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Electronic and vibrational decoupling in chemically exfoliated bilayer 2D-V₂O₅

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Abstract:

Recently emerged transition metal oxide (TMO) based 2D nanostructures are gaining a foothold in advanced applications. Unlike, 2D transition metal dichalcogenides, it is strenuous to obtain high quality thin TMOs due to exotic surface reconstruction during synthesis. Herein, we report the synthesis of bilayer thin 2D-V₂O₅ nanosheets using chemical exfoliation. Synchrotron X-ray diffraction, X-ray photoelectron spectroscopy and atomic force microscopy substantiate the successful formation of bilayer thin 2D-V₂O₅. Ultraviolet-visible absorption spectra exhibit a thickness dependent blue shift in the optical band gap, signifying the emergence of electronic decoupling. Raman spectroscopy fingerprinting shows a thickness dependent vibrational decoupling of phonon modes. Further, it has been verified by computing the lattice vibrational modes using density functional perturbation theory. In this study, the manifestation of the electronic and vibrational decoupling is used as a novel probe to confirm the successful exfoliation of bilayer 2D-V₂O₅ from its bulk counterpart.

KEYWORDS: Bilayer 2D-V₂O₅, Atomic force microscopy, Electronic and vibrational decoupling, Raman spectroscopy, Optical band gap, DFT calculation

Since the discovery of graphene, a new era of two-dimensional (2D) materials originated in material science and nanomaterial based scientific research. The discovery drew enormous attention of material scientists due to the exceptional physical, chemical and electronic properties of graphene. Later on, there were new admissions to the family of 2D materials namely, monolayer transition metal dichalcogenides (TMD)^{1,2,3}, 2D-*h*-BN⁴, MXenes^{5,6}, phosphorene⁷, silicene⁸, germanene⁹ and monolayer transition metal oxides (TMO)^{10,11}. These materials are employed in various applications including photonics, electronics, catalysis, gas sensing and alkali / alkaline earth metal based ion batteries^{11,12,13,14}. Subsequently, the discovery of 2D hybrid hetero-structures broadened the horizon. 2D hetero-structures, fabricated by vertical van der Waals stacking as well as lateral stitching, are employed in various cutting-edge devices^{15,16,17}.

2D-TMOs stand out from other 2D materials due to their capability of existing in different binding configurations¹⁴. Unlike other 2D materials, 2D-TMOs are difficult to synthesis due to possible instability and consecutive surface reconstruction, which can happen during the synthesis process. In most of the cases, the existence of strong ionic bonds causes the creation of many dangling bonds on the surface during the process of synthesis. To compensate the instability, a large structural reconstruction happens on the 2D metal oxide surface¹⁸. There are layered and non-layered TMOs. Layered TMOs can be delaminated using several exfoliation techniques and some bottom-up growth techniques, whereas non-layered TMOs are normally synthesized by oxidizing metal surfaces or by physical vapor deposition techniques^{19, 20}. Layered TMOs like TiO₂ can be exfoliated using cation assisted liquid exfoliation technique²¹. Other layered TMOs such as MoO₃ and V₂O₅ are having layers bound together with weak van der Waals force. For such materials, chemical exfoliation is an appropriate method for large scale synthesis of 2D layers. Liquid exfoliation and gas driven exfoliation are commonly used techniques for the synthesis of 2D nanosheets^{22,23,24}. Electrochemical intercalation with alkali or alkaline earth metals (Li, Na, Mg and others) and micromechanical exfoliation techniques can also be employed for exfoliating layered TMOs²⁵. Besides these top-down approaches, a few bottom-up methods such as atomic layer deposition and hydrothermal synthesis of ultrathin layers of TMOs are also reported in the literature^{26, 27}.

Among the layered TMOs, 2D-V₂O₅ is a less explored van der Waals oxide. There are only very few attempts towards the synthesis of 2D-V₂O₅ using liquid exfoliation^{24,28}, gas-assisted exfoliation^{22,29} and hydrothermal synthesis²⁷. A few layer thick V₂O₅ nanosheets have been employed as cathode material in Li, Zn and S ion batteries^{22,24,27} owing to its augmented properties like improved cycle stability, ultrafast performance and higher charge storage capacity. It also finds use in aerobic oxidative desulfurization applications²⁹ due to higher surface to volume ratio in catalytic applications. Most of these studies deal with the ‘thick 2D layers’ which show enhanced properties from the bulk, and not of a true bilayer or a monolayer. Apart from a few theoretical attempts³⁰, comprehensive studies on the properties of 2D-V₂O₅ nanostructures with thickness down to bilayer or monolayer have not been reported,.

