One-pot liquid-phase synthesis of MoS\textsubscript{2}-WS\textsubscript{2} van der waals heterostructures for broadband photodetection

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Abstract
Two dimensional (2D) van der Waals heterostructures (vdWHs) have unique potential in facilitating the stacking of layers of different 2D materials for optoelectronic devices with superior characteristics. However, the fabrication of large area all-2D heterostructures is still challenging towards realizing practical devices at a reduced cost. In the present work, we have demonstrated a rapid yet simple, impurity-free and efficient sonication-assisted chemical exfoliation approach to synthesize hybrid vdWHs based on 2D molybdenum disulphide (MoS\textsubscript{2}) and tungsten disulphide (WS\textsubscript{2}), with high yield. Microscopic and spectroscopic studies have confirmed the successful exfoliation of layered 2D materials and formation of their hybrid heterostructures. The co-existence of 2D MoS\textsubscript{2} and WS\textsubscript{2} in the vdWH hybrids is established by optical absorption and Raman shift measurements along with their chemical stiochiometry determined by x-ray photoelectron spectroscopy. The spectral response of the vdWH/Si (2D/3D) heterojunction photodetector fabricated using the as-synthesized material is found to exhibit broadband photoresponse compared to that of the individual 2D MoS\textsubscript{2} and WS\textsubscript{2} devices. The peak responsivity and detectivity are found to be as high as \textasciitilde2.15 A W\textsuperscript{−1} and 2.05 \texttimes 10\textsuperscript{11} Jones, respectively for an applied bias of \textasciitilde5 V. The ease of fabrication with appreciable performance of the chemically synthesized vdWH-based devices have revealed their potential use for large area optoelectronic applications on Si-compatible CMOS platforms.

Supplementary material for this article is available online

Keywords: MoS\textsubscript{2}-WS\textsubscript{2}, optoelectronics, van der waals heterostructure, 2D materials, chemical exfoliation, photodetector

(Some figures may appear in colour only in the online journal)

1. Introduction

Along with graphene, which boasts of superior carrier mobility [1] and other fascinating properties [2], many two dimensional (2D) materials like transition metal dichalcogenides (TMDCs) [3, 4], hexagonal boron nitride (hBN) [5], oxides such as Cr\textsubscript{2}O\textsubscript{3} and ZrO\textsubscript{2} [6], etc have drawn research interests [7]. They have a layered structure where the weak interlayer van der Waals forces can be overcome by applying mild external perturbations, facilitating easy exfoliation of individual layers. The band gaps of various 2D materials range from the ultraviolet–visible (UV–vis) to the infrared (IR) region, which can be tuned by changing the number of layers in the materials. In case of 2D TMDCs, however, most optical transitions are excitonic in nature [8] and also, the excitons and higher order excitonic complexes in these materials have high binding energy making them stable at room
temperature. Especially, 2D TMDCs like MoS$_2$ and WS$_2$ have gained the attention of the scientific community due to their abundance, thermal stability under ambient conditions and tunable direct bandgaps useful for band selective optoelectronics [9]. Compared to other popular TMDCs like hBN, MoSe$_2$ and WSe$_2$ which have their absorption peaks in the UV and IR regions respectively, MoS$_2$ and WS$_2$ have theirs in the visible—near IR region [10, 11]. Hence, atomistic MoS$_2$ and WS$_2$ devices have been widely studied for their applications in efficient photodetectors [12], biosensors [13], thin-film transistors [14, 15], energy storage [16], and memory devices [17, 18] etc.

