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.[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.[3,4] The DFT-D3 dispersion correction was included in the calculations to capture the van der Waals interaction between WS_2 layers.[5] Structural relaxation was performed with symmetry constraints and a force and energy threshold of 10^{-3} a.u. and 10^{-4} a.u., respectively, resulting in an in-plane lattice constant of 3.18 Å for both 1L- and 5L-WS_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.[6]

Sample preparation. Template-stripped gold substrates were prepared as reported elsewhere.[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_2 crystals were exfoliated directly over the smooth gold surface. The monolayer and few-layer WS_2 identified from the optical contrast and atomic force microscopy studies were used for further investigations.

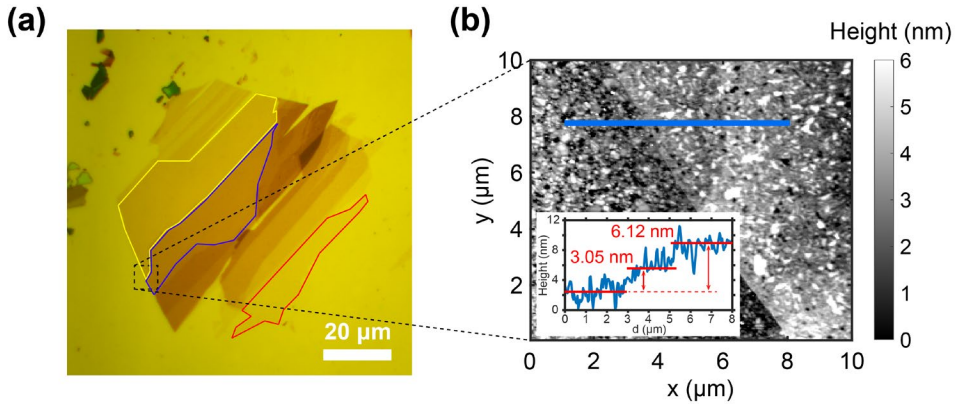

Figure S1. (a) Optical micrograph of the WS_2 layers of various layer thickness on a gold substrate. (b) A height map of the sample measured on a selected area with atomic force microscopy.

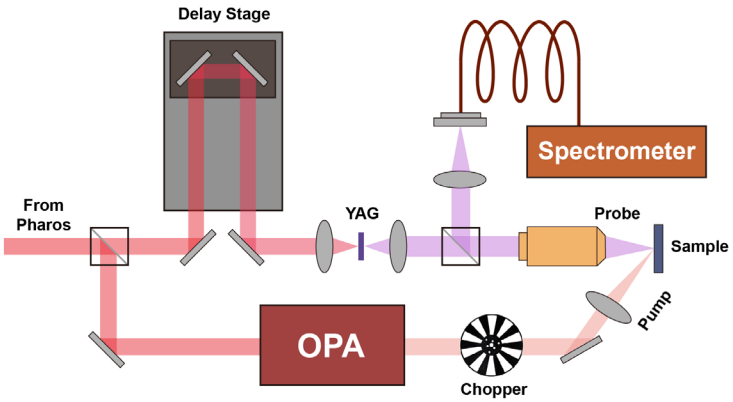

Figure S2. A schematic drawing of the pump-probe transient reflection setup utilizing an optical microscope objective for focusing the probe light onto the sample.

