Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information

Electromechanical behaviour of Violet Phosphorene Nanoflakes

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1. Raman spectra of vP nanoflakes

The Raman (633 nm) spectrum of the sample in the red box area in Fig. S1a is shown in Fig S1b.

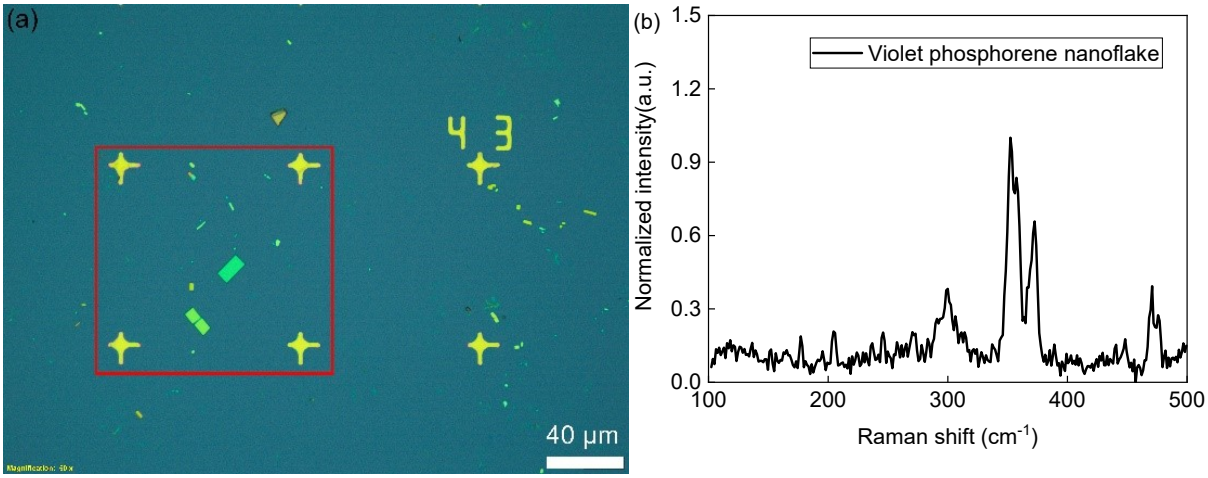

Fig S1. Raman characterization of vP nanoflakes. (a) Microscope image of vP nanoflakes. (b) Raman spectrum of vP nanoflakes.

2. The vP conductivity based on density functional theory

The resistivity was obtained by calculating the conductivity values, which is the reciprocal of resistivity. The BoltzTraP[1] code was employed to calculate the electrical conductivity values. A cutoff energy of 620 eV and a dense Γ-centered k-point mesh of 20x20x8 was utilized, which was considered suitable for the use of the strongly constrained and appropriately normed semilocal density functional[2] with revised Vydrov-van Voorhis nonlocal correlation functional[3] (SCAN-rVV10) within VASP. The calculated conductivity represents a theoretical maximum and that the scattering processes were treated using the relaxation time approximation. The result is shown

in Fig. S2. The carrier concentration of intrinsic vP was demonstrated to be in the range of 10^{15}~10^{16} cm^{-3}.[4, 5] Therefore, the vP conductivity was deduced to be 1.5 $S \cdot m^{-1}$ at room temperature (300 K).

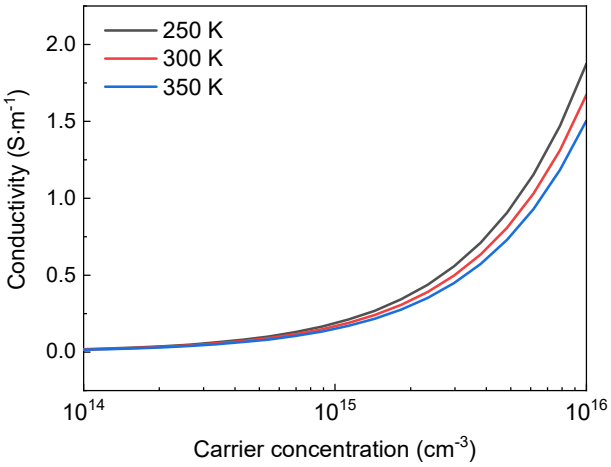

Fig S2. Theoretical analysis of the relationship between the vP conductivity and carrier concentration under different temperature.

