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Gate-tunable trion switch for excitonic device applications

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Trions are excitonic species with a positive or negative charge, and thus, unlike neutral excitons, the flow of trions can generate a net detectable charge current. Trions under favorable doping conditions can be created in a coherent manner using resonant excitation. In this work, we exploit these properties to demonstrate a gate controlled trion switch in a few-layer graphene/monolayer WS2/monolayer graphene vertical heterojunction. By using a high-resolution spectral scan through a temperature controlled variation of the band gap of the WS2 sandwich layer, we obtain a gate voltage dependent vertical photocurrent strongly relying on the spectral position of the excitation, and the photocurrent maximizes when the excitation energy is resonant with the trion peak position. Further, the resonant photocurrent thus generated can be effectively controlled by a back gate voltage applied through the incomplete screening of the bottom monolayer graphene, and the photocurrent strongly correlates with the gate dependent trion intensity, while the nonresonant photocurrent exhibits only a weak gate dependence—unambiguously proving a trion driven photocurrent generation under resonance. We estimate a sub-100 fs switching time of the device. The findings are useful towards demonstration of ultrafast excitonic devices in layered materials.

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I. INTRODUCTION

The monolayer semiconducting transition metal dichalcogenides (MoS2, WS2, MoSe2, and WSe2) exhibit strongly bound two-dimensional excitons with a binding energy on the order of a few hundreds of meV, making these ultrathin monolayers an excellent test bed for excitonic manipulation even at room temperature [1–5]. The neutral excitons (X0) show excellent valley polarization and valley coherence properties that can be readily probed through initialization by circularly and linearly polarized photons, respectively, followed by detection through a circular or linear analyzer [6–11]. However, controlling these excitonic states electrically remains a challenge due to the charge neutral nature of these excitons. In addition, transport of the exciton also remains challenging due to the ultrafast radiative recombination of excitons [12–16] resulting from the high oscillator strength [17–19]—limiting the application of excitonic devices. Recently, this problem has been addressed by creating interlayer excitons [20–24] to suppress the fast radiative decay, and exciton transport over several micrometers in the plane of the layered material has been demonstrated [4]. An external gate control has also been achieved by modulating the binding energy of the neutral exciton [4,5]. In this regard, the charged exciton or trion (X−) is promising since its intensity can be readily controlled electrically by modulating the doping density using a gate voltage. In addition, the trion, while being optically initiated, can be electrically detected in a spatially nonlocal manner through measuring a charge current [25]. The relatively longer radiative lifetime of trions compared to intralayer excitons [6,11] further helps in nonlocal detection. Trions can be valley polarized when initiated through a circularly polarized light [7]. Trions can also carry valley coherence information when resonantly initialized through linearly polarized light [9]. Thus trions are excellent candidates for gate controlled excitonic device applications and also for transferring the valley information into electrical domain. In this work, we demonstrate a fast, gate- and light-tunable vertical trion switch where the trion is coherently initialized through resonant excitation followed by ultrafast interlayer transfer and electrical detection, thus generating a gate controlled photocurrent governed by interlayer trion transport.

