Abstract

We report on a wet chemistry method used to grow PtSe$_2$ nanosheets followed by thermal annealing. The SEM and TEM analysis confirms the formation of PtSe$_2$ nanosheets. Furthermore, XRD, Raman, XPS and SAED patterns were used to analyze the crystal structure and to confirm the formation of the PtSe$_2$ phase. The temperature-dependent Raman spectroscopy investigations were carried out on PtSe$_2$ nanosheets deposited on Si substrates in the temperature range 100–506 K. The shifts in Raman active E$_{2g}$ and A$_{1g}$ modes as a function of temperature were monitored. The temperature coefficient for both modes was calculated and was found to match well with the reported 2D transition metal dichalcogenides. A PtSe$_2$ nanosheet-based sensor device was tested for its applicability as a humidity sensor and photodetector. The humidity sensor based on PtSe$_2$ nanosheets showed an excellent recovery time of $\approx 5$ s, indicating the great potential of PtSe$_2$ for future sensor devices.

Introduction

Graphene, the most well-studied example of the two-dimensional (2D) aromatic compounds, is the building block of all forms of carbon allotropes [1]. In recent years, it has been widely studied due to its extraordinary optical, electrical, mechanical, magnetic and chemical properties [2-5]. Like graphene and its organic analogues [6], inorganic 2D metal dichalcogenides also exhibit outstanding performance in many applications including transistors, sensors, photodetectors, solar cells, field emitters, battery materials, light harvesting and energy storage devices, catalyst for H$_2$ generation, and drug delivery applications [7-12]. Most of the transition metal dichalcogenides (TMDCs) are semiconducting in nature with MX$_2$ type – where M is a metal, M = W, Mo, Sn, Nb, V, etc. from group IV–V and X represents the chalcogenides family, X = S, Se, Te, etc. The metal atom M is sandwiched between layers of chalcogenide (X) atoms in the structure X–M–X. The
TMDCs show diverse functional properties at the monolayer level in contrast to bulk due to the quantum confinement effect. Apart from this, these TMDCs, for example MoS$_2$ and MoSe$_2$, show an indirect to direct band gap transition [13–17].

A 2D platinum diselenide (PtSe$_2$) material has recently joined the growing class of stable TMDCs due to its promising applications. The 2D PtSe$_2$ has not been explored much to date due to difficulties in synthesis. It is well known that bulk PtSe$_2$ is a semimetal in nature with a nearly zero band gap [18,19]. With the help of theoretical calculations such as density functional theory (DFT) and local-density approximations (LDAs), it has been observed that bulk PtSe$_2$ shows a semimetallic nature and single-layer PtSe$_2$ has a semiconducting nature with a bandgap of 1.2 eV. Bilayer PtSe$_2$ is also a semiconducting material but with a slightly smaller band gap than the monolayer material [19]. This layer-dependent conversion of semimetal-to-semiconductor transition has potential for electronic device applications [20–22]. Bulk PtSe$_2$ was first prepared in 1909 by Minozzi from elements [23]. PtSe$_2$ nanosheets have been recently prepared by heating thin foils of platinum in selenium vapors at 400 °C [19,24]. In this paper, we have synthesized few-layer-thick PtSe$_2$ nanosheets by a wet-chemical method [25] at 90 °C using chloroplatinic acid (H$_2$PtCl$_6$) and Se powder as precursors followed by thermal annealing at 500 °C. Temperature-dependent Raman spectroscopic characterization was carried out on the materials.

Materials and Methods

All the chemicals such as chloroplatinic acid, Se powder, hexamethylenetetramine, and NaBH$_4$ were purchased from Sigma-Aldrich for the synthesis of PtSe$_2$ nanosheets.

Synthesis method

The PtSe$_2$ nanosheets were synthesized using a solvothermal method followed by annealing at 500 °C using a previously described method for PtSe$_2$ synthesis [25]. The PtSe$_2$ material was prepared in three steps. The first step is the formation of the PtSe complex on the wall of a container by a wet-chemical method; the second step is the phase transformation of PtSe$_2$ by thermal annealing. 0.5 mL of a 0.015 M solution of H$_2$PtCl$_6$ was mixed with 0.5 mL of 0.5 M hexamethylenetetramine. In order to get a homogeneous solution, the mixture was carefully stirred for 15–20 s until the colour of the solution became slightly yellow; this is referred to as the Pt precursor. In another beaker, 0.8 mg of Se powder was added into a 10 mL ice-cold solution of 0.1 M NaBH$_4$ which acts as a strong reducing agent for the reduction of Se powder. The solution of Se was then heated in an oil bath at 90 °C for ≈20 min in order to completely reduce the Se. After complete reduction, the colour of the solution became dark brown and is referred to as the Se precursor. The Pt precursor was then slowly added into the Se precursor. The colour of the solution was found to suddenly change to greenish brown. The mixture was then kept undisturbed for ≈20 min. After 20 min the complex of Pt and Se was formed on the wall of the beaker. The complex was then washed several times using deionized water. First complex was transferred onto a Si substrate and heated at 100 °C on a hot plate. After complete evaporation, the substrate was annealed in a chemical vapour deposition system at 500 °C in argon gas atmosphere for 5 h.

