

Supporting Information

Unraveling the Ammonia Sensing Behavior and Degradation Pathways of Novel Lead-Free MA₂CuBr₄ based Ammonia Sensor

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Materials and Method:

Methyl amine (33 wt% in ethanol), CuBr₂ (99%), Ethyl acetate, Al₂O₃ paste and Alconox (detergent) are all purchased from Sigma Aldrich. Acetonitrile, Chloroform, Toluene, Hexane, Methanol, Ammonia, Ammonium chloride, Ammonium bromide, Ammonium iodide, Ammonium molybdate, Sodium hydroxide and Acetone are purchased from Merck. Acetone and Isopropyl alcohol (IPA) used for cleaning are purchased from Finar. Diethyl ether is purchased from Spectrochem. Ethanol is purchased from Analytical CSS Reagent. Hydrobromic acid (HBr, 47 wt% in H₂O) is purchased from Merck. Microscopic glass slides are purchased from Borosil. De-ionized water is used for all cleaning purpose.

MABr Synthesis:

A 100 mL round-bottomed (RB) flask is filled with 20 mL of methyl amine (33 wt% in ethanol). 10 mL of ethanol is added to further dilute it. In an ice bath, the reaction mixture is continually cooled to 5 °C. In this reaction mixture, 18 mL of HBr (47 wt% in H₂O) is added drop-wise while being continuously stirred at 500 rpm. After the HBr has been fully added, this mixture is continually swirled for two hours to allow the reaction to finish. A rotary evaporator is used to remove the solvent in order to extract MABr. Diethyl ether is used to repeatedly wash the resulting MABr in order to remove any unreacted starting components. It is utilized in all of the studies after being dried for 12 hours at 60 °C in a vacuum oven.

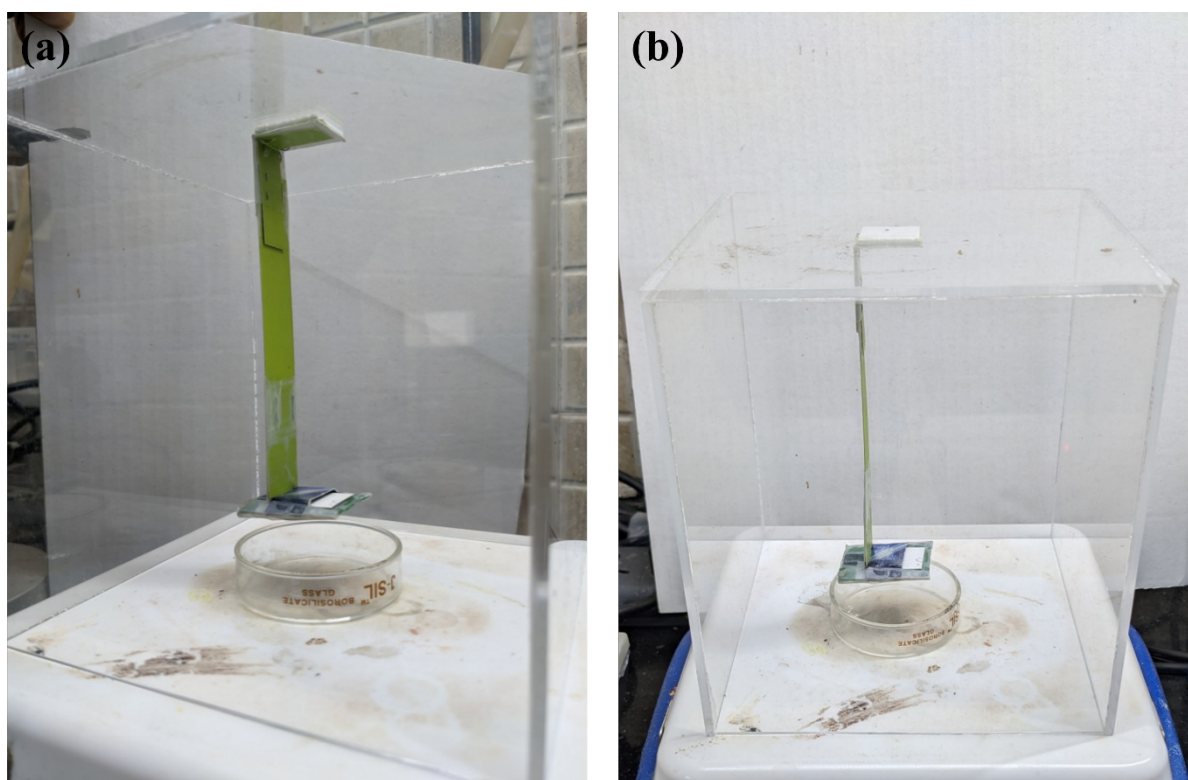
Preparation of MA_2CuBr_4 and $x\text{MABr} + \text{MA}_2\text{CuBr}_4$ ($x=1, 2$) solutions:

1 mmol of CuBr_2 and 2 mmol of MABr is taken in a vial along with 1 mL DMF. It is stirred using a magnetic needle over a stirrer. The resulting purple colored solution is MA_2CuBr_4 solution.

For MABr + MA_2CuBr_4 and 2MABr + MA_2CuBr_4 solutions, 3 mmol and 4 mmol of MABr are mixed with 1 mmol of CuBr_2 in 1 mL DMF, respectively. They are stirred using a magnetic needle over a stirrer. The resulting purple colored solution is $x\text{MABr} + \text{MA}_2\text{CuBr}_4$ ($x=1, 2$) solutions.

Ammonia sensing setup:

The dimension of the ammonia sensing chamber is 15 cm * 15 cm * 15 cm (3.375 L). 1 mL of 28% NH_4OH solution is diluted to 50 mL with water in a volumetric flask. By completely evaporating the appropriate amount of the diluted NH_4OH solution on a heater (50 °C) within the chamber, the concentration of NH_3 is regulated.



Optical ammonia sensor fabrication:

A 1:3.5 (Al_2O_3 paste: Ethanol) suspension is deposited via spin-coating (3000 rpm, 1000 rpm/s, 20 s) over a 1.5 cm * 2.5 cm microscopic glass slide. It is sintered at 450 °C for 30 minutes. Using spin coating (3000 rpm, 1000 rpm/s, 20 s), MA_2CuBr_4 solution is deposited

over it. Following this, the film is annealed on a hot plate at 70 °C for 15 minutes. This fabricated device is used for the ammonia sensing measurements.

Fabrication of optical ammonia sensor with porous PMMA layer:

To the fabricated optical ammonia sensor as described above, we deposit PMMA solution (10 mg PMMA, in 1 mL toluene) at 3000 rpm for 20 s. The solvent is evaporated under vacuum at room temperature, to create a porous layer over the perovskite.

Gas response calculation:

The gas response is determined using the formula,

$$\text{Response} = (A_0 - A_g/A_0) * 100 \quad \text{Equation 1}$$

Here, A_g represents the absorbance of the NH_3 vapor adsorbed film, and A_0 represents the absorbance of the pristine film. The sensing measurement are done at 25 °C room temperature and 40–50% relative humidity.

