Supporting Information

Avoiding Surface Defects Catalyzed Oxidation for Extraordinary Thermoelectric Performance in n-Type Iodine-Doped PbTe Compounds

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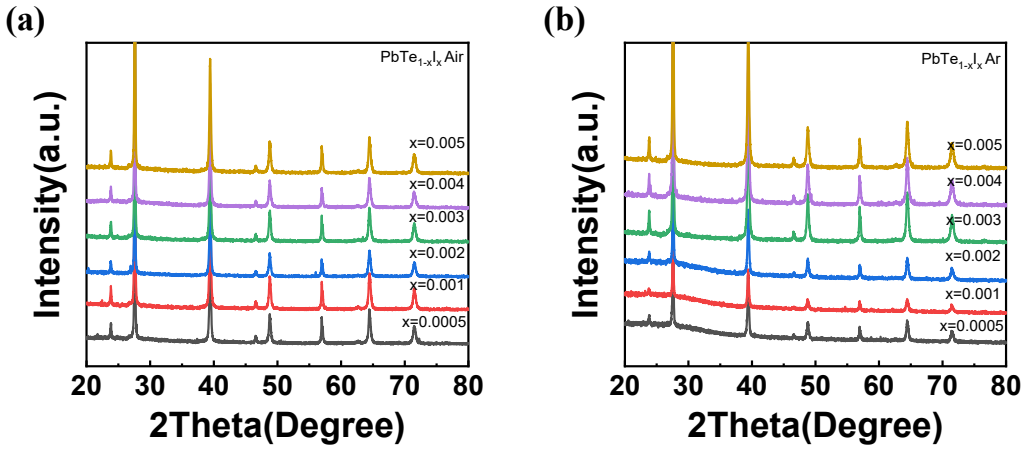

Figure S1. Powder XRD patterns of annealed $PbTe_{1-x}I_x$ samples ground inside and outside the glove box.

