### Trion-Induced Negative Photoconductivity in Monolayer MoS\textsubscript{2}

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Trion-Induced Negative Photoconductivity in Monolayer MoS$_2$


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Optical excitation typically enhances electrical conduction and low-frequency radiation absorption in semiconductors. We, however, observe a pronounced transient decrease of conductivity in doped monolayer molybdenum disulfide (MoS$_2$), a two-dimensional (2D) semiconductor, using ultrafast optical-pump terahertz-probe spectroscopy. In particular, the conductivity is reduced to only 30% of its equilibrium value at high pump fluence. This anomalous phenomenon arises from the strong many-body interactions in the 2D system, where photoexcited electron-hole pairs join the doping-induced charges to form trions, bound states of two electrons and one hole. The resultant increase of the carrier effective mass substantially diminishes the conductivity.

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Atomically thin transition metal dichalcogenides (TMDs, e.g., MoS$_2$, MoSe$_2$, WS$_2$, WSe$_2$) are two-dimensional (2D) semiconductors with rich physical properties, including high mechanical strength and flexibility, strong photoluminescence (PL) [1,2], superior (opto)electronic performance [3,4], and intriguing coupled spin-valley physics [5−8]. These remarkable properties make TMD materials promising for developing next-generation (opto)electronics and (pseudo)spintronics. One distinctive feature of monolayer TMDs is the strong quantum confinement and reduced dielectric screening in the strict 2D limit. The resultant strong Coulomb interactions cause photoexcited electron-hole pairs to form tightly bound excitons, which govern the optical and electronic properties of the materials [9−22]. In samples with excess charges, the excitons can capture additional charges to form trions (charged excitons). These trions possess exceptionally high dissociation energies (20−50 meV), and their concentration and spin-valley configuration can be controlled by electrical gate and optical helicity, respectively [12,23−25]. Although these strong many-body effects have been observed in 2D TMDs, their influence on the materials’ intrinsic conductive behavior and implications for device applications have not been explored thus far.

In this Letter, we report the first experimental signature of a profound trionic effect on the conductive properties of atomically thin TMD materials. By using time-resolved terahertz spectroscopy [26,27], we have observed an anomalous transient decrease of terahertz conductivity in doped monolayer MoS$_2$ after femtosecond laser excitation at $T = 4−350$ K. The negative photoconductivity saturates at high pump fluence, where the conductivity is substantially reduced to $\sim$30% of its equilibrium value. This behavior contrasts with the positive photoconductivity found in multilayer and bulk MoS$_2$, and in other conventional semiconductors (e.g., Si, Ge, and GaAs) [26,27]. Our results reflect the strong many-body interactions in monolayer MoS$_2$, where photoexcited carriers form trions with the original free electrons. The resultant increase of effective mass significantly diminishes the carrier mobility and conductivity. This interaction-driven photo reduction of conductivity represents an intrinsic property of monolayer MoS$_2$ crystals, in contrast to the negative photoconductivity arising from trapping or spatial transfer of charges in some semiconductor systems with high defect density or heterogeneous structure [28,29].

To reveal the intrinsic conductive properties of monolayer MoS$_2$, we used time-domain terahertz spectroscopy. This approach avoids the complication of electrical contacts in transport experiments and, when applied with femtosecond laser excitation, can probe short-lived excited carriers prior to trapping or recombination [26,27]. Our experiment employed a 5-kHz Ti:sapphire amplifier system that generates laser pulses with 1.55-eV photon energy and 90-fs pulse duration. The laser was split into two beams. One beam was frequency converted through an optical parametric amplifier and/or second harmonic generation for pumping the samples. The other beam generated terahertz pulses by optical rectification in a ZnTe crystal for probing the samples. By using electro-optic sampling detection, we could map out the whole waveform of the terahertz electric field $E(t)$ in the time domain, and the pump-induced change of the field $\Delta E(t, \tau)$ at a controllable pump-probe delay time $\tau$ [30−32].

