Layered Compounds

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# $MoS_2$ and $WS_2$ Analogues of Graphene

*H. S. S. Ramakrishna Matte, A. Gomathi, Arun K. Manna, Dattatray J. Late, Ranjan Datta, Swapan K. Pati, and C. N. R. Rao**

Following the discovery of fullerenes[1] in 1985, it was soon recognized that inorganic layered materials such as $MoS_2$ and $WS_2$ can also form fullerene-like structures.[2] After the discovery of carbon nanotubes,[3] inorganic nanotubes analogous to carbon nanotubes were prepared and characterized, nanotubes of $MoS_2$ and $WS_2$ being archetypal examples.[4] With the discovery and characterization of graphene, that is, two-dimensional nanocarbon, which has created great interest in last few years,[5] it would seem natural to explore the synthesis of graphene analogues of layered inorganic materials such as dichalcogenides of molybdenum and tungsten.[6] We aim to prepare graphene-like $MoS_2$ and $WS_2$, which are quasi-two-dimensional compounds in which the atoms within the layer are held together by strong covalent forces while van der Waals interaction enables stacking of the layers. Synthesis of crystals of $MoS_2$ containing several molecular layers by micromechanical cleavage has been reported,[7] and optical absorption and photoconductivity of these films have been studied.[8] There is also a report on the intercalation of alkali metals with layered metal dichalcogenide crystals with controlled stoichiometry, but the products of exfoliation were not examined in this study.[9] There is an early report[10] on graphene-like $MoS_2$ prepared by lithium intercalation and exfoliation, but the material was characterized only by X-ray diffraction, which is not sufficient to determine the exact nature and number of layers. Attempts were made to prepare single layers of $WS_2$ by lithium intercalation and exfoliation as well,[11,12] but here again the product was only characterized on the basis of the (002) reflection in the X-ray diffraction pattern. Schumacher et al.[13] and Gordon et al.[14] prepared $MoS_2$ samples by lithium intercalation followed by exfoliation and characterized the products by means of scanning force microscopy and X-ray absorption fine structure spectroscopy. Yang et al.[15] report that the exfoliated $MoS_2$ forms aqueous suspensions of single layers wherein sulfur atoms are bonded with molybdenum in an octahedral arrangement with $2a_0$ superlattice. Suspensions of layered chalcogenides have also been used to prepare inclusion compounds of various organic molecules[16] and to fabricate light-emitting diodes.[17] Since even $MoS_2$ and $WS_2$ containing five layers do not exhibit the (002) reflection prominently, layered $MoS_2$ and $WS_2$ produced by lithium intercalation and exfoliation must be investigated by transmission electron microscopy and other techniques. Furthermore, it seems desirable to explore alternative syntheses of these graphene-like materials. To this end, we employed three different methods to synthesize graphene-like $MoS_2$ and $WS_2$.

In Method 1, bulk $MoS_2$ and $WS_2$ were intercalated with lithium and exfoliated in water. The reaction between lithium-intercalated $MoS_2$ and $WS_2$ and water forms lithium hydroxide and hydrogen gas and leads to separation of the sulfide layers and loss of periodicity along the *c* axis. In Method 2, molybdic acid and tungstic acid were treated with an excess of thiourea in an $N_2$ atmosphere at 773 K. Method 3 involved the reaction between $MoO_3$ and KSCN under hydrothermal conditions.[18] The products of these reactions were characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), field-emission scanning electron microscopy (FESEM), Raman spectroscopy, and X-ray diffraction (XRD).

The XRD patterns of the molybdenum sulfide samples obtained by the three methods do not exhibit the (002) reflection (Figure 1a). Energy-dispersive analysis of X-rays (EDAX) shows the products to be stoichiometric $MoS_2$. The TEM and AFM images of the products show the presence of one or a few layers of $MoS_2$ (Figures 2 and 3). Figure 2a and b show graphene-like $MoS_2$ layers obtained by methods 2 and 3 with a layer separation in the range of 0.65–0.7 nm. The high-resolution image in Figure 2c shows the hexagonal structure formed by Mo and S atoms with an Mo–S distance of 2.30 Å. The AFM images and height profiles of the products also confirm the formation of few-layer $MoS_2$ (Figure 3a). Figure 4a compares the Raman spectra of graphene-like $MoS_2$ samples with that of bulk $MoS_2$. The bulk sample shows bands at 406.5 and 381.2 $cm^{-1}$ due to the $A_{1g}$ and $E_{2g}$ modes with full-widths at half maximum (FWHM) of 2.7 and 3.1 $cm^{-1}$, respectively. Interestingly, few-layered $MoS_2$ prepared by lithium intercalation exhibits corresponding bands at 404.7 and 379.7 $cm^{-1}$. The sample obtained by Method 2 show these bands at 404.7 and 377.4 $cm^{-1}$. The $A_{1g}$ and $E_{2g}$ modes in the graphene analogues of $MoS_2$ are clearly softened. Furthermore, the FWHM values are larger in the graphene-like samples (10–16 $cm^{-1}$ vs. ca. 3 $cm^{-1}$ in the bulk sample). Broadening of the Raman bands is considered to be due to phonon confinement, and also suggests that the lateral dimensions of these layers are in the nanoregime.[19] We also prepared graphene-like $MoS_2$ by micromechanical cleavage of a $MoS_2$ single crystal using the Scotch-tape technique. Raman spectra of these samples show progressive softening of the $A_{1g}$ and $E_{2g}$ bands with decreasing number of layers.