II. RESULTS AND DISCUSSIONS

Figure 1(a) shows the schematic diagram of the vertical switch with a monolayer WS2 sandwiched between monolayer graphene (MLG) at the bottom and few-layer graphene (FLG) on the top. The heterostructure is prepared on a heavily doped Si substrate coated with 285-nm-thick thermally grown SiO2. The two electrical contacts are deposited to the top and the bottom graphene. More details of the fabrication process are provided in the Methods section. Figure 1(b) shows the optical image of the device delineating the different stacked layers by marking with different colors. The fabricated device is then placed on a thermal stage and the terminals of the device are connected to Keithley 2636B source measure units (SMUs) through micromanipulators for electrical measurements. The temperature (T) of the device is then increased from room temperature to 423 K in steps.
FIG. 1. Photocurrent in FLG/monolayer WS$_2$/MLG vertical heterojunction. (a) Schematic of the experimental device structure where 1L-WS$_2$ is sandwiched between monolayer graphene (MLG) in the bottom and few-layer graphene (FLG) on the top. (b) The optical micrograph of the heterostructure where the MLG, 1L-WS$_2$, and the FLG are marked with blue, yellow, and black outlines, respectively. (c) The transfer characteristics of the device under dark condition at different temperatures with $V_d = 20$ mV. Inset: The dark current-voltage characteristics at 293 K with $V_g = 0$ V. (d) The color plot of temperature dependent PL spectra with 2.33 eV laser excitation. The band gap decreases monotonically with an increase in temperature. The vertical red dashed line corresponds to 1.9591 eV excitation. (e) Variation of exciton ($X^0$) and trion ($X^-$) peak positions as a function of temperature showing enhanced separation (and hence higher trion stability) between the two at higher temperatures. (f) The transient photocurrent at zero external bias with 1.9591 eV laser excitation at different temperatures starting from 303 K and increasing up to 423 K in steps of 20 K.

![Graphical representation of experimental data](image.png)

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of 10 K. At every temperature, the device is illuminated with a linearly polarized laser beam with photon energy of 2.33 and 1.9591 eV through an objective with numerical aperture of 0.5 at different back gate voltages ($V_g$) ranging from $-40$ to $+40$ V. We record the in situ photoluminescence (PL) spectra and photocurrent at each $V_g$ and $T$ step. During measurement, the incident laser power is kept below 8 $\mu$W to avoid any unwanted degradation of the device due to laser-induced heating.

Figure 1(c) shows the transfer characteristics ($I_{dark}$-$V_g$) of the vertical device under dark condition at 295 K, when a $V_d = 20$ mV bias is applied across the two terminals. The graphenelike “V”-shaped curve suggests that the $V_g$ dependence primarily arises from the modulation of the chemical potential in the bottom monolayer graphene and the junction acts like a tunneling series resistance. In the inset, the $I_{dark}$-$V_d$ plot is shown at $V_g = 0$ V confirming the Ohmic nature of the junction arising from strong carrier tunneling between the top and the bottom graphene layers through the band gap of WS$_2$.

The difference in doping-induced work function between the top FLG and the bottom MLG results in an asymmetry in the device along the vertical direction, which results in a built-in electric field, allowing a detectable photocurrent ($I_{ph} = I_{light} - I_{dark}$) between the two electrodes under $V_d = 0$ V. This helps us to reduce the average dark current to zero, suppressing the dark noise of the switch dramatically. The sign of the zero-bias vertical $I_{ph}$ at different $V_g$ suggests a net electron flow from the top FLG to the bottom MLG.

Figure 1(d) depicts the temperature dependent variation of the $A_{1g}$ neutral exciton ($X^0$) peak position as obtained using 2.33 eV laser excitation. The individual spectra at each temperature are shown in Supplemental Material Fig. S1 [26]. The $X^0$ and trion ($X^-$) peak positions, as obtained from a Voigt fitting, are plotted as a function of temperature in Fig. 1(e). One could readily identify that apart from a redshift of the

![Graphical representation of experimental data](image.png)
FIG. 2. Resonant trion mediated $I_{ph}$ generation with 1.9591 eV excitation. (a) Temperature dependent PL spectra of the heterojunction with 2.33 eV excitation. The $X^-$ and $X^0$ energy states, fitted with two Voigt curves (cyan and violet, respectively) are shown separately. The vertical red dashed line shows the spectral position of 1.9591 eV excitation. The $X^-$ state comes in resonance with 1.9591 eV excitation at 343 K while for the $X^0$, it is around 393 K (not shown in the figure). (b) Schematic of the photocurrent generation mechanism with 1.9591 eV excitation at different temperatures. The off-resonance condition is shown in (b) and (h). (b) shows the situation at 303 K with the excitation in the suboptical-band-gap range of 1L WS$_2$ (at 303 K, the optical band gap is 2.014 eV), while (h) shows the situation at 423 K where the excitation is above the optical band gap. The excitation is in resonance with the $X^-$ at 343 K (c)–(e). (c) shows the coherent formation of bright intervalley trions with linear polarization. The resonantly formed $X^-$ can either be transferred directly to the bottom MLG [shown in (d)] or it can recombine radiatively, releasing an electron, which in turn gets transferred to the bottom MLG [shown in (e)]. Both of the processes generate photocurrent; however, the latter process is of weaker efficiency. (f) and (g) show the $X^0$ resonance condition at 393 K, which does not contribute to the photocurrent generation due to the charge neutral nature of $X^0$.

