

# Optoelectronics based on 2D TMDs and heterostructures

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**Abstract:** 2D materials including graphene and TMDs have proven interesting physical properties and promising optoelectronic applications. We reviewed the growth, characterization and optoelectronics based on 2D TMDs and their heterostructures, and demonstrated their unique and high quality of performances. For example, we observed the large mobility, fast response and high photo-responsivity in MoS<sub>2</sub>, WS<sub>2</sub> and WSe<sub>2</sub> phototransistors, as well as the novel performances in vdW heterostructures such as the strong interlayer coupling, am-bipolar and rectifying behaviour, and the obvious photovoltaic effect. It is being possible that 2D family materials could play an increasingly important role in the future nano- and opto-electronics, more even than traditional semiconductors such as silicon.

**Key words:** 2D TMDs; heterostructures; optoelectronics; phototransistors

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## 1. Introduction

Two-dimensional (2D) materials such as graphene and transition metal dichalcogenides (TMDs) are one of the most interesting research topics due to their unique physical properties and great potential in optoelectronic applications. For example, a graphene monolayer with carbon atoms tightly packed into a 2D honeycomb lattice has been proven to possess an exceptionally high carrier mobility exceeding  $10^6$  cm<sup>2</sup>/(V·s) at 2 K and thus have great application potential in ultrafast photodetectors<sup>[1,2]</sup>. However, the band gap of graphene is zero, which limits its applications as the semiconducting active channel in optoelectronics, such as the graphene transistors cannot be turned off due to the high carrier concentration. Graphene also has a very low absorption coefficient leading to very low photo-responsivity and external quantum efficiency (0.1%–0.2%)<sup>[3,4]</sup>. Regarding this disadvantage, Konstantatos *et al.*<sup>[5]</sup> deposited lead sulphide (PbS) quantum dots on top of graphene as a sensitive layer. For these hybrid photodetectors, a huge photo-gain ( $G$ ) was generated due to the high absorption of PbS QDs and high mobility of graphene as well as the efficient charge transfer at the interface.

In contrast to graphene, 2D TMDs with sizable bandgaps around 1–2 eV complement the disadvantages of graphene and attract a great deal of attention due to their interesting physical properties in nanoelectronics, sensing and photonics<sup>[6–11]</sup>. Early start of 2D TMDs is WSe<sub>2</sub> crystal which exhibits high mobility (500 cm<sup>2</sup>/(V·s)), ambipolar behaviour and  $10^4$  on/off ratios at 60 K<sup>[12]</sup>. Then mono or few layer MoS<sub>2</sub> emerged as an interesting material in field effect transistors with excellent on/off ratio ( $10^8$ ) and room-temperature mobility of 200 cm<sup>2</sup>/(V·s)<sup>[13,14]</sup>. Compared to graphene-based devices, MoS<sub>2</sub> based photodetectors can exhibit enhanced responsivity and selectivity with improved responsivity (0.57 A/W) and fast photoresponse (70–110 ms); monolayer MoS<sub>2</sub>-based photodetectors have been demonstrated with a maximum photo-

responsivity of 880 A/W<sup>[15]</sup>. The bulk TMDs (MoS<sub>2</sub>, WS<sub>2</sub>) will become direct bandgap semiconductors when thinned to the monolayer limit. This bandgap transition facilitates the stronger optical emission and absorption, enabling high photon-matter interaction and high efficiency photovoltaic properties. The excellent electrical and optical features including the high mobility and tremendous gate modulation of current as well as strong photoluminescence could offer their opportunity in optoelectronics and energy harvesting applications. Besides, the TMDs based photodetectors show a huge internal photo-gain effect along with the very low dark current by operating the devices in depletion mode, which could produce extremely high responsivity and high sensitivity. Through encapsulation, plasmonic technique and quantum dots (PbS) sensitizing, the performances of TMDs based phototransistors can be further much improved with enhanced mobility and an extended spectrum region into the near and short-infrared spectrum, which is important in the night vision, remote sensing and communications. Besides, TMDs also demonstrate the advantages in the molecular sensing applications due to the high surface-to-volume ratio. For instance, single and few-layer MoS<sub>2</sub> sheets have been demonstrated to be sensitive detectors for NO, NO<sub>2</sub>, NH<sub>3</sub> and trimethylamine gas. The detection mechanism is probably due to the n-doping or p-doping induced by the adsorbed gas molecular, changing the resistivity of the intrinsically n-doped MoS<sub>2</sub>. Another interesting and important feature of atomically thin 2D materials is the large mechanical and bendable characteristics enabling the flexible and wearable sensors and detectors. Recently, other 2D TMDs such as MoSe<sub>2</sub>, WS<sub>2</sub>, WSe<sub>2</sub> etc. and the new 2D family materials such as black phosphorus have also shown great application potential in transistors, photodetectors and gas sensors.

Van der Waals heterostructures assembled by individual 2D layers are currently gaining particularly attention owing to their broad-range of optical bandgap and strong light-matter interactions<sup>[16,17]</sup>. It is proved that TMDs based heterostructures

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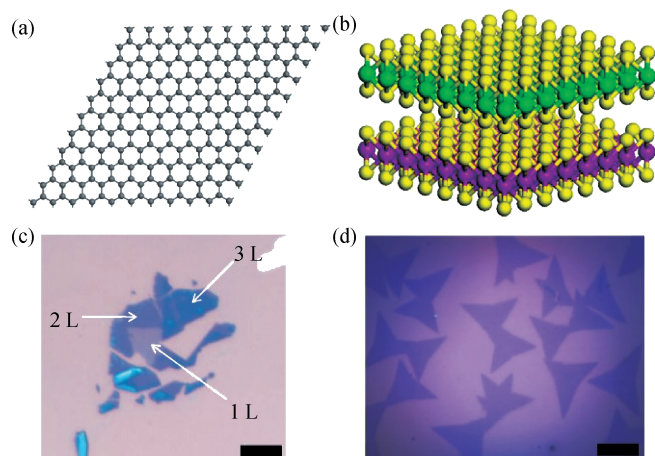


Fig. 1. (Color online) (a, b) Schematic diagram of graphene and TMDs ( $\text{MoS}_2$  or  $\text{WS}_2$ ), respectively. (c, d) Optical microscopy images of exfoliated  $\text{WSe}_2$  and CVD grown  $\text{MoS}_2$ , respectively. The scale bar is  $10\ \mu\text{m}$ .

usually possess type-II band alignment, which can facilitate the efficient electron-hole separation<sup>[18–20]</sup>. For example,  $\text{MoS}_2/\text{WS}_2$  heterostructure can exhibit novel and enhanced optoelectronic performances including the bipolar doping and photovoltaic properties<sup>[21]</sup>. More recently, growing interest has been focused on the p–n van der Waals (vdW) heterostructures since the p–n diode is one of the most fundamental building blocks of modern electronics and optoelectronics. In our recent research work, we found that the p–n  $\text{WSe}_2/\text{MoS}_2$  heterostructures could exhibit strong interlayer coupling and distinct current rectification behaviour<sup>[22]</sup>. Interesting tunable polarity behaviour has also been observed in the  $\text{WS}_2/\text{WSe}_2$  p–n junctions<sup>[23]</sup>. Actually there exist large numbers of 2D TMDs that can be exfoliated and CVD grown easily and assembled to design various heterostructures, which can provide an important platform for developing next-generation electronics and optoelectronics. In this work, we will introduce the development of 2D materials including the growth, physical properties and their optoelectronic applications in transistors, photodetectors and solar cells.