Standard Deviation, σ :

$$\sigma = \sqrt{\left(\sum_{i=1}^n \frac{(X_i - X_m)^2}{n-1}\right)} \quad \text{Equation 2}$$

Where, X_i is the response for the i^{th} measurement and X_m corresponds to the mean of the response observed over three measurement cycles.

Relative standard deviation, RSD:

$$\text{RSD} = \frac{\sigma}{X_m} * 100 \quad \text{Equation 3}$$

Limit of detection, LOD:

$$\text{LOD} = \frac{3\sigma}{m} \quad \text{Equation 4}$$

Where, m is the slope obtained from the linear regression equation of the Response – ammonia concentration plot.

Electrical Device fabrication:

A FTO substrate, 2 cm X 2 cm is laser etched at the centre (80 μm) as such that it creates a configuration FTO/ etched region/ FTO. These substrates are cleaned via the solar cell cleaning

process (Soap solution, DI-water, Acetone, IPA for 10 minutes each) and dried in a lab oven at 70 °C. On this substrate, we deposit MA₂CuBr₄ solution at 3000 rpm for 20 s. The device is annealed at 70 °C for 20 minutes.

Characterizations:

The SEM images with and without ammonia exposure are captured using the Thermoscientific Helios 5 UC Scanning Electron Microscope. The powder-XRD spectrum was obtained using the Rigaku Japan smart lab X-ray diffractometer (Cu target, wavelength: 1.54184 Å). An Integrating sphere integrated Shimadzu UV-Visible spectrophotometer with built-in tungsten and deuterium lamps is used for all UV-Vis absorbance measurements. For the XPS analysis, the PHI 5000 Versa Probe-II equipment was employed. Electrical characterizations are performed using Keithley 2450 sourcemeter.

Sample preparation for different characterizations:

SEM, XRD, XPS analysis: The material is deposited via spin coating over a UV-Ozone treated microscopic glass slide. The coating parameters are 2000 rpm with an acceleration of 500 rpm/s. Following this, the samples are annealed at 70 °C for 15 minutes. Further, for SEM analysis, the surface is sputtered with 5 nm of Pt-coating.

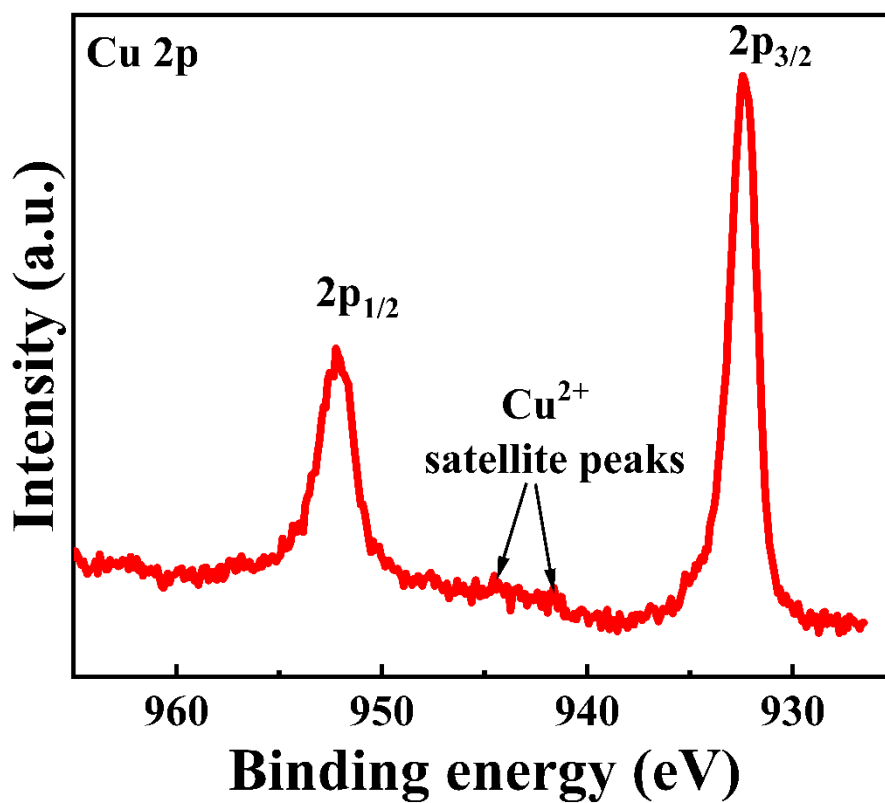


Figure S0.1: XPS spectrum of Cu 2p in MA₂CuBr₄.

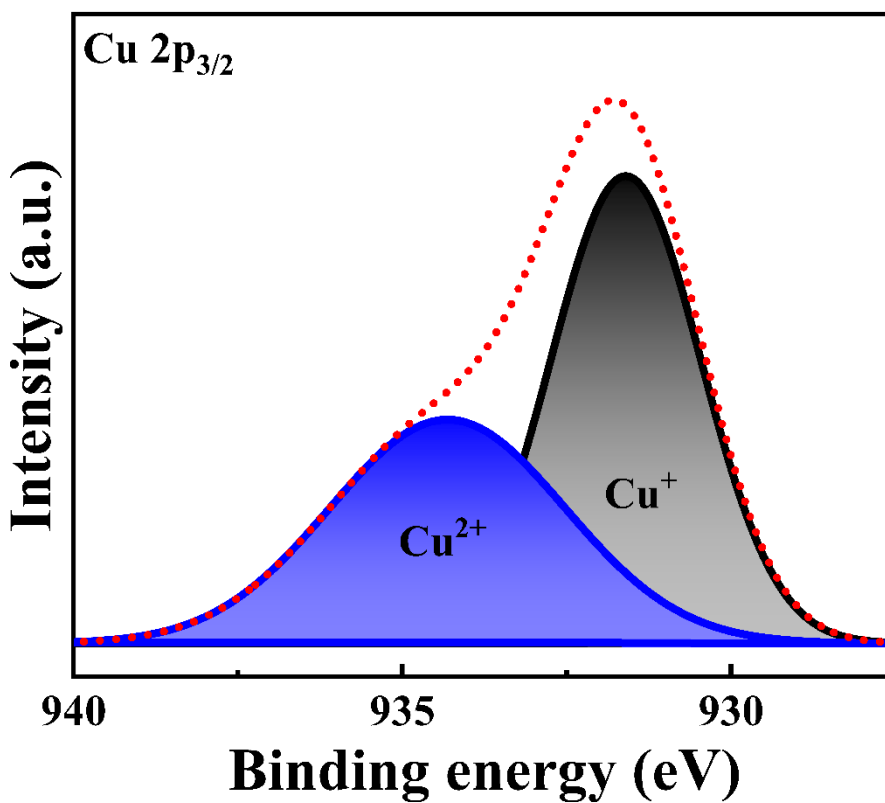


Figure S2: Presence of Cu²⁺ and Cu⁺ phase in the MA₂CuBr₄ film.

