

High-Performance Photodetector Based on Vertical Out-Of-Plane MoS₂/rGO Heterojunction

In this chapter, we discussed the light-sensing performance of the MoS₂ and vertical out-of-plane MoS₂/rGO heterojunction based photodetector in a visible range of wavelengths. First, the synthesis of vertically aligned MoS₂ flakes network via the controlled kinetics conditions of conventional chemical vapor deposition (CVD) process and crumpled reduced graphene oxide (rGO) particles via Hummer method were explained. After fabricating vertical out-of-plane MoS₂/rGO heterojunctions, as-synthesized heterojunction was characterized for examining the morphology, crystal structure, electron doping, elemental analysis and absorption capability. As a proof of concept application, the light-induced electric behavior of the pristine MoS₂ flakes network and vertical out-of-plane MoS₂/rGO heterojunctions under the illumination of visible light was discussed. Moreover, stability in air, lifetime, and reproducibility of the photodetector was evaluated. In the last, light-sensing mechanism of the photodetector was elucidated with the help of experimental results and energy band diagram of the rGO and MoS₂.

7.1 Introduction

The optical energy has been generally recognized as a clean and permanent energy resource. How to effectively realize the conversion and application between optical energy and various energies is a research hotspot nowadays. Therefore, the successful introduction of optical effects into various electronic devices will result in novel properties. Since the isolation of graphene in 2004 by Geim and Novoswlov, two dimensional (2D) materials have shown their great potential for photonics and optoelectronics devices due to their distinct electronic, optical and mechanical properties [Geim et al., 2007; and Novoselov et al., 2005]. Despite the high carrier mobility (20,000 cm² V⁻¹ s) and ultra-broadband absorption by pristine graphene, it suffers from short carrier lifetime and high dark current conductivity due to unavailability of bandgap which limits its uses for photodetection applications.

In recent years, transition metal dichalcogenides or TMDC (i.e., MX₂, where M is transition metal element, M= Mo, or W and X is a chalcogenides element, X= S, Te or Se) materials having layered structure have received considerable attention in a wide range of applications, including transistor, photodiode, and sensor because of its layer dependent properties. For example, molybdenum disulfide (MoS₂) n-type semiconductor tuned its energy band from indirect bandgap (1.2 eV) to direct bandgap (1.8 eV) by changing the number of layers from multilayers to monolayer, respectively, due to quantum confinement effects. The tunable bandgap, low noise, large absorption coefficient, and enhanced luminescence quantum yield pave the way for MoS₂ in next-generation optoelectronic technology. Yin et al. reported first monolayer MoS₂ phototransistor that showed a poor photoresponsivity of 7.5 mA/W under illumination with low optical power (80 μW) and a medium gate voltage (V_g, 50 V). At the meantime, the switching behavior of photocurrent generation and annihilation can be finished within 50 ms, and it shows good stability [Yin et al., 2012]. Due to the excellent photoelectrical properties of the MoS₂, it has attracted great attention in the field of the multifunctional optoelectronic device applications. In particular, the photo-assisted enhancement electronic devices have received extensive attention from researchers. In contrast

to monolayer, multilayer MoS₂ based photodetector exhibits an improved photoresponsivity 100 mA/W due to higher density of states and greater absorption rate of incident photons [Choi et al., 2012]. However, further improvement in the performance of pristine MoS₂ is limited by lower photoelectric conversion efficiency (PCE) and the picosecond ultrashort carrier lifetime. With this consideration, to improve the performance of the MoS₂ based photodetectors, many van der Waals heterostructures with different 2D materials and surface decoration with nanoparticles have been prepared. Vabbina et al. reported a MoS₂/graphene Schottky photodetector that showed a maximum photoresponsivity of 1.26 A/W at 1440 nm [Vabbina et al., 2015]. Kufer et al. deposited p-type PbS quantum dots on n-type MoS₂ to form p-n heterojunction and achieved a high responsivity under applied gate voltage [Kufer et al., 2015]. However, the field-effect transistor-based MoS₂ photodetector requires an extra gate bias and large drain-source voltage to achieve a high photoresponse. The extra gate bias and large drain-source voltage lead to a high value of leakage current in between gate and source, and high dark current along with self-heating effect in the channel, respectively. Consequently, the phototransistor degrades its performance (sensitivity) along with heat dissipation and large power consumption due to all these effects.

7.2 Device fabrication from vertical out-of-plane MoS₂/rGO heterojunction and light-sensing experimental details

Large area vertically aligned MoS₂ flakes network was grown using MoO₃ and sulfur as precursors by conventional CVD technique. The temperatures of the regions containing MoO₃ and sulfur were raised to 1000 and 180 °C, respectively and the Ar flow was kept at 160 SCCM at atmospheric pressure for an hour. The details are given in the previous chapter 3. The reduced graphene oxide (rGO) was synthesized first as graphene oxide nanosheet using a modified Hummers method [Jiang et al., 2016]. Complete fabrication procedure for rGO and MoS₂ heterojunction based photodetector device has been discussed in photodetector characterization section of chapter 2.

