Sub-bandgap activated charges transfer in a graphene-MoS2-graphene heterostructure

Sunil Kumar1 | Arvind Singh1 | Anand Nivedan1 | Sandeep Kumar1 | Seok Joon Yun2 | Young Hee Lee2 | Marc Tondusson3 | Jérôme Degert3 | Jean Oberle3 | Eric Freysz3

1 Femtosecond Spectroscopy and Nonlinear Photonics Laboratory, Department of Physics, Indian Institute of Technology Delhi, New Delhi 110016, India
2 Department of Energy Science, Sungkyunkwan University (SKKU), Suwon 16419, Republic of Korea
3 CNRS, LOMA UMR 5798, Univ. Bordeaux, Talence 33405, France

Correspondence
Eric Freysz, Univ. Bordeaux, CNRS, LOMA UMR 5798, Talence 33405, France. Email: eric.freysz@u-bordeaux.fr
Sunil Kumar, Femtosecond Spectroscopy and Nonlinear Photonics Laboratory, Department of Physics, Indian Institute of Technology Delhi, New Delhi 110016, India. Email: kumarsunil@physics.iitd.ac.in

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Abstract
Monolayers of transition metal dichalcogenides are semiconducting materials which offer many prospects in optoelectronics. A monolayer of molybdenum disulfide (MoS2) has a direct bandgap of 1.88 eV. Hence, when excited with optical photon energies below its bandgap, no photocarriers are generated and a monolayer of MoS2 is not of much use in either photovoltaics or photodetection. Here, we demonstrate that large size MoS2 monolayer sandwiched between two graphene layers makes this heterostructure optically active well below the band gap of MoS2. An ultrafast optical pump-THz probe experiment reveals in real-time, transfer of carriers between graphene and MoS2 monolayer upon photoexcitation with photon energies down to 0.5 eV. It also helps to unravel an unprecedented enhancement in the broadband transient THz response of this tri-layer material system. We propose possible mechanism which can account for this phenomenon. Such specially designed heterostructures, which can be easily built around different transition metal dichalcogenide monolayers, will considerably broaden the scope for modern optoelectronic applications at THz bandwidth.

KEYWORDS
carrier dynamics, graphene, heterostructures, terahertz, transition metal dichalcogenides, ultrafast detector

1 | INTRODUCTION

Suitability of optical materials for applications in photovoltaics and photodetection relies on the efficient conversion of light photons into free electron-hole pairs. In this regard the limiting processes related to carrier-carrier scattering, heat generation through phonon emission by hot carriers and the electron-hole recombination, are important to be known as precisely as possible. In real devices, the latter two processes must be reduced to enhance the conversion of light energy into free carriers only. Moreover, to avoid their recombination, the photogenerated carriers need to be spatially separated almost as soon as they are generated. In practice, multi-layers of different
materials are often employed for many different purposes. Hence, interfacial effects taking place at ultrafast time-scale and within atomistic regions between the layers, are prone to affect their performances in a crucial way. Recently, novel promising optoelectronic devices using quantum materials such as graphene and transition metal dichalcogenides (TMDs), and their heterostructures have been designed. Heterostructures are of special interest as they serve in the study of the atomic interfacial effects and impact the fundamental time-scales involved during the charge carriers exchange and recombination. In many cases, it also has been observed that optical effects are enhanced by appropriate heterojunction between two different monolayers\textsuperscript{[1,2]} and it happens to be very useful for lot-of applications. In fact, near-field coupling through the interlayer charge and energy transfer processes in metal-semiconductor stacks of two-dimensional materials govern the performance of optoelectronic devices made out of them.\textsuperscript{[3]} Very recently, the attention of the scientific community has been driven towards large area heterostructures of graphene with other monolayers of finite band-gap semiconducting TMDs for novel device applications. The latter are easy to synthesize nowadays and exhibit interesting prospects.\textsuperscript{[4–10]} Such heterostructures of varying electronic properties allow us to engineer the interactions/coupling between the layers to address specific applications. Thanks to the remarkable optical properties of molybdenum disulfide (MoS\textsubscript{2}), the high transparency and tunability of the Fermi level in graphene, MoS\textsubscript{2}-graphene heterostructures have shown good promise for flexible and transparent electronic and optoelectronic applications such as ultrathin vertical transistors,\textsuperscript{[11,12]} field-effect transistors,\textsuperscript{[13,14]} photodetectors,\textsuperscript{[15]} energy converters,\textsuperscript{[16]} storage devices,\textsuperscript{[17]} ultrafast saturable absorbers,\textsuperscript{[18]} and so on.\textsuperscript{[19]} For all these applications, it is important to master the mechanisms involved in the generation of carriers and their dynamics in such heterostructures.

