

Type-II WS₂-ReSe₂ Heterostructure and its Charge Transfer Properties

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Abstract

We fabricated a van der Waals heterostructure of WS₂-ReSe₂ and studied its charge transfer properties. Monolayers of WS₂ and ReSe₂ were obtained by mechanical exfoliation and chemical vapor deposition, respectively. The heterostructure sample was fabricated by transferring the WS₂ monolayer on top of ReSe₂ by a dry transfer process. Photoluminescence quenching was observed in the heterostructure, indicating efficient interlayer charge transfer. Transient absorption measurements show that holes can efficiently transfer from WS₂ to ReSe₂ on an ultrafast time scale. Meanwhile, electron

transfer from ReSe_2 to WS_2 was also observed. The charge transfer properties show that monolayers of ReSe_2 and WS_2 form a type-II band alignment, instead of type-I as predicted by theory. The type-II alignment is further confirmed by the observation of extended photocarrier lifetimes in the heterostructure. These results provide useful information for developing van der Waals heterostructure involving ReSe_2 for novel electronic and optoelectronic applications and introduce ReSe_2 to the family of two-dimensional materials to construct van der Waals heterostructures.

Keywords: semiconducting; optical properties

Introduction

Since the discovery of graphene in 2004 [1], many two-dimensional (2D) materials have been fabricated and studied [2-4]. One of the most extensively studied 2D material families is the transition metal chalcogenides (TMDs) [5-7]. Unlike the zero-gap graphene, TMDs have sizeable electronic bandgaps that are strongly dependent on the thickness, allowing thickness-tunable electronic and optical properties. With enhanced Coulomb interactions [8], electrons in 2D TMDs are also strongly coupled to light, resulting in novel optical properties. Hence, TMDs represent enormous potential in applications such as logic electronic and optoelectronic devices.

As layered materials, TMDs can be easily exfoliated to monolayers. Different TMD monolayers can also form van der Waals heterostructures by stacking them together

vertically. Such heterostructures can possess excellent optoelectronic properties that are different from their individual components. Recent studies have revealed that 2D heterostructures can offer exciting new physics and optoelectronic functionalities that can be utilized in solar cells [9-11], photocatalysis, and field effect transistors [12-17]. Since the TMD family has a large number of materials, they can form numerous heterostructures through different combinations for new material discovery and exploration. Indeed, the research on 2D TMD heterostructures has been rapidly growing in recent years [18].

Previously, only several 2D TMDs have been extensively studied, namely MoS_2 , WS_2 , MoSe_2 and WSe_2 . Consequently, most studies of 2D TMD heterostructures are on combining materials from this list. However, incorporating more TMD members, especially those with different crystalline structures and electronic properties, will significantly expand the horizon of this field. Here we report fabrication of WS_2 - ReSe_2 heterostructures and measurements of their charge transfer properties. WS_2 possesses excellent optical properties among the TMDs [19-21]. Meanwhile, ReSe_2 is a newly emerged member of the TMDs family. Its triclinic unit cell has four Re atoms forming a connected parallelogram-shaped cluster, belonging to the bulk space group of P1 [22-23]. Unlike the commonly studied high-symmetry hexagonal TMDs with in-plane isotropic electrical and optical properties, ReSe_2 shows in-plane anisotropic properties due to the lower symmetry of its distorted lattice structure. The anisotropic electrical and optical properties can have potential applications in polarization-sensitive photodetectors [24-25], integrated polarization controllers (such as waveplates) [26-27] and field-effect transistor

s[28-29]. Furthermore, unlike most TMDs, a transition from indirect to direct bandgap is absent in ReSe₂. So far, studies on ReSe₂ have been mostly focused on increasing its crystalline quality [30-32] and understanding its optical [33] and electrical properties [34]. In contrast, there have been few reports on van der Waals heterostructures constructed by this material and the charge transfer properties involving ReSe₂.