7.3 Characterization of vertical out-of-plane MoS₂/rGO heterojunctions

The scanning electron microscopy (SEM) image Figure 7.1 (a) clearly illustrates that as-grown MoS₂ flakes are vertically aligned and uniformly combined, forming a 3D network on the large SiO₂/Si substrate. Figure 7.1 (b) shows the EDX analysis of the crumpled rGO particles decorated MoS₂ film, here, Mo (red color) and S (green color) elements are uniformly distributed over the whole surface. Whereas the C (blue color) and O (yellow color) elements were discretely spread over the film, indicating crumpled rGO particles are randomly decorated over the surface of MoS₂. Also, transmission electron microscopy (TEM) experiments were conducted to provide additional insight into the microstructure analysis of rGO/MoS₂ nanohybrids. Figure 7.1(c) represents the low magnification TEM image of rGO/MoS₂ nanohybrids and in figure 7.1(d), high-resolution transmission electron microscopy (HRTEM) image depicts the interlayer distance of 0.62 nm, corresponding to (002) crystal plane of 2H-MoS₂. Moreover, a clear distinct diffraction ring pattern of selected area electron diffraction (SAED) revealed that rGO/MoS₂ nanohybrids structure is a well-crystallized and the rings are indexed to the (002) and (110) crystal planes of MoS₂ and (002) as well as (110) crystal planes of rGO in the rGO/MoS₂ nanohybrids (Figure 7.1(e)). The TEM image of a crumpled rGO particle is given in Figure 7.2. Further, the pristine MoS₂ flakes network and crumpled rGO particles decorated MoS₂ were characterized by Raman spectroscopy. Two Raman vibrational modes E_{12g} (in-plane vibration) and A_{1g} (out-of-plane vibration) of pristine MoS₂ are located at ~ 381 and ~ 405 cm⁻¹, respectively (Figure 7.3(a)). Whereas, in crumpled rGO particles decorated MoS₂, A_{1g} Raman mode frequency exhibited blue-shift from 405 to 408 cm⁻¹, meanwhile Raman frequency of E_{12g} remained intact at 381 cm⁻¹. The difference between these two Raman modes was increased from 24 to 27 cm⁻¹ with a shift of 3 cm⁻¹ and intensities of both Raman modes were also decreased. The deterioration in intensity, broaden the full width at half maximum

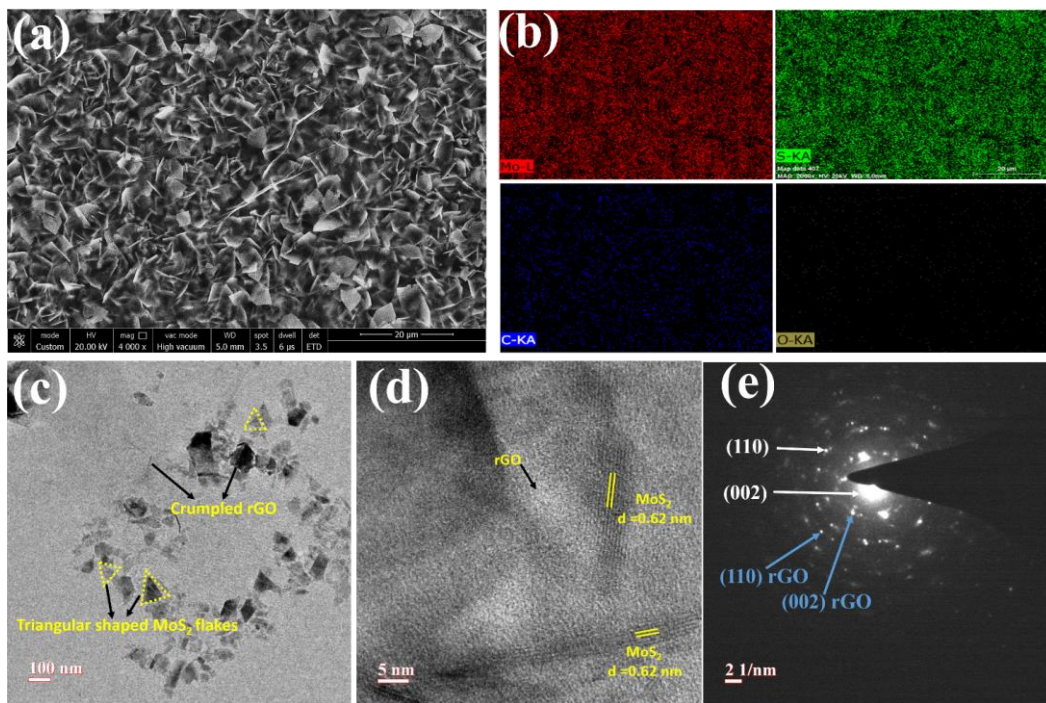


Figure 7.1: (a) SEM image of crumpled rGO particles decorated vertically aligned MoS₂ flakes network. (b) EDX element mapping images of the rGO/MoS₂, confirming the presence of Mo, S, C and O. (c) TEM image, (d) HRTEM image, and (e) SAED pattern of the rGO/MoS₂ nanohybrids.