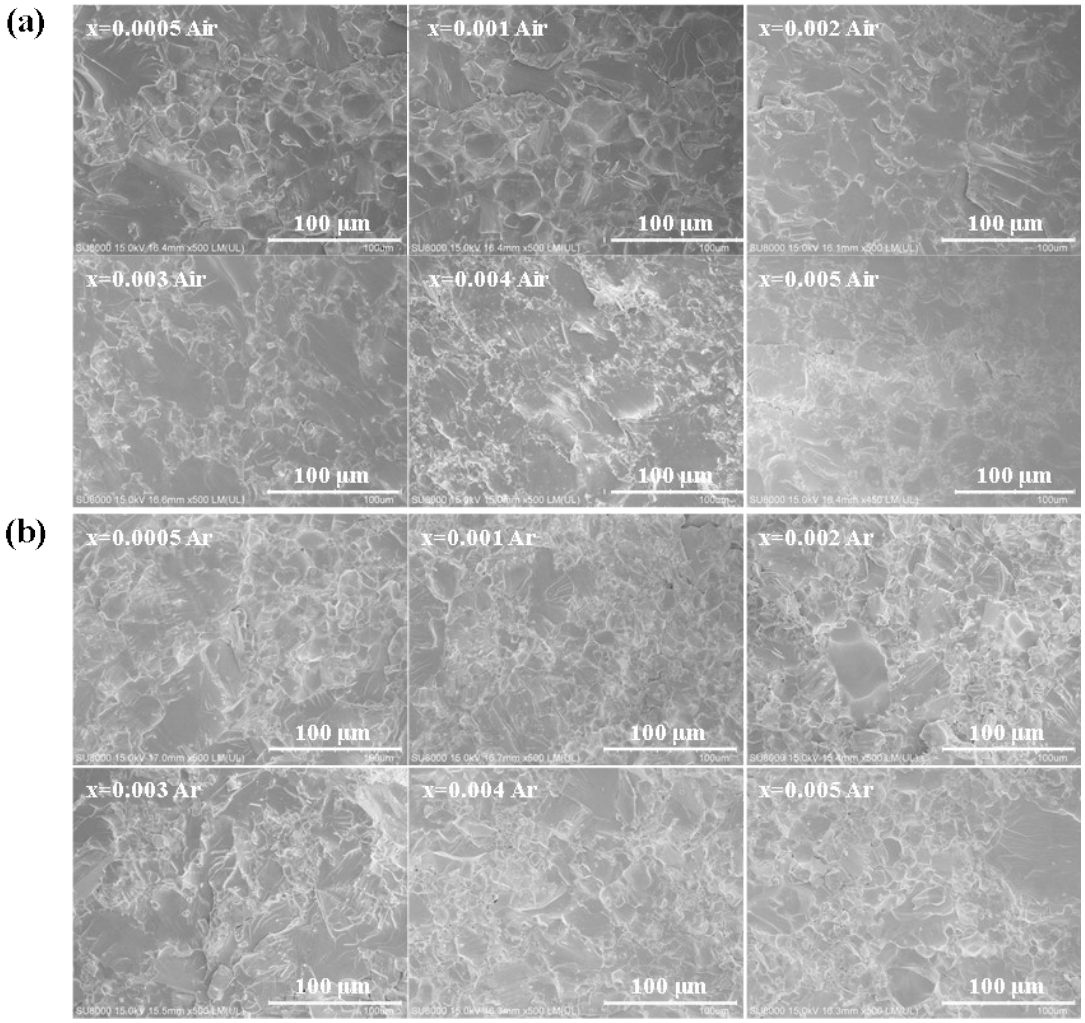

Figure S2. The SEM images for $PbTe_{1-x}I_x$ samples ground inside and outside the glove box.

Table S1. Theoretical positron annihilation lifetimes for the bulk materials of $Pb_{256}Te_{256}$, $Pb_{256}Te255O$, $Pb_{256}Te_{255}I$ and $Pb_{256}Te_{254}IO$, along with the lifetime for the Pb vacancy (V_{Pb}) generation.

Compouds	Bulk/ps	V_{Pb}/ps
$Pb_{256}Te_{256}$	235.1	300.6
$Pb_{256}Te255O$	239.8	304.6
$Pb_{256}Te_{255}I$	235.5	300.5
$Pb_{256}Te_{254}IO$	233.1	298.0

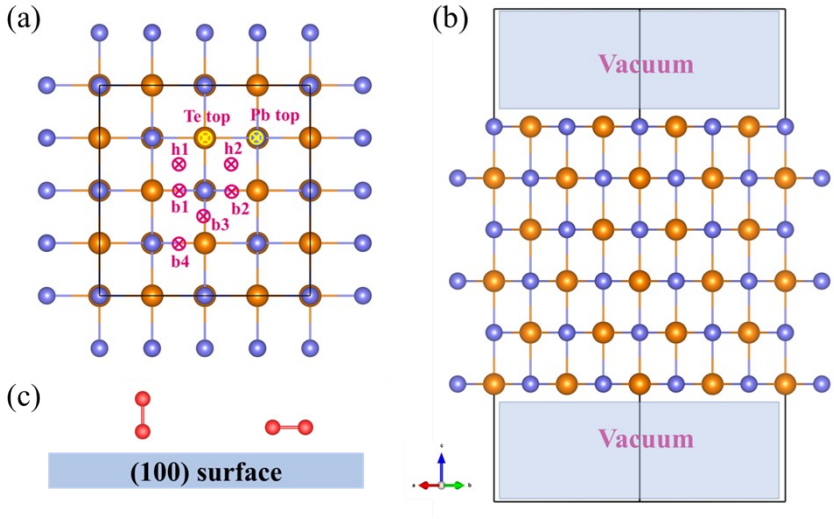

Figure S3 (a) and (b) are schematic diagrams of different adsorption sites of oxygen atoms on the PbTe surface; Figure (c) illustrates the vertical (⊥) and parallel (//) adsorption configurations of oxygen molecules.

Table S2. The formation energy of the vacancy defects on a (100) surface.

μ/eV	V_{Te}/eV	V_{Pb}/eV	V_{PbTe}/eV
Te_{rich}	2.34	1.60	0.91
Pb_{rich}	1.55	2.38	0.91

Table S3 presents the theoretical calculations of the adsorption energies and O–O bond lengths for single oxygen atoms (O), double oxygen atoms (2O), and oxygen molecules

(O_2) at different adsorption sites on the PbTe (001) surface. Various surface states are considered, including the pristine surface, V_{PbTe} (PbTe vacancy), I_{Te}, and I_{Te}+V_{PbTe} surfaces.

