Two-Dimensional WSe₂/MoS₂ p–n Heterojunction-Based Transparent Photovoltaic Cell and Its Performance Enhancement by Fluoropolymer Passivation

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ABSTRACT: As a means to overcome the limitation of installation space and to promote the utilization of the solar cell in various applications, a transparent thin-film solar cell has been studied by many researchers. To achieve a transparent solar cell, the choice of materials which are transparent enough and showing the photovoltaic property at the same time is the key. Here, we suggest a two-dimensional (2D) p–n heterojunction of WSe₂/MoS₂ and an indium tin oxide electrode to fabricate a transparent thin-film photovoltaic cell. Because of advantages that 2D materials possess, a highly transparent (~80%) solar cell with considerable efficiency was achieved. Furthermore, by introducing a transparent passivation layer composed of a fluoropolymer, the photovoltaic performance was much improved. With the passivation layer, our WSe₂/MoS₂ transparent photovoltaic cell reached an efficiency of ~10%. A comparison of photovoltaic parameters before and after applying passivation and analysis on the origin of such differences are also discussed. To the best of our knowledge, this is the first report to fabricate a 2D material-based fully transparent photovoltaic device. Our result exhibits a great potential of the van der Waals p–n heterojunction of 2D semiconductors to be utilized for an active layer of a highly transparent and lightweight thin-film solar cell.

KEYWORDS: transparent solar cell, 2D material, van der Waals heterojunction, WSe₂, MoS₂, fluoropolymer

1. INTRODUCTION

Solar energy is getting great attention as one of the most powerful and reliable renewable energy sources. Many researchers have endeavored to develop a cheap photovoltaic device with high energy conversion efficiency. Nevertheless, the widespread use of the solar cell is often hindered by the limitation of the installation space, which requires a large area, resulting in a high installation cost. The transparent thin-film solar cell is suggested as a solution to overcome such limitations because it can be installed in many places such as the exterior of a building, car, or mobile device, without occupying additional installation space.1–3

To achieve a transparent solar cell, one needs special materials or structures that can meet contradictory requirements of transmitting visible light and utilizing incident photons to convert into electrons and holes at the same time. In this work, we are suggesting two-dimensional (2D) materials as the active layers of the transparent photovoltaic devices. Starting from the advent of graphene, 2D materials have been spotlighted for their peculiar optical, electrical, and mechanical characteristics.4–6 These 2D materials are easily separated into atomic layers because of the unique crystal structural properties of having weak van der Waals (vdW) bonding between each layer. Unlike most bulk materials, 2D materials can maintain their own electrical properties, even in an extremely thin monolayer (∼1 nm).7

In addition, even 2D materials having different crystal structures can form stable heterojunctions, with superior interfacial qualities, free from lattice mismatch problems.8 This can be attributed to the formation of vdW heterostructures unlike the conventional covalent-bonded heterojunction of III–V semiconductors. Therefore, mono- or multilayers of 2D semiconductors are suitable to form a p–n heterojunction, which is thin enough to transmit most of the incident visible light and exhibit a photovoltaic property at the same time.

Here, we suggest a p–n heterojunction of 2D semiconductors, that is, the WSe₂/MoS₂ vdW heterojunction, as an active layer of the transparent photovoltaic cell. WSe₂ and MoS₂ both belong to the family of transition-metal dichalcogenides (TMDs). Among various kinds of TMD materials, WSe₂ and MoS₂ are one of the most famous TMD...
semiconductors; they have been studied a lot in various applications such as a field-effect transistor,9,10 a gas sensor,11 a photodetector,12 and a logic device.13,14 WSe2 and MoS2 are each known to exhibit a p-type and an n-type property, and there have been several reports on the p–n diode and photovoltaic properties of the WSe2/MoS2 heterostructure.15–19 However, there has been no attempt to utilize a WSe2/MoS2 p–n junction as a transparent solar cell and to enhance its photovoltaic performance.