The interaction between graphene and MoS\textsubscript{2} monolayer has been studied by different means. Theoretical calculations using density functional theory have suggested that the linear bands at the Dirac points of graphene are slightly changed in the graphene-MoS\textsubscript{2} heterostructure.\textsuperscript{[20–24]} In the presence of a single graphene layer, the C-exciton binding energy of MoS\textsubscript{2} was reported to be lowered by \(\sim 0.45\) eV.\textsuperscript{[25]} Transfer of photocarriers from MoS\textsubscript{2} to graphene has been reported in the MoS\textsubscript{2}-graphene heterostructure through transient absorption spectroscopy by exciting the excitonic states of MoS\textsubscript{2}.\textsuperscript{[26]} Photoluminescence along with Raman spectroscopy have also been used to demonstrate the saturation of charge transfer from MoSe\textsubscript{2} to graphene in their heterostructure.\textsuperscript{[13]} In addition to photoluminescence quenching, the life time of the excitons was found to reduce to just a picosecond.\textsuperscript{[3]} However, most of the above studies were performed at optical photon energies either above or near the bandgap of MoS\textsubscript{2} and other TMD monolayers. Besides, the techniques involved in these experiments do not directly measure the generated carriers and their dynamics within such heterostructures. In addition, explorations on either TMD “encapsulated” graphene or graphene “encapsulated” TMD monolayer can rarely be found in the literature. Such heterostructures are of particular interest, since a MoS\textsubscript{2} monolayer sandwiched between two graphene layers can exhibit dramatic improvement in its stability against defects formation by powerful incident radiation.\textsuperscript{[27]} Recently, a theoretical study on MoS\textsubscript{2}-graphene-WX\textsubscript{2} (X = S and Se) heterostructure showed not only a much higher thermal stability but also an enhanced carrier concentration and electronic transport in this unique tri-layer heterostructure.\textsuperscript{[22]} Similarly, control on the flow of charges, driven by an external field applied perpendicular to graphene-MoS\textsubscript{2}-graphene and graphene-MoSe\textsubscript{2}-graphene heterostructures, was also studied theoretically\textsuperscript{[23,28]} to explain the extraordinary performance of such heterostructures for high speed and high on-off switching transistor.\textsuperscript{[29]}

Here, we perform optical pump-THz probe experiments to unravel an extraordinary enhancement in the transient THz response from MoS\textsubscript{2} monolayer sandwiched between two graphene layers at optical photon energies in the deep sub-bandgap region of the MoS\textsubscript{2} monolayer. The photoduced dynamic THz conductivity that can be inferred from the transient transmission or reflectivity of the graphene-MoS\textsubscript{2}-graphene heterostructure, is enhanced significantly and it lasts for a few tens of ps. The graphene-like and MoS\textsubscript{2}-like contributions can be distinguished easily in the ultrafast response of the heterostructure. We also find that the MoS\textsubscript{2}-like contribution in the transient THz conductivity of the heterostructure systematically reduces with the decreasing optical excitation photon energy and it becomes negligible at \(\sim 0.45\) eV. On the other hand, due to negligible THz conductivity of MoS\textsubscript{2} monolayer, the stationary THz conductivity of the heterostructure resembles that of graphene in the entire experimental THz bandwidth of \(\sim 0.1-5.0\) THz.