(fwhm) and the blue shift in frequency of A_{1g} mode indicates the electron transfer from MoS₂ to rGO. It has been proved that electron coupling with A_{1g} phonon is stronger than the E_{12g} phonon, which is in good agreement with the previous reports on shifting of A_{1g} Raman vibrational mode with doping of the 2H-MoS₂ [Kim et al., 2015].

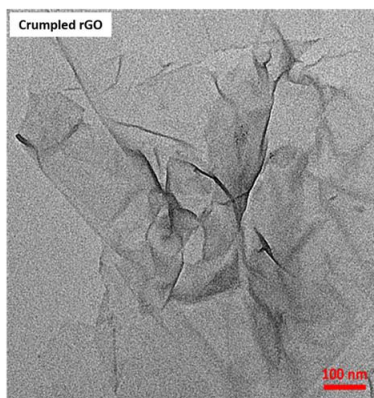


Figure 7.2: TEM image of the crumpled rGO nanoparticles.

Moreover, the two peaks of rGO are located at 1345 and 1584 cm⁻¹, which are ascribed to D band (out-plane vibration due to presence of structural defects) and G band (in-plane vibration of sp² bonded carbon), respectively. The intensity ratio of I_D/I_G was observed as 1.08, which is in agreement with previous rGO report [Khan et al., 2016]. The chemical composition and elements of crumpled rGO particles decorated MoS₂ were determined by using XPS. The deconvolution of the high-resolution peaks Mo 3d and S 2p showed that doublet of Mo 3d_{5/2} and Mo 3d_{3/2} at 229.3 and 232.4 eV and another doublet 2 p_{3/2} and 2 p_{1/2} at 161.9 and 163.1 eV, respectively (Figure 7.3 (b, c)). And the deconvolution of the high-resolution peaks of C 1s

exhibited C-C, C-O, and C=O peaks, as shown in Figure 7.3 (d). The values and shapes of these peaks suggest the coexistence of rGO and MoS₂. Furthermore, to confirm the tunability of optical properties of the MoS₂ after fabricating its hybrid with rGO, the UV-vis absorption experiment was performed for as-synthesized pristine MoS₂ and rGO/MoS₂ hybrid (see Figure 7.4).

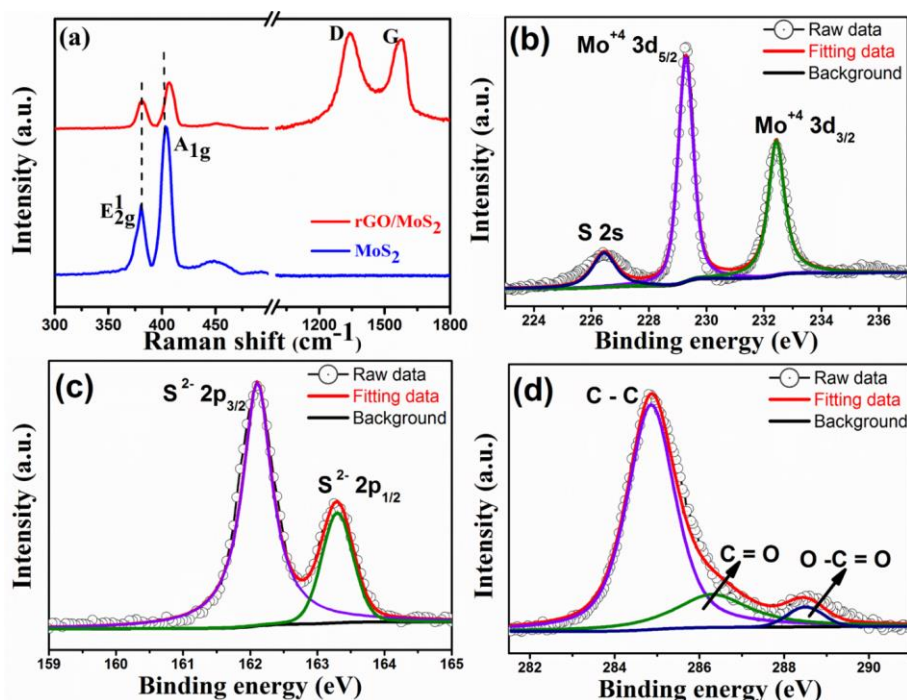


Figure 7.3: (a) Raman spectrum of the rGO/MoS₂ nanohybrids and pristine MoS₂ flakes network. XPS spectra of rGO/ MoS₂ nanohybrids: (b) Mo 3d, (c) S 2p, (d) C 1s.

