# **Electronic Supplementary Information (ESI)**

## Two-Dimensional Magneto-Photoconductivity in Non-van der Waals

### **Manganese Selenide**

Liang Hu,<sup>a,e</sup> Lei Cao,<sup>b</sup> Lingwei Li,<sup>\*a</sup> Juanmei Duan,<sup>b</sup> Xiaoqi Liao,<sup>c</sup> Fangchao Long,<sup>c</sup> Jian Zhou,<sup>a</sup> Yinguo Xiao,<sup>d</sup> Yu-Jia Zeng<sup>\*c</sup> and Shengqiang Zhou<sup>b</sup>

<sup>a</sup> Key Laboratory of Novel Materials for Sensor of Zhejiang Province, Institute of Advanced Magnetic Materials, Hangzhou Dianzi University, Hangzhou 310018, P. R. China.

<sup>b</sup> Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, Dresden 01328, Germany

<sup>c</sup> College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, P. R. China.

<sup>d</sup> School of Advanced Materials, Peking University, Shenzhen Graduate School, Shenzhen 518055, P. R. China

<sup>e</sup> State Key Lab of Silicon Materials, Zhejiang University, Hangzhou 310027, P. R. China

\*Corresponding Author: lingwei@hdu.edu.cn (L.L.) or yjzeng@szu.edu.cn (Y.-J.Z.)

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#### **Experimental Section**

Synthesis of MnSe<sub>2</sub>/Se Composites and MnSe<sub>2</sub> Nanosheets. MnSe<sub>2</sub>/Se was primarily synthesized by optimized hydrothermal procedure. Briefly, 0.2 mmol manganese (II) acetate tetrahydrate (Mn(CH<sub>3</sub>COO)<sub>2</sub>· 4H<sub>2</sub>O, 99.99%, Aladdin) and 0.2 mmol selenium dioxide powder (SeO<sub>2</sub>, 99.99%, Aladdin) were dissolved into 15 mL deionized water (home-made,  $R > 18 \text{ M}\Omega$ ) and keep vigorous stirring. Afterwards, 3 mL hydrazine (N<sub>2</sub>H<sub>4</sub>· H<sub>2</sub>O, 80%, Aladdin) was added to the above solution for ensuring a reducing environment of (Se/Se<sup>2-</sup>). This mixed solution was then transferred to a Teflon-lined stainless-steel autoclave with 25 mL capacity and held at 120°C for 12 h. When the autoclave was cooled to RT, the gray solids were isolated by centrifugation and further purified by anhydrous ethanol (≥99.5%, Aladdin) and citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>· H<sub>2</sub>O, 99.8%, Aladdin) solution (1 M) to remove possible Mn(OH)<sub>2</sub>. To obtain 2D MnSe<sub>2</sub> nanosheets, sodium borohydride (NaBH<sub>4</sub>, 98%, Aladdin) solution (0.3 M) was applied to etch excessive elemental Se in composites. After several-round washing for derived NaHSe, black precipitates of nanosheets can be separated and dried in vacuum at 60°C.

*Characterizations.* The morphologies of cubes and nanosheets were observed by SEM (Hitachi S-4800) and the elemental distribution was confirmed by a combined EDS setup. The observation of atomic arrangement was conducted in HAADF-STEM (JEOL ARM-200F and FEI Titan G<sup>2</sup> 80-200 ChemiSTEM) operating at 200 kV accelerating voltage. The thickness information and magnetic phase signals of nanosheets were collected by NanoWizard 4-NanoScience equipment (JPK Instruments) working in AFM and MFM modes, respectively. XRD patterns were recorded in X-ray diffractometer (Rigaku MiniFlex600) with Cu *Ka* 