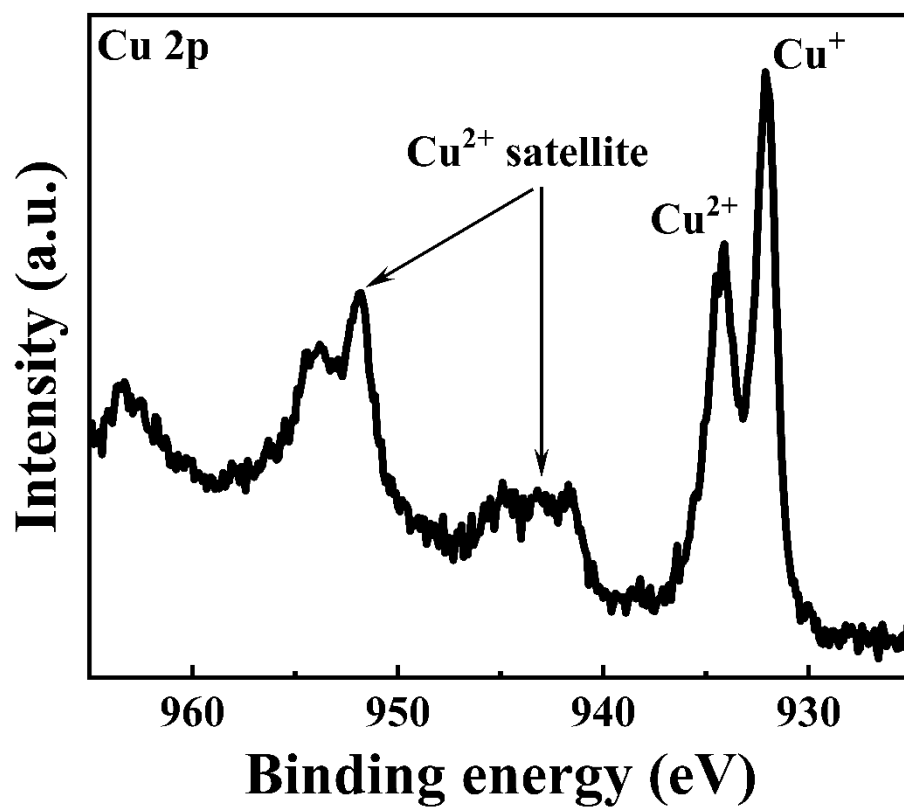


Figure S3: Presence of Cu²⁺ and Cu⁺ phase in the CuBr₂ film.

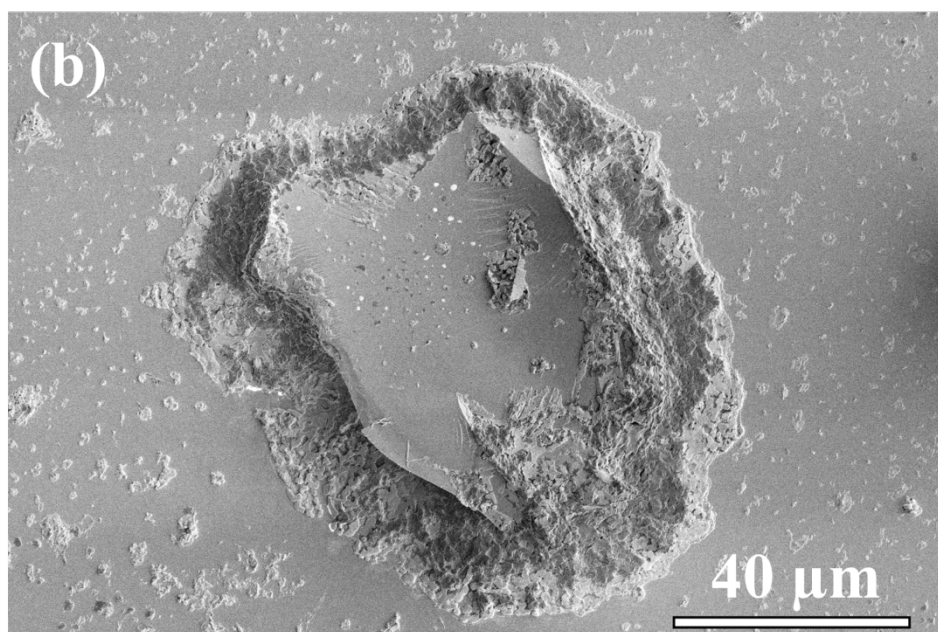
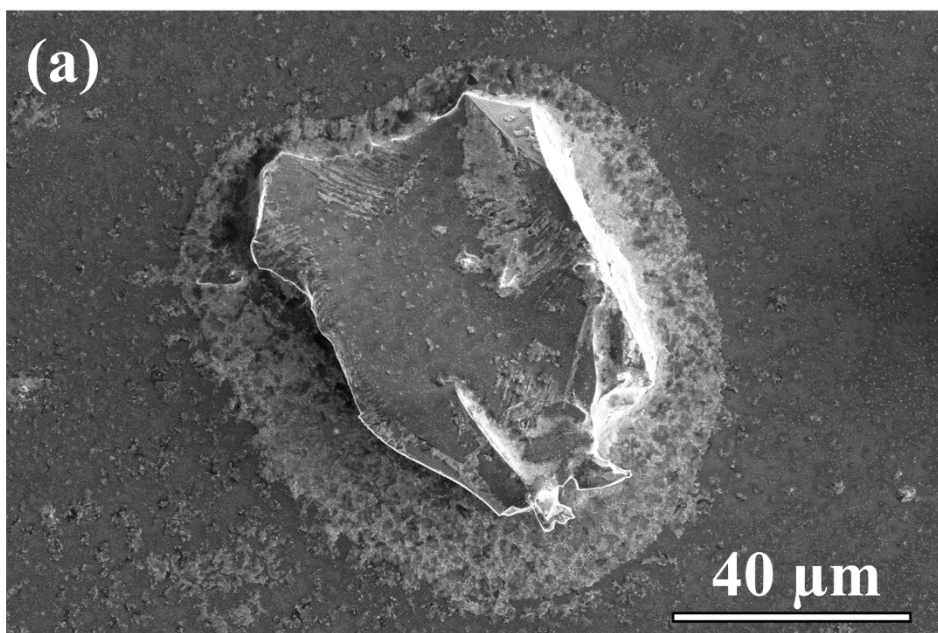


Figure S4: FIB-SEM images of surface peeling in MA_2CuBr_4 crystals with and without ammonia treatment.