2 | EXPERIMENTAL RESULTS

2.1 | THz conductivity measurements

High-quality CVD grown graphene (Gr), MoS\textsubscript{2} single layer (MoS\textsubscript{2},SL), and graphene/MoS\textsubscript{2},SL/graphene (GrMoS\textsubscript{2},Gr) were transferred on Quartz substrates. The broad-band static THz sheet conductivity, \(\sigma\) in mS (milli-Siemens) as determined from THz time-domain spectroscopy is presented in Figure 1 for these three samples. The procedure is detailed in the supporting information (S4). The thick continuous curves, obtained by polynomial fitting of the data,
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**FIGURE 1** A, Real part, Re(σ) and B, imaginary part, Im(σ) of the broadband static THz sheet conductivity of graphene (Gr), MoS$_2$ monolayer, and GrMoS$_2$Gr heterostructure. Thick continuous curves represent the mean behavior obtained by using polynomial fitting.

The real part (Re(σ)) and imaginary part (Im(σ)) of the conductivity represent the mean behavior of the spectral conductivity in each case. Re(σ) is the real part and Im(σ) is the imaginary part of the conductivity. Without a surprise, the THz conductivity of the MoS$_2$ monolayer is almost zero within our experimental uncertainty. This confirms that there are no free carriers present in this high-quality semiconductor MoS$_2$ sample. For the THz conductivity of the graphene, the results show positive values of the real and imaginary parts in the entire frequency range of ∼0.3-5 THz. Likewise, for the GrMoS$_2$Gr, the Re(σ) is almost two times higher than that of graphene, while it continuously decreases with the increasing frequency. For this sample, Im(σ) is negative from ∼0.3 to 1.7 THz, while it is positive and increasing with the frequency beyond 1.6 THz. The interlayer van der Walls (vdW) interaction in the GrMoS$_2$Gr could be a reason for a smaller value of the Im(σ) as compared to that of graphene and the crossover from small negative values to increasing positive values at a frequency above 1.7 THz.

**FIGURE 2** Time-resolved THz reflectivity change, ΔR measured in the lock-in units for A, graphene (Gr), and B, MoS$_2$ monolayer upon femtosecond optical excitation at 3.1 and 1.55 eV using pump-fluence of ∼20 µJ cm$^{-2}$.

For graphene and MoS$_2$ monolayer, are presented in Figure 2A,B, respectively, for a nominal optical-fluence of ∼20 µJ cm$^{-2}$. The underlying quartz substrate is completely inactive at both the excitation wavelengths and pump-fluences up to much > 500 µJ cm$^{-2}$. For the graphene, a characteristic negative ΔR response followed by its nearly complete recovery within ∼8 ps is observed at both the 1.55 and 3.1 eV excitations. Detailed experiments (see Figure S6 in the supporting information) have revealed that the ΔR THz response of graphene has mono-exponential recovery with an average time-constant of ∼2.8 ps. Fluence-dependent experiments show that the time-constant increases from ∼1.5 to ∼3.5 ps by increasing the fluence from very low values to as high as 300 µJ cm$^{-2}$. At any given fluence, the dynamics for 3.1 eV is found to be faster than for 1.55 eV, while the saturation of the THz response takes place at a similar fluence of ∼60 µJ cm$^{-2}$. The relaxation of energetic carriers in graphene is known to occur via production of additional electron–hole pairs by carrier–carrier scattering processes rather than heat production by electron-phonon scattering.[30]

For the MoS$_2$SL, due to absence of photocarrier generation, there is no photoinduced dynamic THz response at 1.55 eV. Only 3.1 eV excitation produces characteristic positive ΔR whose complete recovery seems to take place via two relaxation channels, a fast one at shorter times and another slower one at the longer times. Both the fast relaxation time-constant (mean value $\tau_1$ ∼ 1 ps) and slow relaxation time-constant (mean value $\tau_2$ ∼12 ps) show a very weak fluence-dependence in the experimental range of 0-250 µJ cm$^{-2}$ (see Figure S7 in the supporting information). The fast relaxation component shows saturation at fluences above ∼150 µJ cm$^{-2}$ while the slow component gets saturated at ∼50 µJ cm$^{-2}$. It may be pointed out that in comparison to our single fast relaxation component ($\tau_1$ ∼1 ps), two time-constants with values ∼350 fs and ∼1 ps were reported in the literature for MoS$_2$,[31,32] where it was shown that surface trapping is the dominant mechanism of...
ultrafast THz conductivity quenching.\cite{31} The slower time constant $\tau_2 \sim 12$ ps in the present case is found to be about twice faster than that was attributed to trion relaxation earlier.\cite{32} Nevertheless, the dynamics in MoS$_2$ monolayer is found to be similar to that in the MoSe$_2$ monolayer at 3.1 eV photoexcitation.\cite{2}

