

## Supporting Information

### Highly sensitive and selective ammonia gas sensor based on FAPbCl<sub>3</sub> lead halide perovskite

*Aleksei A. Parfenov, Olga R. Yamilova, Lavrenty G. Gutsev, Diana K. Sagdullina\*, Artyom V. Novikov, Bala R. Ramachandran, Keith J. Stevenson, Sergey M. Aldoshin and Pavel A. Troshin*

#### Theoretical Information

##### *Phase diagram of ordered and disordered FAPbCl<sub>3</sub>*

Since the total energy of FAPbCl<sub>3</sub> was necessary for the calculation of thermodynamics we took the most stable experimentally-known space group of FAPbCl<sub>3</sub> which is P2<sub>1</sub>/c monoclinic<sup>1</sup> and relaxed both the atomic positions and the cell dimensions with PBE+D3. For NH<sub>3</sub> we use a large cell with 15 Angstrom between each gas molecule as our reference. For **Figure 5**, as our references we used the elemental chemical potentials of Cl as Cl<sub>2</sub> and Pb as metallic lead

and  $\mu_{FA} = \frac{1}{2}\mu_{H_2} + \mu_{CH_3NH_2}$ , this choice is motivated by the fact that building simple cubic (2x2x2) supercells of FA or MA and optimizing them will tend to cause the spontaneous formation of H<sub>2</sub> gas in the supercells. To determine these boundary conditions, we consider the heats of formation of FAPbCl<sub>3</sub> and the two main products of degradation:

$$\mu_{FA} + \mu_{Pb} + 3\mu_{Cl} = \Delta H_f(FAPbCl_3) = -6.06 \text{ eV} \#(1)$$

$$\mu_{Pb} + 2\mu_{Cl} = \Delta H_f(PbCl_2) = -3.44 \text{ eV} \#(2)$$

$$\mu_{FA} + \mu_{Cl} = \Delta H_f(FAPbCl) = -2.78 \text{ eV} \#(3)$$

If we consider a limiting Pb-rich case of  $\mu_{Pb} = 0$  we can determine the phase ordering displayed in **Figure 5**.

It is worth noting that our calculations would imply that FAPbCl<sub>3</sub> is unstable; however, this is simply because we took the ordered phase of FAPbCl<sub>3</sub> introducing disorder into the rotations of FA drops the energy of  $\Delta H_f(FAPbCl_3)$  by -0.25 eV. Thus

$$FAPbCl_3 \rightarrow PbCl_2 + FAPbCl \quad \Delta H = -0.09 \text{ eV} \#(4)$$

$$FAPbCl_3(\text{disordered}) \rightarrow PbCl_2 + FAPbCl \quad \Delta H = 0.16 \text{ eV} \#(5)$$

We note that the increased disorder expands the region of stability of the perovskite while shrinking the region of stability of FAPbCl<sub>3</sub> and expanding the region of stability of PbCl<sub>2</sub>.

### *Defect Formation Energies of Vacancies*

We calculated the defect formation energies in the standard fashion:

$$\Delta H_f(X^q) = (E(X^q) + E_{corr}) - E_{pure} - \sum_i \eta_i(\mu_i + \mu_i^{bulk}) + q(\epsilon_{VBM} + V) \quad \#(6)$$

Where  $E(X^q)$  is the energy of the FAPbCl<sub>3</sub> supercell with the defect at that charge state,  $E_{corr}$  is the first-order electrostatic monopole correction for uniform charge distribution in a cubic lattice,  $E_{pure}$  is the energy of the plain FAPbCl<sub>3</sub> ordered supercell.  $\eta$  and  $\mu$  are the amount and chemical potentials of the species removed or added, the  $\mu_i^{bulk}$  term is added to remind the reader that the chemical potential is referenced to the bulk chemical potential, which acts as the upper limit. Finally, the last term is the Fermi level referenced to the valence band maximum.

