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# Flexible solar cell based on CdSe nanobelt/graphene Schottky junction

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Flexible solar cells have attracted intense interests since they have potential in making portable and wearable power sources. We fabricated CdSe nanobelt (NB)/graphene Schottky junction flexible solar cells on polyethylene terephthalate (PET) substrates for the first time. The solar cells have an excellent rectification behavior in dark with typical on/off current ratio of about $2\times10^5$. Under air mass (AM) 1.5 global (1.5 G) illumination, the solar cells perform good photovoltaic (PV) behavior, with typical open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), and fill factor ($FF$) to be about 0.31 V, 4.73 mA cm$^{-2}$, and 36.14%, respectively. The corresponding energy conversion efficiency ($\eta$) is about 0.53%. Under bending conditions, the performance of the solar cells does not change obviously. We attribute the satisfying performance of the flexible solar cells to the ingenious nanomaterials and Schottky junction device structure employed. Our work shows that the semiconductor NBs (NWs) and graphene are promising building blocks in future flexible devices, and the CdSe NB/graphene Schottky junction solar cells have potential application in flexible nano-optoelectronic systems.

## Introduction

Solar cell, which converts solar energy into electrical energy, is one of the important solutions to the energy crisis. Recently, light-weight and bendable flexible solar cells have attracted intense interests,[1-6] because they are potentially useful for portable and wearable power sources. Semiconductor nanowires (NWs) and nanobelts (NBs) can be employed to fabricate flexible devices. NW/NB based solar cells can serve as the novel power sources for nano-optoelectronic systems.[7-10] Moreover, various methods have been developed to assemble nanostructures (nanowires, nanobelts, and nanotubes) over large areas, including electrical field assembling[11], microfluidic flowing[12], and bubble expansion processing[13], etc. These works promise a bright future for the application of the NW/NB based solar cells. Schottky junction based solar cells have many advantages over *p-n* junction based solar cells, such as simple fabrication process, and material universality. For example, it can be made with unipolar semiconductors. However, so far, few work about flexible solar cell based on NW/NB Schottky junction has been reported.

CdSe has a direct bandgap of 1.74 eV, and its absorption spectrum covers most part of the solar light wavelength range, and therefore is an important material for solar energy conversion applications.[14-18] Graphene, a two-dimensional, conjugated, honeycomb lattice structured carbon material, has high electrical conductivity, flexibility, and transparency.[19, 20] Semiconductor NWs (NBs) are proper materials for flexible devices.[21, 22] In this work, we fabricated CdSe NB/graphene Schottky junction flexible solar cells on polyethylene terephthalate (PET) substrates for the first time. Herein, graphene is used to replace the metal in conventional Schottky junction devices. The solar cells have an excellent rectification behavior in dark with typical on/off current ratio of about $2\times10^5$. Under air mass (AM) 1.5 global (1.5 G) illumination, a typical such solar cell performs a good photovoltaic (PV) behavior. The open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), fill factor ($FF$), and energy conversion efficiency ($\eta$) of it are about 0.31 V, 4.73 mA cm$^{-2}$, 36.14%, and 0.53%, respectively. The performance of the solar cells does not change obviously under bending condition.

## Experimental section

Both the *n*-type CdSe NBs and graphene in this work were synthesized by the chemical vapor deposition (CVD) method.[23, 24] For synthesis of CdSe NBs, CdSe (99.99 %) powders and indium particle were used as the source and the donor, respectively. Si substrates covered with 10 nm-thick thermally evaporated Au catalysts were used as the substrates. For the synthesis of graphene, a 25 μm thick high purity (99.99 %) Cu foil and $CH_4$ gas was used as the substrates and the source, respectively. The system was heated by a tube furnace. The graphene was transferred onto the substrates with the stamp method under the help of PMMA (polymethylmethacrylate).[25]

As the first step to fabricate the CdSe NB/graphene Schottky junction solar cell, the CdSe NB suspension in ethanol was dropped on a piece of PET substrate. Then, an In/Au (10/100 nm) ohmic contact electrode was made at one end of a CdSe NB on the substrate using UV lithography, thermal evaporation, and lift-off process. Then, the graphene was transferred onto the PET to form a Schottky contact electrode on the other end of the CdSe NB with the following patterning process, including UV lithography (SUSS MicroTec MJB4), and inductively coupled plasma (ICP) etching. Finally, a 100 nm thick Au ohmic contact electrode was fabricated on the graphene. The schematic diagram of the device is illustrated in Fig. 2a.

