Supplementary Information

Polarization Induced NO_2 Sensing and Amine Generation using Sb Single-Atoms Embedded in Few-Layered $MnPS_3$ Flatlands

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Contents

1. Structural parameters of pristine and nitrobenzene intercalated $MnPS_3$ single crystals

Table S1. Lattice parameters from SXRD measurements.

Sample	$MnPS_3$	Mn_NB_1	Mn_NB_2	Mn_NB_3
Temp	100 K	100 K	100 K	100 K
Space group	C 1 2/m 1	C 1 2/m 1	C 1 2/m 1	C 1 2/m 1
Lattice parameters: *a, b, c* (Å)	5.8032(3), 10.0574(5), 6.5978(5)	5.8101(7), 10.0606(11), 7.8083(9)	5.8096(7), 10.0596(10), 8.9093(9)	5.8103(2), 10.0646(4), 9.6135(3)
α, β (°)	90,107	90,107	90,107	90,107
V(Å^3)	385.08(4)	456.41(8)	520.67(8)	562.18(3)

2. Synthesis of Sb/$MnPS_3$ and Sb Single Atoms (SAs)

30 mg of $KSb(OH)_6$ was dissolved in 250 ml of ultrapure water and 250 mg of nitrobenzene intercalated $MnPS_3$ crystals (Mn_NB_3) were added under sonication for 20 min. The mixture was then stirred rigorously for 24 hours at room temperature and centrifuged. The crystals were washed with ethanol and vacuum dried at 80°C for 12 hours. The as-prepared crystals were transferred to an alumina boat and carbonized at 1000°C for 3 hours with heating rate of 5°C/min. The sample collected was soaked in dil. H_2SO_4 for 6 hours to remove traces of metallic Sb and vacuum dried at 80°C for 12 hours. The concentration of SA loading was varied by increasing amount of $KSb(OH)_6$ precursor.

3. Compositional analyses using SEM-EDX

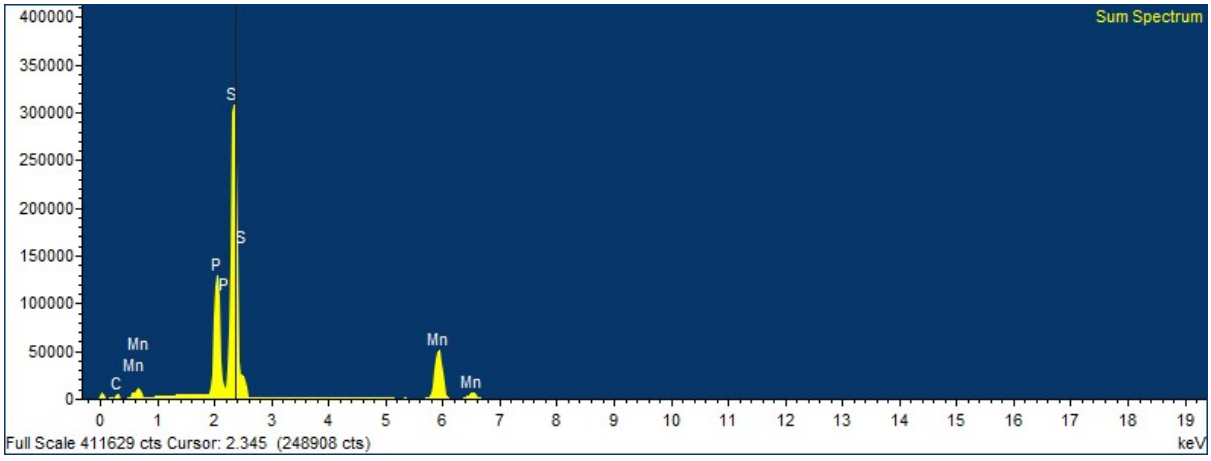

Figure S1. SEM-EDX qualitative estimation of $MnPS_3$ single crystals.