		Sites	Total Energy (eV)	E_{ab} (eV)	O-O Distance (Å)
clean	O	1 - Te Top	-383.75	0.26	\
		2 - Pb Top	-382.62	1.39	\
		3 -h1	-384.03	-0.02	\
		4 - b1	-384.43	-0.42	\
	2O	3-1	-390.40	-1.47	2.30
		3-3'	-390.16	-1.23	2.36
		4-3	-390.39	-1.46	2.30
		4-4	-390.70	-1.77	2.28
		4-4⊥	-390.89	-1.86	2.27
		4-4(180°)	-390.39	-1.46	2.30
	O^2	⊥ 3	-389.06	-0.13	1.25
		// 3-1	-388.75	0.18	1.45
		// 3-2	-389.11	-0.18	1.25
		⊥ 4	-388.31	0.71	1.28
		// 4-1	-388.64	0.29	1.38
		// 4-2	-388.69	0.24	1.38
I_{Te}	O	1 H	-367.44	-1.84	\
		2 Te Top	-367.49	-1.89	\
		3 Pb Top	-365.92	-0.32	\

		4 I Top	-367.06	-1.46	\
	2O	1-1	-373.67	-3.15	2.27
		1-2	-371.73	-1.21	2.36
	O^2	⊥ 1	-371.83	-1.31	1.36
		⊥ 3	-371.17	-0.65	1.26
		// 1-4	-371.56	-1.04	1.35
		// 1-3	-371.86	-1.34	1.33
		// 1-2	-371.83	-1.31	1.35
V_{PbTe}	O	1	-375.80	-0.85	\
		2	-375.81	-0.86	\
		3	-375.89	-0.94	\
		4	-375.49	-0.54	\
		5	-375.66	-0.71	\
		6	-375.82	-0.87	\
	2O	2-3	-380.29	-0.42	1.27
		3-6	-380.44	-0.57	2.21
		2-6	-381.58	-1.71	2.21
		6-6'	-381.44	-1.57	2.08
	O^2	3-5	-380.44	-0.57	1.27
		3-6	-380.44	-0.57	1.38
		⊥3	-380.45	-0.57	1.38
		⊥6	-380.44	-0.57	1.45
$I_{Te}+V_{PbTe}$	O	1	-359.55	-1.43	\
		2	-359.77	-1.65	\
		3	-359.26	-1.14	\

	4	-359.36	-1.24	\
	5	360.03	-1.91	\
	6	359.29	-1.17	\
	7	360.25	-2.13	\
2O	7-5	-364.83	-1.79	1.43
O^2	1、⊥ 7	-364.66	-1.62	/
	2、⊥ 5	-364.11	-1.07	1.35
	3、// 7-5	-364.73	-1.69	1.38
	4、// 7-6	-364.64	-1.60	1.39

Table S4 shows the adsorption energy and chemical adsorption potential barriers for different surfaces.

Surface	Single O E_{ab} (eV)	Double O E_{ab} (eV)	Oxygen E_{ab} (eV)	Barrier E_b (eV)
clean	-0.42	-1.72	-0.17	0.56
I_{Te}	-0.71	-1.49	-0.72	0.98
V_{PbTe}	-0.94	-1.71	-0.57	0.40
I_{Te}+V_{PbTe}	-1.96	-2.95	-1.49	0.17

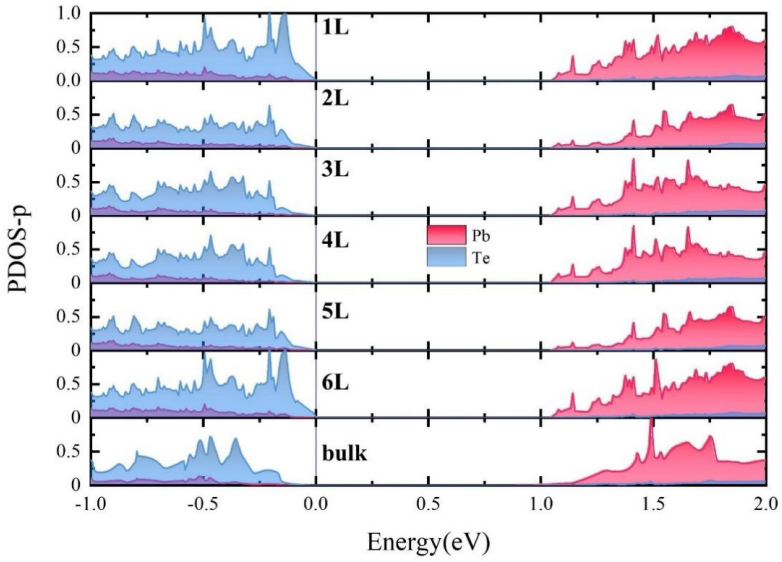

Figure S4. Calculated density of states before and after oxygen adsorption corresponding to different surfaces.