3. The vP specific heat capacity based on density functional theory

The calculation of vP's thermal properties at a constant volume was accomplished by analyzing their phonon density of states relative to their frequencies. Phonon properties were determined via Phonopy code,[6] utilizing the finite displacement method on 2x2x1 supercells generated from the optimized structure consisting of 336 atoms. The optimized structure underwent minimization using PBE-D3 with a force convergence criterion of 2x10-3 eV $Å^{-1}$, and the electronic wavefunction converged to $4x10^{-7}$ eV. The harmonic phonon energy (E) was determined by the following equation:

$$E = \sum_{qv} \hbar\omega(qv)[\frac{1}{2} + \frac{1}{exp(\hbar\omega(qv)/k_B T) - 1}] \quad (1)$$

where q and v represent the wave vector and band index, respectively. $\omega(q,v)$ denotes the phonon frequency at q and v, while T signifies the temperature. k_B is Boltzmann constant and $\hbar$ is Planck constant.

The heat capacity at constant volume (C_V) was calculated by:

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V \quad (2)$$

The capacitance of vP nanoflakes was calculated to be about 1750 $J \cdot K^{-1} mol^{-1}$ at room temperature (300 K), as shown in Fig. S3.

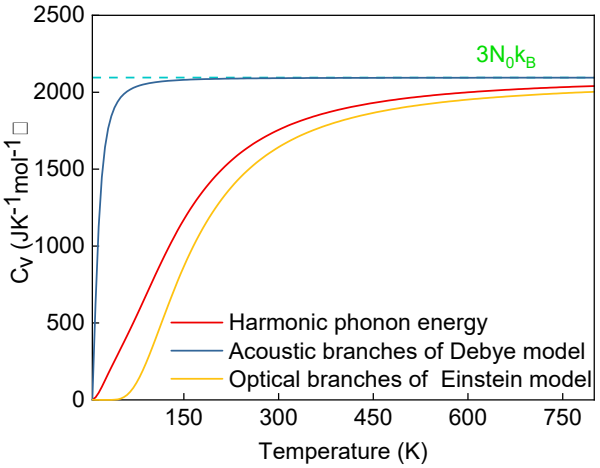

Fig S3. Theoretical analysis of vP capacitance variation curve with temperature.

4. Measurement of thermal conductivity by Raman spectroscopy

Red shift was observed by Raman characteristic peak when vP nanoflakes were irradiated by laser (Fig. S4 a & b). The laser irradiation was assumed to only affect the temperature of the micro-region of 2D material but not the temperature of substrate since the laser irradiation area is very small (1 micron in diameter).[7, 8] Assuming that there is a stable and uniform heat conduction from the 2D material to the substrate, the heat conduction equation is expressed as[9]:

$$\frac{\partial Q}{\partial t} = -k \oint \nabla T \cdot dA \tag{3}$$

where *k* is the thermal conductivity of the material, *A* is the cross-sectional area of heat conduction, *T* is the absolute temperature and *Q* is the heat transferred. Considering the effect of thermal radiation, the equation of thermal conductivity of few-layer vP is described as:

$$k = \frac{1}{2\pi h} \cdot \frac{\Delta P}{\Delta T} \tag{4}$$

where *ΔP* is the change in power, *ΔT* is the change in temperature, and *h* is the thickness of the material. Through the Fig S4c and Fig S4d, the variation law of the vP Raman characteristic peaks with temperature and power was then obtained respectively:

$$\omega(T) = \omega_0 + \chi_T \Delta T \tag{5}$$

$$\omega(P) = \omega_0 + \chi_P \Delta P \tag{6}$$

$\frac{\Delta P}{\Delta T}$ can be obtained by differentiating the power *P*. Substituting $\frac{\Delta P}{\Delta T}$ into Eq (4) results in:

$$k = \left(\frac{1}{2\pi h}\right) \cdot \left(\frac{\chi_T}{\chi_P}\right) \tag{7}$$

The thermal conductivity of the vP nanoflakes was then calculated by combining Eq (5), Eq (6) and Eq (7) to be 47.3±4.6 $W \cdot m^{-1}K^{-1}$, which is close to the thermal conductivity of few-layer MoS_2.[10]

