

Supplementary Information

Bulk and Interfacial Decomposition of Formamidinium Iodide ($\text{HC}(\text{NH}_2)_2\text{I}$) in Contact with Metal Oxide

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Synthesis and Crystalline Phase Characterization of FAPbI₃

The FAPbI₃ powders were synthesized following previously published results.¹ Briefly, 215 mg of FAI was dissolved in 5 ml acetonitrile (ACN, 99.8+%, Alfa Aesar) and then 576 mg of PbI₂ (FAI: PbI₂ = 1:1 molar ratio) was slowly added to the above mixture. The solution was stirred at room temperature for 12 h. The precipitate was washed using diethyl ether ($\geq 99.7\%$, Sigma-Aldrich) in sequence several times by centrifuging at 3000 rpm for 10 min and the powder was obtained by drying in a desiccator overnight. The powder was then dried in a vacuum furnace at 150 °C for 4 h. To determine the crystalline phase of FAPbI₃, we performed powder X-ray diffraction (XRD) using a Rigaku Ultima III diffractometer (40 kV/44 mA) equipped with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Data were collected over a 2θ range from 10° to 50° with a step size of 0.02° and a scan speed of 2°/min. The crystalline phase was identified by comparing it with the reported FAPbI₃ XRD pattern.¹ As shown in Figure S1, the XRD pattern matches well with the reported pattern for the α -phase of FAPbI₃¹, and no additional peaks corresponding to the impurity phase are observed. Thus, a pure α -FAPbI₃ perovskite phase is obtained.

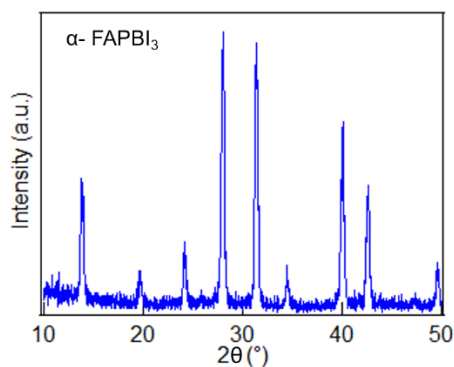


Figure S1. XRD pattern of pure phase α -FAPbI₃ perovskite. The pattern matches well with the reported data in the literature.¹