In the present study, we report the synthesis of a bilayer thin 2D-V₂O₅. There are only a few oxides such as TiO₂, Co₃O₄ and MoO₃^{18,31,32} for which the monolayer or bilayer have been synthesized to date, henceforth adding more importance to our study. The present report is the first experimental observation of electronic and vibrational decoupling in bilayer 2D-V₂O₅. To substantiate this, a detailed investigation using synchrotron XRD, atomic force microscopy, X-ray photoelectron and UV-visible absorption spectroscopy along with density functional theory calculations have been performed in a systematic manner.

RESULTS

Synthesis and characterization of 2D nanosheets of V₂O₅

A modified method of exfoliation by optimizing the concentration of bulk V₂O₅ in formamide was used for the synthesis of 2D-V₂O₅ nanosheets. A schematic diagram of the exfoliation process is given in Figure 1a. After intercalation with the formamide molecules, the bulk V₂O₅ powder swelled due to the increase in interlayer separation. The dispersion was then ultrasonicated to set the layers free which delaminated the swelled crystal into thin nanosheets. The samples made with concentrations of 6 and 1 mM are designated as S1 and S2, respectively. The exfoliated layers form a clear suspension in formamide (Figure 1b)

Figure 1. a) Schematic diagram showing the exfoliation of α - V_2O_5 using formamide as the intercalating agent. b) Photographs of sample suspension in formamide for S1 and S2 (prepared at a concentration of 6 and 1 mM, respectively). c) FESEM images of exfoliated V_2O_5 nanosheets S1 and S2. The inset shows magnified views of the respective images. View of the structure of monolayer 2D- V_2O_5 along d) c -axis and e) a -axis, f) Square pyramidal coordination geometry of V^{5+} . Vanadyl, bridge and chain oxygen are marked as O_I , O_II and O_III respectively. O_III and O_III' are triply coordinated with V atom with different bond lengths. g) X-ray diffraction pattern of bulk V_2O_5 precursor and the exfoliated samples S1 and S2

Figure 1c shows FESEM images of the samples S1 and S2 transferred over SiO_2/Si substrate. It is clear from the images that the layers delaminated at lower concentration (S2) are more flat and less agglomerated than the layers prepared at higher concentration (S1). It can also

be observed that the morphology of the exfoliated layers depends on the concentration. The lateral dimension of exfoliated layers in S2 is in ~100-300 nm range. Structural characterizations of exfoliated samples and the bulk V_2O_5 precursor were carried out using the X-ray diffraction technique. The diffraction patterns are shown in Figure 1g. The bulk V_2O_5 precursor is indexed to the α -polymorph, belonging to the space group $Pmmn$ with lattice parameters $a=11.516\text{\AA}$, $b=3.566\text{\AA}$ and $c=4.372\text{\AA}$ (ICDD 00-041-1426). α - V_2O_5 is a layered orthorhombic crystal with adjacent layers bound with weak van der Waals force. The crystal structure is composed of an arrangement of the corner and edge-sharing VO_5 square pyramidal units along a and b directions, respectively (Figures 1d and 1e). V atom in the VO_5 square pyramidal block is having three types of structurally distinct O atoms. There are singly, doubly and triply coordinated atoms which are named, vanadyl (O_I), chain (O_{II}) and bridge (O_{III}) O atoms^{33, 34}, respectively (Figure 1f). XRD pattern showed persuasive evidence for the exfoliation of V_2O_5 ; exfoliated layers in the sample S1 exhibited a prominent peak corresponding to (001) reflection indicating a massive reduction of the thickness of the V_2O_5 layer in the direction of c -axis (Figure 1g). Hence it can be inferred that the exfoliation has materialized successfully³⁵. The absence of any peaks in the exfoliated layers in sample S2 can be interpreted as further reduction in thickness (Figure 1g)^{36,37}. The broad background in the XRD patterns collected from the samples S1 and S2 are due to the $SiO_2(300\text{ nm})/Si$ substrate on which the sample is deposited.

Raman spectroscopy and XPS studies.

