

Supporting Information

Plasmonic Hot Hole Transfer in Gold Nanoparticle-decorated Transition Metal Dichalcogenide Nanosheets

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Contents: 11 pages (S1-S11), 7 figures (Figure S1-S7), 2 tables (Table S1-S2)

S1. Molybdenum diselenide exfoliation

Bulk MoSe₂ (Materion), MoS₂ (Sigma Aldrich), WS₂ (Sigma Aldrich), WSe₂ (Alfa Aesar) powders were dispersed at a concentration of 25 mg/ml into aqueous sodium cholate surfactant solution (6 mg/ml). The mixture was sonicated in an ice-water bath at 360 W (60% amplitude) in a stainless steel beaker using a probe sonicator with a half inch tip. Sonication was performed for 80 minutes with a 6 second on, 2 second off cycle. Following this initial sonication, the dispersion was centrifuged with a Beckman Coulter ultra-centrifuge for 1.5 hours at 4 krpm (1.7 kg). The supernatant was removed, then discarded. The sediment was re-dispersed in 80 ml of fresh surfactant solution at a concentration of 2 mg/ml. The TMD dispersions were then sonicated for 5 hours using the same parameters as the first sonication step.

S2. Size selection and in situ gold decoration of MoSe₂

Following sonication, the nanosheets were separated by size via centrifugation. In general, nanosheets trapped at higher speeds are thinner and have smaller lateral dimensions.¹ This size separation was performed as reported previously via centrifugation using liquid-cascade centrifugation.² ML-containing dispersions used herein were trapped between 10 and 18 krpm. Au-decoration of each TMD was based on prior work with WS₂.³ Stock MoSe₂ dispersions with an OD of 3.5 at 370 nm were mixed 1:1 by volume with 0.4 mM aqueous AuCl₃. The same

procedure was followed for WSe₂ where 0.4 mM AuCl₃ was mixed with WSe₂ with an OD of 3.5 at 355 nm. WS₂ and MoS₂ were mixed at a 1:2 Au:TMD molar ratio, where TMD concentration was based on previously developed spectral metrics.^{1,2} This approach similar apparent gold loading for each TMD sample. After mixing, samples were covered and refrigerated for 16 hours. Samples were washed by centrifuging at 20 krpm for 1.5 hours, removing supernatant, and topping up with 0.5 mg/ml sodium cholate.

S3. Film deposition

MoSe₂ reference, AuMoSe₂, silica shelled AuNP-MoSe₂ and all films for XPS/UPS were made via blade coating. One-inch square fused quartz substrates (Technical Glass Products) were pre-cleaned by sonicating in acetone for 20 minutes, sonicating in isopropyl alcohol for a few minutes, rinsing with Milli-Q water and drying with N₂. A final clean was performed by soaking in aqua regia (3:1 hydrochloric:nitric acid) for 2-3 hours, rinsing twice with DI water, soaking in DI water overnight, drying with N₂, and further desiccation on a hot plate at 120 °C for 40 minutes. The cleaned glass substrates were stored in a N₂ dry box between cleaning and blade coating. Disposable glass pipettes were cleaned with the glass to be used as the blade coating “blades”. The process for XPS/UPS prepared films was the same, except the films were deposited on ITO glass.

For film deposition, MoSe₂ and AuMoSe₂ solutions (3.5 OD at 370 nm) were mixed in 450 µL of isopropyl alcohol. For blade coating, Kapton tape was placed along opposite sides of the glass affixing it to aluminum foil placed on a hot plate. The tape provided raised edges for the “blade” to rest against during coating. The hot plate was adjusted approximately 60 °C to aid evaporation of the solution. 20 µL of each AuNP and/or TMD containing solution was placed at one end of the glass, between the strips of tape, and drawn across the surface of the glass by hand. Upon reaching the end of the substrate, the direction was reversed without lifting the pipette from the surface; this was repeated until the solution was dried. The rate of coating with the pipette was adjusted to be as fast as possible while maintaining a uniform trailing meniscus of solution between the pipette and substrate without leaving behind streaks or droplets. This process was repeated until a film OD of approximately 0.055 at the A-exciton peak was achieved (with blank substrate subtracted); this took between approximately 400 µL of solution. The films were soaked in Milli-Q water overnight, then dried with N₂. AuNP-containing films were blade coated using the same method. Films were stored in a N₂ dry box after fabrication.