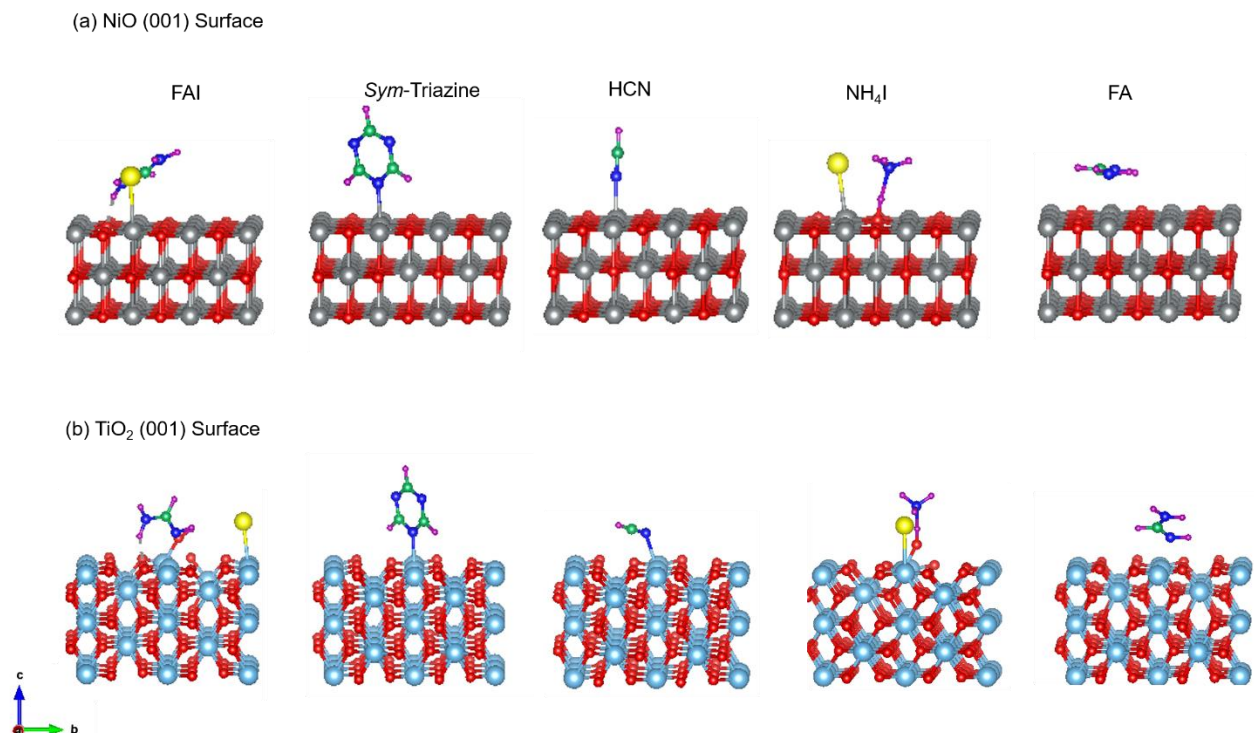


Figure S2. Adsorption configurations of FAI (FA+I), *sym*-triazine, HCN, NH₄I, and FA on (a) NiO (001) and (b) TiO₂ (001) surfaces. Pink, royal blue, green, yellow, grey, light blue, and red balls represent the H, N, C, I, Ni, Ti, and O atoms, respectively.

The TGA-DSC curves for neat FAPbI₃, FAPbI₃ + NiO, and FAPbI₃ + TiO₂ are shown in Figure S3. The neat FAPbI₃ (Figure S3a) undergoes thermal decomposition, the onset of which occurs at ~330 °C (blue dashed line) and 23% weight is lost (black curve) by ~350 °C with corresponding endothermic peak (red curve), in agreement with the weight of FAI in FAPbI₃ (27 %). This result is in good agreement with previous reports.^{2,3} When FAPbI₃ is in contact with NiO (Figure S3b), the onset of decomposition shifts to a much lower temperature of ~220 °C (blue dashed line) with 23% weight lost by 280 °C, consistent with the amount of FAI (24%) in FAPbI₃ + NiO sample. In the case of FAPbI₃ + TiO₂ (Figure S3c), the onset of decomposition occurs at 260 °C (blue dashed line) and completes by 310 °C with 23% weight lost, corresponding

to the weight of FAI (24%) in the $\text{FAPbI}_3 + \text{TiO}_2$ sample. These results indicate that metal oxide affects the thermal stability of FAPbI_3 perovskite.

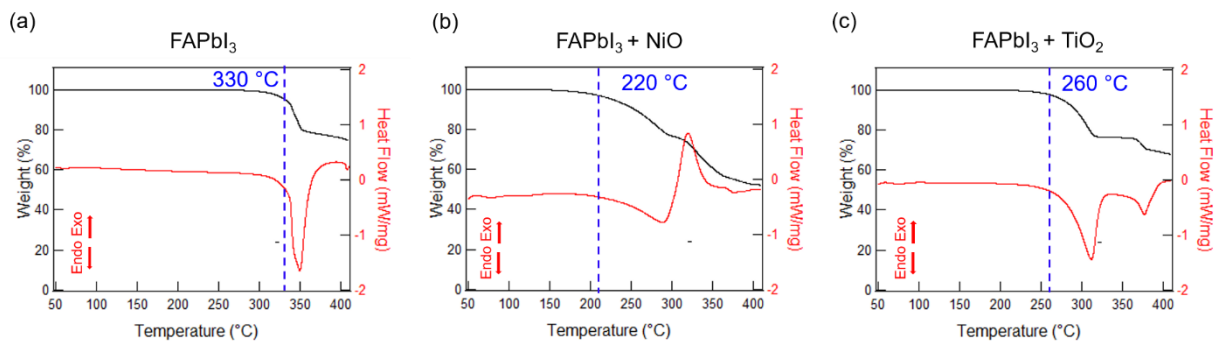


Figure S3. TGA (black, left y-axis) and DSC (red, right y-axis) curves for (a) FAPbI_3 , (b) $\text{FAPbI}_3 + \text{NiO}$ (1:1), and (c) $\text{FAPbI}_3 + \text{TiO}_2$ (1:1) heated from 25 °C to 400 °C at 10 °C/min under 100 sccm of N_2 flow. The blue dashed lines represent the onset of thermal decomposition in each case.