peak position due to a temperature induced reduction in band gap, the trion peak survives up to the highest temperature (423 K) used in the experiment, suggesting a highly stable trion on the junction. This is further supported by an enhancement in the trion dissociation energy (separation between the $X^0$ and $X^-$ peaks) at higher temperature in Fig. 1(e), arising from enhanced doping of monolayer WS$_2$ at higher temperature [25].

The dashed vertical line in Fig. 1(d) indicates the spectral position of the 1.9591 eV excitation. This suggests that using a fixed excitation at 1.9591 eV, with a change in the sample temperature, we can perform a high-resolution spectral scan around the $X^0$ and $X^-$ overlap region. The transient response of the zero-bias $I_{ph}$ under 1.9591 eV excitation is shown at different temperatures in Fig. 1(f). Since $V_d = 0$, the dark current is ideally zero and practically only limited by the noise of the measurement setup. The vertical jumps in $I_{ph}$ when the excitation source is toggled between on and off states indicate that the device works as a fast photonic switch. The magnitude of $I_{ph}$ exhibits a strong nonmonotonic trend with temperature, peaking at $T = 343$ K, which corresponds to the resonant condition between the excitation energy and the $X^-$ peak. This strongly points to the fact that coherently excited trions participate in the detected photocurrent.

The temperature dependent nonmonotonic photocurrent generation mechanism is explained in Fig. 2. When the temperature is around 300 K [top panel of Fig. 2(a)], the band gap of WS$_2$ is higher, and the excitation is well below the $X^0$ and $X^-$ position, thus the resulting photocurrent is weak. The source of this photocurrent from such nonresonant excitation is the photoexcited electrons from the top FLG being driven to the bottom MLG tunneling through the WS$_2$ barrier by the built-in electric field, as schematically depicted in Fig. 2(b). Note that if the temperature changes the relative doping between the top and the bottom graphene, the resulting change in the built-in field would in turn cause a monotonic change in the photocurrent with an increase in temperature. The observed nonmonotonicity in $I_{ph}$ magnitude with temperature thus hints that a separate mechanism other than just photoelectron tunneling must contribute to the nonmonotonicity.

As the sample temperature reaches a value of around 343 K, the linearly polarized photon creates trions in a coherent manner in $K$ and $K'$ valleys, as explained in Fig. 2(c) [9,11]. Each of the trions consists of a bright exciton in one valley electrostatically bound with an electron in the lower spin-split conduction band from the opposite valley. Since interlayer transfer is ultrafast (approximately subpicosecond [12,27–29]), which is faster than trion radiative decay (approximately tens of picoseconds [2,9,10,19,30,31]), the whole negatively charged trion can be transferred to the bottom monolayer graphene driven by the built-in electric field, as illustrated in Fig. 2(d). To account for charge neutrality, the
top layer graphene injects an electron to the WS$_2$, completing the circuit. Thus the trion state acts as an intermediate state to provide a favorable path for the flow of the charge current enhancing the photocurrent. Under resonance, this is the dominating photocurrent transport mechanism in the vertical heterojunction. We also note that after resonant excitation, even if the trion recombines radiatively before being transferred to the bottom graphene layer, the released electron in the conduction band of WS$_2$ can still be driven to the bottom MLG through the built-in field to generate the photocurrent, as depicted in Fig. 2(e). However, noting that the interlayer transfer process is faster than the radiative lifetime, the latter process of photocurrent is less dominant.