Supporting Information File 1, Figure S1 shows the schematic of the PtSe$_2$ nanosheet synthesis steps.

Sensor device fabrication and testing

Sensor devices were fabricated on a tin-doped indium oxide (ITO) substrate with a channel length of ≈300 μm and width ≈5 mm. The PtSe$_2$ nanosheet powder was dispersed in N-methyl-2-pyrrolidone (NMP) solvent and then drop casted between the channels. The devices were further annealed in a vacuum furnace at 170 °C to improve the contact resistance and adhesion of the nanosheets with the substrate. The humidity sensing performance was investigated by exposing the sensor device to various relative humidity (RH) levels ranging from 11.3–97.3% as described in detail previously [26]. All of the electrical tests such as current–voltage (I–V) and current–time (I–t) measurements were carried out using a Keithley 2612A system source meter which was attached to a computer through a GPIB 488A interface. For the photodetection study, a green LED was used. All sensor experiments were carried out at ambient pressure and room temperature.

Results and Discussion

Structural characterization

The structural characterization was carried out using X-ray diffraction (XRD) and Raman spectroscopy. Figure 1a shows the typical XRD pattern of the as-prepared sample deposited on a Si substrate. XRD was performed on a PANalytical X’pert pro dual goniometer diffractometer using Cu Kα radiation. The samples were mounted flat and scanned between 10 to 60°. The XRD pattern of the as-prepared sample shows the strong characteristic peaks around $2θ = 17.41°$ and $33.17°$ belonging to the (001) and (011) planes of PtSe$_2$. These values match well with the JCPDS data card number (88-2281) and as observed in a previous report [27]. Figure 1b shows the Raman spectra of the as-prepared few-layer PtSe$_2$ nanosheets. The Raman spectra were recorded using a Renshaw microscope at a wavelength of 532 nm with laser power ≈25 mW and laser spot diameter ≈1 μm. The typical Raman spectra recorded at room temperature consist of two distinct peaks, one at ≈176 cm$^{-1}$ corresponding to the $E_g$ mode and another slightly less intense peak at ≈205 cm$^{-1}$ corresponding to the $A_{1g}$ mode. The $E_g$ mode in the Raman spectra corresponds to in-plane vibration due to the
opposite motion of the upper and lower Se atoms. The $A_{1g}$ mode in the Raman spectra corresponds to the out-of-plane vibration of Se atoms [22,28].

Morphological investigations were carried out using scanning electron microscopy (SEM). Figure 2a–c shows SEM images of few-layer PtSe$_2$ with typical overlapping of multiple sheets on
each other. Figure 2d shows an SEM image indicating a more transparent thin layer of PtSe$_2$ stacked on each other, exhibiting the few-layer nature of the as-synthesized PtSe$_2$ sample. Figure 3a–c shows the low-resolution TEM images of the as-synthesized PtSe$_2$ sample clearly showing the sheet-like morphology with lateral dimension of $\approx$700 nm. Figure 3d shows a high-resolution TEM image of the PtSe$_2$ nanosheets. The inset of Figure 3d shows the selected area electron diffraction (SAED) pattern for the as-synthesized PtSe$_2$ nanosheets.

Figure 2d shows an SEM image indicating a more transparent thin layer of PtSe$_2$ stacked on each other, exhibiting the few-layer nature of the as-synthesized PtSe$_2$ sample. Figure 3a–c shows the low-resolution TEM images of the as-synthesized PtSe$_2$ sample clearly showing the sheet-like morphology with lateral dimension of $\approx$700 nm. Figure 3d shows a high-resolution TEM image of the PtSe$_2$ nanosheets. The inset of Figure 3d shows the selected area electron diffraction (SAED) pattern which depicts the crystalline nature of the as-synthesized PtSe$_2$ sample. The X-ray photoelectron spectroscopy (XPS) spectra of the Pt 4f and Se 3d regions acquired on a PtSe$_2$ nanosheet sample were carried out on a film deposited on the Si substrate. The Figure 4a represents the fitted spectrum for Pt $4f_{7/2}$ and Pt $4f_{5/2}$ with binding energy 72.55 eV and 75.83 eV, respectively. Similarly, for Se, the binding energy spectrum can be fitted by Gaussian–Lorentzian curves shown in Figure 4b. The two peaks with binding energy 54.8 eV and 55.6 eV are observed for the $3d_{5/2}$ and $3d_{3/2}$ states, respectively.

