

**Electronic supplementary information**

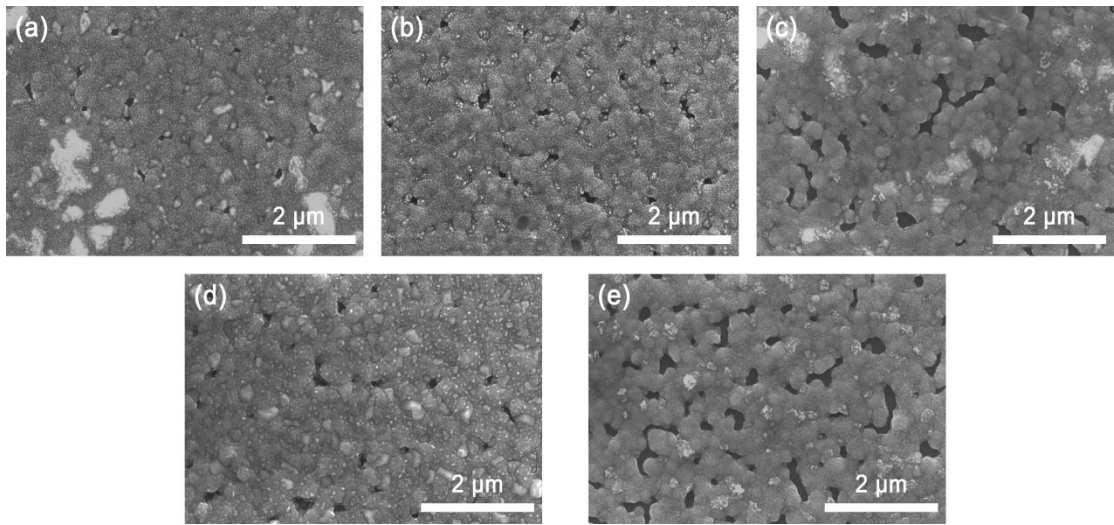
**Alkali doping strategy to improve the photovoltaic properties of  
 $\text{Ag}_2\text{BiI}_5$  solar cells**

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and Daocheng Pan<sup>a, b\*</sup>

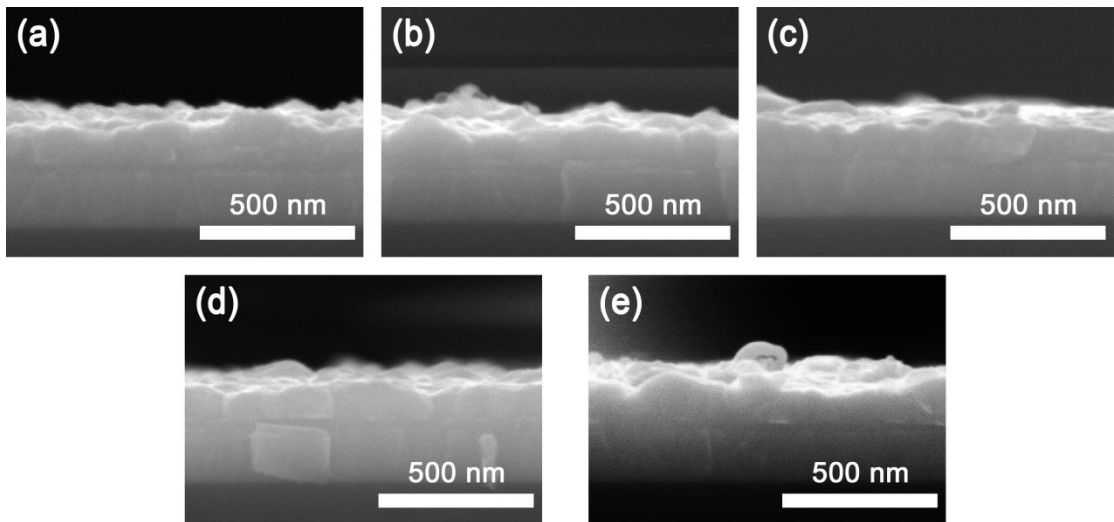
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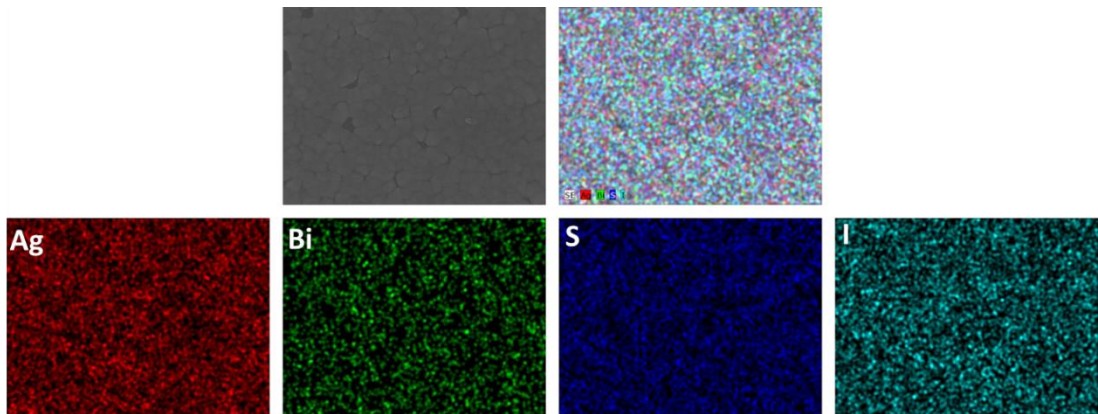
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**Fig. S1.** Top-view SEM images of as-prepared Ag-Bi-S-I films doped with (a)  $\text{Li}^+$ ; (b)  $\text{Na}^+$ ; (c)  $\text{K}^+$ ; (d)  $\text{Rb}^+$  and (e)  $\text{Cs}^+$ .



