Supplementary Information

Study of Surface and Bulk Recombination Kinetics of 2D IO Hybrid Semiconductors Under Linear and Nonlinear Femtosecond Transient Absorption Analysis

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Figure S1 demonstrate the transient absorption pump-probe experimental setup. The 800 nm beam from the Ti:sapphire amplifier is split by a beam splitter. One of the beam passes through the delay stage consisting of a retro-reflector mounted on a computer-controlled motorized translational stage, and is focused on the CaF_2 crystal to generate a broadband white light continuum (WLC) from the UV to IR region and acts as a probe pulse. For optical excitation of the sample, the pump beam is chosen from the TOPAS, which is 350 nm, 800 nm and 1020 nm used in the present work. This strong pump pulse is passed through the optical chopper to avoid the overheating and photo-damage of the sample. After travelling a fixed optical path, the pump pulse is focused onto the sample. A variable neutral density filter is used to control the pump power. Both the pump and probe beams are *temporally and spatially* overlapped on the sample position. The pump is stronger than the probe beam and pump diameter is larger than probe and WLC scans a large area of the sample to collect more information. The WLC probe signals are collected by using point array

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detectors with lock-in detection. This WLC contains a rather intense 800 nm residual and a short pass filter (SPF) is used in the probe path before the sample to eliminate the residual 800 nm light. The relative polarization between the pump and the probe was set at the magic angle (54.7°) in order to eliminate polarization and photo-selection effects. The probe was split by a beam splitter (BS) and one of the probes was used as reference. The pump and probe after the sample were focused on the fiber (pump dumped) which is attached to an imaging spectrometer. Two photodiode arrays are placed after the spectrometer to measure probe and reference pulses. After transmission through the sample, the probe and reference beam is focused on the multi-mode fiber connected to the entrance slit of the imaging spectrometer CDP2022i.

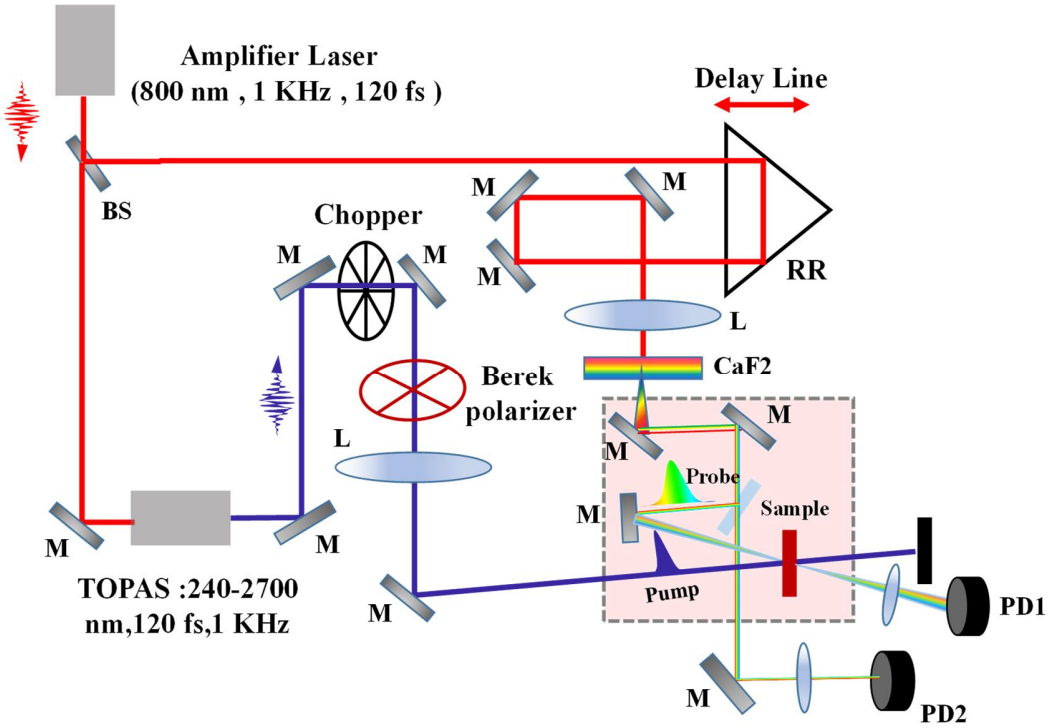

Figure S1 Typical layout of non-degenerate fs-TAS setup with pump pulses from OPA (300-2700 nm, 1 KHz, 120 fs). The weak broad band probe pulse (~400-1000 nm) is generated by focusing μW powers of 800 nm light into CaF_2 crystal.