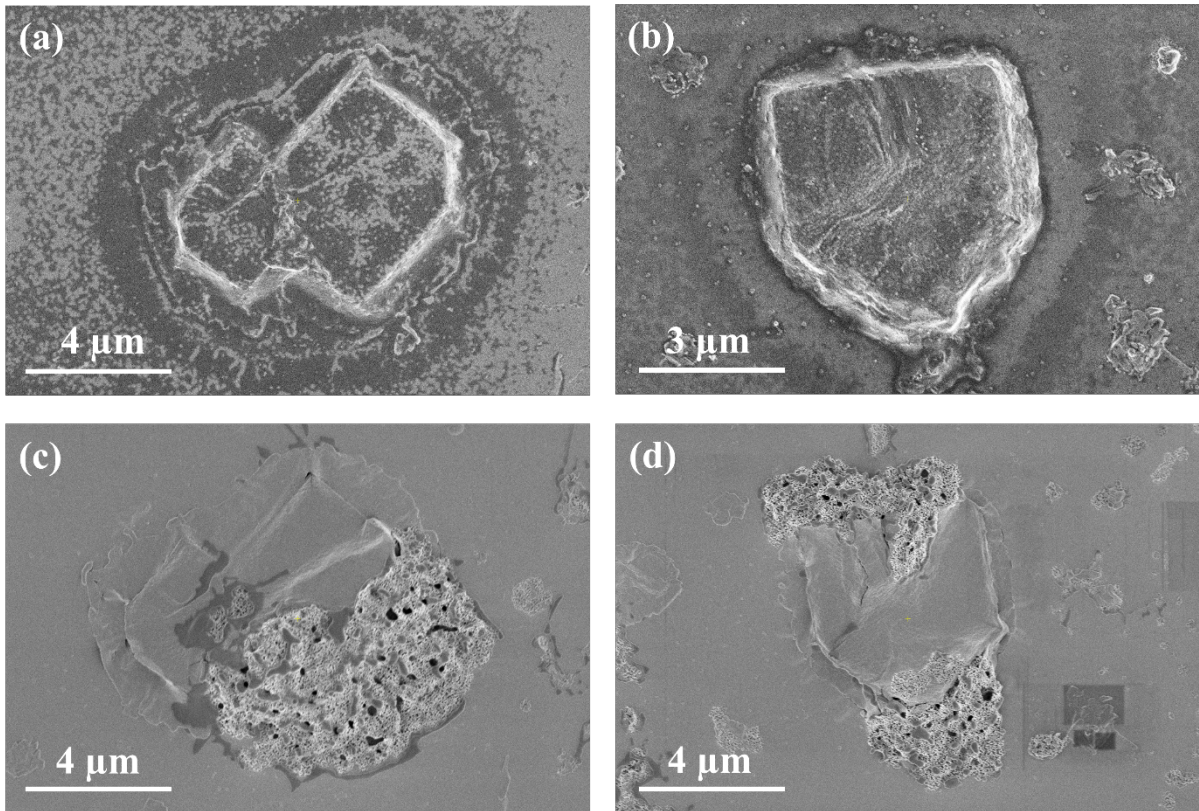


Figure S5: SEM image of MA_2CuBr_4 crystals, without and with ammonia exposures. (a) and (b) are ammonia unexposed films. (c) and (d) are ammonia exposed films. The images are taken at the same location.

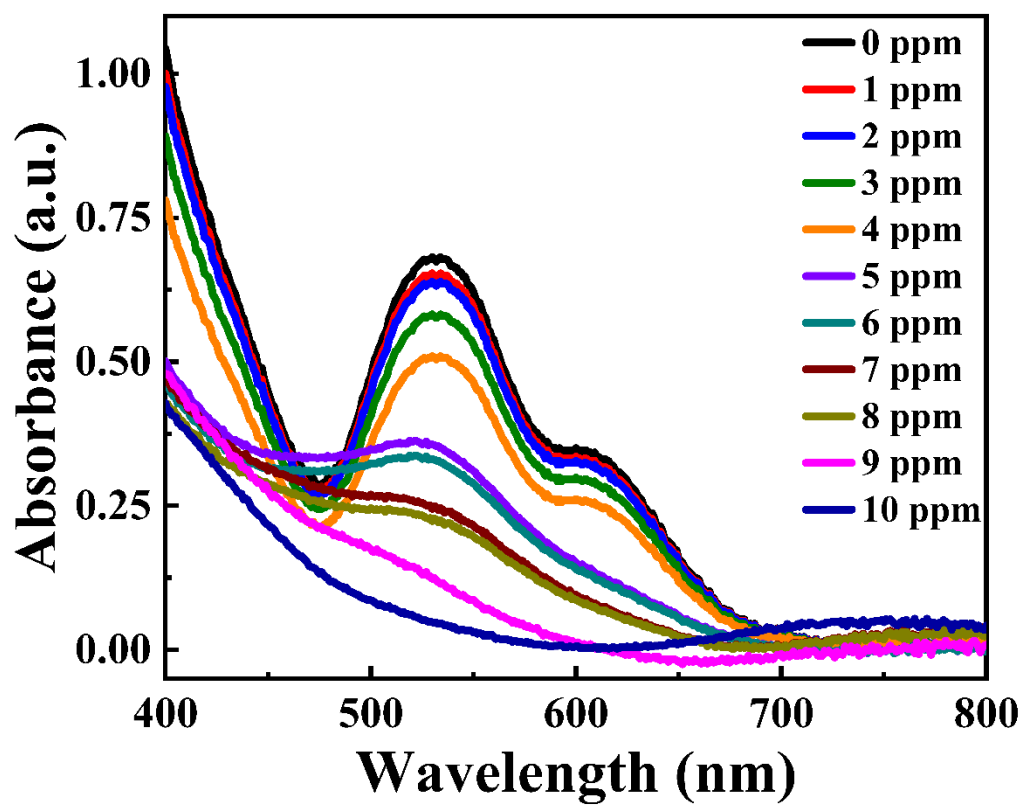


Figure S6: UV-Visible absorbance spectra of the MA₂CuBr₄ films in Figure 2a.

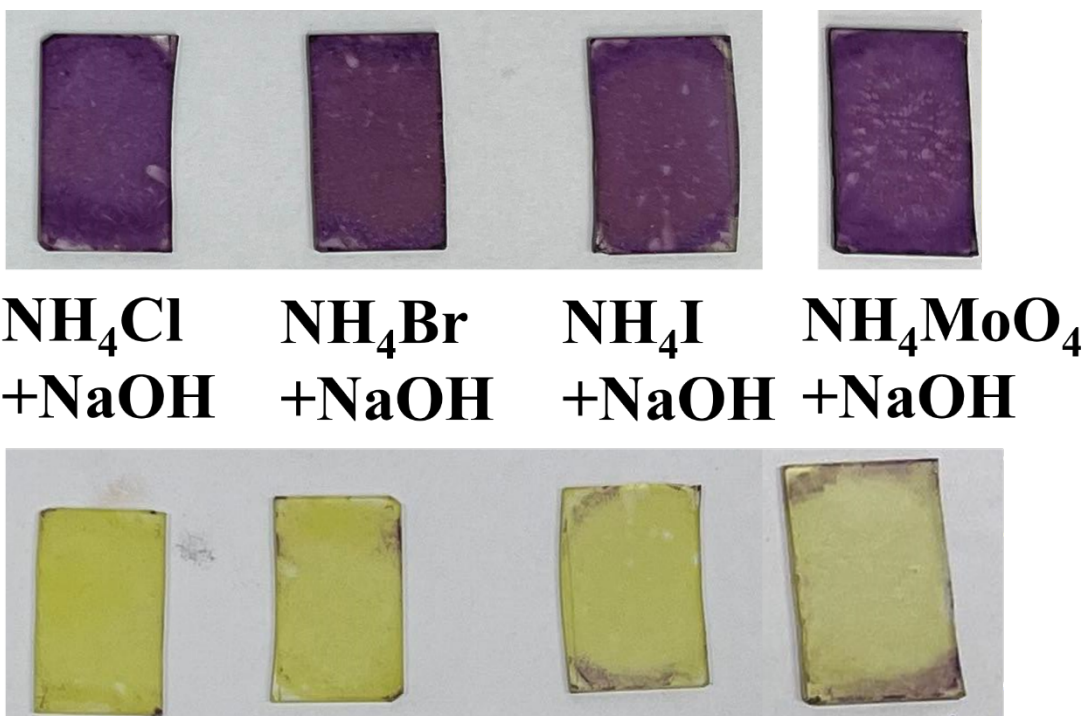


Figure S7: Image of the pristine film and the liberated ammonia treated films.