$E_{corr}$  is defined as

$$E_{corr} = \alpha q^2 / \epsilon L$$

where  $\alpha = 1.8342$  is the Madelung constant of perovskites,  $q$  is the charge of the defect,  $\epsilon$  is the dielectric constant, 4 according to our calculations at 0 K but 28 in the experimental conditions which indicates that the monopole correction becomes less and less significant as temperature rises since our calculations indicate that it is 0.382 eV at 0K and just 0.055 eV at 300K. This indicates that in experimental conditions the lead vacancy with a charge of -2 will be very stable. We note that for this term further increases in the dielectric constant will produce very small differences in defect formation energies, that is, further heating will not stabilize the charged defects any further. Results are in Figure S5.

### *Adsorption Energy of Ammonia*

For examining the adsorption energy of the ammonia, we used the equation:

$$\Delta H_f^{ads}(NH_3^q_X) = E(NH_3_X) - E(X^q) - (\mu_{NH_3} + \mu_{NH_3}^{bulk}) \quad \#(7)$$

Where X is a vacancy which the ammonia occupies, the first term is the geometry with the vacancy filled by ammonia in the most optimal configuration, the second term is the energy of the defect geometry, the third factor we calculated in two modes: in NH<sub>3</sub> rich conditions

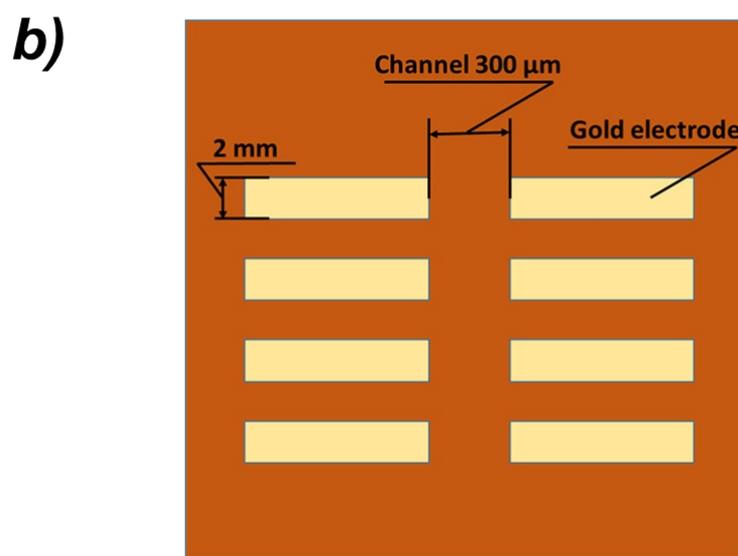
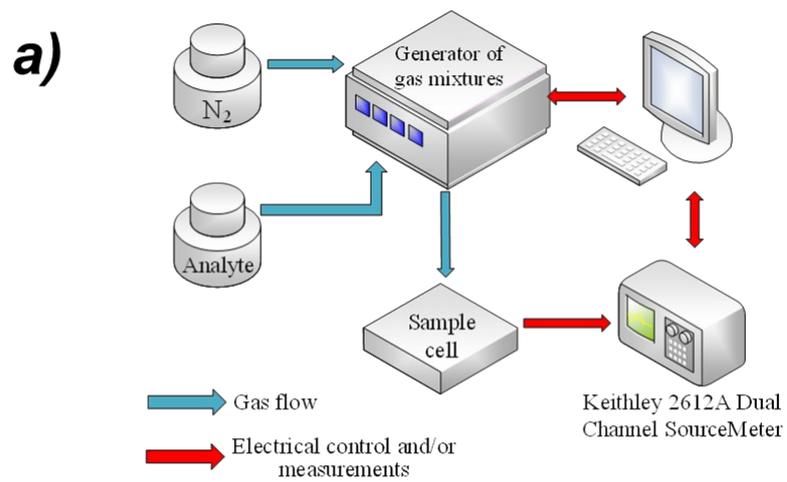
$\mu_{NH_3}=0$  and in experimental conditions, that is when the concentration of ammonia is 1 ppm, this was calculated by the equation<sup>2</sup>:

$$\mu_{NH_3}^{gas} = \mu_{NH_3}^{bulk} + k_B T \ln\left(\frac{PV_Q}{k_B T}\right) + \ln\left(\frac{\sigma B_0}{k_B T}\right) \#(8)$$

