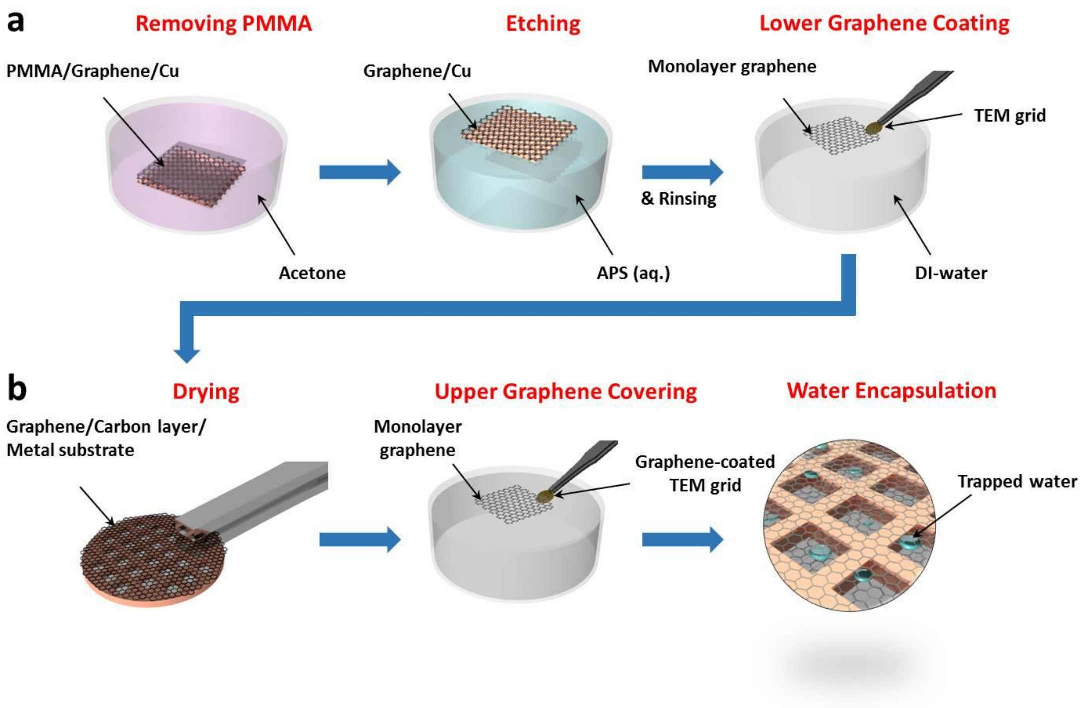
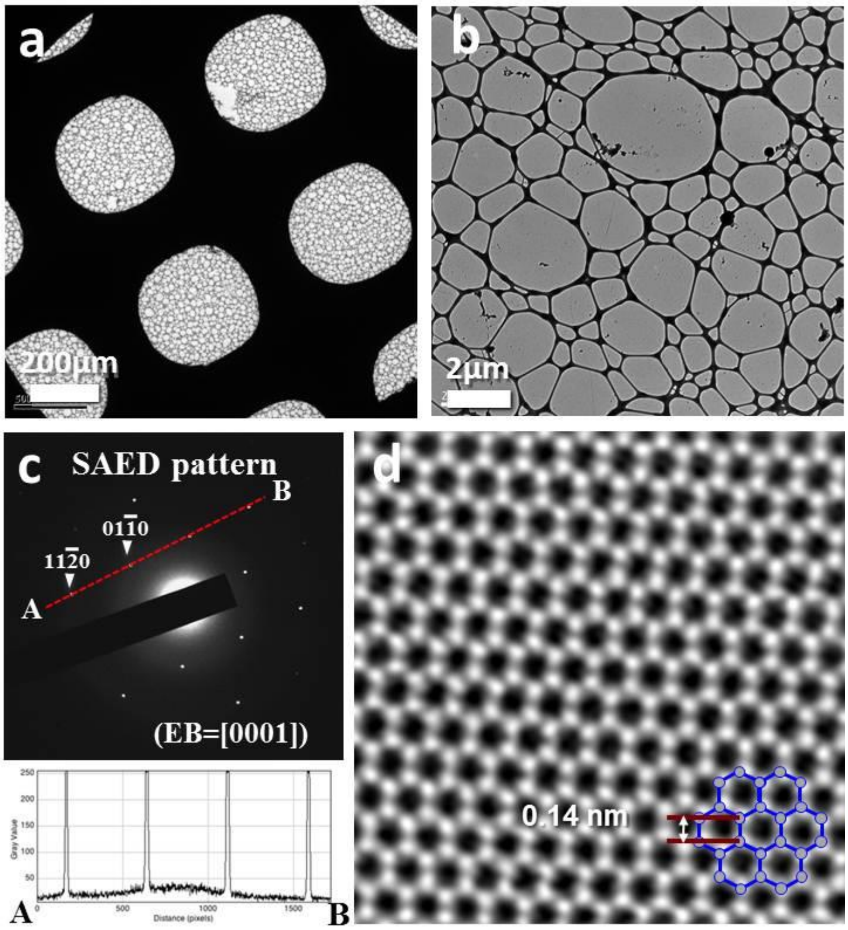
Supplementary Information