In this research, we adopted a 2D WSe2/MoS2 heterojunction to realize the transparent photovoltaic cell and to exhibit its potential. In addition, to enhance the efficiency of our transparent solar cell, the passivation effect of a fluoropolymer was evaluated. Our device, with a best performance has reached a high transparency of ∼80% and a power conversion efficiency (PCE) of ∼10%, which shows sufficient potential of the 2D heterojunction in terms of the transparent photovoltaic material.

2. EXPERIMENTAL SECTION

2.1. Device Fabrication. All of the WSe2 (2D semiconductors) and MoS2 (SPI Supplies) multilayers utilized in our experiment were prepared by mechanically exfoliating commercial bulk crystals. Exfoliated MoS2 flakes were directly transferred onto the top of an alkali-free glass substrate, Eagle 2000 (Corning), using an adhesive tape. In the case of WSe2, they were first transferred onto the polydimethylsiloxane stamp. On the basis of the contrast and color of the flakes under an optical microscope, thin multilayers (∼10 nm) of WSe2 and MoS2 flakes were selected. By utilizing a micromanipulator, the WSe2 flakes were carefully aligned and transferred on top of the target MoS2 flake with overlap. Then, 100 nm thick indium tin oxide (ITO) (deposited by RF sputtering) electrodes with a 300 μm × 300 μm-sized contact pad were connected to the WSe2/MoS2 p–n heterojunction by conventional lithography and lift-off process. All of the devices were annealed under 180 °C and vacuum atmosphere for 1 h to reduce the amount of the photoresist and to enhance the contact properties. After the initial measurement of the properties, the Teflon AF2400 (Dupont) layer was added on top of the previously fabricated device by spin-coating (3000 rpm, 30 s). Figure S1 illustrates the whole fabrication process of our WSe2/MoS2 transparent solar cell.

2.2. Device Characterization. A WSe2/MoS2 heterojunction was characterized by Raman spectroscopy (HORIBA) with a 532 nm laser and atomic force microscopy (Park Systems). A focused ion beam (JEOL) and a spherical aberration correction scanning transmission electron microscope (JEOL) were utilized to cut and observe the cross section of the WSe2/MoS2 heterojunction and measure the exact thickness. The transmittance of our WSe2/MoS2 photovoltaic device was measured with a UV–vis–NIR spectrophotometer (Agilent). As the measuring beam size of the spectrophotometer was much larger (d: ∼5 mm) than our device size (∼tens of μm), the samples were covered with 100 nm thick Ti, except for a 150 μm × 150 μm-sized window. The transparency was then calculated from the measured transmittance data by normalizing it with the reference data. As references, plain glass substrates covered with 100 nm thick Ti except for a 150 μm × 150 μm-sized window (set as 100% transparency) and a dummy sample, which imitates the shape of the real WSe2/MoS2 solar cell using Ti within the same-sized window (set as 0% transparency), were measured. All of the electrical and photovoltaic characteristics were measured inside a vacuum chamber by utilizing a Keithley 4200 parameter analyzer. In this study, a halogen lamp was used as a light source to test the photovoltaic performance. The spectrum of a halogen lamp (Figure S2) differs from that of AM 1.5G illumination, which is a standard condition for solar cell performance evaluation. Because of its high portion of visible light, the photovoltaic parameters extracted from our experiment might be overestimated when compared to the measurement under AM 1.5G illumination.