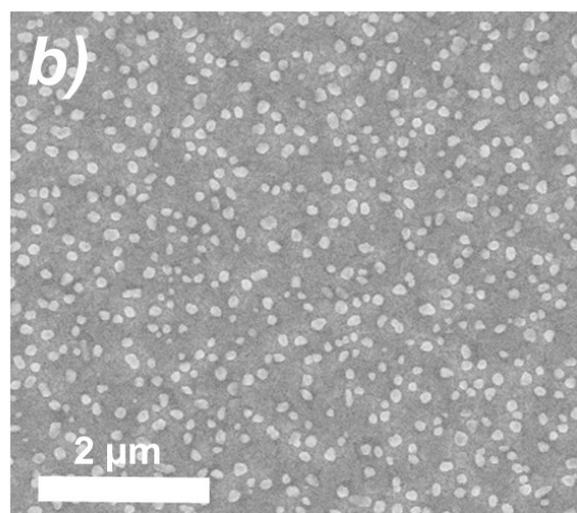
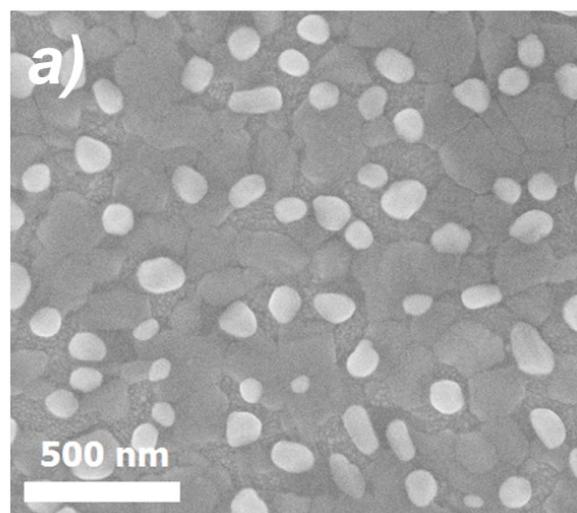
Where P is the partial pressure,  $V_Q = (2\pi\hbar^2/mk_B T)^{3/2}$  is the quantum Volume,  $\sigma = 3$  is the symmetry factor and  $B_0$  is the rotational constant (averaged from Gaussian16 calculation).

### *Band Gap*

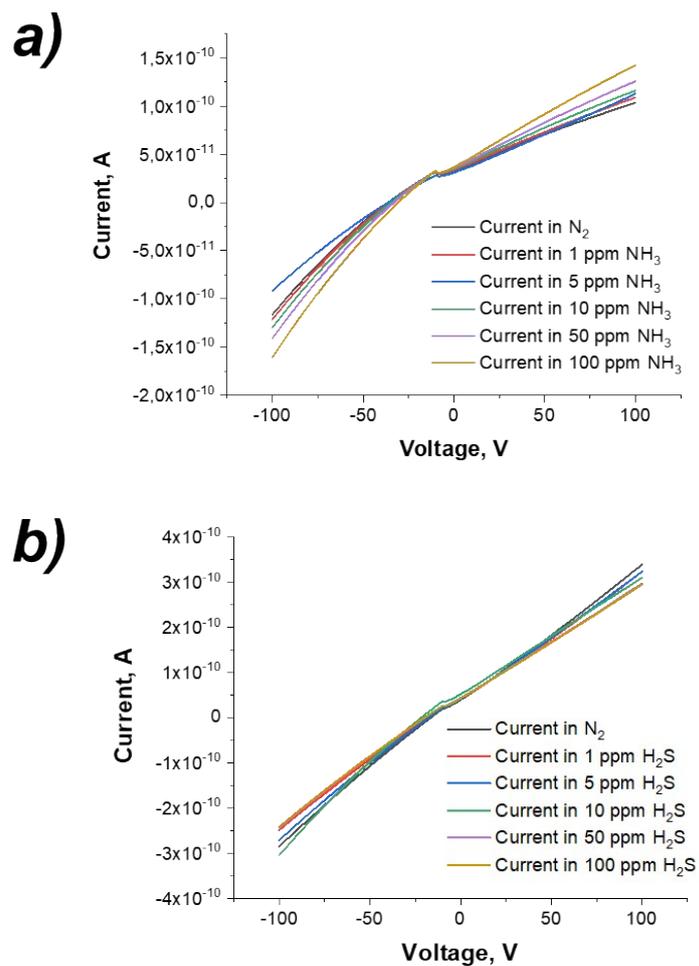
It should be stated that DFT underestimates the band gap of this material by nearly 1 eV; however, the disordered phase underestimates it by significantly less. Thus, the disagreement in perovskites vs experiment can also be partially related to the disordered nature of the material.