radiation ( $\lambda = 1.5104$  Å) and the specimen was prepared by powder compaction. Optical microscopy images and Raman spectra were captured using a confocal microscopic Raman spectrometer (HORIBA LabRAM HR Evolution, 514.5 nm laser excitation, 1800 gr/mm grating, a  $\times 100$  objective lens of NA= 0.90). Temperature dependent Raman study was carried out in a Linkam thermal stage. In order to reduce the damage of laser irradiation (mainly referring to the decomposition of MnSe<sub>2</sub>), Raman tests were maintained below 200 µW. All signals were acquired for 15 seconds and accumulated 2 times. UPS and XPS studies were performed on an ESCALAB 250XI (Thermo Scientific) using He I (21.2 eV) and Al Ka monochromatic source (1486.6 eV), respectively. All binding energy values were corrected by referencing the C 1s peak to 284.6 eV. The optical bandgap is determined by diffuse reflectance spectra (DRS, PerkinElmer LAMBDA). The EPR measurements were implemented on a Bruker ESRA-300 spectrometer operating at X-band with a featured frequency of 9.86 GHz. According to the involvement of external white light source, the variation of signal can be in situ monitored. Magnetic properties were measured using a SQUID magnetometer (Quantum Design). Prior to measurements, all samples were carefully handled using nonmagnetic tweezers, capsules and tapes to avoid unintentional magnetic contamination. The amount of nanosheets dispersed on the substrate is determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Microscopic MOKE measurements on a single nanosheet were carried out on a home-made MOKE setup by using 632 nm He-Ne laser. The sample was fixed on a stage surrounded by a cylindrical permanent magnet and the sweeping field range is fixed between  $\pm 0.1$  T. Prior to magnetotransport measurements (Lakeshore Hall measurement system), the nanosheet powder were ground and pressed into a pellet with a diameter of 1 cm and thickness of 1 mm under the pressure of 70 MPa. For the fabrication of FET devices, MnSe<sub>2</sub> nanosheets were spin-coated on  $p^{++}$ -Si/SiO<sub>2</sub> substrates (SiO<sub>2</sub> layer with a thickness of 300 nm) with prepatterned Cr (5 nm)/Au (45 nm) parallel electrodes with spacing of 10 µm. The photodetection characteristics are also collected on the same device structure with different IR

light ( $\lambda = 1064$  nm) intensities (11.98, 19.20, 40.11 and 80.29 mWcm<sup>-2</sup>). In order to measure magneto-conductivity performance, the device needs to be magnetized in advance under a magnetic field of 2 T. Temporal current tests were conducted in Keysight B2902A semiconductor analyzer.

DFT calculations. First-principles calculations are performed based on DFT by using Vienna Ab initio Simulation Package (VASP) with the projector augmented wave (PAW) method. The cutoff kinetic energy of 500 eV is chosen for the plane wave basis. For the exchange-correlation energy, we employ the Perdew-Burke-Ernzerhof (PBE) functional with generalized gradient approximation (GGA). Because the GGA cannot properly describe strongly correlated systems containing partially filled d subshells, we used the GGA+U method by dividing the electrons into two classes: delocalized s and p electrons, which can be well-described by the GGA, and the localized d electrons, which are described by Coulomb and exchange corrections. In this way, we were able to obtain a qualitative improvement not only for excited-state properties such as energy gaps but also for ground-state properties such as magnetic moments and interatomic exchange parameters. We use the method with  $U_{\rm eff}$  = 3 eV for Mn. A vacuum thickness of 15Å in *a*-direction is used to eliminate the interactions between neighboring layers. Based on the test of convergence accuracy, we use  $(11 \times 11 \times 1)$  Monkhorst-Pack k-point mesh to represent the reciprocal space of the unit cell. By using the conjugated gradient algorithm, the crystal structure is fully optimized, the convergence criteria for energy and force are set to be  $10^{-4}$  eV and 0.01 eV Å<sup>-1</sup>, respectively.



Figure S1. SEM images from (a-b) pristine and (c-d) etched MnS<sub>2</sub>/Se cube composites.



