Supporting Information for

Large-Scale Freestanding Nanometer-thick Graphite Pellicle for Mass Production of Nanodevices beyond 10 nm

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1. Transmission and absorption of NGF at EUV (λ = 13.5 nm), visible (λ = 550 nm), and IR (λ = 800 nm) wavelengths

For EUV, the transmission of the NGF can be expressed in terms of the optical constant for the EUV regime $\beta \approx (r_0 \cdot \lambda^2/2\pi) n_c f_{2c}(0)$, as $T_{EUV} = e^{-4\pi\beta N \cdot d/\lambda}$ where $N \cdot d$ is thickness of the film, λ is wavelength of the EUV, r_0 is classical electron radius, n_c is atomic density of NGF, and $f_{2c}(0)$ is the imaginary part of the atomic scattering factor of carbon at normal incident angle[11]. For visible light, transmission can be expressed as $T = e^{-4\pi\kappa t/\lambda}$ where $\kappa = 1.3$ is the extinction coefficient of graphite at $\lambda = 550$ nm, and t is the thickness of the NGF.

Absorption of light in a material can be expressed as $A = 1 - T - R$, where A is absorption, T is transmission, and R is reflection. With 100-nm-thick NGF, an EUV transmission at 13.5 nm can be calculated with T_{EUV} and β, and the value is 52.6%. Reflectance is not considered because of the very small value. Thus, the absorption of the NGF at the EUV wavelength is 47.4%. At the IR wavelength (800 nm), the transmission

equation is almost the same as that of visible light except the value of κ. κ = 1.7 is introduced and the transmission at a wavelength of 800 nm is 6.9%. Reflectance can be expressed as $R = ((n - n_0)^2 + \kappa^2)/((n + n_0)^2 + \kappa^2)$ and is 36.5%, where $n_0 = 1$ is the refractive index of vacuum and n = 3.0 and κ = 1.7 are the real and imaginary parts of the complex refractive index of the NGF[18]. So, the calculated absorption of the NGF with the thickness of 100 nm is 56.6%. This is very close to the measured value of absorption of NGF, 57.1% (Figure S3).

2. Removal of PMMA by oxygen plasma treatment

A PMMA layer in the scooping and wet and dry transfer (WaDT) methods was used as a support layer for stable transfer of NGF on the frame. Generally, PMMA was removed by thermal annealing and solvent rinses[19]. Although these methods are useful in the case of NGF transfer onto flat substrates, in cases of large-scale freestanding NGF, the sagging problem and the destruction of NGF by thermal annealing and/or surface tension between NGF and solvent were observed. Thus, we used the method of oxygen plasma treatment to remove the PMMA for large-scale freestanding NGFs. The pressure of oxygen was ~ 0.38 Torr, and plasma with a radio frequency of 13.6 MHz and power of 50 W was used. Large-scale freestanding NGFs were treated for 5 min. Figure S7 shows the optical images of as-grown NGF, PMMA/NGF, NGF treated by plasma for 2 min, and 5 min. After oxygen plasma treatment for 5 min, PMMA was completely removed from NGF.

3. Control of NGF thickness by oxygen plasma treatment

NGF synthesized at 1000 °C was coated with PMMA layer, and then it was transferred on a 20 × 20 mm frame by WaDT method after Ni etching and cleaning. The conditions for the oxygen plasma were the same as that for the removal of PMMA. After the removal of PMMA layer on NGF by oxygen plasma treatment for 5 min, NGF was treated by plasma for additional 5 min to 80 min. Figure S8 shows the variation of the transmission of NGF at the visible wavelength of 550 nm as a function of oxygen plasma treatment time and the photo images of NGF/PMMA and NGF treated by oxygen plasma. Thickness of NGF was calculated by Beer-Lambert law (See chapter 2 about transmission and absorption of NGF). As plasma treatment time was increased, thickness of NGF was decreased. The etching rate of NGF by oxygen plasma was ~0.226 nm/min. For 80 min of plasma treatment, the transmission of NGF is enhanced by 9%, and thickness of NGF is reduced by 18.7 nm. The photo image of NGF after oxygen plasma treatment (Figure S8D) is more transparent than that of NGF before treatment (Figure S8C). Graphene (or multi-layered graphene) was generally damaged after oxygen plasma treatment[20]. So, we evaluated the plasma-induced defects of NGF by Raman spectroscopy. Generally, our NGF shows ~0.02 of I_D/I_G in Raman spectroscopy. After removal of PMMA from PMMA/NGF by plasma treatment for 5 min, I_D/I_G was increased from ~0.022 to ~0.053. After 80 min, I_D/I_G was increased to ~0.134, as shown in Figure S8B.

