High yield production of ultrathin fibroid semiconducting nanowire of Ta$_2$Pd$_3$Se$_8$

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ABSTRACT

Immediately after the demonstration of the high-quality electronic properties in various two dimensional (2D) van der Waals (vdW) crystals fabricated with mechanical exfoliation, many methods have been reported to explore and control large scale fabrications. Comparing with recent advancements in fabricating 2D atomic layered crystals, large scale production of one dimensional (1D) nanowires with thickness approaching molecular or atomic level still remains stagnant. Here, we demonstrate the high yield production of a 1D vdW material, semiconducting Ta$_2$Pd$_3$Se$_8$ nanowires, by means of liquid-phase exfoliation. The thinnest nanowire we have readily achieved is around 1 nm, corresponding to a bundle of one or two molecular ribbons. Transmission electron microscopy (TEM) and transport measurements reveal the as-fabricated Ta$_2$Pd$_3$Se$_8$ nanowires exhibit unexpected high crystallinity and chemical stability. Our low-frequency Raman spectroscopy reveals clear evidence of the existing of weak inter-ribbon bindings. The fabricated nanowire transistors exhibit high switching performance and promising applications for photodetectors.

KEYWORDS

van der Waals nanowire, 1D semiconductor, liquid exfoliation, micro Raman spectroscopy, electronic and optoelectronic device

1 Introduction

Van der Waals (vdW) two dimensional (2D) materials, such as graphene [1–3], hexagonal boron nitride (h-BN) [4], transition metal dichalcogenides (TMDCs) [5–9] and black phosphorus [10] have attracted enormous research attention due to their extraordinary properties after thinning down to atomic level. Such high-quality mono or a-few-layer can be achieved with simple mechanical exfoliation, in which adhesive tape is used to effectively separate layers that are originally bonded by weak vdW interactions [1, 3]. The high crystalline films enable comprehensive studies of their novel quantum phenomena. Hidden behind the success of achieving these well preserved 2D film material is the critical role of van der Waals bond, weakly holding the layers together, but also chemically insert enough acting as a protective barrier to prevent degradation caused by the surface reaction. Moreover, the idea of mechanical exfoliation of 2D vdW material can be extended to one dimensional (1D) fibroid crystals, which consist of unit 1D molecular ribbons parallel bonded by vdW forces [11–17]. This presents a new path of fabricating TMDC nanoribbons and avoids the edge problems faced by traditional methods [18–21], in which nanoribbons are directly cut out from the 2D TMDC layers. Indeed, mechanical exfoliation has been successfully applied to exfoliate the vdW fibroid bulk crystal-Ta$_2$Pd$_3$Se$_8$ (TPdS), which can be viewed as an assembly of parallel running zigzag molecular ribbon (also we called it chain in the text below) [11] with edges terminated by Pd atoms and bonded together with interchain vdW bonding. Nanowires composed of a few TPdS molecular chains as thick as a few nanometers have been achieved, demonstrating the feasibility of easy access to ultrathin high-quality 1D nanowires for studying their intrinsic properties as well as potential applications.

However, mechanical exfoliation method is limited only in small laboratory experiments due to the extremely low productivity. To produce large quantities or scales of nanostructures for more practical applications, researchers have made efforts to discover alternative methods. One typical technique, known as liquid-phase exfoliation (LPE), has been proposed to break vdW bonding by utilizing ultra-sonication assisted by chemical solvents. It has been demonstrated to be a
scalable and effective method producing a large number of vdW nano-flakes from their bulk counterpart as mentioned [22–29], and carbon nanotubes from its bundles [30–33]. More interestingly, vdW interactions are widely existing not only in 2D vdW crystals but also in fibroid 1D/quasi-1D vdW crystal systems. Broad fabrication of 1D nanowires is expected to be realized by extending these exfoliation methods from 2D to 1D vdW crystal systems.

