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Graphene analogues of layered metal selenides†

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Graphene analogues of MoSe₂ and WSe₂ have been prepared by three different chemical methods and characterized by electron microscopy and other methods. Graphene analogues of these diselenides as well as of GaSe have also been obtained by liquid-phase exfoliation. Raman spectra of the graphene analogues show significant changes relative to those of the bulk samples.

Inorganic analogues of fullerenes as well as of carbon nanotubes comprising layered metal sulfides and other inorganic materials have been prepared and characterized adequately.^{1–4} These inorganic nanomaterials constitute an important family of nanomaterials. Recent research on graphene^{5–7} has created interest in preparing and characterizing graphene analogues of layered inorganic materials.^{8,9} Some progress has been made in the synthesis of inorganic graphenes in the view of exciting possibilities and potential applications.^{10,11} Exfoliated MoS₂ forms aqueous suspensions of single layers wherein sulphur atoms are bonded with molybdenum in an octahedral arrangement with the 2a₀ superlattice.¹² A structural transition from the hexagonal to the trigonal prismatic structure has been indicated in lithium-intercalated MoS₂.¹³ Exfoliation has been employed to prepare graphene analogues of metal chalcogenides, following the procedure used for graphene.^{14,15} We have been exploring the synthesis of graphene-like inorganic materials, especially those formed by layered metal selenides by different chemical methods. In this communication, we report the successful results obtained in the case of MoSe₂ and WSe₂. We have also obtained graphene analogues of these chalcogenides and of GaSe by exfoliation in *N*-methylpyrrolidone.

In order to prepare graphene-like MoSe₂ and WSe₂ three different chemical methods were employed.‡ Method 1 involved the intercalation of *n*-butyllithium in bulk MoSe₂ and WSe₂ followed by exfoliation in water. In the process of exfoliation, lithium-intercalated MoSe₂ and WSe₂ react with water forming lithium hydroxide and hydrogen gas, causing the separation of layers. In method 2, molybdic acid was reacted with selenium metal under hydrothermal conditions. In Method 3, molybdic

or tungstic acid was reacted with excess selenourea in an N₂ atmosphere at 773 K. Products of these reactions were characterized by transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM) and Raman spectroscopy in addition to X-ray diffraction (XRD).

Molybdenum selenide prepared by the three chemical methods do not show the (002) reflection in the XRD patterns as can be seen from Fig. 1(a). The absence of the (002) reflection in the XRD patterns indicates that the products formed in the reactions contain only a few layers. Similar XRD patterns were also obtained in the case of WSe₂ prepared by these reactions as shown in Fig. 1(b). Energy dispersive X-ray analysis (EDAX) showed the products to be stoichiometric MoSe₂ and WSe₂. Graphene analogues of selenides prepared by different chemical methods were characterized by FESEM (see Fig. S-1†). In Fig. 2, we present TEM and AFM images of MoSe₂ showing the presence of one to three layers. Fig. 2(a) and (b) show graphene-like layers obtained from methods 2 and 3 with a layer separation of 0.65–0.70 nm. AFM images and the corresponding height profiles of 0.9 nm to 1.9 nm in Fig. 2(c) and (d) confirm the presence of one

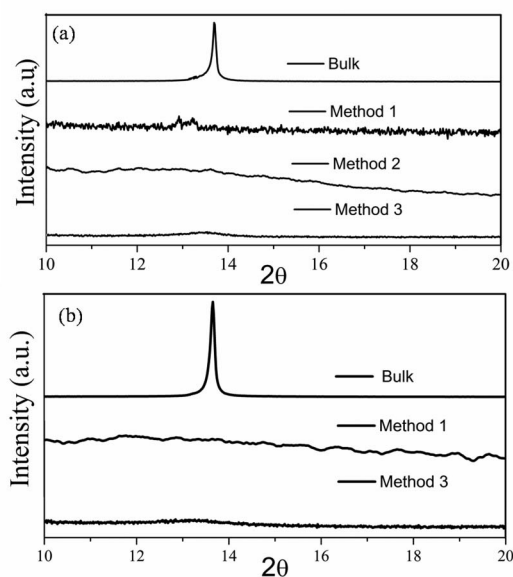


Fig. 1 XRD patterns of (a) bulk MoSe₂ and graphene-like MoSe₂ layers obtained by chemical methods and (b) of bulk WSe₂ and graphene-like WSe₂ layers obtained by chemical methods.