## 2. Growth and methods

Graphene is the monolayer counterpart of graphite which possesses a hexagonal honeycomb structure (Fig. 1(a)). 2D TMDs such as  $\text{MoS}_2$  and  $\text{WS}_2$  possess similar crystalline structures in which each single plane of  $\text{MS}_2$  (M: Mo or W) comprises a trilayer composed of a molybdenum or a tungsten layer sandwiched between two sulphur layers in a trigonal prismatic coordination (Fig. 1(b)). Compared to the traditional materials, the new 2D materials exhibit very unique and excellent physical and chemical properties. Before discussing their optoelectronic properties, we firstly introduce the growth and some methods involved in this paper.

Geim *et al.* developed a very facile tap exfoliation method to prepare the monolayer graphene in 2004 and thus won the Nobel fellowship in 2012 because of his contribution to graphene. Afterward, this simple method has also been proved useful in fabricating other 2D materials such as  $\text{MoS}_2$  thus ex-

tending the studies based on these monolayer materials. For any scientific research, the high quality of materials is most important as a basic fundamental. The exfoliated  $\text{MoS}_2$  exhibits high optoelectronic properties such as the high photoluminescence and mobility, but the size of the samples using the exfoliated method is very small, which limits their wide applications in an actual product. Thus the CVD method for large area and high quality of  $\text{MoS}_2$  has been investigated extensively.

### 2.1. Mechanical exfoliation

2D crystals such as  $\text{MoS}_2$ , and  $\text{WS}_2$  slice were purchased from Lamellae Co. and pasted on magnetic adhesive tape. Folding the sticky side of the tape in half then tearing the tape very slowly, thus the 2D slices are divided into two. This operation is repeated many times until very thin nanoflakes are exfoliated on the tape. The nanoflakes were exfoliated onto  $\text{SiO}_2/\text{Si}$  substrate by pressing the tape gently and then removing it slowly. After the exfoliation, the substrate was placed into hot acetone to remove the residual glue. Thus the 2D materials with different layers can be prepared on the substrate (Fig. 1(c)). The materials using this method usually have large mobility and high photo-response, but the disadvantage is the very small size which limits their large scale applications in optoelectronics.

### 2.2. CVD growth

2D materials ( $\text{MoS}_2$ ) can be grown on different substrates, such as the  $\text{SiO}_2$  and sapphire. Before growth, the substrate should be cleaned in acetone, isopropanol and DI water, followed by 5 min of  $\text{O}_2$  plasma. They were then loaded into a 1-inch CVD furnace and placed face-down above a crucible containing 10 mg of  $\text{MoO}_3$  (99.8% Sigma Aldrich) with another crucible containing 100 mg of sulphur (99.5% Sigma Aldrich) located upstream. The CVD growth is performed at atmospheric pressure while flowing ultrahigh-purity nitrogen at  $700\ ^\circ\text{C}$  for 10 min. Then the furnace is opened, the  $\text{N}_2$  flow is increased and it is cooled down to room temperature. Fig. 1(d) shows the triangle  $\text{MoS}_2$  single crystal using the CVD method. This method can produce large scale 2D materials and facilitate actual applications in the future; however, some problems with the CVD method still remain such as there are lots of defects and low mobility.

### 2.3. Transfer methods for heterostructures

In the case of  $\text{MoS}_2\text{--WS}_2$  heterostructures: The  $\text{MoS}_2\text{--WS}_2$  heterostructures were fabricated with the dry transfer method. Firstly, the multilayer  $\text{MoS}_2$  and  $\text{WS}_2$  nanoflakes were exfoliated onto two pieces of  $\text{SiO}_2/\text{Si}$  ( $300\ \text{nm SiO}_2$ ) substrates respectively from the  $\text{MoS}_2$  and  $\text{WS}_2$  crystals (2D semiconductors.com) with the micromechanical cleavage approach. Secondly, the polymethyl methacrylate (PMMA) liquid was spin-coated on the substrate with  $\text{WS}_2$  nanoflakes with a rotating speed of  $4000\ \text{r/s}$ . After annealing with  $150\ ^\circ\text{C}$  for 30 min, the substrate with PMMA film was soaked into the 2 M NaOH solution. Then, the PMMA film with  $\text{WS}_2$  nanoflakes was floated and transferred onto another substrate to overlap with the  $\text{MoS}_2$  nanoflakes. Finally, the PMMA was dissolved by acetone and the stacked  $\text{MoS}_2\text{--WS}_2$  heterostructures were achieved.