In this paper, a van der Waals heterostructure was fabricated by stacking together monolayers of WS₂ and ReSe₂. Photoluminescence quenching was observed in the heterostructure in comparison to the individual monolayers, indicating efficient interlayer charge transfer processes. The charge carrier dynamics of the heterostructure was studied by transient absorption measurements. We found that holes excited in WS₂ can transfer to ReSe₂ on an ultrafast time scale. The long lifetime of the photocarriers in the heterostructure proves that electrons and holes are separated in the two layers. This observation shows that the WS₂-ReSe₂ heterostructure has a type-II band alignment. The conclusion was further confirmed by the observation of electron transfer from ReSe₂ to WS₂. This work thus proves efficient charge transfer can occur in this heterostructure, and introduces ReSe₂ to the family of 2D materials to construct van der Waals heterostructures.

Results and Discussion

Figure 1a shows schematically the heterostructure studied in this work. A ReSe₂ monolayer and a WS₂ monolayer are vertically stacked together to form a hetero-bilayer structure by the van der Waals interlayer coupling. In general, materials can form different

types of electronic energy band alignments, depending on the relative positions of their band extremes. Previously, both type-I and type-II band alignments have been observed in TMD heterostructures. The type-I alignment is formed when the conduction band minimum (CBM) and the valance band maximum (VBM) are both located in the same materials. With this alignment, both electrons and holes populated in the material with smaller bandgap. The spatial overlap of the wavefunctions of electrons and holes facilitates their radiative recombination, and thus type-I band alignment is favorable for light-emitting applications [35-36]. In the type-II alignment, the CBM and the VBM are located in different materials. Because the electrons and holes populate different layers, their lifetime can be significantly extended, which is desirable for light detection or photovoltaic devices [37-38].

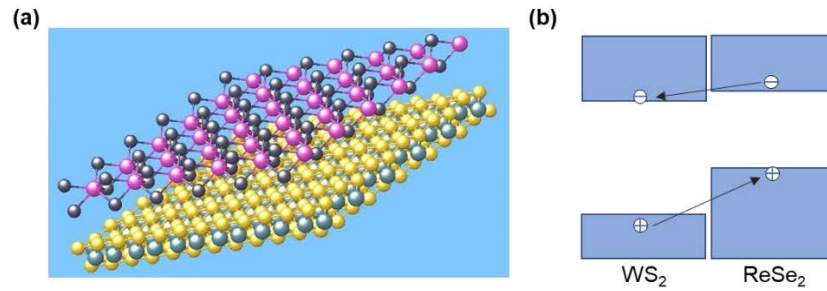


Figure 1: (a) The crystalline structure of the heterostructure sample formed by vertically stacking together monolayers of WS₂ (bottom) and ReSe₂ (top). (b) The band alignment of the WS₂-ReSe₂ heterostructure and the expected electron and hole transfer processes.

So far, the nature of the band alignment of the WS₂-ReSe₂ heterostructure is still an open question that requires experimental studies. The central hypothesis and the conclusion of this study is summarized in Figure 1b. We propose that WS₂-ReSe₂ heterostructure forms

the type-II band alignment, with the CBM and VBM located in the WS_2 and ReSe_2 layers, respectively. Furthermore, due to such an alignment, electrons can efficiently transfer from ReSe_2 to WS_2 , while hole can transfer from WS_2 to ReSe_2 . The transferred electrons and holes are spatially separated in the two layers, resulting in long carrier lifetimes.

According to first-principles calculations, the VBM of ReSe_2 is about 0.3 - 0.4 eV higher than that of WS_2 [36, 39]. Hence, it appears safe to assume that the VBM is located in ReSe_2 . However, the location of the CBM is less certain. Previous calculations have predicted that the CBM of ReSe_2 is only about 0.04 eV lower than that of WS_2 . [36, 39] This would result in the type-I alignment with both band extremes in ReSe_2 . However, due to the challenges in accurately determining the band structures by the first-principles