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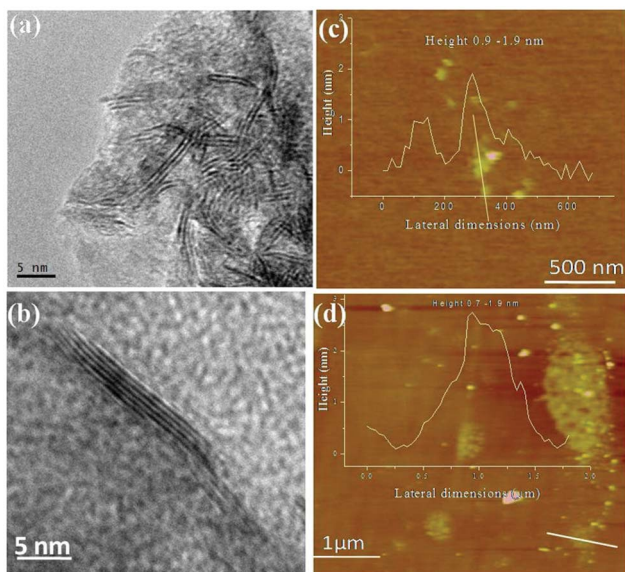


Fig. 2 TEM image of MoSe₂ layers obtained by (a) method 2 and (b) method 3, AFM images and height profiles of MoSe₂ layers from (c) method 2 and (d) method 3.

to three layers with the lateral dimensions varying from 300 nm to few micrometres. We have provided the distribution of layers from the AFM data for method 3 (in Figure S-2†).

In Fig. 3 we show high-resolution transmission electron microscope (HREM) images of MoSe₂ and WSe₂ layers obtained from method 3 recorded with a FEI TITAN³™ aberration-corrected microscope with a negative $C_s \sim 30 \mu\text{m}$ and a positive defocus $\Delta f \sim 8 \text{ nm}$. Here, the atoms appear bright in a dark background. Fig. 3(a) shows graphene-like MoSe₂ with single and bi-layer structures. We have verified the region as single layer using the

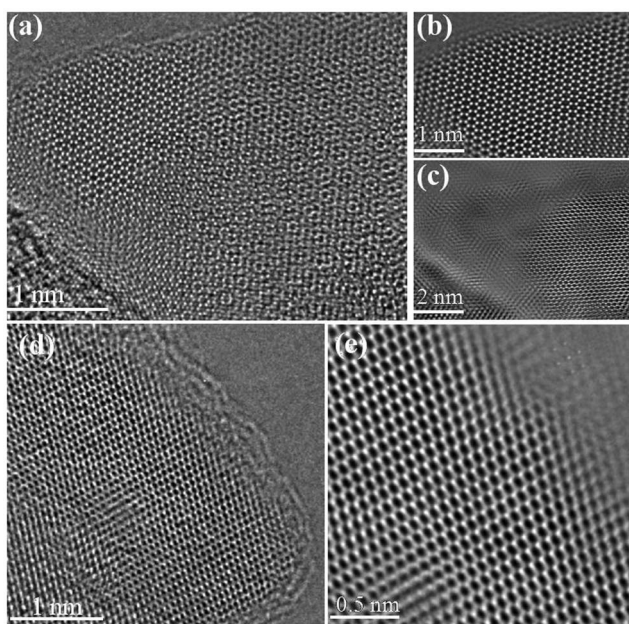


Fig. 3 (a) High-resolution TEM image of layered MoSe₂ from method 3. Fourier transformed images of single and bilayers are shown in (b) and (c). (d) High resolution TEM image of WSe₂ and (e) the Fourier transform image of single layer WSe₂.

Fresnel's contrast¹⁶ before performing HREM. Fresnel contrast is formed under defocus conditions due to abrupt change in inner potential. Fourier filtered HREM images obtained from the same area where one can separate out single-layer MoSe₂ near the edge and the second layer away from the edge (which is slightly rotated with respect to the first layer) are shown in Fig. 3(b) and (c) respectively. The images and the associated Fourier transforms show hexagonal symmetry.

Fig. 4 shows TEM and AFM images of WSe₂ prepared by two chemical methods. The TEM image in the Fig. 4(a) corresponds to WSe₂ prepared by method 1 showing sheet-like morphology. It has lateral dimensions of several micrometres. WSe₂ prepared by the selenourea method contains predominantly 2 layers (Fig. 4(b)). A TEM image showing 4–5 layers is given in the inset of this Figure. Fig. 4(c) and 4 (d) show AFM height profiles of 0.7–1.9 nm supporting the TEM data. Fig. 3(d) presents a HREM image of single-layer WSe₂ prepared by method 3. The corresponding Fourier filtered image is shown in Fig. 3(e), where the bright dots correspond to the heavy W atoms.