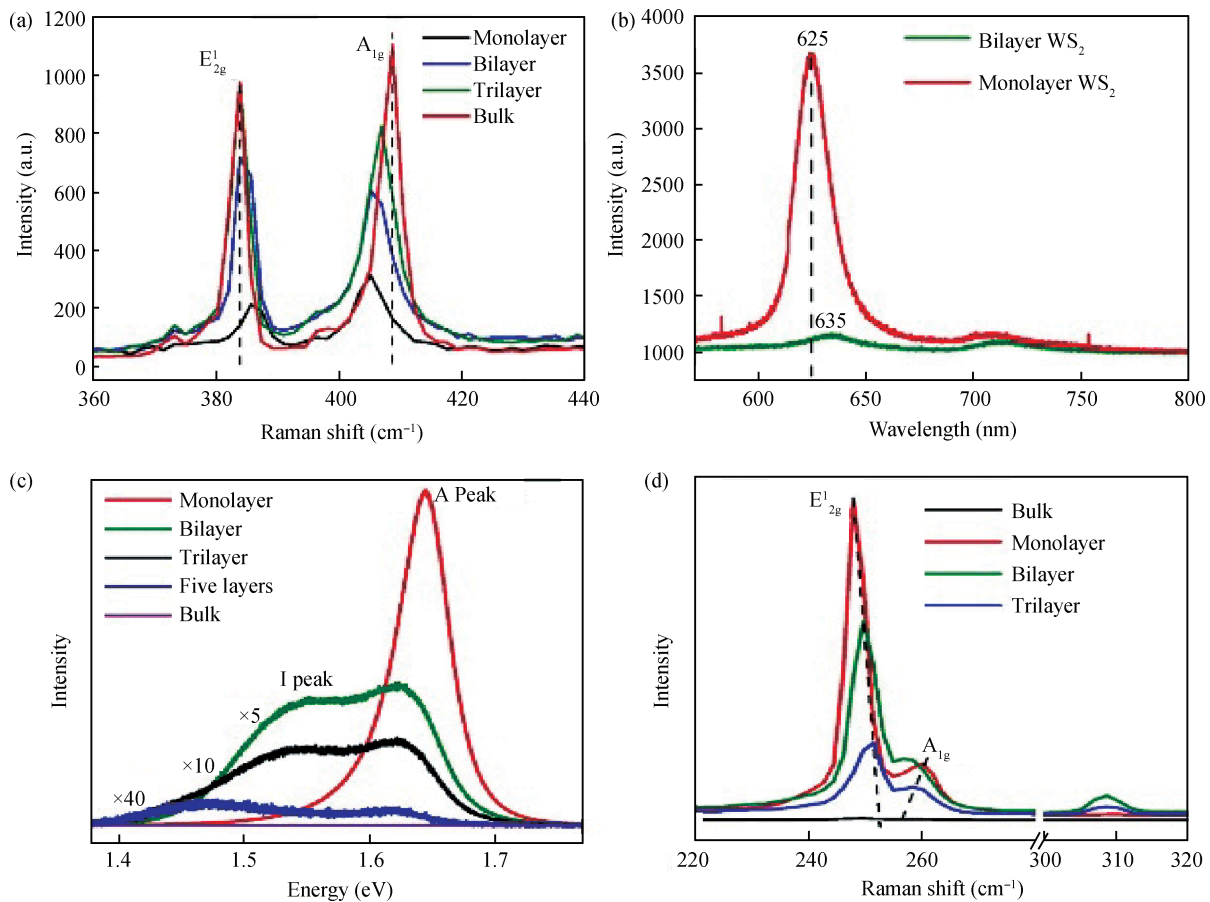


Fig. 2. (Color online) (a) Raman spectra of MoS<sub>2</sub> layers with different layers. (b) PL spectrum of monolayer and bilayer WS<sub>2</sub>. (c, d) PL and Raman spectrum of WSe<sub>2</sub> with different layers.

#### 2.4. Nano-devices fabrication

The general nano-device fabrication technique is photolithography such as the EBL and laser writer, but the fabrication cost is very high. In this work, we used the home-made and low-cost “gold-wire mask moving” technique. Firstly, MoS<sub>2</sub> flakes were exfoliated from the MoS<sub>2</sub> crystals onto 300 nm SiO<sub>2</sub>/Si substrates using the mechanical exfoliation technique, and with vacuum annealing at 350 °C for 2 h to remove the residual glue. Secondly, a micron gold-wire serving as a mask was fixed tightly on the top surface of WS<sub>2</sub> nanoflakes, and then a pair of Au electrodes was deposited onto the substrate by thermal evaporation. To avoid the scattering of metallic atoms onto the side-face of SiO<sub>2</sub>/Si substrates, the sides of the substrate were covered with tin foil. Finally, by slightly removing the Au wire mask and tin foil, the Au electrodes were fabricated and a micron size gap was produced between the two electrodes.

### 3. Optical properties (PL and Raman)

Generally, the band structure and phonon frequency of MS<sub>2</sub> layers are very sensitive to the thickness, i.e. indirect bulk MS<sub>2</sub> can turn into direct bandgap materials when thinned to monolayer, the Raman active mode A<sub>1g</sub> (out-of-plane displacement of S atoms) stiffens, and the E<sub>2g</sub><sup>1</sup> (in-plane displacement of M and S atoms) softens with increasing number of layers, as

shown in Fig. 2(a) for MoS<sub>2</sub>. Fig. 2(b) shows the PL spectrum of WS<sub>2</sub>. The PL intensity decreased with the increased layers. For 2D WSe<sub>2</sub> layers, the crystalline structure is similar to MoS<sub>2</sub> and WS<sub>2</sub>. The indirect-to-direct band gap crossover with decreasing layers to monolayer can also happen from the photoluminescence (PL) spectra (Fig. 2(c)). The monolayer WSe<sub>2</sub> exhibits a strong direct transition emission “A” peak at the energy of 1.65 eV. For the bilayer WSe<sub>2</sub>, the “A” peak becomes one order of magnitude weaker and red-shifts by about 20 meV, accompanied by the emerging indirect transition emission “I” peak at the energy of 1.55 eV. The “I” peak further shifts toward lower energy and outweighs the “A” peak at five layers. No PL signal is observed in bulk WSe<sub>2</sub>[22].

In contrast, the WSe<sub>2</sub> layers exhibit abnormal Raman modes where the Raman intensity is very sensitive to the thickness and decreases sharply with increasing number of layers (Fig. 2(d)). The Raman intensity of bulk WSe<sub>2</sub> is negligible, which is starkly different with MoS<sub>2</sub>. The reason for the unique Raman intensity of WSe<sub>2</sub> can be attributed to the strong interaction with the SiO<sub>2</sub> capping[24]. For the phonon frequency, unlike the obvious separated E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub> modes in MoS<sub>2</sub> and WS<sub>2</sub>, two adjacent modes at around 250 nm are assigned to E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub> modes, respectively[25,26]. Moreover, the E<sub>2g</sub><sup>1</sup> mode stiffens and A<sub>1g</sub> softens with increasing thickness of WSe<sub>2</sub> layers leading to the largest frequency differences in monolayer WSe<sub>2</sub>. The monolayer WSe<sub>2</sub> is most affected by the strain effect resulting in most severe splitting[22]. Overall, the sensitiv-

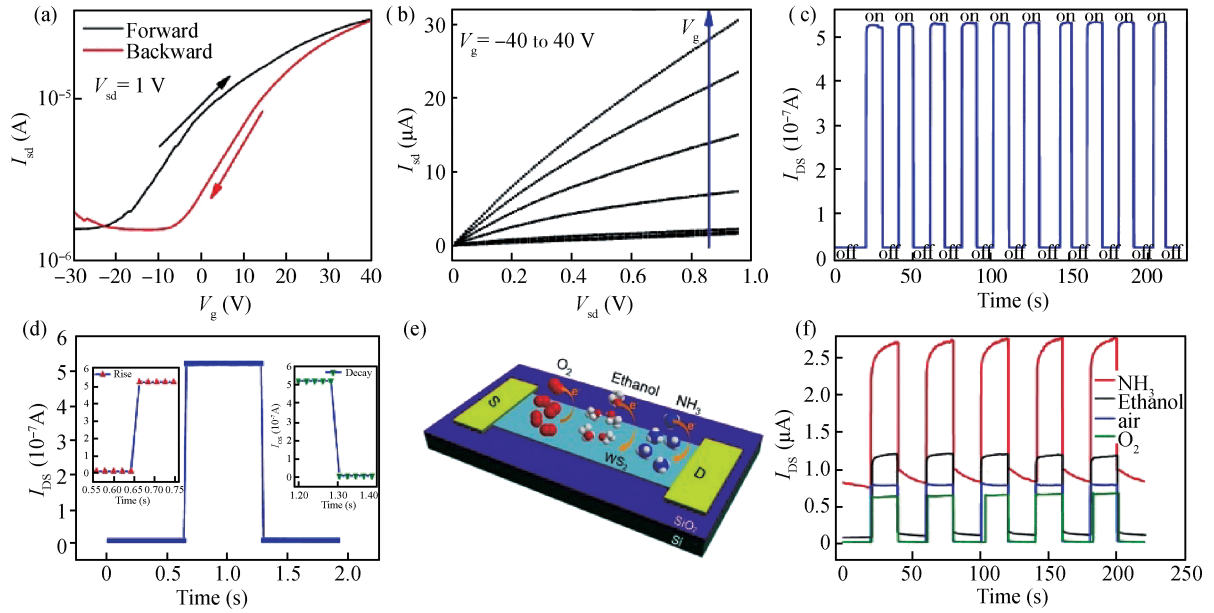


Fig. 3. (Color online) (a) Transfer curves of WS<sub>2</sub> based transistors. (b) Output curves of WS<sub>2</sub>. (c, d) Dynamic response of WS<sub>2</sub> phototransistors. (e) Schematic diagram of the device with different gas molecules. (f) Photoresponse under different gas atmosphere<sup>[27]</sup>.

ity change of phono frequency and PL intensity with various thicknesses in 2D family materials could be a quick and convenient identification of different layers.