The UV-vis absorption spectra of pristine MoS₂ and rGO/MoS₂, and two peaks at 678 and 617 nm are observed and named as A and B, respectively. The peaks A and B are associated to direct excitonic transition at K (K') point of the Brillouin zone because of the spin-orbit splitting of the valance band. Meanwhile, the excitonic transition from the minima of valance band to conduction band at the point M of MoS₂ shows additional broad absorption peaks at 460 nm. It is worth noting that absorption spectra intensity of the rGO/MoS₂ hybrid over the entire range of wavelength was stronger than that of pristine MoS₂ because of intrinsic wide band light absorption of rGO. Therefore, the rGO/MoS₂ hybrid exhibited good gathering of visible light and showed higher responsivity compared to that of pristine MoS₂.

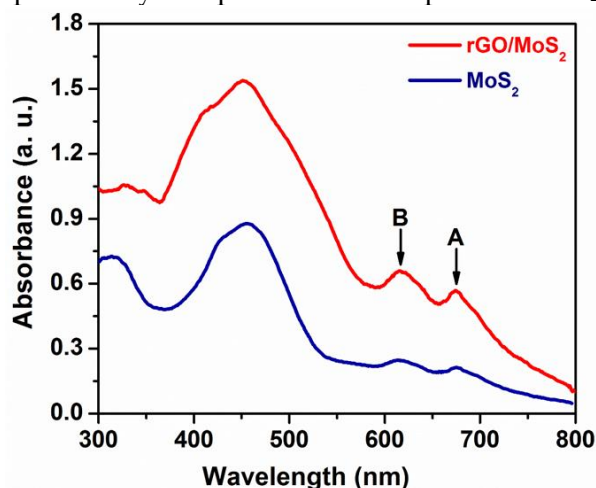


Figure 7.4: UV-visible absorption spectra of as-synthesized MoS₂ and rGO/MoS₂ hybrid.

7.4 Effects of visible range wavelengths on the vertical out-of-plane MoS₂/rGO heterojunctions

To evaluate the light-induced electrical properties of the pristine MoS₂ and crumpled rGO particles decorated MoS₂, the current-voltage (I-V) characteristic measurement was performed for both pristine MoS₂ and rGO/MoS₂ devices in an atmospheric environment under visible light irradiation at specific wavelengths of 460, 520, and 620 nm, as shown in Figure 7.5 (a, b). The currents of both the devices were increased with decreasing the wavelength of the incident visible light source. The different wavelengths of visible light irradiation can excite the electron from valance band to conduction band of the MoS₂ because their optical energies are more than the bandgap of MoS₂ (1.2 eV). While the incident lights were unable to generate photo-induced carriers in rGO due to its wider bandgap of ~ 3.0 eV (large bandgap due to the presence of oxygen-bearing groups that are observed by the XPS). When the pristine MoS₂ device was exposed under the visible light source, photons of shorter wavelength (having high energy) transferred more energy to electrons, which have sufficient energy to reach on electrode after overcome trapping levels (due to defect/impurity) of MoS₂ as well as further, overpass the metal-semiconductor Schottky barrier height (Au/MoS₂), and finally circulated in external circuit under the influence of external applied voltage in between two electrodes and generated photocurrent. However, pristine MoS₂ exhibited low photoresponse because mostly photoexcited electron-hole recombines before reaching on electrode due to low carrier recombination lifetime. As a result, pristine MoS₂ without having p-n junction showed a low photoresponse. However, under the illumination of the incident light, the rGO/MoS₂ device showed the higher photo to the dark current ratio (~ 102 orders of magnitude) due to not only increasing photocurrent but also decreasing dark current (Figure 7.5(c)). Further, we calculated the photodetector's figures of merit such as spectral responsivity (spectral response of the photodetector) and detectivity (sensitivity of the photodetector) to evaluate the performance of the device. The spectral responsivity and detectivity of the device was calculated according to the expressions as, [Khan et al., 2014]

$$R(\lambda) = (I_p - I_d) / (A P_i) \quad (7.1)$$

$$\text{and, } D^* = (A^{1/2} R(\lambda)) / (2q I_d)^{1/2} \quad (7.2)$$

where I_p = current under the light, and I_d = current in absence of light, A is the active area ($7.1 \times 10^{-4} \text{ cm}^2$), and P_i is the incident optical power intensity (8 mW/cm^2). The calculated photo responsivity and detectivity as a function of wavelength are plotted in Figure 7.5 (d). The value of the photoresponsivity as well as detectivity of this photodetector ($R = 2.10 \text{ A/W}$, $D = 5 \times 10^{11} \text{ Jones}$) are much better than that of many previously reported MoS₂ and graphene-based photodetectors. The high detectivity suggest that our rGO/MoS₂ photodetector is highly sensitive even for a small optical signal. This enhanced photo-responsivity and detectivity of the fabricated rGO/MoS₂ photodetector are attributed to an increased absorption rate of incident photons and the low value of dark current.