[*] H. S. S. Ramakrishna Matte, A. Gomathi, A. K. Manna, Dr. D. J. Late, Dr. R. Datta, Prof. Dr. S. K. Pati, Prof. Dr. C. N. R. Rao
Chemistry and Physics of Materials Unit, Theoretical Science Unit and International Centre for Materials Science
Jawaharlal Nehru Centre for Advanced Scientific Research
Jakkur P.O., Bangalore 560 064 (India)
Fax: (+91) 80-2208-2760
E-mail: cnrrao@jncasr.ac.in

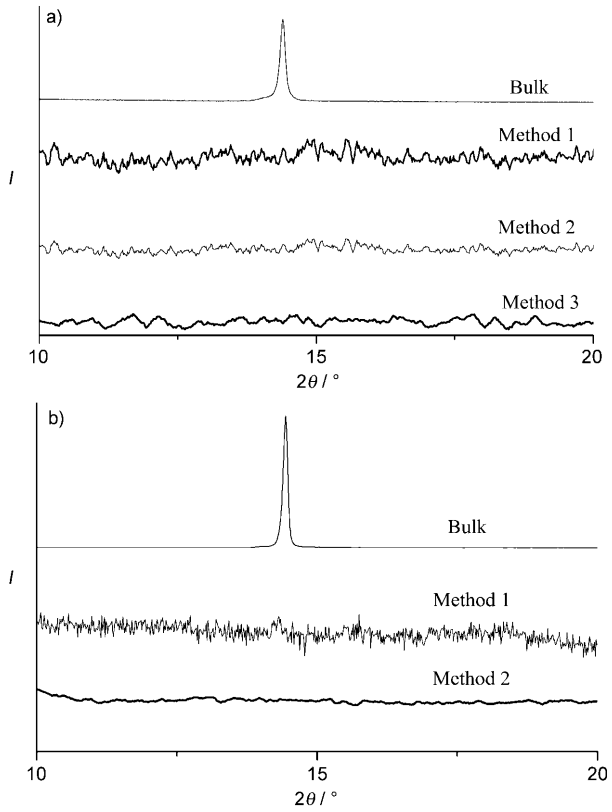


***Figure 1.*** Comparison of XRD patterns of a) bulk $MoS_2$ and $MoS_2$ layers obtained by Methods 1–3 and b) bulk $WS_2$ and $WS_2$ layers obtained by Methods 1 and 2.

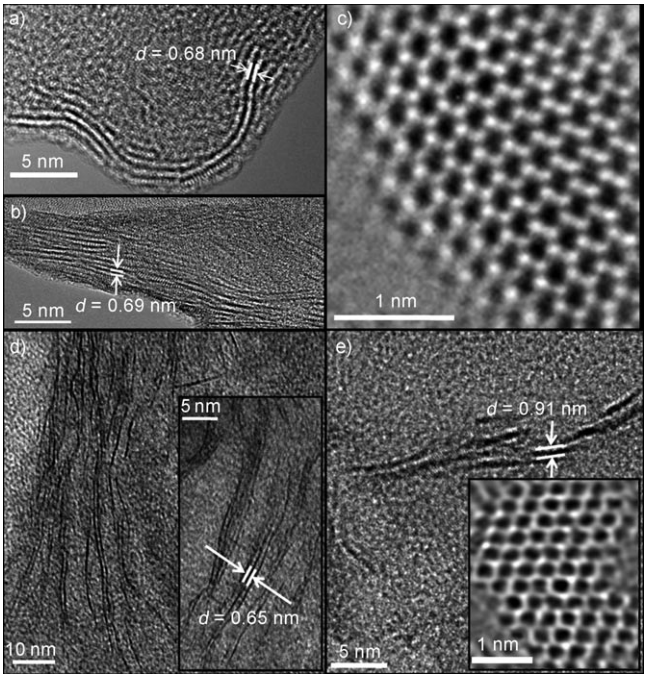


***Figure 2.*** a, b) TEM images of $MoS_2$ layers obtained by Methods 2 and 3. c) High-resolution TEM image of layered $MoS_2$ from Method 3. d, e) Images of $WS_2$ layers from Methods 1 and 2, respectively. The bends in the layers may arise from defects.