#### 4. Optoelectronic applications: FETs, photodetectors and solar cells

2D materials have been demonstrated to have great application potential in various optoelectronics such as transistors, photodetectors and solar cells. In the following we will introduce the excellent properties of the 2D TMDs in these optoelectronics.

The mobility, photoresponsivity  $R$  and external quantum efficiency EQE are critical figures of merit for transistors and photodetectors. The large values of mobility,  $R$  and EQE correspond to high quality materials and high light sensitivity.

The mobility ( $\mu$ ) can be obtained from the equation  $\mu = \frac{\partial I_{DS}}{\partial V_G} \frac{L}{WC_i V_{DS}}$ , where  $L$  is the channel length,  $W$  is the channel width, and  $C_i$  is the gate capacitance between the channel and the silicon back gate per unit area, which can be given by equation  $C_i = \epsilon_0 \epsilon_r / d$ ,  $\epsilon_0$  is the vacuum dielectric constant, and  $\epsilon_r$  (3.9) and  $d$  (300 nm) are dielectric constant and thickness of SiO<sub>2</sub>, respectively.

$R$  and EQE can be expressed as  $R_\lambda = I_{ph}/PS$ ,  $EQE = hcR_\lambda/e\lambda$ , where  $I_{ph}$  is the photo-excited current;  $P$  is the light power intensity;  $S$  is the effective illumination area;  $h$  is Planck's constant;  $c$  is the velocity of light;  $e$  is the electron charge; and  $\lambda$  is the excitation wavelength.

##### 4.1. WS<sub>2</sub> based phototransistors

The multilayer WS<sub>2</sub> phototransistors were fabricated using the gold wire mask method. From the transfer and output characteristic (Figs. 3(a) and 3(b)), we get that the drain current increases largely with increased gate voltage indicating the n-type behaviour. The electron mobility can be calculated to

be 12 cm<sup>2</sup>/(V·s). With light irradiation on/off, the device can also work between low and high impedance states fast and reversibly with an on/off ratio of 25, allowing the device to act as a high quality photosensitive switch. The device also exhibits very fast dynamic response for both rise and decay processes (Figs. 3(c) and 3(d)): the response time is shorter than 20 ms (detection limit of our measurement setup).

The photosensitive properties of the multilayer WS<sub>2</sub> nanoflakes under the various gas environments were also investigated. From the time dependence of the photocurrent at various gas atmospheres during the light switching on/off (Fig. 3(f)), the WS<sub>2</sub> phototransistors can respond to the given gas molecules sensitively which play a different role in the conductivity and photosensitive properties. The drain current of the device is decreased at O<sub>2</sub>, but increased at ethanol and NH<sub>3</sub>. This is from the charge transfer between the WS<sub>2</sub> nanoflakes and the adsorbed gas molecules as shown in Fig. 3(e). Once the vapour molecules come into contact with the surface of WS<sub>2</sub>, the gas molecule would be adsorbed, subsequently changing the charge carrier distribution in WS<sub>2</sub> nanoflakes. O<sub>2</sub> molecules can act as electron acceptors to accept electrons from WS<sub>2</sub>, leading to a reduction in overall conductivity. In contrast, ethanol and NH<sub>3</sub> molecules, serving as electron donors, can donate electrons to the WS<sub>2</sub> nanoflakes, which enhance the total conducting electrons density, resulting in the increased current. It is noted that the  $R$  and EQE of the multilayer WS<sub>2</sub> nanoflakes photodetectors at air are 5.7 A/W and 1118%, respectively, which further improved to 884 A/W and  $1.7 \times 10^5\%$  under the NH<sub>3</sub> atmospheres<sup>[27]</sup>, demonstrating that the 2D multilayer WS<sub>2</sub> nanoflakes can be effectively used in highly sensitive photodetectors and fast photoelectric switches.

##### 4.2. MoS<sub>2</sub> and WSe<sub>2</sub> based phototransistors

Fig. 4(a) shows the transfer curves of the few-layers MoS<sub>2</sub> which performs very well n-type behavior with a large on/off