We investigated large-area monolayer MoS$_2$ samples grown by chemical vapor deposition (CVD) on sapphire substrates [33,34]. The samples were mounted on a helium-flow cryostat in high vacuum. We first measured their
To investigate the optoelectronic response of monolayer MoS$_2$, we excited the sample using 3.1-eV laser pulses. Excitation at this photon energy, with fluences used in our experiment, can generate $\sim 10^{13}$–$10^{14}$ carriers/cm$^2$ in the MoS$_2$ monolayer [1], which is expected to greatly enhance the terahertz absorption (e.g., see Fig. 11 in Ref. [27]). Surprisingly, our result of pump-induced change of transmission (proportional to $\Delta E$) indicates a transient decrease of terahertz absorption in the monolayer MoS$_2$ sample [Fig. 1(b)] [30]. To further explore this unusual behavior, we have measured the temporal ($\tau$) evolution of the fractional change of the terahertz field, i.e., the ratio between the maximum values of waveforms $E(t, \tau)$ and $E(t)$ [Fig. 1(c)]. The terahertz dynamics exhibit a short component with lifetime $\tau_1 \approx 1$ ps, followed by a long component with lifetime $\tau_2 \approx 42$ ps. From the measured transmission spectra, we extracted the change of complex sheet conductivity $\Delta \sigma(\omega, \tau)$ of monolayer MoS$_2$ [30]. Both the real and imaginary parts of $\Delta \sigma(\omega, \tau)$ exhibit negative values for all delay times ($\tau$) and frequencies ($\omega$) in our measurement range [Fig. 1(d)].

The observed negative photoconductivity is a robust and substantial effect in monolayer MoS$_2$. It persists for all incident pump fluences ($F = 0.4$–$170$ $\mu$J/cm$^2$) and temperatures ($T = 4$–$350$ K) in our experiment [see, for example, the fluence dependence in Figs. 2(a)–2(b) and data for $T = 300$ K in Fig. 2(c)]. As the pump fluence increases, the reduction of the terahertz absorption increases and gradually saturates at an almost 70% decrease of the total absorption [Fig. 2(b)], indicating that the conductivity of monolayer MoS$_2$ is reduced to only $\sim 30\%$ of its equilibrium value. The long component exhibits a considerable increase of magnitude and relaxation time with the fluence, and becomes the dominant contribution to the overall dynamical response in the saturation regime [Figs. 2(a)–2(b)].

Negative photoconductivity was observed in monolayer MoS$_2$ samples deposited on sapphire and quartz substrates, with and without HfO$_2$ or polymer electrolyte top layers. The insensitivity to the dielectric and interfacial environment implies that the phenomenon originates from the intrinsic property of the MoS$_2$ material. We also examined multilayer CVD MoS$_2$ films and bulk MoS$_2$ crystals. We did not observe any photoreduction of conductivity in these thicker samples, but only the expected photoenhancement (see the Supplemental Material [30]).

We can understand the above observations by considering the substantially enhanced Coulomb interaction and excitonic effects in monolayer MoS$_2$. The binding energies of excitons in MoS$_2$ and other TMD monolayers have been estimated to be a few hundred meV [9–22], an order of magnitude larger than the values of their respective multilayer and bulk crystals [11,37]. As excited carriers in MoS$_2$ are known to relax within 100 fs [38], we expect the photogenerated electrons and holes to form tightly bound excitons in monolayer MoS$_2$ almost instantaneously. These excitons are charge neutral and have resonance energies much higher than the terahertz photon energy ($\sim 4$ meV).

FIG. 1 (color online). (a) Terahertz response of monolayer MoS$_2$ on a sapphire substrate in equilibrium conditions. The red and blue lines show the terahertz electric field transmitted through areas with and without the sample, respectively. The left inset is a zoomed-in view of the peak (dashed square). The measurement uncertainty at the peak is $3.5 \times 10^{-5}$, corresponding to 0.06% of the total terahertz signal. The right inset shows the terahertz power spectra. (b) Change of terahertz transmission after pulsed excitation. The red and green lines denote, respectively, the equilibrium transmitted terahertz field and the pump-induced waveforms $E(t, \tau)$ at $\tau = 3$ ps. The inset is a schematic of our experiment. (c) Temporal evolution of the ratio between the maximum values of waveforms $E(t, \tau)$ and $E(t)$. A biexponential fit (red line) yields lifetimes $\tau_1 = 1$ ps and $\tau_2 = 42$ ps. The inset is a zoomed-in view of the short component. (d) The extracted pump-induced change of complex sheet conductivity $\Delta \sigma(\omega, \tau)$ at $\tau = 3$ and 40 ps. The measurements were made at $T = 15$ K, with incident pump fluence $50 \mu$J/cm$^2$ and photon energy 3.1 eV.