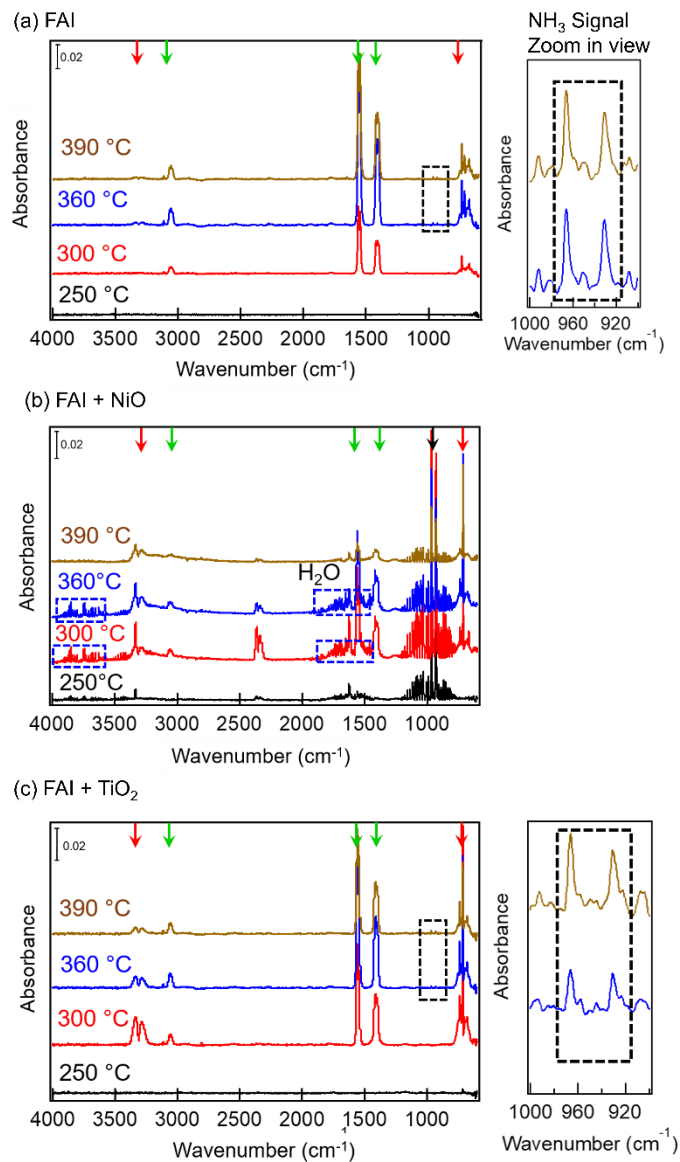


Figure S4. FTIR spectra at selected temperatures for 1:1 molar ratio of (a) FAI, (b) FAI + NiO, and (c) FAI + TiO₂ collected at 250 °C (black), 300 °C (red), 360 °C (blue), and 390 °C (brown). The characteristic vibrational frequencies of NH₃, HCN, and *sym*-triazine ((HCN)₃) gases are marked with black, red, and green arrows, respectively. The dotted black (zoom in view in (a,c)) and blue rectangles (in (b)) represent NH₃ and H₂O, respectively. All assignments are based on NIST database.⁴