3. RESULTS AND DISCUSSION

After fabricating the WSe2/MoS2 p–n heterojunction-based photovoltaic cell, we first tried to confirm whether the heterostructure has formed successfully. Figure 1a shows the cross section of our device and indicates the points where the laser was focused for Raman spectroscopy. Point “A” is a MoS2-only region, and point “C” is a WSe2-only region, whereas point “B” is the overlapped region where the MoS2/WSe2 heterostructure is formed. Using a 532 nm laser, Raman characteristics of each point were measured (Figure 1b). The Raman spectra at point “A” showed major peaks at 379.9 and 405.4 cm−1, respectively, which correspond to the E2g1 and A1g peaks of MoS2.20 In the case of point “C”, the largest peak was observed at 247.2 cm−1, and it is mainly A1g peaks of WSe2 combined with a small E2g peak.21 For the overlapped region of MoS2, and WSe2, point “B”, the superpositions of Raman spectra of MoS2-only and WSe2-only regions were observed, which confirms the formation of a MoS2/WSe2 heterostructure. Especially for the Raman peaks that appeared at the range of 330–430 nm, further analysis was conducted and arrived at the same conclusion (Figure S3). To observe the real structure and check the interface status, scanning transmission electron microscopy (STEM) analysis was conducted to one of our WSe2/MoS2 transparent photovoltaic device. Figure 1c is a cross-sectional STEM image of the 2D heterojunction. It shows that the multilayers of MoS2 and WSe2 are staked in a row with a clear interface between them. The TEM image of the same sample is also included in Figure S4. The thicknesses of each layer were measured from the TEM image as 7.06 (MoS2) and 4.51 nm (WSe2) individually. From the STEM image, the number of layers for MoS2 and WSe2 can be calculated as 11 and 7 layers, respectively. As we have used exfoliated 2D flakes for our experiment, the exact thickness...
varies sample by sample, but on average, flakes with thickness range between 4 and 20 nm were utilized. As the photovoltaic device was fabricated on a glass substrate using a 2D WSe2/MoS2 p–n heterojunction as an active layer and ITO as an electrode, it is fully transparent. Figure 2a is a photograph of our sample, exhibiting high transparency. Figure 2b is the optical microscopic image of the real sample, showing the lateral structure (p–n junction, anode, and cathode all lie on the same plane) of our 2D semiconductor-based solar cell. To quantify the transparency of our WSe2/MoS2 photovoltaic cell, a UV–vis–NIR spectrophotometer was utilized to measure the transmittance of visible light (Figure 2c). The beam size of the spectrophotometer is too large (d: ~5 mm) to directly measure the transparency of our micrometer-sized device; therefore, the region that we do not want to include as a measuring range was blocked by depositing 100 nm thick Ti before the measurement. As described in detail in the “Experimental Section” of this paper, the real measurement was conducted through a 150 μm²-sized window, patterned on the device. Then, the transparency (calculated value) was defined as a relative transmittance (experimentally measured value) of the real sample normalized by the transmittance of the reference sample. Considering that the transmittance of a baseline reference sample (Ti pattern imitating the real device) was measured as 0.143% and a fully transparent reference sample (no pattern at all within the window) showed a transmittance of 0.243%, the transparency of a real WSe2/MoS2 solar cell (transmittance: 0.223%) was calculated as 80% within the 400–750 nm wavelength range. Figure S5 contains the real images of the samples and additional explanations on how we have calculated the transparency of the WSe2/MoS2 solar cell. The device utilized for this measurement included a hexagonal-boron nitride (h-BN) encapsulating layer on top; therefore, the transparency of a WSe2/MoS2 photovoltaic device without encapsulation will be around 80% or even higher.

The as-fabricated device was measured inside a vacuum probe station, using a parameter analyzer. Figure 3a indicates the I–V characteristic of the WSe2/MoS2 p–n junction-based transparent solar cell. The blue line is a linear I–V plot, and the red line is a semilog plot of the same device. The inset shows the current rectifying I–V curve in a wide voltage range. (b) J–V curves of the photovoltaic cell under various intensities of white light. (c) FF and PCE values with respect to the incident light intensity, which were calculated from the J–V curves shown at (b). (d) Power–voltage plot of the device under illumination of 4.42 mW/cm² forming maximum power rectangle at V = 0.135 V.
Figure 4. Effect of fluoropolymer passivation to the WSe2/MoS2 transparent solar cell. (a) Schematic image of our WSe2/MoS2 transparent solar cell and the chemical structure of Teflon AF2400, a fluoropolymer that we have utilized as a passivation layer. (b) J−V characteristics under dark state and related diode parameters extracted from the fitted line for the initial device and the one with passivation. (c) J−V characteristics under illumination (1.91 mW/cm²) and related photovoltaic parameters before and after applying fluoropolymer passivation.

heterostructures of 2D p- and n-type semiconductors successfully operate as a p–n diode. The 2D material-based p–n junction device also maintained a low leakage current level of less than 10⁻¹² under the negative bias.