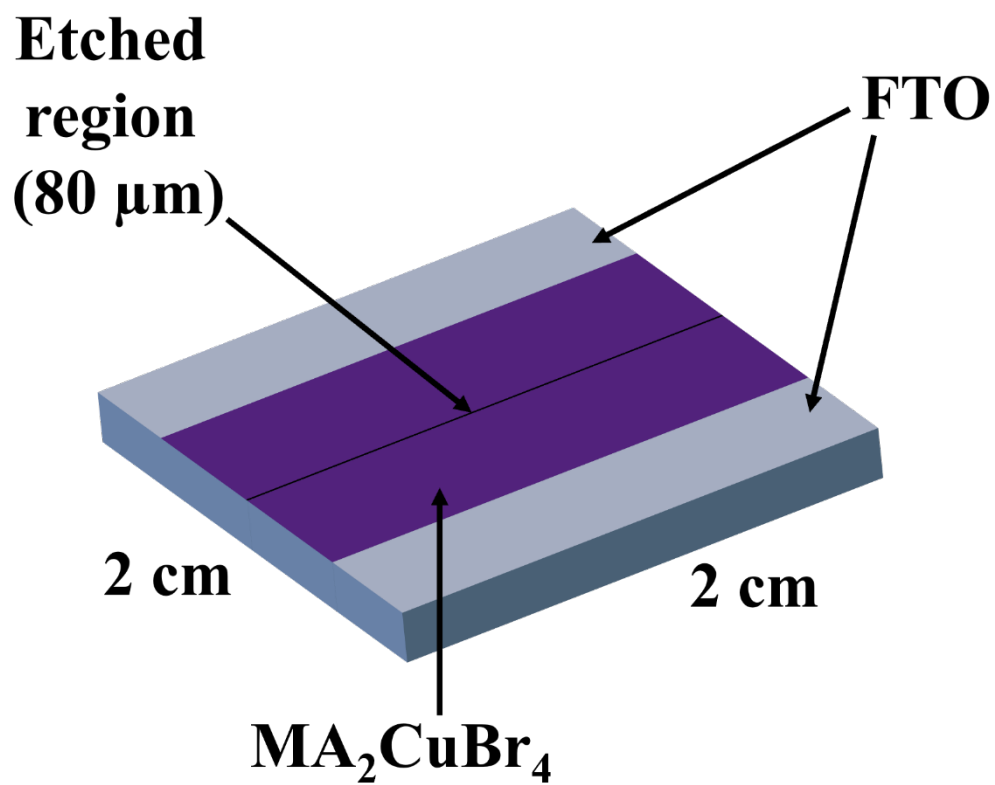


Figure S8: Schematics of the device used for ammonia sensing via resistance change.

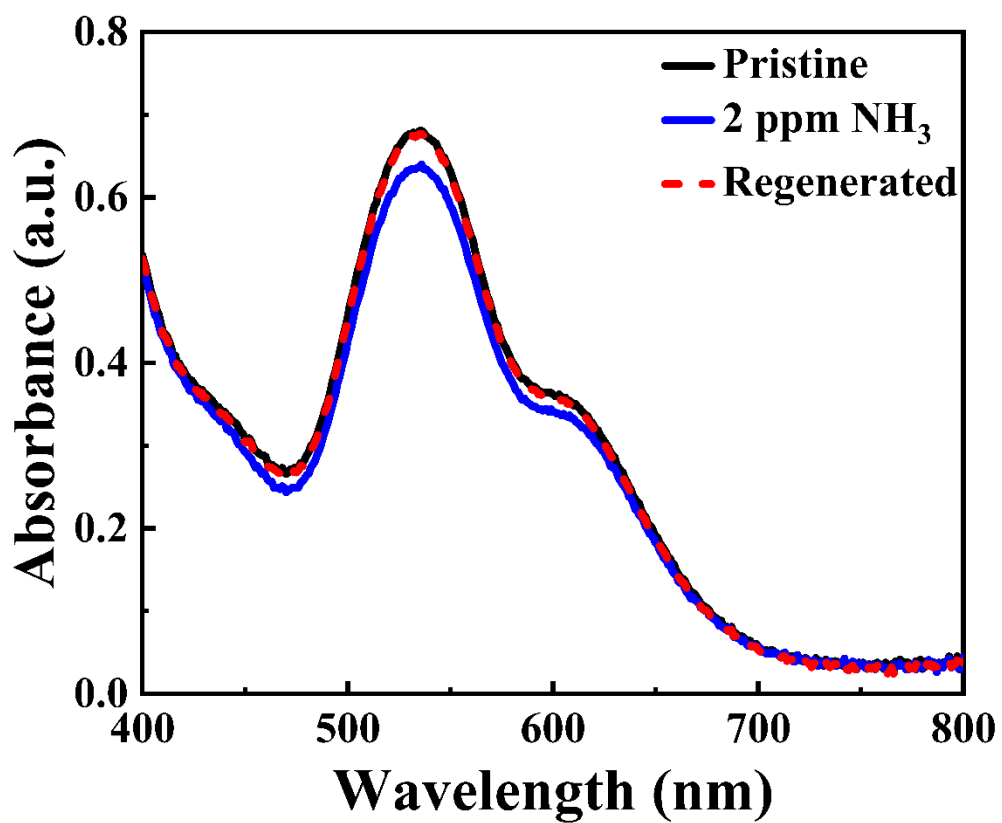


Figure S9: UV-visible absorbance of pristine, ammonia exposed and regenerated film.