Dongha Shin et al., "Growth dynamics and gas transport mechanism of nanobubbles in graphene liquid cells".

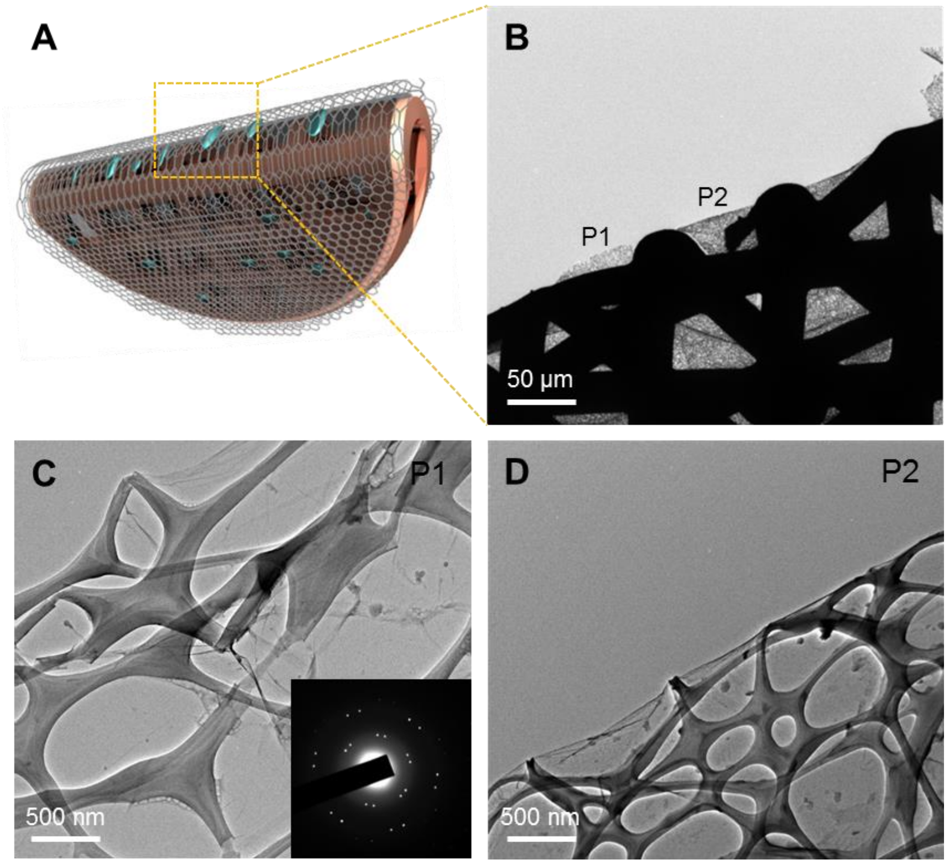
A. Supplementary Figures



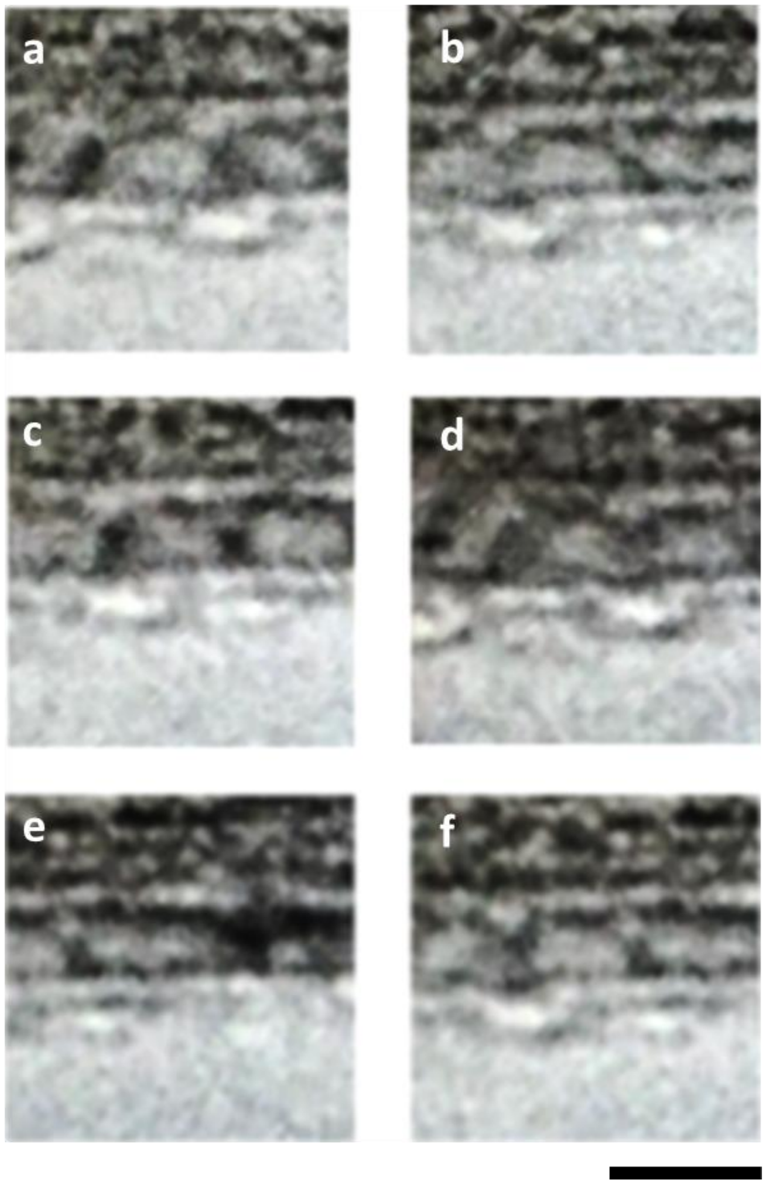
Supplementary Figure 1. Schematic representation for the preparation processes of graphene liquid cells. a, Fabrication of graphene coated TEM grid. The monolayer graphene without PMMA support was prepared by removing PMMA with acetone, followed by Cu etching with 1.8 wt% ammonium persulfate (APS) solution. Finally rinsing and transferring complete the graphene-supported TEM grid. **b**, Capturing water islands by transferring the second layer graphene. After drying, another monolayer graphene floating on water was transferred on to the graphene-supported TEM grid, where residual water on graphene can be trapped naturally between two graphene layers.