As the temperature increases further, the resonance condition breaks and thus the photocurrent also lowers. Around 393 K, the excitation comes in resonance with $X^-$ [Figs. 2(f) and 2(g)] peak; however, the $I_{ph}$ is still quite low. The net charge in the neutral exciton being zero, the exciton flow does not contribute to the charge current in spite of being resonantly created and transferred to the bottom graphene layer as evidenced from quenching of photoluminescence in several studies [32–34]. It is also possible that the resonantly created exciton can form trions with the emission of phonons, which could eventually generate a charge current. However, the time it takes to form the trion through phonon emission is much longer than interlayer exciton transfer, suppressing this process, and hence the photocurrent at exciton resonance is also suppressed compared to trion resonance. With further spectral detuning through an increase in temperature [Fig. 2(h)], $I_{ph}$ is even more suppressed.

Figure 3(a) shows the transient response of $I_{ph}$ with $V_g$ varying from $-40$ to $40$ V, keeping the temperature fixed at 343 K, suggesting a monotonic increment of $I_{ph}$ with $V_g$. Figure 3(b) shows the strong tunability of $I_{ph}$ with $T$ as well as $V_g$ through a color plot. With an increase in $V_g$ at the back gate, the WS$_2$ film can be gated through the bottom MLG film due to its incomplete screening. The gate tunability of $I_{ph}$ is maximum when the excitation is around the resonance with the $X^-$ peak, and tunability reduces on both sides. This is further evidence regarding the strong role of the trion in the photocurrent generation mechanism. With larger positive $V_g$, the formation of $X^-$ is favored, which in turn increases the photocurrent. The point is further elaborated in Figs. 3(c) and 3(d), by taking horizontal slices from Fig. 3(b) along $V_g = 40$, $0$, and $-40$ V. In Fig. 3(d), the relative $X^0$ (solid circles) and $X^-$ (open circles) peak shifts with respect to 1.9591 eV excitation at different temperatures. The resonance conditions with $X^0$ and $X^-$ are indicated by the vertical dashed lines.
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FIG. 4. Correlation of $V_g$ modulation with $X^-$ intensity under resonance. (a) The color plot of the PL intensity obtained with 1.9591 eV excitation as a function of $V_g$ (in horizontal axis) and the relative emission energy positions of $X^-$ with respect to the excitation energy (in vertical axis). The green open symbols denote the position of the $X^-$ peak obtained from 2.33 eV excitation. (b) Normalized PL spectra with 2.33 eV excitation at 343 K showing the $X^-$ and $X^0$ energy states separately at five different $V_g$ conditions. The red arrows indicate the position of the 1.9591 eV excitation, with which photocurrent is measured. (c) Normalized $I_{ph}$ (in brown symbols, left axis) and trion intensity along the horizontal dashed line in (a) (in orange symbols, right axis) for different $V_g$ with 1.9591 eV excitation at 343 K, showing a strong correlation between the two independent measurements.

trion resonance, we clearly notice a monotonic increase in the intensity with an increase in $V_g$. The individual spectra with 2.33 eV excitation at different gate voltages are depicted in Fig. 4(b), clearly indicating the increasing strength of trions with an increase in the gate voltage. In Fig. 4(c), we plot the normalized PL intensity as a function of gate voltage along the dashed line ($T = 343$ K) in Fig. 4(a). The normalization of the PL intensity is performed as $\frac{PL(V_g) - PL_{min}}{PL_{max} - PL_{min}}$, where $PL_{min(max)}$ is the minimum (maximum) PL intensity with varying $V_g$ at 343 K. In the right axis of the same figure, we also plot the normalized $I_{ph}$ [normalized as $\frac{I_{ph}(V_g) - I_{ph_{min}}}{I_{ph_{max}} - I_{ph_{min}}}$, where $I_{ph_{min(max)}}$ is the minimum (maximum) $I_{ph}$ with varying $V_g$]. The correlation between the two independent measurements is remarkable, unambiguously suggesting the origin of $I_{ph}$ from transport of negatively charged trions in the vertical direction.