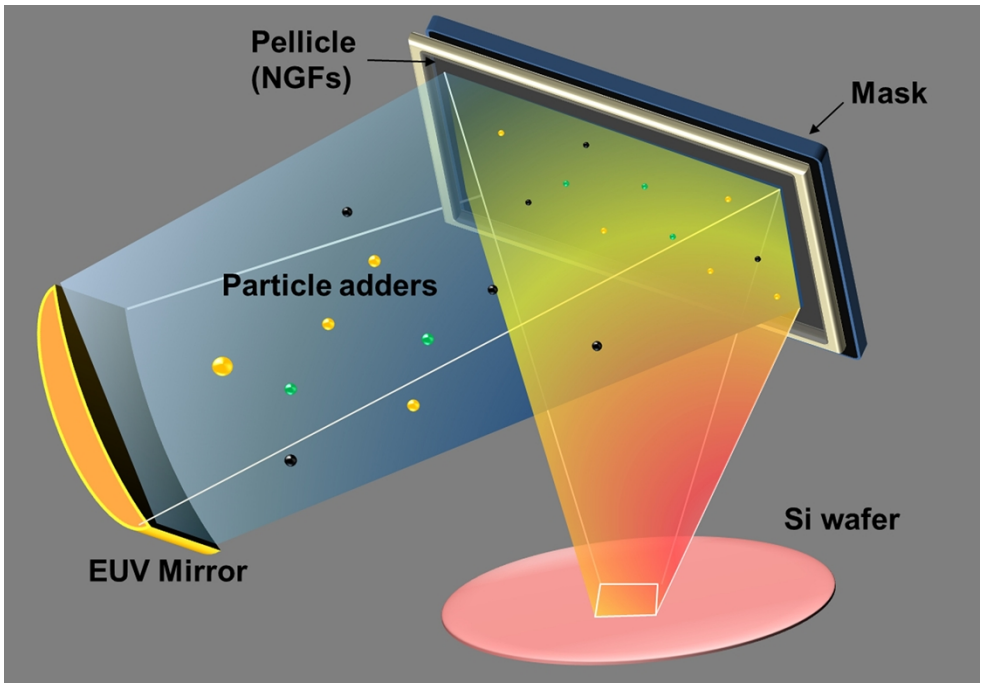

Figure S1. Scheme of EUV lithography. An EUV beam generated from an EUV source is reflected via an EUV mirror and goes through the pellicle twice by a reflection mask. Energy efficiency transferred onto Si wafer that directly affects production efficiency is proportional to the square of the pellicle transmission, and thus improvement of EUV transmission of the EUVL pellicle is required.