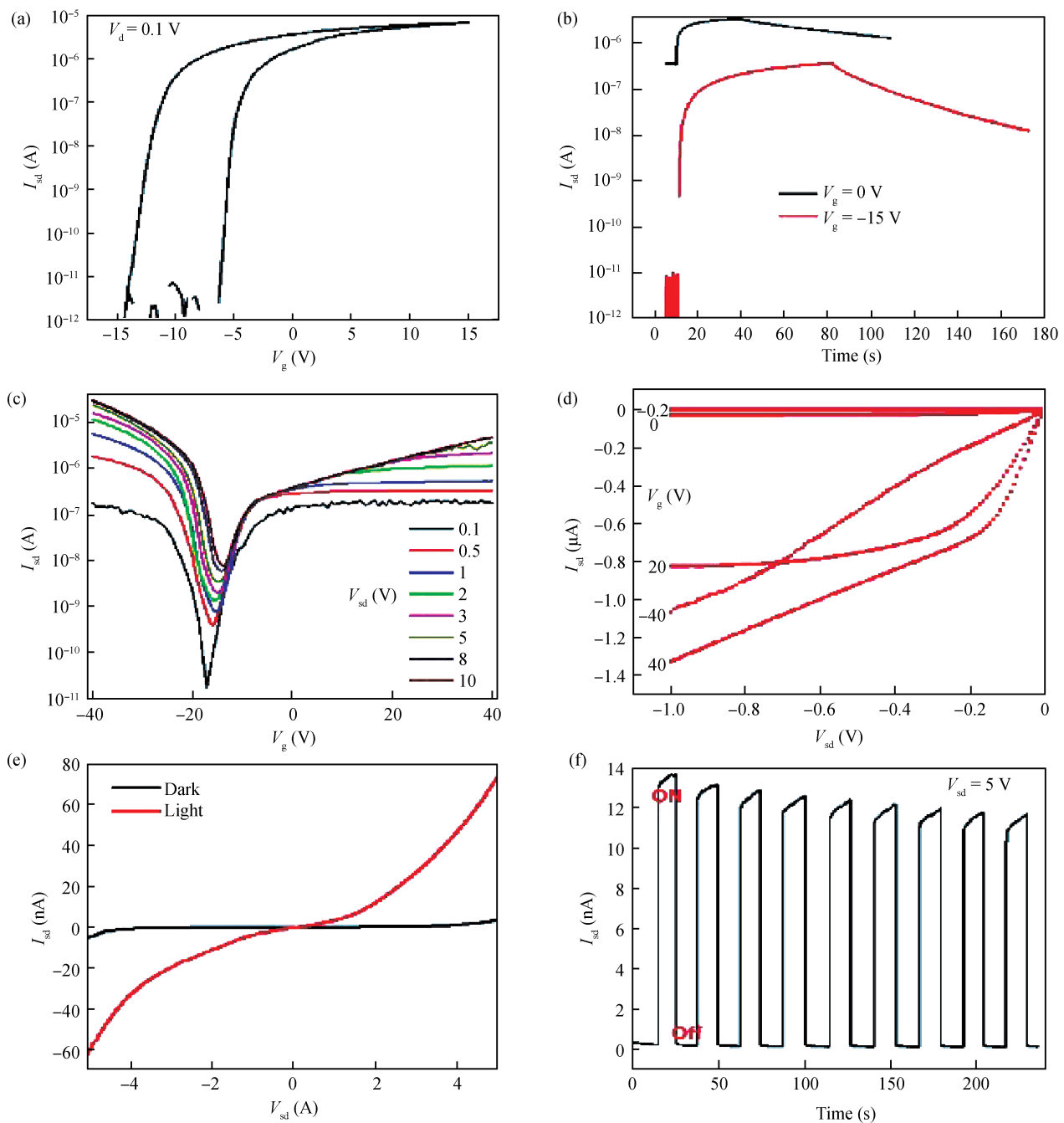


Fig. 4. (Color online) (a) Transfer and (b) output characteristics of pure atomically thin MoS<sub>2</sub> layers, the  $I_{sd}$  can increase with increasing gate voltage and the on/off ratio can reach higher than  $10^6$ , indicating the well n-type behaviour of MoS<sub>2</sub> layers. (c) Transfer and (d) output characteristics of pure atomically thin WSe<sub>2</sub> layers, indicating the well p-type behavior of WSe<sub>2</sub> layers with on/off ratio of about  $10^4$ . (e)  $I$ - $V$  curves of WSe<sub>2</sub> transistors under dark and light. (f) Dynamic response of WSe<sub>2</sub> devices.

ratio of  $10^6$  and large electron mobility; from the output characteristics, it is the Ohmic contact between Ti/Au electrodes and MoS<sub>2</sub> channel. The high performance of MoS<sub>2</sub> transistors indicates its great application potential in future nanoelectronics and integrated circuits. But the photo-response is very slow due to the large amounts of defects such as the H<sub>2</sub>O and O<sub>2</sub> absorbed on the surface of MoS<sub>2</sub>. Fig. 4(b) shows the time dependences of drain current under the different gate voltage. Once light illuminated the devices, the current increases relatively fast but decreases very slowly once the light is turned off, even

the current cannot recover to the initial value. It is also found that under the negative gate voltage ( $-15$  V) the dark current is very small (pA) resulting in the low noise and high sensitivity. The photocurrent is over 200 nA and photo-responsivity is calculated to be 1057 A/W, which is much higher than that under zero gate (63 A/W). As the slow response limits their application in photodetectors, different methods have been tried in attempts to improve the performances. For example, after the encapsulation with ALD Al<sub>2</sub>O<sub>3</sub> the performances of MoS<sub>2</sub> phototransistors are much improved with a fast response of only

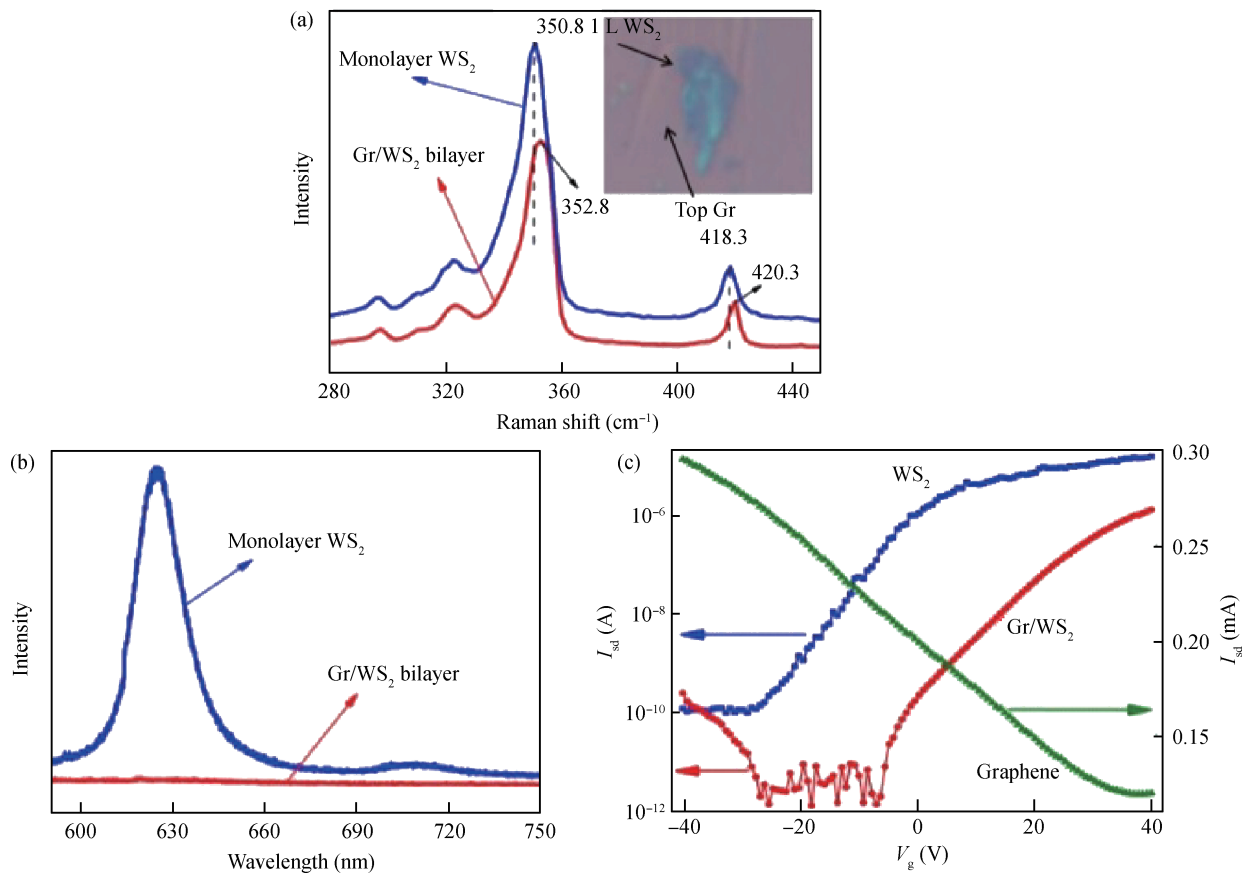


Fig. 5. (Color online) (a) Raman and (b) PL spectra of monolayer  $\text{WS}_2$  and the bilayer graphene/ $\text{WS}_2$  heterostructure. The inset of (a) is an optical image of graphene/ $\text{WS}_2$  bilayer. (c) Transfer curves of graphene,  $\text{WS}_2$  and Gr/ $\text{WS}_2$  devices<sup>[29]</sup>.

10 ms<sup>[28]</sup>.

In contrast to the n-type of  $\text{WS}_2$  and  $\text{MoS}_2$  as discussed above, the  $\text{WSe}_2$  can exhibit different behaviors depending on the contact metal. Based on the previous literature, the Ag metal with low work function can lead to the n-type behavior of  $\text{WSe}_2$  but the metal with high work function such as Pd or Pt can result in the p-type behavior because the high work function metal can facilitate the holes transport in the  $\text{WSe}_2$  channel. Here we used Au as the source and drain electrodes and found the ambipolar behavior as shown in the Fig. 4(c). The on/off ratio ranged from  $10^3$  to  $10^4$  with varying bias for both electrons and holes. The output curves (Fig. 4(d)) also demonstrated the typical ambipolar behavior. From both  $I$ - $V$  and  $I$ - $t$  curves (Figs. 4(e) and 4(f)), the drain current is much improved under light illumination and the response is very fast with a raise and delay time of only 20 ms indicating the sensitive photo-detections.

