Supporting Information

for

Efficient liquid exfoliation of KP$_{15}$ nanowires aided by Hansen's empirical theory

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Strong temperature-dependent Raman response of exfoliated KP$_{15}$
The KP$_{15}$ nanowires with a defect-free surface and high carrier mobility are suitable for the development of novel electric nanodevices. The vibrational properties of KP$_{15}$ nanowires can play an important role in the electronic performance of nanodevices [1].

Here we found that exfoliated KP$_{15}$ nanowires had a strong temperature-dependent Raman response. Due to the resolution of the Raman system at a low-temperature mode, a KP$_{15}$ nanowire with a thickness of 80.9 nm and a width of 139.1 nm was chosen for the temperature-dependent Raman test (Figure S1a and Figure S1b). When the laser power values were 20 and 80 $\mu$W, respectively, the positions of those Raman peaks were the same (Figure S1c). This means that when the laser power was below 80 $\mu$W, the laser heating did not significantly increase the temperature of the KP$_{15}$ nanowires. Here, for low-temperature Raman measurements, the laser power was kept below 20 $\mu$W.

Figure S1d shows Raman spectra of the tested KP$_{15}$ nanowire under different temperatures. The space group of KP$_{15}$ is $\overline{P1}$, so all the Raman peaks in KP$_{15}$ are in the $A_g$ mode. There were seven Raman peaks with a high signal-to-noise ratio located at 90.6, 126.1, 354.2, 369.6, 378.7, 453.9, and 476.2 cm$^{-1}$. These peaks were named as No. 1, 4, 7, 8, 9, 11, and 12 Raman peaks for an easy identification in Figure S1d. As the temperature increased, all the Raman peaks of the liquid-exfoliated KP$_{15}$ nanowire shifted towards lower wave numbers (Figure S1). The vibration frequencies of those Raman peaks have a linear relationship with temperature (Figure S2). The peak position and temperature data can be fitted by the following Equation S1.

\[
\omega = \omega_0 + \chi T, \quad (S1)
\]

where $\omega_0$ is the vibration frequency of the corresponding Raman mode at absolute zero, $\chi$ is the first-order temperature coefficient of the Raman mode, and $\omega$ is the vibration frequency of the Raman mode at T [2]. The second-order term was not considered because it usually appeared at high temperature. The temperature evolutions of those Raman modes in the tested KP$_{15}$ are shown in Figure S2. For peak 1, $\chi_1=-0.00942$ cm$^{-1}$K$^{-1}$; for peak 4, $\chi_4=-0.01756$ cm$^{-1}$K$^{-1}$; for peak 7, $\chi_7=-0.02118$ cm$^{-1}$K$^{-1}$; for peak 8, $\chi_8=-0.02065$ cm$^{-1}$K$^{-1}$; for peak 9, $\chi_9=-0.01327$ cm$^{-1}$K$^{-1}$; for peak 11, $\chi_{11}=-0.01892$ cm$^{-1}$K$^{-1}$; and for peak 12, $\chi_{12}=-0.01724$ cm$^{-1}$K$^{-1}$. The highest temperature coefficient ($\chi_7=-0.02118$ cm$^{-1}$K$^{-1}$) in
KP$_{15}$ nanowire Raman modes is near to the highest value of black phosphorus ($-0.028$ cm$^{-1}$K$^{-1}$) and is higher than the highest value of MoS$_2$ ($-0.0132$ cm$^{-1}$K$^{-1}$) and graphene ($-0.016$ cm$^{-1}$K$^{-1}$) [2-4].

**Figure S1**: The size of the tested KP$_{15}$ nanowire and its Raman results at different temperatures. (a) Optical result of the tested KP$_{15}$ nanowire. (b) AFM result of the tested KP$_{15}$ nanowire marked in Figure S1a. (c) Raman results of the tested KP$_{15}$ nanowire marked in Figure S1a with different laser power values at room temperature. (d) Raman results of the tested KP$_{15}$ nanowire marked in Figure S1a at different temperatures.
Figure S2: The peak positions of the Raman peaks of the KP$_{15}$ nanowire at different temperatures. Temperature dependence of Raman peaks No. 1(a), 4(b), 7(c), 8(d), 9(e), 11(f), 12(g).

The frequency changes could be attributed to two reasons: the anharmonic coupling of phonons and phonon energy changes caused by thermal expansion of the lattice [4]. The measured frequency change $\Delta \omega$ can be written as:

$$\Delta \omega = (\chi_T + \chi_V) \Delta_T + \left(\frac{d\omega}{dT}\right)_V \Delta T + \left(\frac{d\omega}{dV}\right)_T \Delta V,$$

(S2)

where $\chi_T$ is the “self-energy” shift due to the direct coupling of the phonon modes and $\chi_V$ is the shift due to the thermal-expansion-induced volume change [5]. However, concrete contributions of “self-energy” and thermal expansion to the temperature coefficient in KP$_{15}$ still lack theoretical research. Due to the lower thermal expansion of KP$_{15}$ (4.84×10$^{-6}$K$^{-1}$) [6], the temperature coefficient of KP$_{15}$ nanowires is mainly due to the contribution of “self-energy” rather than to thermal expansion [4]. Therefore,
the strong temperature-dependent Raman response indicates a strong phonon–phonon coupling in KP$_{15}$ nanowires. This result may help with non-invasive temperature measurements of KP$_{15}$ nanodevices.

References