Finally, we comment on the estimated switching speed of the trion switch. Since trions are coherently generated through optical excitation, the primary step limiting the intrinsic speed of switching is the interlayer transfer time of the trion. This interlayer transfer timescale can be roughly estimated through the difference in homogeneous linewidth broadening of the trion emission between WS$_2$ at the junction and from WS$_2$ lying on SiO$_2$. The total homogeneous linewidth of the trion emission can be estimated from the radiative recombination rate ($\Gamma_r$), nonradiative scattering rate ($\Gamma_{nr}$), and interlayer transfer rate ($\Gamma_{tr}$) by $\Gamma = \Gamma_r + \Gamma_{nr} + \Gamma_{tr}$. The last term is present only for the heterojunction, and absent for a control WS$_2$ sample placed on SiO$_2$. Thus, we have

$$\tau = \frac{\hbar}{2\Gamma_r} = \frac{\hbar}{\Delta\Gamma},$$

where $\Delta\Gamma$ is the difference in the Lorentzian component of the full width at half maximum of the $X^-$ peaks between the junction and the control sample, after fitting each of them using a Voigt function [18,32]. We estimate a value of $\tau \approx 65$ fs suggesting the ultrafast nature of the trion switch.

In summary, we have demonstrated a gate- and light-controlled trion switch, where trion is optically initiated in a resonant manner and the readout is performed electrically. This can lead to a new paradigm of exciton-based optoelectronic switches. The proposed technique exploits the vertical interlayer transfer of excitonic species, which thus can be extremely fast, compared to relatively slow planar transport of heavy excitons. The efficient controllability through both electrical gating as well as photogating marks an important step towards the realization of a trion-based transistor. Since trions can be valley polarized, the valley information can be optically initiated, followed by an electrical sensing, thus transferring the valley information into the electrical domain. The proposed technique can also be used for efficient...
generation and injection of spin current by resonantly exciting the trion using circularly polarized light—an important step toward realizing spintronic devices.

III. METHODS

A. Device fabrication

To prepare the heterojunction of MLG/monolayer WS$_2$/FLG we have used a dry transfer technique on a highly doped Si substrate covered with a 285-nm-thick thermally grown oxide layer. The different layers have been heated subsequently on a hot plate at 70 °C for 2 min in order to get improved adhesion between layers. Device contacts are fabricated using standard nanofabrication methods. The substrate is spin coated with PMMA 950C3 and baked on a hot plate at 180 °C for 2 min. This is followed by e-beam lithography with an acceleration voltage of 20 kV, an electron beam current of 220 pA, and an electron beam dose of 200 μC cm$^{-2}$. Patterns are developed using methyl isobutyl ketone:isopropyl alcohol (MIBK:IPA) solution in the ratio 1:3. Later, samples are washed with IPA and dried in N$_2$ blow. Electrodes are then made by deposition of 10 nm Ni/50 nm Au films using DC magnetron sputtering at 3 × 10$^{-3}$ mbar and subsequent lift off by dipping the substrate in acetone for 15 min, followed by washing in IPA and N$_2$ drying. The oxide at the back side of the wafer is also etched by dilute hydrofluoric acid (HF) solution.

B. Photocurrent measurement

Devices are kept on a Linkam thermal stage along with a heater underneath. The laser beam (2.33 or 1.9591 eV) is focused through a 50× objective (NA of 0.5) to the heterostructure with a spot size of approximately 2 μm. The devices are electrically probed using micromanipulators and a Keithley 2636B is used as source meter. The temperature of the stage is increased from 295 to 423 K in steps of 10 K. A gate bias $V_g$ is applied at the Si substrate ranging from −40 to +40 V in steps of 5 V. At each temperature and at each biasing point, photocurrent measurements are carried out and in situ photoluminescence spectra are obtained.

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