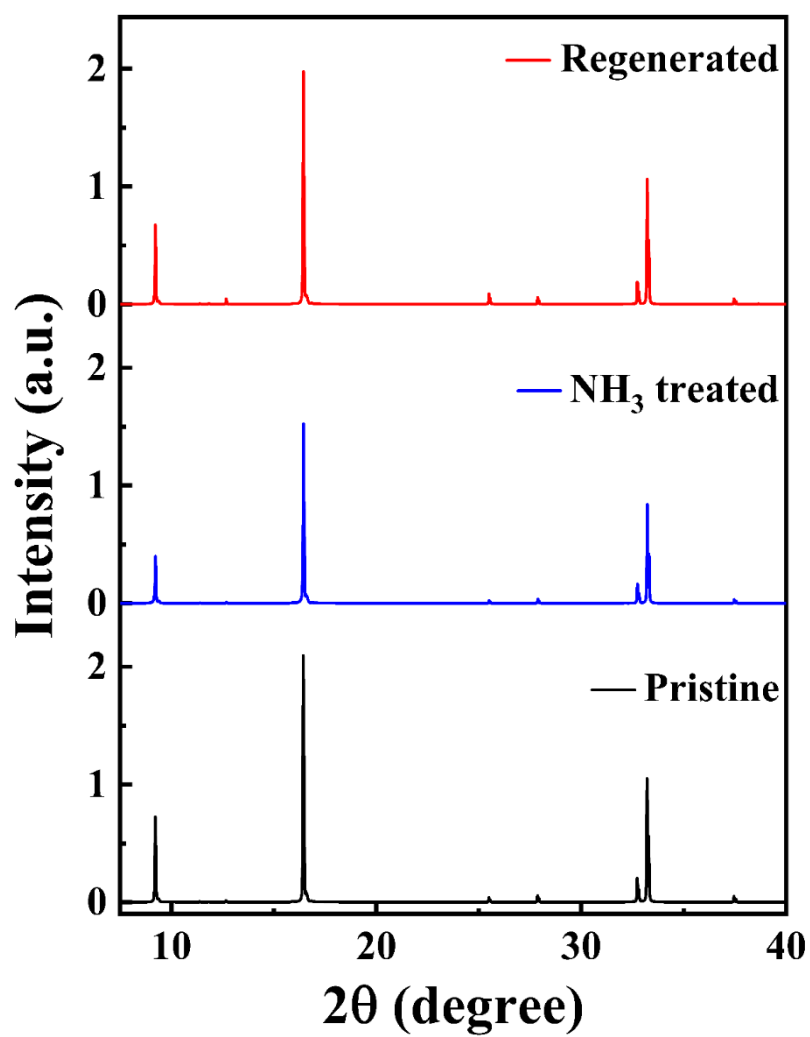


Figure S10: XRD of pristine, ammonia exposed and regenerated film.

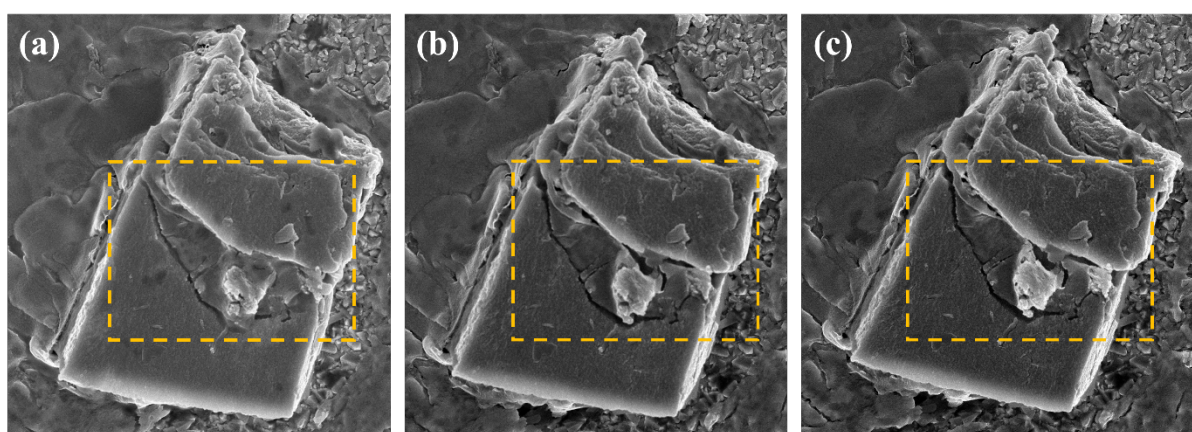


Figure S11: SEM of (a) pristine, (b) ammonia exposed and (c) regenerated film.

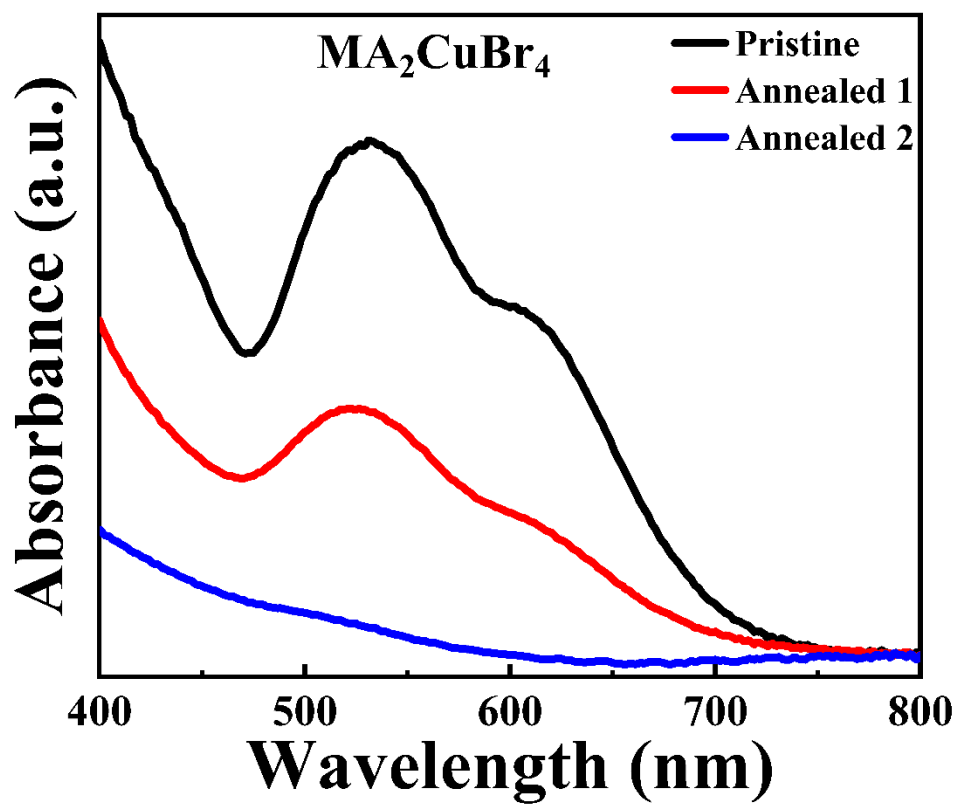


Figure S12: UV-Visible spectra of MA₂CuBr₄ film on subsequent ammonia exposures.

