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

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Abstract

The KP$_{15}$ nanowires with one-dimensional properties has a defect-free surface, high anisotropy, and carrier mobility which is desirable for the development of novel nanodevices. However, the preparation of nanoscale KP$_{15}$ is still inefficient. In this work, the Hansen solubility parameters of KP$_{15}$ were first obtained. Based on the Hansen's empirical theory, the concentration of liquid-exfoliated KP$_{15}$ nanowires was improved to 0.0458 mg·mL$^{-1}$ by a solution containing 50% water and 50% acetone. Approximately 79% of the KP$_{15}$ nanowires had a thickness value below 50 nm and 60.9% of them had a width value below 100 nm. The thinnest KP$_{15}$ nanowires reached 5.1 nm and had smooth boundaries. Meanwhile, strong temperature-dependent Raman response in exfoliated KP$_{15}$ nanowires has been observed, which indicates a strong phonon–phonon coupling in those nanowires. This is helpful for non-invasive temperature measurements of KP$_{15}$ nanodevices.

Introduction

Low-dimensional materials have drawn significant attention in recent years. So far, not only new composite materials with excellent properties have been obtained by the synthesis of different materials, but also low-dimensional materials with different properties than those of bulk materials have been synthesized by physical and chemical methods. For instance, Bingjun
Meanwhile, a strong temperature-dependent Raman response nanowires reached 5.1 nm and had smooth boundaries. 15 nanowires had width values below 100 nm. The thinnest KP wires had thickness values below 50 nm and 60.9% of these respectively improved. Our results show that 79% of the KP and 50% acetone, the exfoliation efficiency of KP were also obtained in this work. By using a solution containing 50% water phase exfoliation efficiency of KP. This theory has been successfully used for improving this method was still inefficient [13]. Herein, the Hansen’s empirical theory was firstly introduced to improve the liquid-phase exfoliation efficiency in several low-dimensional materials, [15-17]. This theory has been successfully used for improving the exfoliation efficiency in several low-dimensional materials, such as carbon, graphene, metal oxides, and fibrous phosphorus. [18].

In a previous study, we exfoliated KP in alcohol; however, this method was still inefficient [13]. Herein, the Hansen’s empirical theory was firstly introduced to improve the liquid-phase exfoliation efficiency of KP nanowires. In addition, Hansen solubility parameters (HSPs) for KP were also obtained in this work. By using a solution containing 50% water and 50% acetone, the exfoliation efficiency of KP was effectively improved. Our results show that 79% of the KP nanowires had thickness values below 50 nm and 60.9% of these nanowires had width values below 100 nm. The thinnest KP nanowires reached 5.1 nm and had smooth boundaries. Meanwhile, a strong temperature-dependent Raman response was found in exfoliated KP nanowires. This indicates a strong phonon–phonon coupling in KP nanowires, which favors non-invasive temperature measurements of KP nanodevices.

Methods
Synthesis of KP bulks
The KP bulks were prepared by the gas-phase transfer method. High-purity red phosphorus (1.37 g, 99.9999%) and metallic potassium (0.130 g, 97%) were mixed in a quartz tube. The temperature gradient in the quartz tube was 650 °C/400 °C and the heat treatment time was 12 h. After annealed, dark-red KP bulks were finally obtained.

Liquid exfoliation
For the liquid-exfoliation process, 1 mg of KP was mixed in 20 mL of solvent and ultrasonically processed at a power of 80 W in an ice bath for 6 h, followed by centrifugation at 2000 rpm for 20 min. For the samples with predetermined concentration, centrifugation was not used.

Measurement equipment
UV–visible spectrophotometry was performed by using a Shimadzu UV-3101PC system. Atomic force microscopy (AFM) tests were performed in a Multimode 8 system. The Raman tests were performed on a WITec alpha300 RA confocal Raman microscopy system. For the Raman tests, KP samples were spun on SiO(2)(300 nm)/Si substrates. The excitation wavelength used was 532 nm, the spot size was approx. 1 μm, and the laser power was kept below 20 μW. For low-temperature Raman measurements, a Linkam THMS600 cryostat cooled by liquid nitrogen was used to control the temperature. To prevent sample drift, SiO(2) (300 nm)/Si substrates with tested KP samples were attached by fixtures to the Linkam THMS600 cryostat.

Results and Discussion
KP bulks, prepared by the gas-phase-transfer method, had a flat and smooth surface shown in Figure 1a. The X-ray diffraction patterns of the synthesized KP were both theoretically calculated and experimentally measured. The consistency between the two patterns shows that there is no impurity phase (Figure 1b), which confirms an excellent crystallization quality of the KP bulks.