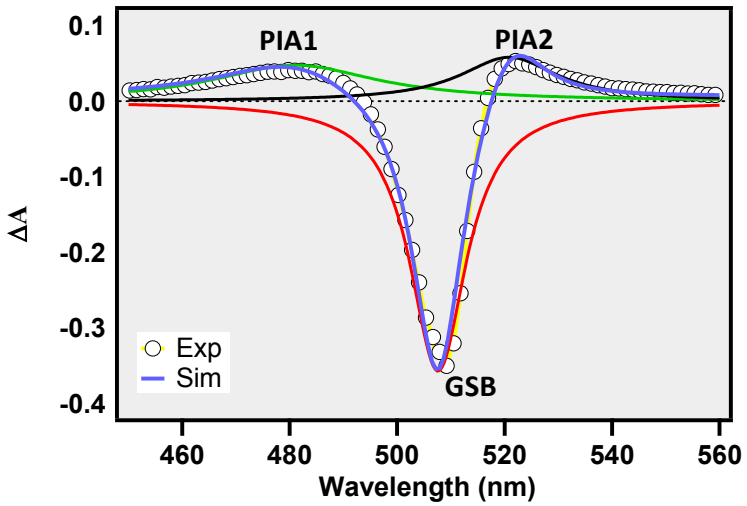

Figure S2 Zero delay transient absorption spectra under 350 nm excitation. The spectra was fitted using three Lorentzian peaks attributed to PIA1, GSB and PIA2 using phenomenological expression $\Delta A = y_0 + \sum_{i=1}^{3} \frac{A_i}{(x - x_i)^2 + B_i}$.

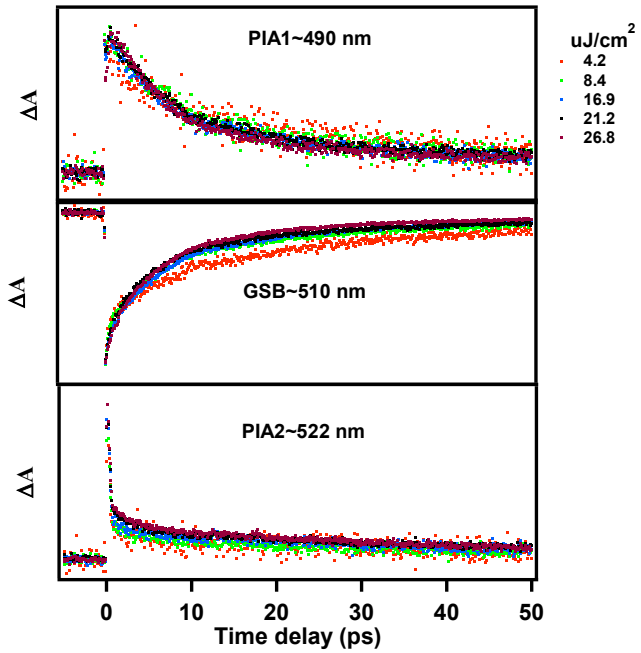

Figure S3 Fluence dependent transient dynamics of (a) PIA1 at 490 nm, (b) GSB at 510 nm and (c) PIA2 at 522 nm in CHPI thin film. Ex: 350 nm, 1 KHz, 120 fs. Fluences: 4.2, 8.4, 16.9, 21.2 and 26.8 μJ/cm^2.

