Supporting Information

High-performance Silicon-compatible Large - area UV-to-visible Broadband Photodetector Based on Integrated Lattice-matched type II Se/n-Si Heterojunctions

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Morphology Tailoring

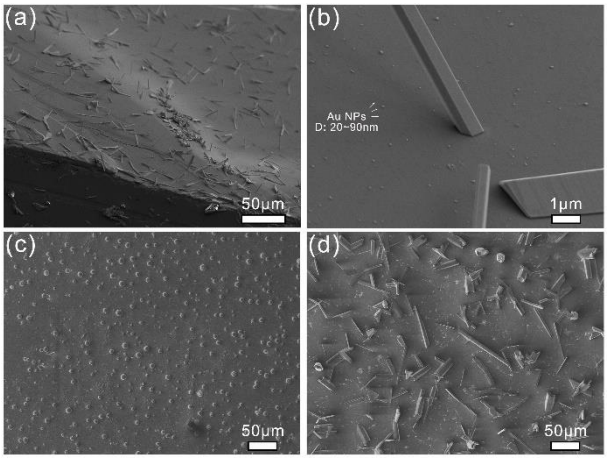

Figure S1. SEM images of the fabricated Se crystals on (111) silicon wafer without (a) NH_4Cl assistance or (b) Au NP inducement, and (c, d) selenium growth on the cleavage surface of (100) silicon wafer.

Material calculations

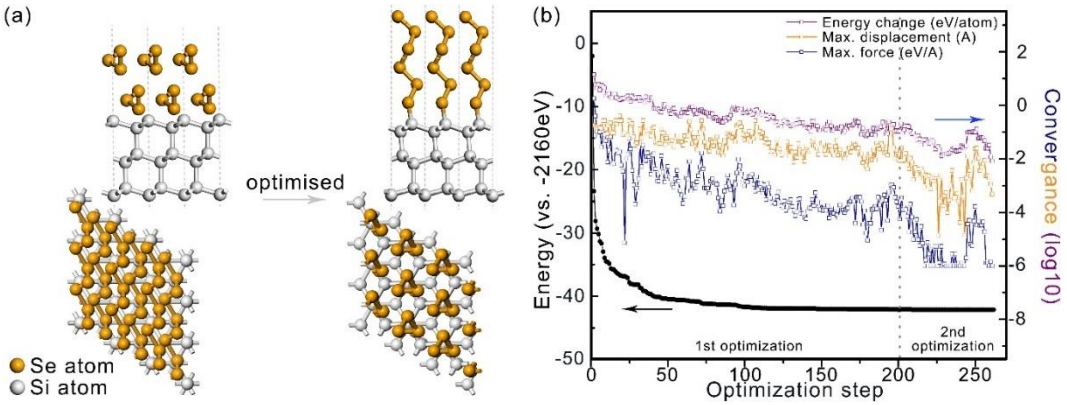

Figure S2. (a) First-principles structure optimization started with Se (100)-Si contact using CASTEP, and (b) the energy minimization and geometry optimization during optimization process.

We first started the structure optimization with Se (100)-Si contact (as showed in the left of **Figure S2a**). The orientation of Se (001) axis gets perpendicular to Si (111) plane and Se-Si bonds are formed between the outmost Si atom and the starting point of selenium molecular chain to achieve lowest energy and highest geometry optimization. The final result is displayed in Figure a, which is well corresponding to our experimental results.

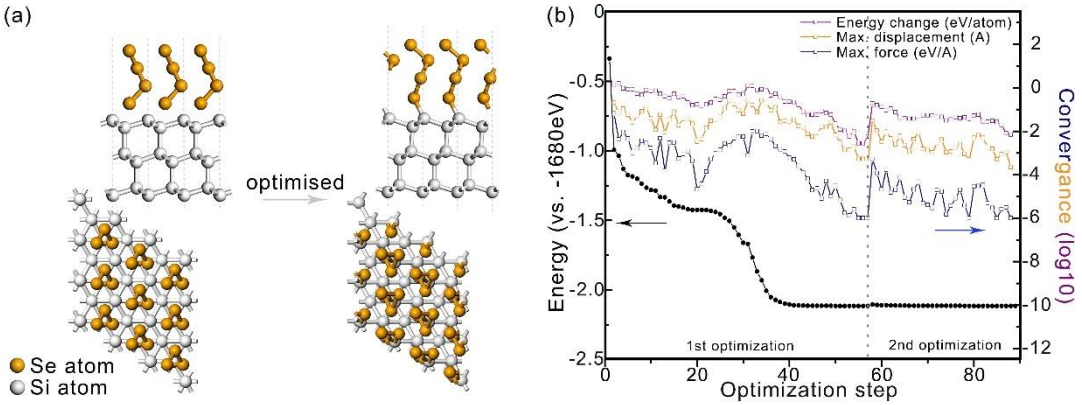

Figure S3. (a) First-principles structure optimization started with Se (001)-Si contact using CASTEP, and (b) the energy minimization and geometry optimization during

optimization process.