MoS₂, WS₂, and WSe₂ reference and AuNP-decorated films for TA were fabricated via a membrane filtration technique. This technique yields slightly less film uniformity relative to blade coating but was more facile and required fewer TMD nanosheets. For membrane filtration, 100 μ L of each diluted solution was dropped on a Whatman polycarbonate membrane with 30 nm pore size. After the solution dried, the membrane was stamped onto a pre-clean quartz slide. The slide was placed in chloroform to dissolve the polycarbonate, thereby leaving the TMD film on the quartz slide. The films were then soaked in water overnight.

S4. X-ray/Ultraviolet photoelectron spectroscopy (XPS/UPS)

XPS was used for core level spectra of Au, Mo, Se, etc. UPS was used for energetic information; it is preferable to XPS since it does not penetrate as deeply, thereby minimizing substrate contributions. Table S1 summarizes key XPS/UPS results. Molar ratios are from high-resolution XPS, where X:M is the molar ratio of transition metal (M; Mo/W) to chalcogenide (X; Se/S) and X:Au is the ratio of transition metal to Au, Φ is the work function from UPS, and $E_F - E_{VBM}$ is the UPS-derived difference between the Fermi level and valence band. Fig. S1 shows a) Mo 4f, b) Se 2p, c) W 4f, and d) S 2p core level spectra obtained from high-resolution XPS. Fig. S2 plots a) Au 4f core level spectra, which shows a high-binding energy shoulder on the Au⁰ peak at 86 eV attributed to Au-Se bonds for both AuMoSe₂ and AuWSe₂.³ Fig. S2 b) and c) plot UPS spectra used to derive the $E_F - E_{VBM}$ of each sample and work function (Φ), respectively. Fig. S2 d) yields estimated valence and conduction band positions of each sample based on UPS results.

Sample	X:M ratio	X:Au ratio	Φ	$E_F - E_{VBM}$
AuMoSe ₂	1.84	5.25	4.62	0.74
MoSe ₂	1.86		4.59	0.81
AuWSe ₂	2.95	0.8	3.43	0.58
AuMoS ₂	2.11	3.24	4.79	0.93
AuWS ₂	1.94	3.05	4.60	0.89

Table S1: Summary of extracted values from XPS/UPS. X:M is the ratio of transition metal (M; Mo/W) to chalcogenide (X; Se/S), X:Au is the ratio of transition metal to Au, Φ is the work function, and $E_F - E_{VBM}$ is the difference between the Fermi level and valence band maximum.