2.3 Optical pump-induced THz response of GrMoS$_2$Gr

The evolution of the GrMoS$_2$Gr reflectivity in the THz range upon excitation at 3.1 eV, that is, above the bandgap of MoS$_2$, for the pump-fluence of $\sim 14 \mu$J cm$^{-2}$ is displayed in Figure 3A. Upon excitation, the transient response first decreases slightly and then increases rapidly to large values, following which, a slow decrease occurs. An enhancement in the ultrafast THz response at 3.1 eV as compared to that at 1.55 eV, is expected here, because photocarriers are generated in both the MoS$_2$ and graphene layers for the prior. However, the signal cannot naively be accounted for by adding the contributions of graphene and MoS$_2$, displayed in Figure 3A. Indeed, it has been shown that, upon excitation above its bandgap, the electrons photogenerated in both the MoS$_2$ and graphene layers are rapidly transferred towards graphene. Fluence-dependent experiments at 3.1 eV reveal that at the zero delay, there appears a contribution from a THz pulse-like response (Figure S9 in the supplementary information) that is superimposed with the main THz transient signal of GrMoS$_2$Gr. This additional contribution may arise due to THz emission from the optical pump-induced charge separation at the interface which has been seen earlier in MoS$_2$/MoSe$_2$ heterostructure.\cite{1}

Typical variations and kinetics of the optical pump-induced THz reflectivity, $\Delta R$ and transmission, $\Delta T$ changes for GrMoS$_2$Gr are presented in Figure 3B,C, respectively, at the excitation photon energy of 1.55 eV (below the MoS$_2$SL bandgap) and fixed fluence of $\sim 20 \mu$J cm$^{-2}$. It is obvious that, except the polarity reversal, the THz response of the heterostructure through both the $\Delta R$ and $\Delta T$, is exactly the same. Therefore, analysis of any of the two is sufficient for extracting the relaxation kinetics. The characteristic THz responses of both, the graphene and the MoS$_2$ constituents of this tri-layer stack, are observed here and marked by red (Gr-like at short times) and blue (MoS$_2$-like at longer times) in the figure. Compared to the data in Figure 2 for the MoS$_2$ monolayer, a surprising enhancement in the MoS$_2$-like contribution in the transient THz reflectivity of the photoexcited GrMoS$_2$Gr heterostructure, is recorded. This is true for both the excitation photon energies here. Besides, since at 1.55 eV, no photocarriers are generated in MoS$_2$SL, a MoS$_2$-like contribution is not expected in the THz response of GrMoS$_2$Gr in the first place.

2.4 Kinetics of the THz response of GrMoS$_2$Gr

Figure 4A displays the temporal evolution of the THz reflectivity, $\Delta R(t)$ of the GrMoS$_2$Gr sample upon excitation at 1.55 eV taken at various fluences. Similar results were obtained in transmission mode (see supporting information Figure S8). The data are well fitted using bi-exponential relaxation components in the convolution. As we already mentioned, the amplitude, $A$ and the relaxation constant, $\tau$ of these components will be considered
FIGURE 4  Femtosecond optical pulse-induced modifications in the THz reflectivity, ΔR of GrMoS\textsubscript{2}Gr heterostructure in the lock-in units. A, Evolution of ΔR dynamics at various pump-fluences following optical excitation at 1.55 eV. The Gr-like and MoS\textsubscript{2}-like components are marked. The fit of the data and corresponding relaxation components (A\textsubscript{1}, τ\textsubscript{1}, A\textsubscript{2}, τ\textsubscript{2}) are also indicated. Pump-fluence dependent evolution of the amplitudes and time-constants of the Gr-like (A\textsubscript{1}, τ\textsubscript{1}) and MoS\textsubscript{2}-like (A\textsubscript{2}, τ\textsubscript{2}) components for optical excitation at B, 1.55 eV and C, 3.1 eV.