Stacking layers of different TMDCs by forming all 2D heterostructures are expected to provide wider absorption/emission bands in the system using combinatorial properties, which has been proved to be beneficial for photovalaic [19] devices and broadband photodetection [20]. Field effect transistors based on heterostructures of graphene with hBN and MoS$_2$ have been fabricated which gave high switching ratios of $\sim$50 and $\sim$10000 respectively, demonstrating their potential in high frequency applications [21]. MoSe$_2$/WSe$_2$-based photodetectors have also been found to exhibit a high photoreponsivity of 127 mA W$^{-1}$ in the infrared region [22]. Actually, the availability of a wide range of tunable bandgaps in TMDCs allows precise stitching of different compositions, giving rise to highly suitable quantum materials for fabricating broadband optoelectronic devices [23–25]. MoS$_2$ and WS$_2$ have the added advantage of having lattice constants with very close values of 3.15 Å and 3.153 Å respectively [26], which make them perfect candidates for 2D van der Waals heterostructures (vdWHs) with the least in-plane strain and by forming a type-II band alignment that results in faster charge separation across the heterostructure. Mechanically exfoliated (ME) and transferred vertical stacks of pristine TMDC layers have outstanding physical properties but offer very small active area, requiring complex nanolithography for device fabrication [27, 28] and thus are not scalable for practical applications. For example, Lopez et al produced a photodetector based on ME’ed monolayer MoS$_2$ with an ultra high responsivity of 880 A W$^{-1}$ at a wavelength of 560 nm; however, they first had to identify the monolayered flake using optical microscope and then perform electron beam lithography followed by wire-bonding to form the metallic contacts [12]. Chemical vapour deposition synthesizes high quality and large-area flakes with sharp and clean heterointerfaces and hence provides superior quality films; but this process involves the usage of hazardous chemical precursors and capital-intensive instrumentation [29]. In this regard, a simple chemical exfoliation method, where the use of hazardous chemicals and sophisticated instrumentation is not a necessity, can be one of the ways out for an easier, faster and cheaper route to synthesize vdW heterostructures. Being a versatile and low-cost synthesis process, this is the main pathway to exfoliate various 2D materials like MoS$_2$ [30], black phosphorus [31], etc. Furthermore, solution-processed 2D heterostructures provide a high yield of flakes with variable shapes and sizes within a short period of time [32] and therefore, suitable for large area flexible device applications. Here, we report one-pot sonochemical synthesis of MoS$_2$-WS$_2$ hybrid vdW heterostructures using ethylenediamine (EDA)—assisted chemical exfoliation in a facile manner [33]. Successful exfoliation and subsequent mixing of few layered MoS$_2$ and WS$_2$ after prolonged sonication result in multiple local heterojunctions. Atomic force microscopy (AFM), high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, and Auger electron spectroscopy (AES) have been used to evaluate the micro-structure and quality of the heterostructures. The utilization of MoS$_2$-WS$_2$ vdWHs for Si-complementary metal oxide semiconductor (CMOS) compatible vertical heterojunctions (in 2D/3D configuration) is demonstrated by fabricating photodetector devices. The MoS$_2$-WS$_2$ vdWH device exhibits better current rectification and enhanced photoresponse characteristics, as compared to control devices with few-layered MoS$_2$ and WS$_2$ flakes due to combinatorial properties, which can be beneficial for wideband optoelectronic devices with superior performance.

2. Experimental section

2.1. Sample synthesis

Here 0.5 g MoS$_2$ and 0.5 g WS$_2$ (1:1 ratio) powders (bought from Sigma Aldrich, with CAS no. 1317–33–5 and used without further purification) were taken separately and added to 25 ml ethylenediamine (EDA). The mixture was subjected to magnetic stirring for 24 h at room temperature to let EDA get absorbed on the basal plane of MoS$_2$ and WS$_2$. A schematic representation of the synthesis method is shown in figure 1. EDA acted as a chelating agent as well as a hydrogen bond donor here and bound to the surface of the MoS$_2$ or WS$_2$ layers. This upward pull by EDA weakens the interlayer attraction and promotes layer by layer exfoliation [34]. After complete surface adsorption, the excess EDA was discarded by centrifugation and washed several times using N,N-dimethylformamide (DMF) to remove traces of unreacted EDA. Thereafter, the mixture was redispersed in DMF, followed by ultrasonication for two hours, as shown in figure 1(b). The reduction of interlayer attraction through hydrogen bond formation with EDA was augmented by the hydrodynamic forces generated by the ultrasonic waves, leading to the efficient exfoliation of few layers of TMDCs. The resulting mixture containing flakes of different sizes was separated from the bulk unexfoliated part by centrifugation. These exfoliated flakes with an obtained concentration of 5 mg ml$^{-1}$, formed a colloidal suspension in DMF that was stable for a long period. Suspended MoS$_2$ and WS$_2$ layers were arranged in close proximity forming local vdWHs, as depicted in figures 1(d) and (e). The ultrasonication process leads to a polydispersity in the resulting solution and by gradient centrifugation, we can selectively filter out nanosheets of different dimensions [35, 36]. Thus, to obtain variations in the lateral dimension of the flakes, the supernatant was then centrifuged at different speeds of 2000, 5000 and 10 000 rpm (hereafter referred to as 2k, 5k and 10k samples respectively). The digital images of their colloidal dispersions are shown in figure 1(f). The same procedure was followed for synthesizing individual 2D MoS$_2$ and WS$_2$ flakes with varying sizes to compare their properties with their hybrid vdWH.
Figure 1. Schematic representation of the different steps of solvent exfoliation: (a) Bulk powders of MoS2 and WS2 were added to EDA solution, (b) After magnetic stirring for 24 h, EDA was washed out and the mixture of MoS2 and WS2 was re-dispersed into fresh DMF and sonicated for 2 h and (c) centrifugation at different rotational speeds to extract few layers of exfoliated MoS2-WS2 vdWH. Schematic representation of this vdWH formation is shown in (d). After detachment from bulk body, (e) MoS2 is placed on top of WS2 layers or vice versa. (f) Digital photograph of as-synthesized MoS2-WS2 vdWH.