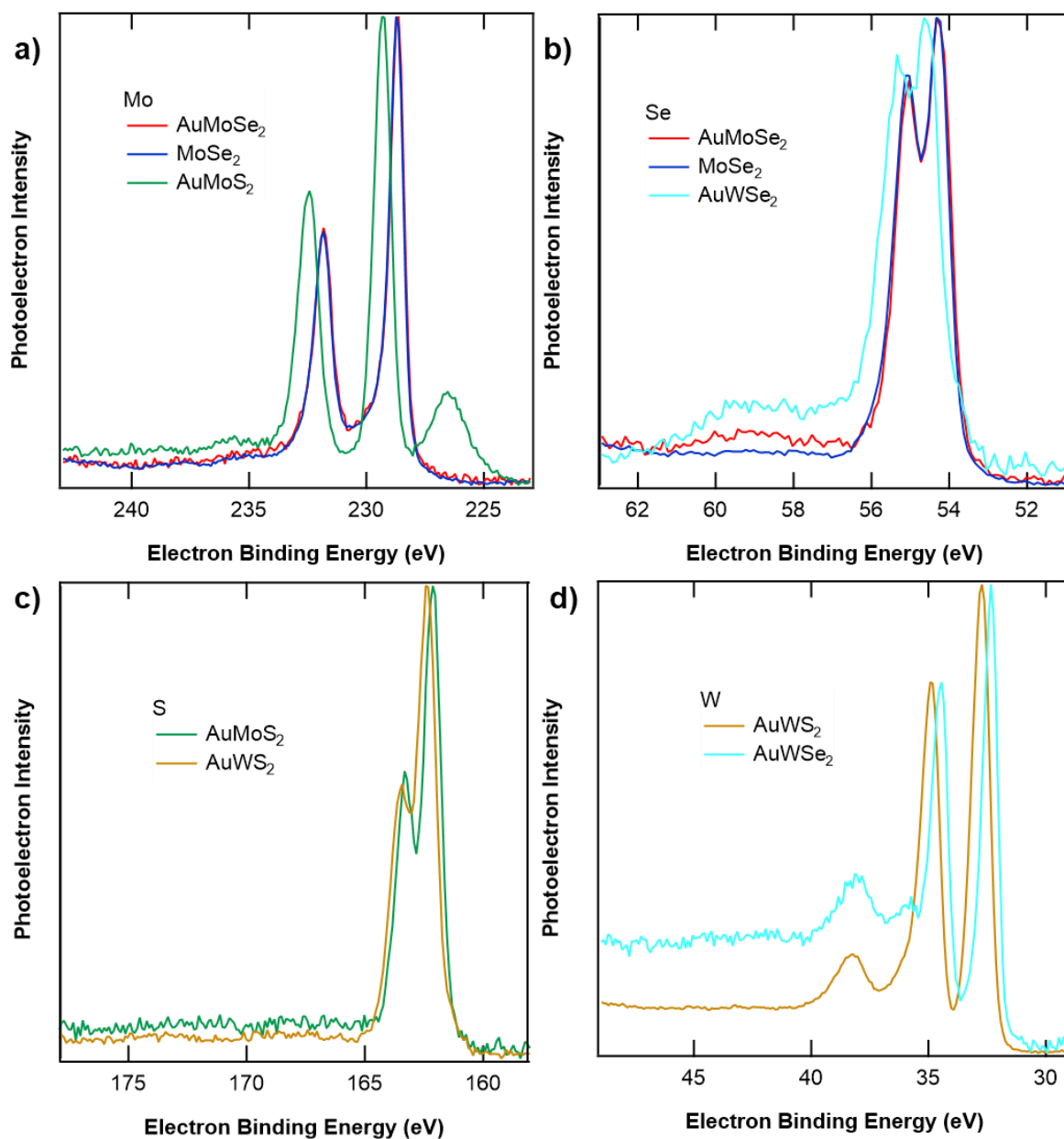


Figure S1: XPS a) Mo 4f, b) Se 2p, c) d) S 2p , and d) W 4f core level spectra for various Au-decorated and reference TMD films.

