Supporting Information

High-capacity zinc-iodine flow batteries enabled by a polymer-polyiodide complex cathode

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S1. Volumetric Capacity and Energy Density

Given the stoichiometric ratio of transferred electron to iodine or iodide reactant (*ξ*), Faraday's constant (*F*), concentration of iodine or iodide reactant in the catholyte (*c*), and open circuit voltage (*OCV*), the theoretical volumetric capacity (C_V, Ah/L) and volumetric energy density (E_V, Wh/L) in the flow battery can be calculated by the following equations:

$$C_V = \frac{F \times C \times \xi}{3600} \tag{S1}$$

$$E_V = C_V \times OCV \tag{S2}$$

For 6 M KI, we can calculate the theoretical volumetric capacity and energy density of the ZIFB as follows:

$$Zn^{2+} + 3I^{-} \rightarrow Zn + I_3^{-} \qquad E = -1.299\ V \tag{S3}$$

$$C_V = \frac{96485 \times 6 \times \frac{2}{3}}{3600} = 107.2\ \ (Ah/L)$$

$$E_V = 107.2 \times 1.299 = 139.25\ \ (Wh/L)$$

For 6 M KI with PVP, we can calculate the theoretical volumetric capacity and energy density of the PVP-ZIFB as follows:

$$Zn^{2+} + 3I^{-} + PVP \rightarrow Zn + PVP\text{?}I_3^{-} \qquad E = -1.299\ V \tag{S4}$$

$$C_V = \frac{96485 \times 6 \times 1}{3600} = 160.8 \ \ (Ah/L)$$

$$E_V = 160.8 \times 1.299 = 208.87 \ \ (Wh/L)$$

It is noted that both reaction (S3) and (S4) can exist in the catholyte of PVP-ZIFB. For 6 M I^-, therefore, the volumetric capacity would be a value between 107.2 to 160.8 Ah/L, while the energy density is between 139.25 and 208.87 Wh/L, as summarized in Table S4.

S2. Molar Capacity

Molar capacity (C_n) is defined as the volumetric discharge capacity per molar concentration of I^- initially dissolved in catholyte, as given in Eq. (S5)

$$C_n = \frac{C_V}{C_s} \tag{S5}$$

where C_V is the volumetric capacity for a given salt concentration of C_s in catholyte, which can be further derived as shown in Eq. (S6)

$$C_V = \frac{Q_e}{V_s} = \frac{n_e F}{\frac{n_s}{c_s}} = \frac{n_e}{n_s} F c_s = \xi_{e/s} F c_s \tag{S6}$$

where Q_e is the total quantity of electric charge from the electrochemical conversion between iodide and triiodide/iodine in catholyte, V_s is the volume of the catholyte, F is Faraday constant, n_e is the molar amount of transferred electrons and n_s is the molar amount of the salt in the fixed volume of catholyte where the subscript s means KI or ZnI_2 dissolved in catholyte, $\xi_{e/s}$ means the stoichiometric number of transferred electrons with respect to different salt solutes. Combining Eq. (S5) and Eq. (S6), one can obtain Eq. (S7)

$$C_n = \xi_{e/s} F \tag{S7}$$

where $\xi_{e/s}$ is 2/3 for KI, 1 for KI with PVP and 2 for ZnI_2. Based on Eq. (S7), the theoretical molar capacities of KI, KI with PVP and ZnI_2 are calculated to be 17.87 26.8 and 35.74 Ah/mol, respectively.

$$C_n = \xi_{e/s} F \ = \frac{2}{3} \times 96484 = 17.86 \ \ (Ah/mol)$$

$$C_n = \xi_{e/s} F \ = 1 \times 96484 = 26.8 \ \ (Ah/mol)$$

$$C_n = \xi_{e/s} F \ = 2 \times 96484 = 35.74 \ \ (Ah/mol)$$

Finally, the unlock capacity can be defined as

$$\text{Unlock capacity (\%)} = \frac{C_n(KI + PVP) - C_n(KI)}{C_n(KI)} \times 100\%$$

$$\text{Unlock capacity (\%)} = \frac{C_n(ZnI_2 + complexing\ agent) - C_n(ZnI_2)}{C_n(ZnI_2)} \times 100\%$$

The unlocking capacities for different catholyte compositions are summarized in

Table S7.