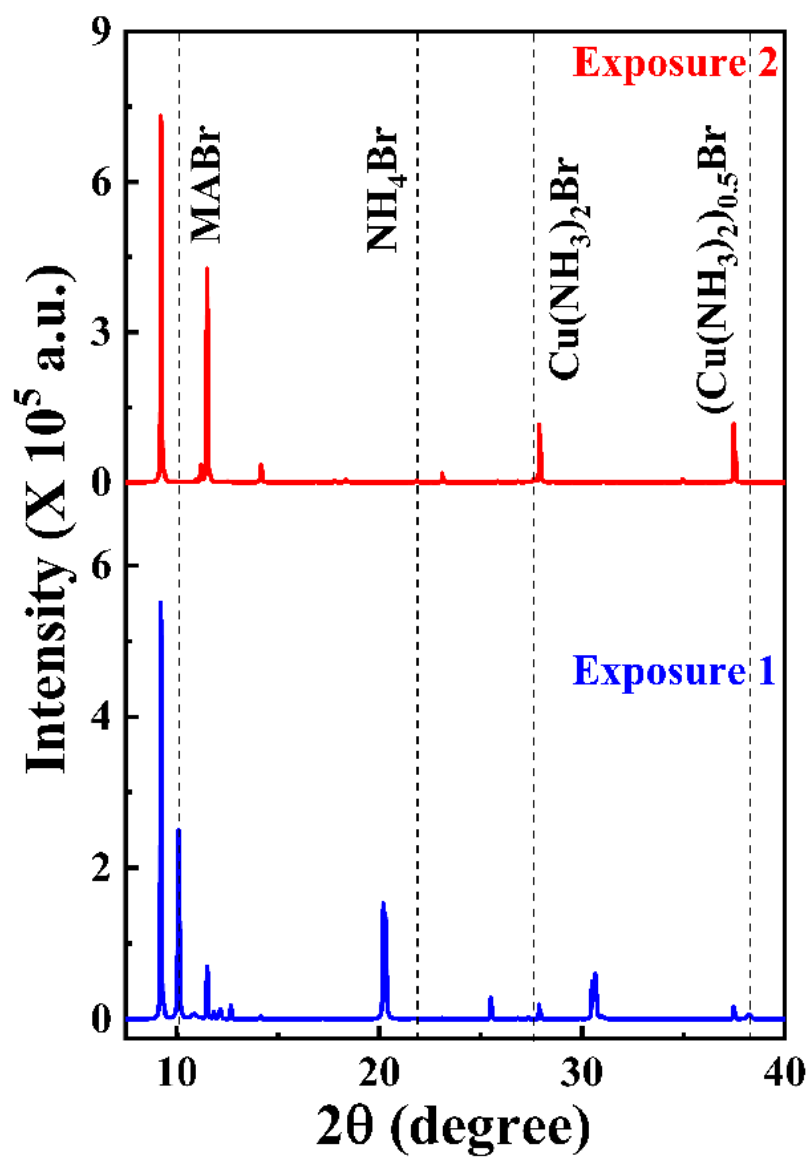


Figure S13: XRD of MA_2CuBr_4 film on subsequent ammonia exposures.

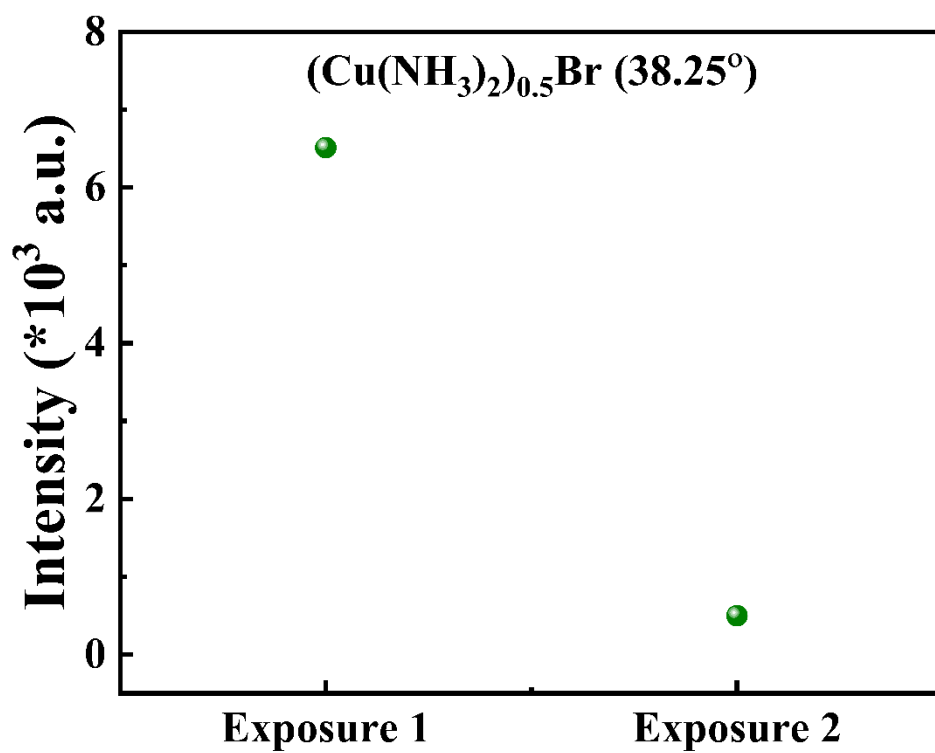


Figure S14: XRD evolution of (111) plane of $(\text{Cu}(\text{NH}_3)_2)_{0.5}\text{Br}$ (38.25°) phase, after subsequent ammonia exposures.

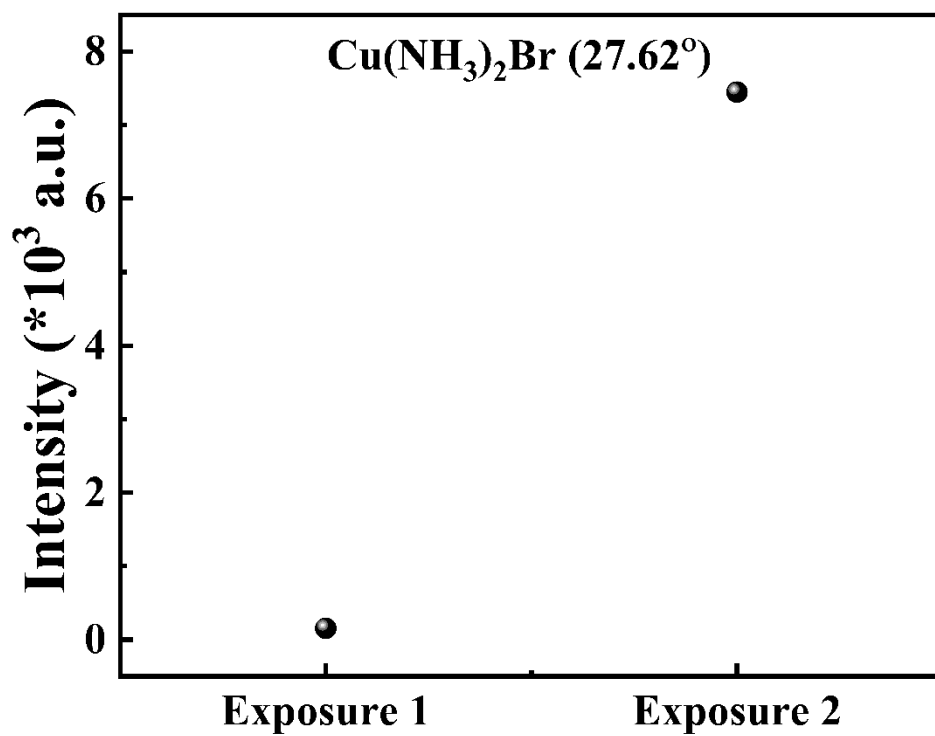


Figure S15: XRD evolution of (111) plane of $\text{Cu}(\text{NH}_3)_2\text{Br}$ (27.62°) phase, after subsequent ammonia exposures.