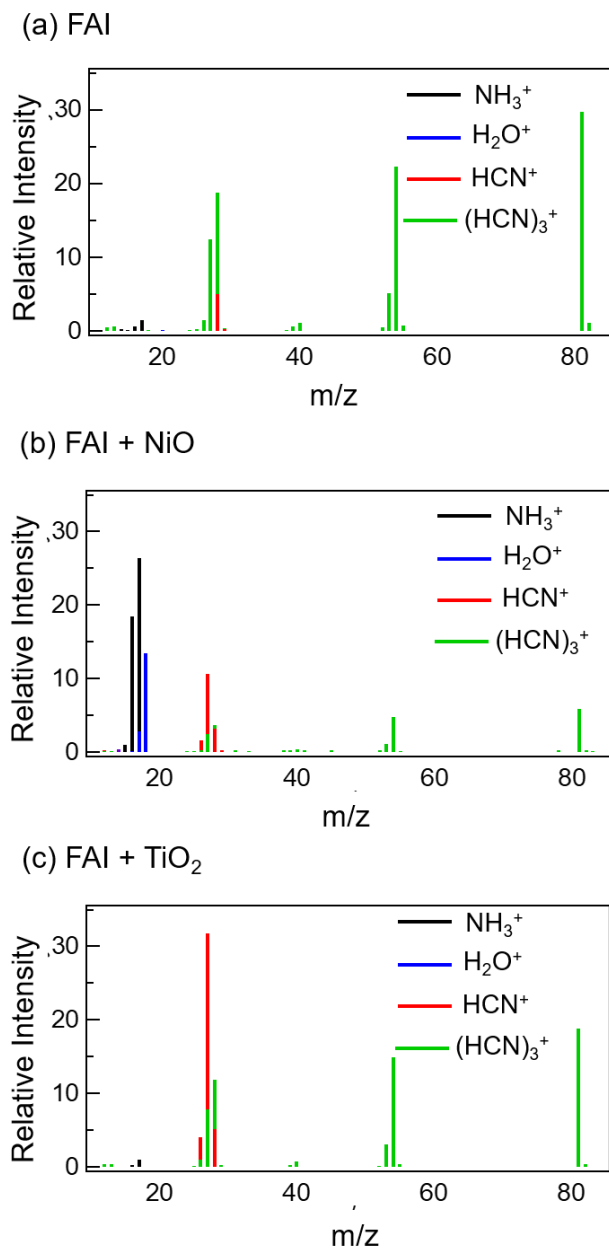


Figure S5. TPD-MS bar charts for 1:1 molar ratio of (a) FAI, (b) FAI + NiO, and (c) FAI + TiO₂ showing fragmentation patterns for NH₃⁺, H₂O⁺, HCN⁺, and (HCN)₃⁺ based on NIST database.⁵

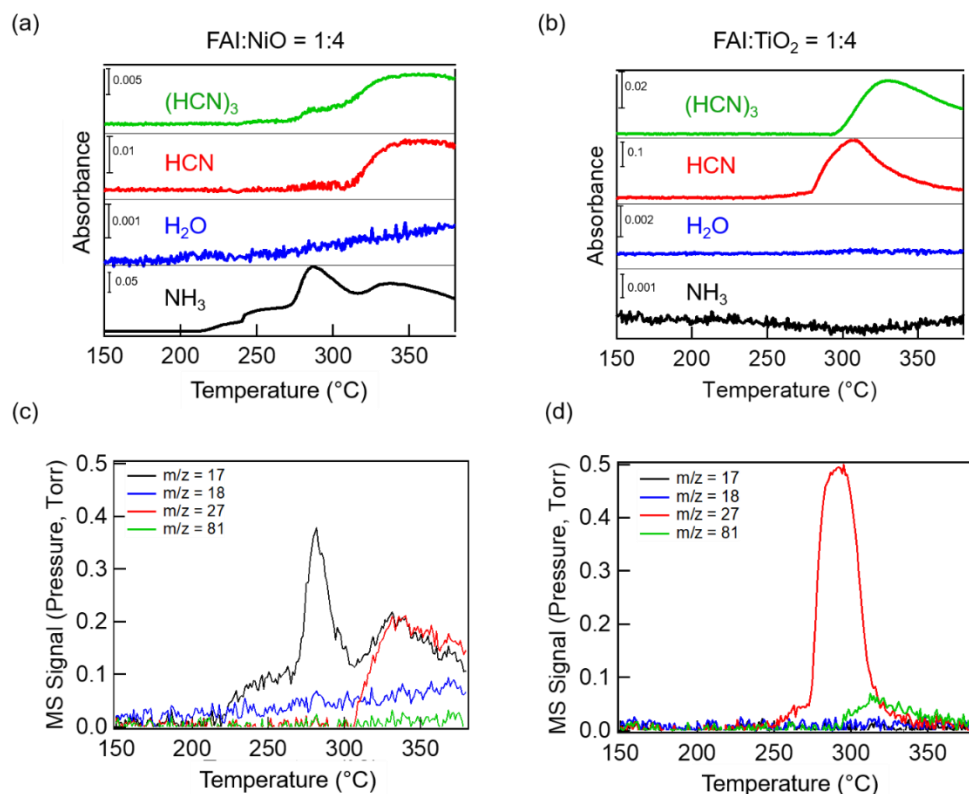
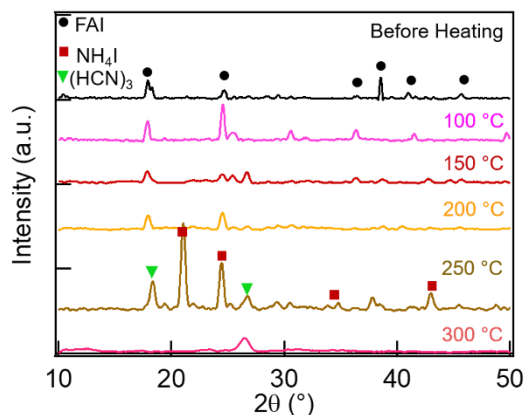