Figure 2. a) Raman spectra of bulk V_2O_5 precursor and exfoliated samples S1 and S2, prepared at concentrations 6 and 1mM respectively. b) Change in Raman mode frequencies of exfoliated samples from bulk. Dotted lines are a guide to the eye. c) XPS survey spectra of S1 and S2. d) Core level V2p spectra with peaks corresponding to binding energy of $V_{2p_{3/2}}$ and $V_{2p_{1/2}}$. The deconvoluted peaks show the existence of oxygen vacancy defects in the samples S1 and S2.

Figure 2a shows the Raman spectra for bulk and exfoliated nanosheets of V_2O_5 . The bulk V_2O_5 and sample S1 showed peaks corresponds to 10 Raman active modes^{30,38,39}. Raman spectroscopic study of sample S2 revealed nine vibrational modes at 111, 162, 267, 324, 493, 539, 619, 711 and 1010 cm^{-1} . All modes except the one centered at 1010 cm^{-1} are fitted with Gaussian-Lorentzian line shape (Figure *S-1a* in supplementary information). The mode at 1010 cm^{-1} is separately fitted with Breit–Wigner–Fano (BWF) line shape function owing to its asymmetric nature (Figure *S-1b* in supplementary information). Mode frequencies of B_{2g}^2 and A_{1g}^4 at around 198 and 405 cm^{-1} , respectively, are not detected in bilayer 2D- V_2O_5 since the intensity of both the modes decreases beyond the detection limit due to very less amount of sample in the laser exposed area. The observed Raman shift and the corresponding linewidth for bulk V_2O_5 , samples S1 and S2 are shown in Figure 2b and Figure *S-2* in supplementary information, respectively. Ultrathin layers of V_2O_5 in sample S2 showed significantly broadened peaks along with considerable shifts from the mode frequencies of bulk V_2O_5 . There is a blue shift from the bulk values, observed for the modes at 111, 162, 324, 493, 539, 711 and 1010 cm^{-1} . On the other hand, a red shift is observed for the mode at 267 cm^{-1} . The peak at 619 cm^{-1} appears due to the possible removal of vanadyl oxygen (O_i) during the exfoliation process. To elucidate the presence of oxygen vacancy defects in the sample, XPS studies were carried out. The XPS survey spectra of samples S1 and S2 are shown in Figure 2c. Both the samples show peaks at 517.4 ($V2p_{3/2}$), 524.8 ($V2p_{1/2}$) and 530.1 ($O1s$) indicating the presence of V_2O_5 in the samples⁴⁰. The deconvoluted peaks at 517.4 and 516.3 eV in the core level spectrum corresponds to the binding energy of $V2p_{3/2}$ for V^{5+} and V^{4+} states, respectively (Figure 2d). The peaks corresponding to the binding energy of $V2p_{1/2}$ for V^{5+} and V^{4+} states are observed at 524.8 and 523.1 eV, respectively⁴⁰. These observations indicate the presence of oxygen vacancy defects in the samples. The oxygen vacancy defect in both the samples were calculated using the area under the curve and it is ~18 and 17%, respectively, for S1 and S2. In addition, the peak at 400.2 eV is identified to appear due to the presence of quarternary nitrogen functional group^{41,42}. It can be observed that the presence of this functional group is marginal in S2. The observed oxygen vacancies are predominantly attributed to the loss of O_i owing to the lowest formation energy^{39,43}. On the removal of O_i , the appearance of a new mode can occur due to the local reduction, resulting in other VO_x phase with a possible change in the local symmetry. A Raman mode at 615 cm^{-1} is

reported elsewhere for VO_2 ^{44,45}. The peak at 621 cm^{-1} is observed only in S2, because of the possible surface reconstruction in the thinnest exfoliated nanosheets in the sample. An asymmetry is observed for the peak at 1010 cm^{-1} in the Raman spectrum of S2 (Figure *S-1b* in supplementary). This mode appears due to the stretching vibration of $\text{V}-\text{O}_i$ along the c -axis³⁰. It may be noted that this high-frequency mode is an out-of-plane vibration and the other phonon modes are either in-plane or a combination of both in-plane and out-of-plane modes. The observed asymmetry in the high frequency mode indicates that the exclusive out-of-plane mode is more prone to changes while reducing the number of layers than the other modes. The mode at 1010 cm^{-1} is fitted with Fano line shape (Figure *S-1b* in supplementary information) because of the possible increase in electronic activities with the loss of O and resultant surface reconstruction. The broadened peaks are indications of a decrease in phonon lifetime, which occurs because of the presence of O vacancy defects in the exfoliated layer and the decrease in thickness. Though the thickness reduction is conspicuous in sample S1 from synchrotron XRD, the change in vibrational modes is marginal in this sample in comparison to bulk (Figure 2b). At the same time, the change in mode frequency shift and broadening is more apparent in the thinnest sample S2, indicating a vibrational decoupling of modes from bulk to reduced thickness sample.