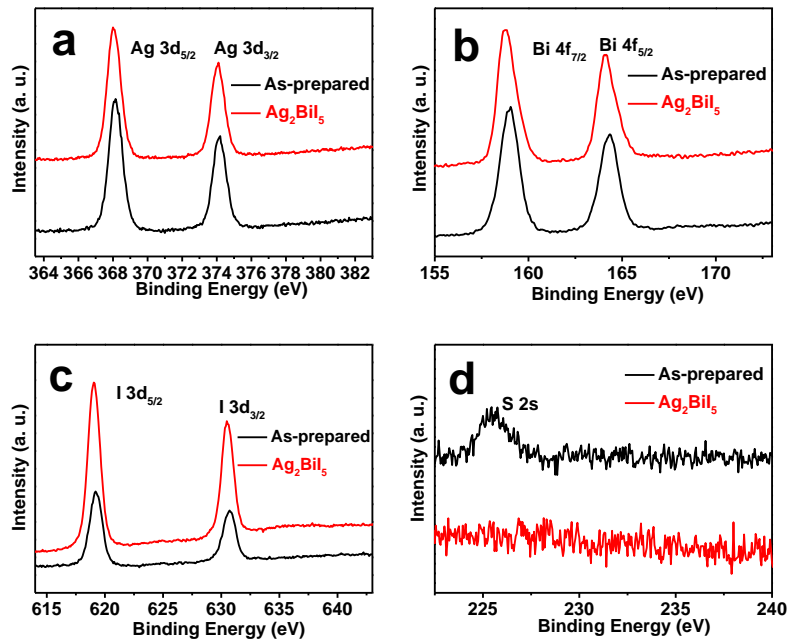
**Fig. S2.** Cross-sectional SEM images of as-prepared Ag-Bi-S-I films doped with (a)  $\text{Li}^+$ ; (b)  $\text{Na}^+$ ; (c)  $\text{K}^+$ ; (d)  $\text{Rb}^+$  and (e)  $\text{Cs}^+$ .