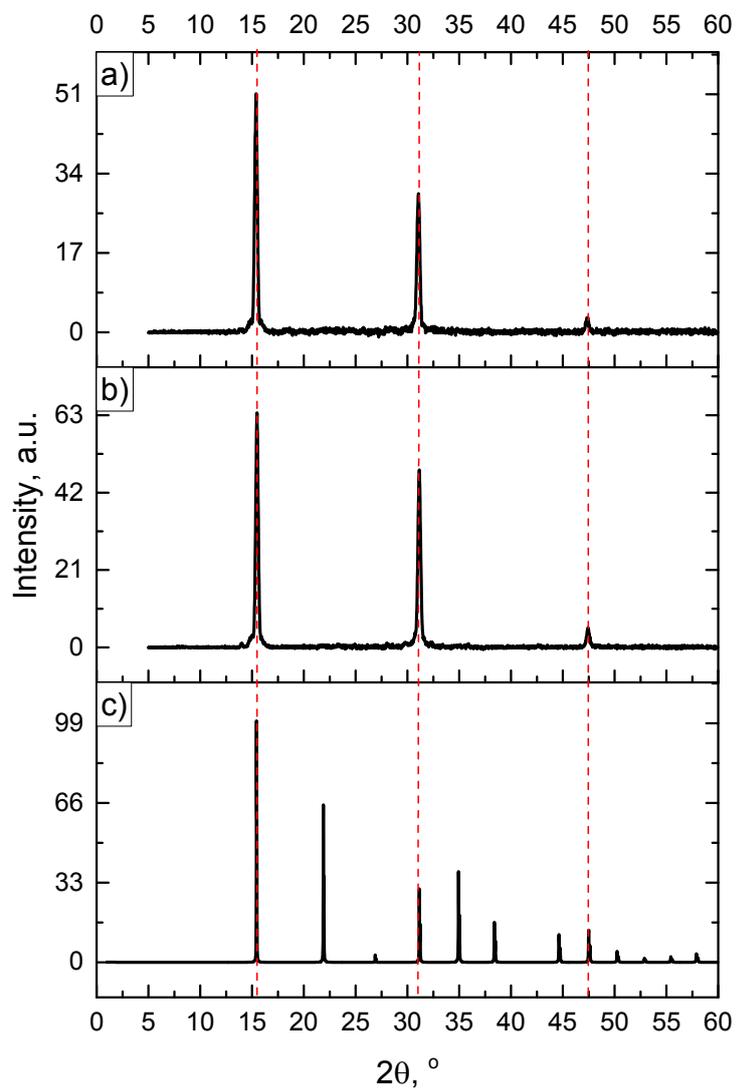
**Figure S1.** a) Experimental setup for gas sensor testing and (b) layout of the used sample geometry with 4 resistor-type devices fabricated on the same substrate.