Then we cut the Se-Si bonds and switched the optimized Se molecular chains to the sub-outmost Si atoms (**Figure S3a**) to confirm the bonding location. As the optimization lasts (**Figure S3b**), Se-Si bonds forms again on the outmost Si atoms and generate a highly similar structure to that in **Figure S2a**. These calculation results prove that Se crystals is liable to form a vertical growth on $Si_{(111)}$ substrates due to the lattice match and the Se-Si bonds.

Electrode Material Selection

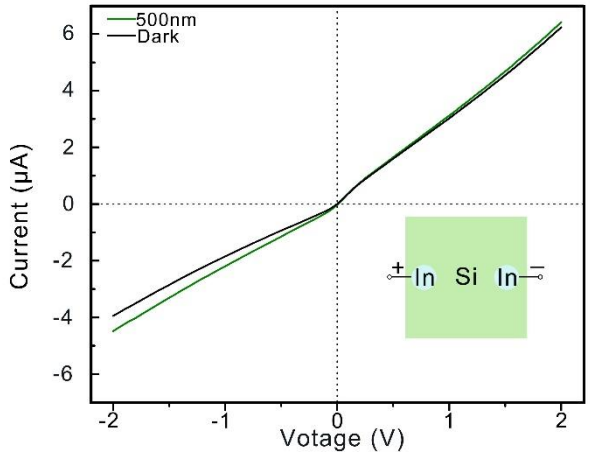

Figure S4. The I-V curves of indium-Si-indium MSM structure in dark and under 500 nm luminance (1.02 mW cm^{-2})

For silicon side, we choose low work function material indium (4.12 eV) to form quasi-ohmic contact with n-Si. The work function of p-doped n-type silicon is regarded as 4.094 eV (χ_{Si}=4.05 eV, ΔE_D=0.044 eV according to handbook), thus only a small Schottky barrier of ~0.026 eV is formed between Si and In. We believe that such a small Schottky barrier would not obviously influence the device performances.

The quasi-ohmic contact is proved by the I-V tests (**Figure S4**), where only a slight bending is observed under small bias and current generally varies linearly with voltage change.

For selenium side, we proposed and prepared nickel coated silver nanowires as high work function transparent electrode material to ensure the ohmic contact with selenium crystals. The reported work function of selenium is 4.92 eV, 0.23 eV lower than that of nickel (5.15 eV), thus nickel modified silver nanowires may form ohmic contact with selenium.

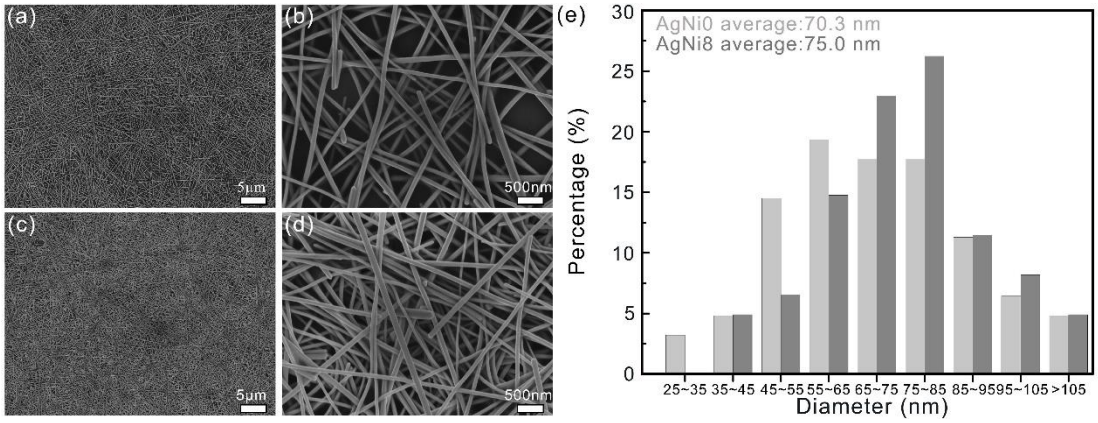

Figure S5. The SEM images of (a, b) AgNi0 and (c, d) AgNi1, and (e) the statistic results of nanowire sizes in AgNi0 and AgNi1.