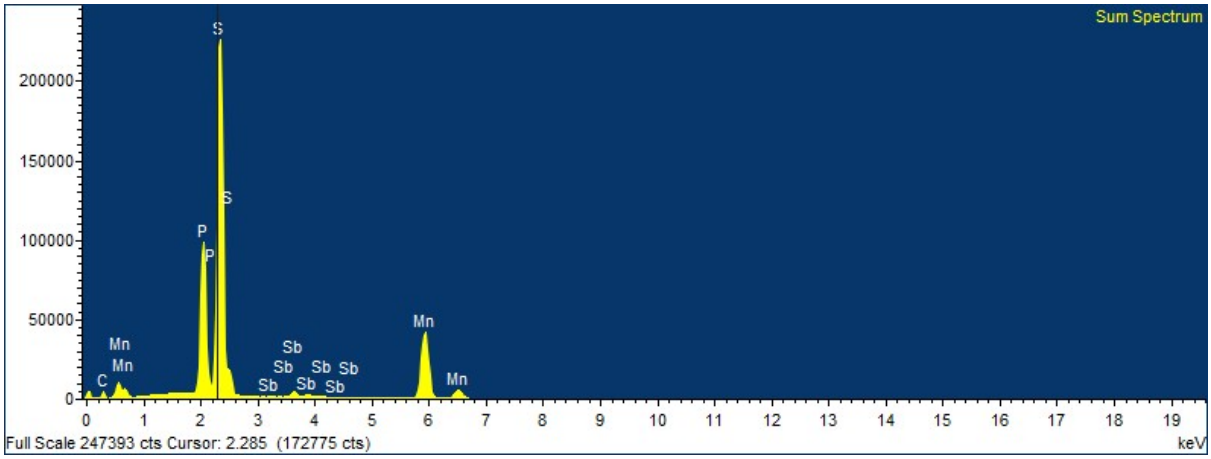

Figure S2. SEM-EDX qualitative estimation of Mn_Sb_3.5 sample.

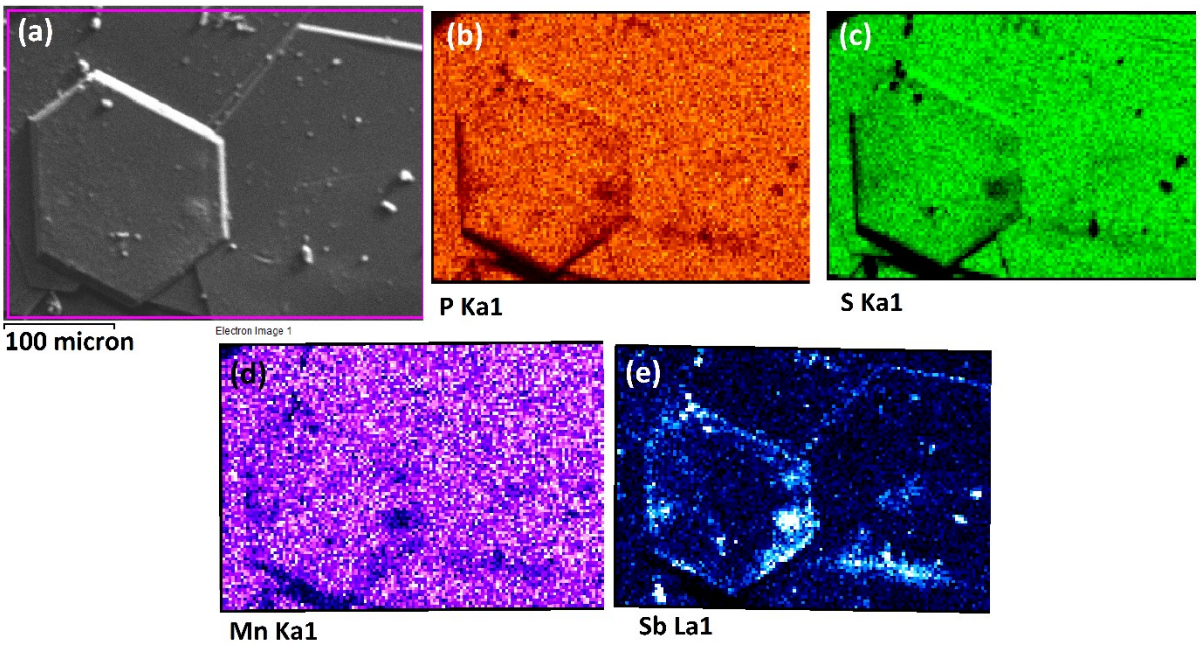

Figure S3. SEM-EDX colour mapping of Mn_Sb_3.5 sample.