**Figure S2.** AFM height image and randomly selected profile lines for thickness statistical analysis of nanosheets.



Figure S3. Raman spectral evolution with thickness

For some 2D materials (including vdW and non-vdW ones), the dependence of Raman spectra on thickness appears very sensitive. For example, SnSe nanosheets (9–20 nm) are synthesized on molten polydimethylsiloxane by chemical vapor deposition (Adv. Electron. Mater., 2016, 2, 1600292). Thickness-dependent Raman shift persists even with thickness over 20 nm. The underlying mechanism is still unclear but it is widely believed to originate from weakened bond force. Likewise, Li et al. reported SnS flakes synthesized by physical vapor deposition (RSC Adv., 2017, 7, 48759). The shift of Raman can take place for the flake with thickness of 21.4 nm. The change of bond angle is ascribed to this phenomenon. Recently, this anomaly is also reported in mechanically-exfoliated 2D non-vdW tellurium (Appl. Surf. Sci., 2020, 531, 147303). Their vibrational behavior is attributed to Te chains deformation, which is verified by DFT calculations. For MnSe<sub>2</sub> nanosheets, an analogous mechanism might affect the bonding of Mn-Se with the decrease of thickness. We note that the lattice of bulk region in nanosheets expands about 2%, which may weaken the bond force and soften in-plane and out-of-plane phonon vibrational modes. To further support our viewpoint, we choose several flakes with different featured thickness (12 nm, 20 nm and 38 nm) and implement the Raman measurements. As shown in Fig. S3, with the flakes thinned, an obvious Raman blueshift trend can be observed for the thickness of 20 and 38 nm. But for the thickest flake (38 nm), the peak changed hardly at all. This demonstrates that Se dissolution process easily affect Mn-Se bonds of nanosheets with thickness below 20 nm, which might be beneficial for ferromagnetic exchange and the opening of bandgap.



**Figure S4.** Temperature-dependent Raman spectral measurements of 2D MnSe<sub>2</sub> from 300 K to 335 K. There is an obvious drop of Raman intensity around 320 K, which well accords with the critical transition temperature of magnetization.



**Figure S5.** (a) Interface of MnSe<sub>2</sub>/Se nanocomposites. Inset is the enlarged view of helical Se atomic chains for crystalline Se (denoted as c-Se). (b) Etching induced amorphization of surface Se atoms (denoted as a-Se). (c) Zoom-in region from the black dashed box shown in (b). (d) Fold edge of a MnSe<sub>2</sub> nanosheet. (e) Magnified edge of the etched surface. (f) Atomic arrangement of edge region. For better observation, the corresponding lattice models are marked nearby.

Figure S5 reveals a group of images of structural evolution before and after etching MnSe<sub>2</sub>/Se. For starters, because of the unique helical characteristics of Se atoms in crystalline Se (c-Se) [*ACS Nano* 2017, 11, 10222–10229], we can easily observe the interface between MnSe<sub>2</sub> and c-Se before etching procedure (Figure S3a). When c-Se was softened by NaBH<sub>4</sub> aqueous solution (Figure S3b), the disorder of surface Se atoms induced the formation of amorphous Se layer (a-Se), which can be evidenced by the following elemental distribution data. Not only that, a thin layer (~2 nm) with low contrast appears near MnSe<sub>2</sub> core, which is capped by amorphous Se layer. Furthermore, this layer is clearly displayed in Figure S3c, which we call as the Se-poor layer in previous manuscript. When Se atoms are fully dissolved and washed by deionized water, the core-shell structured nanosheets are extracted by a typical centrifugation process (Figure S3d). We next focus on their edge section. In Figure S3e, a similar capping structure can be also seen, where the exposed (200) surface is determined by measuring lattice fringe spacing (d~0.328 nm). As you expected, we further explore the atomic arrangement of cross-section by spherical aberration-corrected STEM in Figure S3f. For the left part, it corresponds to pure MnSe<sub>2</sub> lattice and the periodic armchair-like Se-Mn-Se chains can be explicitly captured. In contrast, the missing of Se atoms occurs in the right section, which leads to the formation of a distorted atomic arrangement. For better observation, the corresponding space-filling atomic models are marked nearby.



**Figure S6.** (a, c) High-angle annular dark field (HAADF) images and (b, d) the corresponding elemental line-scan profiles for MnSe<sub>2</sub> nanosheets with the etched layer capped (b) and uncapped (d) by amorphous Se layer. (e) Single-point elemental ratio collected from core and shell regions in (c).

From the perspective of elemental distribution, through line-scans and single-point signal collection (Figure S4), it is concluded that Se atoms are indeed missing in the shell region. The Se/Mn atomic ratio in thin shell layer can be accurately determined as 1:1. Meanwhile, the ratio in the core section approaches 2:1, which is consistent with the stoichiometric MnSe<sub>2</sub>. As depicted in Figure S4c, the thickness of thin shell layer varies to ~5 nm under elemental analysis, which is larger than what we have observed in Figure S3e (~2 nm). The reason is mainly from persistent electron irradiation (accelerating voltage 200 kV) towards specimen.