7.5 Speed and stability of the photodetector

To understand the reproducibility and speed of the MoS₂ and rGO/MoS₂ devices, we measured the temporal response of the devices at 4 V for blue light (460 nm) in ambient air. Both devices showed good repeatability and stability without degradation of photoresponse in its cyclic test, as shown in Figure 7.6 (a). In addition, the response time of the devices is calculated as time required to change the current from 10% to 90 % of the photocurrent. The rGO/MoS₂ photodetector exhibited a significantly improved response time of ~ 18 ms compared to the slow response of ~ 0.2 s of the pristine MoS₂ device (Figure 7.6 (b)). Further, to verify the influence of air, we examined the temporal response of the rGO/MoS₂ device again after three months, while the device was put in atmospheric environments for three months. From Figure 7.6 (c) it is observed that the device was stable and exhibited good reproducibility

with nearly unchanged photoresponse in ambient air for all 100 cycles. This stability and excellent repeatability are ascribed to a reduction in the interaction of photoexcited carriers with environmental adsorbates due to surface passivation of the MoS₂ by crumpled rGO particles.

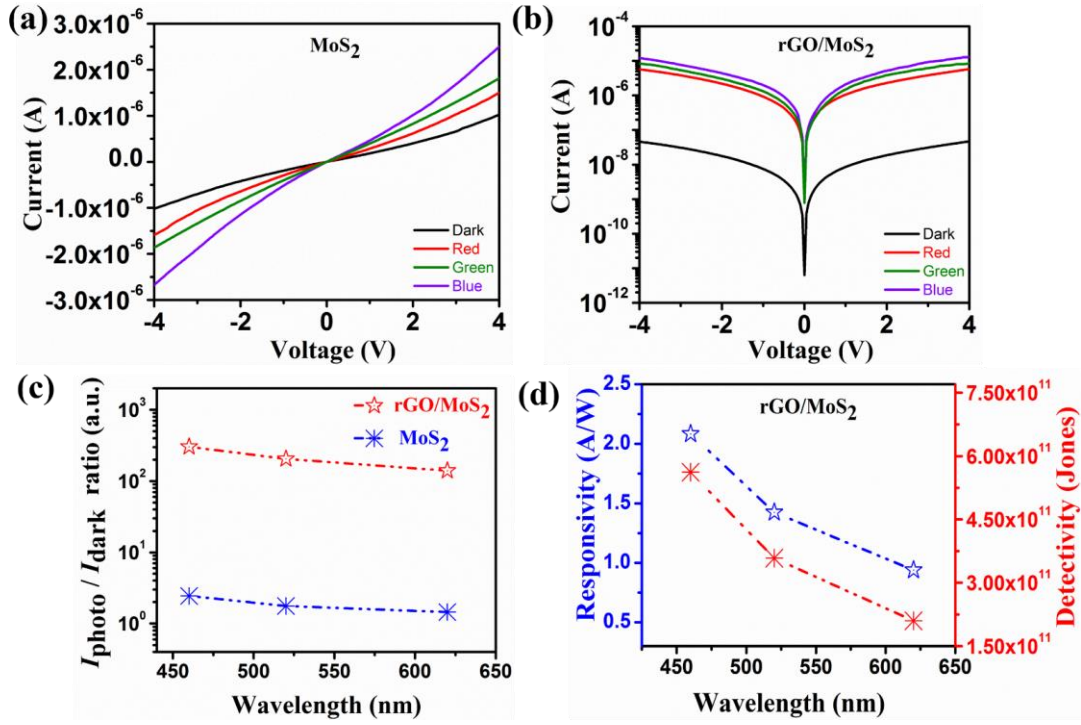


Figure 7.5: Current-voltage (I-V) characteristics measured in the dark and under different wavelengths at room temperature (a) in linear scale for pristine MoS₂, (b) in log scale for rGO/MoS₂ device. (c) $I_{\text{photo}} / I_{\text{dark}}$ ratio in log scale for both devices at a different wavelength in a log scale (d) Calculated responsivity and detectivity of the rGO/MoS₂ photodiode at different wavelengths.