Measurement of the absorption coefficient and the Hansen solubility parameters for KP
According to the Hansen’s theory [19], the dispersed concentration C of a KP dispersion prepared by liquid exfoliation can be expressed by Equation 1 as follows.
δ_D is the intermolecular dispersion force, δ_H is the intermolecular hydrogen bond; δ_P is the intermolecular polar force; δ_{A,D}, δ_{A,P}, δ_{A,H} are the Hansen solubility parameters (HSPs) of the solute; and δ_{B,D}, δ_{B,P}, δ_{B,H} are the HSPs of the solvent. Therefore, to get a high concentration of KP_{15} in dispersion, the HSPs of the solvent for the exfoliation of KP_{15} should be close to those of KP_{15}. A weighted average method was used to calculate the HSPs of KP_{15}. The concentration of KP_{15} was used as a weight factor for each suspension. This way, the HSPs of KP_{15} can be expressed according to Equation 2 [19].

\[
\frac{1}{C} \propto \frac{\delta_{A,D} \delta_{B,D}}{\delta_{A,D} + 2 \delta_{B,D}} \left( \frac{\delta_{A,P} \delta_{B,P}}{4 \delta_{A,P} + \delta_{B,P}} + \frac{\delta_{A,H} \delta_{B,H}}{4 \delta_{A,H} + \delta_{B,H}} \right),
\]

(1)

where δ_{j,sol} are the HSPs of the solvent and C is the concentration of the KP_{15} dispersions. The Lambert–Beer law (Equation 3) was then used to measure the concentration of the KP_{15} dispersions:

\[
A = KCbC,
\]

(3)

where A is the absorbance, K is the absorption coefficient of the material, b is the absorbing layer thickness (which in this work is the width of the cuvette, i.e., 1 cm), and C is the concentration of the KP_{15} dispersions. The absorbance A and the absorption coefficient K are related to the wavelength of the incident light. To determine A and K, it is necessary to choose a specific incident wavelength. The bandgap of bulk KP_{15} is approx. 1.75 eV [20]. However, according to our previous study, with thickness reduction of the KP_{15} nanowires, a surface-state luminescence at 693 nm gradually dominates in the KP_{15} nanowire [14]. This could affect light absorption properties of KP_{15} due to its decreased size.

To avoid the generation of concentration error caused by the absorbance influence of the surface state, a wavelength (800 nm) which is far away from the bandgap of KP_{15} bulk and surface state in the KP_{15} nanowires was chosen. Some dispersions for which we predetermined the concentration were prepared to fit and determine the absorption coefficient K. Solutions of five different concentrations of KP_{15} dispersions in butyrolactone were prepared by liquid exfoliation with a predetermined concentration. UV–visible absorption spectra results are shown in Figure 2. The concentration linearly varies with absorbance. The slope of this fitted linear equation is 3.86 ± 0.13. This means that the absorption coefficient of KP_{15} is 3.86 ± 0.13 mL·mg^{-1}·cm^{-1}.

We selected 20 common solvents, including benzyl benzoate, toluene, ethyl acetate, acetone, alcohol, butyrolactone, N,N'-dimethylpropyleneurea, bromobenzene, cyclopentanone, N-dodecyl-2-pyrrlidone, glycol, vinyl acetate, hexane, isopropyl alcohol, N,N-dimethylformamide, O-phthalic dimethyl ester, dimethyl sulfoxide, N-methylpyrrlidone, water, and cyclohexanone. The HSPs of those solvents are listed in Table 1.

Figure 3 exhibits the concentrations of KP_{15} dispersions exfoliated in different solvents. Cyclopentanone and butyrolactone were more suitable than the other solvents to exfoliate KP_{15}. Figure 4 shows the relationship between the HSPs of different solvents and the concentration of the KP_{15} suspension. Based on Equation 2, the HSPs of KP_{15} were δ_D = 17.60 MPa^{1/2},
Figure 2: Absorbance of predetermined KP$_{15}$ dispersions exfoliated in butyrolactone. (a) Absorbance of different concentrations of predetermined KP$_{15}$ dispersions exfoliated in butyrolactone. (b) Absorbance (800 nm) as a function of concentration of predetermined KP$_{15}$ dispersions. The absorption coefficient (800 nm) is 3.86 ± 0.13 mL·mg$^{-1}$·cm$^{-1}$.