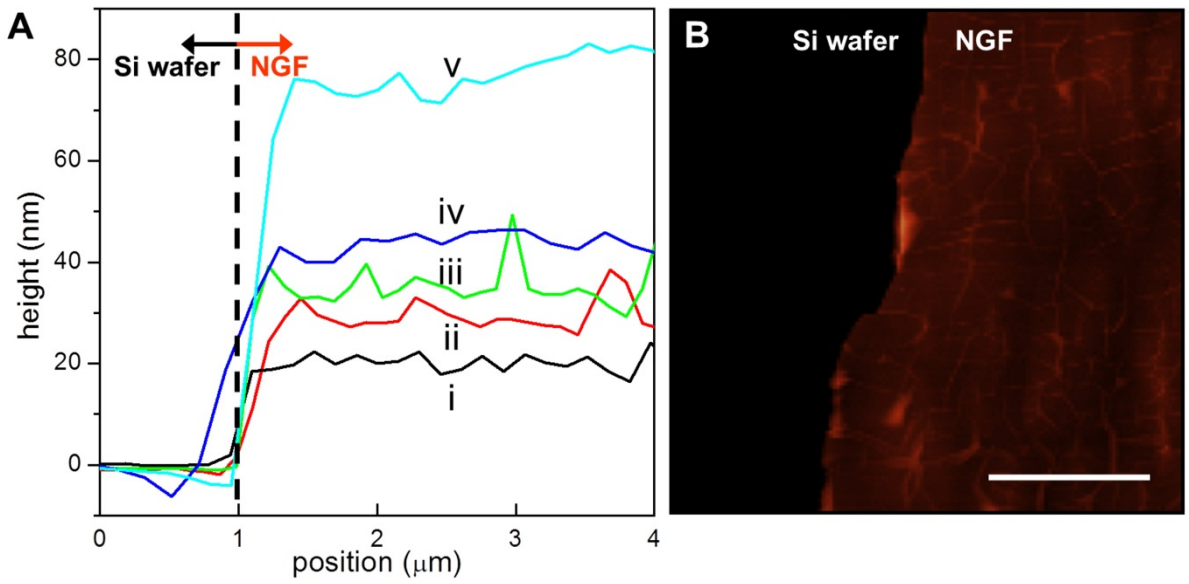

Figure S2. Thickness of nanometer-thick graphite film (NGF) measured by AFM. (A) AFM line profiles obtained at the edge of the NGF from 18 nm (i) to 78 nm (v). Each thickness was obtained after transfer of the NGF on to a Si wafer. (B) Typical AFM topographic image of NGF (34 nm thick). The scale bar of (B) is 5 μm.

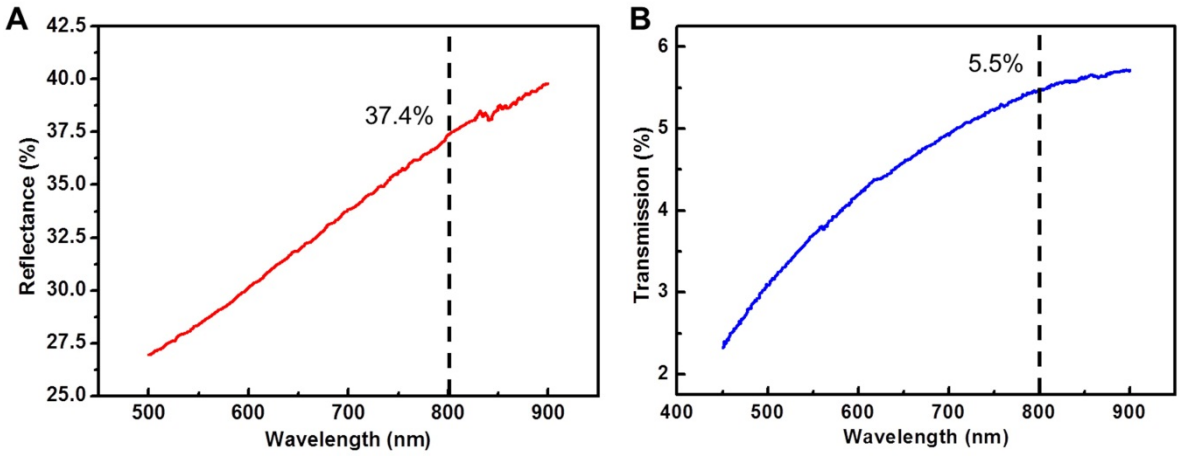

Figure S3. Reflectance and transmission of the 100 nm thick NGF measured by UV-vis NIR spectrometer. (A) Reflectance and (B) transmission of the NGF to the incident light were measured as 37.4% and 5.5%, respectively. At a wavelength of 800 nm, 57.1% of the incident laser power was absorbed and converted into heat in NGF.

