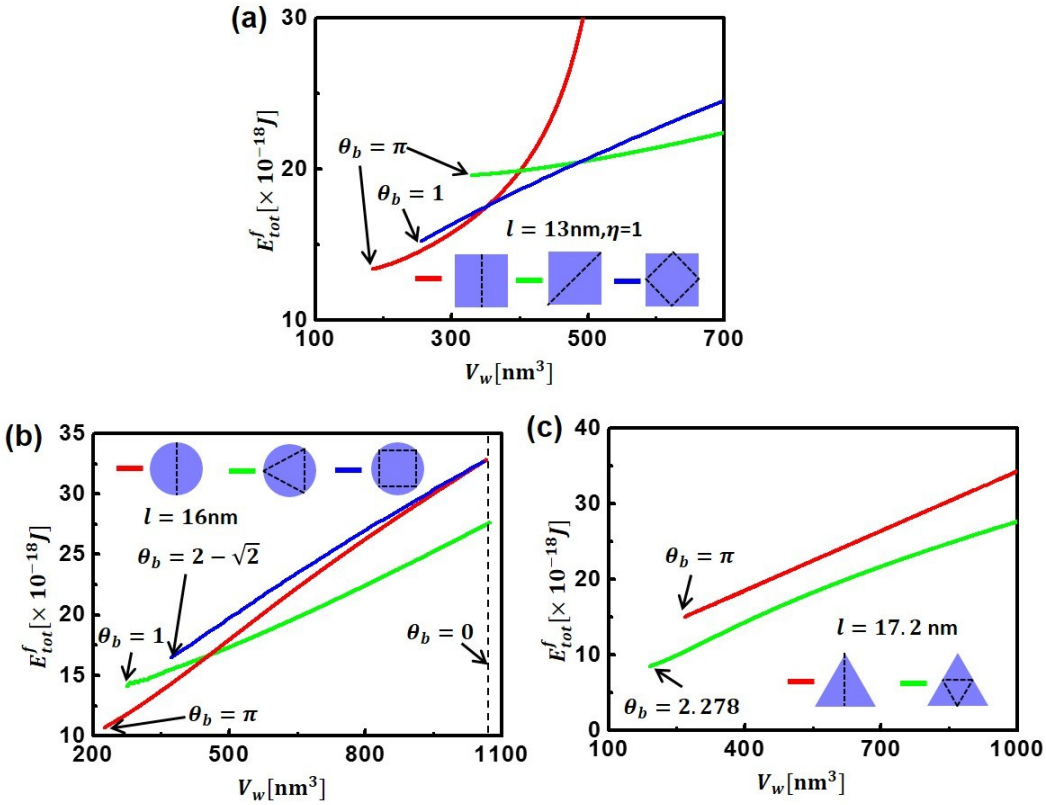

Figure S7. The energy variation with water volume for self-folding (a) square graphene (b) circular graphene and (c) triangular graphene. Insets show the graphene geometry and possible folding paths (black dashed line in insets)

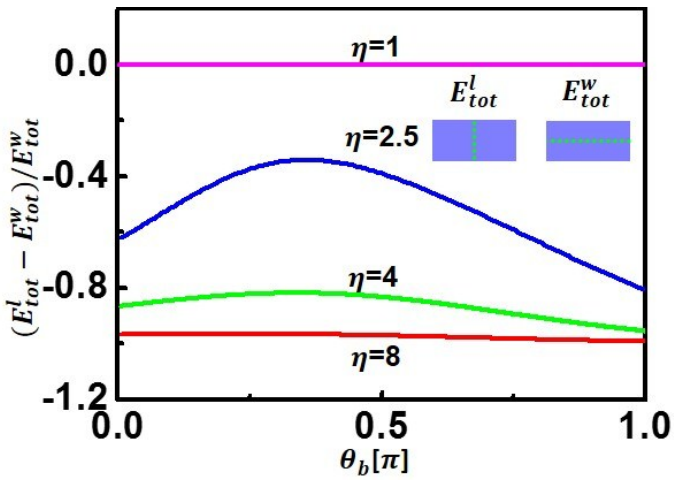

Figure S8. Normalized energy difference when the rectangular graphene is folded along its symmetric axis (green dotted line in insets) parallel to the length and width of the rectangle, respectively, where $\eta = l/w$ (≥ 1) is the aspect ratio of graphene.