Table 1: Hansen parameters for the solvents [21].

| solvent                        | δ$_D$ (MPa$^{1/2}$) | δ$_P$ (MPa$^{1/2}$) | δ$_H$ (MPa$^{1/2}$) |
|-------------------------------|---------------------|---------------------|---------------------|
| benzyl benzoate               | 20                  | 5.1                 | 5.2                 |
| toluene                       | 18                  | 1.4                 | 2                   |
| ethyl acetate                 | 15.8                | 5.3                 | 7.2                 |
| acetone                       | 15.5                | 10.4                | 7                   |
| alcohol                       | 18.1                | 17.1                | 16.9                |
| butyrolactone                 | 18                  | 16.6                | 7.4                 |
| N,N’-dimethylpropyleneurea    | 17.8                | 9.5                 | 9.3                 |
| bromobenzene                  | 19.2                | 5.5                 | 4.1                 |
| cyclopentanone                | 17.9                | 11.9                | 5.2                 |
| N-dodecyl-2-pyrrolidone       | 17.5                | 4.1                 | 3.2                 |
| glycol                        | 17                  | 11                  | 26                  |
| vinyl acetate                 | 16                  | 7.2                 | 5.9                 |
| hexane                        | 14.9                | 0                   | 0                   |
| isopropyl alcohol             | 15.8                | 6.1                 | 16.4                |
| N,N-dimethylformamide         | 17.4                | 13.7                | 11.3                |
| O-phthalic dimethyl ester     | 18.6                | 10.8                | 4.9                 |
| dimethyl sulfoxide            | 18.4                | 16.4                | 10.2                |
| N-methylpyrrolidone           | 18                  | 12.3                | 7.2                 |
| water                         | 15.8                | 8.8                 | 19.4                |
| cyclohexanone                 | 17.8                | 8.4                 | 5.1                 |

δ$_P$ = 11.19 MPa$^{1/2}$, and δ$_H$ = 8.95 MPa$^{1/2}$. As long as the difference between the HSPs of KP$_{15}$ and the HSPs of a given solvent is reduced, $\tau$ can be reduced with an improved exfoliation efficiency. Figure 5 shows the concentration of KP$_{15}$ dispersions as a function of $\tau$. When $\tau$ tends to zero, the concentration of the KP$_{15}$ dispersion reaches the maximum value, which corresponds to the results of the aforementioned equation.

Liquid exfoliation of one-dimensional KP$_{15}$

The HSPs obtained for KP$_{15}$ were $\delta_D = 17.60$ MPa$^{1/2}$, $\delta_P = 11.19$ MPa$^{1/2}$, and $\delta_H = 8.95$ MPa$^{1/2}$. We chose a mixed solution containing water and acetone to exfoliate KP$_{15}$. The HSPs of water were $\delta_D = 15.8$ MPa$^{1/2}$, $\delta_P = 8.8$ MPa$^{1/2}$, and $\delta_H = 19.4$ MPa$^{1/2}$. The HSPs of acetone were $\delta_D = 15.5$ MPa$^{1/2}$, $\delta_P = 10.4$ MPa$^{1/2}$, and $\delta_H = 7.0$ MPa$^{1/2}$. The HSP range of a mixed solution of water and acetone can cover the HSPs of KP$_{15}$, however, both of them can be easily removed. The HSPs ($\delta_i$) in a mixed solution containing water and acetone can be expressed by Equation 4.

$$\delta_i = \sum \delta_{i,\text{comp}} \delta_{i,\text{comp}}, \quad (4)$$
where $\phi_{i,\text{comp}}$ is the volume fraction of the corresponding solvent and $\delta_{i,\text{comp}}$ is the HSPs of the solvent. The concentration of the KP$_{15}$ dispersion can be measured by the Lambert–Beer law (Equation 3). As shown in Figure 6a, by tuning the volume fraction of acetone in the mixed solution, the HSPs of the mixed solution can be close to those of KP$_{15}$, and the exfoliation efficiency can be clearly improved. The concentration values of the KP$_{15}$ suspension in the solutions were 0.0268 mg·mL$^{-1}$ (exfoliated in deionized water), 0.0079 mg·mL$^{-1}$ (acetone), and 0.0236 mg·mL$^{-1}$ (alcohol), respectively [13]. When the solvent mixture with a 50% volume fraction of acetone is used for stripping, the concentration of the KP$_{15}$ dispersion finally increases to 0.0458 mg·mL$^{-1}$. At this point, the parameter $\tau$ is close to the minimum value.

The Raman result for the KP$_{15}$ nanowires exfoliated in water–acetone mixed solution is shown in Figure 7c. At least 11 distinguishable Raman peaks located at 476.6, 453.0, 408.8, 378.3, 368.4, 354.1, 303.7, 288.5, 126.1, 114.1, and 90.7 cm$^{-1}$ were seen and those Raman results were similar to the Raman modes of mechanically exfoliated KP$_{15}$ [11]. As shown in Figure 7d, Figure 7e, and Figure 8, the thinnest KP$_{15}$ nanowires obtained by liquid exfoliation could reach 5.1 nm and had smooth boundaries. The thicknesses of 79% of the liquid-exfoli-

**Figure 3:** UV–visible spectrum of the KP$_{15}$ dispersions using various solvents.

**Figure 4:** Concentration of KP$_{15}$ dispersions as a function of the Hansen parameters. (a) Concentration of KP$_{15}$ dispersions as a function of $\delta_C$. (b) Concentration of KP$_{15}$ dispersions as a function of $\delta_P$. (c) Concentration of KP$_{15}$ dispersions as a function of $\delta_H$. 