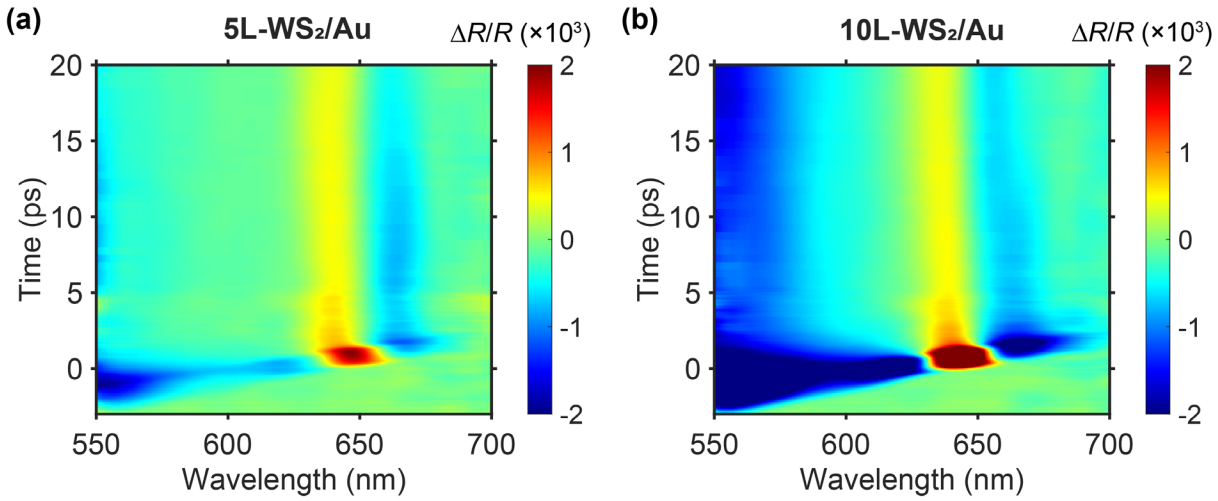

Figure S3. Transient $\Delta R/R$ spectral map of (a) 5L-WS_2/Au, and (b) 10L-WS_2/Au excited by below-bandgap pump with a wavelength of 1100 nm from 0 to 20 ps after pump excitation.

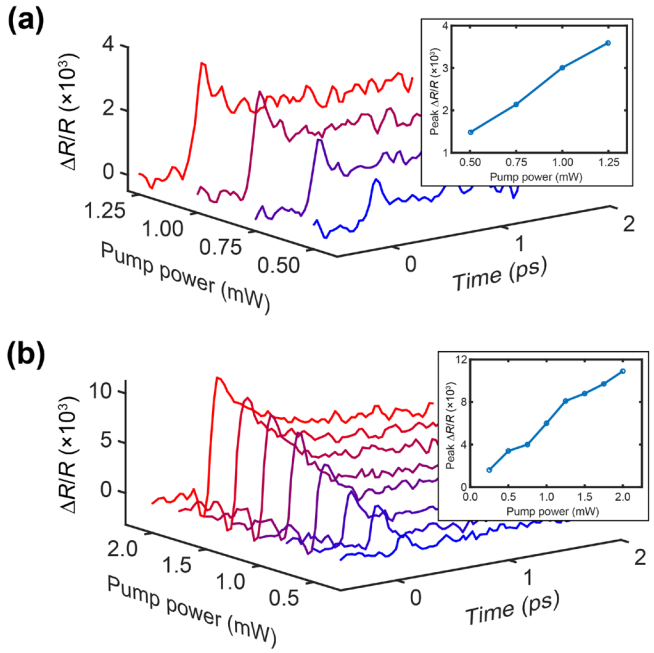

Figure S4. Pump-dependent kinetics of $\Delta R/R$ of (a) monolayer-WS_2 and (b) 5L-WS_2 on gold substrate, extracted at their corresponding excitonic absorption peaks. The inlets in (a)(b) show linear relationship between the peak $\Delta R/R$ value and pump power.

