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Direct Determination of Band Gap Renormalization in Photo-Excited Monolayer MoS₂

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A key feature of monolayer semiconductors, such as transition-metal dichalcogenides, is the poorly screened Coulomb potential, which leads to large exciton binding energy (E_b) and strong renormalization of the quasiparticle bandgap (E_g) by carriers. The latter has been difficult to determine due to cancellation in changes of E_b and E_g , resulting in little change in optical transition energy at different carrier densities. Here we quantify bandgap renormalization in macroscopic single crystal MoS₂ monolayers on SiO₂ using time and angle resolved photoemission spectroscopy (TR-ARPES). At excitation density above the Mott threshold, E_g decreases by as much as 360 meV. We compare the carrier density dependent E_g with previous theoretical calculations and show the necessity of knowing both doping and excitation densities in quantifying the bandgap.

Atomically thin transition-metal dichalcogenide (TMDC) monolayers and heterojunctions are being broadly explored as model systems for a wide range of electronic, optoelectronic, and quantum processes. The commonly studied TMDC monolayers possess direct bandgaps in the visible to near-IR region [1–3]. Because of the strong many-body Coulomb interactions in monolayer TMDCs, both exciton binding energy (E_b) and bandgap renormalization energy are large [3]. The former lowers the optical transition energy by hundreds meV from E_g , while the latter decreases E_g by similar amounts in the presence of charge carriers or excitons. The bandgap renormalization energy (ΔE_g) and decrease in exciton binding energy (ΔE_b) tend to be of similar magnitudes but counteract each other, leading to comparatively modest changes in optical transition energies [4,5]. Since the quasiparticle bandgap E_g is the most fundamental quantity and is predicted to be exceptionally sensitive to carrier or exciton densities [4,6,7], there

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is clearly a need to determine bandgap renormalization and its dependence on carrier/exciton densities.

Past attempts at measuring ΔE_g required analysis of subtle or small features in optical spectra [8–11]. Examples include estimating the gain threshold in transient reflectance spectra from photo-excited TMDC monolayer and bilayer above the Mott density [8], extrapolating E_g from the experimental Rydberg exciton series in conjunction with theoretical models [9,10], and identifying features attributed to bandgap transition on the broad fluorescence excitation spectra of gate-doped monolayer MoS₂ [11]. The ideal technique to determine quasiparticle energies is angle resolved photoelectron spectroscopy (ARPES), which directly maps band energies with momentum resolution. ARPES typically probes the valence bands and populating the conduction band would require either a) heavy chemical doping via K or H atom deposition [12–15] or b) photo-doping via above-gap optical excitation in time-resolved (TR) ARPES [16–18]. The chemical doping approach may lead to undesirable changes to the dielectric environment and lattice structure of TMDC monolayers [12–15,19]. TR-ARPES of transiently excited TMDCs can in principle probe both the quasiparticle bandgap and the dynamics of bandgap renormalization. However, past attempts of TR-ARPES on TMDC monolayers have used CVD grown polycrystalline monolayers on metal or semimetal substrates [16–18]. These conductive substrates drastically modify both the energetics and dynamics of excited states in TMDC monolayers [16–18]. Others TR-ARPES studies have used bulk TMDC crystals, instead of monolayers [20–23]. To overcome these limitations, here we prepare single crystal MoS₂ monolayers with macroscopic sizes (mm-cm) on dielectric substrates (285 nm thick SiO₂ on n-doped Si). We use TR-ARPES to monitor the time evolution of the valence band maximum (VBM) and conduction band minimum (CBM) following above-gap optical excitation. We directly quantify bandgap energies with excitation density across the Mott threshold and compare experimental results with recent theoretical calculations.

In our femtosecond TR-ARPES experiment (Fig. 1a and Fig. S3), the visible excitation pulse ($h\nu_1 = 2.2$ eV, 40 fs pulse width, s-polarized) is obtained from a home-built non-collinear optical parametric amplifier (NOPA), pumped by a Ti:Sapphire laser (Coherent Legend, 10 W, 10 kHz, 800 nm, 35 fs). Part of the Ti:Sapphire laser output is frequency-doubled for high harmonic generation (HHG) in Kr gas (KM Labs, XUUS) to produce EUV probe pulses ($h\nu_2 = 22$ eV,

pulse duration <100 fs, p-polarized) [24]. The EUV pulse ionizes electrons from both valence and conduction bands for detection by a hemispherical analyzer with angular resolution. Note that the use of EUV, instead UV probe, is necessary to access the high momentum K point at the Brillouin zone corner. The plane of light incidence and analyzer slit is parallel to the Γ -K direction, with the sample azimuthal geometry fixed for the collection of photoemission from the K valley.