terahertz absorption in equilibrium conditions at $T = 15$ K. We recorded the terahertz electric field transmitted through the MoS$_2$/substrate area, $E(t)$, and as a reference, through an area without MoS$_2$ flakes, $E_0(t)$ [Fig. 1(a)]. The maximum value of $E(t)$ was 2.1% smaller than that of $E_0(t)$. This attenuation of the terahertz transmission [insets of Fig. 1(a)] arises from intraband absorption of excess free electrons in the doped sample. From the measured transmission spectra, we extracted the complex sheet conductivity of monolayer MoS$_2$ by applying the standard thin-film approximation [30,35,36]. We determined in the spectral range of 0.5–2.0 THz an average (real) conductivity $\sigma_1 \approx 2 \pm 0.5$ $G_0$, where $G_0 = 2e^2/h$ is the quantum of conductance. We estimated the doping electron density of our samples to be $n \approx 5.5 \pm 2 \times 10^{12}$ cm$^{-2}$ from the trion dissociation energy ($\sim 40$ meV) [see the PL spectra in the inset of Fig. 5(a)], which increases with the Fermi level according to Ref. [23]. We then obtained an electron mobility $\mu = \sigma_1 / ne \approx 180 \pm 70$ cm$^2$ V$^{-1}$ s$^{-1}$ for our samples at $T = 15$ K.
They will not interact with the terahertz radiation and change the terahertz conductivity. This accounts for the lack of positive terahertz photoconductivity in monolayer MoS$_2$ at all pump fluences in our experiment. We note that our terahertz technique is different from conventional transport methods, in which a large dc electric field is applied across the samples to break the excitons into free carriers, thus leading to positive photoconductivity [1,4,21,39].

To account for the negative photoconductivity, we further consider the interactions between the excitons and free charges. Previous experiments [12,23–25] have shown that when excess doped electrons are available, the excitons can capture free electrons to form three-body bound states with two electrons and one hole in monolayer MoS$_2$ and other TMDs. These complex quasiparticles, the so-called trions, possess large dissociation energies (20–50 meV) and are stable even at room temperature. Trion formation can adequately account for our experimental observations: after pulsed excitation, the generated electron-hole pairs form trions with the excess free charges within the rise time of the pump-probe signal ($\sim 1$ ps). The trions behave as free charged particles with increased effective mass [40], resulting in lower carrier mobility ($\mu$) and hence lower conductivity ($\sigma = ne\mu$). In other words, instead of increasing the free-carrier concentration, photoexcitation adds mass to the original free charges and dulls their response to the electric field (Fig. 3).

A straightforward way to confirm the trion scheme is to compare the terahertz dynamics with the trion decay dynamics. We have carried out time-resolved PL measurements on our monolayer MoS$_2$ samples at $T = 300$ K [Fig. 2(d)] [30]. The PL intensity in the emission photon energy range of 1.7–2.0 eV [inset of Fig. 5(a)] is proportional to the trion population and decayed with a lifetime of $\tau_2 = 33 \pm 5$ ps. This decay time, comparable to results in other experiments [41–44], reflects the nonradiative recombination of trions in the defect sites. The trion lifetime agrees with the terahertz recovery time under similar conditions ($\tau_2 = 29$ ps) [Fig. 2(c)].

To further verify the trion mechanism, we have conducted the terahertz experiment with tunable pump photon energy from 0.77 to 2.11 eV (Fig. 4). The overall terahertz dynamical response is suppressed sharply and the major
FIG. 4 (color online). (a) Temporal terahertz dynamics of monolayer MoS$_2$ at $T = 50$ K, with the same incident pump fluence (65 $\mu$J/cm$^2$), but different pump photon energy (0.77–2.11 eV). The inset shows the long-component lifetime ($\tau_2$) from biexponential fits as a function of photon energy. No systematic energy dependence was found for the short-component lifetime ($\tau_1 \approx 2$ ps). (b) The maximum pump-induced signal at $\tau \approx 2$ ps and at $\tau = 8$ ps (representing the long-component contribution) as a function of photon energy, with the same left y-axis as (a). The dashed curve is the absorption spectrum measured on a representative monolayer MoS$_2$ flake at $T = 20$ K using the method in Ref. [1].