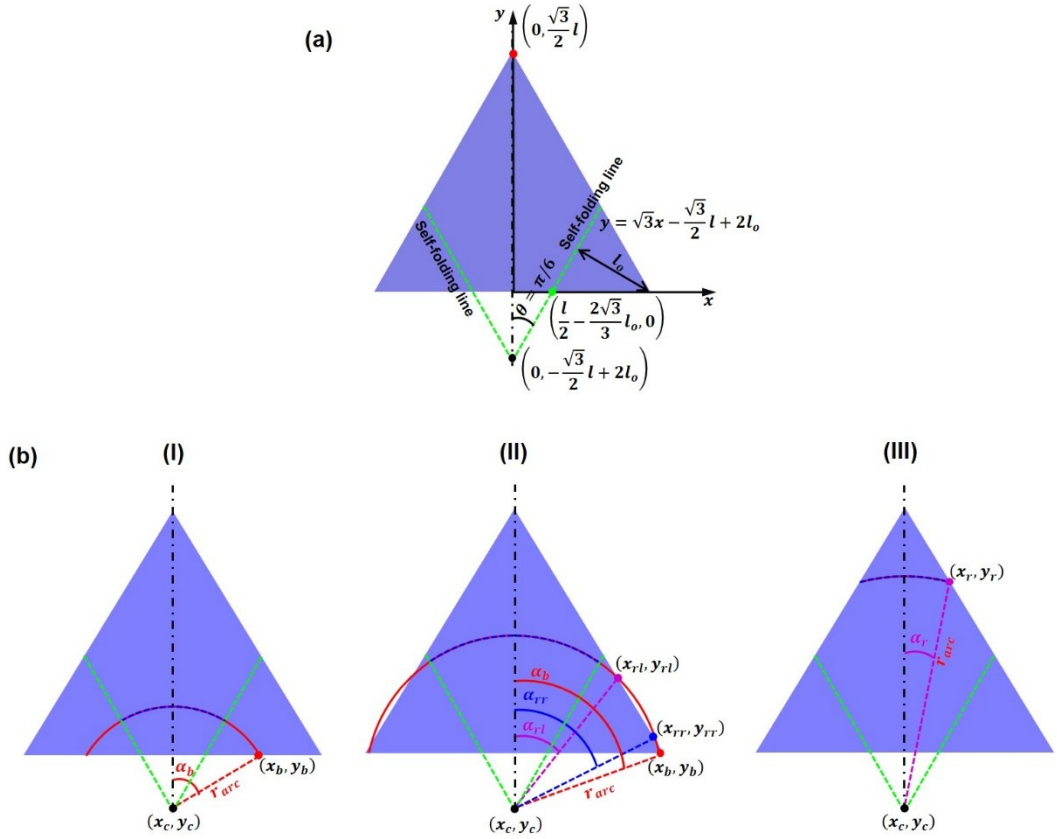

Figure S9. Schematics to show the overlap length l_o, self-folding line to determine the parameters in a "cone-like" folded triangular graphene. (a)The dashed green lines illustrate the self-folding line and the overlap length l_o is the distance of tip of graphene to the self-folding line. (b) The radius of arcs (r_{arc}) centered at the intersection point between self-folding line and symmetric axis of triangle will increase. And the arc may have b.I) two intersection points with the bottom boundary of triangle, (b.II) two intersection points with the left and right boundary of triangle, respectively, and two intersection point with the bottom boundary of triangle and (b.III) one intersection point with the left and right boundary of triangle, respectively. Atoms on the same arc will be in the same cross-section of the "cone-like" pattern and the averaged radius of curvature at this cross-section is $r_{arc}/6$.