## 5. Heterostructures based on the 2D materials

### 5.1. $\text{WS}_2$ -graphene heterostructures

The van der Waals heterostructures are assembled by individual 2D layers using the transfer method. Due to the broad-range of optical bandgap and strong light-matter interactions, they exhibit unique and excellent properties and thus are gaining particular attention. Now we will introduce some interesting optoelectronic properties in different heterostruc-

tures. Figs. 5(a) and 5(b) show the Raman spectrum of bilayer graphene- $\text{WS}_2$  heterostructures, which exhibited distinctive Raman and PL characteristics compared with each constituent layer. First-principles calculations showed that graphene bound to the  $\text{WS}_2$  monolayer with an interlayer spacing of about 3.9 Å indicated a strong interaction between graphene and  $\text{WS}_2$  ( $\text{MoS}_2$ ) monolayers. The Raman modes  $A_{1g}$  and  $E_{2g}^1$  significantly stiffen by  $2 \text{ cm}^{-1}$  in this bilayer heterostructure, implying the strong interlayer coupling between graphene and  $\text{WS}_2$ . We found that both  $A_{1g}$  and  $E_{2g}^1$  modes of  $\text{WS}_2$  stiffen by coupling with graphene. Considering the strong interlayer coupling between graphene and  $\text{WS}_2$ , two possible physical models were proposed to explain the phonon stiffening in Gr- $\text{WS}_2$  heterostructures<sup>[29]</sup>. One is the electron-phonon interaction model, where lower electron concentration leads to weaker electron-phonon coupling, and thus induced stiffening in the Raman modes  $A_{1g}$ . The other model is the interlayer interaction. The strong interlayer coupling between graphene and  $\text{WS}_2$  can surpass the Coulomb interactions and strengthen both in-plane and out-of-plane effective restoring forces acting on the atoms, hence resulting in the higher frequencies of  $A_{1g}$  and  $E_{2g}^1$  modes.

Fig. 5(c) shows the typical transfer characteristics of  $\text{WS}_2$ , graphene and Gr- $\text{WS}_2$  heterostructure separately. The ultra-thin  $\text{WS}_2$  layers and monolayer graphene exhibit n-type and p-type behavior respectively. However, the Gr- $\text{WS}_2$  heterostructures exhibited obvious ambipolar properties with a high n-type on/off ratio of almost  $10^6$  and a p-type on/off ratio of about  $10^2$ ,

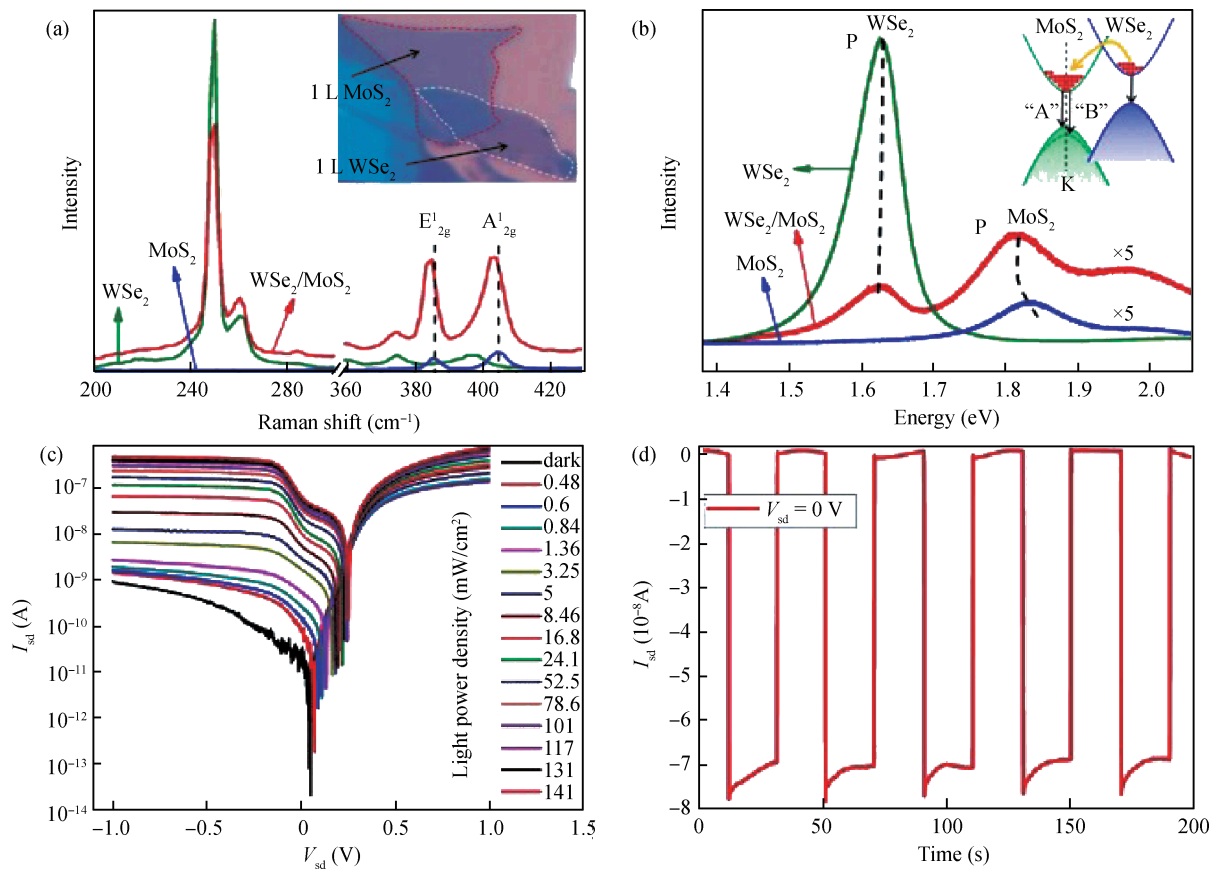


Fig. 6. (Color online) (a, b) Raman and PL spectrum of MoS<sub>2</sub>/WSe<sub>2</sub> heterostructures, respectively. (c)  $I$ – $V$  curves of MoS<sub>2</sub>/WSe<sub>2</sub> heterojunctions under light illumination with different light power. (d) Dynamic response under zero bias<sup>[21, 22]</sup>.

which could be derived from n-type WS<sub>2</sub> and p-type graphene. Gate-induced electrons in WS<sub>2</sub> were dominated under positive  $V_g$ , thus forming an n-type conducting channel. But, the electrons in WS<sub>2</sub> were exhausted under negative  $V_g$  and the holes from the p-type graphene can modulatingly dope the WS<sub>2</sub> at the interface, resulting in the p-type behavior<sup>[29]</sup>.