4. TEM grid preparation and additional TEM images

Standard "Blue Tape" (Ultron systems, INC. Silicon Free Blue Adhesive Film P/N 1007R-6.0) was cut into small pieces, and the few layer crystals were transferred onto them by an antimagnetic tweezer. The scotch tape was now held between two pieces of weighing paper and the TEM grid (carbon coated Cu grid from Ted Pella Inc.) was placed on the exfoliated sample (attached to scotch tape) on the carbon side and rubbed gently with a third piece of weighing paper. The whole arrangement was transferred to a 2D heater at 80°C and rubbed gently on the grid to enable transfer of sample from scotch tape on grid. The residual organic

molecules (glue from scotch tape) were removed by heating the grids under vacuum at 120°C for 2 hours. The samples were then ready for loading in the TEM machine.

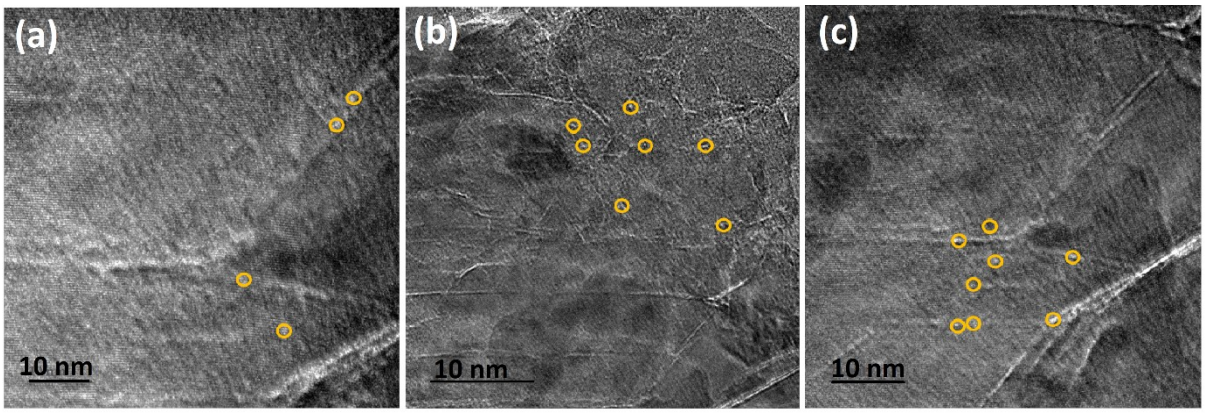

Figure S4. Bright field TEM images of (a) Mn_Sb_1.2 (b, c) Mn_Sb_2.0 samples, with Sb SAs highlighted in yellow colour circles.

5. XPS and BET results

Table S2. Values of binding energies (eV) of core-level spectra of different elements in all samples and their respective BET surface areas.

Elements	$MnPS_3$	Mn_NB_Sb_1.2	Mn_NB_Sb_3.5	Mn_NB_Sb_5
Mn $2p_{3/2}$	640.51	640.44	640.23	640.33
P-Sb (P $2p_{3/2}$)	134.17	134.21	134.25	134.22
S $2p_{3/2}$	161.76	161.70	161.32	161.21
N 1s C-N/N-O	—	400.13/402.04	400.13/402.04	400.13/402.04
Sb $3d_{5/2}$	530.0	530.89	530.94	529.98
BET surface area (m^2/g)	43	75	103	105

Table S3. Quantitative estimation of surface Sb composition (per formula unit of $MnPS_3$).