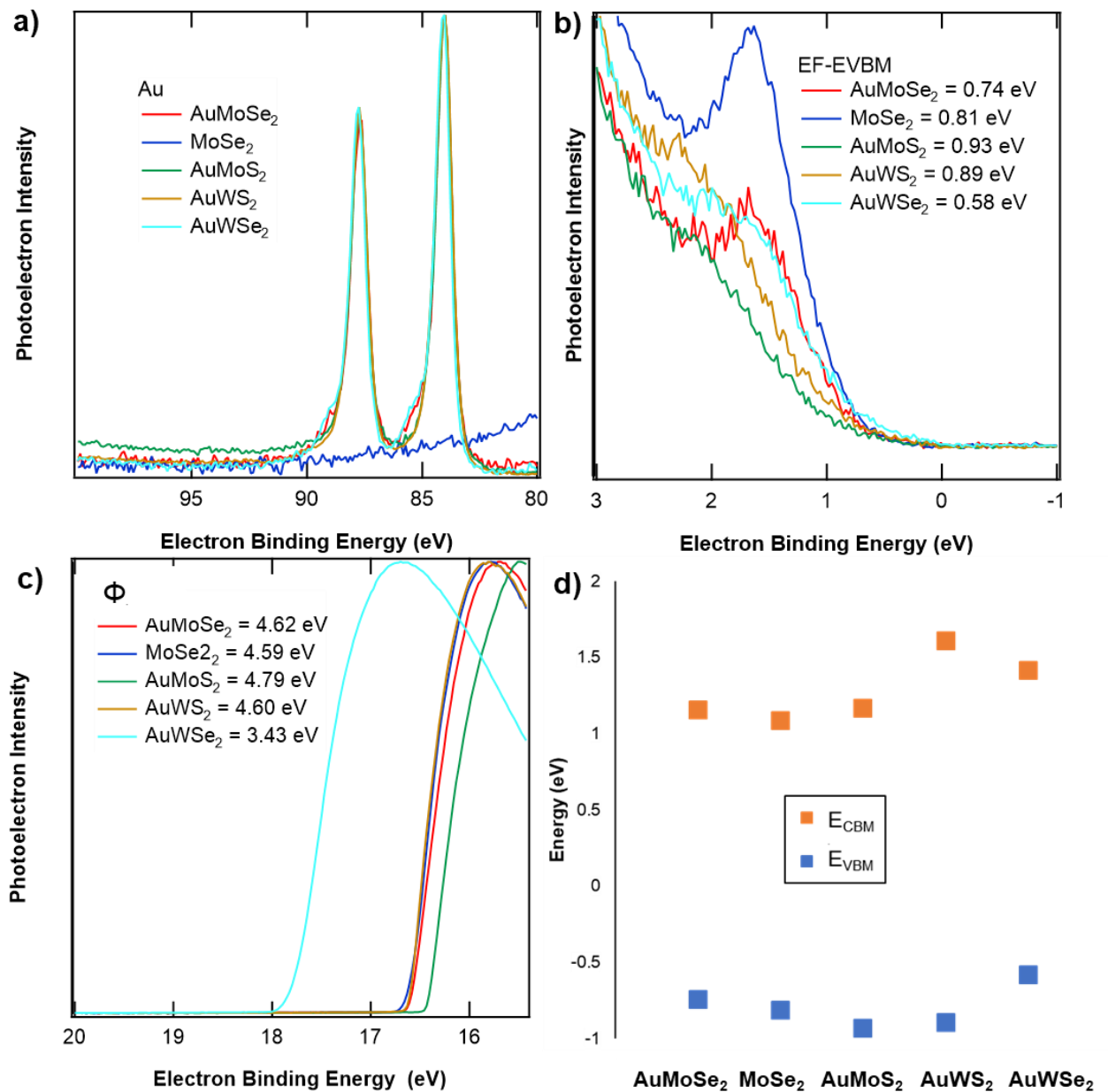


Figure S2: a) Au 4f core level spectra b) and c) plot UPS spectra used to derive the $E_F - E_{VBM}$ of each sample and work function (Φ), respectively, d) estimated valence and conduction band positions of each sample based on UPS results.

The XPS data were obtained on a Physical Electronics 5600 system using Al K α radiation (1486 eV) and the UPS data was obtained by incorporating a home-built He plasma gun into the existing XPS setup, where the He 1 α line is centered at 21.22 eV. Briefly, the XPS and UPS setup was calibrated with Au metal, which was cleaned via Ar-ion sputtering. The raw atomic

concentration has a 5% error due to surface inhomogeneities, surface roughness, literature sensitivity values for peak integration, *etc.* The high-resolution XPS energy uncertainty is ± 0.05 eV. The UPS energy uncertainty is ± 0.025 eV for both $E_F - E_{VBM}$ and Φ , where the UPS data has been corrected for the higher emission lines of 1β and 1γ .

S5. Optical absorptivity measurements

Absorptivity, A , was calculated from transmissivity, T , and reflectivity, R , as $A = 1 - T - R$. Transmissivity and reflectivity were collected with a Cary 6000i spectrophotometer with a DRA-1800 integrating sphere to account for diffusely scattered light. The lamps were warmed for one hour prior to collecting data. The transmission reference was taken with no sample while the reflection reference was a standard Spectralon film. The % absorptivity of MoSe_2 , AuMoSe_2 , AuNP-silica reference, and layered AuNP-silica- MoSe_2 films is shown in Fig. S3.

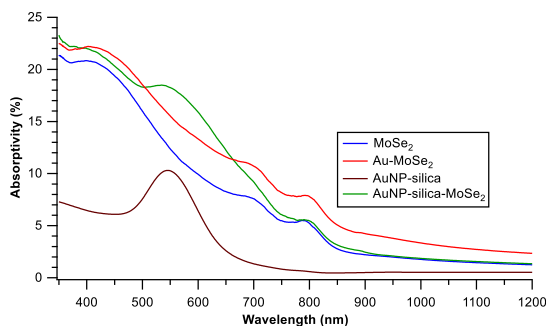


Figure S3: Absorptivity for MoSe_2 , AuMoSe_2 , silica shelled AuNP, and layered silica shelled AuNP- MoSe_2 films.

S6. Photoluminescence (PL) measurements

PL spectroscopy was performed on the TMD films in a Renishaw confocal Raman microscope using 532 nm and 633 nm excitation with 50x objective. Fig. S4 illustrates the PL intensity dependence of AuMoSe₂ on excitation energy.