Measurement of thickness of exfoliated nanosheets using AFM

Further to measure the thickness of the “thinnest” nanosheets in the sample S2, atomic force microscopic (AFM) studies are carried out. Figure 3 shows the AFM image of the well dispersed layers. As shown in the height profile, thicknesses of the individual layers are observed to be in the range of 1.0-1.5 nm. The standard deviation of the measured step height is about 0.1 nm. The thickness of monolayer $2\text{D}-\text{V}_2\text{O}_5$ is approximately 0.43 nm and thus a typical bilayer V_2O_5 should have a thickness of about 0.87 nm, while trilayer should have a thickness greater than 1.3 nm (Figure *S-3* in supplementary information). In the present study, thicknesses of the individual layers in S2 are in the range of 1.0 - 1.5 nm, which counts upto 2 to 3 monolayers. Though the sample is an ensemble of bilayer or trilayer $2\text{D}-\text{V}_2\text{O}_5$, the number distribution of the thickness of flakes shown in Figure 3, indicate the presence of considerably higher number of bilayer thin nanosheets in the sample. Fig *S-4* (in supplementary) shows the line profiles in several other areas used to obtain the statistical average.

Figure 3. AFM image of exfoliated ultrathin layers of V_2O_5 , line profile of height measured across the nanosheets, labeled as 1 and 2 and the number distribution of exfoliated layers with the thickness are shown in the right side. Thicknesses from 1.0 to 1.5 nm are observed, which counts to 2 -3 layers of V_2O_5 .

Ultraviolet-Visible absorption spectroscopy.

The optical properties of materials are very sensitive to their dimension, and the variation is drastic when the dimension decreases down to nanometer-scale. For this reason, bulk and exfoliated V_2O_5 samples are characterized using ultraviolet-visible (UV-Vis) absorption spectroscopy. V_2O_5 is having O-2p derived main valence band and V-3d derived conduction band. Herein, the optical absorption energy of allowed direct transition was found using Tauc's method. The UV-Visible absorption spectra of bulk and exfoliated samples are given in Figure 4a. The direct band transition which is allowed by momentum conservation obeys the relation, $\alpha h\nu \propto (h\nu - E_g)^{1/2}$ (α - absorption coefficient of the material, E_g - band gap). Consequently, the x -intercept of the extrapolation of linear portion of the curve in Tauc's plot provides the value of direct band gap.

Figure 4 a) UV-Vis absorption spectra of bulk V_2O_5 and exfoliated samples S1 and S2. b) Tauc's plot for three samples showing the direct band gap. The values of band gap for bulk V_2O_5 , S1 and S2 are around 2.39, 2.67 and 3.72 eV, respectively.

Optical band gap of bulk V_2O_5 , S1 and S2 are measured to be 2.39, 2.67 and 3.72 eV, respectively (Figure 4b). The GW calculations with polarization correction predict a direct band gap at 2.6 eV and an indirect band of 1.98 eV for bulk V_2O_5 . At the same time, the direct band gap of 4.91 eV is predicted for monolayer 2D- V_2O_5 . There is a substantial change in the band gap with thickness reduction. In the present study, the band gap values obtained are in qualitative agreement with theoretical predictions. The observed blue shift in optical band gap from bulk to bilayer 2D- V_2O_5 is 1.33 eV, which is in trend with the theoretically predicted shift of ~ 2.3 eV for monolayer⁴⁶. The discrepancy in magnitude of the shift stems from the existence of strong excitonic effects in bilayer 2D- V_2O_5 ^{46,47}. The observation of absorption edge blue shift from bulk to bilayer 2D- V_2O_5 indicates the electronic decoupling with the decrease in layer thickness and further confirms the formation of two layer thick flakes of 2D- V_2O_5 in the sample S2.