(long) component is quenched as the photon energy falls below 1.9 eV. This critical energy value matches the resonance of the A exciton and trion from the absorption spectrum of monolayer MoS$_2$ [Fig. 4(b)] [1,23]. Near the excitonic resonance, we expect only excitons and trions to be produced, with minimum free-carrier generation and carrier heating. As the neutral excitons do not interact with the terahertz radiation, the strong signal of negative photoconductivity must arise from the charged trions.

In the trion scheme, the reduction of conductivity is expected to saturate at a value proportional to the doping electron density, when most of the excess electrons are transformed into trions. To this end, we have examined the terahertz dynamics and PL of a MoS$_2$ sample at different doping stages. At the initial stage, the pristine sample exhibited a pronounced terahertz response (black line in Fig. 5). Its PL spectrum was centered at the trion ($A^-$) recombination energy (1.844 eV), indicating strong unintentional electron doping [inset of Fig. 5(a)]. We next doped the sample with chemical solutions according to the method described in Ref. [45]. We first deposited tetrafluorotetracyanoquinodimethane (F$_4$TCNQ) molecules as $p$-type chemical dopants to lower the electron density of the sample [45]. The PL of the sample increased and the peak position blueshifted to the exciton energy (1.885 eV), indicating the suppression of trion formation [23,45]. Correspondingly, the terahertz response was suppressed and subsequently quenched. The response also saturated at lower pump fluence (red and green lines in Fig. 5). The process could be reversed by depositing nicotinamide adenine dinucleotide (NADH) molecules as $n$-type dopants to increase the electron density [45]. Both the PL spectrum and the terahertz response were partially recovered (blue lines in Fig. 5). The observed doping dependence agrees qualitatively with the expected behavior for trion formation.

Finally, the trion formation provides a straightforward explanation for the $\sim 70\%$ reduction of terahertz conductivity in the saturation regime [Fig. 2(b)], which simply reflects the threefold increase of carrier effective mass. It also naturally accounts for the fluence and photon-energy dependence of the terahertz recovery time. As shown in the insets of Figs. 2(a) and 4(a), the long-component lifetime ($\tau_2$) increases with increasing pump fluence or photon energy, both corresponding to the increase of trion density. Excitons and trions in MoS$_2$ decay predominantly through defect-mediated processes. The probability to trap a trion will decrease when the defect sites gradually fill up at increasing excitation density. This will prolong the trion lifetime and hence, the terahertz recovery time.

The evidence and analysis above strongly suggest that trion formation is the dominant mechanism for the negative photocconductivity in monolayer MoS$_2$, particularly the major (long) component of the terahertz dynamics. For the terahertz response at a shorter time scale ($\sim 1$ ps) and optical excitation with photon energy below 1.8 eV, trion-trion annihilation, defect-mediated absorption, and the carrier heating effect might become important. These secondary factors are discussed in the Supplemental Material [30].

In conclusion, we have observed a dramatic reduction of terahertz conductivity in monolayer MoS$_2$ under optical excitation. This unusual phenomenon originates from the strong many-body interactions in the material,

FIG. 5 (color online). (a) Temporal terahertz dynamics of monolayer MoS$_2$ at different chemical doping stages. The measurements were made on a pristine MoS$_2$ sample on sapphire (black), the same sample after being doped lightly (red) and heavily (green) with $p$-type F$_4$TCNQ molecules and further doped with $n$-type NADH molecules. The sample is different from that used in Fig. 2. All measurements were made with the same pump photon energy (1.98 eV) and fluence (174 $\mu$J/cm$^2$) at $T = 50$ K. The inset shows the PL spectra of the MoS$_2$ sample at the corresponding doping stages, taken at room temperature with 532-nm laser excitation. The A and B excitons and trion ($A^-$) are denoted. (b) The maximum pump-induced signal (at $\tau \approx 2$ ps) as a function of pump fluence at the corresponding doping stages in (a). Both (a) and (b) have the same y-axis.
which convert the 2D electron gas into a charged trion gas with the same charge density but much heavier effective mass. Similar photoconductivity phenomena are expected in other 2D materials with strong trionic effects. Our research reveals that charge transport in 2D TMD materials can be conducted by trions, which respond to the electric field as free charged particles [40]. The trionic effects can be conducted by trions, which respond to the electric field. This unique feature provides new device concepts for developing novel excitonic and spintronic devices that are operational at room temperature.

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