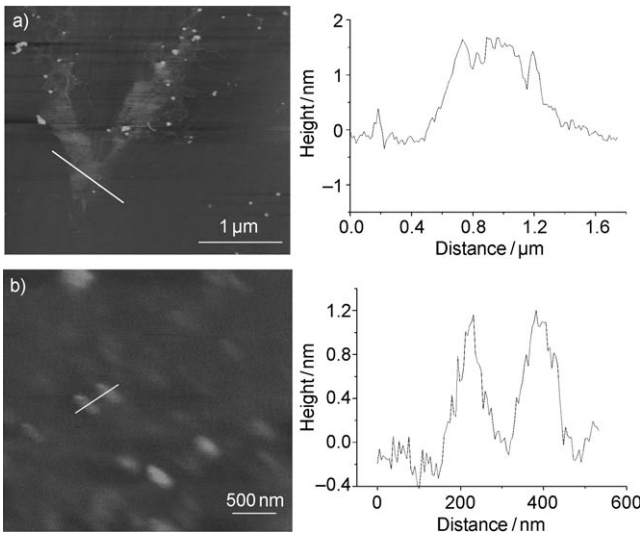


***Figure 3.*** AFM images and associated height profiles of a) $MoS_2$ layers obtained by Method 2 and b) $WS_2$ layers obtained by Method 1.

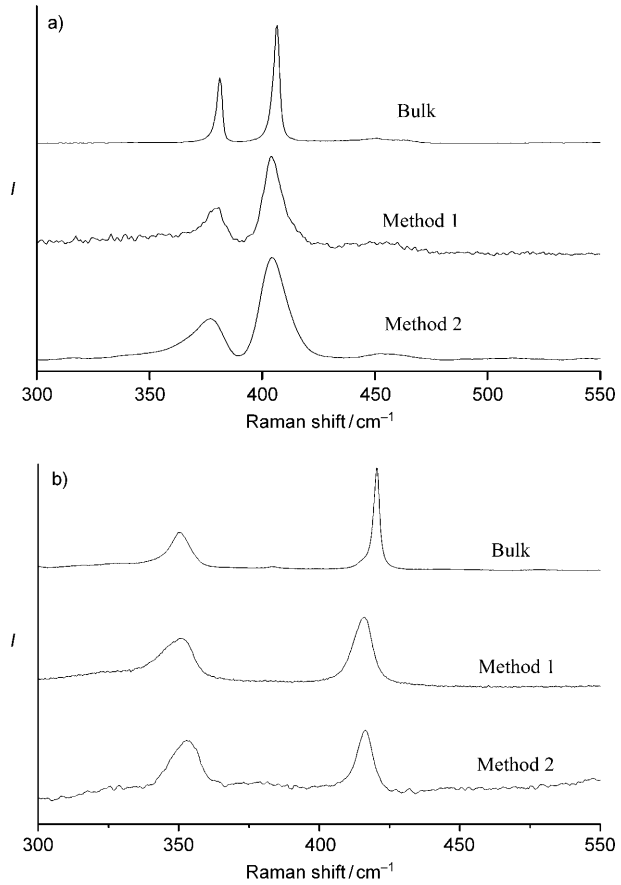


***Figure 4.*** Raman spectra of a) bulk $MoS_2$ and $MoS_2$ layers obtained by Methods 1 and 2 and b) of bulk $WS_2$ and $WS_2$ layers obtained by Methods 1 and 2.

Graphene analogues of $WS_2$ were prepared by Methods 1 and 2. The XRD patterns of these samples show the absence of the (002) reflection (Figure 1 b), while EDAX analysis confirms the stoichiometry of the products to be $WS_2$. The

  

TEM images in Figure 2d and e reveal that $WS_2$ obtained by both methods 1 and 2 mostly consists of bilayers and single layers. The separation between the $WS_2$ layers in the bilayer sample is in the range of 0.65–0.70 nm. $WS_2$ layers obtained by the thiourea method show an interlayer spacing of 0.9 nm.