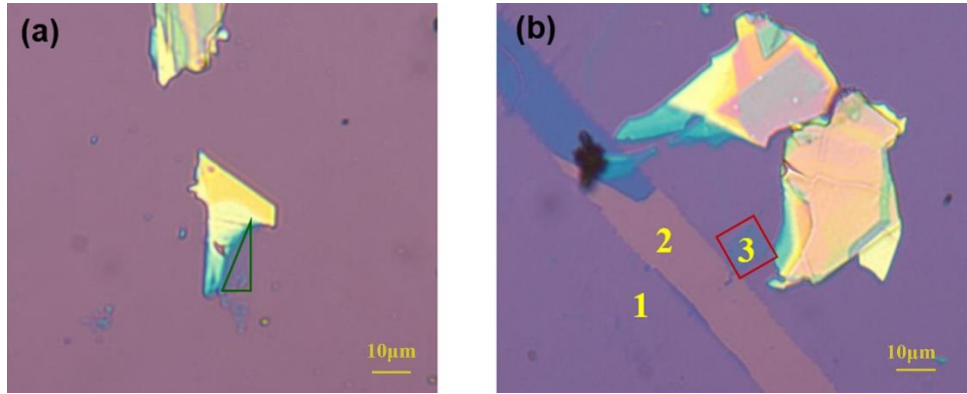


Figure 2: (a) An optical microscope image of the WS_2 flakes. (b) An optical microscope image of the ReSe_2 film and the WS_2 - ReSe_2 heterostructure.

calculations, such a small offset could be within the uncertainties of the theory. Thus, experimental studies on the nature of the band alignment is desirable.

To understand the nature of the band alignment and to probe the charge transfer properties of WS_2 - ReSe_2 , we fabricate samples shown in Figure 2. Figure 2(a) and 2(b) are

the optical microscope images of the monolayer WS₂ and the WS₂-ReSe₂ heterostructure sample, respectively. The WS₂ monolayer was obtained by mechanical exfoliation from a bulk crystal. The ReSe₂ monolayer film was grown by chemical vapor deposition. The WS₂ monolayer flake was transferred on top of the ReSe₂ film by a dry transfer technique. The samples were thermally annealed to improve the interface quality (see Methods for details). The areas marked 1, 2, 3 in Figure 2(b) are the monolayer ReSe₂, the Si/SiO₂ substrate, and the WS₂-ReSe₂ heterostructure, respectively.

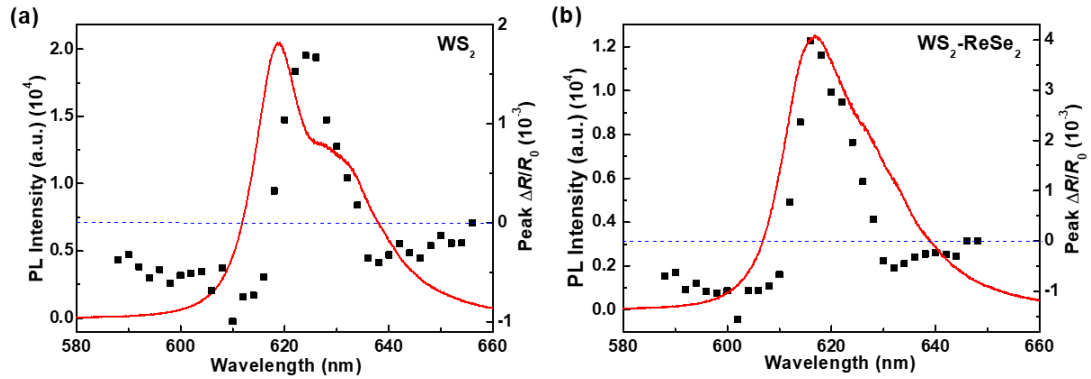


Figure 3: (a) Peak differential reflection signal from the monolayer WS₂ as a function of the probe wavelength (symbols, right axis) and PL of the same sample under 532-nm (2.33-eV) laser excitation. (b) Same as (a) but for the heterostructure sample.