Here we report on our LPE study of single-crystal 1D semiconducting TPdS fibroid nanowires. In particular, we find that by using the LPE method ultrathin TPdS nanowires as thin as 1 to 4 nm can be efficiently produced. Our comprehensive studies through low-frequency Raman spectroscopy and high-resolution scanning transmission electron microscopy (STEM) demonstrate highly preserved crystal quality and weak inter-ribbon bindings. Then, the 1D nanowire transistors fabricated from liquid exfoliated TPdS show promising potential in electrical switching applications, and a photothermal dominated photoresponse mechanism has also been revealed. Our work demonstrates a successful large-quantity fabrication of ultra-thin fibroid nanowires through a simple and clean technique. At this early stage, although our semiconducting TPdS nanowires exhibit relative low mobility when compared to up-to-date record best carbon nanotubes [34–37] and silicon nanowires [38, 39], our fabrication method avoids the complexity caused by selection, separation, and protection problems remaining in current 1D system studies [40]. Besides, our STEM and transport results simultaneously indicate the outstanding stability of TPdS nanostructures even down to the nanometer scale, which is crucial for next-generation modern electronics.

2 Results and discussion

2.1 Exfoliations and basic characterizations

Ta:Pd:Se belongs to the isostructure group of ternary chalcogenides M₂X₃Y₈ (M = Ta, Nb; X = Ni, Pd, Pt; Y = S, Se), which has a linear crystal structure with bonding strengths differ near 20 times between and within unit “ribbons” (the smallest repeating unit in crystal structure) as highlighted by the dashed rectangular in Fig. 1(a) [11]. For each ribbon, it contains two chains of edge-sharing Se trigonal prisms centered by Ta atoms and bridged by Pd atoms. The chains are further capped by additional Pd atoms at the two sides. The lateral dimension of one unit ribbon is 1.0 nm × 0.4 nm. The ribbons are interconnected via weak bindings between terminated-Pd (trans-Se) atoms and trans-Se (terminated-Pd) atoms with neighboring ribbons, forming a windmill shape framework extending along c-axis. From the crystal structure, we believe that the existence of isotropic vdW bonds in TPdS crystal is crucial for successful isolation of ultrathin nanostructures or even single molecular chain out from the bulk counterparts. In the LPE process, a powerful sonication is applied to effectively break the inter-ribbon interactions so as to obtain separated thin nanowires, as illustrated by Fig. 1(b). To process the exfoliation, we surveyed different solvents including isopropyl alcohol (IPA), N-methyl-2-pyrrolidone (NMP), chloroform, etc. (see Fig. S1 and Table S1 in the Electronic Supplementary Material (ESM)). The bulk TPdS crystal of 0.5 mg was immersed into different solvents (20 mL) and then ultra-sonicated for 4 hours at 50 °C with a total input power of 0.6 MJ. After analyzing the exfoliation results, we note that NMP and IPA were the most appropriate solvents resulting in TPdS nanowires dispersions as shown in Fig. 1(c), and NMP mixture was more stable without significant reaggregation after a few hours. The different exfoliation processes are supposed to be closely related to their surface tension and corresponded dispersive and polar components matching with our TPdS nanowires [41]. We suggest the NMP with a surface tension of 40.79 mJ·m⁻² and polar component/dispersive component ratio of ~ 0.4 match better with the TPdS nanowires (see Note S1 in the ESM). The sonicated mixtures were then centrifuged at 500 rpm for 1 h, the sediment was weighted as ~ 21 wt.% of the initial bulk material, and the supernatants were collected as the resultant liquids indicated by Fig. 1(d). We performed further characterizations based on deposited nanowires on substrate (SiO₂/Si wafer), referred to as on-chip sample (see Methods). Figures 1(e) and 1(f) show the as-prepared samples (NMP solvent) under scanning electron microscopy (SEM) before and after centrifugation, respectively. Before centrifugation, the TPdS nanowires were densely overlapped on the wafer. After centrifugation, individual nanowires with random orientations can be easily found.