## 5.2. MoS<sub>2</sub>–WSe<sub>2</sub> (WS<sub>2</sub>) heterostructures

The monolayer MoS<sub>2</sub> and monolayer WSe<sub>2</sub> are vertically stacked forming the bilayer heterostructures (inset of Fig. 6(a)). In the WSe<sub>2</sub>/MoS<sub>2</sub> bilayers, the typical Raman modes A<sub>1g</sub> and E<sub>2g</sub><sup>1</sup> of both MoS<sub>2</sub> and WSe<sub>2</sub> monolayers appear at the same frequencies as in their isolated monolayers (Fig. 6(a)), indicating that the interlayer coupling is very weak between the constituent layers. The PL signal in the heterostructures changes greatly: emission from WSe<sub>2</sub> sharply drops and emission from MoS<sub>2</sub> slightly increases (Fig. 6(b)). This is probably from the inefficient charge transfer due to the very weak interlayer coupling<sup>[22]</sup>.

We now turn into the MoS<sub>2</sub>/WS<sub>2</sub> heterojunctions. Similar Raman and PL spectrum of the heterostructures were observed in MoS<sub>2</sub>/WSe<sub>2</sub> heterostructures. The interesting point is that we made the vertical and planar transistors based on the multilayer MoS<sub>2</sub>–WS<sub>2</sub> heterostructures and found novel and excellent field-effect and photosensitivity with new functionalities and superior electrical and optoelectronic properties that far exceed the one for their constituents. The vertical device ex-

hibits a rectifying property with forward to reverse bias current ratios of 10<sup>3</sup> and a bipolar behaviour, which has an n-type behavior with an ON/OFF ratio of more than 10<sup>4</sup> under positive  $V_{sd}$  and a p-type behavior with an ON/OFF ratio of 10 times under negative  $V_{sd}$ . The observed behaviour can be attributed to the type-II band alignment between MoS<sub>2</sub> and WS<sub>2</sub> and the band slope induced by the gate voltage<sup>[21]</sup>. Fig. 6(c) shows  $I$ – $V$  curves under dark and upon light illumination with different light power density, depicting the formation of short-circuit current  $I_{sc}$  and open circuit voltage  $V_{oc}$  upon light illumination, which increases with the light power, indicating an excellent photovoltaic property. The maximum  $V_{oc}$  can reach 0.25 V. Another important phenomenon is that the vertical transistors can also perform as a self-driven photodetector without applying source-drain bias (Fig. 6(d)), and the photocurrent can change sensitively and rapidly with light switching on/off<sup>[22]</sup>.

## 5.3. WS<sub>2</sub>–WSe<sub>2</sub> PN heterojunctions

Moreover we also investigated the p-WSe<sub>2</sub>/n-WS<sub>2</sub> heterojunctions and demonstrate their unusual electrical transport and photo-responsive properties. Obvious current rectification and symmetrical ambipolar characteristics as well as large current hysteresis are observed in this artificial heterojunction. Interestingly, the polarity behaviours of the heterostructures system can be modulated by source drain voltage  $V_{sd}$  and gate voltage  $V_g$  ranging from n- or p-type to ambipolar or “anti-bipolar” behaviour. A unique transport model is proposed to explain this

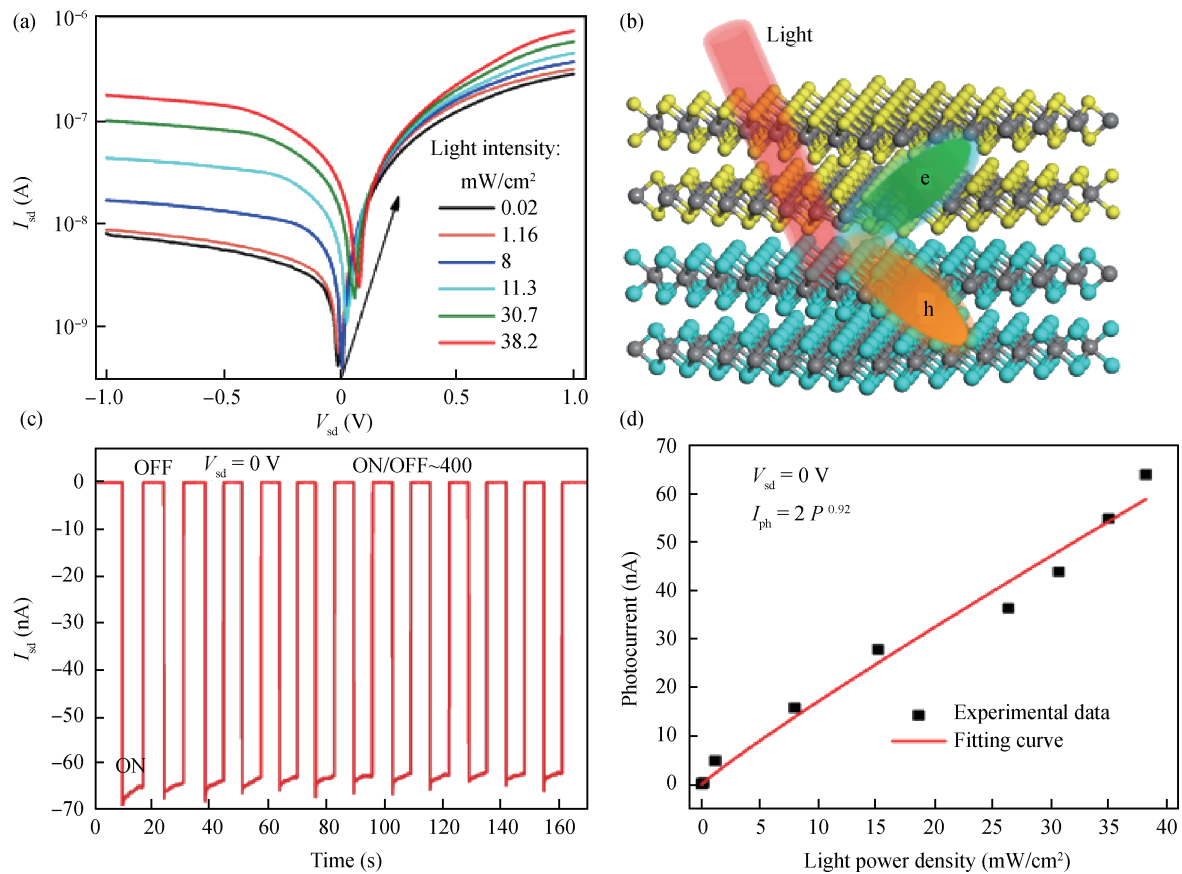


Fig. 7. (Color online) (a)  $I$ - $V$  curves of WS<sub>2</sub>-WS<sub>2</sub> PN heterojunctions under light with different light power density. (b) Schematic diagram of photo-generated electron-hole separation in this junction. (c) Time dependences of  $I_{sd}$  during the incident light switched on/off. (d) Photocurrent as function of light power density with  $V_{sd}$  of 0 V<sup>[23]</sup>.

phenomenon in which the conducting channels of junctions, p-WS<sub>2</sub> and n-WS<sub>2</sub> will successively work on electrical transport with gradually improving  $V_{sd}$ <sup>[23]</sup>.