**Figure 5:** Concentration of KP$_{15}$ dispersions as a function of $\tau$, $\tau = (\delta_{A,D} - \delta_{B,D})^2/4 + (\delta_{A,P} - \delta_{B,P})^2/4 + (\delta_{A,H} - \delta_{B,H})^2/4$.

**Figure 5:** Concentration of KP$_{15}$ dispersions as a function of $\tau$, $\tau = (\delta_{A,D} - \delta_{B,D})^2/4 + (\delta_{A,P} - \delta_{B,P})^2/4 + (\delta_{A,H} - \delta_{B,H})^2/4$. 

**Figure 6:** (a) Concentration of KP$_{15}$ dispersions as a function of $\delta_C$. (b) Concentration of KP$_{15}$ dispersions as a function of $\delta_P$. (c) Concentration of KP$_{15}$ dispersions as a function of $\delta_H$. 

**Figure 6:** (a) Concentration of KP$_{15}$ dispersions as a function of $\delta_C$. (b) Concentration of KP$_{15}$ dispersions as a function of $\delta_P$. (c) Concentration of KP$_{15}$ dispersions as a function of $\delta_H$. 

**Figure 7:** (c) Raman spectrum of the KP$_{15}$ nanowires exfoliated in water–acetone mixed solution. At least 11 distinguishable Raman peaks located at 476.6, 453.0, 408.8, 378.3, 368.4, 354.1, 303.7, 288.5, 126.1, 114.1, and 90.7 cm$^{-1}$ were seen and those Raman results were similar to the Raman modes of mechanically exfoliated KP$_{15}$ [11]. As shown in Figure 7d, Figure 7e, and Figure 8, the thinnest KP$_{15}$ nanowires obtained by liquid exfoliation could reach 5.1 nm and had smooth boundaries. The thicknesses of 79% of the liquid-exfoli-
Figure 6: Results of KP\textsubscript{15} dispersions exfoliated in acetone/water mixtures. (a) Absorbance of KP\textsubscript{15} dispersions exfoliated in acetone/water mixtures with different acetone volume fractions. (b) KP\textsubscript{15} suspension concentration and the calculated $\tau$ as a function of the acetone volume fraction.

Figure 7: (a) Height distribution of KP\textsubscript{15} nanowires after liquid exfoliation. (b) Cross sections of KP\textsubscript{15} nanowires after liquid exfoliation. (c) Raman spectra of KP\textsubscript{15} nanowires after liquid exfoliation. (d) Thickness histograms of KP\textsubscript{15} nanowires after liquid exfoliation. (e) Width histograms of KP\textsubscript{15} nanowires after liquid exfoliation.

ated KP\textsubscript{15} nanowires were below 50 nm; the widths of 60.9\% of the KP\textsubscript{15} nanowires were below 100 nm. The sizes of the obtained KP\textsubscript{15} nanowires were much smaller than those obtained in our previous studies [13]. Meanwhile, a strong temperature-dependent Raman response in exfoliated KP\textsubscript{15} nanowires has been observed. That may help with non-invasive temperature measurements of KP\textsubscript{15} nanodevices (details are demonstrated in Supporting Information File 1).

Conclusion

In summary, based on the Hansen's empirical theory, the liquid phase exfoliation efficiency of KP\textsubscript{15} nanowires has been improved. The HSPs of KP\textsubscript{15} were calculated to be $\delta_D = 17.60$ MPa$^{1/2}$, $\delta_P = 11.19$ MPa$^{1/2}$, and $\delta_H = 8.95$ MPa$^{1/2}$. In addition, based on the Hansen's empirical theory, the exfoliation efficiency was improved by adjusting the ratio of water and acetone. When the mixed solvents had the smallest $\tau$, the thick-
Figure 8: Sizes of exfoliated KP$_{15}$ nanowires. (a) Cross section of the KP$_{15}$ nanowire marked in the upper right corner inset image. (b) Cross section of the KP$_{15}$ nanowire marked in the upper right corner inset image. (c) Cross section of the KP$_{15}$ nanowire marked in the upper right corner inset image. (d) Cross section of the KP$_{15}$ nanowire marked in the upper right corner inset image.

Supporting Information

Supporting Information File 1
Strong temperature-dependent Raman response of exfoliated KP$_{15}$.
[https://www.beilstein-journals.org/bjnano/content/supplementary/2190-4286-13-69-S1.pdf]

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