as Gr-like (-A\textsubscript{1}, τ\textsubscript{1}) and MoS\textsubscript{2}-like (A\textsubscript{2}, τ\textsubscript{2}), respectively. The amplitude A\textsubscript{1} of the Gr-like component is negative and it relaxes with a short time constant (1.6 ps < τ\textsubscript{1} < 1.9 ps). The amplitude A\textsubscript{2} of the MoS\textsubscript{2}-like component is positive and it relaxes with a longer time constant (13 ps < τ\textsubscript{2} < 16 ps). The fluence-dependence of these parameters is given in Figure 4B for the negative Gr-like and positive MoS\textsubscript{2}-like relaxation components. Like in graphene alone, the Gr-like component in GrMoS\textsubscript{2}Gr, quickly saturates above a fluence of ~60 µJ cm\textsuperscript{-2} and the time-constant, τ\textsubscript{1} also shows an increase with the increasing fluence to attain a constant value at very high fluences. The latter is slightly smaller (mean value ~1.8 ps) than the mean value obtained for graphene alone (~2.5 ps). The MoS\textsubscript{2}-like component is rather interesting. The amplitude A\textsubscript{2} shows saturation at fluences above ~150 µJ cm\textsuperscript{-2}, exactly like the behavior of the MoS\textsubscript{2} monolayer alone as discussed above for 3.1 eV excitation (also Figure S7 of the supplementary information). The corresponding time-constant, τ\textsubscript{2}, increases from ~13 ps at the low fluences (same value as in MoS\textsubscript{2} alone, Figure S7) to ~16 ps at higher fluences in Figure 4B. Since the contribution (area under the curve) of the MoS\textsubscript{2}-like component in the THz response of the GrMoS\textsubscript{2}Gr, is much larger, a higher value of τ\textsubscript{2} means that the overall THz response from GrMoS\textsubscript{2}Gr has got enhanced as compared to that of MoS\textsubscript{2} monolayer at 3.1 eV.

The transient THz reflectivity data for the GrMoS\textsubscript{2}Gr at 3.1 eV and a fixed fluence was shown in Figure 3A.
From the raw traces taken at various fluences (Figure S9 in the supplementary information), the Gr-like contribution, just near the zero-delay, appears less prominent due to an overlapping THz pulse-like feature. However, the data beyond time $\sim 0.8$ ps can be reproduced well by using a bi-exponential function in the convolution, exactly like what was done for the response at 1.55 eV. The fluence-dependence of the amplitudes and the time-constants of the negative ($A_1, \tau_1$) Gr-like and positive ($A_2, \tau_2$) MoS$_2$-like components in $\Delta R$ response at 3.1 eV, is given in Figure 4C. As the amplitudes of the two contributions saturate above $\sim 70$ $\mu$J cm$^{-2}$, the time-constant, $\tau_1$ of Gr-like component remains almost steady at $\sim 1$ ps, while, the time-constant, $\tau_2$ of the MoS$_2$-like component slightly decreases from $\sim 14$ to $\sim 12$ ps. Importantly, at low fluences for both the pump photon energies, 1.55 and 3.1 eV, the two time-constants are similar to each other suggesting the same origin. Hence, in absence of any direct photoexcitation of the carriers in the MoS$_2$ layer of the GrMoS$_2$Gr at 1.55 eV, our observations indicate that a significant fraction of the photocarriers generated in the graphene layers migrate towards the MoS$_2$ layer so as to enhance the THz response from GrMoS$_2$Gr. The carriers’ transfer to MoS$_2$ is likely to take place during the excitation pulse itself. Later, these carriers will have to return back to graphene for the recombination to take place, thereby slowing down the overall carrier relaxation process in GrMoS$_2$Gr.

2.5 Deep sub-bandgap optically-induced THz response of GrMoS$_2$Gr

To strengthen the above observation regarding the THz response of GrMoS$_2$Gr excited below the MoS$_2$-bandgap and get more details before discussing the possible mechanism for this effect, we present here additional experimental results obtained at excitation photon energies much smaller than 1.55 eV. Transient THz transmission response, $\Delta T$ of the GrMoS$_2$Gr with excitation photon energies of $\sim 1.1$ eV (1140 nm), 0.92 eV (1240 nm) and 0.46 eV (2700 nm), that is, going deeper into the sub-bandgap region of the MoS$_2$SL are presented in Figure 5 taken at a pump fluence of $\sim 50$ $\mu$J cm$^{-2}$. For a one-to-one comparison, the corresponding results for graphene alone, are also presented in Figure 5.