From our observation, there is no significant un-separated or aggregated big chunk of crystals after exfoliations. This indicates that the bulk TPdS has been extensively separated and become nanowires with certain thickness and length distributions. Then, we systematically investigated the thickness and length distributions of the nanowires produced by IPA and NMP solvents using atomic force microscopy (AFM). As shown in Figs. 2(a) and 2(b), a variable range of thicknesses and lengths of TPdS nanowires are demonstrated by the AFM images of randomly selected areas from IPA and NMP samples, respectively. Zoom-in views of 5 µm × 2.5 µm squares indicate TPdS nanowires as thin as 1.4 nm can be readily achieved. It is worth noting that the thinnest nanowire observed from our AFM is ~ 1 nm (Fig. S4 in the ESM), which should correspond to nanostructures consisting of 1–2 unit molecular chains as compared with the simulation (see Fig. S3 in the ESM). To better compare the results, the contour plots of the histograms of the nanowire thickness and length distributions, as obtained from 400 individual nanowires, are shown in Figs. 2(c) and 2(d) for IPA and NMP exfoliations, respectively. Both of the IPA and NMP exfoliated nanowires have thicknesses that are most distributed (> 90% number fraction) below 10 nm, while the NMP exfoliation yields slightly thinner and shorter nanowires
in average, for which we can achieve ~ 45.57% nanowires below 4 nm. We also estimated the mass fractions of different thicknesses after centrifugation (see Methods). The mass fraction for nanowires below 10 nm is 48.3 wt.%, and 4.8 wt.% for nanowires below 4 nm. Thus the total yield from the initial material can be estimated as 38.2% for nanowires below 10 nm and 3.8% below 4 nm. Our following discussions are all based on NMP prepared sample. We would like to note that for low-wavenumber Raman spectroscopy and electrical device measurements, we focused on relatively thick TPdS nanowires so as to get strong signal for the Raman spectra and achieve good contacts for electrical devices.

2.2 Low-wavenumber Raman spectroscopy and transmission electron microscopy studies

Based on the on-chip deposited nanowires, we performed low-wavenumber Raman spectroscopy study (see Methods). Vibrational modes located at low-wavenumber range less than 100 cm$^{-1}$ can denote the movement of atoms or molecules governed by weak forces, including vdW, quasi-vdW and hydrogen bond. Low-wavenumber Raman spectroscopy has been successfully used to investigate the interlayer phonon modes in 2D materials [42] and the intermolecular interactions between aromatic molecules [43–45]. Our detailed Raman spectroscopy studies provide guidance for further understanding of one-dimensional crystal structure and symmetries. As shown in Fig. 2(e), Raman spectra at different polarization configurations for a relatively thick nanowire (diameter ~ 1 μm), have been stacking plotted together. We measured the excitation-angle dependences of the Raman peaks, where 0° and 90° represent parallel (Γ(xx)z) and cross (Γ(yx)z) polarization configurations. A few peaks in the low wavenumber region (< 100 cm$^{-1}$) are examined under different configurations, i.e. 18.1, 26.9, 32.5, 60, and 72.9 cm$^{-1}$ can be clearly resolved at Γ(yx)z configuration. The successful demonstrations of low wavenumber Raman peaks indicate the existence of inter-chain vibrations in our TPdS system. In addition, these measured Raman peaks exhibit distinct excitation-angle dependent polarizations, as demonstrated by the intensity polarization angle dependences in Fig. 2(f). Here, we take P1 (32.5 cm$^{-1}$), P2 (72.9 cm$^{-1}$), and P3 (201.5 cm$^{-1}$) as the examples of these different polarizations. More specifically, the Raman intensity of P1 is consistent with the laser polarization which reaches maximum at parallel configuration and minimum at cross configuration, while P2 intensity shows the opposite evolution and P3 intensity stays almost constant. These different polarization dependences indicate distinguishable symmetries related to these Raman modes [42, 46]. Since the detector polarization is aligned with our TPdS chain direction, vibrations along the chain and totally symmetric vibration modes will preserve the laser polarization in Raman scattering. Therefore, we can see that the P1 mode reflects the breathing-like vibration between chains or shearing-like vibration along the chain, and the P2 mode corresponds to the shearing-like vibration perpendicular to the chain. P3 mode shows a slightly broader peak which may correspond to a combination of two vibrations with close energy, one is mainly along the chain direction and another shows significant component perpendicular to the chain. We have simulated the possible corresponded atoms vibration modes, as shown in Figs. S5 and S6 in the ESM. However, due to the complexity of the crystal structures, we are not able to correlate the irreducible representations for these peaks, which is beyond the scope of this research work. In fact, we also performed simulation of Raman spectra evolution with different thicknesses, as can be seen in Fig. S7 in the ESM, only single and double ribbons produce unique spectra. For example, in Raman spectrum of single ribbon, the modes corresponded to the vibration of the bonds between ribbons are absent. With increasing nanowire size, its Raman peaks tend to the bulk spectrum.