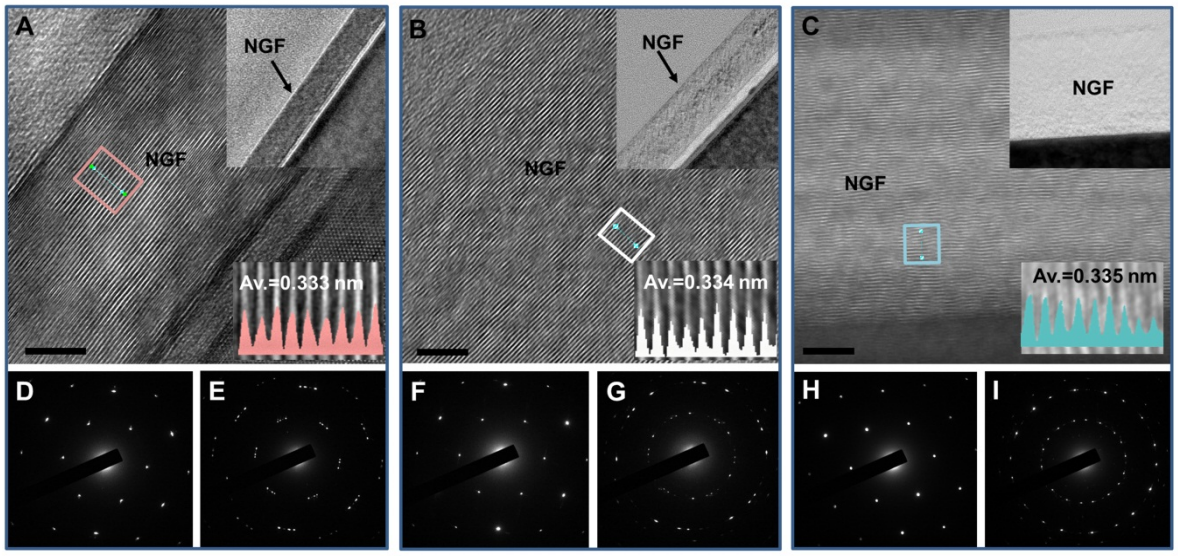

Figure S4. TEM cross-section image and electron diffraction pattern of NGFs. (A-C) High-resolution TEM cross-section images of the NGFs of various thicknesses. The thicknesses of NGF synthesized at 910, 925, and 1000 °C were 18, 28, and 67 nm, respectively. The top-right inset of (A-C) show the cross-sectional view of each film. The bottom-right inset of (A-C) show the magnified image of the marked area in (A-C) and the layer distance from the intensity profile. They are very close to theoretical layer distance of the graphite, 0.335 nm, and show a well-arranged layer structure. (D-I) The selected area electron diffraction (SAED) patterns of (A-C). Each NGF has similar SAED patterns: (i) well-defined hexagonal and (ii) hexagonal patterns by overlapped grain, indicating the polycrystalline structure of the NGFs. Each SAED pattern was collected using a 1.2 μm aperture. The scale bar is 5 nm.