There is one more peak observed in the Se region with low intensity at 52.9 eV which corresponds to Pt $5d_{3/2}$ [24]. The thickness of the as-prepared PtSe$_2$ nanosheets was calculated using atomic force microscopy (AFM). Figure 5a shows the AFM image which clearly shows that the lateral dimensions of the nanosheets are $\approx$700 nm. Figure 5b represents the corresponding height profile plot for the PtSe$_2$ nanosheet with thickness found to be $\approx$47 nm.

**Temperature-dependent Raman spectroscopy of few-layer PtSe$_2$ nanosheets**

The temperature-dependent Raman spectroscopy investigations of few-layer PtSe$_2$ nanosheets were carried out between 100–506 K. The Raman spectra of the PtSe$_2$ nanosheets at different temperatures are provided in Supporting Information File 1, Figures S2 and S3. The Raman mode $E_g$ and $A_{1g}$ as a function of temperature is shown in Figure 6a,b. It can be clearly seen that the position of the $A_{1g}$ and $E_g$ modes shifts to...
lower wavenumbers as the temperature increases from 100 K to 506 K. The Raman modes $E_g$ and $A_{1g}$ for PtSe$_2$ behave linearly within the temperature range 100–506 K. Furthermore, it was observed that the full width half maximum (FWHM) increases with an increase in temperature. The peak positions in the Raman spectra were calculated by fitting the Lorentzian function to the $A_{1g}$ and $E_g$ modes. The temperature coefficient can be calculated by Equation 1 [29]:

$$\omega(T) = \omega_0 + \chi T,$$

where $\omega_0$ is the peak position of the $A_{1g}$ and $E_g$ mode at zero Kelvin, $\chi$ is the temperature coefficient of the $A_{1g}$ and $E_g$ modes, and $\omega$ is a Raman phonon frequency. The slope of the Raman modes vs temperature plot directly gives the value of the temperature coefficient and is given in Table 1. Further, it was clearly seen that the Raman peak position and peak broadening was affected by temperature. This change in Raman modes is mainly due to the contribution from the thermal anharmonicity.

The Raman phonon frequency as a function of volume and temperature is given by Equation 2 [30]:

$$\left(\frac{\partial \ln \omega}{\partial T}\right)_P = \left(\frac{\partial \ln V}{\partial T}\right)_P \left(\frac{\partial \ln \omega}{\partial \ln V}\right)_T + \left(\frac{\partial \ln \omega}{\partial T}\right)_V,$$

$$\left(\frac{\partial \ln \omega}{\partial T}\right)_P = -\frac{\gamma}{K} \left(\frac{\partial \ln \omega}{\partial P}\right)_T + \left(\frac{\partial \ln \omega}{\partial T}\right)_V,$$

where $\gamma$ is the volume thermal coefficient and $K$ represents the isothermal volume compressibility. The first term on the right hand side, $-\gamma/K (\partial \ln \omega/\partial P)_T$, represents the volume contribution at a constant temperature. The second term, $(\partial \ln \omega/\partial T)_V$, represents the temperature contribution at constant volume. In single-layer TMDCs due to the direct band gap, the double resonance phenomenon is useful to explain the change in FWHM, intensity and the peak shift as a function of temperature. The double resonance phenomenon can be attributed to several process including absorption of an incident photon, creation of a hole pair,
double scattering of a created hole pair with phonon, and recombination of an electron–hole pair with emission of phonon. The temperature coefficient for the $E_g$ and $A_{1g}$ modes was found to be $-0.014$ and $-0.008$, respectively. The nature of the temperature dependence of the Raman spectra of PtSe$_2$ nanosheets is found to be similar in nature to that of graphene and other 2D materials such as MoS$_2$, WS$_2$, MoSe$_2$, WSe$_2$, BP, TiS$_3$, multilayer graphene, and MoTe$_2$ [29,31-34]. A comparison of the temperature coefficient values corresponding to various 2D materials are shown in Table 2. The value of $\Delta \omega$ for both $E_g$ and $A_{1g}$ modes was found to be $6.11$ cm$^{-1}$ and $3.14$ cm$^{-1}$, respectively.