The optical image of the device was taken by an optical microscope (Zeiss Axio Imager A2m). The PL and Raman spectra were collected by a microzone confocal Raman spectroscope (HORIBA Jobin Yvon, LabRam HR800) excited by the 632.8 nm He-Ne laser. The synthesized CdSe NBs were characterized by a field emission scanning electron microscope (FESEM; Nova Nano SEM 430) and a high-resolution transmission electron microscope (HRTEM; FEI Tecnai F30). The electrical properties of the graphene were measured with a Hall measurement system (Accent HL5500). The transparency spectrum was measured by a UV-VIS-NIR recording spectrophotometer (Shimadzu UV-3100). Room temperature electrical transport and PV properties of the solar cells were characterized by two semiconductor characterization systems (Keithley 4200, 2400) together with a solar simulator (Newport 91160-1000) with a calibrated illumination power density of 100 mW $cm^{-2}$.

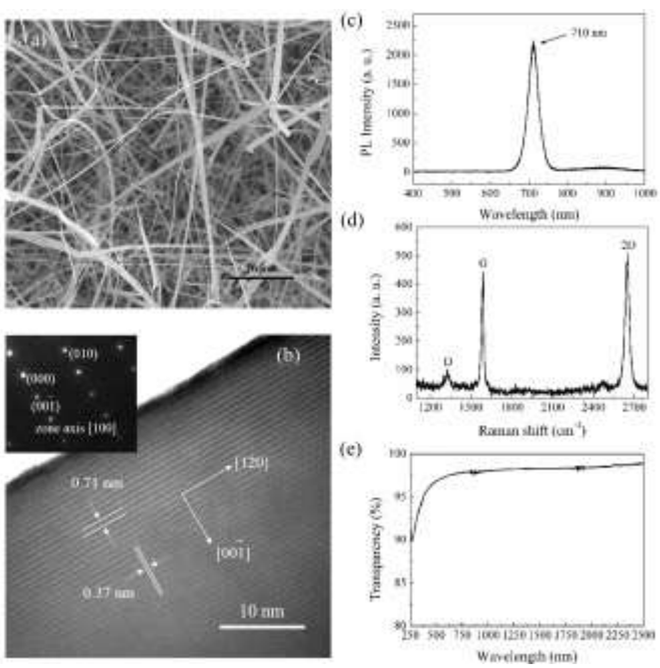


**Figure 1.** (a) FESEM image of as-synthesized CdSe NBs. (b) The typical HRTEM image of a CdSe NB. Inset: The corresponding SAED pattern of the CdSe NB. (c) Room-temperature PL spectrum of a single CdSe NB. (d) Typical Raman spectrum of the graphene transferred on a $Si/SiO_2$ (300 nm) substrate. (e) The transparency spectrum of the graphene transferred on a quartz substrate.