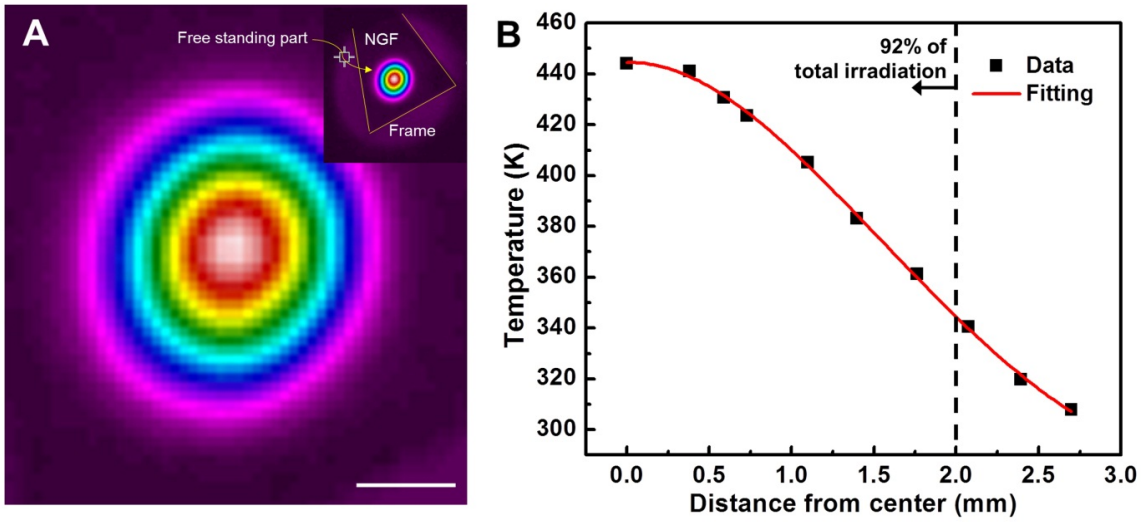

Figure S5. Temperature profile of NGF with IR laser irradiation. (A) The thermal image of the NGF pellicle with 5.1 W/cm^2 of IR laser irradiation, and (B) temperature profile. The scale bar of (A) is 2 mm. The inner diameter of the free-standing pellicle was 5.3 mm and outer diameter of the frame was 12.0 mm. An IR laser with a wavelength of 800 nm was illuminated onto the center of the pellicle. About 92% of total intensity of the incident beam was focused within 2 mm from the center of the beam. Temperatures profile of the NGF was obtained from the analysis of thermal image, and the temperature profile (Figure S5B) was fitted using polynomials.

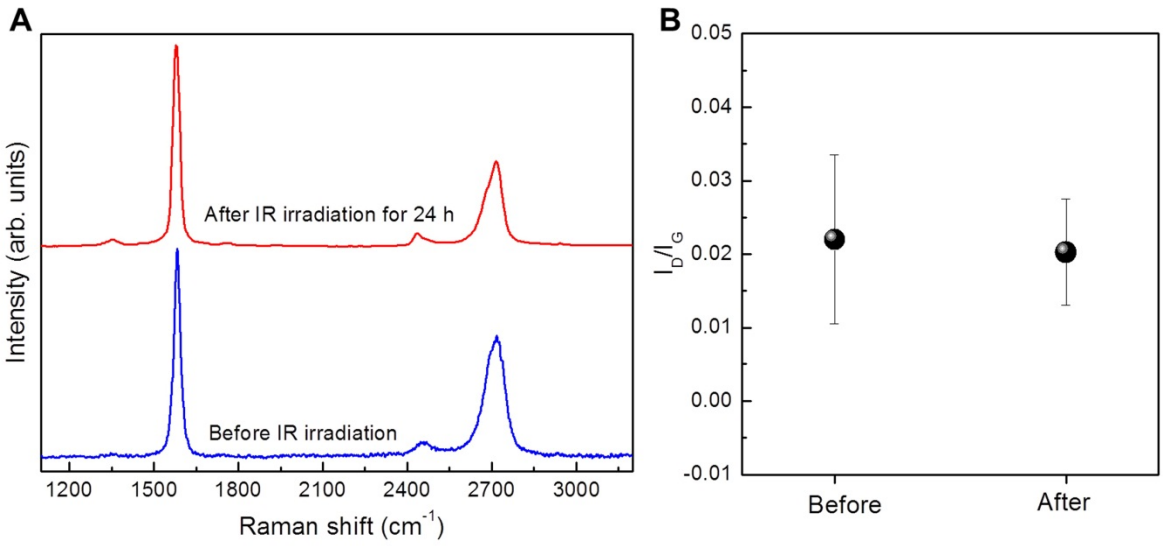

Figure S6. Raman spectra of the NGF pellicle before and after IR laser irradiation.

(A) Raman spectra of the freestanding NGF pellicle before and after IR laser irradiation.

(B) No enhancement of the D-band was observed after IR irradiation.