However, the ratio determined by single-point analysis is still comparable to our previously proposed model but we have to admit that, the speculation of Se/Mn atomic ratio of unity only by comparing the difference between XPS and EDS results is arbitrary. After adding the above depth analysis to the revised manuscript, it is believed that the DFT calculations in the early version is reasonable. We have put these supplementary STEM images to the revised manuscript and the ESI file, corrected the relevant description and adjusted the logic of this article to make the transition between experimental results and theoretical calculations appear more natural and appropriate.



Figure S7. Integrated EPR spectra of 2D  $MnSe_2$  nanosheets with and without white light illumination



Figure S8. Magnetization curves of  $MnSe_2$  nanosheets powder with and without light illumination. The increase of saturation magnetic moment is about 57.1% of the original magnetic moment.



**Figure S9.** (a) The supercells before and after structural relaxation. (b) Simulated lattice parameters. (c) TEM image of reconstructed step surface and corresponding FFT pattern.

The contraction of 22.5% is theoretically predicted based on a fully-relaxed MnSe<sub>2</sub> monolayer with half of the Se atoms etched in (200) surface. This contraction appears to be rather large because enough vacuum layer is built in DFT calculations. Actually, according to STEM calibration, the degree of contraction is decreased to the level of ~18%. Such a change might come from strain relaxation in interface region. On the other hand, the strong shrinkage of a-axis leads to the extension of b- and c-axis for reconstructing surfaces (see Fig. R2a-b). After relaxation, the value of b/c changes to 1.048, very close to the SAED result in Fig. 2e. To check surface atomic arrangement, we have performed STEM measurements on the etched surface. A clear layered texture can be captured in Fig. R2c and we further conduct FFT operation. It is found that a new rhombohedral symmetry appears in pattern, in accordance with simulated symmetry of Mn atoms.



**Figure S10.** Calculated 2D  $MnSe_2$  supercells with different exposed surfaces and the corresponding spin-polarized electronic energy bands. There is a small gap in 2D  $MnSe_2$  with an exposed (200) surface, which indicates that engineering this surface has the possibility to open the bandgap.



**Figure S11.** Calculated 2D MnSe<sub>x</sub> supercells with different stoichiometric ratios (x= 1.3, 1.5, 1.6) and the corresponding spin-polarized electronic energy bands. Except for x=1, no bandgaps can be observed in other ratios.



**Figure S12.** Orbital-projected PDOS diagrams of 2D defective MnSe<sub>2</sub> in (a) up- and (b) down-spin channel.

**Table S1.** The total energies (TOTEN) and adsorption energies ( $E_{ads}$ ) of different VASPcalculated slabs. For 4 hydrogen atoms and 4 hydroxyls adsorbed Mn<sub>4</sub>Se<sub>4</sub> slabs, the  $E_{ads}$  is determined by the expression of  $E_{ads} = E_{TOTEN}$  (slab)-  $E_{TOTKEN}$  (Mn<sub>4</sub>Se<sub>4</sub>)-  $E_{TOTKEN}$  (H/OH), where  $E_{TOTEN}$  (slab),  $E_{TOTKEN}$  (Mn<sub>4</sub>Se<sub>4</sub>) and  $E_{TOTKEN}$  (H/OH) are the total energies of adsorbed Mn<sub>4</sub>Se<sub>4</sub> slabs, pristine slab, and free hydrogen atoms or hydroxyls, respectively.

Calculated slabs	Formula	TOTEN (eV)	$E_{\rm ads}({\rm eV})$
	Mn <sub>4</sub> Se <sub>4</sub>	-46.33	
	Mn <sub>4</sub> Se <sub>4</sub> H <sub>4</sub>	-53.84	-2.87
	Mn <sub>4</sub> Se <sub>4</sub> (OH) <sub>4</sub>	-81.37	-3.04



**Figure S13.** A pair pictures of MnSe<sub>2</sub> nanosheets dispersed in alkaline (left,  $M_{\text{KOH}}=1 \text{ mol/L}$ ) and acid (right, M<sub>HCl</sub>=1 mol/L) solutions.