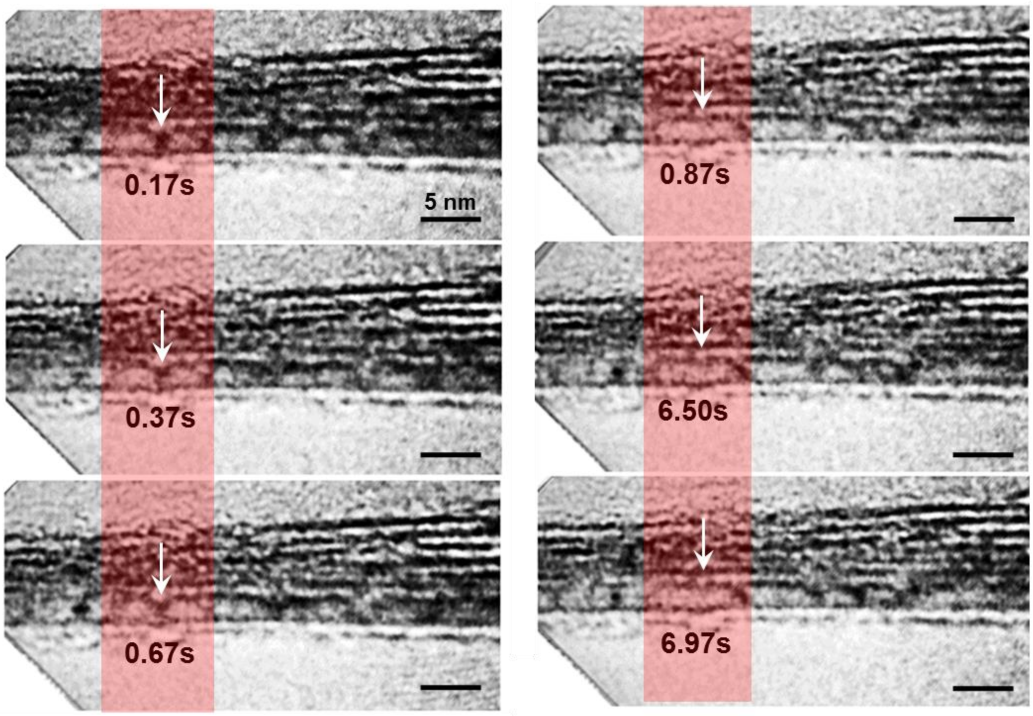
Supplementary Figure 2. Characterization of high quality CVD graphene using HR-TEM and HAADF-STEM. a and **b**, TEM images of monolayer graphene on a Cu grid with amorphous carbon as support layer. **c**, Selected area electron diffraction (SAED) pattern of graphene monolayer, evidenced by the same intensity along the A-B line profile. **d**, Atomic resolution image of high quality graphene obtained by high-angle annular dark filed (HAADF) scanning transmission electron microscope (STEM).



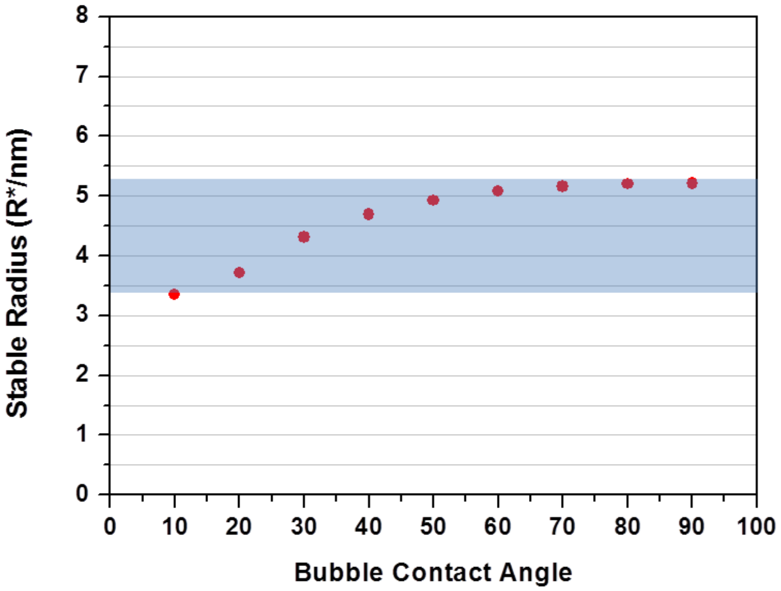
Supplementary Figure 3. Morphology of folded graphene liquid cells on a TEM grid. **a,** Schematic illustration of folded graphene liquid cell on a TEM grid. **b-d**, Low and high magnification TEM images of the folded graphene liquid cells. The P1 and P2 indicate the cut and folded parts of graphene liquid cells, respectively. The inset image in C shows the selected area electron diffraction (SAED) pattern of two overlapping graphene monolayers.