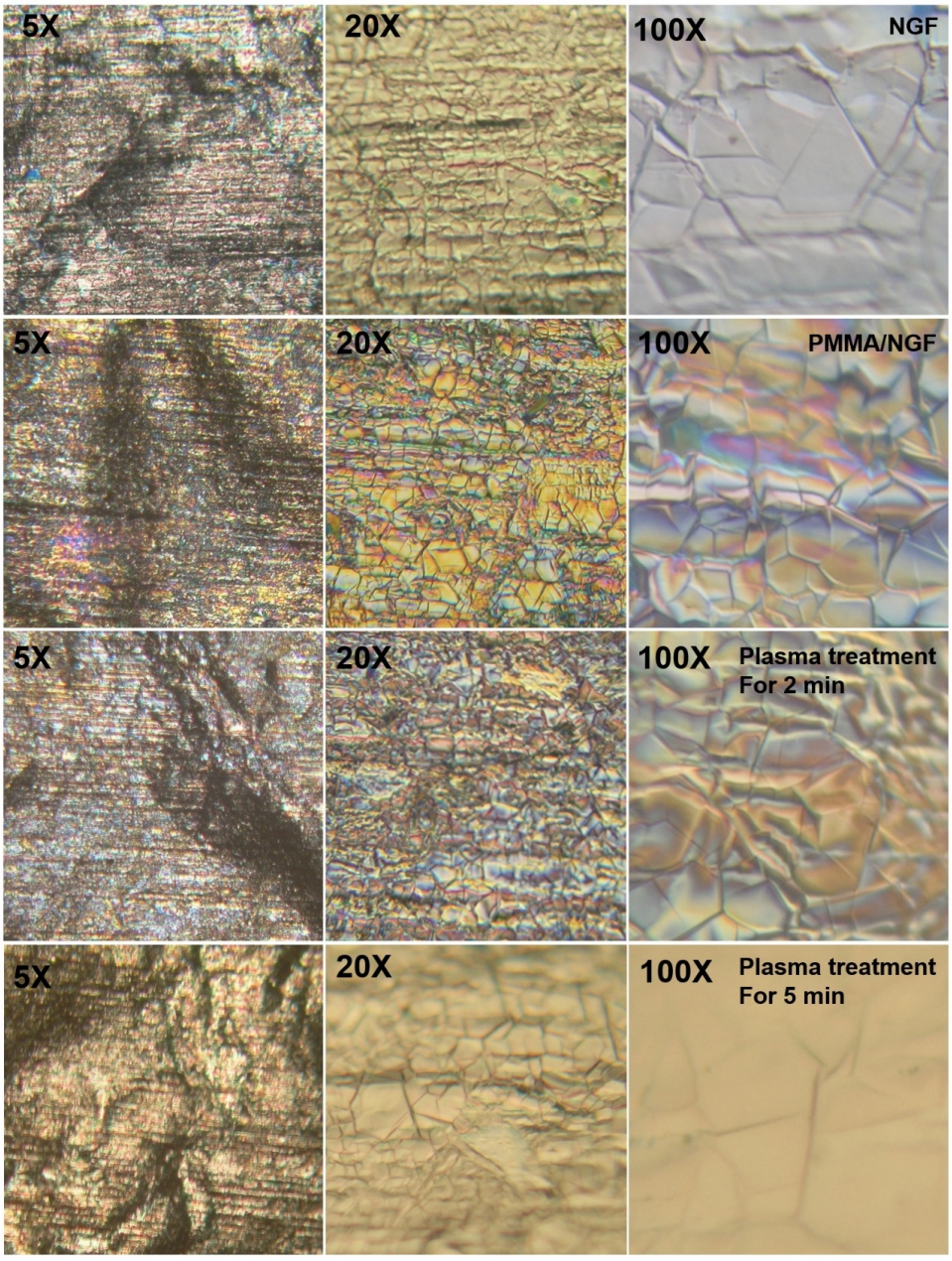

Figure S7. Optical images of NGFs and PMMA/NGFs before and after O_2 plasma treatment. After oxygen plasma treatment for 5 min, PMMA was completely removed from NGF. The pressure of oxygen was ~ 0.38 Torr, and plasma with a radio frequency of 13.6 MHz and power of 50 W was used.

