Supplemental Material for "Temperature coefficients of phonon frequencies and thermal conductivity in thin black phosphorus layers"

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Figure S1. Raman spectra of BP samples before and after temperature-dependent Raman measurements.

The Raman spectra of samples S1 and S2 before and after temperature-dependent Raman measurements are shown in Fig. S1, as (a) and (b), respectively. Both S1 and S2 exhibit no decrease in their Raman intensities, indicating no photodegradation of the films after heating.

Regarding to the linewidth, for S1, the thicker BP film, the FWHM values of all the three modes generally keep the same before and after the measurements; whereas, for S2, the thinner film, they exhibit a slight increase, which, as mentioned in the main text, is attributed to the strain effect on the linewidth. For thinner films, they are more susceptible to the substrate influence, and with increasing temperature the change of film morphology tends to be more significant. As a result, when the temperature goes back to room temperature, the residual strain may increase the linewidth of Raman modes. Even though the strain can change the FWHM, the primary origin of the broadening of FWHM for all the samples is attributed to the decay of phonons.

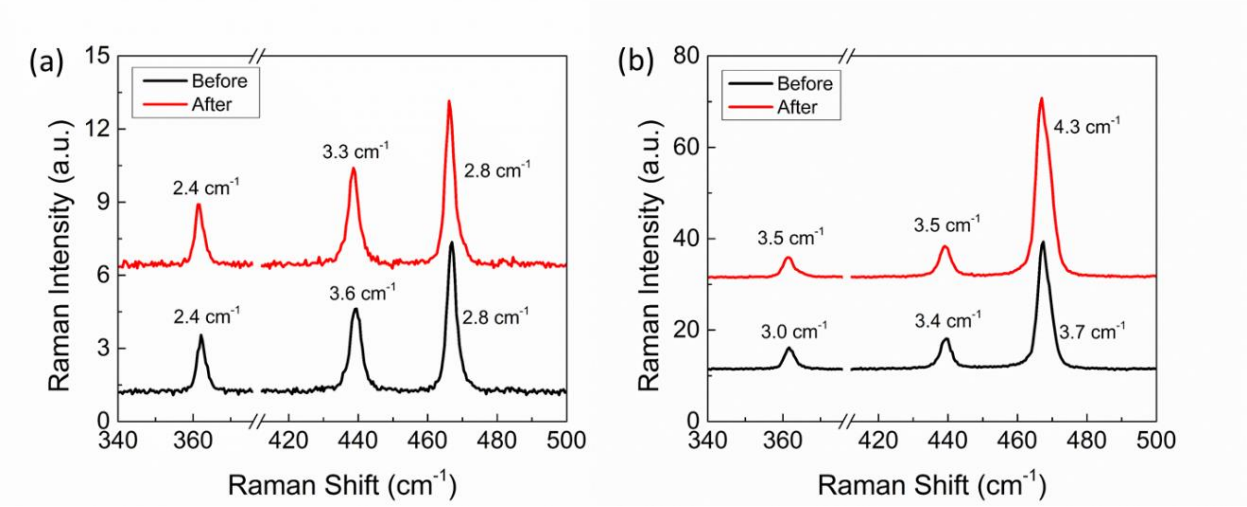

Figure S1. Raman spectra of (a) S1 and (b) S2 collected before and after temperature-dependent Raman measurements at room temperature.

Figure S2. Angle-resolved Raman spectroscopy.

Figure S2 shows the angle-dependent Raman measurements of the suspended BP film shown in Figure 3(a). The polarizations of the laser and the analyzer are at the same direction. With the rotation of the sample, it is able to collect the Raman signals as a function of polarization angle. Figs. S2(a)-(b) shows that the peak position does not change with varying angle. Figs. S2(c)-(e) give the polar plots of all the three Raman modes, which can help to determine the crystal orientation of the sample. In the measurements of laser power dependent Raman spectroscopy, based on the measured Raman spectrum we were able to estimate the angle between the laser polarization and the zigzag direction to be ~30 °, using the polar plot of A_g^2 mode.[1]

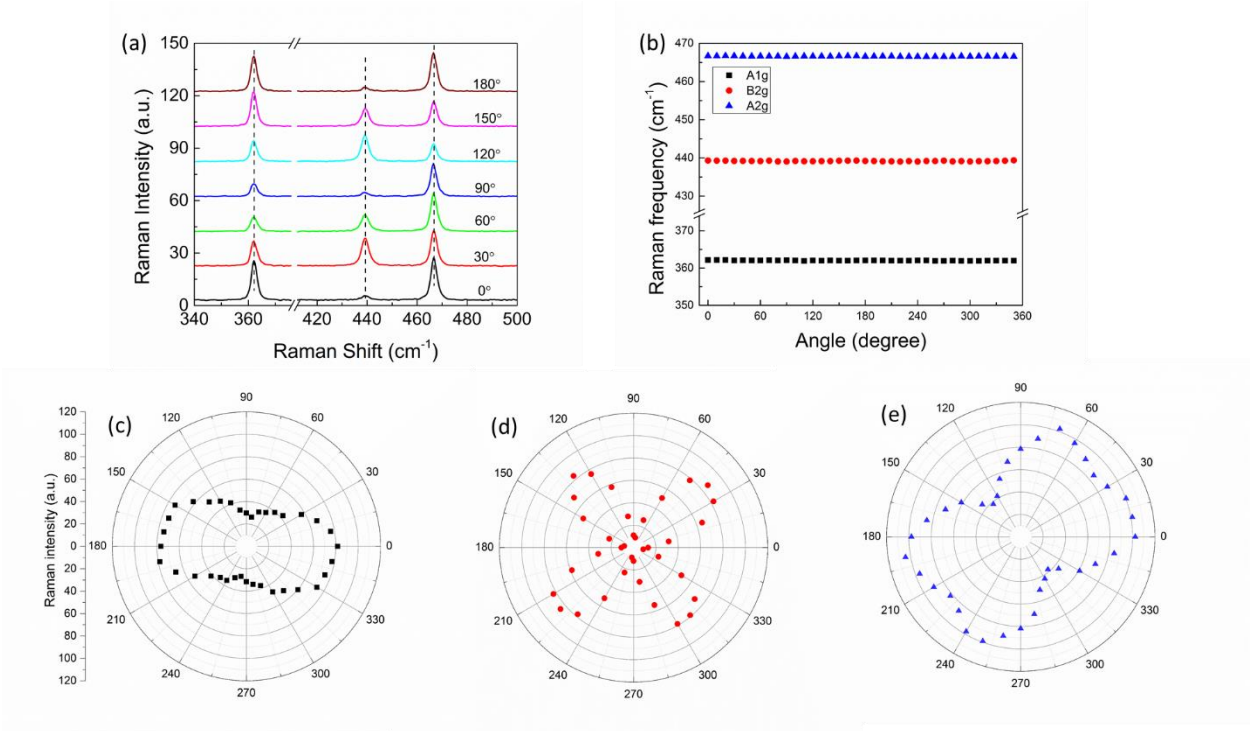

Figure S2. (a) Representative Raman spectra of suspended BP film at different polarization angles. (b) Peak positions of all the three Raman modes as a function of polarization angle. (c)-(e) Polar plots of Raman intensity for (c) A_g^1, (d) B_{2g}, and (e) A_g^2 modes, respectively.

References:

1. J. Wu, N. Mao, L. Xie, H. Xu, and J. Zhang, Angewandte Chemie International Edition **54** (8), 2366 (2015).