2.2. Characterisation

The surface morphology of the exfoliated flakes was studied by an AFM, in the tapping mode [model: Agilent Technology, 5500]. The micro-structural characterizations were carried out using a HRTEM [model: JEOL, JEM-2100F equipped with a CCD from Gatan, Inc. USA] and a x-ray diffractometer [model: Philips MRD x-ray diffractometer] with Cu-Kα, line of wavelength 1.5418 Å. Raman spectra were recorded using Ar–Kr gas laser of 514 nm equipped with an optical microscope having 100x objective lens. Chemical composition of the samples were investigated by x-ray photoelectron spectroscopy (XPS) with characteristic Al-Kα, radiation of energy 1486.6 eV [model: PHI 5000 Versa Probe II, ULVAC PHI, INC, Japan] and AES using a spectroscope [model: PHI 710, ULVAC PHI, INC, Japan]. Optical characterization was carried out by absorption spectroscopy of as-synthesized samples, placed in a quartz cuvette with a fiber-probe based UV–vis-NIR photo-spectrometer, [model: Avaspec 23648]. Electrical and optical measurements of the fabricated heterostructure were done using a Keithley semiconductor parameter analyzer [model: 4200A SCS], a broadband light source of power one sun, a monochromator, and a mechanical chopper.

2.3. Results and discussions

A high density of exfoliated flakes is obtained by the synthesis method at 2000 rpm centrifugation speed, as revealed by the TEM micrographs presented in figures 2(a)–(c), for the MoS2–WS2 vdWHs and individual MoS2 and WS2 2D nanoflakes, respectively. Prolonged ultrasonication causes the flakes to undergo size reduction in the basal plane, resulting in an average lateral size of ~100–200 nm for MoS2–WS2, MoS2, and WS2 samples, as observed in the TEM micrographs of figures 2(a)–(c), respectively. This reaffirms the efficacy of the EDA-assisted sonochemical exfoliation process to exfoliate 2D TMDCs. A typical HRTEM micrograph recorded around an overlapping region of MoS2 and WS2 flakes present in the heterostructure sample, as depicted in figure 2(d), reveals two different sets of planes, displaced and rotated by some angle, as shown in figure 2(e). The measured interplanar spacing of ~0.27 nm corresponds to the (100) planes of MoS2 while that of ~0.25 nm corresponds to the (101) planes of WS2 [34]. The selected area electron diffraction (SAED) pattern of this overlapping region shown in figure 2(f), exhibits two closely spaced hexagonal lattices. This confirms the retention of the hexagonal symmetry of MoS2 and WS2 in the vdWH, even in their exfoliated low dimensional form, preserving superior crystalline quality in the heterostructure. The exfoliated nanosheets from the bulk materials have been further studied by AFM, as shown in figure S1 of the electronic supporting information (ESI) and average thickness is found to be ~ 8.0 nm. It indicates the formation of few-layered flakes in the hybrid heterostructure.