Clearly, the characteristic positive $\Delta T$ response of graphene remains intact in GrMoS$_2$Gr at all the excitation wavelengths in Figure 5. However, the MoS$_2$-like contribution keeps reducing with the lowering of the excitation photon energy. At excitation photon energy of 0.46 eV, the MoS$_2$-like contribution becomes negligibly small, in comparison, and the overall THz response of GrMoS$_2$Gr quite resembles that of the graphene. It is evident that the MoS$_2$-like contribution will vanish completely, if the excitation photon energy is reduced further down. We may also note from Figure 5 that the THz response of graphene at 0.46 eV (2700 nm) possesses a second slow relaxation component with its time-constant of $\sim 10$ ps.

3 DISCUSSION

A possible mechanism accounting for our experimental observations is provided in Figure 6 through charge creation and relaxation in the real and momentum space representations of the GrMoS$_2$Gr. The upper panel in Figure 6 displays the physical stack which undergoes optical pulse excitation and THz pulse probing. The
free electrons generation in graphene and their back and forth movement between Graphene and MoS$_2$ is indicated. Time-dependent THz absorption by these free carriers is what is captured through the THz probing with controllable delay after the pump pulse excitation. The electronic energy structures of graphene and MoS$_2$ layer along with their density of states (DOS)\textsuperscript{[33]} are drawn in the lower panel. At room temperature, even without any intentional doping, there are a finite number of free carriers in graphene. This could be the reason for the occurrence of the slow relaxation component in the transient THz response of graphene due to optical excitation at 0.46 eV (2700 nm) as discussed in the previous section. In the GrMoS$_2$Gr, the layers are physically separated by about 0.5 nm and electrostatically bonded through vdW interaction. As soon as the interface between graphene and MoS$_2$ layer is formed, the bottom of the conduction band of MoS$_2$ equilibrates at an energy $\sim$0.5 eV above the K-point of graphene\textsuperscript{[21,23,24]} as indicated in the Figure 6.

Consider the optical excitation at 1.08 eV (1140 nm) and both the excitation and the probe beams travelling towards right (top panel in Figure 6), the first graphene layer absorbs about 3% of the excitation light.\textsuperscript{[34]} Since the MoS$_2$ layer is mostly transparent at this excitation photon energy, the second graphene layer receives lesser amount of light than the first graphene layer. Hence, less photocarriers are generated in the second graphene layer. This difference results into a photocarrier concentration gradient across the heterostructure. Of course, the strength of the photocarrier concentration gradient would depend on the excitation photon energy and the fluence. Accordingly, an electric field develops across the GrMoS$_2$Gr heterostructure. It lifts the degeneracy around the K-points and gives rise to a small direct bandgap.\textsuperscript{[23]}

Energetic electrons are generated by the excitation pulse (photon energy $> 0.5$ eV) in the graphene at sufficiently high energy states. Due to the photocarrier concentration gradient, while relaxing, these energetic electrons are dragged towards MoS$_2$ layer during the excitation pulse itself. Taking, the out of plane component of the electronic velocity to be $10^5$ m s$^{-1}$, interlayer separation between graphene and MoS$_2$ to be 0.6 nm, the photocarriers would take a time of $\sim$6 fs, that is, mainly during the excitation pulse duration itself, to move across the Gr/MoS$_2$ interface. Once in the MoS$_2$ and relaxed to its conduction band minimum, the energetic electrons have to go...
back towards the graphene layer to be recombined with the corresponding photogenerated holes. Due to the smaller DOS in graphene, the photoelectrons transferred to MoS$_2$ layer would keep piling up there until states are available for their return at lower energies in graphene. The later occurs within the time-scale of electron-hole recombination in graphene. Therefore, the additional pathway in the carrier relaxation trajectories results into slowing down of the overall relaxation dynamics in the GrMoS$_2$Gr through the occurrence of MoS$_2$-like relaxation component (A$_{2,r_2}$) in Figures 3–5. Clearly, at excitation photon energies below 0.5 eV (energy difference between the bottom of the conduction band of MoS$_2$ and the K-point of graphene), the energetic photoelectrons in the graphene are not created in states sufficiently high in energy so that they can be dragged towards MoS$_2$ due to concentration gradient field. Therefore, for excitation photon energies close and below 0.5 eV (2700 nm), the relaxation of all the photocarriers occurs within the graphene layers only resulting into a transient THz response of the GrMoS$_2$Gr resembling that of the graphene sample.