Figure S6. TPD-FTIR-MS results for 1:4 molar ratios of FAI:NiO (left) and FAI:TiO₂ (right). (a,b) FTIR temperature profiles and (c,d) MS temperature profiles. The black, blue, red, and green lines represent NH₃, H₂O, HCN, and *sym*-triazine, respectively. All assignments are based on NIST database.^{4,5}

In Figure S7a, we present XRD patterns of neat FAI. Before heating the sample (black), the reflections of crystalline FAI (black circles) are observed. With heating, the FAI peaks decrease and by 250 °C (brown), obvious changes are observed, consistent with the onset of decomposition shown in TGA-DSC results (Figure 1a). The main peaks can be indexed to NH₄I phase (maroon squares) and the minor peaks correspond to *sym*-triazine phase (green inverted triangles). On further heating to 300 °C (magenta), we see the loss of NH₄I and *sym*-triazine signals, indicating the complete decomposition of the solid organic compound. When FAI is mixed with NiO (Figure S7b), before heating (black), reflections associated with crystalline FAI (black circles) and NiO (pink pentagons) are seen. After heating to 200 °C (orange), we see the appearance of new peaks

corresponding to NiI_2 (violet diamonds), consistent with the onset of decomposition. NH_4I peaks (maroon squares) are also observed, but with much weaker intensity than in neat FAI. On further heating to 250 °C (brown), we see the growth of NiI_2 . By 300 °C (magenta), only NiI_2 peaks are evident, providing support for the interfacial reaction. In the case of FAI mixed with TiO_2 (Figure S7c), the XRD patterns before heating (black) show the presence of FAI (black circles) and TiO_2 (blue dumbbells). However, after heating to 250 °C (brown), only TiO_2 peaks are present. No peaks corresponding to NH_4I are observed as in the case of FAI. No TiI_4 is found, further validating that as FAI decomposes, there are no reactions with TiO_2 .

(a) FAI



(b) FAI + NiO

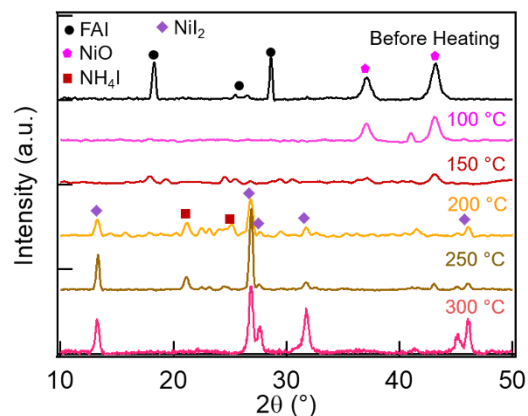
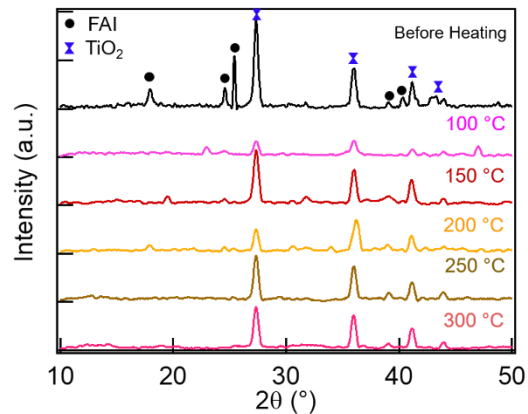
(c) FAI + TiO₂

Figure S7. XRD patterns for 1:1 molar ratio of (a) FAI, (b) FAI + NiO, and (c) FAI + TiO₂ powders before heating (black) and after heating to 100 °C (pink), 150 °C (maroon), 200 °C (orange), 250 °C (brown), and 300 °C (magenta) for 10 min. Peaks associated with crystalline FAI, NiO, TiO₂, NH₄I, *sym*-triazine, and NiI₂ are marked by black circles, pink pentagons, blue dumbbells, maroon squares, green inverted triangles, and violet diamonds, respectively.