The crystalline nature of MoS2 and WS2 in the hybrid heterostructure has been further investigated by x-ray diffraction measurements at 2.0° grazing angle of incidence, as shown in figure 3(a), for various samples where all the characteristic diffraction peaks are duly indexed. The intense peak at 2θ ~ 14.6° for MoS2, WS2, and MoS2–WS2 vdWH is associated with the (002) planes of MoS2 and WS2 flakes [37, 38], indicating the formation of their hexagonal 2H phase. The dominance of this
peak is due to the high density of vertically stacked 2D sheets. The full-width-half-maximum (FWHM) of this peak in the vdWH sample is 1.02°, as compared to that of 1.00° and 0.90° for individual MoS2 and WS2 samples, respectively. The finite broadening of the FWHM in the vdWH is due to the presence of the two constituent compounds. XRD spectra thus clearly support the retention of crystallinity and semiconducting 2H phase in all the samples after EDA assisted solvent exfoliation. Molecular vibrations of these samples have been probed by the measurement of Raman shift using a 488 nm laser. The Raman spectrum of WS2 presented in figure 3(b), shows two peaks at ~359 and ~428 cm⁻¹, which are attributed to the in-plane $E_{2g}$ and out-of-plane $A_{1g}$ vibrational modes, respectively. The corresponding vibrational modes for MoS2 nanoflakes appear at ~383 cm⁻¹ and ~408 cm⁻¹, respectively, in agreement with the existing report [39]. However, the MoS2-WS2 vdWH sample exhibits Raman peaks at ~351 and ~419 cm⁻¹ owing to the contribution from WS2 and those at ~380 and ~407 cm⁻¹ are attributed to the MoS2 flakes. It is to be noted that the Raman peaks have an overall red shift in the vdWHs, which depends on...
the stacking pattern (Mo-W or W-Mo-W, etc) in our multi-layered flakes [40], compared to the Raman shifts in the individual MoS2 and WS2 nanoflakes, indicating the possible development of in-plane π stacking in MoS2 [41] and hence the formation of in situ local heterojunction. The absence of any new vibrational mode or unusual change in the Raman spectra of the vdWH in comparison with that of bare MoS2 and WS2 reaffirms the crystalline quality of the exfoliated sample. In addition, the difference between the out-of-plane $A_{1g}$ and in-plane $E_{2g}$ modes of vibrations is found to be $\sim 25$ cm$^{-1}$ for MoS2 and the intensity ratio of the $A_{1g}$ and $E_{2g}$ modes for WS2 is calculated to be 1.13, both of which confirm that the 2D sheets contain only few-layers [42] in the heterostructure sample. Thus, both the XRD and Raman characterizations confirm the semiconductor phase of the synthesized samples [43, 44].

The investigation of the chemical state and composition of the as-synthesized vdWH has been performed using high-resolution XPS. The spectral features of Mo 3d, W 4f, and S 2p doublets have been deconvoluted and the results are presented in figure 4. The spin-orbit split 3d orbitals of Mo, namely Mo 3d_{3/2} and Mo 3d_{5/2}, are observed at $\sim 229.5$ eV and $\sim 232.6$ eV, respectively, as shown in figure 4(a). On the other hand, in figure 4(b), two distinct peaks of W 4f_{1/2} and W 4f_{3/2} are recorded at $\sim 32.7$ eV and $\sim 35$ eV, respectively. The absence of any higher energy peak for Mo and W reveals that the sample has not been oxidized to form sub-oxides of MoO_x or WO_x during exfoliation. The binding energies for Mo and W agree well with the existing literature values for the Mo$^{4+}$ and W$^{4+}$ states [45, 46]. In figure 4(c), the S 2p_{1/2} and 2p_{3/2} peaks found at $\sim 162.3$ eV and 163.5 eV, respectively, also agree well with reports for the S$^{-2}$ state [30]. These results indicate the formation of desired chemical bonds like S–Mo–S and S–W–S and the absence of any elemental states of M or W. Therefore, the mechanism employed in synthesizing the hybrid vdWH has not triggered any side reaction to render these materials in any other undesirable chemical or oxidized state. Thus, the chemically pure colloidal vdWH is potentially attractive to fabricate multifunctional devices. The atomic percentage of various elements present in the MoS2-WS2 vdWH sample has been calculated to be Mo $\sim 21\%$, W $\sim 20\%$ and S $\sim 59\%$. These elements are also homogeneously distributed in the sample, as evident from the elemental maps recorded by AES mapping and their elemental RGB overlay presented in figure 5. Figure 5(a) shows the scanning electron micrograph of the sample on Si substrate and figures 5(b)–(d) display the elemental maps of Mo, W, and S, respectively. The overlapping region of Mo, W and S represents the formation of the MoS2-WS2 vdWH, which is shown in figure 5(e). The elemental distribution has been quantized by the system and the extracted percentages of Mo, W and S in this area are presented in figure 5(f). The corresponding elemental concentrations are found to be $\sim 20.1\%$, $\sim 22.6\%$, and $\sim 57.3\%$ for Mo, W and S respectively, which are in close agreement with the XPS measurements. It is also seen that the Auger signals generated by the S, Mo and W atoms belong to the LMM, MNN and MNN electron transitions in them respectively [47]. AES elemental maps of the individual 2D MoS2 and WS2, along with their atomic concentrations are presented in figures S2 and S3 (ESI) respectively. A larger fraction of S in the MoS2-WS2 vdWH sample is accounted due to the contribution from both the constituent compounds, which is in close agreement with our calculated fraction of individual elements using XPS.