Note that for photoexcitation with > 0.5 eV photons, the energetic photocarriers move, only partially, towards the MoS$_2$ layer, and a fraction of them still relaxes within the graphene layer. The ratio between the magnitudes of the Gr- and MoS$_2$-like components in the THz response of GrMoS$_2$Gr provides directly the fraction of the photocarriers migrating from the graphene to the MoS$_2$ layer of the heterostructure due to photocarrier concentration gradient in the GrMoS$_2$Gr heterostructure. From Figures 3 and 4, we find that at 1.55 eV excitation, about 35% of the photoexcited carriers relax within the graphene layer while about two third of the total, instantly migrate to the MoS$_2$ layer. At optical excitation of ~0.46 eV, the fraction of migrating photocarriers abruptly decreases below 10% (Figure 5).

4 | CONCLUSIONS

To summarize, we have presented optically induced transient THz reflectivity and transmission changes and their recovery in high quality graphene, MoS$_2$ single layer and graphene-MoS$_2$-graphene heterostructure. From the GrMoS$_2$Gr heterostructure, an enhanced transient THz response is produced even for excitation photon energies deep in the band gap region of the MoS$_2$ single layer. The excitation photon energy dependent measurements clearly suggest that, only below 0.45 eV, the MoS$_2$-like contribution vanishes from the ultrafast THz response of the heterostructure. This is a clear case of an all-optical control of THz conductivity in MoS$_2$ monolayer even at those optical frequencies for which MoS$_2$ layer is completely transparent, by encapsulating it with graphene from either sides. This effect may have many implications in fast electronic devices at GHz to THz frequencies, such as in FETs, where, without creating electrons within the MoS$_2$ layer by the application of an electrical bias, the external light can help in modulating the conductivity of the MoS$_2$ layer through top and bottom graphene layers. This phenomenon seems to be quite general and should occur in heterostructures for a large variety of TMD layers and other semiconductor layers sandwiched in between two graphene or metallic layers, thereby, opening up new avenues for generation of interesting material heterostructures to enhance certain device performances in the optoelectronics and THz photonics.

5 | MATERIALS AND EXPERIMENTS

5.1 | Sample preparation

Large area (~15 mm × 15 mm) MoS$_2$ monolayer was grown on SiO$_2$/Si substrate by two-zone furnace atmospheric pressure CVD. Ammonium heptamolybdate ((NH$_4$)$_6$Mo$_7$O$_{24}$, Sigma-Aldrich, 431346) and sodium hydroxide (NaOH, Sigma-Aldrich, S8045) were dissolved in deionized water as a Mo precursor and promoter, respectively. The precursor solution was coated onto the substrate by spin-coating at 3000 r.p.m. for 1 minute. The details are described in our previous work.[35] Then, the precursor-coated substrate and 0.2 g of sulfur (Sigma, 344621) were separately introduced in to a two-zone furnace. The sulfur zone was heated up to 210°C at a rate of 50 °C min$^{-1}$, while the substrate zone was set to 800°C with a ramping rate of 80°C min$^{-1}$. For the entire process, N$_2$ gas (500 sccm) was injected as a carrier gas. A Cu foil (Nilaco, CU-113173, 99.9% with 100 µm thickness) was annealed in H$_2$ and Ar atmosphere at 1050°C for 2 hours to increase its crystallinity and remove any contamination. 5 sccm of diluted CH$_4$ gas (0.1% diluted in Ar) was then injected into the CVD chamber for 15 minutes to synthesize graphene on the Cu foil. After the growth, the CVD chamber was naturally cooled to room temperature. For transferring the MoS$_2$ and graphene to quartz substrates, poly(methyl methacrylate) (PMMA C4, MicroChem) assisted wet-etching method was adopted. PMMA was coated onto the sample (MoS$_2$ on the SiO$_2$/Si, and Gr on Cu foil) following which the PMMA-supported samples were immersed into respective etchants (diluted hydrofluoric acid for MoS$_2$ and Cu-etchant for Gr) to detach the samples from the as-grown substrates. The PMMA-supported samples were transferred to quartz substrates. Finally, PMMA was removed by dipping the PMMA-supported samples on quartz substrates into acetone for 5 min. A tri-layer graphene-MoS$_2$-graphene...
(GrMoS2Gr) heterostructure was fabricated for our current studies. Initially a monolayer MoS2 was transferred onto the graphene sample. Prior to the stacking of MoS2 and graphene layers, the graphene sample was annealed at 300°C in a vacuum chamber at a pressure of \( \sim 5 \times 10^{-5} \) Torr for 2 hours to avoid any contamination between the interface. The same procedure was followed for stacking the top graphene layer on the MoS2/graphene sample supported on quartz substrate. Thus obtained large area layers are not continuous entirely, but cover about 80% area on the surface on the substrate.\(^2\) High quality and crystallinity of our layered samples and their vertical stacks were confirmed by various characterization tools.\(^35\) Characterization by Raman and optical absorption spectroscopy are given in the supporting information.