Table S1. Reaction energies of neat FAI, FAI on NiO(001), and FAI on TiO₂(001).

	Neat FAI (eV)	FAI on NiO (001) (eV)	FAI on TiO ₂ (001) (eV)
$\text{CH}(\text{NH}_2)_2\text{I} = \frac{1}{3}(\text{HCN})_3 + \text{NH}_3 + \text{HI}$	0.69	-0.09	0.42
$\text{CH}(\text{NH}_2)_2\text{I} = \text{HCN} + \text{NH}_3 + \text{HI}$	1.63	0.75	1.0
$\text{CH}(\text{NH}_2)_2\text{I} = \text{NH-CH-NH}_2 + \text{HI}$	0.81	0.35	0.82
$\text{NH}_3 + \text{HI} = \text{NH}_4\text{I}$	-0.45	0.21	0.67
$\text{HCN} = \frac{1}{3}(\text{HCN})_3$	-0.94	-0.84	-0.58

Note that the * symbol is neglected for molecules on NiO (001) and TiO₂ (001) in this table.

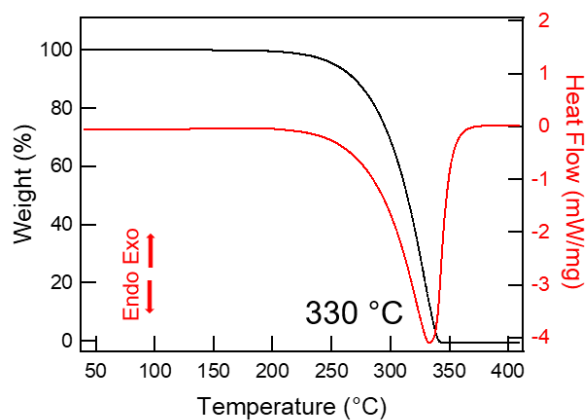


Figure S8. TGA (black, y-axis) and DSC (red, y-axis) curves for NH₄I from 25 °C to 400 °C at 10 °C/min under 100 sccm N₂ flow.

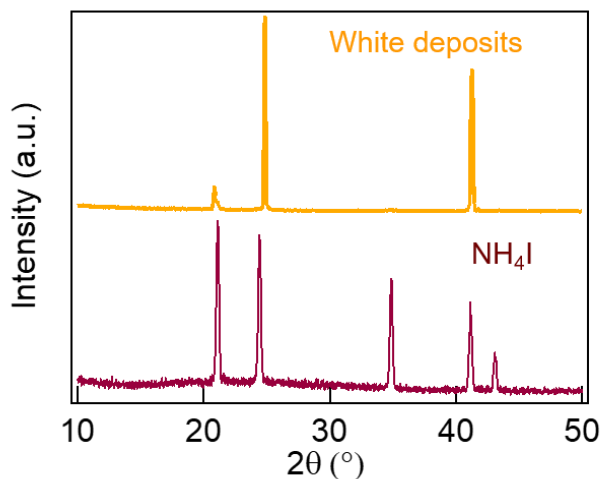


Figure S9. XRD patterns of white deposit (orange), collected from the exhaust capillary of the sample cell after TPD experiment of neat FAI and neat NH_4I powder (maroon).