AgNixs generally maintain the morphology of silver nanowires, and the SEM images of AgNi0 and AgNi1 are provided in Figure. The reduced nickel on Ag NWs slightly increases the metal nanowires, and the average diameter changes from 70.3 nm to 75.0 nm when nickel reaches 8% (see **Figure S5** for details).

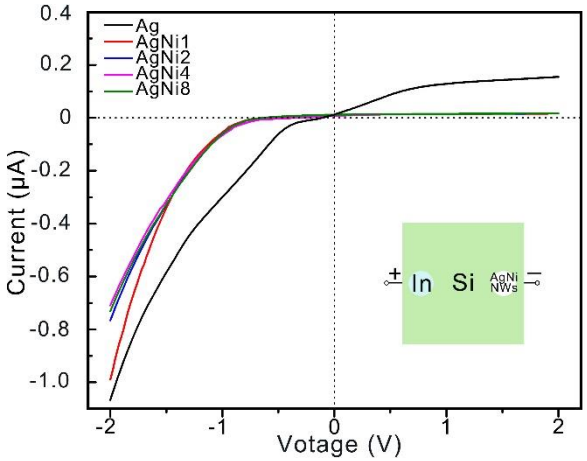

Figure S6. The I-V curves of indium-Si-AgNi NWs MSM structure in dark.

The work function variation of AgNix (x=0, 1, 2, 4, 8) is compared by the I-V curves showed in the following, where In forms quasi-ohmic contact with n-Si as mentioned above. As displayed in the **Figure S6**, the on/off ratio of the prepared Schottky diode changes from 7.3 to over 60, indicating that the Schottky barrier between n-type silicon and Ag nanowires is obviously enhanced after nickel modification. The high work function of nickel modified Ag NWs guarantees excellent ohmic contact with Se materials, and the ohmic contact is also examined by the I-V tests of carbon-Se-AgNi8 MSM structure (**Figure S7**).

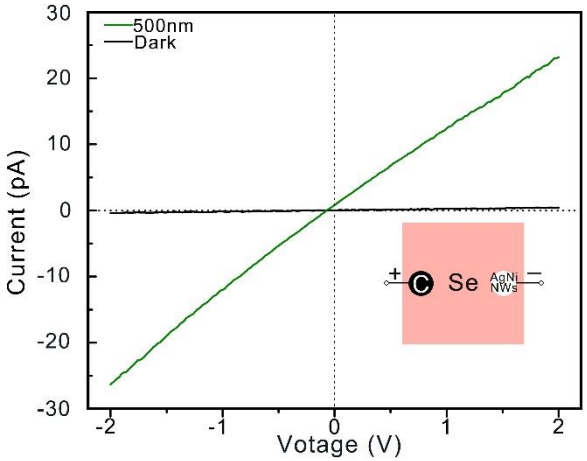

Figure S7. The I-V curves of carbon-Se-AgNi8 MSM structure in dark and under 500 nm luminance (1.02 mW cm^{-2})

Additional Figures

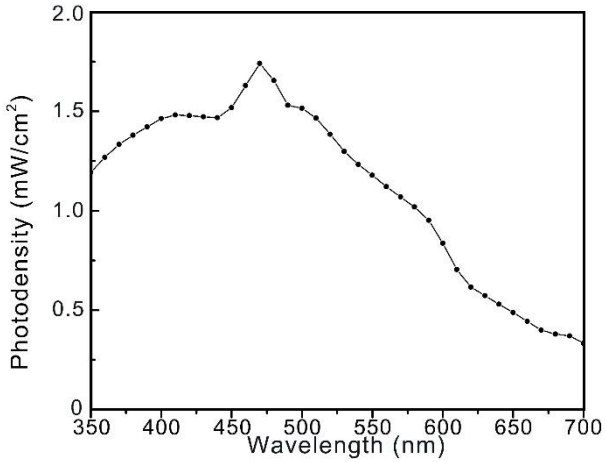

Figure S8. Photodensity curves of the xenon lamp used in **Figure 3a-b** and **Figure 4c-d**.