S3. Cost calculation

The cost of each of the chemicals is referred to the website (www.macklin.cn), which is listed in Table S5. Based on Table S5 and S6, the cost of the iodine-based catholyte can be estimated according to the following equations:

For inorganic additives:

$$Cost\ of\ catholyte\ (\$/(mol \cdot L^{-1})) = \left[P_a \times \frac{1}{C_a} + P_{a,s} \times \frac{1}{C_{a,s}}\right] \times \frac{1\ Ah}{Cap_a} \tag{S8}$$

For polymer additives:

$$Cost\ of\ catholyte\ (\$/(mol \cdot L^{-1})) = [P_a \times \frac{1\ Ah}{Cap_a}] \times \frac{1}{C_a} + \frac{P_{1,a,s} \times m_{a.s}}{C_a} \tag{S9}$$

where in the catholyte, the P_a is the price of active material (\$/mol), C_a is the concentration of the active material (mol/L), $P_{a,s}$ is the cost of the supporting material (\$/mol), $P_{1,a,s}$ is the cost of the supporting material (\$/g), C_a is the concentration of active material (mol/L), $C_{a,s}$ is the concentration of supporting electrolyte (mol/L), and Cap_a are the capacity at the given active material (Ah/mol), the $m_{a,s}$ is the mass of the supporting material (g).

For KI:

$$P_{KI} = 0.09\frac{\$}{g} \times 166\frac{g}{mol} = 14.96\frac{\$}{mol}$$

$$Cost\ of\ (KI) = P_{KI} \times \frac{1\ Ah}{Cap_{KI}}$$

$$= 14.96 \times \frac{1}{12} \times 1 = 1.186\ (\$/(mol \cdot L^{-1}))$$

For KI+PVP:

$$P_{KI} = 0.09\frac{\$}{g} \times 166\frac{g}{mol} = 14.96\frac{\$}{mol}$$

$$Cost\ of\ (PVP) = \left(0.03\frac{\$}{g} \times 0.18\ g\right) = 0.005\ (\$)$$

$$Cost\ of\ (KI + PVP) = [P_{KI} \times \frac{1\ Ah}{Cap_{KI}}] \times \frac{1}{C_{KI}} + \frac{P_{PVP} \times m_{PVP}}{C_{KI}}$$

$$= \frac{14.96}{19} + 0.005 = 0.754\ (\$/(mol \cdot L^{-1}))$$

For ZnI_2:

$$P_{ZnI_2} = \left(0.16\,\frac{\$}{g} \times 319\,\frac{g}{mol}\right) = 51.04\,\left(\frac{\$}{mol}\right)$$

$$Cost\ of\ (ZnI_2) = P_{ZnI_2} \times \frac{1\ Ah}{Cap_{ZnI_2}} \times \frac{1}{C_{ZnI_2}} = \frac{51.04}{28} = 1.82\ (\$/(mol \cdot L^{-1}))$$

For ZnI_2+$ZnBr_2$:

$$P_{ZnI_2} = \left(0.16\,\frac{\$}{g} \times 319\,\frac{g}{mol}\right) = 51.04\,\left(\frac{\$}{mol}\right)$$

$$P_{ZnBr_2} = \left(0.06\,\frac{\$}{g} \times\ 225\,\frac{g}{mol}\right) = 11.18\,\left(\frac{\$}{mol}\right)$$

$$Cost\ of\ (ZnI_2 + ZnBr_2) = \left[P_{ZnI_2} \times \frac{1}{C_{ZnI_2}} + P_{ZnBr_2} \times \frac{1}{C_{ZnBr_2}}\right] \times \frac{1\ Ah}{Cap_{ZnI_2}}$$

$$= \frac{51.04 + 14.18 \times 2}{35} = 2.09\ (\$/(mol \cdot L^{-1}))$$

For NH_4I+NH_4Cl:

$$P_{NH_4I} = \left(0.16\,\frac{\$}{g} \times 144.94\frac{g}{mol}\right) = 23.19\,\left(\frac{\$}{mol}\right)$$

$$P_{NH_4Cl} = \left(0.006\,\frac{\$}{g} \times 53.49\frac{g}{mol}\right) = 0.33\,\left(\frac{\$}{mol}\right)$$

$$Cost\ of\ (NH_4I + NH_4Cl) = \left[P_{NH_4I} \times \frac{1}{C_{NH_4I}} + P_{NH_4Cl} \times \frac{1}{C_{NH_4Cl}}\right] \times \frac{1\ Ah}{Cap_{NH_4I}}$$