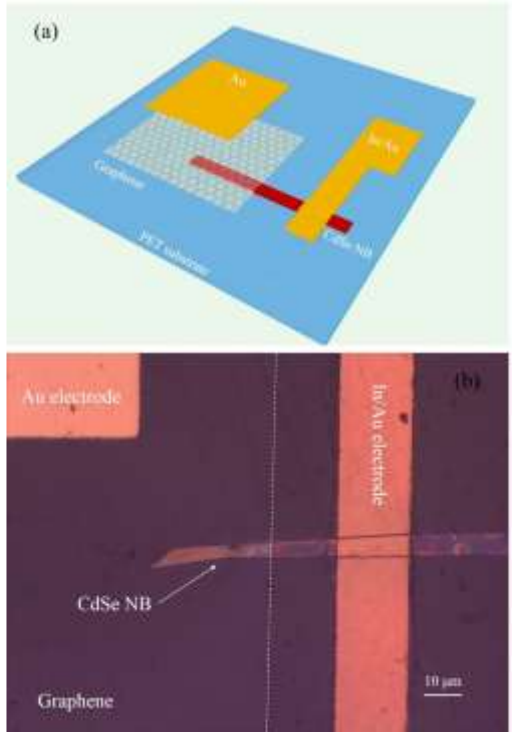


**Figure 2**. (a) The schematic diagram of the CdSe NB/graphene Schottky junction solar cell on a PET substrate. (b) Optical image of a CdSe NB/graphene Schottky junction solar cell on a PET substrate.

## Results and discussion

Figure 1a shows the typical FESEM image of the CdSe NBs. The NBs are about ten to hundreds of micrometers in length,sub-micrometer to several micrometers in width, and hundreds of nanometers in thickness. The typical HRTEM image of a CdSe NB is shown in Fig. 1b. The crystal planes with spacing distance of about 0.71 nm and 0.37 nm are clearly seen. According to the JCPDS card (no. 77-2307), these planes can be indexed, respectively, as $\{00\bar{1}\}$ and {010} crystal planes of hexagonal CdSe. The corresponding selected area electron diffraction (SAED) pattern is shown in the inset. By carefully checking the included angles of the SAED pattern and the corresponding spacing distances of the crystal planes, we can index the zone axis of the NB to be [100], and the growth direction of it to be <120>. Corresponding Miller indices are labelled in the figures. Figure 1c shows the typical room-temperature photoluminescence (PL) spectrum of a single CdSe NB. Only a strong near-bandedge emission centered around 710 nm (~1.74 eV) is observed, indicating the high quality of the CdSe NBs.[26] Typical Raman spectrum of the graphene transferred on a $Si/SiO_2$ (300 nm) substrate is shown in Fig. 1d. The G peak (~ 1588 $cm^{-1}$) and 2D peak (~ 2649 $cm^{-1}$) are clearly observed. The intensity ratio of the G peak to the 2D peak ($I_G/I_{2D}$) is about 0.86, indicating the formation of bilayer graphene. A tiny D peak (about 1324 $cm^{-1}$) is observed, which reveals a small percentage of defects.[27, 28] The transparency