Fig. 1b shows optical image of a single crystal MoS₂ monolayer (blue color) on the SiO₂/Si substrate. Our improvement to the gold - assisted exfoliation technique [25] has yielded macroscopic single crystal samples (lateral dimension in the mm-cm range). See Fig. S1 and S2 in Supporting Materials for characterization with atomic force microscope (AFM) for sample cleanness and second harmonic generation (SHG) for alignment of crystal axis. The complex dielectric function (Fig. 1c) obtained from white light reflection shows the characteristic A and B excitons and photoluminescence spectrum (Fig. 1d) shows emission from the A exciton ($E_A = 1.865 \pm 0.05$ eV). These optical spectra are consistent with those of previous reports [1,26].

In a TR-ARPES experiment, the visible pump pulse induces a direct transition in the K and K' valleys. Following a controlled time delay (Δt), the EUV probe pulse ionizes the electrons in the valence and conduction bands. Fig. 2 shows momentum-resolved ARPES from monolayer MoS₂ around the K valley without (a) and with (b) visible pump ($\Delta t = 0$). The two spectra are integrated over the 1.1 - 1.4 \AA^{-1} parallel

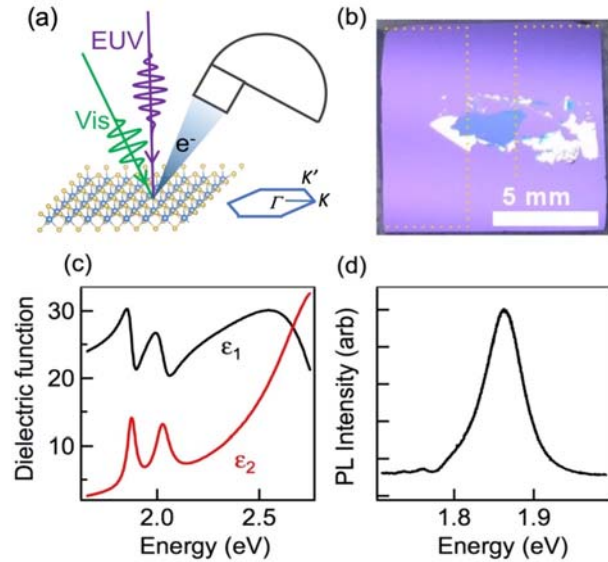


Figure 1. The macroscopic single crystal MoS₂ monolayer sample and characterization. (a) Schematics of TR-ARPES experiment, combining the femtosecond visible pump (green) and EUV probe (purple). The photoelectrons are collected by the hemispherical analyzer at a specific angle θ from the surface normal, corresponding to emission from a K valley. (b) Image of the single crystal MoS₂ monolayer. We deposit Au films in the dashed areas for electrical contact and grounding. (c) Complex dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$) of the monolayer MoS₂ determined from reflection spectroscopy and (d) Photoluminescence of the MoS₂ monolayer at room temperature.

momentum window to yield the corresponding energy distribution curves (EDCs), shown in Fig. 2c. The MoS₂ monolayer sample is n-doped, with the Fermi energy close to the CBM. As a result, weak photoelectron signal from intrinsic population in the conduction band near CBM is observed in Fig. 2a. This signal is used to determine a doping density of $n_0 = (4.9 \pm 1.0) \times 10^{12} \text{ cm}^{-2}$ (see Supporting Information, Fig. S6). Mechanically exfoliated MoS₂ monolayers are commonly known to be of n-type at similar doping levels [27–29].