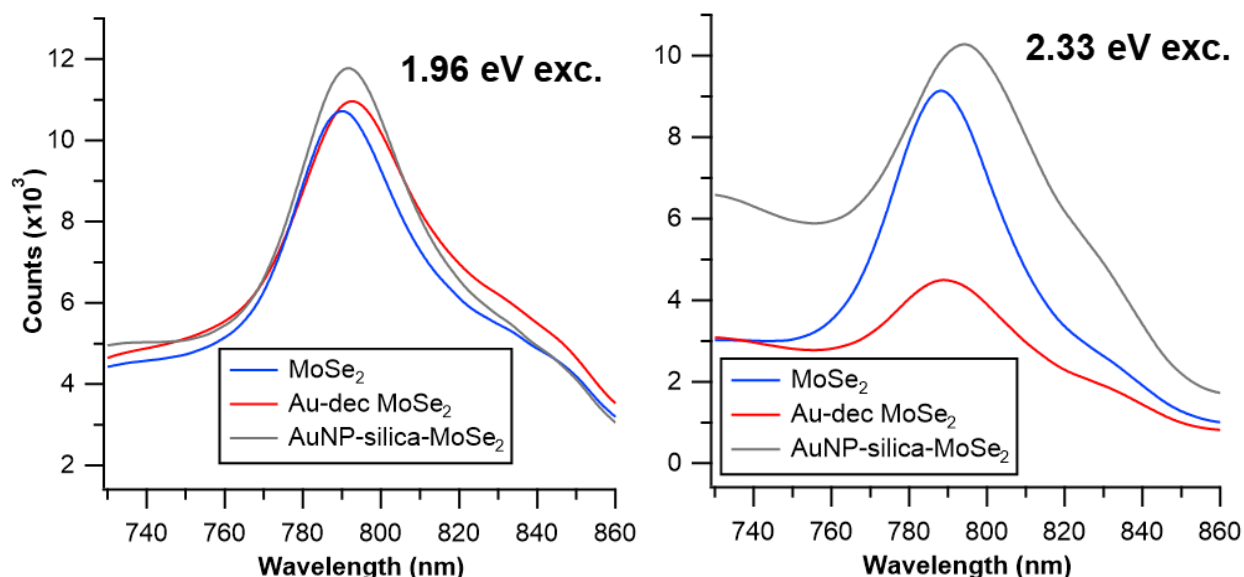


Figure S4: PL spectroscopy for MoSe₂, AuMoSe₂, and AuNP-silica-MoSe₂ films at 1.96 eV (left) and 2.33 eV (right) excitation.

S7. Transient absorption spectroscopy setup

Femtosecond transient absorption spectroscopy measurements used a Coherent Ti:sapphire laser with a ca. 100 fs pulse width (at 800 nm) and 4 W output (both at 800 nm) featuring a 1kHz rep rate. The pump beam generates the desired excitation wavelength via a TOPAS optical parametric amplifier. A beam splitter diverts part of the pump to generate the broadband (ca. 420-800 nm for visible, 800-1600 nm for near infrared) probe beam. This white-light probe is split to provide a secondary reference probe spectrum. The main pump beam is attenuated by neutral density filters and chopped at 500 Hz such that every other probe pulse coincides with the pump pulse. The total pump intensity for all trials was 50 nJ, estimated by measuring the power output through a series of pinholes apertures.

S8. Additional transient absorption spectra and kinetics

Fig. S5 plots additional TA results including a) A-PIA kinetics for MoSe₂, AuMoSe₂, and AuNP-silica-MoSe₂ films at 2.48 eV excitation, as well as b-d) A-PIA and A-PB kinetics for WSe₂, WS₂, and MoS₂ respectively at 2.48 eV excitation. Note extended A-PIA lifetimes for AuWSe₂, but not for AuWS₂ and AuMoS₂.