To further analyze the crystallinity of the exfoliated TPdS nanowires, we preformed aberration-corrected STEM characterization. High-quality nanowires with various thicknesses can be easily identified. Figure 3(a) shows annular dark-field (ADF) images of a thicker (9.3 nm) TPdS nanowire along the <100> zone axis. The orientation can be corroborated by the
fast Fourier transform (FFT) as indicated by the top right inset. The interplanar distances correspond to the (100), (2 1 1), and (2 T 0) planes (compared with the result of crystal structure simulation). The atomic resolution image of the TPdS nanowire clearly shows a smooth and clean surface without significant degradations, as shown by bottom right inset of Fig. 3(a). Figure 3(b) shows the ADF images of an ultra-thin (~3.0 nm) TPdS nanowire. The nanowire shows a few segments oriented in different directions as highlighted in the image. At a higher magnification, we observed atomic resolution images of this specific nanowire at three selected areas. The crystal orientation can be identified by comparing to the simulated crystal structure with six-unit chains as shown by Fig. 3(b) inset. The view directions of area 1 and area 2 are [120] and [100], respectively. Area 3 shows a twist of the nanowire from [100] to [120]. The TEM analysis beyond both thicker and ultra-thin TPdS nanowires indicates an extremely high level of crystallinity, which has been successfully preserved during the LPE process.

More interestingly, we didn’t observe a significantly oxidized or amorphous layer on the exfoliated nanowires even after storing in ambient environment for more than one month. This phenomenon is consistent with our calculations of H₂O and O₂ adsorptions on TPdS surface, as shown by Fig. 10. For the TPdS crystal, the adsorption energy for O₂ molecule is 1.12 eV/molecule, indicating adsorption of O₂ is not favorable. Although the TPdS crystal shows favorable adsorption of H₂O molecule with an adsorption energy of −0.33 eV/molecule, the TPdS structural geometry is stable upon such adsorption as indicated by Fig. S10 in the ESM. In fact, this stable crystal structure even at nanometer scale is crucial for modern electronic applications. Thus, we further characterize the device performance based on high-quality TPdS nanowires.