The AFM images and height profiles of $WS_2$ obtained by method 1 confirm the existence of two or three layers of $WS_2$ with an average thickness of 1.3 nm (Figure 3b). The presence of bilayers of $WS_2$ in the sample obtained by the thiourea method was also confirmed by AFM studies. Raman spectra of $WS_2$ obtained by both methods show softening of the bands due to the $A_{1g}$ mode (see Figure 4b). Compared to the narrow bands at 351 ($E_{2g}$) and 420 $cm^{-1}$ ($A_{1g}$) of bulk $WS_2$ with FWHM values around 7.8 and 2.4 $cm^{-1,}$ respectively, the spectrum of $WS_2$ obtained by lithium intercalation shows bands at 350 and 415 $cm^{-1}$ with FWHM values of 13.7 and 8.4 $cm^{-1}$, respectively. The Raman spectrum of $WS_2$ layers synthesized by Method 2 also show similar softening of the Raman bands and increased FWHM.

We studied 3D and 2D $MoS_2$ structures and their electronic and phonon properties using the density functional theory package SIESTA[20] within the generalized gradient approximation (GGA), considering Perdew–Burke–Ernzerhof (PBE) exchange and correlation functional[21] with double-ζ polarized (DZP) basis sets. From the optimized geometry of layered $MoS_2$, it is clear that the Mo and S atoms are covalently linked in the triple layers with effective coordination numbers of six and three for Mo and S atoms, respectively. The Mo–S bond length and Mo-S-Mo (or S-Mo-S) bond angle are 2.41 Å and 82.41°, respectively, and the estimated thickness of the triple layer is 3.17 Å. Layered $MoS_2$ has an indirect band gap (Γ→K) and a direct gap of 1.70 eV at the K point, whereas bulk $MoS_2$ has an indirect band gap (Γ→K) of 1.06 eV (see Figure 5a and b). The total and projected density of states for layered and bulk $MoS_2$ show that both systems have a nonzero indirect band gap near $E_F$ with a smaller gap value for the bulk system, the major contribution to which comes from the outermost d orbitals of the Mo atoms.

We calculated the full phonon dispersion along all the high-symmetry points in the Brillouin zone. Layered $MoS_2$ has three atoms per unit cell, and nine phonon modes are therefore expected (thee acoustic and six optical modes). Considering the point group for this system to be $C_{3v}$, there will be three $A_1$ modes and three doubly degenerate E modes. In the case of bulk $MoS_2$, the unit cell consists of six atoms resulting in 18 phonon modes (three acoustic and 15 optical modes). Similarly, at the Γ point, all modes can be assigned by the irreducible representations of the $D_{6h}^4$ ($P6_3/mmc$) space group. The phonons soften on going from the bulk system to layered $MoS_2$. The two E optical and one E acoustic phonons are nearly doubly degenerate at the Γ point (Figure 5c). Interestingly, the layer phonons have lower energies than bulk phonons, in corroboration of the current and earlier experimental findings.[22,23]

The $A_1$ optical phonon modes soften by 6–9 $cm^{-1}$ on going from bulk to single-layer $MoS_2$ structure. However, the softening of the doubly degenerate optical E phonon modes is comparatively smaller (ca. 3–7 $cm^{-1}$), because the in-plane vibration of the layered atoms creates the doubly degenerate E modes, whereas the out-of plane vibration gives rise to $A_1$ modes, which are thereby affected to a greater extent. The overall softening of phonon energies can be attributed to the fact that, in contrast to the bulk sample, the surface S atoms are not vibrationally frozen by the next layer in the layered sample, and lower force constants result.

In summary, we have prepared $MoS_2$ and $WS_2$ analogues of graphene with one or two to three layers by different chemical methods. Graphene-like $MoS_2$ may find applications as a solid-state lubricant. It should be possible to prepare graphene analogues of other layered materials as well, and these may be useful to prepare novel polymer composites. Inorganic analogues of graphene are new two-dimensional members of the larger family of inorganic nanocarbon analogues, of which the zero-dimensional fullerenes and one-dimensional nanotubes are already well known.