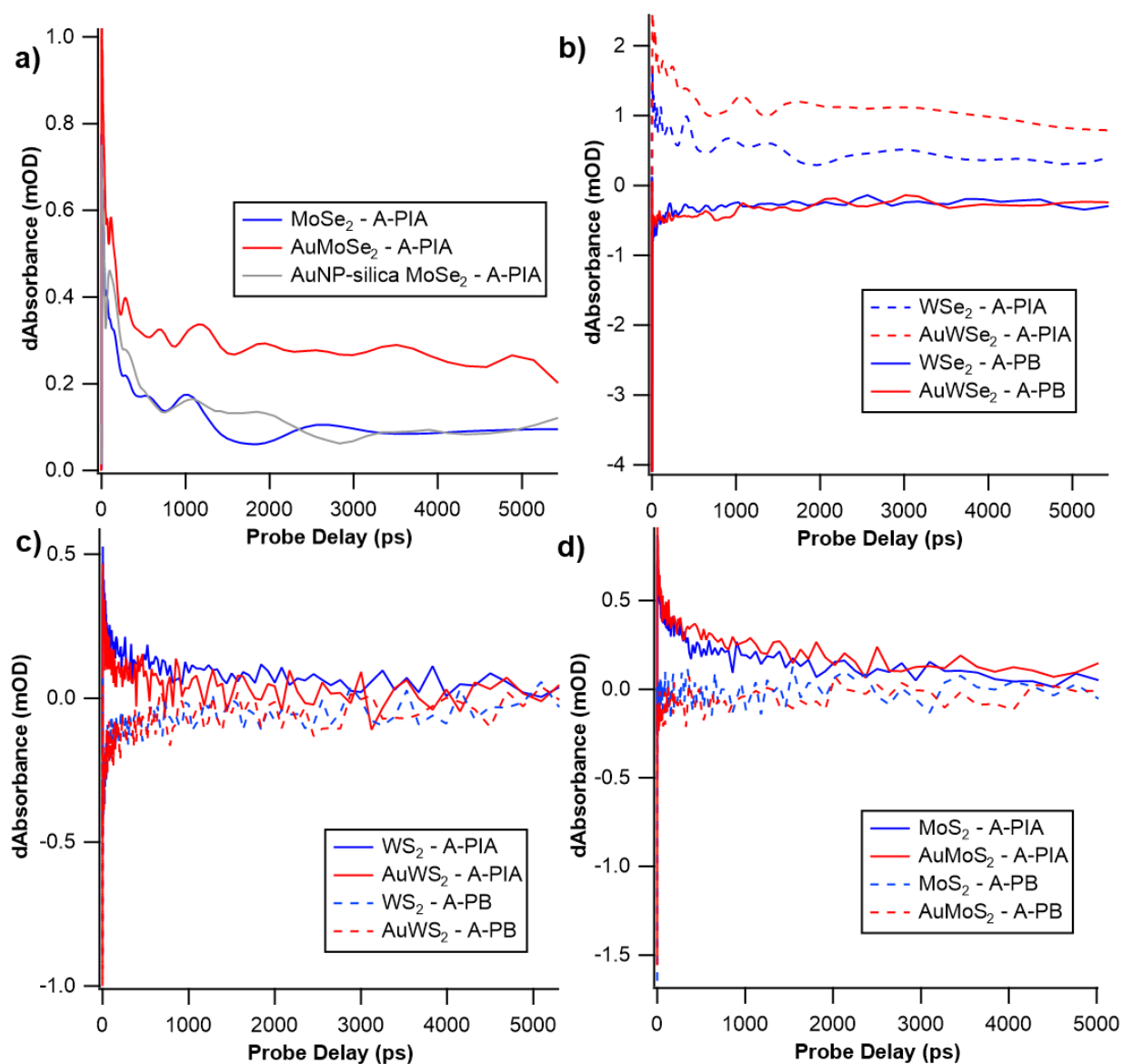


Figure S5: a) TA A-PIA kinetics for MoSe₂, AuMoSe₂, and AuNP-silica-MoSe₂ films at 2.48 eV excitation, b-d) A-PIA and A-PB kinetics for WSe₂, WS₂, and MoS₂ respectively at 2.48 eV excitation. Note extended A-PIA lifetimes for AuWSe₂, but not for AuWS₂ and AuMoS₂.