Figure S14. (a) Hydroxyl modified Mn<sub>4</sub>Se<sub>4</sub> slab. (b) Spin-polarized electronic band structure.(c) Orbital-projected PDOS diagrams. (d) Calculated atomic magnetic moment



**Figure S15.** Absorption spectra of home-made MnSe, MnSe<sub>2</sub>, MnSe<sub>2</sub>/Se and MnSe<sub>2</sub> nanosheets. It can be found that the extra presence of elemental Se in MnSe<sub>2</sub>/Se leads to an absorption bump at ~500 nm, which can be attributed to Se sol [*Mater. Res. Bull.* 2010, 45, 56–62]. When Se is dissolved, the bump disappears and the feature of absorption band (600~800 nm, which is also reported in Ref. [*Chin. Phys. B*, 2016, 25, 107405]) is between MnSe<sub>2</sub> and MnSe, manifesting itself as an intermediate state. Interestingly, the MnSe<sub>2</sub>/Se composites also have a weak absorption near 1100 nm, which is not seen in home-made MnSe<sub>2</sub> powder. It means that the infrared absorption might originate from the unique complex structure. When Se is completely removed, this part is effectively improved in nanosheets.



**Figure S16.** (a) Transfer and (b) output characteristics curves of the FET device based on MnSe<sub>2</sub> nanosheets. The 3D AFM height image of device is shown in the inset. Nanosheets are densely spin-coated on Si/SiO<sub>2</sub> substrate followed by the deposition of patterned Cr/Au electrodes by magnetron sputtering. The positive gating voltage ( $V_{GS}$ ) has an observable modulation effect on source-drain current ( $I_{DS}$ ) when fixing source-drain voltage ( $V_{DS}$ ) at 100 mV, which indicates an electron-dominated transport behavior. The threshold voltage ( $V_{th}$ ) is about +13 V and demonstrates that the device works in an enhancement mode. A moderate on/off current ratio of ~10<sup>2</sup> and subthreshold slope of 3.9 V/dec can be determined from the

transfer curve. Since the output curves maintain linear within  $V_{\rm DS}$ =100 mV, the linear mobility value ( $\mu_{\rm lin}$ ) can be deduced as ~2.7 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> according to the definition of linear mobility (

 $\mu_{\text{lin}} = \frac{L \quad \text{d}I_{\text{DS}}}{WC_{\text{i}}V_{\text{DS}}\text{d}V_{\text{GS}}}, \text{ where } W/L = 466, C_{\text{i}} \text{ is the capacitance density per unit area (1.151 \times 10^{-8} \text{ F cm}^{-2}), \text{ and the maximum of transconductance } g_{\text{m}} = \text{d}I_{\text{DS}}/\text{d}V_{\text{GS}} = 1.427 \times 10^{-6} \text{ S}.$ 

Surface Localized Etched Layer Charge Transfer  $SiO_2$  $V_{DS} = +100 \text{ mV}$  $CBM \bigoplus K_{F}$   $V_{GS} = +13 \text{ V}$  $E_F$   $V_{GS} = 0$ Si  $V_{GS} = 0$ 

Figure S17. Left panel: Calculated supercell ( $Mn_{16}Se_{28}$ ) with enough vacuum layer and the corresponding differential charge density distribution diagram. Right panel: Mechanism illustration of field effect modulated energy band offset in  $MnSe_{2[metal]}/MnSe_{2[semiconductor]}$  coreshell structure.

For the MnSe<sub>2[metal]</sub>/MnSe<sub>2[semiconductor]</sub> core-shell structure, we built a similar model (Mn<sub>16</sub>Se<sub>28</sub>) and calculated the differential charge density. As shown in the Figure S14, a small number of electrons in the semiconductor shell are transferred to the interface between the two, forming an upward-bending energy barrier in heterojunction region. The existence of space charge region can block the further flow of electrons in semiconducting MnSe<sub>2</sub> into the metallic

MnSe<sub>2</sub>. Furthermore, the loss of electrons inside the semiconductor increases the resistance and thus reduces the dark current of device, which is conducive to the improvement of photoconductivity performance. Such a charge transfer trend can be also qualitatively proved by calculating their Fermi levels ( $E_F$  for bulk MnSe<sub>2</sub>: -3.45 eV;  $E_F$  for Mn<sub>4</sub>Se<sub>4</sub> slab: -2.59 eV).