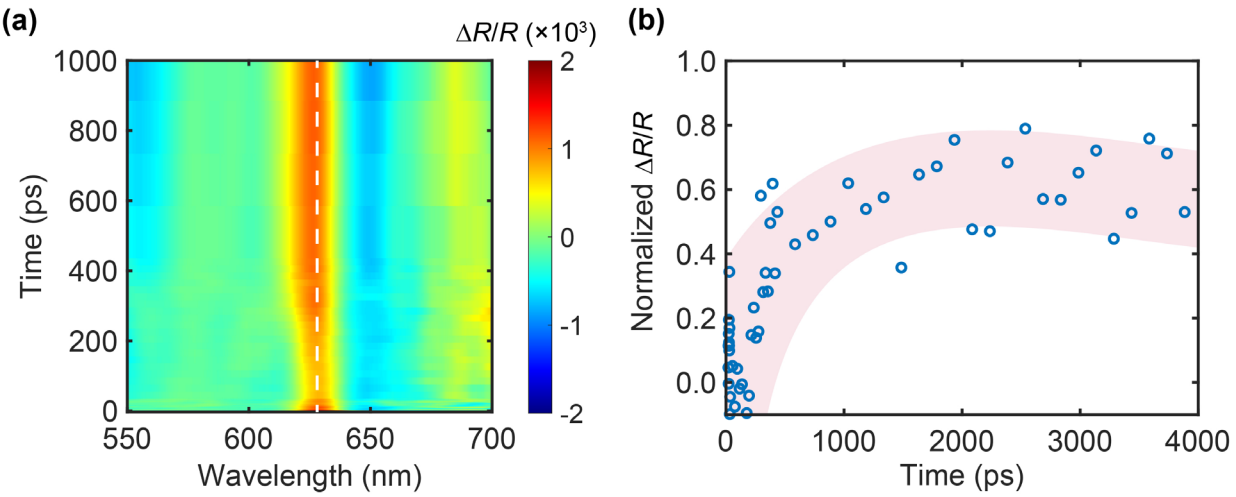

Figure S5. (a) Transient $\Delta R/R$ spectral map of 1L-WS_2/Au excited by below-bandgap pump with a wavelength of 1100 nm from 0 to 1000 ps after pump excitation. (b) The kinetics of $\Delta R/R$ extracted at 630 nm, corresponding to the A-exciton wavelength. The kinetics rise to a peak at approximately 1200 ps, followed by a slow decay up to 4000 ps.

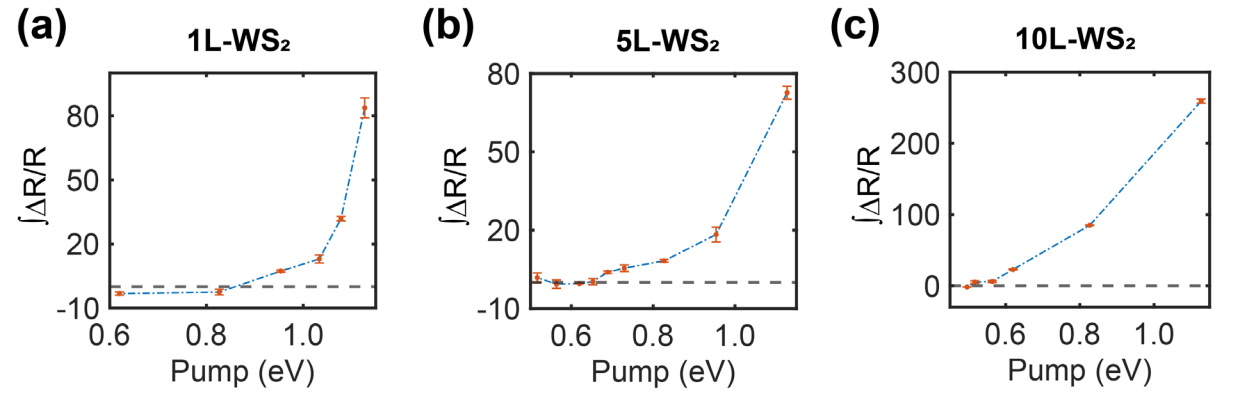

Figure S6. The $\Delta R/R$ kinetics extracted at the A exciton resonance and integrated over the first 4 ps for (d) 1L-WS_2/Au, (e) 5L-WS_2/Au, and (f) 10L-WS_2/Au, with pump wavelength converted to pump photon energy in eV. For a certain thickness of sample, measurements under each wavelength are repeated three times with the standard errors presented by the error bars.

Supporting References

1. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari and R. M. Wentzcovitch, *J. Phys.: Condens. Matt.*, 2009, **21**, 395502.
2. P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. Buongiorno Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. Dal Corso, S. de Gironcoli, P. Delugas, R. A. DiStasio, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H. Y. Ko, A. Kokalj, E. Küçükbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N. L. Nguyen, H. V. Nguyen, A. Otero-de-la-Roza, L. Paulatto, S. Poncé, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu and S. Baroni, *J. Phys.: Condens. Matt.* 2017, **29**, 465901.
3. D. R. Hamann, *Phys. Rev. B*, 2013, **88**, 085117.
4. M. Schlipf and F. Gygi, *Comput. Phys. Commun.*, 2015, **196**, 36-44.
5. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
6. P. E. Blöchl, O. Jepsen and O. K. Andersen, *Phys. Rev. B*, 1994, **49**, 16223-16233.
7. D. Jariwala, A. R. Davoyan, G. Tagliabue, M. C. Sherrott, J. Wong and H. A. Atwater, *Nano Lett.*, 2016, **16**, 5482-5487.