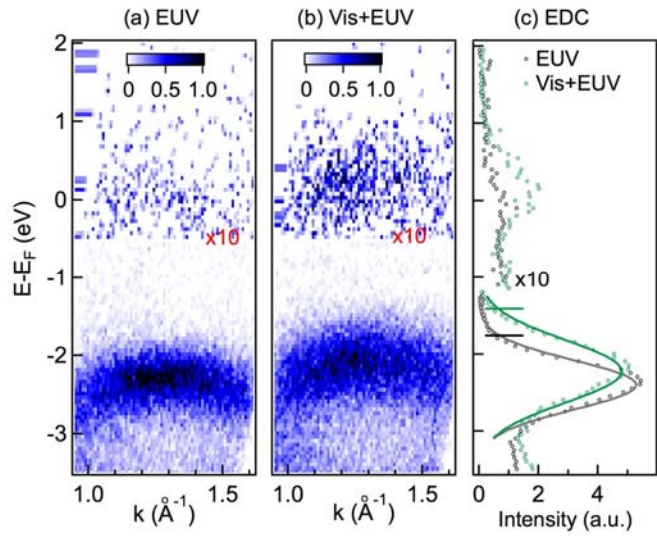


Figure 2. TR-ARPES from monolayer MoS₂. (a) (b) EUV ARPES of single crystal MoS₂ monolayer without and with the visible pump excitation ($\Delta t=0$). The APRES spectra is collected at K valley along Γ to K direction. The visible pump is at a photon energy of 2.2 eV. (c) Corresponding electron energy distribution curves (EDC). The solid lines are Gaussian functional fits. The horizontal marks represent the edges of the EDCs, corresponding to $E_0+2\sigma$. The spin orbit splitting at K valley is not resolved under the current energy resolution. The excitation density from the pump pulse is $n_{e,h} = (2.3\pm 0.5) \times 10^{13} \text{ cm}^{-2}$. The conduction band signal is magnified by 10x for clarity.

With the addition of the pump pulse, photo-excitation across the bandgap creates exciton

and/or electron/hole carrier density, $n_{e/h}$, on top of n_0 . In the experiment, we vary the excitation

densities $n_{e/h}$ in the range of 3.8×10^{12} to $2.3 \times 10^{13} \text{ cm}^{-2}$. For reference, the Mott density for the

transition from exciton gas to electron-hole plasma is $n_{\text{Mott}} \sim 4.3 \times 10^{12} \text{ cm}^{-2}$, estimated from the

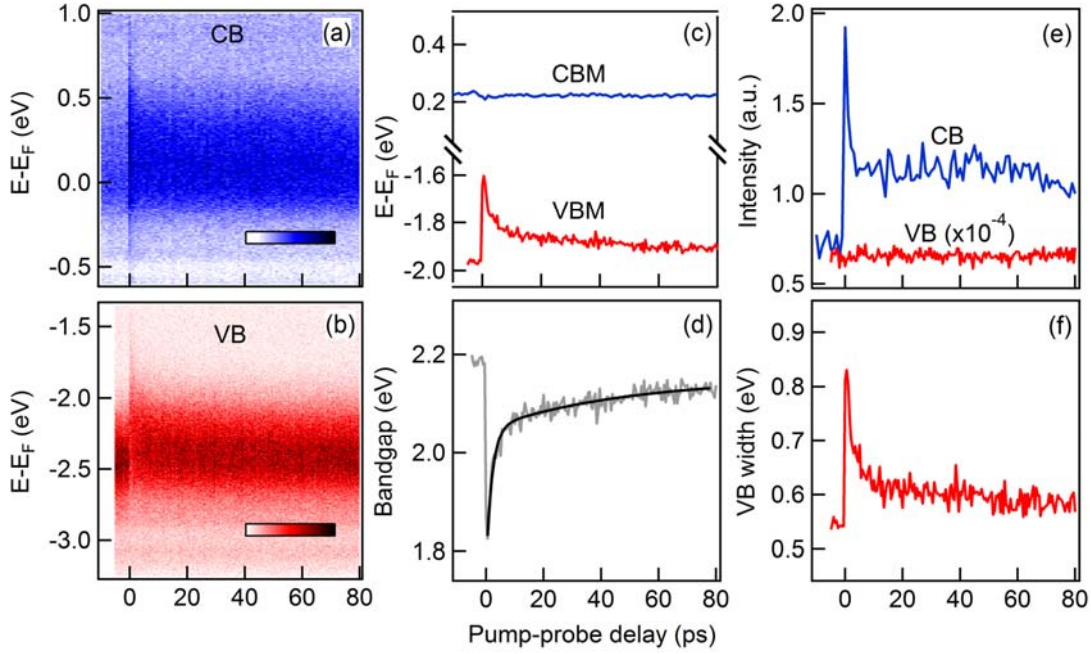


Figure 3. Dynamics of band renormalization. All panels are shown as a function of pump-probe delay: (a) and (b) are 2D pseudo-color (intensity) plots of EDC spectra collected individually for conduction band and valence band, respectively; (c) CBM and VBM positions extracted from EDC scans shown in panel a and b; (d) band gap E_g (grey) with bi-exponential fit (black solid line); (e) conduction (blue) and valence (red) band photoelectron intensities; and (f) full width at half maximum of valence band. To obtain the EDCs in (a) and (b), the photoelectron signal is integrated from 1.1 \AA^{-1} to 1.4 \AA^{-1} . The CBM is fixed at the time-averaged value of 0.223 eV in the calculation of the bandgap in (d). The initial excitation density is $n_{e/h} = 1.3 \times 10^{13} \text{ cm}^{-2}$ and sample is at 295 K . The color scales in (a) and (b) are normalized (0-1).