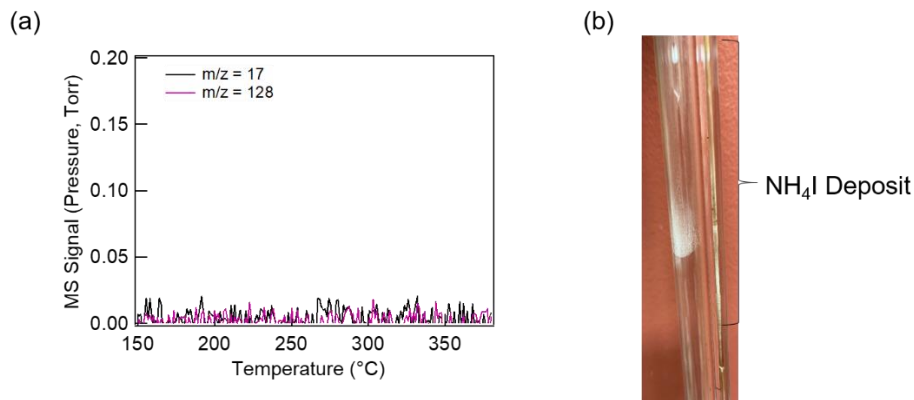


Figure S10. (a) TPD-MS temperature profile for neat NH_4I . MS signals of $m/z = 17$ (black) and $m/z = 128$ (purple) represent NH_3^+ and HI^+ parent ions, respectively. (b) Image of TPD a sample cell showing the white deposits in the exhaust capillary. Assignments are based on NIST database.⁵

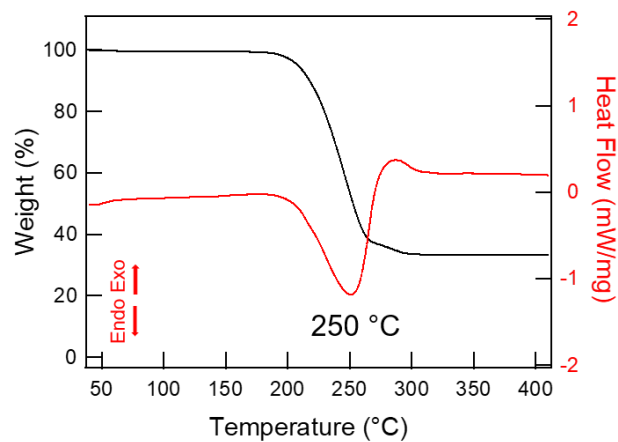


Figure S11. TGA (black, y-axis) and DSC (red, y-axis) curves for 1:1 molar ratio of $\text{NH}_4\text{I} + \text{NiO}$ from 25 °C to 400 °C at 10 °C/min under 100 sccm N_2 flow.

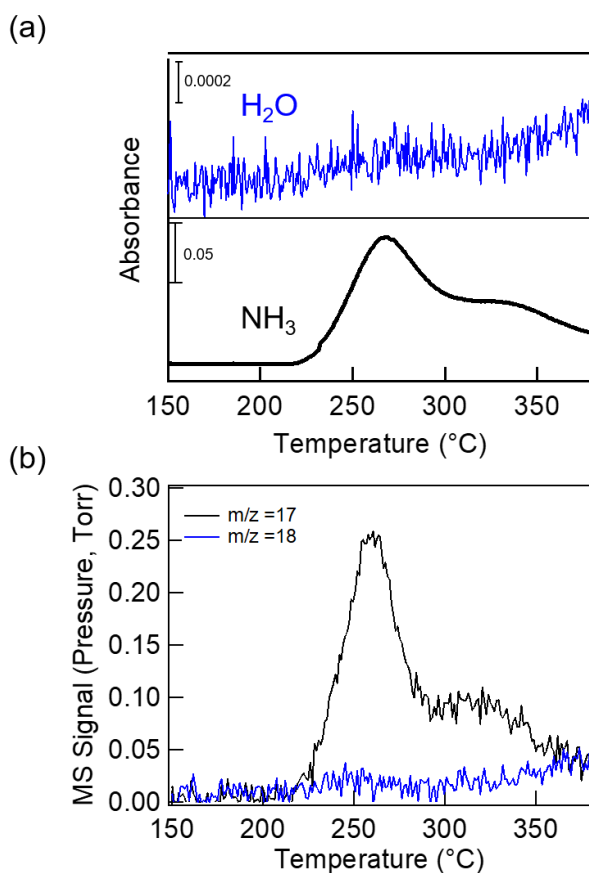


Figure S12. TPD-(a) FTIR and (b) MS temperature profiles for 1:1 molar ratio of $\text{NH}_4\text{I} + \text{NiO}$. The black and blue lines represent NH_3 and H_2O , respectively. All assignments are based on NIST database.^{4,5}

References

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- 5 W. E. Wallace, 'Mass Spectra' in *NIST Chemistry WebBook NIST Standard Reference Database Number 69*, 2017.