Optical properties of the samples have been analyzed by the UV–vis absorption spectroscopy of MoS2, WS2, and the hybrid heterostructure samples collected at a centrifugation speed of 2k rpm is shown in figure 6. The samples collected at the other speeds of 5k and 10k rpm are presented in figure S4. The absorption spectra for MoS2 nanoflakes in figure 6(a) show two distinct peaks at $\sim 620$ and $\sim 680$ nm arising from the absorptions associated with B and A excitons, respectively [33]. These peaks are ascribed to the formation of excitons due to electronic transitions from the spin-split valence bands to the conduction band at the K-point of the Brillouin zone [48]. With an increase in centrifugation speed, the absorption peaks undergo a blue shift as shown in figure S4(a), in accordance with the quantum confinement effect arising from the gradual decrease in the dimension of MoS2 nanoflakes. Similarly, WS2 nanoflakes exhibit two characteristic peaks at $\sim 537$ and $\sim 644$ nm ascribed to the B and A excitons [35], respectively, as shown in figure 6(a). On the other hand, the MoS2-WS2 heterostructure shows three distinct absorption peaks at $\sim 532$, $\sim 630$ and $\sim 677$ nm in the same figure. The feature at $\sim 630$ nm can be deconvoluted into two peaks at $\sim 613$ and $\sim 637$ nm, as shown in figure 6(b), attributed to the combined absorption of the B-exciton of MoS2 and A-exciton of WS2 [48]. The resultant absorption from the hybrid heterostructure combining 2D MoS2 and WS2 is found to be broader than either of the individual materials. The co-existence of MoS2 and WS2 in the hybrid heterostructure thus leads to wideband and enhanced absorption.

![Figure 4](image-url) XPS core level spectra of (a) Mo, (b) W, and (c) S of the as-synthesized MoS2-WS2 vdWH.
as compared to that of the constituent materials, making it a potential candidate for optoelectronic devices.

Vertical p-n junction devices have been fabricated using the as-synthesized samples to analyze their performance as a photodetector. The samples collected at a centrifugation speed of 2000 rpm, with an average lateral size of $\sim 100 – 200$ nm were chosen to fabricate the devices, as these flakes had larger areas compared to the ones centrifuged at 5000 and 10 000 rpm. The MoS$_2$ and WS$_2$ nanoflakes and MoS$_2$-WS$_2$ vdWHs were spin-coated onto freshly cleaned silicon substrates at 1500 rpm for a duration of 30 s to ensure total substrate coverage, as shown in the cross-sectional SEM images of the vdWH device in figure S5, ESI. Gold (Au) and aluminium (Al) metal electrodes were deposited on top of the film and

Figure 5. (a) SEM micrograph of the vdW heterostructure used for Auger electron mapping. AES maps for elemental distribution of (b) Mo, (c) W, (d) S and (e) their combination. (f) Elemental percentages of the above mapped elements, deduced from their Auger signals are: 57.3% of S, 22.6% of W, and 20.1% of Mo.

