Thermal degradation of formamidinium based lead halide perovskites into sym-triazine and hydrogen cyanide observed by coupled thermogravimetry - mass spectrometry analysis

Emilio J. Juarez-Perez²,³, Luis K. Ono³, Yabing Qi*³

*e-mail: ejjuarezperez@unizar.es; Yabing.Qi@OIST.jp

²Energy Materials and Surface Sciences Unit (EMSSU), Okinawa Institute of Science and Technology Graduate University (OIST), 1919-1 Tancha, Onna-son, Okinawa 904-0495, Japan

³ARAID Foundation, Institute of Nanoscience of Aragon (INA), University of Zaragoza. 50018 Zaragoza, Spain
Detailed calculations for estimation of maximum release achievable per meter-square of FA based perovskite based solar cell and hydrogen cyanide instantaneous concentration observed during low temperature heating tests and.

**Maximum release achievable per meter-square of FA based perovskite solar cell**

The weight of one thin-film of 1 m² of surface and 500 nm thickness of FAPbI₃ or FAPbBr₃ is

\[ W_{\text{FAPbX}_3/m^2} = V_m \cdot \rho_{\text{FAPbX}_3} \]

Where \( W_{\text{FAPbX}_3/m^2} \) is the weight of perovskite contained in the thin-film of 1 m² of surface and 500 nm thickness. \( V_m \) is the volume of this thin-film, \( V_m = 0.5 \text{ cm}^3 \) and \( \rho_{\text{FAPbX}_3} \) is the crystal density obtained from cif files reported for the α-FAPbI₃¹ or FAPbBr₃².

\[ W_{\text{FAPbI}_3/m^2} = 2505 \text{ mg} \]

\[ W_{\text{FAPbBr}_3/m^2} = 1880 \text{ mg} \]

Atomic weight percent of FAPbI₃ (\( M_{w\text{FAPbI}_3} = 632.98 \text{ mg/mmol} \))

- C 1.90 %
- H 0.80 %
- N 4.43 %
- Pb 32.73 %
- I 60.15 %

Atomic weight percent of FAPbBr₃ (\( M_{w\text{FAPbBr}_3} = 491.98 \text{ mg/mmol} \))

- C 2.44 %
- H 1.02 %
- N 5.69 %
- Pb 42.12 %
- Br 48.72 %

\( M_{w\text{FA+}} = 45.06 \text{ mg/mmol} \); \( M_{w\text{HCN}} = 27.02 \text{ mg/mmol} \)

The maximum HCN release achievable per meter-square of FA based perovskite solar cell is,

\[ W_{\text{HCN}/m^2} = W_{\text{FAPbX}_3/m^2} \cdot (\% \text{ CHN})_{\text{FAPbX}_3} \cdot M_{w\text{HCN}}/M_{wFA} \]

The maximum observed hydrogen cyanide instantaneous partial pressure during low temperature heating tests was \( P_{\text{HCN}} = 1.36 \times 10^{-7} \text{ torr} \) at 85 °C, see Figure S6. The equivalent HCN concentration in mg/m³ is obtained as,

\[ C_{\text{max-\text{HCN}/m}^2} = \frac{P_{\text{HCN}} M_{w\text{HCN}}}{S_{\text{HCN}} R T} \cdot \frac{W_{\text{FAPbBr}_3/m^2}}{W_{\text{sample}}} \]
Figure S1. Tandem TG-DTA/MS coupled experiments for FAI. Top panel shows a one-step type mass loss TG pattern (green line). Bottom panel shows the MS traces simultaneously recorded (1-100 amu) during the experiments. Gray dash line indicates the initial temperature (time) of the first detection of the released gases during the high-temperature thermal degradation.
Figure S2. Tandem TG-DTA/MS coupled experiments for FAac (formamidinium acetate). Top panel shows a one-step type mass loss TG pattern (green line). Bottom panel shows the MS traces simultaneously recorded (1-100 amu) during the experiments. There is a concurrent process of sublimation of FAac obscuring clear observation of released products during degradation.
Figure S3. Full MS spectra (1-200 amu) for the tandem TG-DTA/MS coupled experiments shown in Figure 1 for a) FAPbI$_3$ and b) FAPbBr$_3$. 
Figure S4. Tandem TG-DTA/MS coupled experiments for FAPbBr$_3$ at 3 different heating rates, 5 ºC/min (left), 10 ºC/min (center) and 20 ºC/min (right). Top panels show the archetypal two-step type mass loss TG patterns (green line) for FAPbBr$_3$. Bottom panels show MS traces simultaneously recorded (1-100 amu) during the experiments. Gray dash lines indicate the initial temperature (time) of the first detection of the released gases during the high-temperature thermal degradation.
Figure S5. Graphical comparisons of the theoretical fittings (solid lines) and experimental data (symbols) for TG curves during the first mass loss step of MAPbBr$_3$, FAPbBr$_3$, MAPbI$_3$, FAPbI$_3$, and the unique mass loss step of precursors FAI, FABr and FAac, and all inorganic perovskite CsPbI$_3$. 
Figure S6. Raw m/z ratio traces (non-calibrated) recorded for NH$_3$ (17 amu), NH$_4^+$ (18 amu), HCN (27 amu), N$_2^+$ (28 amu), formamidine HCN$_2$H$_3$ (44 amu) and sym-triazine (54 amu) fragment.
Figure S7. a) Mass spectrometry profiles of the empty 6-ways cross chamber recorded during illumination and heating-in-the-dark pulsed experiments. The sample holder temperature is recorded during light pulses and heating on/off intervals on the empty sample holder. b) Time dependent m/z traces of selected relevant amu registered during the thermal test of the chamber under light or dark conditions.
Figure S8. Fragmentation patterns m/z peaks retrieved from the NIST MS library data (http://webbook.nist.gov/chemistry/) for a) ammonia, b) hydrogen cyanide, c) sym-triazine and d) hydrogen bromide.