### 5.2 THz time-domain spectroscopy for broadband static THz conductivity

The schematic of the experimental setup is shown in Figure S3. THz pulses of sub-200 fs duration are generated in dual color air plasma and detected in a \(<110>\) cut GaP crystal by electro-optic sampling technique in the usual manner.\(^2\) For driving the THz setup, femtosecond pulses with time-duration of \( \sim 50 \text{ fs} \) are taken from a Ti:Sapphire based regenerative amplifier operating at 1 kHz repetition rate and central wavelength (photon energy) 800 nm (\( \sim 1.55 \text{ eV} \)). A strong part (\( \sim 1 \text{ W} \) average power) of the laser output is used for THz generation. A biconvex lens of focal length 250 mm is used to focus the fundamental and second harmonic from a beta barium borate (BBO crystal, thickness 100 \( \mu \text{m} \)) into the air. Highly resistive silicon wafer was used to block the unused optical beam and let through the THz beam in the main experimental setup until the GaP crystal. A set of four off-axis parabolic mirrors with focal length of 150 mm were used to route the THz beam through a sample, placed at the center between the inner two parabolic mirrors and finally to the 200 \( \mu \text{m} \) thick GaP crystal for detection of the THz pulses. A synchronous gating optical beam (average power \( \sim 5 \text{ mW} \)) taken from the laser and routed through a linear time-delay stage (controllable time-delay) is made to collinearly fall onto the GaP crystal. The gating pulse samples the THz beam in the GaP crystal through an imbalance in intensity of its two orthogonal polarization components detected in a lock-in amplifier with the help of a quarter wave plate, a Wollaston prism and two photodiodes. The complete THz setup was enclosed in a box under continuous purging of dry air to minimize THz losses in between from the generation point in the air-plasma to the detection point at the GaP crystal.

### 5.3 Optical pump-THz probe experiments

The same setup as described above and shown in Figure S3, was used for optical pump-THz probe time-resolved spectroscopy by adding a pump pulse travelling through another linear translational stage. For optical excitation of the materials studied in our paper, either 800 nm pulses taken directly from the laser or its second harmonic at wavelength (energy) 400 nm (\( \sim 3.10 \text{ eV} \)) were used. For optical excitation at wavelengths other than the above, we have used an optical parametric amplifier providing \( \sim 100 \text{ fs} \) pulses in a variable wavelength range. The time-delay between the optical pump and a fixed position corresponding to the maximum of the THz pulse, either reflected from or transmitted through the sample under study, was varied to obtain the time-resolved optically induced THz response from the samples in both the THz transmission and reflection modes. In all of the experimental results discussed in our paper, the optical excitation beam diameter on the sample was \( \sim 3 \text{ mm} \) while the THz probe beam size was slightly larger. The pump-fluence was varied using continuously variable neutral density filters.

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### DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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