### 2.3 Functionality demonstrations and zero-bias photo-response

It has been demonstrated that the mechanical exfoliated TPdS nanowire is a good candidate for the channel material of 1D field-effect transistor [11]. In order to study the electronic transport properties of TPdS nanowires through LPE method, we fabricated FETs with a double-gate layout. As indicated by Fig. 4(a), a DC current is flowing through TPdS nanowire which is tuned by a back gate and a top ionic liquid gate separately (ionic liquid N,N-diethyl-N-(2-methoxyethyl)-N-methylammonium bis(trifluoromethylsulphonyl) imide (DEME-TFSI) has been used as the gate medium) [47]. Figure 4(b) shows the transconductance for a typical FET based on a 31.4 nm TPdS nanowire as indicated by the AFM image (Fig. 4(b) inset). Under the back gate, at a source-drain bias of 0.5 V, the TPdS nanowire clearly shows n-type semiconducting behavior. The device can be switched to on-state with $I_{DS} = 5.1 \times 10^{-8}$ A at $V_{DS} = 80$ V, and turned into off-state with $I_{DS} < 1 \times 10^{-10}$ A at $V_{DS} = -50$ V, resulting in an on/off ratio larger than 500. Based on the back gate sweeps, the field-effect mobility $\mu_{FE}$ can be extracted from the standard FET model $I_{DS} = \frac{W}{2L} \mu_{FE} C_{ox} \left( V_{DS} - \frac{V_{GS}-V_{th}}{2} \right)$, where $L$ is the channel length which is 6.7 μm, $W$ is the channel width as 31.4 nm, $C_{ox}$ is the capacitance per unit area which can be determined from $C_{ox} = \varepsilon_{r} \varepsilon_{0} / d_{ox}$, where $\varepsilon_{r}$ is the dielectric constant of vacuum, $\varepsilon_{0}$ represents the relative dielectric constant of 3.9 for SiO₂, and $d_{ox}$ is 300 nm as the dielectric layer thickness. For this specific device, $\mu_{FE}$ equals to 32.5 cm²V⁻¹s⁻¹ at $V_{DS} = 80$ V, which is comparable with that achieved through mechanical exfoliated TPdS nanowire (with an average of 80 cm²V⁻¹s⁻¹). Our TPdS nanowires exhibit comparable or even better performance compared with other solution-processed semiconducting nanostructures, i.e. MoS₂ [48], black phosphorus [26, 49], and carbon nanotubes [33, 50, 51] (see Table S3 in the ESM). To further improve the gate response of the TPdS FETs, a top ionic liquid gate is applied in a range of −2 to 2 V when the back gate is grounded instead. The device shows significant bipolar behavior with an on-current of $4.5 \times 10^{-7}$ A at the electron side and $1.4 \times 10^{-4}$ A at the hole side. The off-state current is as low as $10^{-10}$ A, indicating a higher on/off ratio near $10^{4}$. The swing slope extracted from the gate sweeps has been improved from 23 V·dec⁻¹ for back gate to 517 V·dec⁻¹ for ionic liquid gate. Figure 4(c) shows the linear $I_{DS}$–$V_{DS}$ dependence at different liquid gate voltages from −2 to 2 V, indicating nearly ohmic contacts between TPdS nanowire and the gold metal.
Then, we further checked the stability of our TPdS nanowires from the transport analysis. As shown in Fig. S11 in the ESM, the 1D TPdS transistor shows very good stability with almost unchanged transconductance after stored in ambient environment for more than two months. We believe that the oxidation process is quite slow since it will increase the resistance or make the contacts worsen significantly. This result is in good consistency with our STEM studies and theoretical calculations, as discussed above. They have simultaneously provided solid supports for the good stability of our TPdS nanostructures.

From the above analysis, our exfoliated TPdS nanowires exhibit outstanding semiconducting properties. In such a quasi-1D semiconducting system, its promising application as photodetectors is worth being pursued [52–57]. Our following discussions will focus on the photo-response study based on TPdS nano-devices. Figure 5(a) shows the optical image of a two-terminal photodetector device. Under our confocal microscope system, the 532 nm green laser as the excitation light was focused at the center of the device. A typical time-resolved photoresponse is plotted in Fig. 5(b). $I_{\text{photo}}$, at zero source-drain bias rises upon turning on the laser and decays after switching off the laser. As shown by the rise and decay process in Fig. 5(c), the response curve can be characterized by a single exponential function expressed as

$$I_{\text{photo}} = A_t \exp \left( -\frac{t - t_0}{\tau} \right) + B_o,$$

where $t_0$ is the time when the laser is switched on, $A_t$ and $B_o$ are fitting constants, and $\tau$ is the time constant. The fitted time constants for rising ($\tau_r$) and decay ($\tau_d$) processes are 110 and 117 ms, respectively. Actually, there have been intensive studies on the photoresponse of a wide range of low dimensional materials. The response time varies significantly for different materials. For example, the rising and decay time is 1.5 ps in graphene [58], ~1 ms in black phosphorus [59], and ranging from 5 ms to 4 s in TMDC thin flakes [60–64]. It is worth noting that, even in the same material, such as MoS$_2$ monolayer [60, 63], the rising and decay time is in good consistency with our STEM studies and theoretical calculations, as discussed above. They have simultaneously provided solid supports for the good stability of our TPdS nanostructures.

For different samples or materials. In nanoscale semiconducting photodetectors, two different mechanisms have been identified including photovoltaic effect and photothermoelectric effect. The response time in latter process is generically limited by the phonons since heat transfer is the essential step. On the other hand, the response speed also can be significantly affected by external factors, i.e. in disorder rich metal oxide nanowires such as ZnO, Nb$_2$O$_5$, and Cu$_2$O, the rising and decay time can be as long as 100 s due to surface trapping and disorders [65, 66]. Our previous study based on mechanical exfoliated TPdS nanowires has reported a variable range hopping dominated transport, which indicates the disorder and surface trapping play an important role in device properties [11]. Thus, the disorder and surface trapping states may cause trapping of photoexcited carriers, which is expected to contribute to the slow response for our TPdS photodetectors.