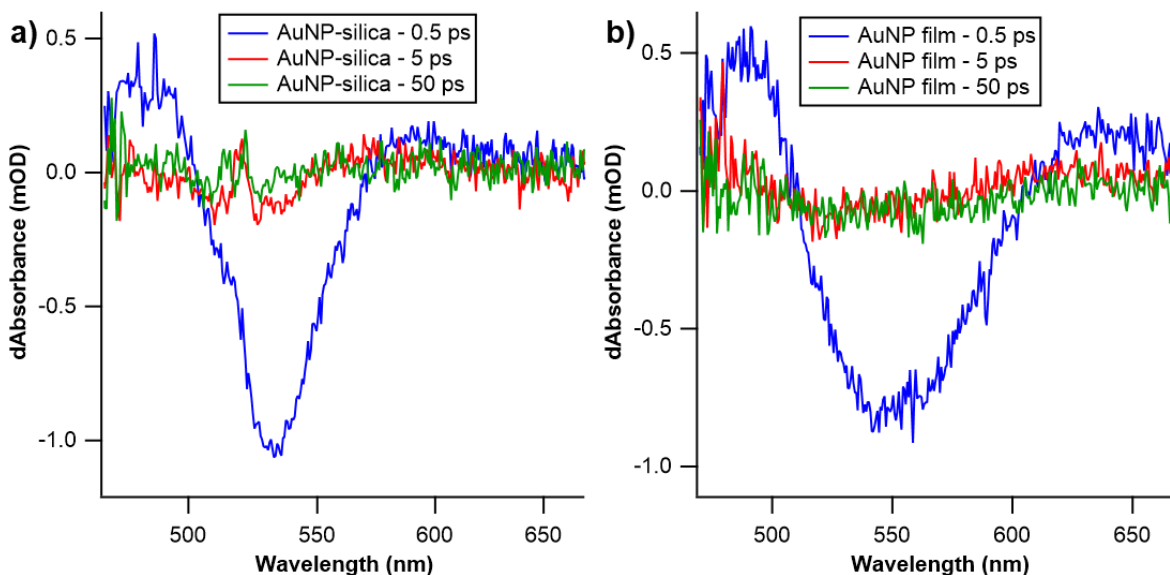


Figure S6: a) TA spectra at 2.4 eV excitation for silica shelled AuNP and AuNP films.

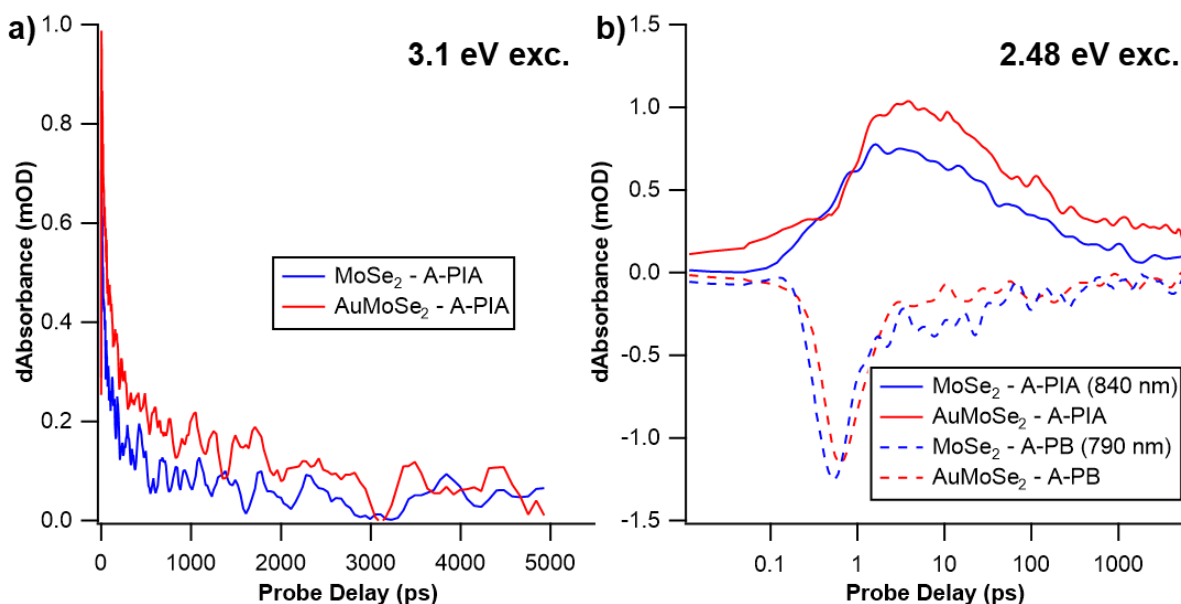


Figure S7: a) TA A-PIA kinetics for MoSe₂ and AuMoSe₂ at 3.1 eV excitation, b) A-PIA and A-PB kinetics for MoSe₂ and AuMoSe₂ at 2.48 eV excitation plotted on log scale.

