Supporting Information for

Electronic state evolution of oxygen-doped monolayer WSe_2 assisted by femtosecond laser irradiation

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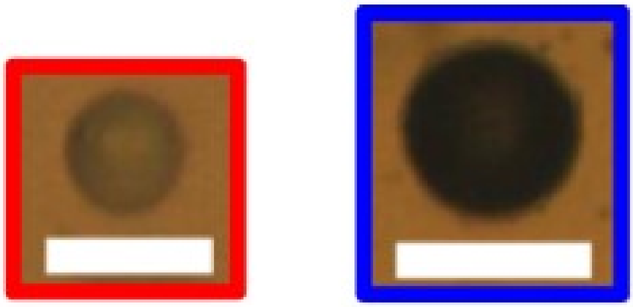

Figure S1. Micro-zone optical images for IFsLI case 1 in a red square and IFsLI case 2 in a blue square, respectively (scale bar, 500 μm), where the light-yellow background is covered by the pristine monolayer WSe_2 film, the brown spot with a diameter of ~300 μm for IFsLI case 1 and a darker and larger modified spot with a diameter of ~400 μm for IFsLI case 2 are the femtosecond laser modification areas caused by pump pulses..

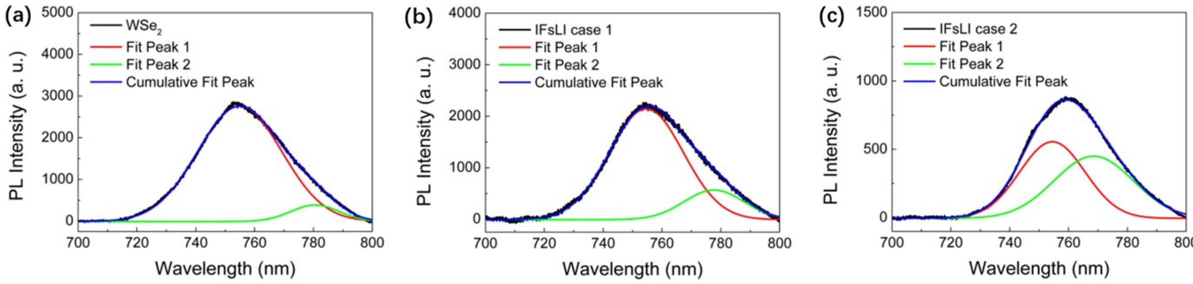

Figure S2. Two-peak fitting for the steady-state PL spectra of (a) pristine monolayer WSe_2 on the sapphire substrate, (b) monolayer WSe_2 with a moderate modification (IFsLI case 1) and (c) monolayer WSe_2 with a strong modification (IFsLI case 2). The peak 1 could be the radiative recombination of band-edge excitons. The peak 2 could be attributed to the defects.[1]

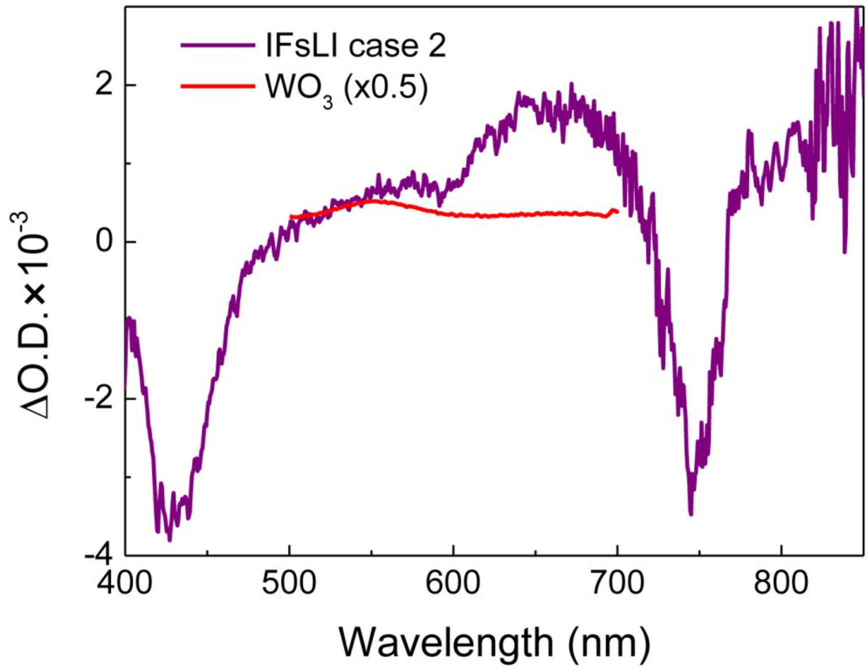

Figure S3. Comparison between initial TA spectra at 1 ps of monolayer WSe_2 with a strong modification (IFsLI case 2) and WO_3 (multiplying by a factor of 0.5) in ref. S2, where the transient signal at ~550 nm is assigned to the photogenerated holes on WO_3.