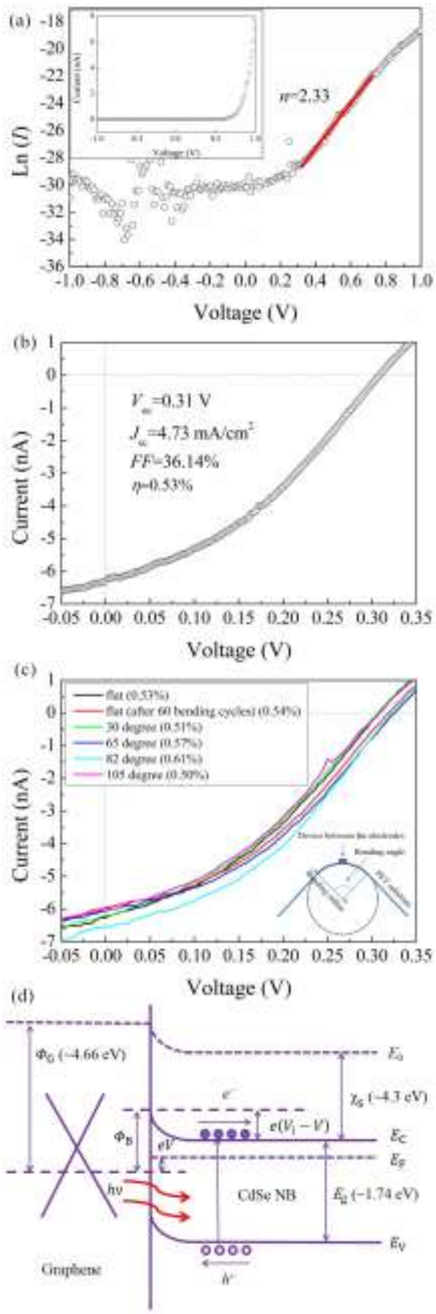


**Figure 3.** (a) Room-temperature *I-V* characteristic of a typical CdSe NB/graphene Schottky junction solar cell in dark on a semi-log scale. The red straight line shows the curve fitting result by the equation $I = I_0[\exp(eV/nkT)-1]$. Inset: Room-temperature *I-V* curve in dark on linear scale. (b) Room-temperature *I-V* curve of the same solar cell under AM 1.5G illumination with light intensity of 100 mW $cm^{-2}$. (c) Room-temperature *I-V* curves of the solar cell under bending angles of 0°, 30°, 65°, 82°, and 105°, as well as after 60 bending cycles. The schematic diagram of the measuring method is depicted in the inset. (d) The energy band diagram of the CdSe NB/graphene Schottky junction under light illumination. $\Phi_G$ is the work function of graphene, $\Phi_B$ is the Schottky barrier height, $V_i$ is the build-in potential, $V$ is the output voltage of the solar cell, and $\chi_S$ is the electron affinity of CdSe. $E_0$, $E_C$, $E_V$, and $E_F$ are the vacuum level, conduction band edge, valence band edge, and Fermi level of CdSe, respectively.

spectrum of the graphene is shown in Fig. 1e. The transparency of graphene is high (>97%) in the range with wavelength longer than 500 nm. The sheet resistance, hole concentration, and mobility of the graphene, obtained by the Hall measurement, are about 714.8 Ω $sq^{-1}$, $9.26\times10^{12}$ $cm^{-2}$, and 943 $cm^2$ $V^{-1}$ $s^{-1}$, respectively.

Figure 2b is the optical image of an as-fabricated CdSe NB/graphene Schottky junction solar cell on a PET substrate. For clarity, the graphene edge is marked by a white dotted line.

Figure 3a shows the room-temperature current (*I*)-voltage (*V*) curve of an as-fabricated solar cell in dark. The *I-V* curve shows an excellent rectification behavior. The on/off current ratio between −1 V to 1 V is about $2\times10^5$. For high-mobility semiconductors, such as CdSe etc., we can use the theory of thermionic emission of electrons to describe the *I-V* relation of a Schottky junction diode. Therefore, by curving fitting the measured *I-V* curve with the equation $I = I_0[\exp(eV/nkT)-1]$, where $I_0$, $e$, $V$, $n$, $k$, and $T$ are the reverse saturation current, the electronic charge, applied bias, diode ideality factor, Boltzmann constant, and the absolute temperature, respectively,[29] we can obtain the ideality factor $n$ to be about 2.33.

The room-temperature *I-V* curve of the solar cell under AM 1.5G illumination is plotted in Fig. 3b. We can see that the device exhibits a clear PV behavior, with $V_{oc}$, $J_{sc}$, and $FF$ to be about 0.31 V, 4.73 mA $cm^{-2}$, and 36.14%, respectively. The effective Schottky junction area (the overlapping area of CdSe NB and graphene, where the electrons and holes are separated) used to calculate the current density is about 133.4 $\mu m^2$, as shown in Fig. 2b. Then we evaluated the solar cell by calculating the energy conversion efficiency with equation $\eta = FF\cdot J_{sc}\cdot V_{oc}/P_{in}$, where $P_{in}$ is the illumination light power density (100 mW $cm^{-2}$). We obtain the energy conversion efficiency to be about 0.53%. Furthermore, as a flexible application, we investigated the performance of the device under different bending conditions. Typical PV behaviors of the solar cell under bending angles of about 0°, 30°, 65°, 82°, and 105° are shown in Fig. 3c. Herein, the bending angle is defined as the corresponding central angle when the bending region was regarded as a circular arc of a whole circle, as shown in the inset. The performance of the solar cell after 60 bending cycles is also shown in Fig. 3c. The energy conversion efficiencies under different bending conditions are given in the legend. We can see that the performance of the solar cell does not change obviously under these bending conditions. We attribute the satisfying performance of the flexible solar cell to the high quality of the CdSe NB, the high transparency and conductivity of the graphene, which is used to replace the metal in conventional Schottky junction devices.