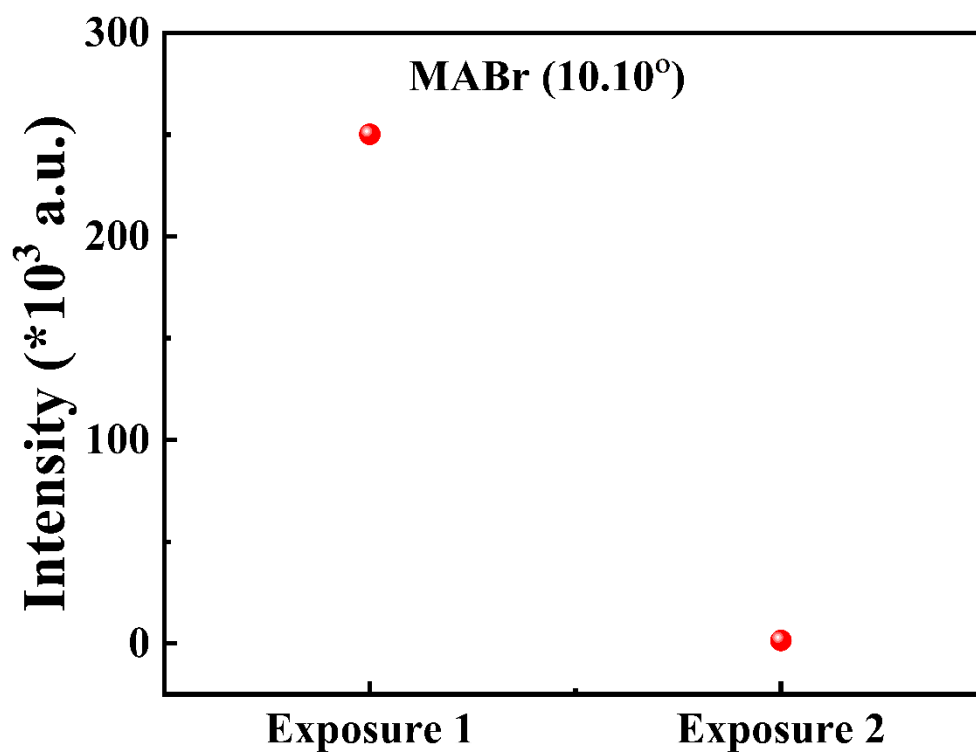


Figure S16: XRD evolution of (001) plane of MABr (10.10°) phase, after subsequent ammonia exposures.

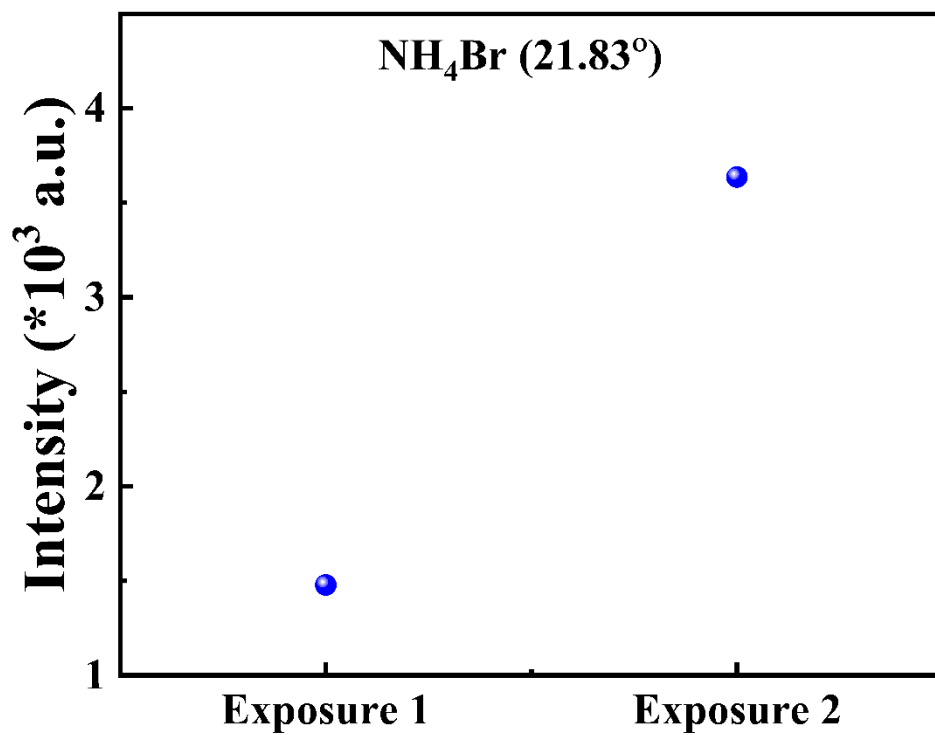


Figure S17: XRD evolution of (001) plane of NH₄Br (21.83°) phase, after subsequent ammonia exposures.

Table S1: RSD of the sensor at different ammonia concentrations.

C_{Ammonia} (ppm)	Response (%)	Standard Deviation	Relative Standard Deviation (%)
1	3.52	0.0752	2.13
2	6.31	0.2	3.18
3	14.52	0.5	3.45
4	25.22	1.2	4.75
5	46.19	1.51	3.26
6	50.15	1.9	3.78
7	62.76	2.46	3.93
8	64.52	2.06	3.2
9	78.01	2.86	3.65
10	96.63	3.18	3.31
11	95.89	2.83	2.95

Table S2: Literature comparison of halide perovskite based optical ammonia sensors.

Sl. No.	Material	Range	Sensitivity	Selectivity	Method	Reference
1.	MAPbI ₃	-	-	-	Absorbance (colorimetric)	30
2.	MAPbBr ₃	0.3 wt%	60%	NH ₃	Fluorescence	29
3.	MAPbBr ₃ / m-TiO ₂	5-100 ppm	72% (5 ppm)	NH ₃ and amine molecules	Fluorescence	6
4.	MAPbBr ₃ -TBA/GeO ₂	10-100 ppm	62% (100 ppm)	NH ₃	Fluorescence	28
5.	FAPbI ₃	80-100 ppm (o)	65% (20 ppm)	NH ₃	Absorbance (colorimetric)	25
6.	MAPbI ₃	10-100 ppm	96% (20 ppm)	NH ₃	Absorbance (colorimetric)	25

7.	MAPbBr ₃	50-100 ppm	82% (20 ppm)	NH ₃	Absorbance (colorimetric)	25
8.	CsPbBr ₃ quantum dots	25-300 ppm	8.85	NH ₃	Fluorescence	27
9.	CsPbBr ₃ quantum dots	20-200 ppm	-	NH ₃ , Ethanol, water	Fluorescence	26
10.	CsPbBr _{1.5} Cl _{1.5} quantum dots	20-200 ppm	-	NH ₃ , Ethanol, water	Fluorescence	26
11.	CsPbBr _{1.5} I _{1.5} quantum dots	20-200 ppm	-	NH ₃ , Ethanol, water	Fluorescence	26
12.	MASnI ₃	5-100 ppm	87% (100 ppm)	-	Absorbance (colorimetric)	31
13.	MA ₂ CuBr ₄	2-15 ppm	95% (10 ppm)	NH ₃	Absorbance (colorimetric)	This work