$$= \frac{23.19 + 0.33 \times 2}{17.9} = 1.33\ (\$/(mol \cdot L^{-1}))$$

For ZnI_2+ NH_4Br:

$$P_{ZnI_2} = \left(0.16\,\frac{\$}{g} \times 319\,\frac{g}{mol}\right) = 51.04\,\left(\frac{\$}{mol}\right)$$

$$P_{NH_4Br} = \left(0.016\,\frac{\$}{g} \times 97.94\frac{g}{mol}\right) = 1.57\left(\frac{\$}{mol}\right)$$

$$Cost\ of\ (ZnI_2 + NH_4Br) = \left[P_{ZnI_2} \times \frac{1}{C_{ZnI_2}} + P_{NH_4Br} \times \frac{1}{C_{NH_4Br}}\right] \times \frac{1\ Ah}{Cap_{ZnI_2}}$$

$$= \frac{51.04 + 1.57}{35} = 1.50\ (\$/(mol \cdot L^{-1}))$$

For NaI:

$$P_{NaI} = \left(0.11\,\frac{\$}{g} \times 149.89\,\frac{g}{mol}\right) = 16.49\,\left(\frac{\$}{mol}\right)$$

$$Cost\ of\ (NaI) = \left[P_{NaI} \times \frac{1}{C_{NaI}}\right] \times \frac{1\ Ah}{Cap_{NaI}}$$

$$= \frac{16.49}{17.86} = 0.92\ (\$/(mol \cdot L^{-1}))$$

$$Cost\ of\ (NaI + PC) > 0.92\ (\$/(mol \cdot L^{-1}))$$

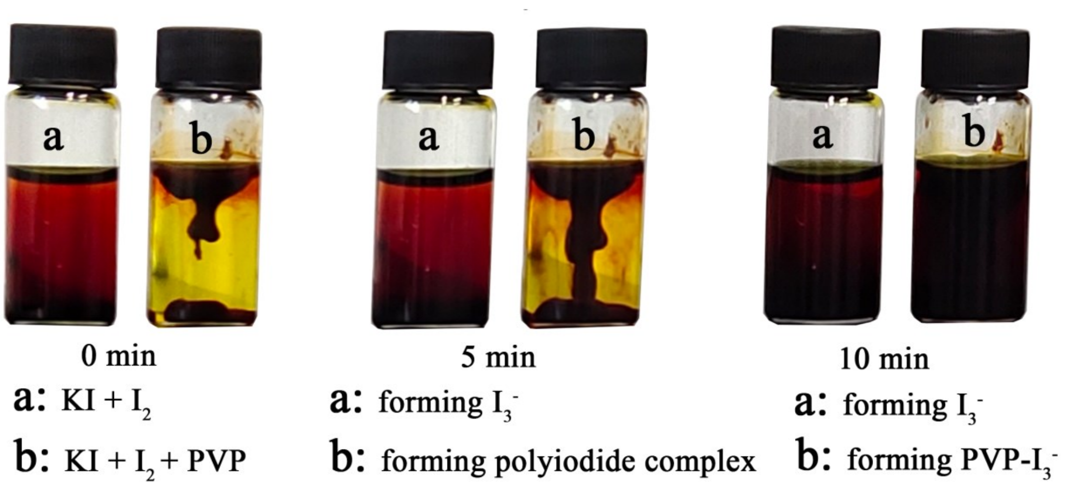

Fig. S1. Variations of the KI solutions with and without PVP additives over time (a) 0 min; (b) 5 min; (c) 10 min.

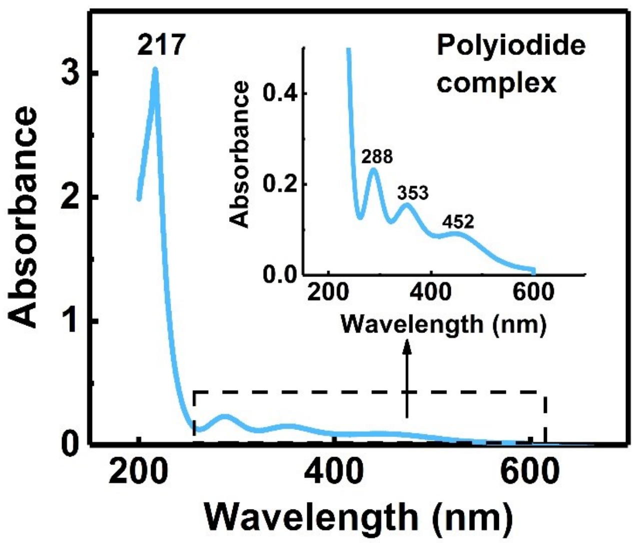

Fig. S2. Ultraviolet spectrum of polyiodide complex.