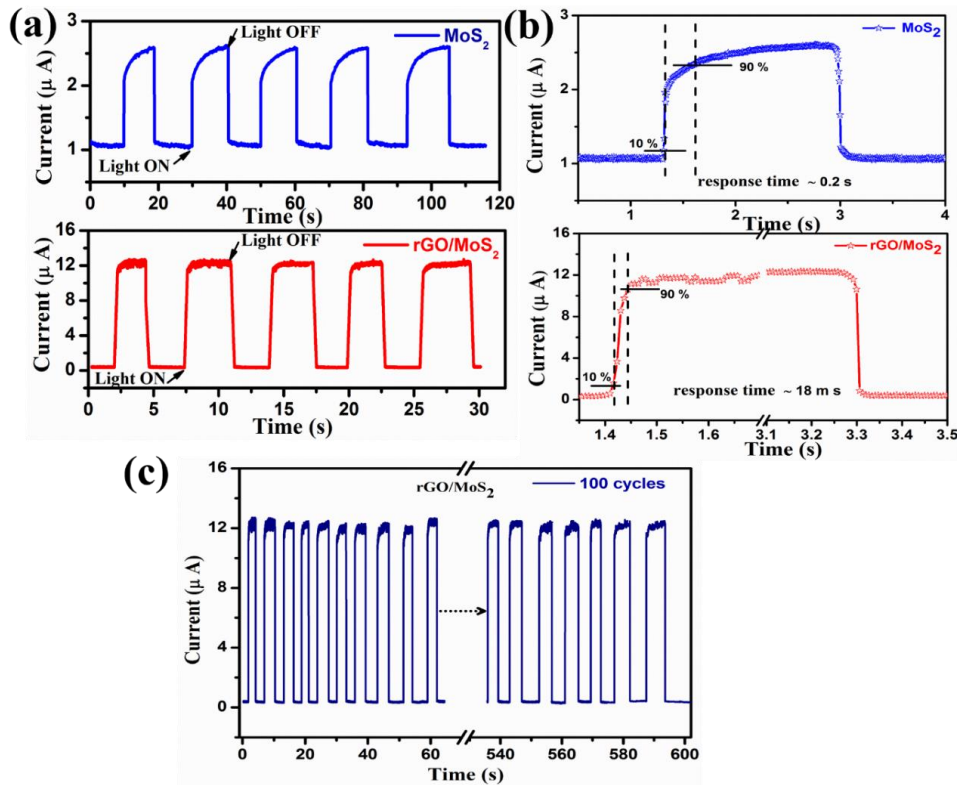


Figure 7.6: (a) A temporal response, (b) calculated response time, of the pristine MoS₂ and rGO/MoS₂ photodiodes at 4 V under blue (460 nm) light illumination. (c) Stability test of rGO/MoS₂ photodiode with 100 cycles under blue (460 nm) light illumination after 3 months in ambient air.

Whereas pristine MoS₂ deteriorates its photoelectric performance in ambient air. Because, MoS₂ having a high surface to volume ratio is very sensitive to the environmental adsorbates, for instance, H₂O and O₂ gas molecules withdraw the electrons from the MoS₂ surface, results in decreasing the photoresponse of the MoS₂ device.

In addition, to get additional insight on reproducibility, stability, repeatability and reliability of the device, we fabricated twelve devices (D1, D2, D3, ..., and D12) from each pristine MoS₂ and rGO/MoS₂ structures. The photo to dark current ratio was calculated for all devices at different wavelengths of each pristine MoS₂ and rGO/MoS₂ structure (see Table 7.1 and 7.2). Moreover, histograms of the pristine MoS₂ and rGO/MoS₂ devices with vertical error bars are shown in figure 7.7 and 7.8, respectively. The mean values of the $I_{\text{photo}}/I_{\text{dark}}$ ratio (in order of 10²) with low relative standard deviation (RSD) of ~ 1.01 % with standard deviation of < 3.5 demonstrating reliability with precise as well as stable photoresponse, and excellent manufacturability of new photodetector in the range of visible wavelengths by using the rGO/MoS₂ based structure.

Table 7.1: Calculated $I_{\text{photo}}/I_{\text{dark}}$ ratio values in the range of visible wavelengths (460, 520, 620 nm) for all 12 devices of pristine MoS₂.

Device	$I_{\text{photo}}/I_{\text{dark}}$ @ $\lambda = 460$ nm	$I_{\text{photo}}/I_{\text{dark}}$ @ $\lambda = 520$ nm	$I_{\text{photo}}/I_{\text{dark}}$ @ $\lambda = 620$ nm
D1	2.48	1.76	1.45
D2	2.54	1.98	2.01
D3	1.89	1.03	1.02
D4	3.01	2.01	1.89
D5	2.46	1.84	1.32
D6	2.65	2.04	1.86
D7	1.96	1.64	1.4
D8	1.99	1.74	0.98
D9	2.14	1.46	1.24
D10	2.28	1.83	1.36
D11	2.98	2.1	1.98
D12	3.1	2.22	1.9
Mean value	2.45	1.81	1.53
SD	0.40	0.31	0.36

Table 7.2: Calculated $I_{\text{photo}}/I_{\text{dark}}$ ratio values in the range of visible wavelengths (460, 520, 620 nm) for all 12 devices of the rGO/MoS₂.