Elements	$MnPS_3$	Mn_NB_Sb_1.2	Mn_NB_Sb_3.5	Mn_NB_Sb_5
Mn 2p	1.002	1.002	1.002	1.002
P 2p	1.010	1.009	1.007	1.009
S 2p	2.998	2.995	2.988	2.994

Sb 3d	▬▬	1.172	3.411	4.759

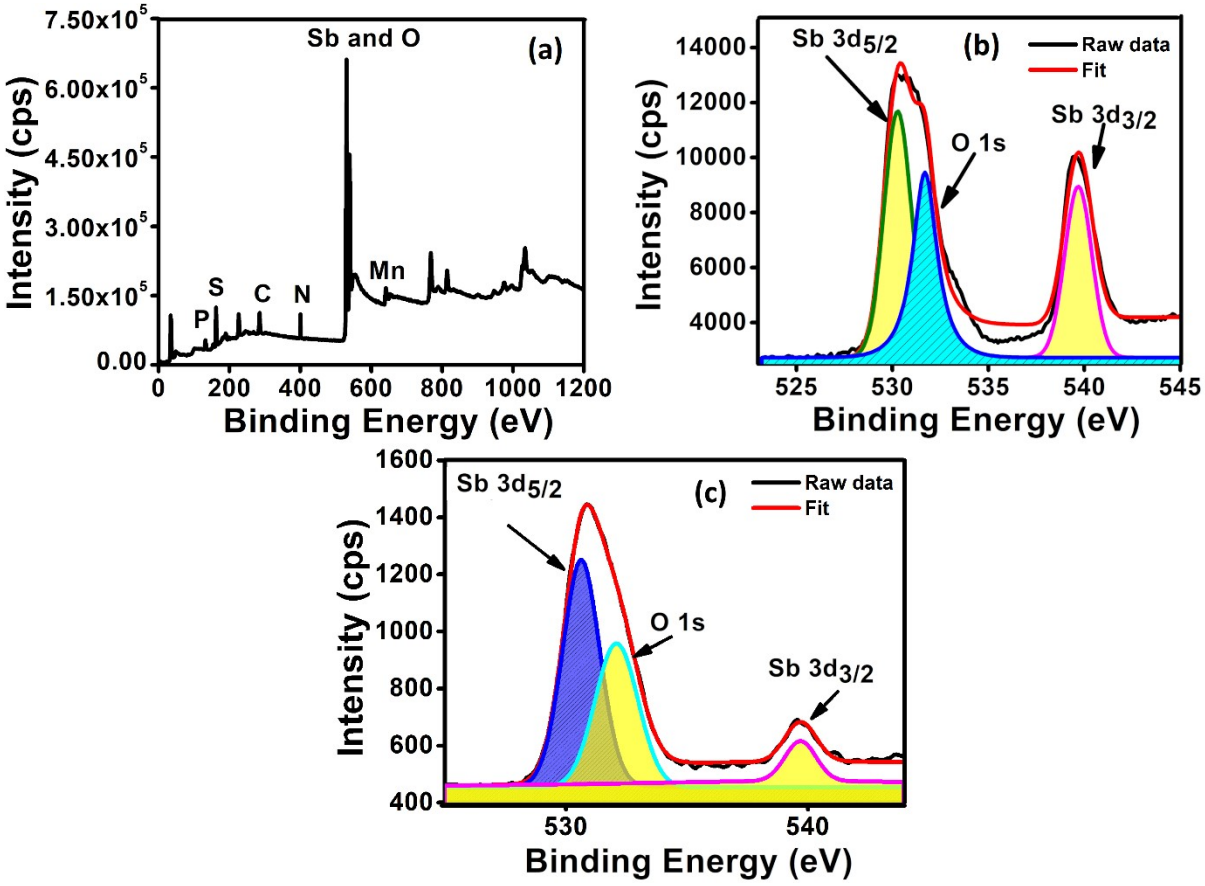

Figure S5. (a) Survey scan of Mn_Sb_3.5 sample, with all elements marked. (b) Sb 3d core level spectrum of Mn_NB_Sb_1.2 sample. (c) Sb 3d core level spectrum of Mn_NB_Sb_3.5 sample post catalytic measurements.