2D scaling relationship [7] of $a_0 n_{Mott}^{1/2} \approx 0.25$ with a_0 (exciton Bohr radius) = 1.2 nm for undoped monolayer MoS_2 on SiO_2 [30]. The excitation density probed here is mostly in the e-h plasma region. Fig. 2b shows ARPES spectra at excitation density of $n_{e/h} = (2.3 \pm 0.5) \times 10^{13} \text{ cm}^{-2}$ at $\Delta t = 0$. Compared to Fig. 2a, we observe three major changes: 1) an increase in conduction band electron intensity; 2) an up-shift in the VBM; and 3) a broadening in the valence band EDC. Photoelectron signal from the conduction band at $\Delta t = 0$ probes $n_0 + n_{e/h}$; therefore the prompt increase in CB photoemission signal, observation 1), is proportional to the excitation density $n_{e/h}$. To understand observations 2) and 3), we point out that the depletion in the valence band by optical excitation is $\sim 1\%$ of the total electron density in the band and not detectable in our experiment. Thus, the up-shift in VBM and broadening of the valence band results from

manybody effects resulting from the excitation. The former measures the band renormalization [4,6,7] and the latter attributed to dephasing from hole-hole scattering [31].

We now turn to the dynamics of the manybody effects following optical excitation. Figs. 3a and 3b are 2D pseudo-color EDC plots showing the conduction band and valence band photoemission signal, respectively, as a function of pump probe delay Δt . Note that EDC spectra were taken with analyzer energies focused on CB and VB, resulting in a better S/N than that shown in Figure 2, especially for CB. A representative EDC at single a time slice is shown in Figure S5. Because of the low electron population in the conduction band, we assume these electrons reside close to the CBM and take the intensity-weighted average of the CB photoelectron energies as the CBM position. For the VBM, a common practice in photoemission studies is to use linear extrapolation near the threshold, which may introduce large uncertainty. Instead, each valence band EDC from the K valley is well described by a Gaussian function, and therefore we use the high-energy cutoff at $E_a+2\sigma$ (E_a is the intensity-weighted average of the valence band energy and σ is variance of the Gaussian fit) to represent the VBM. These two approaches yield similar VBM values, as shown in Supporting Information (Fig. S5).

Fig. 3c show the VBM/CBM positions as a function of Δt . Interestingly, the photo-excitation induced bandgap renormalization is reflected exclusively in the up-shift in the VBM while the CBM remains constant, suggesting that the CBM is pinned to the Fermi-level of the metal contact in our n-doped sample, in agreement with Bampoulis et al. [27]. The difference between CBM and VBM gives the time-dependent E_g . In the calculation of the bandgap, a CBM is fixed at the time-averaged value of 0.223 eV. As is shown in Fig. 3d, E_g is measured to be 2.19 ± 0.10 eV in the absence of optical excitation ($\Delta t < 0$), which is ~ 0.4 eV lower than $E_g = 2.6 \pm 0.2$ eV in undoped monolayer MoS₂ [6,11]. This difference reflects band renormalization from the intrinsic n-type doping of $n_0 = (4.9 \pm 1.0) \times 10^{12}$ cm⁻² [6,11]. At $\Delta t = 0$, photoexcitation across the bandgap further lower E_g by as much as $\Delta E_g = -0.36 \pm 0.04$ eV.

The large photo-induced bandgap renormalization results from the poorly screened Coulomb potential and strong manybody interactions in the TMDC monolayer. The renormalized bandgap, initially by $\Delta E_g = -0.36 \pm 0.04$ eV at $\Delta t = 0$, recovers with increasing Δt due to carrier recombination. This recovery can be described by a bi-exponential fit (solid curve in Fig. 3d), with time constants of $\tau_d = 2$ ps and 80 ps, respectively. The time-dependence in E_g is consistent

with the population decay of conduction band photoelectron intensity (blue curve in Fig. 3e), as well as in the recovery of valence bandwidth (Fig. 3f). For comparison, the photoelectron intensity from the valence band (red curve in Fig. 3e) remains constant, as expected from the small depletion of the valence band ($\sim 1\%$) due to photo-excitation. At such a high excitation density, the fast decay ($\tau_d = 2$ ps) likely results from Auger recombination [33], while the slow-decay can be attributed to intrinsic radiative/nonradiative decays in the MoS₂ monolayer [34]. We point out that electronic interaction with or screening by the SiO₂ dielectric substrate is minimal for our single crystal MoS₂ monolayer and photo-excited carrier populations survive for over 400 ps at room temperature (see Fig. S9). For comparison, previous experiments of polycrystalline TMDC monolayers on metal or graphene substrates show lifetimes up to four-orders of magnitude shorter [17,18]. Thus, the band renormalization determined here reflects close-to intrinsic manybody interactions in the MoS₂ monolayer [30]. The time dependent band renormalization quantified in our TR-ARPES measurement is also in qualitative agreement with previous optical measurements on monolayer TMDCs [7,8,11,36–38].