Table S5 displays the charge transfer between different atomic layers on the pristine PbTe (100) surface and in the bulk.

Positions	Charge transfer (e)	Bader(e)	Te-Pb Distance (Å)
1/6L-Te	-0.67	6.667	3.28
2/5L-Te	-0.61	6.607	3.28
3/4L-Te	-0.62	6.617	3.28
1/6L-Pb	+0.65	3.348	3.28
2/5L-Pb	+0.62	3.381	3.28
3/4L-Pb	+0.62	3.380	3.28
Bulk-Te	-0.66	6.662	3.28
Bulk-Pb	+0.66	3.338	3.28

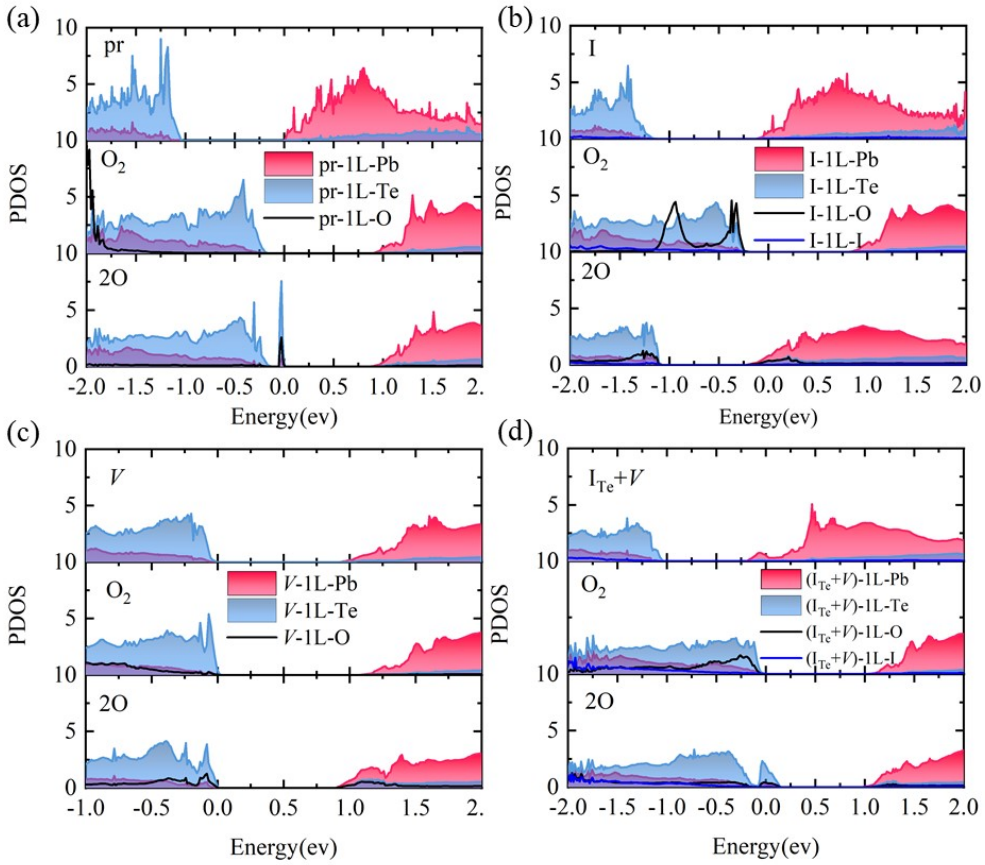

Figure S5. Calculated density of states before and after oxygen adsorption corresponding to different surfaces.

Table S6 presents the charge redistribution of surface atoms under various surface states.

	Te	Pb	2O-Te	2O-Pb	O^2-Te	O^2-Pb	2O-O	O^2-O
clean	-0.67	+0.65	+0.98	+0.81	-0.62	+0.68	-1.06	-0.08
I_{Te}	-0.67	+0.65	+0.04	+0.80	-0.62	+0.91	-1.06	-0.08
V_{PbTe}	-0.67	+0.65	+0.09	+0.77	-0.64	+0.71	-1.05	-0.32
$I_{Te+}V_{PbTe}$	-0.67	+0.55	+0.21	+0.80	-0.64	+0.80	-1.05	-0.44