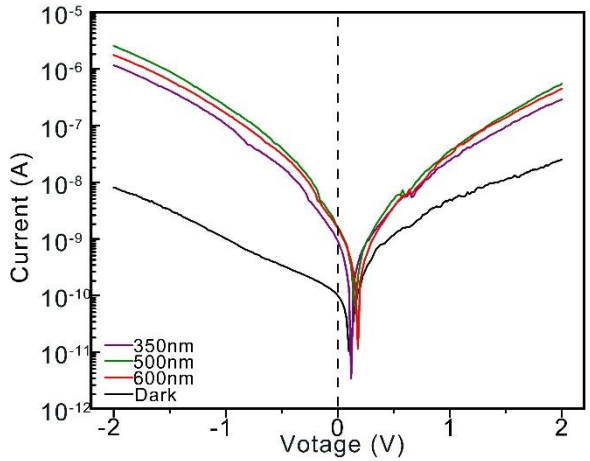

Figure S9. I-V curves of the Se/Si p-n heterojunction photodetector fabricated from samples in **Figure S1d**.

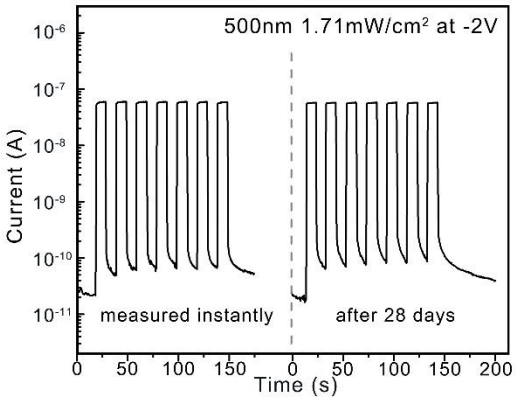

Figure S10. I-t curves of Se-Si devices measured instantly and 28 days after device construction.

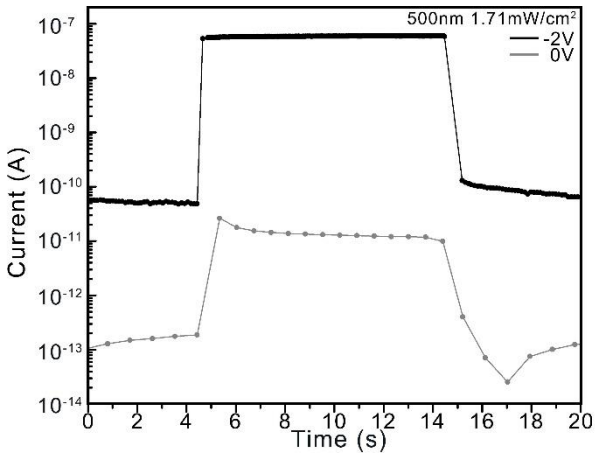

Figure S11. (a) Amplified scatter-line plots in one on/off period from **Figure 3b**.

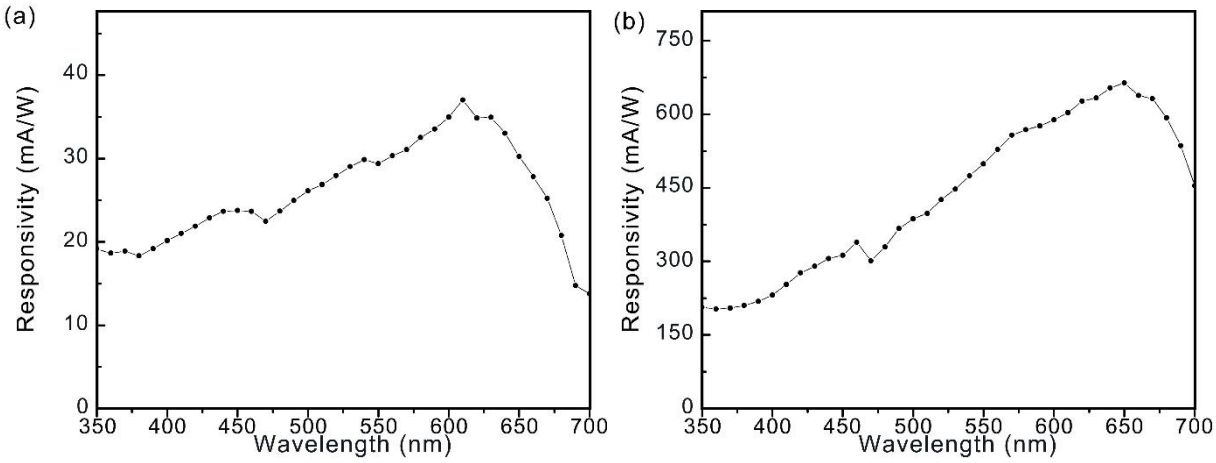

Figure S12. The measured responsivity of the Se/Si p-n heterojunction photodetector

under (a) -2 V and (b) -5 V bias.