6. Gas sensing and ORR experiments

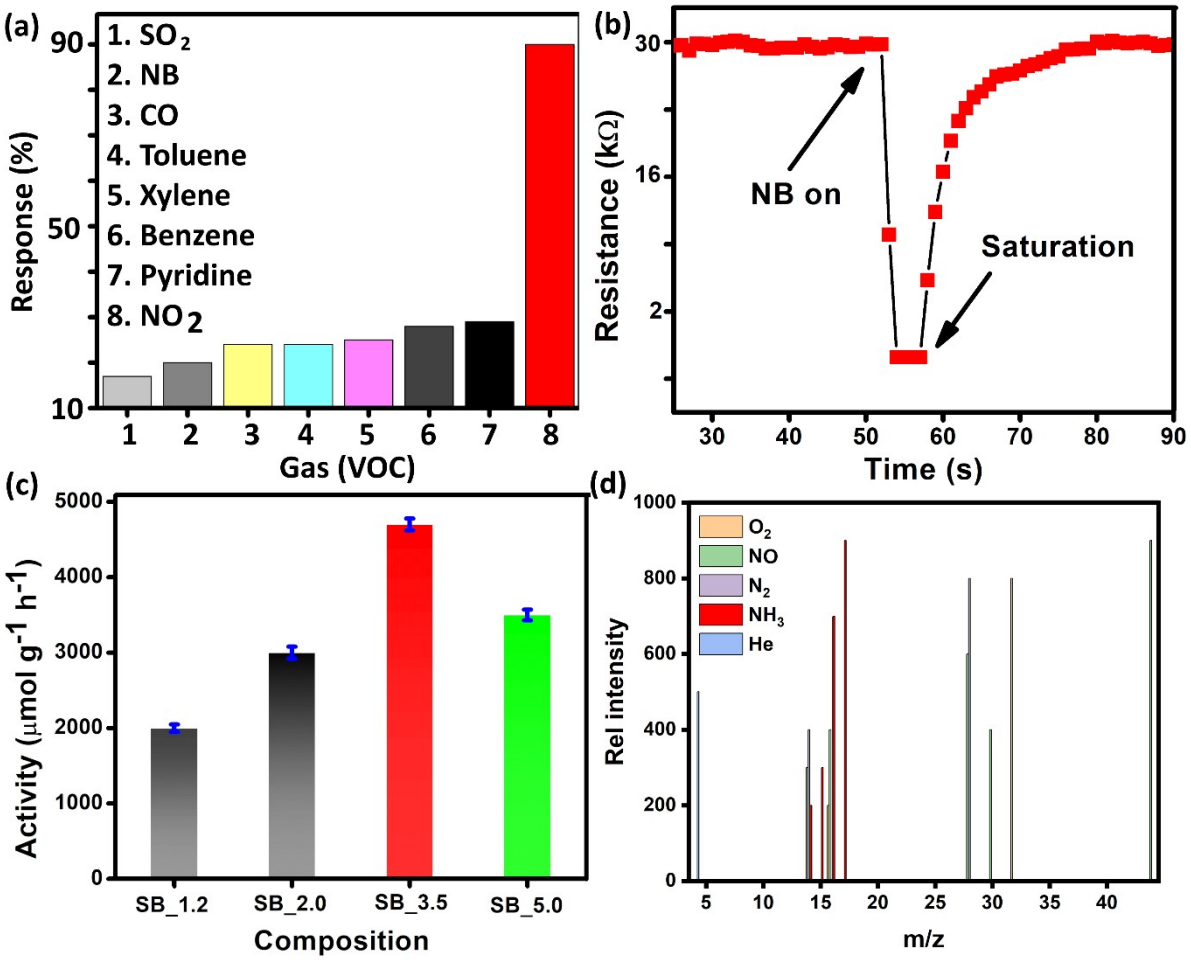

Figure S6. (a) Cross-sensitivity results of Mn_NB_Sb_3.5 sample, under 10 ppm of different gases and VOCs, at room temperature, in presence of 50μW green light, at θ=50°. (b) Dynamic response of Mn_NB_Sb_3.5 sample, on saturation, with 10 ppm NO_2 in presence of 50μW green light, at θ=50°**.** Response and recovery times were estimated as 10 s and 20 s, respectively. (c) Activity comparison of various compositions. (d) Gas chromatography results showing major components of catalytic reaction. [1-3]