Photoluminescence (PL) spectra of the monolayer WS₂ and the heterostructure at room temperature were obtained under a 532-nm (2.33-eV) laser excitation, as shown as the curves in Figure 3. The peak at about 615 nm and the shoulder at about 625 nm can be attributed to the excitons and trions, respectively. The PL intensity of the heterostructure is

about 60% of the WS₂ monolayer. Since the two spectra were measured under the same conditions, without interlayer interactions, the PL would be similar. The reduction of PL in the heterostructure could thus be attributed to transfer of photocarriers from WS₂ to ReSe₂ before they recombined in WS₂. Figure 3 also shows the spectra of differential reflection (symbols, right axis). In these measurements, a 410-nm (3.02-eV) pump pulse with a peak fluence of 5.6 $\mu\text{J cm}^{-2}$ was used to inject photocarriers. Differential reflection of the probe with various probe wavelengths was measured as a function of the probe delay. The differential reflection is defined as $\Delta R/R_0 = (R - R_0)/R_0$, where R and R_0 are the reflectance of the sample at the probe wavelength with and without the presence of the pump, respectively. The peak differential reflection signal at each probe wavelength is plotted in Figure 3 as the black squares. The strong dependence of the signal near the PL peak proves that in both samples, the differential reflection signal originates from the change of the exciton resonance of WS₂ due to the pump-injected carriers. Therefore, the differential reflection signal monitors population of the photocarriers in WS₂. The largest signal was obtained with the probes of 1.98 eV and 2.02 eV for the monolayer WS₂ and the WS₂-ReSe₂ heterostructure samples, respectively. Hence, these probe photon energies will be used in the following experiments.

One way to test our central hypothesis of the type-II band alignment is to observe electron transfer from ReSe₂ to WS₂, which would prove that the CBM of ReSe₂ is higher than that of WS₂. We designed an experimental configuration as illustrated in Figure 4(a).

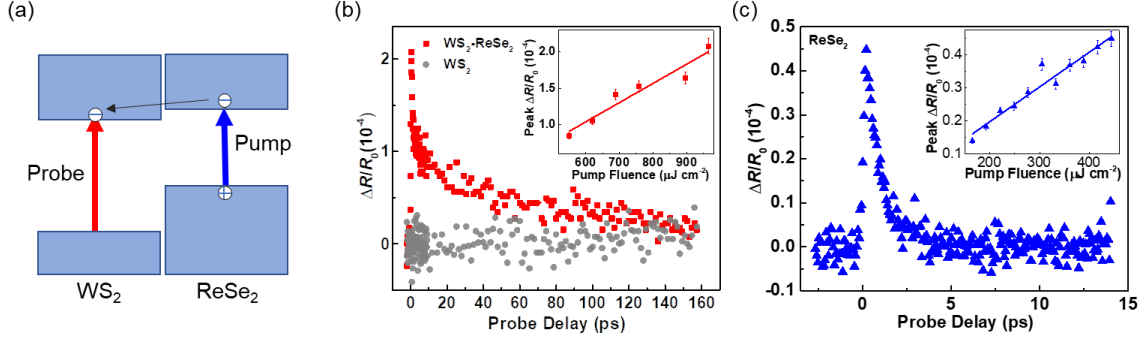


Figure 4: (a) The pump-probe configuration to study electron transfer from ReSe₂ to WS₂. A 1.51-eV pump excites ReSe₂ only (blue vertical arrow). The excited electrons can transfer to WS₂ if the conduction band minimum of WS₂ is lower than ReSe₂. The presence of the electrons in WS₂ is detected by a 2.01-eV probe pulse. (b) Differential reflection measured by using the configuration shown in (a) from the WS₂-ReSe₂ heterostructure (red squares) and the WS₂ monolayer sample (gray circles). The inset shows that the peak signal from the heterostructure is proportional to the pump fluence. (c) Differential reflection signal from a monolayer ReSe₂ measured by using a 2.01-eV pump and a 1.51-eV probe. The inset shows that the peak signal is proportional to the pump fluence.

A less energetic pump of 1.51 eV is used to excite the heterostructure sample. Since its photon energy is far below the optical bandgap of WS₂ of 2.01 eV, it can only excite the ReSe₂ layer, which has a 1.3-eV bandgap. If the electrons excited in ReSe₂ can transfer to WS₂, they will be sensed by the probe pulse of 2.01 eV. The results of such a measurement are shown in Figure 4(b) as the red squares. The existence of the differential reflection signal in this configuration confirms that electrons excited in ReSe₂ can transfer to WS₂.