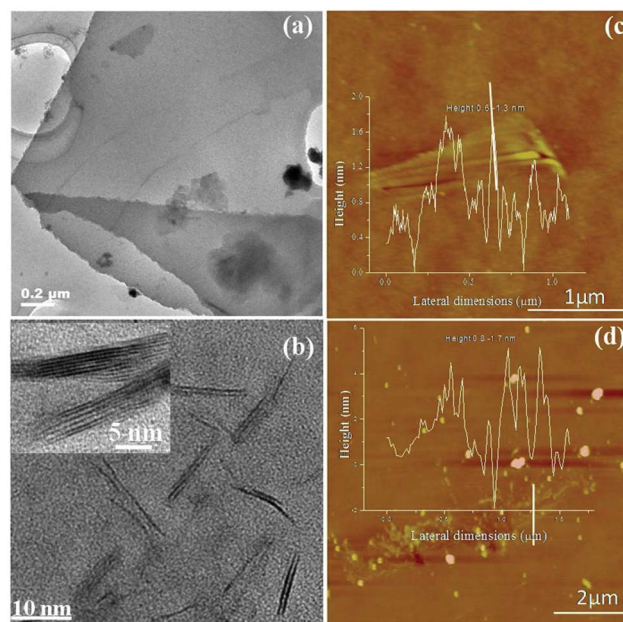


Fig. 4 TEM image of WSe₂ layers obtained by (a) methods 1 and (b) method 3, AFM images and height profiles of MoSe₂ layers from (c) method 1 and (d) method 3.

We have obtained few-layer WSe₂ by liquid-phase exfoliation of bulk WSe₂ in *N*-methylpyrrolidone (NMP). The dispersion formed after 10 min of sonication, characterized by microscopic techniques revealed the formation of few-layer WSe₂.

Raman spectra of graphene-like MoSe₂ prepared by different methods were compared with the spectrum of bulk MoSe₂. The bulk sample gives Raman bands at 168.8 and 242 cm⁻¹ due to the E_{1g} and A_{1g} modes with the full-width half maxima (FWHM) of 4.1 and 3.7 cm⁻¹ respectively.

Interestingly, few-layered MoSe₂ prepared by method 1 exhibits the corresponding bands at 168.1 and 239.4 cm⁻¹. The sample obtained by method 3 shows these bands at 168 and 239.9 cm⁻¹ (See Fig. 5). There is a clear softening of the A_{1g} and E_{1g} modes in the graphene analogues of MoSe₂. The softening of modes observed

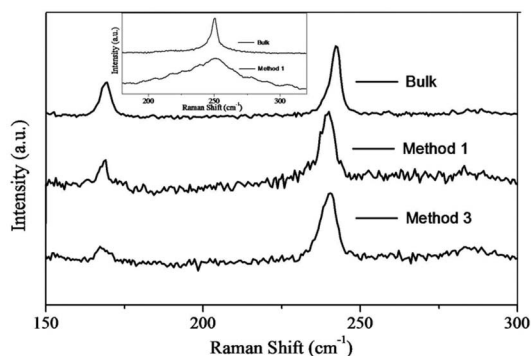


Fig. 5 Raman spectra of bulk MoSe₂ and graphene-like MoSe₂ layers obtained by chemical methods and inset is bulk WSe₂ and graphene-like WSe₂ layers obtained by method 1.

here is similar that reported in the case of graphene analogues of MoS₂.⁹ The FWHM values are larger in the graphene-like samples, the values varying from 6–8 cm⁻¹ compared to ~4 cm⁻¹ in bulk MoSe₂. Raman spectra of graphene-like WSe₂ obtained by both the methods show softening of the bands due to the A_{1g} and E_{1g} modes. Compared to the narrow bands at 175 cm⁻¹ (E_{1g}) and 255 cm⁻¹ (A_{1g}) of bulk WSe₂ with FWHM values around 3.1 and 5.1 cm⁻¹ respectively, (see inset of Fig. 5) the spectrum of WSe₂ obtained from method 1 shows bands at 171 and 249.7 cm⁻¹ with FWHM values of 24 and 43 cm⁻¹. The Raman spectrum of WSe₂ layers synthesized by method 3 shows similar softening of the Raman bands and increase in the FWHM values. The broadening of the Raman bands is considered to be due to phonon confinement.¹⁷

GaS and GaSe are both layered materials having mica-like morphology. We could exfoliate bulk GaS and GaSe in *N*-methylpyrrolidone (NMP) to form stable dispersions of the materials mainly containing one to three layers. Fig. 6(a) shows the sheet-like morphology of GaSe while Fig. 6(b) gives the AFM image with a height profile of 1.3 nm confirming the formation of few-layered GaSe.