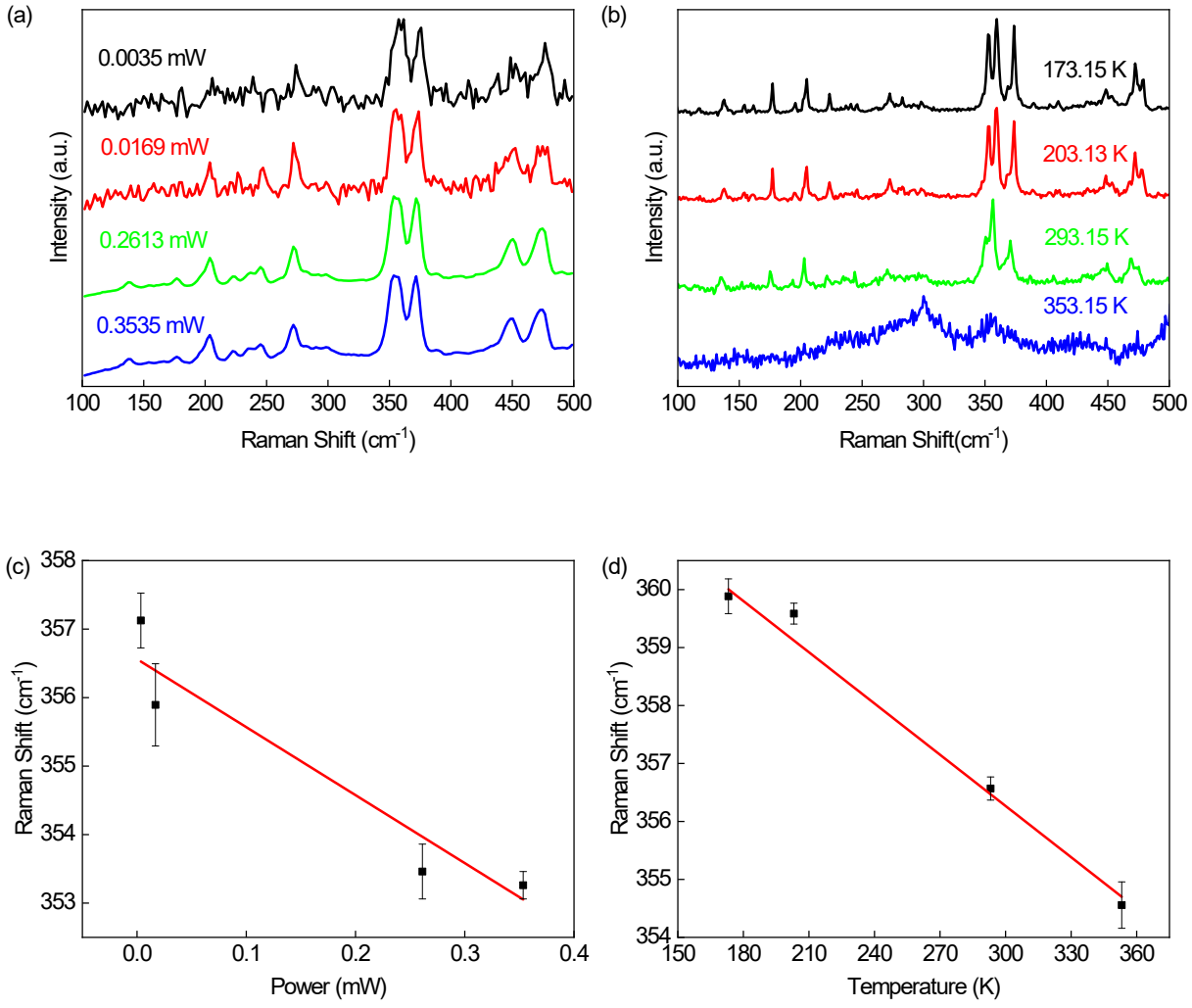

Fig S4. Raman spectra of vP nanoflakes under different power laser irradiation and temperature. (a) Raman spectra of vP nanoflakes at laser irradiation with different power. (b) Raman spectra of vP nanoflakes at different temperature. (c) Variation of vP nanoflakes characteristic peaks with power. (d) Variation of vP nanoflakes characteristic peaks with temperature.

5. SThM characterize thermal conductivity of vP nanoflakes

The 2D materials thermal conductivity was studied by scanning thermal microscopy (SThM), as shown in Fig. S5. The probe model is VITA-DM-GLA-1. The signal value of the characterization is negatively correlated with the thermal conductivity. The smaller the signal value is, the higher the thermal conductivity is.[11-13] The signals of MoS_2 nanoflakes, black phosphorene nanoflakes, vP nanoflakes, and graphene were demonstrated to be 91 mV, 51 mV, 16 mV and -21 mV, respectively. This indicates that vP nanoflakes has good thermal conductivity, although not as good as graphene nanoflakes.