Our ability to determine bandgap renormalization in macroscopic MoS₂ monolayers on an dielectric substrate allows us to carry out quantitative comparisons to theoretical predictions [4,6,7,39]. The solid circles in Fig. 4 are bandgap values determined in our TR-ARPES measurements at different excitation densities. The photoinduced electron/hole density $n_{e/h}$ coexists with the intrinsic electron density of $n_0 = (4.9 \pm 1.0) \times 10^{12} \text{ cm}^{-2}$ from n-type doping. Both e/h pairs from optical excitation and excess electrons from n-type doping screen the Coulomb interactions, leading to renormalization of the bandgap. We use the total carrier

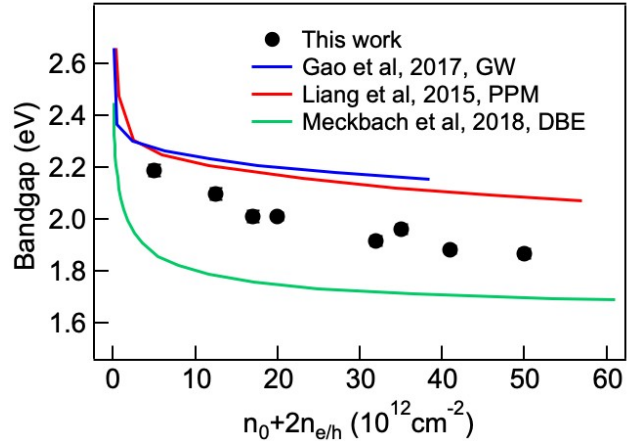


Figure 4. Comparison of experimental bandgaps with theoretical calculations. Solids circles are experimental bandgaps for monolayer MoS₂ determined by TR-ARPES as a function of total doping density ($n_0 + 2n_{e/h}$). The solid curves are theoretical results for electron doping (red [6] and blue [39]) or e/h pair generation from optical excitation (green) [7].

density, i.e., n_0+2n_{e-h} , in comparison to previous calculations for either electron doping or e/h pair excitation. Liang et al. calculated band renormalization (red curve) from the quasiparticle self-energies of valence and conduction bands in monolayer MoS₂ using a new plasmon-pole model that takes into account carrier occupation and carrier screening at high electron doping levels [6]. The result is close to that of a more recent GW calculation (blue curve) by the same group [39]. Mechbach et al. incorporated plasma dielectric screening into a four band Hamiltonian and solved the Dirac-Bloch equation to obtain renormalized band gaps at different excitation densities ($n_{e/h}$) [7]. The resulting bandgap values (green curve) is below those predicted for only electron doping (red and blue curves). While the first data point for $n_0 = (4.9\pm 1.0) \times 10^{12} \text{ cm}^{-2}$ in our measurement (without photo-excitation) is very close to the theoretical results for the same electron doping density [6,39], the experiment data points move closer to the results of Mechbach et al. for photo-doping [7]. This comparison reveals the critical importance of knowing both intrinsic doping levels and additional photo-excitation densities in quantifying the bandgap in 2D TMDCs.

In summary, we carry out direct and quantitative measurement of bandgap renormalization in photo-excited MoS₂ monolayers using TR-ARPES. The use of macroscopic and single crystal MoS₂ samples on a dielectric (SiO₂) surface allows us to access the close-to-intrinsic bandgap renormalization and carrier decay dynamics in the 2D semiconductor. We show reduction in the bandgap by as much -0.36 eV for photo-excitation above the Mott density in an n-type MoS₂ monolayer. The measured density-dependent bandgap provides a benchmark for the validation of theoretical models and for the understanding of strong manybody interactions in TMDC monolayers.

Supplemental Material. Experimental methods, including 1) the preparation of macroscopic MoS₂ single crystal monolayer; 2) characterization by reflectance spectroscopy and photoluminescence spectroscopy; and 3) time-resolved ARPES measurements. Additional data and analysis. This file also includes references [40-45].

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