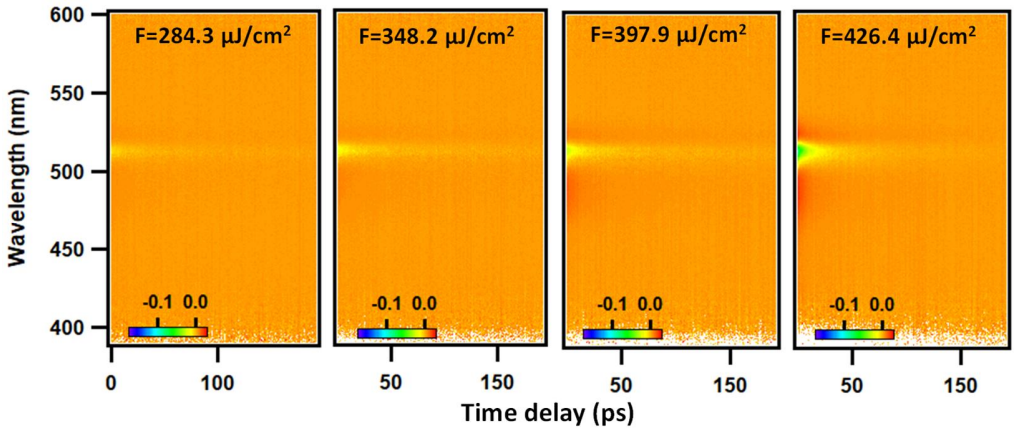

Figure S4 Fluence dependent transient absorption spectral mapping pumped at 800 nm (2PA) at different fluence values viz 284.3, 348.2, 397.9 and 426.4 µJ/cm^2.

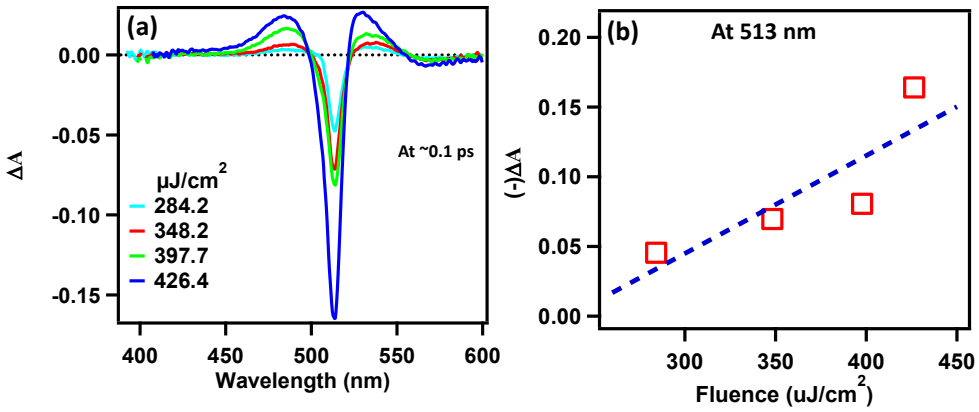

Figure S5 (a) Fluence dependent zero delay transient absorption spectra (b) plot of bleach intensity (~513 nm) with fluence. Ex: 800 nm, 1 KHz, 120 fs

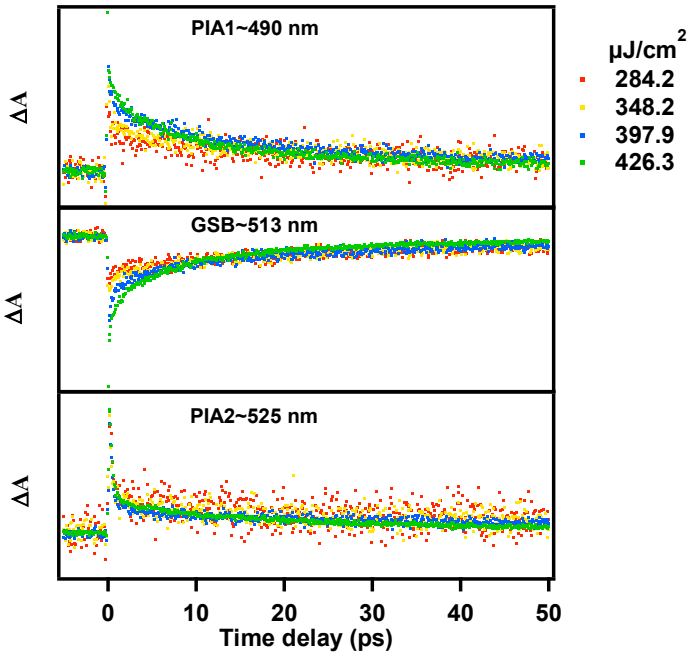

Figure S6 Fluence dependent transient dynamics of (a) PIA1 at 490 nm, (b) GSB at 513 nm and (c) PIA2 at 525 nm in CHPI thin film. Ex: 800 nm, 1 KHz, 120 fs. Fluences: 284.2, 348.2, 397.9 and 426.3 μJ/cm^2.