Device	$I_{\text{photo}}/I_{\text{dark}}$ @ $\lambda = 460$ nm	$I_{\text{photo}}/I_{\text{dark}}$ @ $\lambda = 520$ nm	$I_{\text{photo}}/I_{\text{dark}}$ @ $\lambda = 620$ nm
D1	301.54	204.62	140.10
D2	302.82	205.02	140.4
D3	304.54	206.24	141.56
D4	299.86	202.45	139.86
D5	300.24	203.64	138.67
D6	305.28	207.56	142.56
D7	298.56	201.25	138.54
D8	300.58	202.56	136.58
D9	306.82	208.52	146.54
D10	296.45	199.35	137.98
D11	301.68	204.82	138.57
D12	297.52	196.58	136.58
Mean value	301.32	203.55	139.82
SD	3.01	3.24	2.66

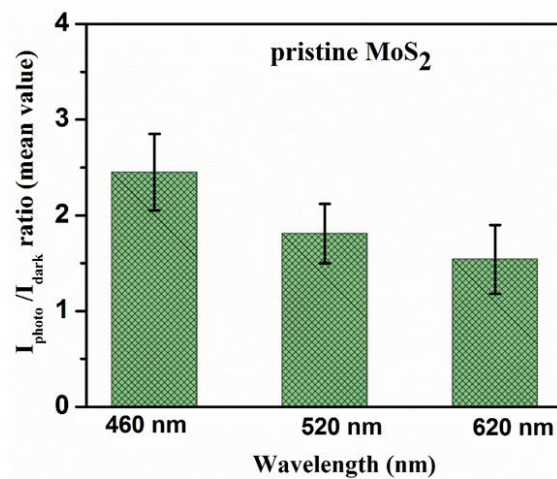


Figure 7.7: A histogram of the mean value of $I_{\text{photo}}/I_{\text{dark}}$ ratio of the pristine MoS₂ structure-based twelve devices (D1, D2, D3, ..., and D12) at three different wavelengths. and vertical error bar depicts the standard deviation from the mean value.

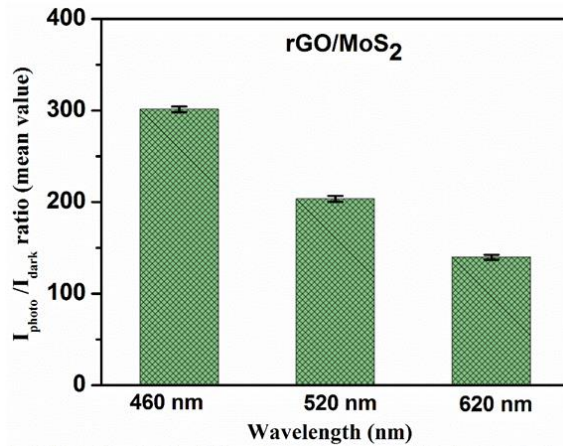


Figure 7.8: A histogram of the mean value of $I_{\text{photo}}/I_{\text{dark}}$ ratio of the rGO/MoS₂ structure-based twelve devices (D1, D2, D3, ..., and D12) at three different wavelengths and vertical error bar depicts the standard deviation from the mean value.

7.6 Light sensing mechanism of the photodetector

We have also elucidated the generation and movements of charge carriers at the rGO/MoS₂ interface under the light irradiation of different wavelengths by energy band diagram of rGO particles and vertically aligned MoS₂ flakes network (Figure 7.9), and utilize the photo-gating effect to explain the enhanced photoresponse in the rGO/MoS₂ device. The work function of p-type rGO is about 4.9 eV, which is more than that of n-type MoS₂ of 4.6 eV and electron affinity of MoS₂ is 4.2 eV, as shown in Figure 7.9 (b). The high quality vertically oriented MoS₂ flakes network provides the high active surface area, strong optical adsorption and fast carrier transport to enhance the performance of photodetector. And, this MoS₂ flakes network enhanced the contact area with the crumpled rGO particles as compared to the plane nanosheet MoS₂ because plane nanosheet makes only point contact with crumpled rGO particles. Moreover, exposed edge sites of vertically aligned MoS₂ facilitate the strong electronic coupling with sp² hybridized carbon atom of the rGO. As a result, multiple open-circuit nanoscale p-n heterojunctions are formed in between crumpled rGO particles and vertically aligned MoS₂ flakes (Figure 7.9(a)). Thereby, band bending and space charge regions are occurred at these multiple nano junctions due to electron transfer that is derived by the work function difference between the rGO and MoS₂. This electron transfer from MoS₂ is also confirmed by observing the reduced dark current of the rGO/MoS₂ device and also by Raman spectroscopy. The space charge region, d , at each nano junction, enhanced the generation of electron-hole pairs under the light irradiation and suppress the recombination of photoexcited electron-hole pairs. Because, a local built-in electric field directed from MoS₂ to rGO drives a force for separating photoexcited carrier and rises carrier lifetime, as shown in Figure 7.9(c). Thereby, photoexcited electrons moved into MoS₂, which are same as majority carrier of n-type MoS₂ and whereas, hole transferred into rGO due to built-in electric field at the interface. The electrons in MoS₂ channel are circulated under the influence of applied external electric field in between two electrodes and generate photocurrent.