Then, the photovoltaic characteristics was tested by shining white light onto the device. For all of the experiments measuring the photovoltaic performance, a halogen lamp was utilized as an irradiation source and was connected to the vacuum chamber by an optic fiber. Figure 3b exhibits the J−V plots of the transparent WSe2/MoS2 heterojunction device under various intensities of illumination. When the light is on, open-circuit voltage (VOC) and short-circuit current density (JSC) are clearly observed, demonstrating that our device operates as a photovoltaic cell. As the light intensity gets stronger, JSC tends to increase from 0.93 to 2.21 mA/cm², whereas VOC remains at a similar value of 0.265 V. Along with the slight decrease of fill factor (FF) from 33 to 31%, PCE of the device turned out to show a maximum value of 4.32% under a light intensity of 3.34 mW/cm² (Figure 3c). The active area was defined as an overlapped region of n-type MoS2 and p-type WSe2, which was measured to be 17.11 µm² for the sample shown in Figure 3. Figure 3d shows the power curve with respect to the voltage. Under illumination of 4.42 mW/cm², the generated power of our WSe2/MoS2 photovoltaic cell has reached its maximum value of 31.38 pW at the voltage of 135 mV. We have fabricated many WSe2/MoS2 heterojunction photovoltaics with the same process and the champion sample has reached PCE of 8.27% (Figure S6). Considering that a transparent thin-film solar cell can offset its shortage of efficiency by increasing the installation area, because of its main advantage of having a large freedom in installation space, we tried to enhance the PCE of our 2D transparent photovoltaic cell. There are several reports that 2D materials are easily affected by environmental factors like the adsorption of moisture or other gas molecules.23,24 Such adsorbents tend to work as a surface trap site or induce charge transfer.25 To suppress such effect and enhance the efficiency, we introduced fluoropolymer passivation. Figure 4a shows the device structure and chemical structure of the passivation layer that we used. Teflon AF2400 is an amorphous fluoropolymer, which is highly transparent throughout the whole visible light region. In addition, it can be deposited as a thin film by a simple spin-coating process; therefore, we applied it to our WSe2/MoS2 transparent solar cell.

Figure 4b,c shows the effect of a passivation layer to the device characteristics under dark and illuminated conditions. Figure 4b compares the dark current density (J) versus voltage (V) plots of the same 2D heterojunction device before and after spin-coating Teflon AF2400. Using the Shockley diode model, the J−V characteristics of the diode can be expressed simply by

\[ J = J_0 \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right] \]

where \( J_0 \) denotes the saturation current density, \( n \) is the diode ideality factor, and \( k, T, \) and \( q \) represent the Boltzmann’s constant, temperature, and elementary charge, respectively. Under the voltage bias of around 0.3 V and temperature of 300 K, \( \exp[ qV/kT ] \) becomes much larger than 1; therefore, by fitting \( \ln(J)−V \) plot, \( J_0 \) and \( n \) values can be directly estimated from the intercept and slope (Figure S8), respectively. The result shows that both \( J_0 (1.47 \times 10^{-4} \text{ to } 1.19 \times 10^{-4} \text{ mA/} \)
cm$^2$) and $n$ (2.88 to 2.23) tend to decrease after the fluoropolymer passivation is applied. As both parameters are known to be closely related to the recombination rate, it suggests that the carrier recombination at the solar cell was suppressed by a Teflon coating.