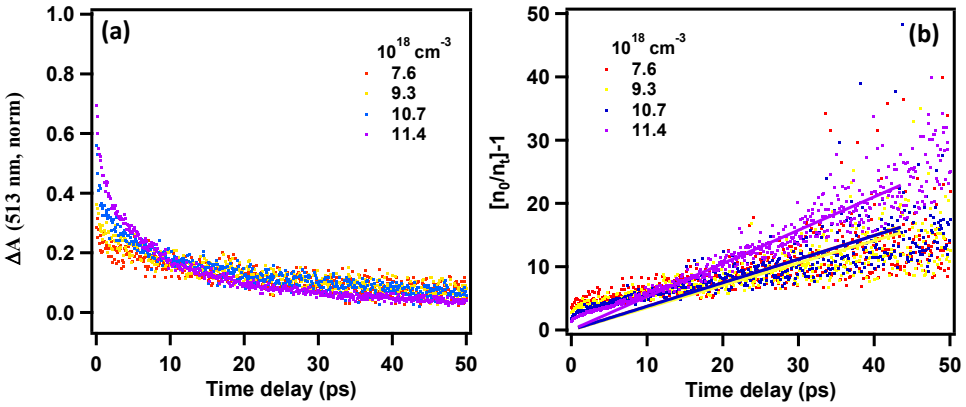

Figure S7 (a) Kinetic profiles of 513 nm bleach recovery at various excitation densities. Traces are normalized to the maximum bleach signal at each excitation energy density. (b) Reciprocal of kinetic traces shown in (a). Solid lines are linear fits to the second order rate equation $n_0/n_t-1=kn_0t$, at various excitation densities where kn_0 is slope, n_0 and k are initial carrier density and second order recombination rate constant. Ex: 800 nm, 1 KHz, 120 fs.

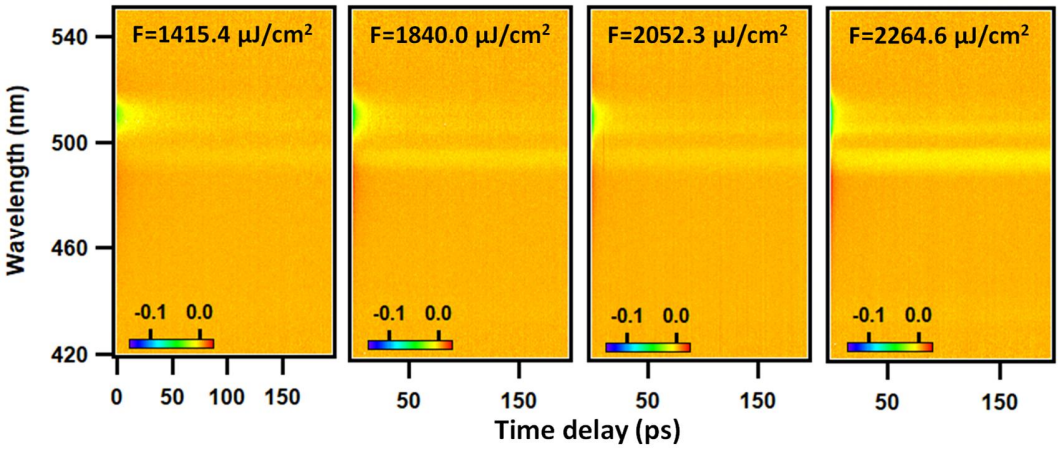

Figure S8 Fluence dependent three-photon transient absorption spectral mapping pumped at 1020 nm (3PA) at different fluence values viz 1415.4, 1840, 2052.3 and 2264.6 μJ/cm^2.

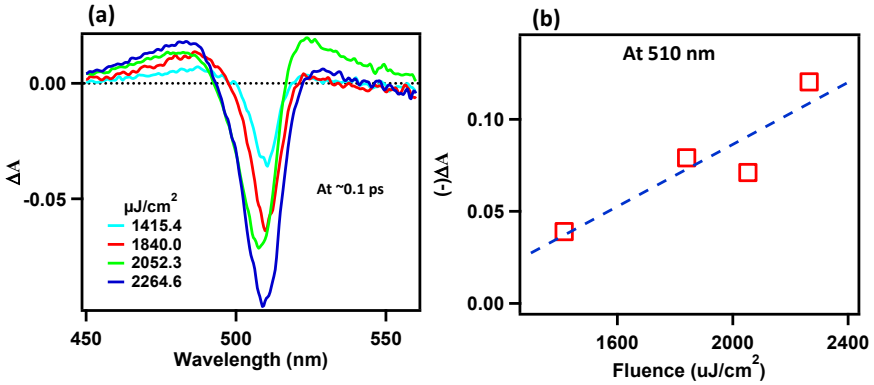

Figure S9 (a) Fluence dependent zero delay transient absorption spectra (b) plot of bleach intensity (~510 nm) with fluence. Ex: 1020 nm, 1 KHz, 120 fs