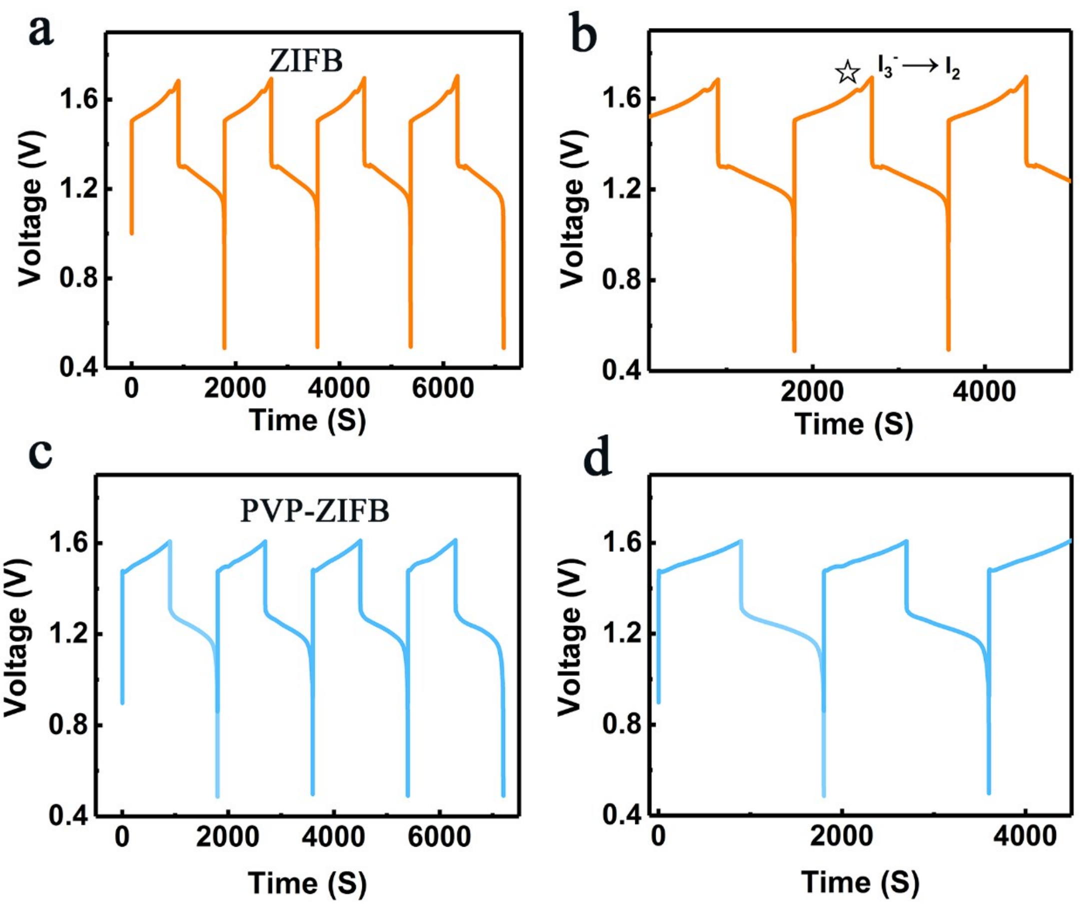

Fig. S3. Charge-discharge voltage profiles at 20 mA cm^{-2}. (a)-(b) ZIFB; (c)-(d) PVP-ZIFB.