In order to explore the photocurrent generation mechanism, we presented scanning photocurrent microscopy measurements on our TPdS device (see Methods). Figure 5(d) shows the 2D contour plot of the photocurrent depending on the laser spot (~1 μm diameter) locations at the device (see Note S2 in the ESM for laser spot determination). The photocurrent exhibits a sign switching when the laser spot is scanned from source to drain electrodes, with maximum magnitudes at these metal-semiconductor contact edges. Besides, when the laser spot is located micrometer away from these two edges, either in-between or at the two sides, the photocurrent is still existing but with smaller magnitude. This is in controversy with the p-n junction or Schottky barrier driven photovoltaic effect, which is supposed to be constrained at the p-n or metal-semiconductor interfaces [67, 68]. However, it can be explained by the photothermoelectric effect, because when the laser is heating up the metal contacts which generate temperature differences and gradients. This laser heating is generally existing and not a negligible effect in microscopy experiments. The local temperature of gold contacts can easily rise about 0.4 K even with a laser heating power as low as 60 μW [69]. Besides, we performed all the measurements at room temperature when the Schottky barrier in our TPdS transistor is negligible as evidenced by the fairly linear $I_{\text{D}}$-$V_{\text{DS}}$ curves in Fig. 4(c). Thus, we propose a photothermoelectric effect dominated mechanism in our TPdS 1D photodetector, as illustrated by Fig. 5(f). In particular, a local temperature gradient induced by light absorption drives electrons to travel through the device. When the laser is heating up the contacts, the Seebeck coefficient difference between Au metal and TPdS nanowire generates a photothermal voltage across the junction, which could explain the maximum photocurrent observed at the contact edges but not only constrained there [69–72]. Meanwhile, as shown in Fig. 5(e) and Fig. S14 in the ESM, the photocurrent profile along the line-cut from the red to blue dashed circles in Fig. 5(d) does not show clear gate dependence, which provides evidence for the photothermal dominated mechanism as the photovoltaic effect should depend on the band alignments significantly [52, 73].

Figure 5  Photoresponse study based on Ta$_2$Pd$_3$Se$_8$ transistors. (a) Optical image of the fabricated nanowire device and schematic drawing for the photocurrent mapping setup. The laser used in this experiment is 532 nm solid laser. (b) Room-temperature photoresponse with a few lights on/off cycles based on the device in (a). Note: the source-drain bias has been set to zero. (c) Zoom-in view of one cycle showing the rise and decay processes. Black dots: measured photo-response curve. Red solid line: fitted curve with exponential decay function. (d) Photocurrent mapping contour plot based on the device in (a). (e) Gate dependent photocurrent profiles across the line-cut starting from red dashed circle to the blue dashed circle in (d), from left to right, the back gate voltage is set to –60, 0, and 60 V. (f) Band diagram of the photothermoelectric mechanism.
3 Conclusion
In summary, we have demonstrated the large-quantity production of high-quality ultra-thin TPdS nanowires using liquid-phase exfoliation with selected solvents. The resultant TPdS nanowires show highly preserved crystallinity and can be considered as an important step toward the fabrication of perfect 1D TMDC nanoribbons with naturally semiconducting properties. 1D field-effect transistors based on exfoliated TPdS nanowires exhibit competitive electrical transport properties and high mobility among liquid exfoliated van der Waals semiconductors. Besides, the as-fabricated devices show significant photoresponse with a clear photothermal dominated mechanism. Our work sheds light on the extension of wet exfoliation technique to 1D or quasi 1D van der Waals materials, which contains a large group of candidates. The efficient production of 1D semiconducting TPdS nanowires can provide a wide range of applications, referred to as 1D field-effect transistor, optoelectronics, energy harvesting, chemical sensing, and biological sensing, etc.