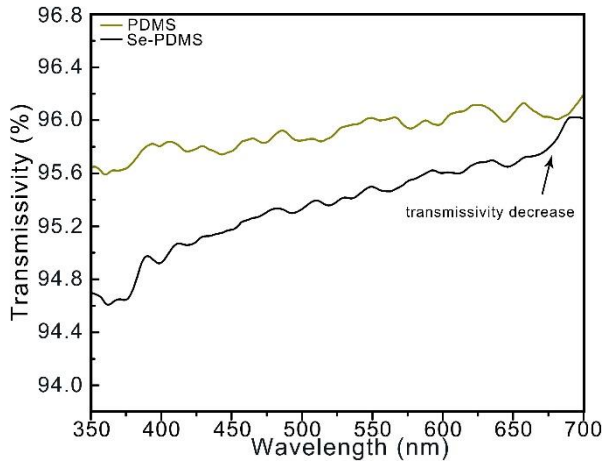

Figure S13. Transmissivity curves of mechanically peeled off Se-PDMS film and the contrast PDMS film fabricated in the same way.

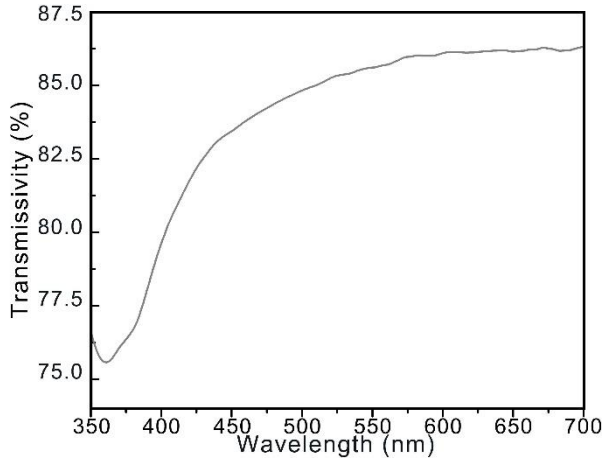

Figure S14. Transmissivity curves of the utilized transparent electrode.

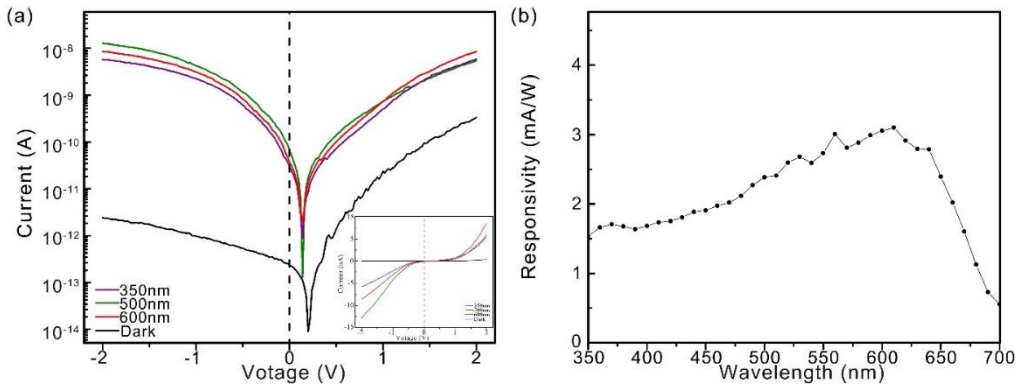

Figure S15. (a) I-t curves and (b) responsivity data of Se/Si device using ITO glass as transparent top electrode.

Experimental Section

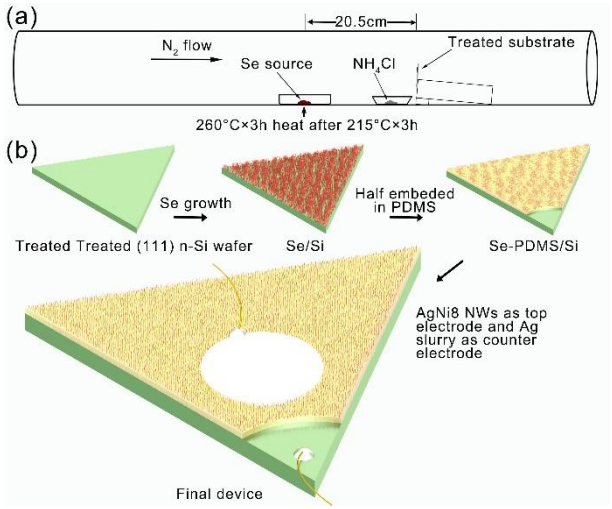

Figure S16. Schematic description of (a) material fabrication and (b) device construction.