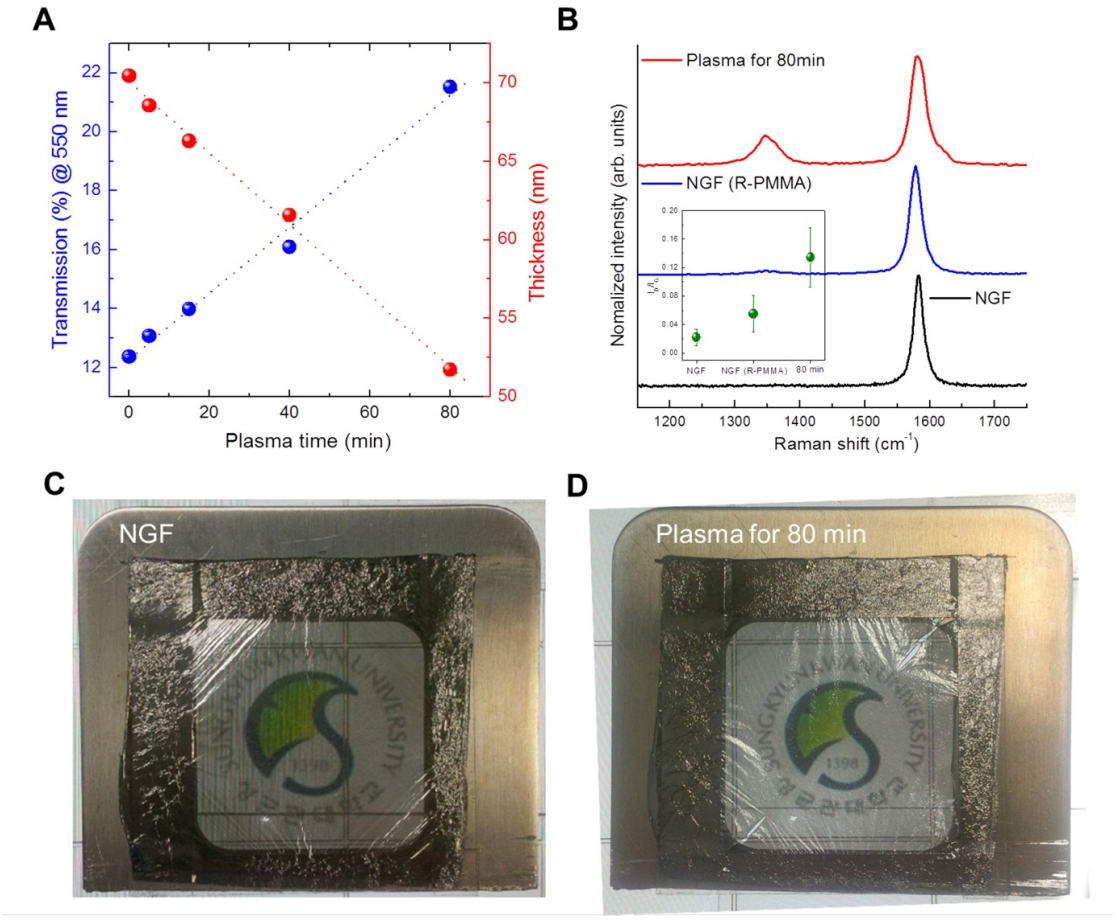

Figure S8. Control of NGF thickness by oxygen plasma treatment (20 × 20 mm frame). (A) Variation of the transmission of NGF and calculated thickness at visible wavelength of 550 nm as a function of oxygen plasma treatment time. Thickness of NGF was calculated by Beer-Lambert law (See chapter 2). For 80 min of etching time, the transmission of NGF was enhanced by 9% and the thickness of the NGF was reduced by 18.7 nm. (B) Raman spectra of NGF, NGF (R-PMMA) (PMMA removed from NGF), and NGF treated by plasma for 80 min, and (C-D) the photo images of NGF (after removal of PMMA) and NGF treated by oxygen plasma for 80 min. The inset of (B) is I_D/I_G ratio of each film.