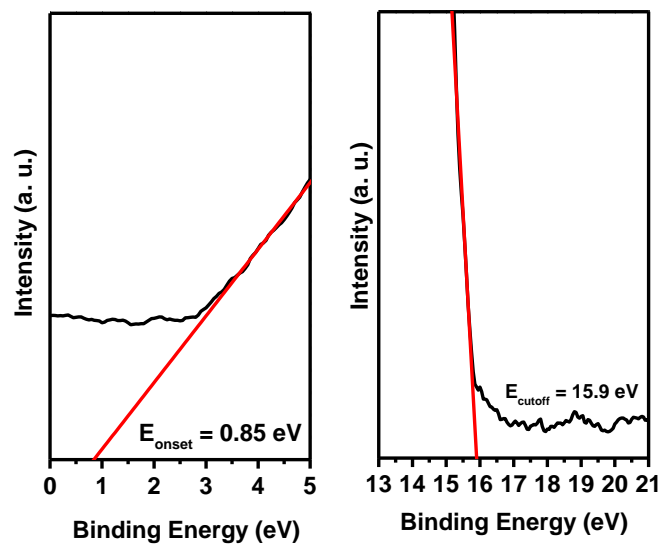
**Fig. S3.** The energy dispersive spectroscopy (EDS) mapping of as-prepared undoped  $\text{Ag}_2\text{BiI}_5$  film.

**Table S1.** The elements contents of the as-prepared  $\text{Ag}_2\text{BiI}_5$  thin films doped with different alkali ions.

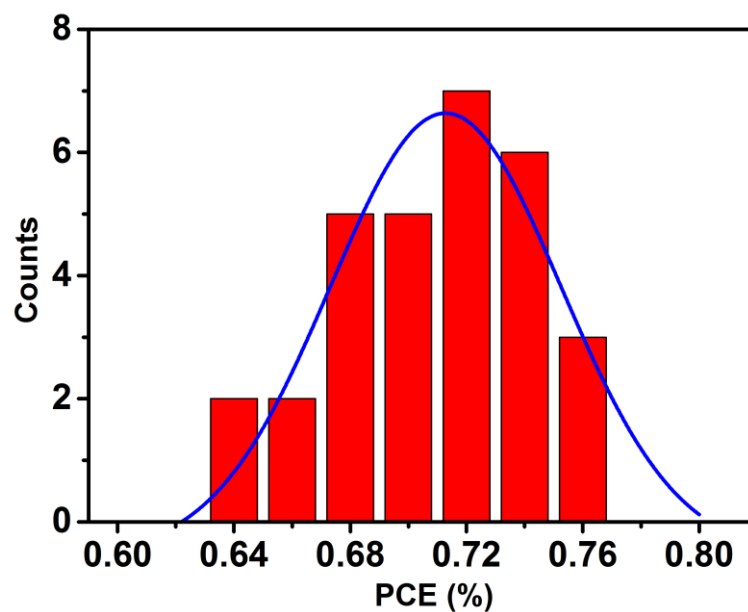
Sample	Ag (at.%)	Bi (at.%)	I (at.%)	alkali (at.%)	alkali/(Ag+Bi) (%)
$\text{Ag}_2\text{BiI}_5$	28.38	12.06	59.56	-	-
$\text{Ag}_2\text{BiI}_5:\text{Li}$	24.75	12.55	61.61	1.09	2.92
$\text{Ag}_2\text{BiI}_5:\text{Na}$	25.06	12.59	61.24	1.11	2.95
$\text{Ag}_2\text{BiI}_5:\text{K}$	25.29	12.72	61.86	1.13	2.97
$\text{Ag}_2\text{BiI}_5:\text{Rb}$	25.55	12.86	60.45	1.14	2.97
$\text{Ag}_2\text{BiI}_5:\text{Cs}$	25.70	13.07	60.05	1.18	3.04



**Fig. S4.** XPS spectra (a) Ag 3d, (b) Bi 4f, (c) I 3d, (d) S 2s of Ag<sub>2</sub>BiI<sub>5</sub> and as-prepared Ag-Bi-S-I thin films.