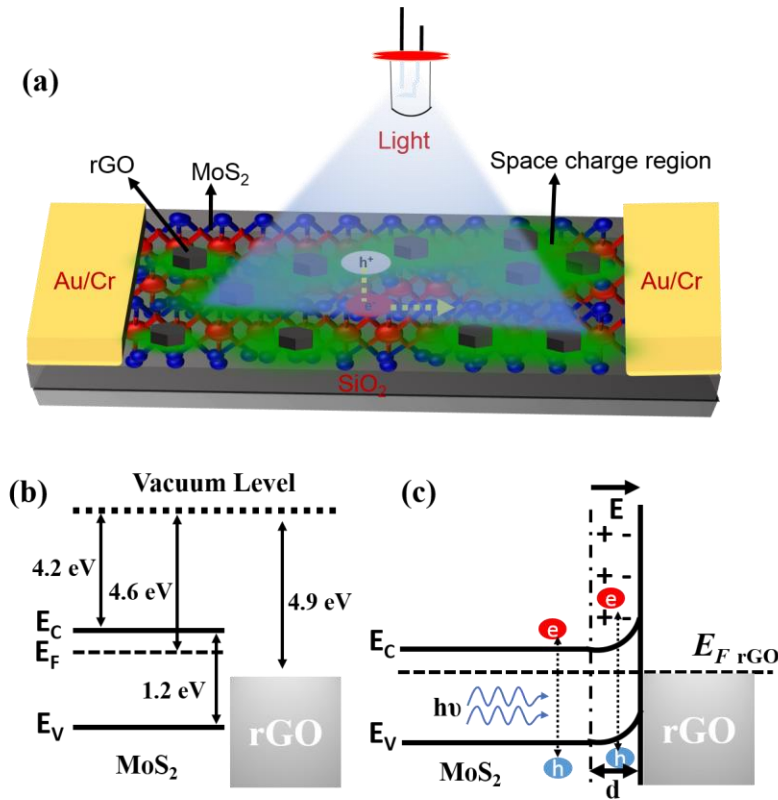


Figure 7.9: (a) A sketch of crumpled rGO particles decorated MoS₂ based photodiode and space charge region formed at the interface. Energy band diagram of the MoS₂ and rGO (b) before the contact, (c) after the contact under light illumination.

Meanwhile, accumulated holes in the rGO modulate the conduction of the channel (MoS₂) after exploiting the photo-gating effect through capacitive coupling [Zhenhua et al., 2016, and Chao et al., 2016]. Thereby, photo-response of the rGO/MoS₂ based device was significantly enhanced by the photo-gating effect. On the other hand, the rGO/MoS₂ nanohybrids also absorbed more light compared to pristine MoS₂, as shown in figure 7.4. So, electron-hole pairs generation was increased in the rGO/MoS₂ nanohybrids due to gathering of visible light and showed higher photoresponse. As a result, the improved photoresponse of the rGO/MoS₂ device was because of synergism of increased optical absorption and photo-gating effect.

7.7 Conclusion

In summary, we fabricated a device using crumpled rGO particles decorated vertically aligned MoS₂ flakes network to form p-rGO/n-MoS₂ heterostructure and investigated its light-induced electric properties under the visible spectra. The multiple nano junctions between p-rGO and n-MoS₂ formed the p-n heterojunctions at the interface which improved the spatial separation of the photoexcited carrier due to a developed high built-in electric field at the interface. So, the rGO/MoS₂ photodetector showed high performance in term of photo responsivity (~ 2.10 A/W) and detectivity ($\sim 5 \times 10^{11}$ Jones) in atmospheric environments. Moreover, crumpled rGO particles decoration on MoS₂ improved the response time of the MoS₂ photodetector from 0.2 s to 18 ms and showed stability in ambient air at room temperature via surface passivation. The high photoresponse and its stability in air suggest that the integration of rGO particles with MoS₂ pave the way to develop a high-performance practical photodetector.

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