Table S4. Error calculation in sensing measurements due to ambient light conditions.

Sample	Error (%)
Mn_NB_Sb_1.2	4.6
Mn_NB_Sb_3.5	5.1

Mn_NB_Sb_5.0	5.6

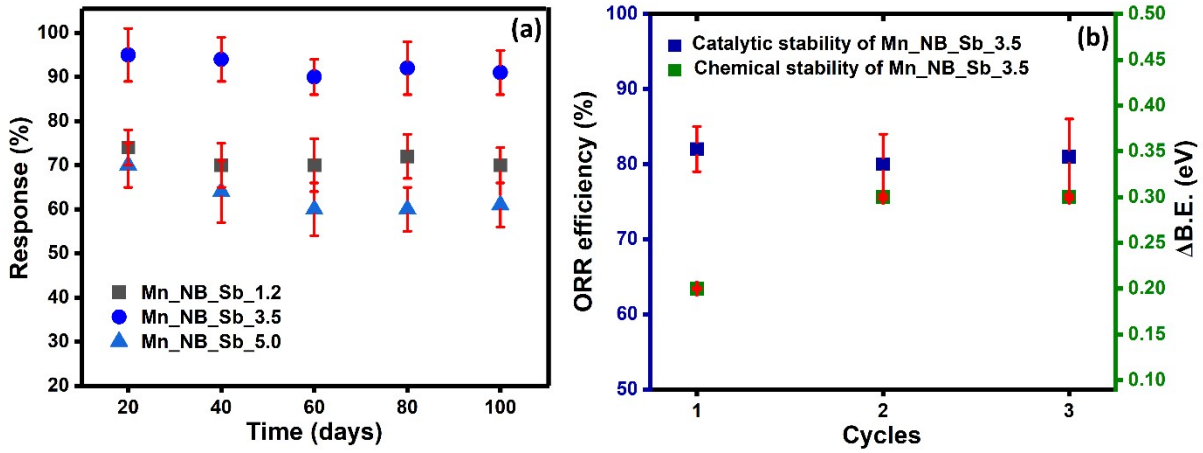

Figure S7. (a) Long term stability of the sensors with 10 ppm NO_2 in presence of 50µW green light, at θ=50° (b) Catalytic and chemical stability studies of Mn_NB_Sb_3.5 sample over three consecutive cycles.

Table S5. Statistical estimation of errors (%) in response estimation in sensing measurements.

θ◦	Mn_NB_Sb_1.2	Mn_NB_Sb_3.5	Mn_NB_Sb_5.0
0	1.2	1.4	2
30	2.7	2.1	2.2
60	1.4	1.8	2
90	1.7	1.8	1.6
120	1.1	1.8	1.9
150	2	1.3	1.6
180	1.6	2.5	1.4
210	2.4	2.2	2.1
240	2.2	2	2
270	2.8	2.3	2.5
300	2	1.9	2.6
330	1.7	1.9	1.8
360	1.9	1.6	1.5