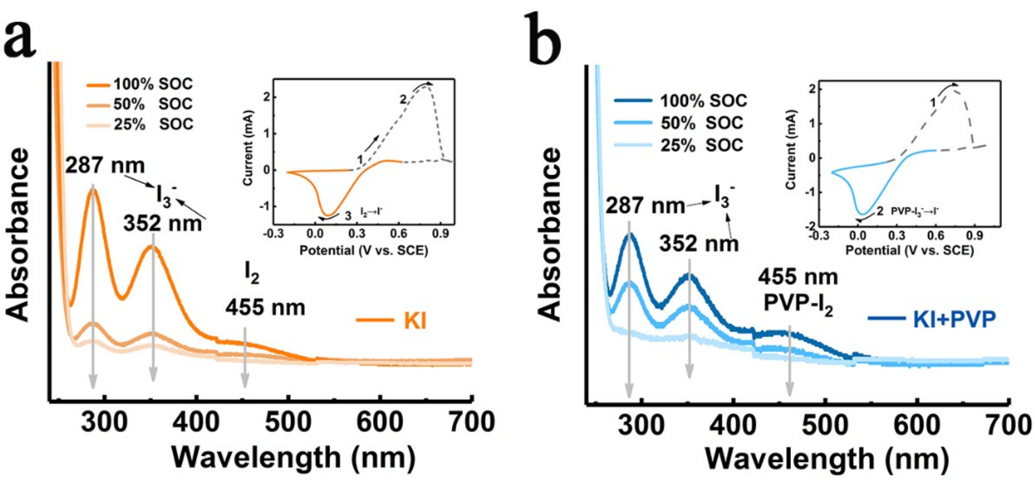

Fig. S4. The variations of UV-Vis spectra upon reduction for (a) 1 M KI and (b) 1 M KI + PVP.

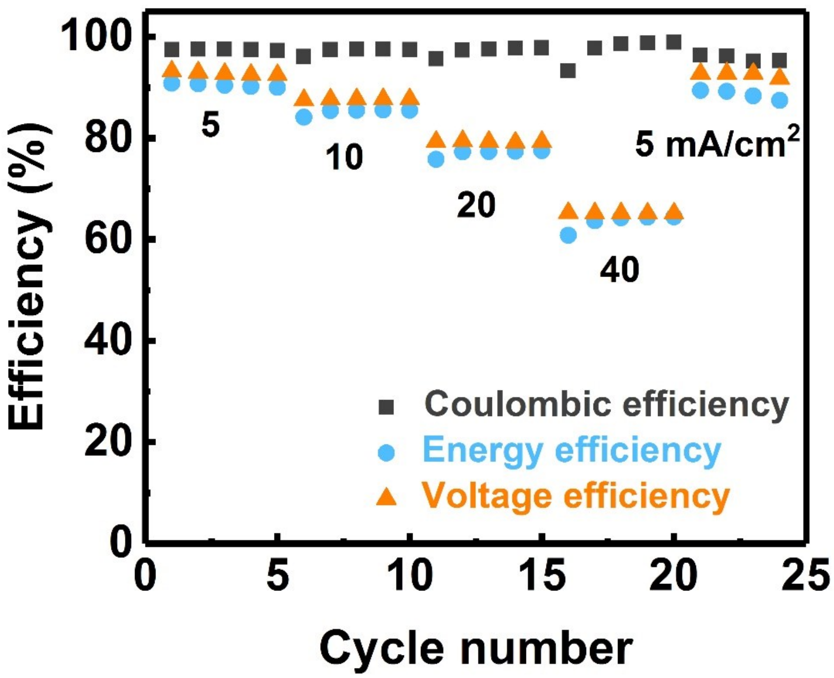

Fig. S5. Rate performance of PVP-ZIFB.