### Table 2: Temperature coefficient values for various 2D materials.

<table>
<thead>
<tr>
<th>TMDCs</th>
<th>Raman modes</th>
<th>Temperature coefficient ($\chi$)</th>
<th>$\Delta \omega$ (cm$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoSe$_2$</td>
<td>$A_{1g}$</td>
<td>$-0.0096$</td>
<td>$4.75$</td>
<td>[29]</td>
</tr>
<tr>
<td>WSe$_2$</td>
<td>$A_{1g}$</td>
<td>$-0.0071$</td>
<td>$3.81$</td>
<td>[29]</td>
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<td>MoS$_2$</td>
<td>$E_g$</td>
<td>$-0.0136$</td>
<td>$8$</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td>$A_{1g}$</td>
<td>$-0.0113$</td>
<td>$6.11$</td>
<td></td>
</tr>
<tr>
<td>WS$_2$</td>
<td>$E_g$</td>
<td>$-0.0098$</td>
<td>$4.51$</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td>$A_{1g}$</td>
<td>$-0.014$</td>
<td>$6.43$</td>
<td></td>
</tr>
<tr>
<td>black phosphorous</td>
<td>$B_{2g}$</td>
<td>$-0.008$</td>
<td>$4.39$</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>$A_{1g}$</td>
<td>$-0.013$</td>
<td>$18.4$</td>
<td></td>
</tr>
<tr>
<td>TiS$_3$</td>
<td>$A_{1g}$</td>
<td>$-0.022, -0.025$</td>
<td>$-0.024, -0.017$</td>
<td>[32]</td>
</tr>
<tr>
<td>single-layer graphene</td>
<td>$G$</td>
<td>$-0.0162$</td>
<td>$-$</td>
<td>[33]</td>
</tr>
<tr>
<td>bilayer graphene</td>
<td>$G$</td>
<td>$-0.0154$</td>
<td>$-$</td>
<td></td>
</tr>
<tr>
<td>MoTe$_2$ (bilayer)</td>
<td>$E_{2g}$</td>
<td>$-0.0116$</td>
<td>$-$</td>
<td>[34]</td>
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<tr>
<td></td>
<td>$B'_{2g}$</td>
<td>$-0.0181$</td>
<td>$-$</td>
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<tr>
<td>PtSe$_2$</td>
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<td>$6.11$</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>$A_{1g}$</td>
<td>$-0.008$</td>
<td>$3.14$</td>
<td></td>
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</table>

Humidity sensor and photodetector based on few-layer PtSe$_2$ nanosheets

Figure 7a shows the typical resistance of the sensor device vs relative humidity plot. The resistance is significantly decreased from 3.75 G$\Omega$ to 0.83 M$\Omega$. The humidity sensing mechanism for the PtSe$_2$ sensor can be explained as follows. When the PtSe$_2$ nanosheet sensor device was exposed to water molecules/vapors, a charge transfer between the water molecules and the PtSe$_2$ nanosheets occurs. This results in the decrease in resistance of the PtSe$_2$ nanosheet sensor device with an increase in the relative humidity. The interactions among the water molecules (electron donor) and the PtSe$_2$ nanosheets results in an enhancement in the conductivity of the sensor device, similar to that observed for other 2D materials such as SnSe$_2$ [35], MoS$_2$ [36], BP [26], and MoSe$_2$ [37]. Figure 7b shows a typical current–time ($I$–$t$) plot where cycles of 11.3% and 97.3% RH levels were used to calculate the response and recovery time. The response and recovery time for the PtSe$_2$-based humidity sensor device was found to be 118 s and 5 s, respectively. The advantage of the PtSe$_2$-based humidity sensor device is its rapid recovery and its functionality at room temperature. Figure 7c shows a typical $I$–$V$ plot in dark conditions and under green light illumination. Figure 7d shows the $I$–$t$ plot for the photodetector based on PtSe$_2$ nanosheets with a response time of $\approx 110$ s and a recovery time of $\approx 129$ s.

### Conclusion

In conclusion, we report on a wet chemistry method to grow PtSe$_2$ nanosheets. The SEM and TEM analysis confirm the for-
formation of PtSe₂ nanosheets. Further, the XRD, Raman and SAED pattern results were used to analyze the crystal structure and to confirm the formation of the PtSe₂ phase. Temperature-dependent Raman spectroscopy investigations were carried out on PtSe₂ nanosheet films grown on Si substrates between 100–506 K. The temperature coefficient for the E₈ and A₁g modes was found to be −0.014 and −0.008, respectively. A room temperature humidity sensor based on the PtSe₂ nanosheets demonstrated an excellent recovery time of ≈5 s, indicating the great potential of PtSe₂-based sensors for future nano-electronics and sensor devices.

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Supporting Information
Supporting Information File 1
Additional figures.
[https://www.beilstein-journals.org/bjnano/content/supplementary/2190-4286-10-46-S1.pdf]