Like the MoS<sub>2</sub>/WS<sub>2</sub> heterostructures, the p-n junctions also exhibit excellent photovoltaic, self-driven and enhanced photo-switching properties. Fig. 7(a) shows  $I_{sd}$ - $V$  characteristics of the heterojunctions devices under light illumination (633 nm) with different incident light power densities. With the increasing light power, the open-circuit voltage  $V_{oc}$  and short-circuit current  $I_{sc}$  are forming and increasing, indicating the excellent photovoltaic properties. Due to the energy gradient from type-II band alignment and the built-in potential between WS<sub>2</sub> and WS<sub>2</sub>, the photo-excited electron-hole pairs can be efficiently separated (Fig. 7(b)). Under light illumination, the photo-excited electrons in WS<sub>2</sub> and holes in WS<sub>2</sub> can easily drift into the other layer, thus resulting in the significant photocurrent and photovoltaic effect. From the dynamic response of photocurrent with zero bias (Fig. 7(c)), the photocurrent can be produced and annihilated quickly and sensitively with the light switching on/off. The photo-switching on/off ratio can reach higher than 400 times and the response time is less than 20 ms revealing the high efficient electron-hole separation and high quality of self-driven photo-switching<sup>[23]</sup>.

## 6. Conclusion

In summary, the growth, characterization and nano-

devices performances of 2D materials (graphene and TMDs) and their heterostructures were systemically introduced. The 2D TMDs were prepared by CVD and the exfoliation method, which can exhibit excellent performances of phototransistors with high mobility and fast response. The heterostructures were fabricated by stacking different 2D layers on top of each other, which also performs unique physical and device properties such as the enhanced performances, strong interlayer coupling as well as high photovoltaic effect. All results demonstrate their huge application potential in future electronic and optoelectronic fields.

## References

- [1] Elias D C, Gorbachev R V, Mayorov A S, et al. Dirac cones reshaped by interaction effects in suspended graphene. *Nat Phys*, 2011, 7: 701
- [2] Geim A K, Novoselov K S. The rise of graphene. *Nat Mater*, 2007, 6: 183
- [3] Mueller T, Xia F, Avouris P. Graphene photodetectors for high-speed optical communications. *Nat Photonics*, 2010, 4: 297
- [4] Nair R R, Blake P, Grigorenko A N, et al. Fine structure constant defines visual transparency of graphene. *Science*, 2008, 320: 1308
- [5] Konstantatos G, Badioli M, Gaudreau L, et al. Hybrid graphene-quantum dot phototransistors with ultrahigh gain. *Nat Nanotechnol*, 2012, 7: 363
- [6] Tsai D S, Liu K, Lien D H, et al. Few-layer MoS<sub>2</sub> with high



- broadband photogain and fast optical switching for use in harsh environments. *ACS Nano*, 2013, 7: 3905
- [7] Tongay S, Zhou J, Ataca C, et al. Broad-range modulation of light emission in two-dimensional semiconductors by molecular physisorption gating. *Nano Lett*, 2013, 13: 2831
- [8] Hu P A, Wang L, Yoon M, et al. Highly responsive ultrathin GaS nanosheet photodetectors on rigid and flexible substrates. *Nano Lett*, 2013, 13: 1649
- [9] Hu P A, Wen Z, Wang L, et al. Synthesis of few-layer GaSe nanosheets for high performance photodetectors. *ACS Nano*, 2013, 6: 5988
- [10] Liu W, Kang J, Sarkar D, et al. Role of metal contacts in designing high-performance monolayer n-type WSe<sub>2</sub> field effect transistors. *Nano Lett*, 2013, 13: 1983
- [11] Mak K, He K, Shan J, et al. Control of valley polarization in monolayer MoS<sub>2</sub> by optical helicity. *Nat Nanotechnol*, 2012, 7: 494
- [12] Podzorov V, Gershenson M E, Kloc C, et al. High-mobility field-effect transistors based on transition metal dichalcogenides. *Appl Phys Lett*, 2004, 84: 3301
- [13] Ayari A, Cobas E, Ogundadegbe O, et al. Realization and electrical characterization of ultrathin crystals of layered transition-metal dichalcogenides. *J Appl Phys*, 2007, 101: 014507
- [14] Radisavljevic B, Radenovic A, Brivio J, et al. Single-layer MoS<sub>2</sub> transistors. *Nat Nanotechnol*, 2011, 6: 147
- [15] Lopez-Sanchez O, Lembke D, Kayci M, et al. Ultrasensitive photodetectors based on monolayer MoS<sub>2</sub>. *Nat Nanotechnol*, 2013, 8: 497
- [16] Britnell L, Gorbachev R V, Jalil R, et al. Field-effect tunnelling transistor based on vertical graphene heterostructures. *Science*, 2012, 335: 947
- [17] Yu W J, Li Z, Zhou H L, et al. Vertically stacked multi-heterostructures of layered materials for logic transistors and complementary inverters. *Nat Mater*, 2013, 12: 246
- [18] Gong C, Zhang H, Wang W, et al. Band alignment of two-dimensional transition metal dichalcogenides: application in tunnel field effect transistors. *Appl Phys Lett*, 2013, 103: 053513
- [19] Kang J, Tongay S, Zhou J, et al. Band offsets and heterostructures of two-dimensional semiconductors. *Appl Phys Lett*, 2013, 102: 012111
- [20] Komsa H, Krashenninnikov A. Electronic structures and optical properties of realistic transition metal dichalcogenide heterostructures from first principles. *Phys Rev B*, 2013, 88: 085318
- [21] Huo N J, Kang J, Wei Z M, et al. Novel and enhanced optoelectronic performances of multilayer MoS<sub>2</sub>–WS<sub>2</sub> heterostructure transistors. *Adv Funct Mater*, 2014, 24: 7025
- [22] Hao N J, Tangay S, Guo W L, et al. Novel optical and electrical transport properties in atomically thin WSe<sub>2</sub>/MoS<sub>2</sub> p–n heterostructures. *Adv Electron Mater*, 2015, 1: 1400066
- [23] Huo N J, Yang J H, Huang L, et al. Tunable polarity behavior and self-driven photoswitching in p-WSe<sub>2</sub>/n-WS<sub>2</sub> heterojunctions. *Small*, 2015, 11: 5430
- [24] Wang Y, Ni Z H, Shen Z X. Interference enhancement of Raman signal of graphene. *Appl Phys Lett*, 2008, 92: 043121
- [25] Zhao Y, Luo X, Li H, et al. Interlayer breathing and shear modes in few-trilayer MoS<sub>2</sub> and WSe<sub>2</sub>. *Nano Lett*, 2013, 13: 1007
- [26] Li H, Lu G, Wang Y, et al. Mechanical exfoliation and characterization of single- and few-layer nanosheets of WSe<sub>2</sub>, TaS<sub>2</sub>, and TaSe<sub>2</sub>. *Small*, 2013, 9: 1974
- [27] Huo N J, Yang S X, Wei Z M, et al. Photoresponsive and gas sensing field-effect transistors based on multilayer WS<sub>2</sub> nanoflakes. *Sci Rep*, 2014, 4: 5209
- [28] Kufer D, Nikitskiy I, Lasanta T, et al. Hybrid 2D–0D MoS<sub>2</sub>–PbS quantum dot photodetector. *Adv Mater*, 2015, 27: 176
- [29] Huo N J, Wei Z M, Meng X Q, et al. Interlayer coupling and optoelectronic properties of ultrathin two-dimensional heterostructures based on graphene, MoS<sub>2</sub> and WS<sub>2</sub>. *J Mater Chem C*, 2015, 3: 5467