Theoretical calculations

To further validate the vibrational decoupling from bulk to the lower thickness and a consequent shift in Raman mode frequencies, the phonon modes of bulk and monolayer 2D- V_2O_5 were computed using first principle density functional theory (DFT) calculations. Schematic views of the structure of monolayer 2D- V_2O_5 along c - and a - axes are shown in Figure 1d and e,

respectively. In Figure 1f, O_{III} and O_{III'} are triply coordinated with V atom with different bond lengths, 1.8844 Å and 1.9787 Å, respectively. The unit cell contains 14 atoms and it is composed of two formula units of V₂O₅. Group theoretical analysis showed that monolayer V₂O₅ belongs to D_{2h} point group. Since the unit cell contains 14 atoms, 42 vibrational modes are expected; in which 3 are acoustic and the remaining 39 are optic modes. From the factor group analysis, the optic modes at Γ point can be written as, $\Gamma_{\text{optic}} = 3A_{1u} + 6B_{1u} + 3B_{2u} + 6B_{3u} + 7A_{1g} + 3B_{1g} + 7B_{2g} + 4B_{3g}$. Out of these 39 vibrational modes, 21 are Raman active modes. The phonon dispersion of monolayer V₂O₅ is shown in Figure S-5. All modes are real and positive, indicating the structural stability of the monolayer V₂O₅. It is worth noting that all phonon modes are least dispersive along the out-of-plane direction in the Brillouin zone ($\Gamma \rightarrow Z$), which is a consequence of the 2D nature of the system.

DISCUSSION

The calculated phonon frequencies of monolayer and bulk V₂O₅ were compared with the experimental observation and compiled in Table 1. All low-frequency modes with a frequency less than 336 cm⁻¹ show red shift, while all higher frequency phonon modes tend to blue shift from the mode frequencies of bulk V₂O₅. Hence, the vibrational decoupling in monolayer 2D-V₂O₅ structure from bulk analogue is reflected in the theoretical calculation as well. A detailed explanation of the nature of bond vibrations is given in supplementary information (Figure S-6). Experimentally, 8 out of the 21 Raman active modes were detected. The observed shift in Raman modes from bulk to the bilayer, particularly for out-of-plane modes, is in line with DFT predictions. As mentioned earlier, the mode at 1010 cm⁻¹ (A_{1g}^7) is exclusively an out-of-plane vibrational mode which experimentally shows a blue shift for the 2D layers (Figure 2b and Table 1). The blue shift from the bulk value in the mode A_{1g}^7 was theoretically predicted for the monolayer (Table 1). Since the out-of-plane vibrational modes are very sensitive to the change in thickness down to 2D layers, this observation can be identified as the signature of vibrational decoupling.

Table 1. Calculated phonon modes and experimentally observed Raman active modes for bilayer 2D-V₂O₅

Mode	LDA		Experiment		Mode	LDA		Experiment	
	Bulk (cm ⁻¹)	Monolayer (cm ⁻¹)	Bulk (cm ⁻¹)	Bilayer 2D-V ₂ O ₅ (cm ⁻¹)		Bulk (cm ⁻¹)	Monolayer (cm ⁻¹)	Bulk (cm ⁻¹)	Bilayer 2D-V ₂ O ₅ (cm ⁻¹)
A_{1u}^1	100	94			B_{2g}^4	353	366		
B_{3u}^1	127	103			B_{1u}^3	363	390		
A_{1g}^1	151	105	103	111	A_{1g}^4	381	408	404	
B_{1u}^1	176	138			B_{3u}^4	420	486		
B_{2g}^1	177	144			B_{1u}^4	434	510		
B_{1g}^1	178	166	145	162	A_{1g}^5	442	525	483	493
B_{3g}^1	218	173			B_{2g}^5	474	551		
A_{1g}^2	234	196			A_{1u}^3	529	563		
B_{2g}^2	238	205	198		B_{2u}^3	555	573		
B_{2u}^1	241	241			A_{1g}^6	555	575	527	539
B_{3g}^2	253	253			B_{1u}^5	600	661		
B_{3u}^2	267	263			B_{1g}^3	722	752	703	711
A_{1u}^2	291	266			B_{3g}^4	723	755		
B_{2u}^2	296	281			B_{3u}^5	813	830		
B_{1g}^2	297	282			B_{2g}^6	880	948		
B_{3g}^3	306	286	285	267	B_{3u}^1	882	1099		
B_{1u}^2	325	297			B_{1u}^6	886	1101		
A_{1g}^3	329	298			B_{2g}^7	886	1116		
B_{2g}^3	336	299	306	324	A_{1g}^7	1001	1117	994	1010
B_{3u}^3	342	365							