4 Methods

4.1 Bulk synthesis
Bulk Ta2Pd3Se8 single crystal is synthesized using chemical vapor transport method. The mixture of thoroughly ground stoichiometric Ta, Pd, and Se element powders was sealed in a quartz tube under vacuum and pre-heated for a week at 750 °C. The resultant powder was ground again and sealed in a new vapor transport method. The mixture of thoroughly ground

4.2 Sample preparations
Part A, liquid form sample preparations. 0.5 mg bulk TPdS single crystal was immersed in 20 mL solvents (IPA or NMP). The mixture was sonicated for 4 h at a bath temperature of 50 °C. The obtained dispersion was centrifuged at 500 rpm for 1 h, and the top half of the centrifuged solution was collected as the liquid form sample.

Part B, on-chip sample preparations. The on-chip samples were prepared using drop-casting methods. The substrate is 1 cm² square Si/SiO2 (300 nm) wafer. The solution was drop cast on the substrate and dried by using a spin-coater to spin at 1,000 rpm for 10 s. Then, the samples were rinsed in IPA for 2 min and dried by using compressed air.

4.3 Characterizations
Raman scattering spectroscopy measurements were carried out at room temperature using a micro-Raman spectrometer (Horiba-JY T64000) equipped with liquid nitrogen cooled charge-coupled device (CCD). The measurements were conducted in a backscattering configuration under a triple subtractive mode, excited with a diode green laser (λ = 532 nm). We used a reflecting Bragg grating followed by another ruled reflecting grating to filter out the laser sidebands, and as such, we can achieve the limit of detection ~ 5 cm⁻¹. The backscattered signal was collected through a 100× objective and dispersed by an 1,800 g-mm⁻2 grating with a spectral resolution of 0.7 cm⁻¹. For polarization measurement, we fix the analyzer before detector and the sample and rotate the polarization direction of the laser excitation.

SEM was performed using Hitachi S-4800 FESEM. The images under all magnifications were acquired at 5 kV acceleration voltage. 1 nm thick carbon layer was uniformly deposited on the samples to reduce the charging effect caused by the SiO2 substrate.

Atomic resolution ADF-STEM images of TPdS nanowires were obtained using a JEOL annular field detector with a fine-imaging probe. The probe current was approximately 23 pA with a convergence semi-angle of 22 mrad and an inner semi-angle of 45–50 mrad.

4.4 Mass fraction and yield estimations
The mass fraction of the exfoliated Ta2Pd3Se8 nanowires can be estimated according to our AFM length and thickness distribution analysis. Given that the volume of individual nanowire is assumed as V = ρD²L, where D is the diameter (thickness), L is the length, and ρ is the density, the mass fraction of individual thickness can be estimated as

\[ F = \frac{\sum \text{individual } D_{\text{ind}}^2 L_{\text{ind}}}{\sum D_{\text{ind}}^2 L_{\text{ind}}} \]

Then, since the sediment after centrifugation (500 rpm, 1 h) has been weighted as ~ 21 wt.% of the initial bulk material, which indicates ~ 79 wt.% remaining in the supernatant used for the AFM analysis. The total yield from the initial bulk TPdS crystals can be calculated as Y = F × 79%.

4.5 Raman active vibration modes simulations
All calculations of the atomic and electronic structure of Ta2Pd3Se8 nanowires were performed using a density functional theory [74, 75] within the PBE-PAW approximation [76] with the periodic boundary conditions using a Vienna Ab-initio Simulation Package [77–79]. The plane-wave energy cutoff was equal to 300 eV. For the calculation of the equilibrium atomic structure, the Brillouin zone was sampled according to the Monkhorst–Pack [80] scheme with a grid not less than 4×6×10 k-point for bulk structure and 1×1×12 k-point for quasi 1D nanowires structures. The structural relaxation was performed until the forces acting on each atom were less 0.01 eV Å⁻¹.

The Raman spectra spectrum simulation was performed using python script vasp_raman.py [81] based on computation of the derivative of the polarizability (or macroscopic dielectric tensor) with respect to that normal mode coordinate: dP/dQ (or dε/dQ) [82].

4.6 Photocurrent measurement setup
The photoresponse measurements were performed based on a confocal microscopy setup. A ~ 1 mW 532 nm green laser beam was focused onto a ~ 450 nm 1/e² radius spot using a 50× microscope objective lens. The sample was mounted on an Attocube scanning stage with a scanning resolution of 100 nm both along x and y directions. The photocurrent at zero source-drain bias was measured using a DC current amplifier and recorded by home-designed Labview software.

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