Figure 6. UV–vis absorption spectra of as-synthesized (a) MoS$_2$, WS$_2$ and MoS$_2$-WS$_2$ vdWHs and (b) deconvolution of the peak at 630 nm (shaded portion) in (a).
bottom of the substrate, respectively, by thermal evaporation technique at a base pressure of $\sim 2 \times 10^{-6}$ mbar. A typical planar view of the fabricated device is shown in figure 7(a). The effective active area of each device is $\sim 2 \times 10^{-5}$ mm$^2$. Control MoS$_2$ and WS$_2$ devices have also been fabricated alongside to systematically compare their performances. Typical current–voltage ($I$–$V$) characteristics are shown in figure 7(b) for devices made with MoS$_2$, WS$_2$ and the vdWH under dark and illumination conditions. The variation of current as a function of voltage in the n-MoS$_2$/p-Si heterojunction device shows a good rectification behavior at an applied bias of $-5$ V, as presented in the middle panel of figure 7(b), with a rectification ratio of $\sim 1.8 \times 10^2$ and a moderately low dark current of $\sim 7.6 \times 10^{-6}$ A. In the p-WS$_2$/n-Si heterojunction device, a rectification ratio of $\sim 3.6 \times 10^4$ and low dark current of $\sim 1.35 \times 10^{-8}$ A are noted from the bottom panel of figure 7(b). The low dark current in the WS$_2$/Si heterojunction may be attributed to low defect concentration and higher generation-recombination of carriers in WS$_2$ in the reverse-biased condition and hence the realization of a good heterointerface. The photo-to-dark current ratio of both MoS$_2$ and WS$_2$ is found to be $10^2$. However, the device with MoS$_2$-WS$_2$ vdWH/p-Si shows the maximum photo-to-dark current ratio of $\sim 10^3$, with a rectification ratio of $\sim 10^3$ and moderately low dark current of $\sim 2.3 \times 10^{-6}$ A, at $-5$ V applied bias, as shown in the top panel of figure 7(b). Overall, the device made of vdWH shows superior photoresponse in comparison to those of MoS$_2$ and WS$_2$ nanoflakes individually. Therefore, the combination of MoS$_2$ and WS$_2$ provides an enhanced light harvesting capability. The optical switching behavior of all the devices including MoS$_2$-WS$_2$ vdWH/p-Si heterojunctions at an applied bias of $-3$ V upon periodic illumination from a source of broadband light is shown in figure 7(c) and the vdWH device exhibits the best optical response, consistent with the $I$–$V$ characteristics in figure 7(b). The switching characteristics of the vdWH/Si photodetector for different applied bias is shown in figure 7(d). With increasing reverse bias, there is an enhanced collection efficiency of the photogenerated electrons and holes across the vdWH/Si heterojunctions, resulting in an increased output current. It should be noted that the possible local (2D–2D) heterojunctions, which are distributed throughout the device have a cumulative effect on the output current, leaving no control over a single (2D–2D) heterojunction. Response time, a key parameter determining the speed of a photodetector, has been calculated by measuring the time taken by the output
current to rise from 10% to 90% of its maximum value and vice versa. The average response time ($\tau_{res}$) of our vdWH/Si photodetector, estimated from the magnified view of an optical switching cycle at $-3$ V, as shown in figure S6, ESI, is found to be $\sim 50$ ms. This fast photoresponse can be attributed to the realization of a good heterojunction between Si and MoS$_2$/WS$_2$. Hence, the photoresponse of the device fabricated using chemically exfoliated vdWH is moderately sharp and can be employed for various optoelectronic devices.

Spectral responsivity of a photodetector is a measure of the change in output current with incident radiation. The responsivity profiles for various photodetectors have been recorded with a broadband light source and the results are presented in figure 8(a). The vdWH/Si photodetector yields a much higher responsivity over a range of 400–800 nm, compared to the individual MoS$_2$/Si or WS$_2$/Si heterojunction devices. The vdWH/Si photodetector covers the spectral range of both MoS$_2$ and WS$_2$ based devices, and thus it has an extended spectral range of operation in the visible region with superior responsivity. The NIR contribution to the responsivity with a peak value of $\sim 0.97$ A W$^{-1}$ @5 V around $\sim 1020$ nm is due to the intrinsic absorptions in the underlying Si substrate and this response remains almost unchanged for all the devices. A maximum responsivity of $\sim 2.15$ A W$^{-1}$ (at $-5$ V) is noted over a range of 550–670 nm in the vdWH device. This operational range of wavelengths is closer to the bandgap of MoS$_2$ and WS$_2$ ($\sim 1.8$–2.2 eV), leading to higher absorption of photons. In comparison, the peak responsivities for MoS$_2$/Si and WS$_2$/Si devices are found to be $\sim 1.6$ A W$^{-1}$ and $\sim 1.04$ A W$^{-1}$ respectively, in the visible region, which are much lower than that of the vdWH/Si device. For comparison, the commercial silicon-based photodetector, Newport, Model 818-BB-21, has a peak responsivity of 0.47 A W$^{-1}$ [49]. The spectral variation of the external quantum efficiency of the devices is given in figure S7, ESI, where it is seen that the MoS$_2$/WS$_2$ device exhibits the highest EQE of 470% at the expected wavelength of $\sim 560$ nm. The specific detectivity of a device reflects how efficiently the device can detect the required signal in the presence of a background noise. The MoS$_2$/WS$_2$ vdWH/Si device is found to exhibit the highest detectivity of $\sim 2 \times 10^{11}$ Jones at $\sim 560$ nm (figure 8(b)), which is superior to the devices fabricated using the individual layers. The optical characteristics in terms of responsivity and detectivity are thus found to be enhanced in the vdWH device, which are presented in table 1.