In general, the field effect can only deplete and accumulate carriers for thin layers below 5 nm. Under field-effect mode ( $V_{GS}$ = +13 V), if the accumulated carriers cannot exceed the energy barrier, the junction region will always exist and these carriers cannot be transferred to the metal region in large quantities. In this regard, the metallic core will have no significant influence on the electrical characteristics in semiconductor shell layer. We can make a simple estimation for the degree of field-effect regulation by the equation of  $E_{\rm F}$  '= $E_{\rm F}$  +  $k_{\rm B}T \ln(n'/n)$ , where  $E_{\rm F}$  and  $E_{\rm F}$ ' are Fermi levels, n and n' are the densities of electron before and after modulation, respectively,  $k_{\rm B}$  is Boltzmann constant and T is the room temperature (300 K) during FET tests. Since the current is proportional to the density of carrier, the increasement of two orders of magnitude in on-state current means that the value of  $\ln(n'/n)$  is about 2. Hence, we can conclude that  $E_{\rm F}$  '- $E_{\rm F}\approx 2k_{\rm B}T=52$  meV, which is far lower than the energy barrier (0.86 eV). On the other aspect, owing to a considerable electron mobility, the carriers in narrow channel region (10 µm) can quickly transport between electrodes at a  $V_{\rm DS}$  of 100 mV. Therefore, the leaking current towards the metallic core can be ignored.



**Figure S18.** The fittings of  $\ln \sigma$  as a function of (a)  $T^{1/2}$ , ES VRH conduction and (b)  $T^{1/4}$ , 3D-Mott VRH conduction.



**Figure S19.** (a) ZFC/FC and (b) *M*-*H* curves of pristine MnSe<sub>2</sub>/Se. The appearance of Néel transition ( $T_{N}$ ~38 K) corresponds to the MnSe<sub>2</sub> component of composites.



Figure S20. Magnetization curves of (a)  $MnSe_2$  nanosheets without subtracting the contribution of substrate and (b) bare Si/SiO<sub>2</sub> substrate.



**Figure S21.** *M*-*H* curves of (a)  $MnSe_2$  nanosheets dispersed on  $Si/SiO_2$  after subtracting diamagnetic contribution and (b) nanosheets powder at 300 K. Obviously, their saturation moment levels are comparable and the difference of magnetic permeability at low fields stems from the random orientation of nanosheets in powder.

Ions	s-orbit	<i>p</i> -orbit	<i>d</i> -orbit	Total/µ <sub>B</sub>
Mn#1	0.066	0.047	4.450	4.563
Mn#2	0.067	0.046	4.450	4.563
Mn#3	0.066	0.047	4.450	4.563
Mn#4	0.067	0.046	4.450	4.563
Se#1	0.005	0.006	0.009	0.019
Se#2	0.005	0.006	0.009	0.019
Se#3	0.005	0.006	0.009	0.019
Se#4	0.005	0.006	0.009	0.019
Total/µ <sub>B</sub>	0.284	0.211	17.835	18.329

Table S2. Calculated atomic magnetic moment in 2D defective Mn<sub>4</sub>Se<sub>4</sub>



**Figure S22**. Hall resistance  $R_{xy}$  at 200 K for 2D MnSe<sub>2</sub>. A pronounced anomalous Hall effect can be observed in this curve, which is evidenced by a non-linear dependence of  $R_{xy}$  with external magnetic field. A negative slope indicates a *n*-type conduction behavior.



**Figure S23.** Temporal current measurements under IR illumination and response time constant fittings for the device (a) without magnetization and (b) with magnetization.



**Figure S24.** The fitting curves of photocurrent versus laser power density at RT. According to  $I_{ph}=\alpha P^{\theta}$ , where  $\alpha$  is the constant for a certain wavelength, *P* is power density, and  $\theta$  is also the constant for evaluating photosensitivity. Before and after magnetization, different exponential terms can be obtained. In general, this  $\theta$  value is correlated with trapping process in photoconductivity. Photogating effect plays an important role on the deviation of  $\theta$  value from one, which also results in a well-known high photo gain and a slow recombination process. In current work, the device working under magnetization appears to be weaker photogating effect, thus leading to a  $\theta$  value near one. Therefore, a faster respond speed should stem from the optimization of spin alignments.