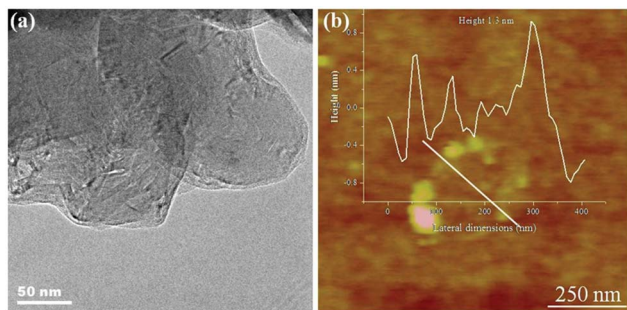


Fig. 6 (a) TEM image of GaSe sheets obtained by liquid-phase exfoliation (b) AFM image and the associated height profile of GaSe.

In conclusion, it has been possible to synthesize graphene analogues of layered metal selenides by chemical methods as well as by liquid-phase exfoliation in NMP. The chemical methods employed here can be extended to obtain graphene analogues of other layered materials. These graphene-like materials may find applications in the fabrication of devices. We have been

able to fabricate transistors with graphene-like molybdenum chalcogenides.

Notes and references

‡ Synthesis:

Method 1: MoSe₂ and WSe₂ were intercalated and exfoliated in two steps. In the first step, 100 mg MoSe₂/WSe₂ were weighed and soaked in 10 ml of *n*-butyllithium¹⁸ in 20 ml of hexane and refluxed in a nitrogen atmosphere for 48 h at 373 K. The intercalated samples were washed with hexane several times to remove any excess *n*-butyllithium. In the second step exfoliation of the Li-intercalated samples was carried out in distilled water, followed by ultra-sonication for 10 min. In the process, evolution of H₂ gas occurred with the formation of an opaque suspension of the layered selenide. The suspension was centrifuged and the solid product was collected for further characterization. **Method 2:** MoSe₂ layers were prepared using a hydrothermal method wherein 1 mmol of molybdic acid, 2 mmol of selenium metal and 30 mmol of NaBH₄ were taken in 10 ml of deionised water in a 23 ml capacity of Teflon-coated autoclave and heated at 453 K for 24 h to yield few-layer MoSe₂. The product obtained was washed with ethanol and dried at 278 K and characterized further. (yield ~75%) **Method 3:** Layered MoSe₂ and WSe₂ were prepared using selenourea as the selenium source. In a typical synthesis, molybdic acid or tungstic acid was ground with excess of selenourea (molybdic acid (0.032 g)/tungstic acid (0.049 g):thiourea (1.18 g) ≡ 1:48) and heated at 773 K for 3 h under nitrogen atmosphere with heating rate of 20 °C min⁻¹. The product was cooled to room temperature in a nitrogen atmosphere (yield ~60%).

Characterization: The products of the above reactions were characterized by various techniques. X-Ray diffraction (XRD) patterns were recorded using Cu-Kα radiation on a Rich-Siefert XRD-3000-TT diffractometer. FESEM images were obtained using a FEI NOVA NANOSEM 600. EDAX was carried out with the same system. TEM images and atomic arrangement of hexagonal MoSe₂ and WSe₂ in Fig. 3 (no reconstruction) were obtained from the FEI TITAN (cube) 80–300 kV aberration corrected transmission electron microscope with a negative spherical aberration coefficient (Cs) of ~–30 μm and a positive defocus about +8 nm, where atomic potentials appear with bright contrast in a dark background. AFM measurements were carried out with Veeco digital instruments, di Innova. Samples for AFM measurements were prepared by spin coating the MoSe₂ and WSe₂ solutions on Si substrate. Raman spectra of samples were recorded with a 515.5 nm Ar laser using JobinYvon Lab Ram HR spectrometre.

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