Figure 4c exhibits the $I$–$V$ characteristics of the transparent WSe$_2$/MoS$_2$ heterojunction device under light, comparing the effect of fluoropolymer passivation on top. Although $V_{OC}$ and FF are slightly decreased, enhancement in $J_{SC}$ far outweighs those factors, resulting in a higher PCE value from 7.99 to 10.00%. Teflon AF2400, a fluoropolymer, contains lots of C–F bonds and the fluorine atom is one of the most powerful electronegative elements. Therefore, the molecular dipole field is induced in the end groups of Teflon AF2400, which can also affect the charge distribution of the surroundings. Furthermore, there is a report that such electrostatic dipole moments of the fluoropolymer greatly promote the hole accumulation in thin WSe$_2$, while suppressing the electron concentration of MoS$_2$. It may have induced the imbalance of hole and electron concentrations in our WSe$_2$/MoS$_2$ photovoltaic cell, which results in the suppression of recombination at the junction area. In addition, the strong hydrophobicity of Teflon AF2400 can effectively repel the ambient molecules, which are easily adsorbed onto the bare 2D materials and activate surface recombination. As Teflon AF2400 has refractive index of 1.29, it also works as an antireflective coating. Figure 5 exhibits the reflectivity of the glass substrate before and after applying the Teflon AF2400 thin film (∼95 nm) that we have used in our experiment. Within the visible light range, the average reflectivity has decreased from 8.28% (bare glass substrate) to 5.09% (Teflon AF2400 coated glass substrate), which may have contributed to the large increase of $J_{SC}$ of the WSe$_2$/MoS$_2$ transparent solar cell.

4. CONCLUSIONS

In this paper, we have demonstrated a 2D heterojunction-based fully transparent solar cell for the first time. Multilayers of n-type MoS$_2$ and p-type WSe$_2$ successfully met the contradictory requirements of being transparent and generating electricity from the incident light by the peculiar characteristic of maintaining a good photovoltaic property in a very thin form. Our WSe$_2$/MoS$_2$ transparent solar cell exhibited a high transparency of ∼80% and moderate PCE of 4–8%. Furthermore, we tried to evaluate its performance enhancement by introducing fluoropolymer passivation. The 2D p–n junction-based photovoltaic cell, with a Teflon AF2400 coating, has shown great improvement in its performance with a PCE up to ∼10%. It seems that the field-effect passivation effect, strong hydrophobicity, and antireflective effect of the fluoropolymer have contributed to the enhancement of the device performance.

Considering that the device in this work was a lateral structure, which is not an optimized structure for efficient photocarrier extraction, the vertically structured 2D heterojunction solar cell will further enhance the performance of the solar cell; this will be enabled by wafer-scale, high-quality multilayer 2D material synthesis. Recently, various 2D materials and their vdW heterostructures have been evaluated as a good candidate for photovoltaic applications. This work not only demonstrates the potential of a 2D vdW p–n heterojunction as a photovoltaic device but also expands its applications to a transparent thin-film solar cell which will enhance the freedom of installation space.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b12250.

Process flow of device fabrication; spectral intensity of the halogen lamp; peak analysis on the Raman spectra of MoS$_2$, WSe$_2$, and their overlapped region within the wavelength of 330–430 nm; TEM image of a WSe$_2$/Mo$_x$/ MoS$_2$ heterojunction; optical microscopy images of samples which are utilized for the transmittance measurement and resulting transparency values; $I$–$V$ characteristics and the photovoltaic parameters of various WSe$_2$/MoS$_2$ photovoltaic cells; summary on the CBM, VBM, and band gap size of MoS$_2$ and WSe$_2$ from the previous reports and their resulting band alignment; and linear fitting of dark current–voltage plots of a WSe$_2$/MoS$_2$ photovoltaic cell before and after applying passivation for $J_0$ and $n$ value extraction (PDF)

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Notes

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