Supplementary Figure 4. Cross-sectional TEM images of nanobubbles in a graphene liquid cell. a-f, TEM images showing the side view of various nanobubbles in water trapped between sandwiched graphene. (see supplementary Movie 1). Scale bar, 5 nm.



Supplementary Figure 5. Snap shots of TEM movies showing the side views of nanobubbles**.** The white arrows indicate the two coalescing nanobubbles. Scale bars, 5 nm.



Supplementary Figure 6. Calculated stable radii of nanobubbles with varying contact angles with graphene.

B. Supplementary Note 1

Calculation on the stable radius of plano-convex shaped nanobubbles

The stable radius of nanobubbles was calculated considering the structural parameters from TEM observation and the molecular dynamics simulation results by Matsumoto *et al.* (Ref. 27). The setting temperature of water is 300K, and the system volume was fixed at V = 30 x 30 x 7.5 (nm)^3. The liquid pressure of system P_{sys} can be estimated from the density of liquid ρ_{liq} as

$$\mathrm{P}_{sys} = A\ \frac{mN}{V - V_{bubble}} + B \tag{1}$$

where m is the molecular mass of water, N is the number of molecules, and $V_{bubbule}$ is the volume of nanobubble. A and B are the constants determined approximately by a linear function of P_{sys} with respect to ρ_{liq}. Considering the plano-convex shape of nanobubbles, $V_{bubbule}$ was calculated by simple integral as

$$\mathrm{V}_{bubble} = \int_{R_c - H}^{R_c} \left({R_c}^2 - y^2\right)\pi dy = \pi R^3 \left\{ \frac{\left(\tan\frac{\theta_c}{2}\right)^2}{\sin\theta_c} - \frac{1}{3}\left(\tan\frac{\theta_c}{2}\right)^3 \right\} \tag{2}$$

The surrounding liquid pressure of nanobubble, P_{liq} is given by $P_{liq} = P_{vap} - \Delta P$, where P_{vap} is the gas pressure inside the nanobubble and ΔP is Young-Laplace pressure. At 300K, the vapor density inside nanobubble is very low, so it can be set as P_{vap} = 0 in our calculation. Thus, P_{liq} simply can be expressed as ~ – ΔP. Now the radius of stable nanobubble can be derived from the equilibrium equation between liquid and system pressure, $P_{liq} = P_{sys}$ as following:

$$-\frac{2\gamma\sin\theta_c}{R} = \frac{AmN}{6750 - \pi R^3 \left\{ \frac{\left(\tan\frac{\theta_c}{2}\right)}{(\sin\theta_c)^2} - \frac{1}{3}\left(\tan\frac{\theta_c}{2}\right)^3 \right\}} + B \tag{3}$$

The constant values are approximated as A = 2 x 10^{24}, B = - 1980, γ= 71.97 mN m^{-1} and N = 211,003. A and B are adopted from the MD simulation by Matsumoto *et al.* (Ref. 27), θc is roughly measured to be 60~90^0 based on the TEM results, and γ is the surface tension of water. In this way, the stable radius of a nanobubble was calculated to be 5.04~5.21 nm as shown in Supplementary Figure 6.