7. Raman spectroscopy

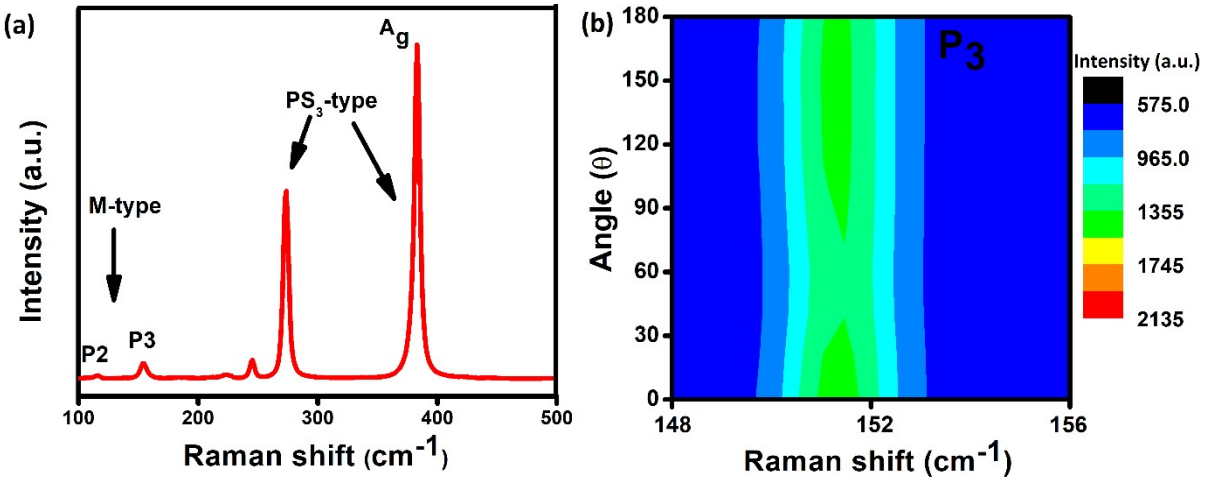

Figure S8. (a) Raman spectrum of $MnPS_3$ single crystal using a 532 nm laser source. (b) Polarization dependent Raman spectra of Mn_NB_3 sample, highlighting the P3 vibration mode (corresponding to the Mn^{2+} vibrations).

8. Theoretical results

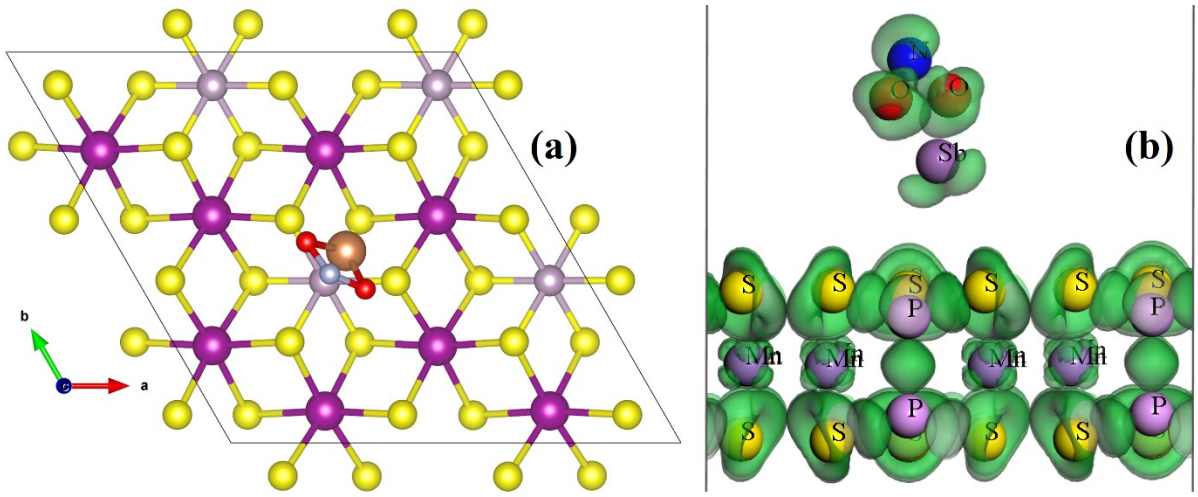

Figure S9. (a) Optimized atomic structure (top view) for NO_2 attached with single Sb atom over 2×2×1 supercell of $MnPS_3$ monolayer; (b) Electron density difference map (side view).