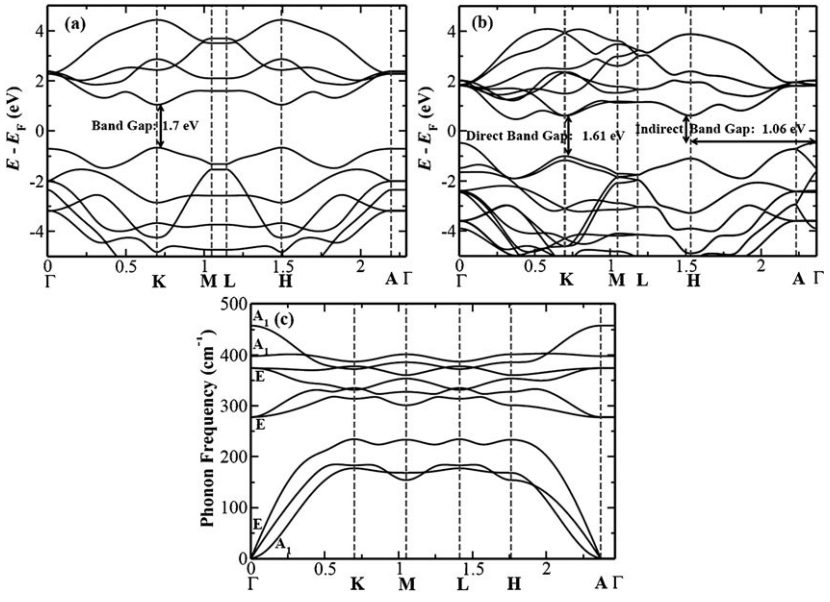


***Figure 5.*** Electronic band structure of a) single-layered $MoS_2$, b) bulk $MoS_2$, and c) full phonon dispersion of single-layered $MoS_2$ at all high-symmetry points in the Brillouin zone. The energy is scaled with respect to the Fermi energy $E_F$.

## *Experimental Section*

Method 1: Intercalation and exfoliation of $MoS_2$ and $WS_2$ were done in two steps. The first step was to intercalate the sulfide with lithium by soaking 100 mg of the sulfide in 10 mL of *n*-butyllithium in 5 mL of hexane in a nitrogen atmosphere for 72 h at 373 K. The intercalated samples were washed with hexane several times to remove any unreacted *n*-butyllithium. The intercalated sample was exfoliated by ultrasonication with distilled water in a closed vial, during which profuse evolution of gas was observed and an opaque suspension of the layered sulfide was

  

formed. The suspension was centrifuged and the solid product collected for further characterization.

Method 2: In a typical synthesis, molybdic acid or tungstic acid was ground with an excess of thiourea (molybdic acid/tungstic acid:thiourea 1:48) and heated at 773 K for 3 h under nitrogen atmosphere. After 3 h, the sample was cooled to room temperature under nitrogen atmosphere. The black product obtained was used as such for further analysis.

Method 3: $MoS_2$ layers were prepared by hydrothermal treatment of 1 mmol of molybdic oxide and 2.5 mmol of KSCN in 10 mL of deionized water in a 23 mL Teflon-coated autoclave at 453 K for 24 h. The product was washed with water, and dried at 278 K, and characterized further.

Characterization: XRD patterns were recorded with $Cu_{K\alpha}$ radiation on a Rich-Siefert XRD-3000-TT diffractometer. FESEM images were obtained with an FEI Nova NanoSEM 600. TEM images and atomic arrangements of hexagonal $MoS_2$ and $WS_2$ in Figure 2 (no reconstruction) were obtained from an FEI Titan (cube) 80–300 kV aberration-corrected transmission electron microscope with a negative spherical aberration coefficient of $C_s \approx -30$ μm and a positive defocus of $+8$ nm, whereby atomic potentials appear with bright contrast on a dark background. Raman spectra of $MoS_2$ samples were obtained with a 514 nm Ar laser, and those of $WS_2$ samples were recorded with a 632 nm HeNe laser in a Jobin Yvon LabRam HR spectrometer. AFM measurements were carried on Vecco digital instruments, di Innova. Samples for AFM measurements were prepared by spin coating $MoS_2$ and $WS_2$ solutions onto mica substrate.

Methods of calculation: We treated the three-dimensional bulk system as two triple layers per unit cell stacked in hexagonal symmetry. We considered six- and three-atom unit cells for bulk and 2D layered $MoS_2$, repectively, for electronic-structure calculations. We considered a 300 Rydberg energy cutoff for a real-space mesh size and a *k*-point sampling of 28 for structural relaxation, and 60 and 600 *k*-points for the single-point calculations, uniformly distributed along the 2D and 3D hexagonal Brillouin zone, respectively. We calculated the full phonon dispersion by the finite difference approach, setting up the dynamical matrix from the induced forces.

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