The modes designated as B_{3g}^3 , A_{1g}^5 , A_{1g}^6 and B_{1g}^3 are also found to follow the theoretically predicted frequency shift from the bulk values of Raman mode frequency. A similar observation of vibrational decoupling of layers is reported in other 2D materials like MoS₂⁴⁸. In the present study, the inferences from AFM analysis showed that the exfoliated flakes are having a thickness from bilayer to trilayer (Figure 3). It can be expected that the intercalation of formamide molecules into the interlayer gap can cause a lattice expansion along the *c*- axis. The thicknesses of exfoliated 2D layers are measured as 1.0 to 1.5 nm which are slightly greater than the theoretical bilayer and trilayer thicknesses of 0.87 and 1.3 nm, respectively, indicating the effect of intercalation. However, anomalous blue shifts are observed for A_{1g}^1 , B_{1g}^1 and B_{2g}^3 mode frequencies. The discrepancy with the theoretical prediction may happen because of the surface reconstructions caused by the following reasons; the formation of O vacancies and enlarged interlayer separation of the bilayer 2D-V₂O₅ during exfoliation process. The Raman spectroscopic studies of Li intercalated V₂O₅ demonstrated that the B_{1g}^1 mode of Li intercalated structure showed a blue shift due to the possible increase in interlayer separation⁴⁹. Moreover, there are several reports on the anomalous shift of Raman mode frequencies observed in TMDs depending on the method of exfoliation, indicating that the nature and extent of surface reconstruction differ with the method of synthesis which eventually causes the anomalous shift in Raman mode frequencies^{50, 51}. The presence of oxygen vacancy defects and a small amount of quaternary nitrogen functional group in bilayer 2D-V₂O₅, observed from XPS studies (Figures 2c and 2d), can be accounted as the reason for the anomalous shifts and broadening of Raman active lattice vibrational modes of bilayer 2D-V₂O₅.

In summary, we used a modified method of intercalation by formamide molecules to exfoliate the bulk V₂O₅. We could achieve bilayer thin 2D-V₂O₅ nanosheets with the lateral dimension of 100-300 nm. The formation of bilayer 2D-V₂O₅ nanosheets is confirmed using Synchrotron XRD, FESEM, XPS and AFM characterizations. Using UV-Vis spectroscopy, thickness dependant absorption edge blue shift from the bulk is manifested in bilayer V₂O₅ indicating electronic decoupling. The Raman spectroscopic studies on the exfoliated sample showed that the mode frequencies of bilayer 2D-V₂O₅ were shifted from bulk values due to vibrational decoupling. The experimental observations were further confirmed by computing lattice vibrational modes using density functional perturbation theory. This is the first report on the

electronic and vibrational decoupling in bilayer thin 2D-V₂O₅, and this novel observation can be used for fingerprinting the formation of 2D or few layer thick transition metal oxide samples from their bulk counterparts.

METHODS

Formamide is a strong intercalating agent and is often used for exfoliating layered materials. The formamide intercalated V₂O₅ can form a stable suspension of thin flakes of V₂O₅²⁴. Bulk V₂O₅ powder (Merck, 99.99%) was exfoliated by dispersing in formamide (Merck, 99%) with concentrations of 6 (S1) and 1mM (S2) for 24 h. The dispersion was ultrasonicated for 1 h at room temperature for separating the exfoliated nanosheets. The suspension of exfoliated 2D-V₂O₅ flakes in formamide was directly drop coated on the SiO₂/Si substrate and high pure Au substrate and heated at 100°C for removing remnants of formamide. Post annealing treatment was performed at 250°C for 3 h in O₂ atmosphere. The addition of any other liquid for washing the exfoliated particles was avoided since the particles might cluster together in other liquids. The synthesis process was simplified by directly coating the dispersion onto the substrate. The complete removal of formamide was confirmed by further characterizations.