Fig. S6 illustrates rapid, ps-scale carrier relaxation for silica shelled AuNP and AuNP films excited at 2.48 eV. Fig. S7a plots A-PIA kinetics for AuMoSe₂ and MoSe₂ at 3.1 eV excitation; an increase in kinetic lifetimes is apparent for AuMoSe₂. Fig. S7b plots AuMoSe₂ and MoSe₂ at 2.48 eV excitation, the same data shown in main manuscript Fig. 2b, on a log scale to more clearly

show the 1-3 ps rise time of the additional TA component. Table S2 summarizes the long-component lifetime from the bi-exponential fits for all samples studied herein as a function of excitation energy.

Sample	Pump (eV)	A-PIA (ns)	A-PB (ns)
MoSe ₂	2.48	1.7±0.6	1.3±0.5
AuMoSe ₂	2.48	4.2±0.9	1.1±0.4
MoSe ₂	1.65	2.4±0.7	0.7±0.3
AuMoSe ₂	1.65	2.6±0.8	0.6±0.4
MoSe ₂	3.10	1.0±0.5	
AuMoSe ₂	3.10	2.5±1.0	
WSe ₂	2.48	1.7±0.6	1.1±0.8
AuWSe ₂	2.48	2.8±0.8	0.8±0.7
MoS ₂	2.48	2.1±0.9	0.7±0.5
AuMoS ₂	2.48	1.6±0.8	0.6±0.6
WS ₂	2.48	1.9±0.9	1.0±0.5
AuWS ₂	2.48	1.1±1.0	0.9±0.4

Table S2: Extracted bi-exponential lifetimes for kinetic traces at the A-PIA for each TMD-containing film at various excitation energies.

S9. Atomic Force Microscopy (AFM) characterization

The stock MoSe₂ dispersion was characterized via AFM prior to Au-decoration. AFM was performed with a Bruker Innova AFM system under ambient conditions. The MoSe₂ nanosheets were deposited on a polished sapphire substrate via spincoating at 3000 rpm. The samples were soaked in DI briefly to remove surfactant residue. Fig. S8 shows 3 scans from which the mean nanosheet length and thicknesses of 54.2 ± 32.8 nm and 3.1 ± 2.5 nm, respectively, were determined. These estimates are likely on the high side as residual surfactant and difficulty in measuring small nanosheets likely increases the number of larger nanosheets sampled in this analysis relative to the overall distribution.

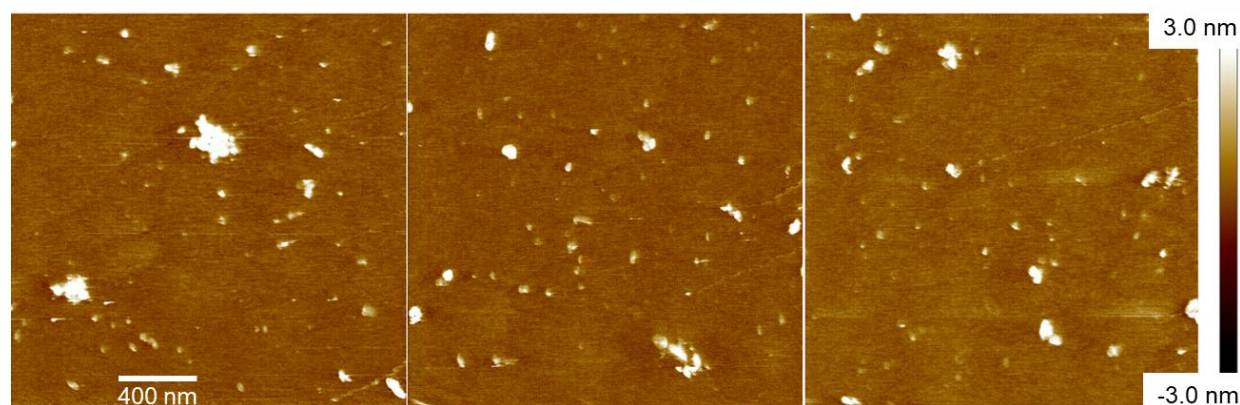


Figure S8: AFM scans for the stock MoSe₂ dispersion prior to Au-decoration.

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