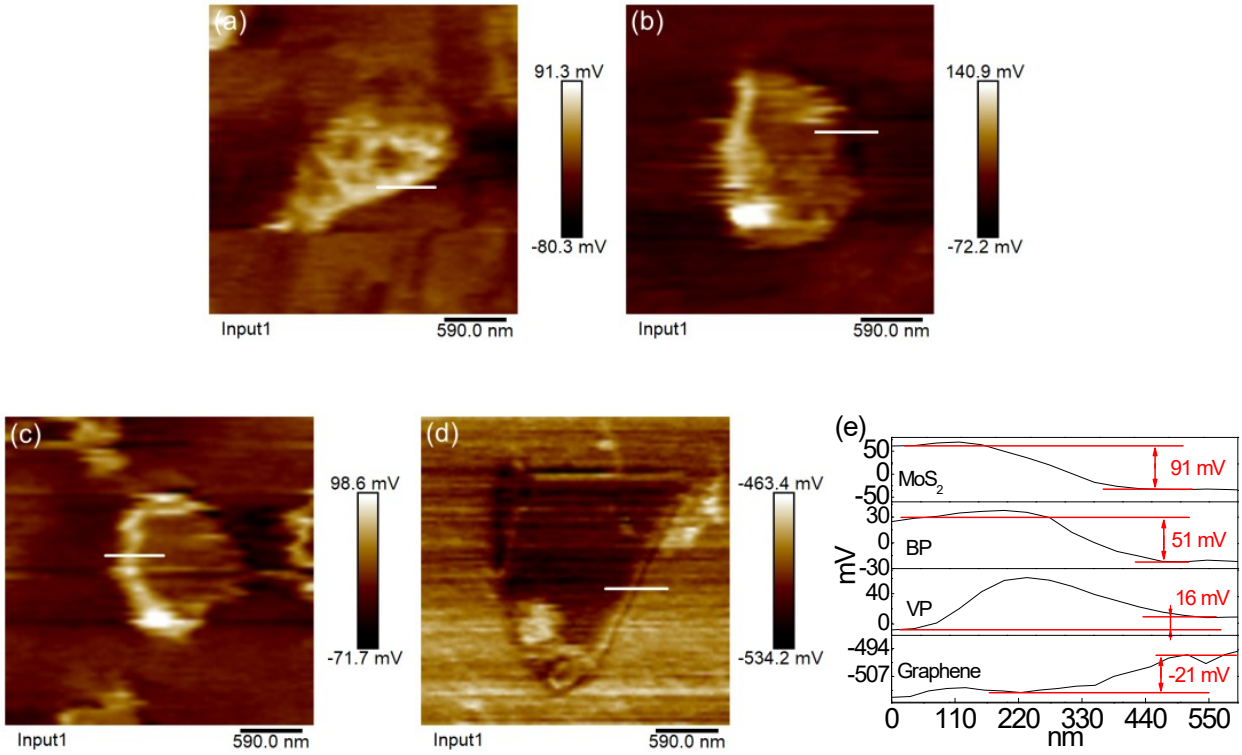

Fig S5. SThM thermal conductivity signal diagram. (a) MoS_2 nanoflakes. (b) Black phosphorene nanoflakes. (c) vP nanoflakes. (d) Graphene nanoflakes. (e) Cross-sectional height of the white line in fig S5a, b, c and d.

6. Raman spectra of vP nanoflakes in the nanoindentation region

The Raman (633 nm) spectrum of vP and the sample in the nanoindentation region (Oxidized).

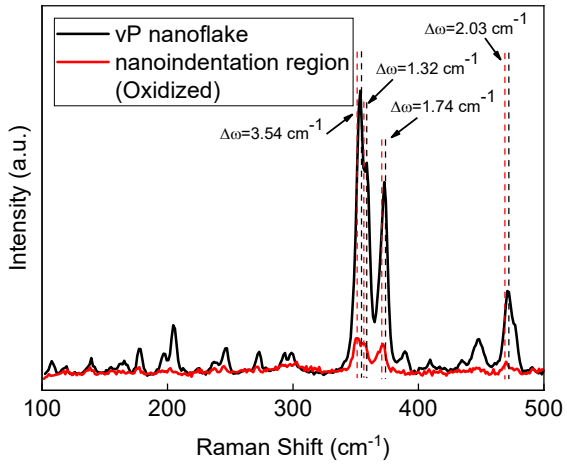

Fig S6. Raman characterization of vP and the vP in the nanoindentation region.

Notes and references

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