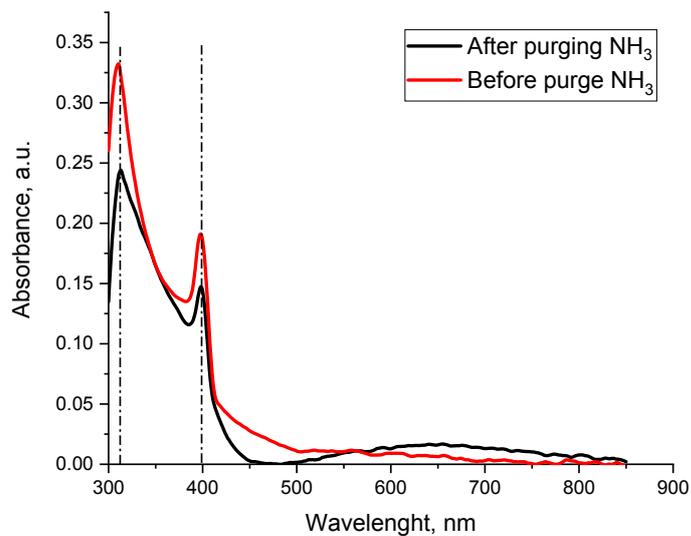
**Figure S2.** SEM images of the FAPbCl<sub>3</sub> film.



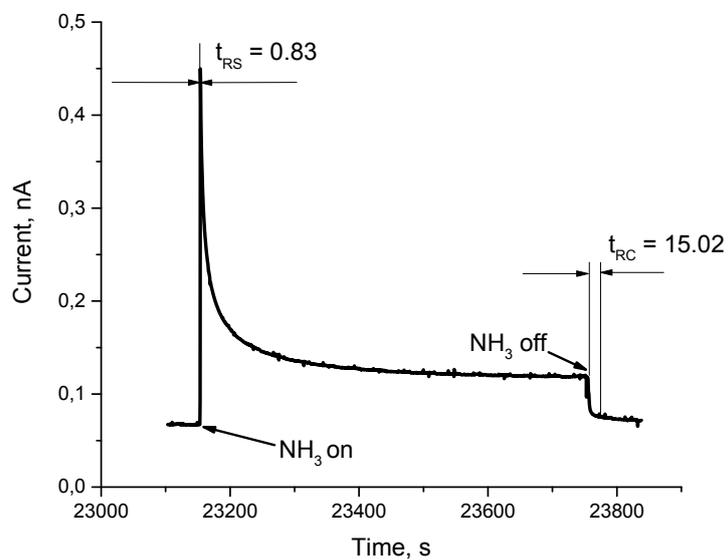
**Figure S3.** I–V curves for FAPbCl<sub>3</sub>-based resistor device measured in the presence of different concentrations of NH<sub>3</sub> (a) or H<sub>2</sub>S (b)



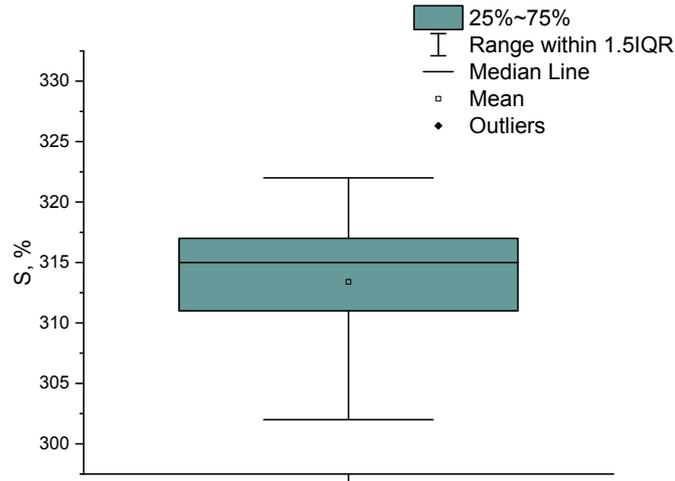
**Figure S4.** XRD pattern of the FAPbCl<sub>3</sub> film before (a) and after (b) exposure to the 1 ppm NH<sub>3</sub> compared to the reference pattern simulated from single crystal x-ray diffraction data (c).