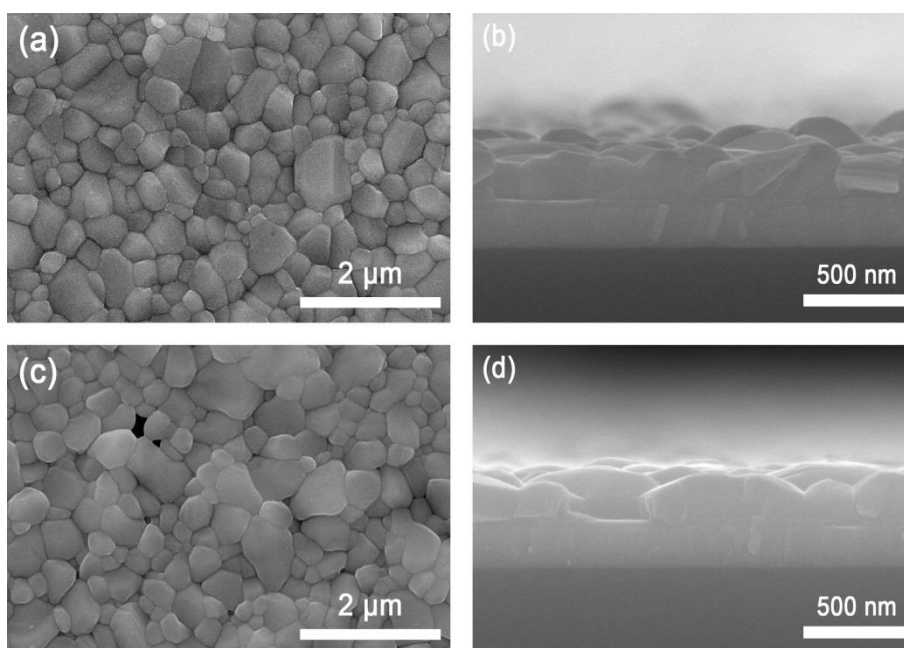
**Fig. S5.** UPS spectra of Ag<sub>2</sub>BiI<sub>5</sub> thin film.



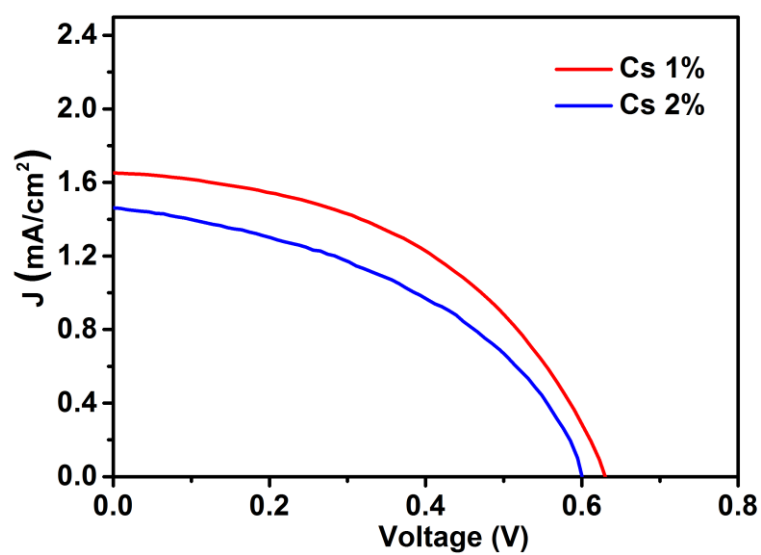
**Fig. S6.** Statistical efficiency distribution of 30 devices with the  $K^+$ -doped  $Ag_2BiI_5$  absorber layers.

**Table S2.** PV parameters of the  $Ag_2BiI_5$  solar cells with and without alkali doping (PTAA for HTL).

Sample	$J_{sc}$ ( $mA/cm^2$ )	$V_{oc}$ (V)	$FF$ (%)	PCE (%)
w/o	1.21	0.68	45.97	0.38
$Li^+$	1.31	0.70	53.61	0.49
$Na^+$	1.55	0.69	54.89	0.59
$K^+$	1.95	0.68	56.20	0.75
$Rb^+$	1.64	0.69	54.43	0.62
$Cs^+$	1.42	0.42	43.17	0.26



**Fig. S7.** Top-view and cross-sectional SEM images of 1% (a and b) and 2% (c and d) Cs<sup>+</sup>-doped Ag<sub>2</sub>BiI<sub>5</sub> thin films.



**Fig. S8.** *J-V* curves of 1% and 2% Cs<sup>+</sup>-doped Ag<sub>2</sub>BiI<sub>5</sub> solar cells.

**Table S3.** PV parameters of the 1% and 2% Cs<sup>+</sup>-doped Ag<sub>2</sub>BiI<sub>5</sub> solar cells (PTAA for HTL).

Sample	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	$FF$ (%)	PCE (%)
1%	1.65	0.63	46.96	0.49
2%	1.46	0.60	44.03	0.39