Table S6. Optimized Crystallographic parameters

Optimized CIF of the $MnPS_3$ bulk

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data_MnPS3
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_symmetry_Int_Tables_number       12
_symmetry_cell_setting            monoclinic
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_symmetry_equiv_pos_as_xyz
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  -x,y,-z
  -x,-y,-z
  x,-y,z
  x+1/2,y+1/2,z
  -x+1/2,y+1/2,-z
  -x+1/2,-y+1/2,-z
  x+1/2,-y+1/2,z
_cell_length_a                 6.2422
_cell_length_b                 11.0275
_cell_length_c                 7.2324
_cell_angle_alpha               90.0000
_cell_angle_beta               105.8931
_cell_angle_gamma                90.0000
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
S1    S    0.73344   0.34527   0.73816   0.00515  Uani   1.00
Mn1   Mn   0.50000   0.16639   0.50000   0.00631  Uani   1.00
S2    S    0.26261   0.50000   0.73914   0.00533  Uani   1.00
P1    P    0.55116   0.50000   0.65945   0.00440  Uani   1.00
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_atom_site_aniso_U_23
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Mn1     0.00408   0.00639   0.00881   0.00000   0.00234   0.00000
S2      0.00376   0.00551   0.00776   0.00000   0.00335   0.00000
P1      0.00343   0.00529   0.00498   0.00000   0.00201   0.00000
loop_
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_geom_bond_site_symmetry_2
_ccdc_geom_bond_type
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S1    P1     2.043   .    S
S1    Mn1    2.706   7_656 S
Mn1   S1     2.758   2_656 S
Mn1   S1     2.706   8_455 S
Mn1   S1     2.706   7_656 S
Mn1   S2     2.737   6_546 S
Mn1   S2     2.737   5_545 S
S2    P1     2.036   .    S
S2    Mn1    2.737   5_455 S
S2    Mn1    2.737   7_556 S
P1    S1     2.043   4_565 S
P1    P1     2.218   2_656 S
```

Optimized CIF of the $MnPS_3$ monolayer

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_symmetry_Int_Tables_number      1
_symmetry_cell_setting           triclinic
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
_cell_length_a                   6.2823
_cell_length_b                   6.2825
_cell_length_c                   22.9087
_cell_angle_alpha                 90.0000
_cell_angle_beta                  90.0000
_cell_angle_gamma                 120.0000
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
Mn1   Mn   0.33326  0.66669  0.50000  0.01267 Uiso  1.00
Mn2   Mn   0.66674  0.33331  0.50000  0.01267 Uiso  1.00
P1    P    0.00067  0.00095  0.45146  0.01267 Uiso  1.00
P2    P    0.99933  0.99905  0.54854  0.01267 Uiso  1.00
S1    S    0.00100  0.68878  0.42719  0.01267 Uiso  1.00
S2    S    0.99900  0.31122  0.57281  0.01267 Uiso  1.00
```

S3	S	0.31370	0.31412	0.42724	0.01267	Uiso	1.00
S4	S	0.68630	0.68588	0.57276	0.01267	Uiso	1.00
S5	S	0.68835	0.00141	0.42721	0.01267	Uiso	1.00
S6	S	0.31165	0.99859	0.57279	0.01267	Uiso	1.00

Table S7. Estimation of Gibb's Free Energy with contribution from laser source.

Reaction product	ΔG (eV)	hγ (eV)
NO_3^-	-1.7	1.2
HNO_3	-1.9	1.1
NO_2	-2.9	1.1
HNO_2	-3	1.2
NO	-4.2	1.1
HNO	-4	1.2
N	-4.3	1.1
NH	-4.4	1.1
NH_2	-5.3	1.2
NH_3	-6.2	1.1

References

1. Kovats, E., Helv. Chim. Acta, 1958, 41, 1915.

2. Van Den Dool, H., Kratz, P.D., J. Chromatography, 1963, 11, 463-471.

3. Lee, M.L., Vassilaros, D.L., White, C.M., Novotny, M., Anal. Chem., 1979, 51(6), 768-773.