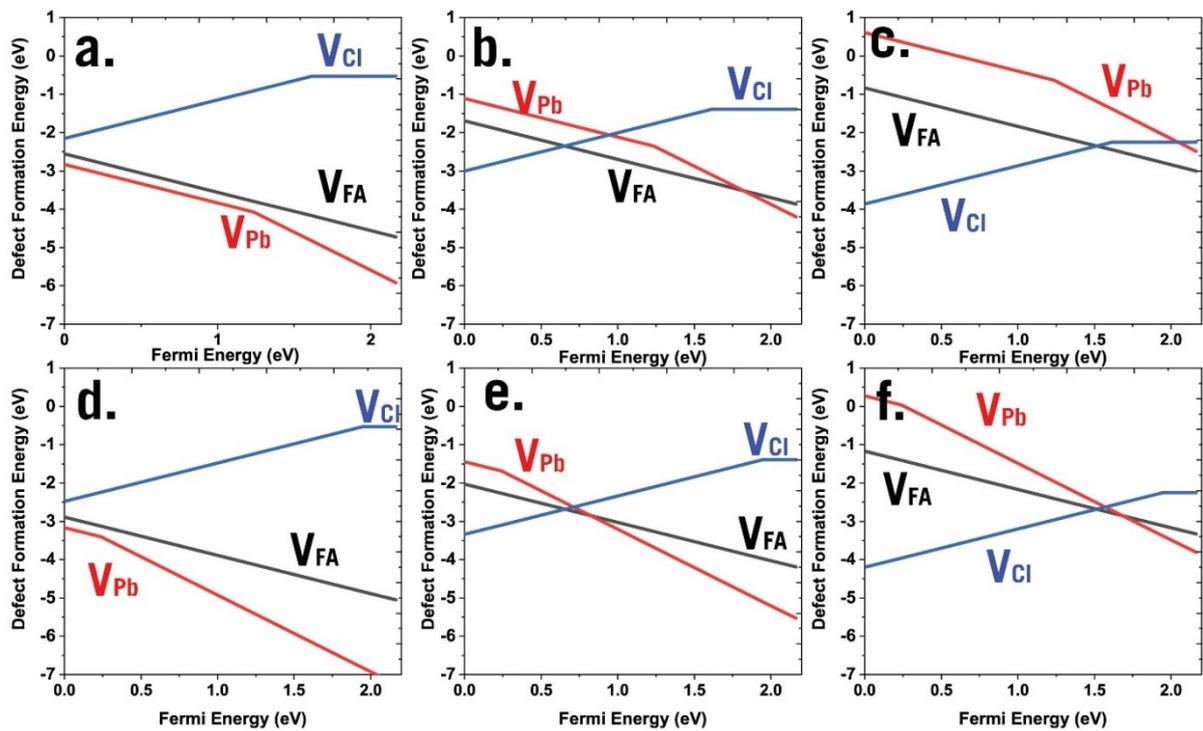
**Figure S5.** Absorption spectra of FAPbCl<sub>3</sub> before and after exposure to the 100 ppm of NH<sub>3</sub>



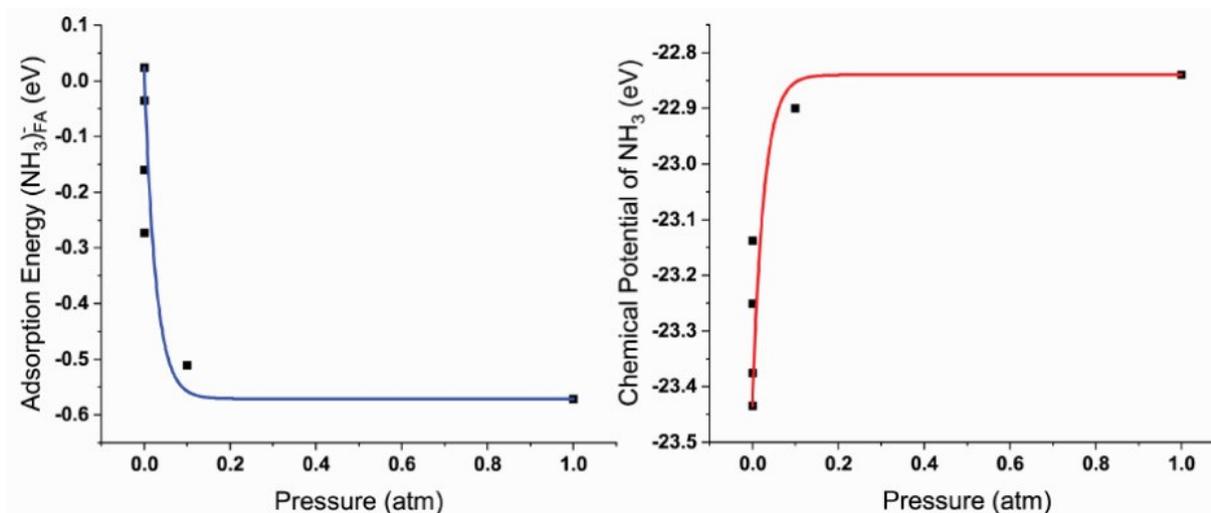
**Figure S6.** The response/recovery time of the gas sensor to 1 ppm ammonia.