Fabrication of selenium crystals: A JS-1600 ion sputtering apparatus (HTCY Tec., Ltd, Beijing) and a gold target (>99.999% HTCY Tec., Ltd, Beijing) are used to sputter Au NPs on phosphor-doped silicon substrates (10~20 Ω cm LiJing Silicon Mater., Ltd,

Zhejiang). The Au NP-induced selenium growth is then carried out in a horizontal single-temperature-zone tube furnace. As showed in **Figure S16a**, Se powder (>99.95% Meixing Chem., Ltd, Shanghai) is put in the center of the quartz tube and the substrate is placed 20.5 cm from the Se source. NH_4Cl (>99.5% Sinopharm Chem. Reag., Ltd, Shanghai) is added between Se powder and the substrate. Then the quartz tube is heated as the following steps under a constant nitrogen flow (>99.999%) of 50 standard cubic centimeter (sccm): 1. Slowly heated to 50 °C in 2 h to flush out the residual air; 2. Heated to 215°C at 8 °C min^{-1} and maintained at 215 °C for 3 h; 3. Heated up to 260 °C in 5 min and stayed for 3h, then naturally cooled down to room temperature.

Preparation of AgNi nanowires: The prepafration of Ag nanowires is similar to Ran *et al.*'s work [Y. Ran et al. Chem. Commun. 2014, 50, 14877-14880] and the details are described as follows. 0.180 g $AgNO_3$ (>99.8% Sinopharm Chemical Reagent Co., Ltd, Shanghai) is dissolved in to 3 mL of ethylene glycol (EG, >99% Sinopharm Chemical Reagent Co., Ltd, Shanghai). Then the $AgNO_3$ solution is added to 22 mL Polyvinylpyrrolidone (PVP) solution (0.163 g PVP dissolved in total (M_W55000: M_W1300000=1:2), Sigma-Aldrich Co, Ltd, USA) with 2.5 mL 600 μM $FeCl_3$ solution (also in EG). After fully stirring, the mixture is heated up to 140 °C and maintained for 3 h. Then the silk white product is cooled down for further treatments. After that, 19.5, 39.4, 80.3, 168 μL 0.1M $NiNO_3$ (aq) is added to 5 mL of the prepared silk white product (containing 20.8 mg Ag NWs) for AgNi NWs contain 1, 2, 4, 8 % nickel, named as AgNi1, AgNi2, AgNi4, AgNi8, respectively. Then the mixture was mixed with 141 μL hydrazine (35 wt%) under fully stirring and heated at 120 ℃ for 10 min. Nickel is

reduced onto Ag NWs during this process and modifies the work function of Ag NWs.

Device construction: The device construction process is graphically described in **Figure S16b**. The base and curing agents of PDMS (SYLGARD 184) are mixed at a mass ratio of 10:1 and spincoated on the fabricated material. Then the whole sample is heated at 120°C for 1h in a drying oven. In this way, the synthesized selenium crystals are half-embedded in insulating polymer film on silicon wafer. The prepared AgNi8 NWs are then dropped on the Se-PDMS layer and spread as transparent top electrode along with gold wires as leg wires and silver slurry as welding material.

Material Characterization: A field emission SEM (FESEM, Zeiss Sigma) is employed to examine the morphology of the prepared samples, and further characterizations are operated in a HRTEM (TECNAI G2 S-TWIN) with an EDS equipment.

Optical and Photoelectric Measurements: The transmissivity results are collected from a UV-vis spectrophotometer (Hitachi U-4100). The photoelectric properties are evaluated through a semiconductor characterization system (Keithley 4200) connected to Xe lamp and monochromator, and a NOVA II power meter (OPHIR photonics) is used to detect the light density. In order to measure the instant photo response, a YAG:Nd laser (pulse duration: 3-5 ns, 355 nm, Continuum Electro-Optics, MINILITE II), a 1 GΩ resistor and an oscilloscope (Tektronix MSO/DPO5000) are employed as the insert circuit in **Figure 3c**. All the photoelectric measurements are operated at room temperature under ambient conditions.