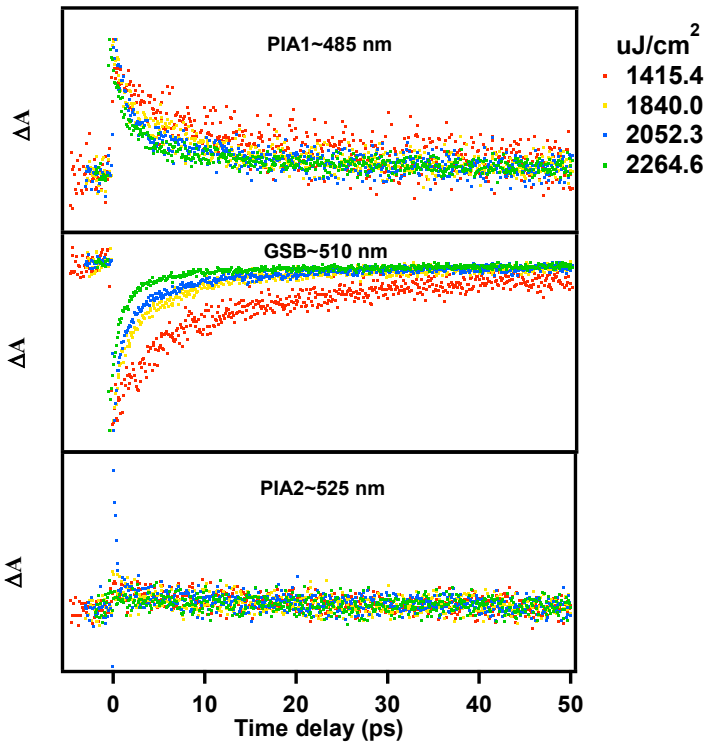

Figure S10 Fluence dependent transient dynamics of (a) PIA1 at 485 nm, (b) GSB at 510 nm and (c) PIA2 at 525 nm in CHPI thin film. Ex: 1020 nm, 1 KHz, 120 fs. Fluences: 1415.4, 1840, 2052.3 and 2264.6 μJ/cm^2.

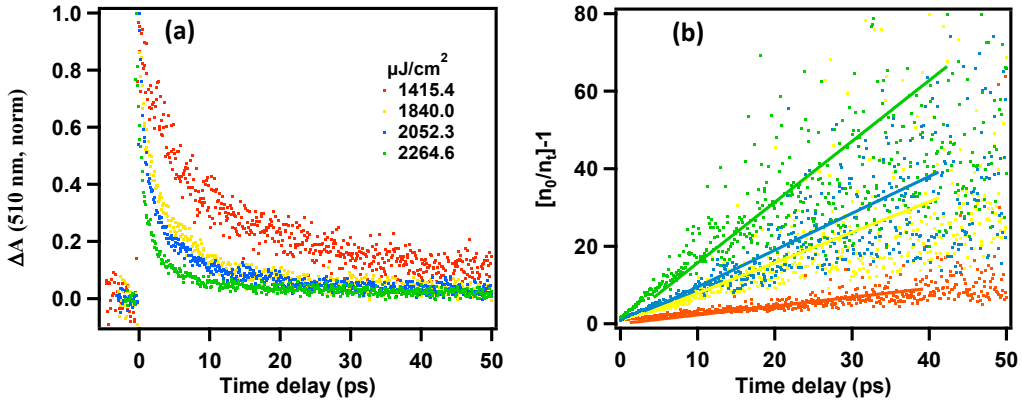

Figure S11 (a) The normalized kinetic profiles of 510 nm ground state bleaching region at various excitation fluences. (b) Reciprocal of kinetic traces shown in (a) Solid lines are linear fits to the second order rate equation $n_0/n_t-1=kn_0t$, at various excitation densities where kn_0 is slope, n_0 and k are initial carrier density and second order recombination rate constant. Ex: 1020 nm, 1 KHz, 120 fs