Morphology of the samples transferred on SiO₂/Si substrate were studied using a field emission scanning electron microscope (FESEM, SUPRA 55 Zeiss). Crystallographic studies using a six-circle diffractometer (HUBER 5020) were carried out in reflection geometry using Synchrotron X-ray with a wavelength of 0.7174 Å (BL12, INDUS2, RRCAT, India). Raman spectroscopic studies were carried out using 532 nm excitation wavelength (InVia, Renishaw, UK) in the back-scattering geometry with a 2400 gr/mm grating and thermoelectrically cooled charged coupled device as the detector. Sample coated on Au substrate was used for Raman spectroscopic studies in order to avoid the dominant Raman peak intensity from Si substrate. Raman spectra were collected from well dispersed samples on the substrate. XPS measurements (SPECS Surface Nano Analysis GmbH, Germany) were carried out with a monochromatic Al K α X-ray (1486.7 eV) source.

Topographical image was collected by AFM, to measure the thickness of individual V₂O₅ flakes. AFM studies of sample coated on SiO₂/Si substrate were carried out using a multimode scanning probe microscope (INTEGRA, NT-MDT, Russia). Imaging was performed in intermittent contact mode. UV-Vis spectroscopic studies (Avantes) were performed in the exfoliated sample

suspension. Pure formamide (Merck, 99%) was used as the reference. The absorption spectra for the samples were collected by subtracting the effect of reference liquid. UV-Vis spectrum of bulk V_2O_5 was collected by taking distilled water (MilliQ, 18 M Ω) as the reference.

Spin polarized *ab initio* DFT calculations were executed using Vienna *ab initio* simulation package (VASP)⁵². The exchange correlation functional was computed using local density approximation (LDA) of Perdew–Zunger⁵³, and this choice was justified by the earlier calculation³⁰. A kinetic energy cut-off of 520 eV was used to truncate the size of plane wave basis set. To treat the local Coulombic correlation associated with vanadium 3*d* states a Hubbard correction ($U-J = 3.25$ eV) was incorporated. A supercell of size 3×2×1 was employed for phonon calculations. A vacuum separation of 25 Å was provided along *c*-axis to eliminate the unphysical interactions between the periodic images. Monkhorst pack grid of size 5×2×1 was used to integrate over the Brillouin zone. Geometries were optimized with a force convergence of the order of 10⁻⁴ eV/Å. Density functional perturbation theory (DFPT)⁵⁴ in conjunction with auxiliary phonon post-process package PHONOPY⁵⁵ was used for phonon calculations.

Data availability

Data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

The central idea was conceived by P.R.R, S.D and A.K.P. Sample synthesis was carried out by P.R.R. AFM topography were recorded by K.G. Rest of the characterizations and data analysis were done by P.R.R. Theoretical calculations were carried out by P.A. Manuscript was written by P.R.R and all authors discussed the results and the manuscript.

Competing interests

The authors declare no competing interests.

Figures

Figure 1

a) Schematic diagram showing the exfoliation of α -V₂O₅ using formamide as the intercalating agent. b) Photographs of sample suspension in formamide for S1 and S2 (prepared at a concentration of 6 and 1 mM, respectively). c) FESEM images of exfoliated V₂O₅ nanosheets S1 and S2. The inset shows

magnified views of the respective images. View of the structure of monolayer 2D-V2O5 along d) c-axis and e) a-axis, f) Square pyramidal coordination geometry of V5+. Vanadyl, bridge and chain oxygen are marked as OI, OII and OIII respectively. OIII and OIII' are triply coordinated with V atom with different bond lengths. g) X-ray diffraction pattern of bulk V2O5 precursor and the exfoliated samples S1 and S2

Figure 2

a) Raman spectra of bulk V2O5 precursor and exfoliated samples S1 and S2, prepared at concentrations 6 and 1mM respectively. b) Change in Raman mode frequencies of exfoliated samples from bulk. Dotted lines are a guide to the eye. a) XPS survey spectra of S1 and S2. d) Core level V2p spectra with peaks corresponding to binding energy of V2p3/2 and V2p1/2. The deconvoluted peaks show the existence of oxygen vacancy defects in the samples S1 and S2.

Figure 3

AFM image of exfoliated ultrathin layers of V2O5. line profile of height measured across the nanosheets, labeled as 1 and 2 and the number distribution of exfoliated layers with the thickness are shown in the right side. Thicknesses from 1.0 to 1.5 nm are observed, which counts to 2 -3 layers of V2O5.

Figure 4

a) UV-Vis absorption spectra of bulk V_2O_5 and exfoliated samples S1 and S2. b) Tauc's plot for three samples showing the direct band gap. The values of band gap for bulk V_2O_5 , S1 and S2 are around 2.39, 2.67 and 3.72 eV, respectively.

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