This observation thus proves that the CBM of ReSe₂ is higher than WS₂, as we hypothesized in Figure 1(b). To confirm our interpretation, three additional measurements were performed to rule out other potential origins of the signal: First, we repeated the measurement on the individual WS₂ monolayer sample, and observed no signal, as indicated by the gray circles in Figure 4(b). This shows that, indeed, the pump does not excite WS₂. Second, we studied the pump-fluence-dependence of the signal from the heterostructure. As shown in the inset of Figure 4(b), the signal is proportional to the pump fluence. This confirmed that the pump does not excite the WS₂ layer of the heterostructure by two-photon absorption. Indeed, two-photon absorption of WS₂ is negligible at this pump fluence according to previously reported values of its coefficient [40]. Third, to rule out the possibility that the probe senses electrons in the ReSe₂ layer of the heterostructure through mechanisms other than phase-space state filling, such as screening, we studied photocarrier dynamics in an individual ReSe₂ monolayer sample by using the 2.01-eV pulse as the pump and the 1.51-eV pulse as the probe. As shown in Figure 4(c), the dynamics of the photocarriers in ReSe₂ is very different from the signal observed from the heterostructure sample, featuring a very fast decay time. Hence, we conclude that the signal observed from the heterostructure is due to electrons in WS₂. Since WS₂ is not excited, the only possible origin of these electrons is those transferred from ReSe₂. Furthermore, the sub-picosecond rising time of the signal indicates that the electron transfer from ReSe₂ to WS₂ occurs on an ultrafast time scale.

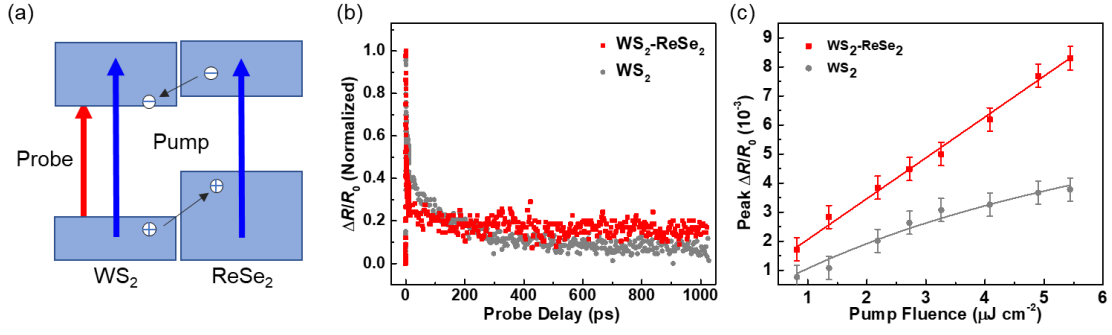


Figure 5: (a) The pump-probe scheme to study hole transfer from WS₂ to ReSe₂ and charge separation. The sample is excited by a 3.02-eV pump pulse and detected by a 2.01-eV probe pulse. (b) Normalized differential reflection signals from the WS₂-ReSe₂ heterostructure (red squares) and WS₂ monolayer (gray circles). (c) The peak differential reflection signals from the two samples as a function of the pump fluence.

According to theory, the VBM of ReSe₂ is about 0.3 - 0.4 eV higher than that of WS₂ [36, 39]. Thus, the VBM of the heterostructure is located in ReSe₂ and holes excited in WS₂ are expected to transfer to ReSe₂ to lower their potential energy. To study this process, we used the 3.02-eV pump pulse to excite the heterostructure and the 2.01-eV probe to monitor carriers in WS₂. Figure 5(a) shows schematically the pump -probe scheme and the expected charge transfer. Here, both layers are excited and electrons and holes are expected to transfer along opposite directions and separate into the two layers. The red squares and gray circles in Figure 5(b) show the normalized differential reflection signal from the heterostructure and the WS₂ monolayer, respectively. Clearly, the two samples show different carrier dynamics. The signal from the heterostructure show a slow-decaying

component that persist for more than 1 ns. Such a long carrier lifetime confirms the layer-separation of electrons and holes - a signature of type-II band alignment - and thus hole transfer from WS₂ to ReSe₂. Furthermore, Figure 5(c) shows the peak signals from the two samples as a function of the pump fluence. For the same fluence, the signal from the heterostructure is about twice of the signal from WS₂, further confirming the existence of charge transfer. In addition, while the signal from the heterostructure is proportional to the pump fluence (and thus the injected carrier density), a saturation effect was observed in WS₂ [the gray curve in Figure 5(c)]. This can be attributed to different physics mechanisms responsible for the differential reflection signal of the two samples. In the WS₂ monolayer, the signal is caused by excitons and thus mainly through the phase-space state filling effect which has a lower saturation density. In the heterostructure only electrons populate the WS₂ layer and thus their charge screening effect could be significant.