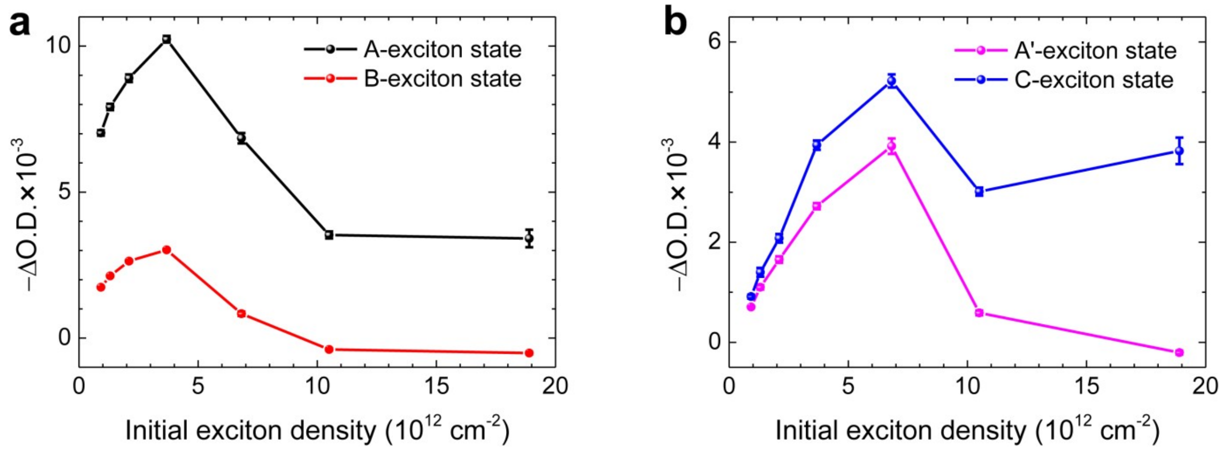

Figure S4. The exciton-density-dependent initial amplitude of GSB signals for (a) A-/B-exciton states, and (b) A′-/C-exciton states.

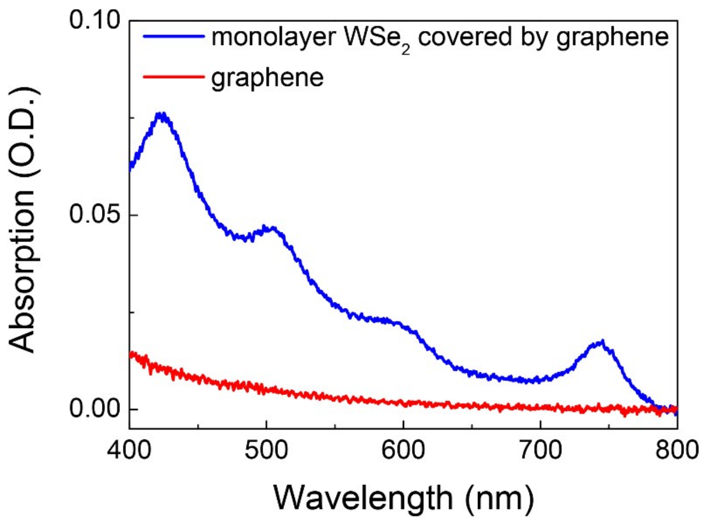

Figure S5. Steady-state absorption spectra of graphene and monolayer WSe_2 covered by graphene.

Table S1. Parameters for the PL peak fitting of monolayer WSe_2 with/without IFsLI treatments

	Peak 1 (nm)	Peak 2 (nm)	Spectral weight for Peak 1 %	Spectral weight for Peak 2 %
Pristine monolayer WSe_2	754.9	780.5	92	8
IFsLI case 1	754.7	777.7	82	18
IFsLI case 2	754.5	768.5	51	49

Table S2. Parameters for the XPS peak fitting of monolayer WSe_2 with/without IFsLI treatments

Bonding	Pristine monolayer WSe_2			IFsLI case 1			IFsLI case 2		
	Binding energy (eV)	FWHM (eV)	Area %	Binding energy (eV)	FWHM (eV)	Area %	Binding energy (eV)	FWHM (eV)	Area %
$W4f_{7/2}$ WSe_2	32.49	1.25	35.69	32.77	0.96	36.54	32.43	0.97	32.25
$W4f_{5/2}$ WSe_2	34.90	1.84	46.00	34.93	1.04	29.69	34.55	0.99	24.18
$W5p_{3/2}$ WSe_2	37.77	2.10	18.31						
$W4f_{7/2}$ WO_3				36.26	1.36	16.37	36.04	1.54	22.99
Overlapping of $W4f_{5/2}$ WO_3 and $W5p_{3/2}$ WSe_2				38.32	1.51	17.40	38.19	1.59	20.58

Table S3. Formation energy of V_{Se} and O_{Se} under the W-rich condition and Se-rich condition.

Formation energy (eV)	W-rich	Se-rich
V_{Se}	1.61	2.44
O_{Se} (O_2 reservoir)	-2.63	-1.81
O_{Se} (WO_3 reservoir)	0.15	0.42

Table S4. Femtosecond time-resolved TA dynamics parameters obtained by multiple-exponential fitting under 400 nm excitation.

	Lifetime component	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_{ave} (ps)	
monolayer WSe_2	A exciton	3.7 (57.7%)	39 (33.3)	605 (9.0%)	69.5	
	B exciton	0.37 (37.5%)	4.5 (43.6%)	63 (18.9%)	14.0	
	C exciton	12 (56.9%)	84 (43.1%)		43	
	Lifetime component	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_{ave} (ps)	η
monolayer WSe_2 /Graphene	A exciton	0.60 (55.4%)	2.8 (38.9%)	114 (5.7%)	7.9	0.89
	B exciton	0.37 (66.2%)	1.7 (25.3%)	15 (8.5%)	2.0	0.86
	C exciton	0.69 (56.5%)	20 (43.5%)		9.1	0.79

carrier extraction efficiency: $\eta = 1 - \tau_{WSe_2-Graphene} / \tau_{WSe_2}$

REFERENCES

(1) H. G. Ji, P. Solís-Fernández, D. Yoshimura, M. Maruyama, T. Endo, Y. Miyata, S. Okada, H. Ago, *Adv. Mater.*, **2019,** 31, 1903613.

(2) D. Li, R. T. Chen, S. Y. Wang, X. W. Zhang, Y. Zhang, J. X. Liu, H. Yin, F. T. Fan, J. Y. Shi, C. Li, *J. Phys. Chem. Lett.*, **2020,** 11, 412-418.