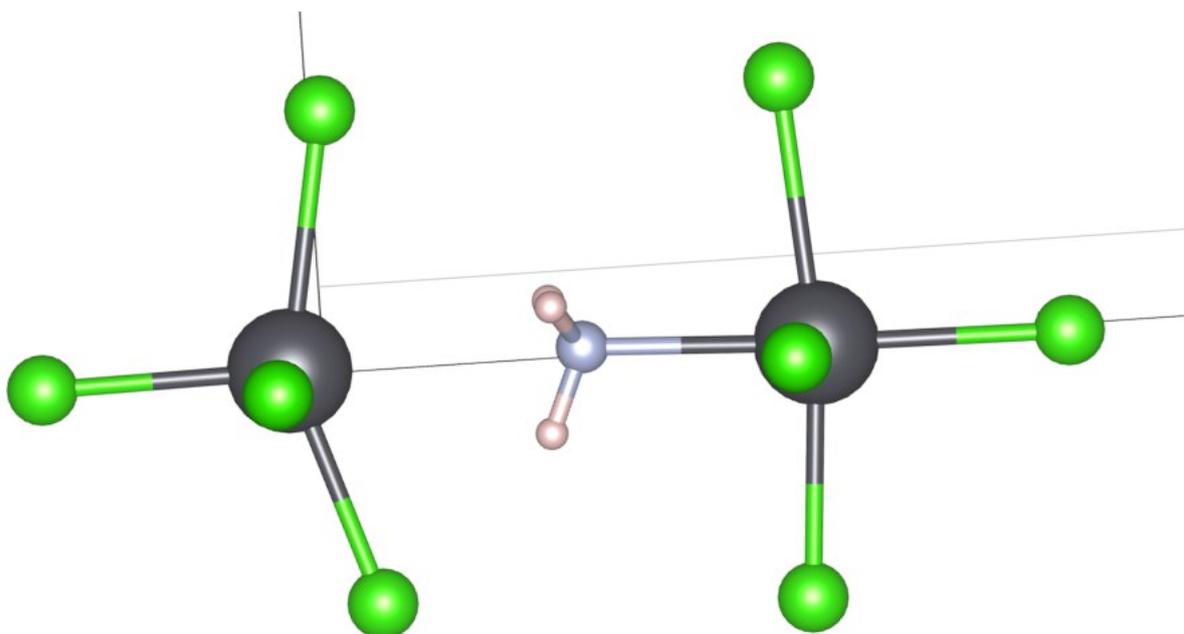
**Figure S7.** Statistical data obtained from ten sensors illustrating reproducibility of the sensor response to 1 ppm of ammonia.



**Figure S8.** The defect formation energies of  $V_{Cl}$ ,  $V_{FA}$ ,  $V_{Pb}$  for a. Cl Rich, b. Moderate, c. Pb Rich regimes at 0K and d. Cl Rich, e. Moderate, f. Pb Rich regimes at 300K.



**Figure S9.** (left) The pressure-dependent adsorption energy of NH<sub>3</sub> in a  $V_{FA}^-$  defect at 300K (right) Pressure-dependent chemical potential of ammonia gas at 300K. The pressures are partial pressures of ammonia.



**Figure S10.** Local alignment of NH<sub>3</sub> in a  $V_{cl}^+$  defect. Green = Cl, gray = Pb, blue = N, white = H.

## References

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