The energy band diagram for the CdSe NB/graphene Schottky junction is shown in Fig. 3d. Based on it, the mechanism of the Schottky junction solar cell can be explained as follows: A Schottky barrier forms in CdSe NB near the interface due to the difference between the work-function of the graphene (~4.66 eV) and the electron affinity of CdSe (~4.3 eV). Under light illumination, the photo-generated holes ($h^+$) and electrons ($e^-$) within the depletion region together with a diffusion length away from the depletion region are driven by the built-in electric field toward graphene and CdSe NB, respectively, and produce an output voltage. If the solar cell is open-circuited, the forward bias is the open-circuit voltage ($V_{oc}$). When the solar cell is short-circuited, the extracted photo-generated electrons and holes will transit through the external circuit to produce a short-circuited current ($I_{sc}$).

## Conclusions

In summary, we have fabricated flexible CdSe NB/graphene Schottky junction solar cells for the first time. In this work, we used graphene to replace the metal in a conventional Schottky junction. Compared to traditional metal, graphene has the advantage of high light transparency and flexibility. The CdSe NB/graphene Schottky junctions have excellent rectification behavior with typical on/off current ratio of about $2\times10^5$. Under AM 1.5G light illumination, the devices perform good PV behavior, with typical $V_{oc}$, $J_{sc}$, and *FF* values to be about 0.31 V, 4.73 mA $cm^{-2}$, and 36.14%, respectively. The corresponding energy conversion efficiency is about 0.53%. The performance of the solar cells do not change obviously under bending conditions. We attribute the satisfying performance of the flexible solar cells to the ingenious nanomaterials and Schottky junction device structure employed. Our work shows that the semiconductor NBs (NWs) and graphene are promising building blocks in future flexible devices, and the CdSe NB/graphene Schottky junction solar cells have potential application in flexible nano-optoelectronic system.

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## Notes and references

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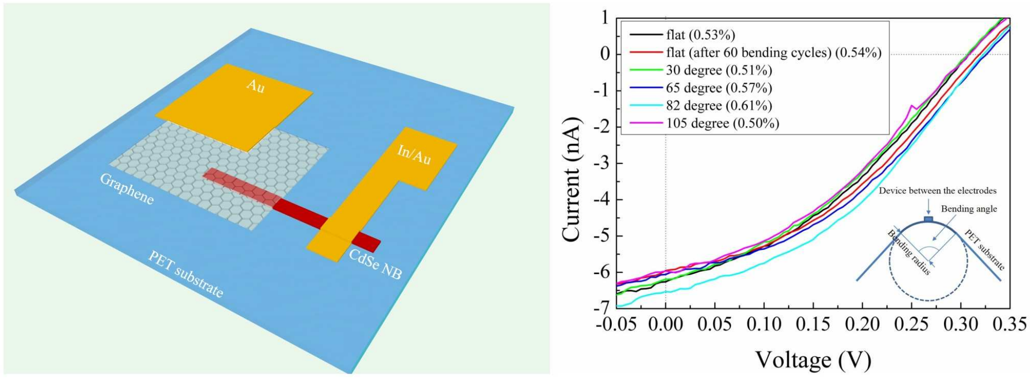


Flexible solar cells based on CdSe NB/graphene Schottky junction are fabricated and evaluated under different bending conditions.