Conclusion

In summary, we have studied charge transfer in a van der Waals heterostructure fabricated by stacking together monolayers of WS₂ and ReSe₂. Photoluminescence quenching observed in the heterostructure indicates efficient interlayer charge transfer. The results of transient absorption measurements show that electrons excited in ReSe₂ can transfer to WS₂ on an ultrafast time scale. Meanwhile, holes excited in WS₂ can transfer to ReSe₂. These observations establish that monolayers of WS₂ and ReSe₂ forms a type-II heterostructure with excellent charge transfer properties. This work introduces ReSe₂ as a

new building block to construct van der Waals heterostructure with good charge transfer properties and provides a strategy for its applications in electronic and optoelectronic devices. Although unexplored in this study, the in-plane anisotropic absorption of ReSe₂ could be utilized in such heterostructures for polarization-sensitive photodetection devices.

Methods

The WS₂ bulk crystal used in the experiment was acquired from 2D Semiconductors. A monolayer WS₂ was prepared by mechanical exfoliation from the bulk crystal and then was transferred to a Si/SiO₂ substrate. Another exfoliated monolayer was transferred to a monolayer ReSe₂ film which was grown on a Si/SiO₂ substrate by chemical vapor deposition (acquired from 6 Carbon Technology Corporation, where information about the material characteristics is available). The WS₂-ReSe₂ heterostructure sample and the monolayer WS₂ sample were both annealed for 6 hours at 200 °C in Ar environment at a base pressure of about 5 Torr.

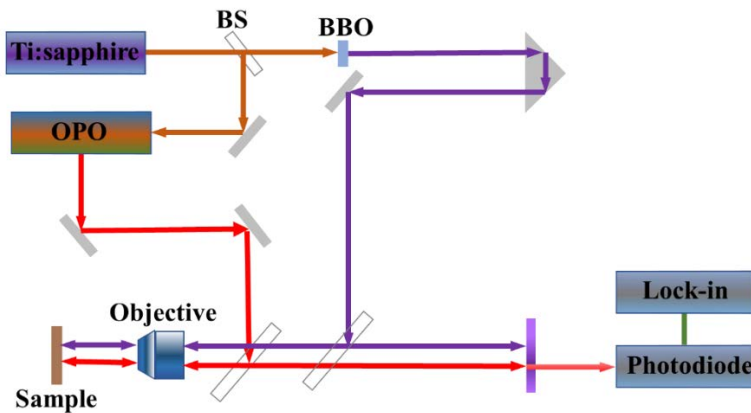


Figure 6: Schematics of the transient absorption setup.

The photocarrier dynamics in these samples was studied by a transient absorption technique [38, 41]. The principle of this technique and the experimental setup have been described previously [42]. Figure 6 shows schematically the experimental configuration. Here, three pulses with wavelengths of 410, 620, and 820 nm were utilized as pump or probe pulses. The 820 nm pulse was obtained from a 80-MHz Ti:sapphire laser. The 410 nm pulse was obtained from second harmonic generation of the 820 nm pulse in a beta barium borate crystal. The 620 nm pulse was obtained from an optical parametric oscillator (OPO) that was pump by the 820 nm pulse. The selected pump and probe beams are combined by a beam splitter (BS) and co-focused to the sample. Their relative arrival time at the sample was controlled by changing the path length of the probe beam with a linear motor stage. In the transient absorption measurements, photocarriers are inject by the pump pulse and monitored by measuring the differential reflection of the probe, which is defined as $\Delta R/R_0 = (R - R_0)/R_0$, where R and R_0 are the probe reflection with the without the pump.

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