Supplementary Materials

Methods

First-principles calculations. The first-principles Kohn-Sham density functional theory (DFT) calculations of the band structure and density of states (DOS) utilized the Quantum ESPRESSO package.\textsuperscript{1,2} The generalized gradient approximation (GGA) was used in the scheme of Perdew-Burke-Ernzerhof (PBE) with normal-conserving and fully relativistic ONCV SG15 pseudopotentials to support non-collinear spin-orbital coupling (SOC) calculations.\textsuperscript{3,4} The DFT-D3 dispersion correction was included in the calculations to capture the van der Waals interaction between WS\textsubscript{2} layers.\textsuperscript{5} Structural relaxation was performed with symmetry constraints and a force and energy threshold of 10\textsuperscript{-3} a.u. and 10\textsuperscript{-4} a.u., respectively, resulting in an in-plane lattice constant of 3.18 Å for both 1L- and 5L-WS\textsubscript{2}. The self-consistent DFT calculations were performed on a 40×40×1 Monkhorst-Pack $k$-grid with an 80 Ry cutoff energy. A non-self-consistent calculation with tetrahedral occupations on a 100×100×1 grid was then performed, from which the DOS plots were obtained.\textsuperscript{6}

Sample preparation. Template-stripped gold substrates were prepared as reported elsewhere.\textsuperscript{7} Briefly, a two-component epoxy was dropped on 100-nm thick gold, which was pre-deposited on Si substrates. The epoxy was covered with Si chips as a carrier wafer. Upon drying at 100 ºC and flipping the chips, the buried flat gold surface was exposed for TMD exfoliation. Using the scotch-tape method, the WS\textsubscript{2} crystals were exfoliated directly over the smooth gold surface. The monolayer and few-layer WS\textsubscript{2} identified from the optical contrast and atomic force microscopy studies were used for further investigations.
Figure S1. (a) Optical micrograph of the WS$_2$ layers of various layer thickness on a gold substrate. (b) A height map of the sample measured on a selected area with atomic force microscopy.

Figure S2. A schematic drawing of the pump-probe transient reflection setup utilizing an optical microscope objective for focusing the probe light onto the sample.
Figure S3. Transient $\Delta R/R$ spectral map of (a) 5L-WS$_2$/Au, and (b) 10L-WS$_2$/Au excited by below-bandgap pump with a wavelength of 1100 nm from 0 to 20 ps after pump excitation.

Figure S4. Pump-dependent kinetics of $\Delta R/R$ of (a) monolayer-WS$_2$ and (b) 5L-WS$_2$ on gold substrate, extracted at their corresponding excitonic absorption peaks. The inlets in (a)(b) show linear relationship between the peak $\Delta R/R$ value and pump power.
Figure S5. (a) Transient $\Delta R/R$ spectral map of 1L-WS$_2$/Au excited by below-bandgap pump with a wavelength of 1100 nm from 0 to 1000 ps after pump excitation. (b) The kinetics of $\Delta R/R$ extracted at 630 nm, corresponding to the A-exciton wavelength. The kinetics rise to a peak at approximately 1200 ps, followed by a slow decay up to 4000 ps.

Figure S6. The $\Delta R/R$ kinetics extracted at the A exciton resonance and integrated over the first 4 ps for (d) 1L-WS$_2$/Au, (e) 5L-WS$_2$/Au, and (f) 10L-WS$_2$/Au, with pump wavelength converted to pump photon energy in eV. For a certain thickness of sample, measurements under each wavelength are repeated three times with the standard errors presented by the error bars.
Supporting References