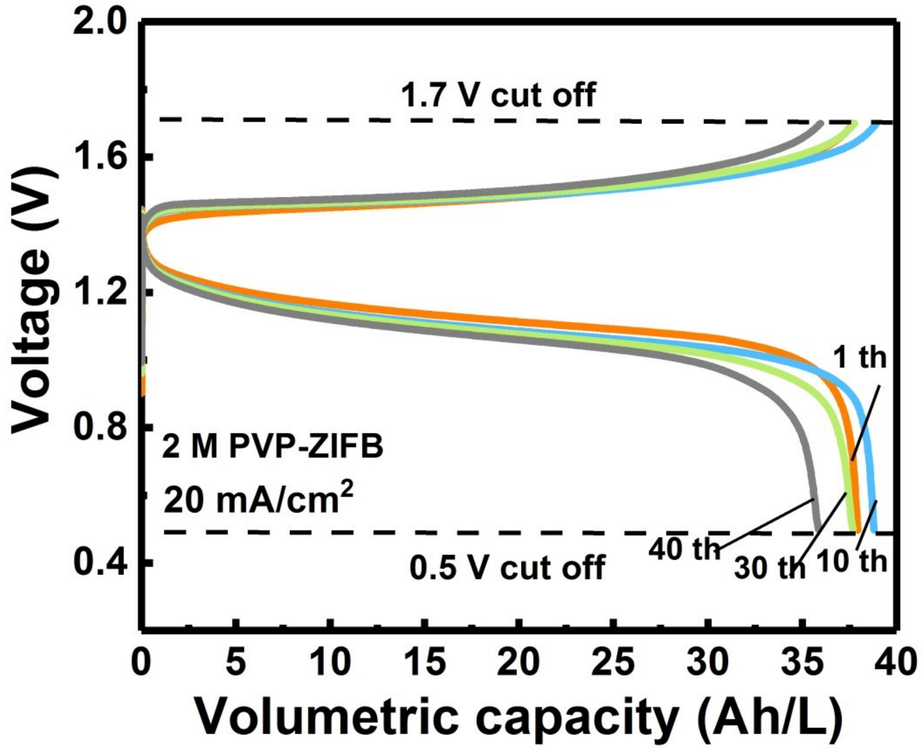

Fig. S6. Charge-discharge curves of PVP-ZIFB at 20 mA cm^{-2} with 2 M I^-.

Fig. S7. Carbon felts after long-term charge-discharge cycling (120 h).

Table S1. Calculated binding energy of NVP-I_2

NVP-I_2/Hatree	NVP/Hatree	I_2/Hatree	Binding energy (Ha)
-14203.8274268	-363.6827210	-13840.1294754	-0.0152

Table S2. Summary of ZIFB and PVP-ZIFB performance for 1 M I^- at 20 mA cm^{-2}

System	Average charge voltage (V)	Average discharge voltage (V)	Volumetric discharge capacity (Ah/L)
ZIFB	1.65	1.2	12
PVP-ZIFB	1.55	1.3	19

Table S3. Summary of PVP-ZIFB performance at 20 mA cm^{-2} with different concentrations of I^-

Catholyte composition	Average charge Voltage (V)	Average discharge Voltage (V)	Volumetric discharge capacity (Ah/L)
1 M I^-	1.55	1.3	19
2 M I^-	1.5	1.2	37
6 M I^-	1.45	1.15	115

Table S4. Theoretical volumetric capacity and energy density of PVP-ZIFB

Catholyte composition	Theoretical volumetric capacity (Ah/L)	Theoretical energy density (Wh/L)
1 M I^-	17.86-26.8	23.2-34.8
4 M I^-	71.47-107.2	92.83-139.2
6 M I^-	107.2-160.8	139.2-208

Table S5. The costs of chemicals

Chemical materials	Price ($/kg)	Molar mass (g/mol)
KI	85.7	166
ZnI_2	159.88	319
$ZnBr_2$	49.7	225
NH_4Br	15.83	97.94
NH_4Cl	6.114	53.49
NH_4I	160.68	144.94
PVP	27.77	N/A

Table S6. Molar capacity for different catholyte compositions

Catholyte composition	Molar capacity (Ah/mol)	Reference
KI	12	This work
ZnI_2	28	[20]
ZnI_2+NH_4Br	39	[20]
ZnI_2+$ZnBr_2$	35	[27]
ZnI_2	34	[18]
NH_4I/NH_4Cl	17.9	[22]
KI+PVP	19	This work

Table S7. Comparison of the PVP-ZIFB system with other ZIFB systems

Catholyte	Concentration of I^- (mol L^{-1})	Electrode area (cm^2)	Unlocking capacity (%)	Price (\$/mol L^{-1})	No. of cycles	Current density (mA/cm^2)	CE/EE	Reference
KI	6	28	0	1.19	50	20	99%/78%	This work
ZnI_2	1	5	0	1.82	30	40	99%/82%	[20]
ZnI_2	7	40	21%	1.5	40	10	99%/82%	[18]
ZnI_2+NH_4Br	1	5	39.2%	1.5	100	40	99%/85%	[20]
ZnI_2+$ZnBr_2$	7	4	38.8%	3.72	50	10	~95%/N/A	[27]
NH_4I+NH_4Cl	2.5	9	49.2%	1.33	1200	20	99%/88%	[22]
NaI+PC	1.5	5 *	48.8%	> 0.92**	50	20	90%/68%	[25]
KI+PVP	6	28	58.3%	0.75	600	20	99%/79%	This work

* Based on observation from the photo [25]

** Mass of PC is not available in [25]