The mechanism of generation and collection of charge carriers in the MoS$_2$/WS$_2$ vdWH/Si heterojunction can be explained with the help of an energy band diagram, which is presented in figure 8. The energy levels (conduction and valence band edges) of various materials [30] before they are brought in contact are shown in figure 8(c). The energy band alignment of vdWH on Si leads to a type-II heterojunction between MoS$_2$ and WS$_2$, as shown in figure 8(d), which is favorable for the movement of charge carriers in the device. As for the heterojunction of the sample with the underlying Si substrate, two scenarios are possible: n-MoS$_2$/p-Si and p-WS$_2$/p-Si. Here, we have represented the band alignment at the WS$_2$/Si heterointerface. In this case, the p-WS$_2$/p-Si junction forms a typical type-I p-p heterojunction as shown in figure 8(d). n-MoS$_2$/Si would form a type-II p-n heterojunction. Under a reverse bias, the depletion region at the p-n junction between WS$_2$ and MoS$_2$ widens, facilitating generation of higher density of photocarriers. As the applied reverse bias is increased, it facilitates efficient separation of
The structure and their application in broadband photodetection on Si substrates. This study shows the potential use of energy levels, as shown in figure 8(e). When light is incident across the depletion region with energy higher than the band gap of the materials, electron–hole (e–h) pairs are generated in all the possible MoS2/WS2, MoS2/Si and WS2/Si heterojunctions. Photogenerated electrons and holes move in the opposite direction under an applied external bias and get collected in the external circuit as photocurrent. The presence of both MoS2 and WS2 broadens the range of wavelengths of photons that can be absorbed by the vdWH device due to combinatorial effect. Greater the width of the extended depletion region encountered by photons, higher is the rate of e–h pair generation and hence higher is the photocurrent. Thus, our photodetector exhibits photoresponse comparable to those reported in literature for photodetectors fabricated in a similar fashion, as shown in table S1. Therefore, this study reveals the potential of chemically synthesized MoS2–WS2 vdWHs for applications in broadband, large-area photosensing devices.

3. Conclusions

We have demonstrated a simple one-pot and inexpensive, EDA-assisted sonochemical exfoliation process of 2D MoS2 and WS2 layers to form hybrid vdWH without altering their crystal structure and phase. Various structural, spectroscopic, and microscopic characterizations have confirmed the presence of both MoS2 and WS2 2D sheets in the vdWH and the formation of local heterojunctions. The heterojunction (vdWH/Si) photodetector shows moderately good rectification behavior with sharp photoresponse characteristics under broadband illumination. The spectral response from the photodetector fabricated using MoS2–WS2 vdWH on Si has shown superior responsivity over an extended spectral range of 400–800 nm with combined response from MoS2 and WS2 nanoflakes. A maximum responsivity of $\sim 2.15 \, \text{A} \, \text{W}^{-1}$ in the visible range of 550–670 nm and a detectivity of $\sim 2 \times 10^{11}$ Jones at $\sim 560$ nm have been achieved from the hetero-structure on Si substrates. This study shows the potential use of chemical routes for the synthesis of hybrid vdWH heterostructure and their application in broadband photodetection on Si CMOS platforms.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflict of interest

The authors declare no conflict of interest.

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