Supplementary Information (SI) for Journal of Materials Chemistry C.

SUPPORTING INFORMATION

Heterostructured binary/ternary MoO_3/Bi_2MoO_6 metal oxides based acetone sensing devices relevant to non-invasive disease monitoring

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1. Characterization tools

To confirm the composition of the desired material, various characterization tools were employed. Surface morphology was investigated using a Field Emission Scanning Electron Microscope (SEM) from JEOL India Pvt. Ltd. (Model: JEOL JSM 7610f). Crystallographic analysis was conducted using a Bruker X-ray Diffractometer (XRD) (Model: D8 Advance Eco). Elemental analysis was carried out using X-ray Photoelectron Spectroscopy (XPS) from Physical Electronics (Model: PHI 5000 VersaProbe III). The functional groups of the materials under investigation were confirmed using a Fourier Transform Infrared Spectrometer (FTIR) from Thermo-Scientific (Model: Nicolet 6700). UV-Visible absorption and energy band gap measurements were performed using a UV-Visible Spectrophotometer from Thermo-Scientific (Model: Evolution 201). Exhaled human breath was collected in Tedlar bags from Shilpent Enterprises India. The acetone gas sensing performance of the prepared sensing device was evaluated using an Electrometer/Source Meter from Keithley (Model: 6517B) to measure electrical parameters. Molecular structures were generated using the Gaussian 09 program, and optimization was carried out using the LanL2DZ basis set in conjunction with the ground state B3LYP density functional theory model.

2. Device fabrication

The spin coating method was used to create the sensing components, which entails applying a continuously thin layer of sensing material onto a substrate that has been well-cleaned. Making a solution with the sensing material dissolved in distilled water was the first stage in this procedure. To guarantee homogeneity, the sensing materials were then coated five times at 1000 rpm on each glass substrate. The film was annealed at 150°C after deposition in order to improve its properties and eliminate any solvent residue. Each gadget was then covered with silver electrodes in preparation for further electrical tests.

3. Experimental set-up

A temperature controller, four sensors, and a heater made up the gas sensing setup in which all of the tests were conducted. The current variations were recorded with the Keithley electrometer. The gas sensor system's interior design consists of four 2-liter sample containers that are each attached to a heated plate. A programmable temperature controller may be used to change the temperature. A micropipette was used to add acetone to the sensing chamber. Human breath was first collected in Tedlar gas collection bags and then injected to observe the response to exhaled breath. The relationship given in (S1) was used to calculate the acetone concentration, which was expressed in parts per million (ppm).

$$V_x = \frac{V \times C \times M}{22.4 \times d \times p} \times 10^{-9} \times \frac{273 + T_r}{273 + T_c} \quad \text{(S1)}$$

Where V_x represents the volume of injected acetone, V represents the volume of the gas sensing setup, C represents the part-per-million (ppm) concentration of the injected acetone, M represents the acetone's molar mass in g/mol, d represents the specific gravity of the injected liquid in g/cm^3, p represents the liquid's purity in percentage, T_r represents the room temperature, and T_c represents the temperature of the internal hot plate.

4. SEM and EDS

Table S1: Atomic and weight percentage of the elements estimated by EDS spectra

MoO_3			**Bi_2MoO_6**			**MoO_3/Bi_2MoO_6**		
Element	Weight%	Atomic%	Element	Weight%	Atomic%	Element	Weight%	Atomic%
O K	37.74	78.43	O K	26.66	69.41	O K	31.23	75.04
Mo L	62.26	21.57	Mo L	68.00	29.52	Mo L	56.80	22.76
Total	100.00		Bi M	5.34	1.06	Bi M	11.97	2.20
			Total	100.00		Total	100.00	

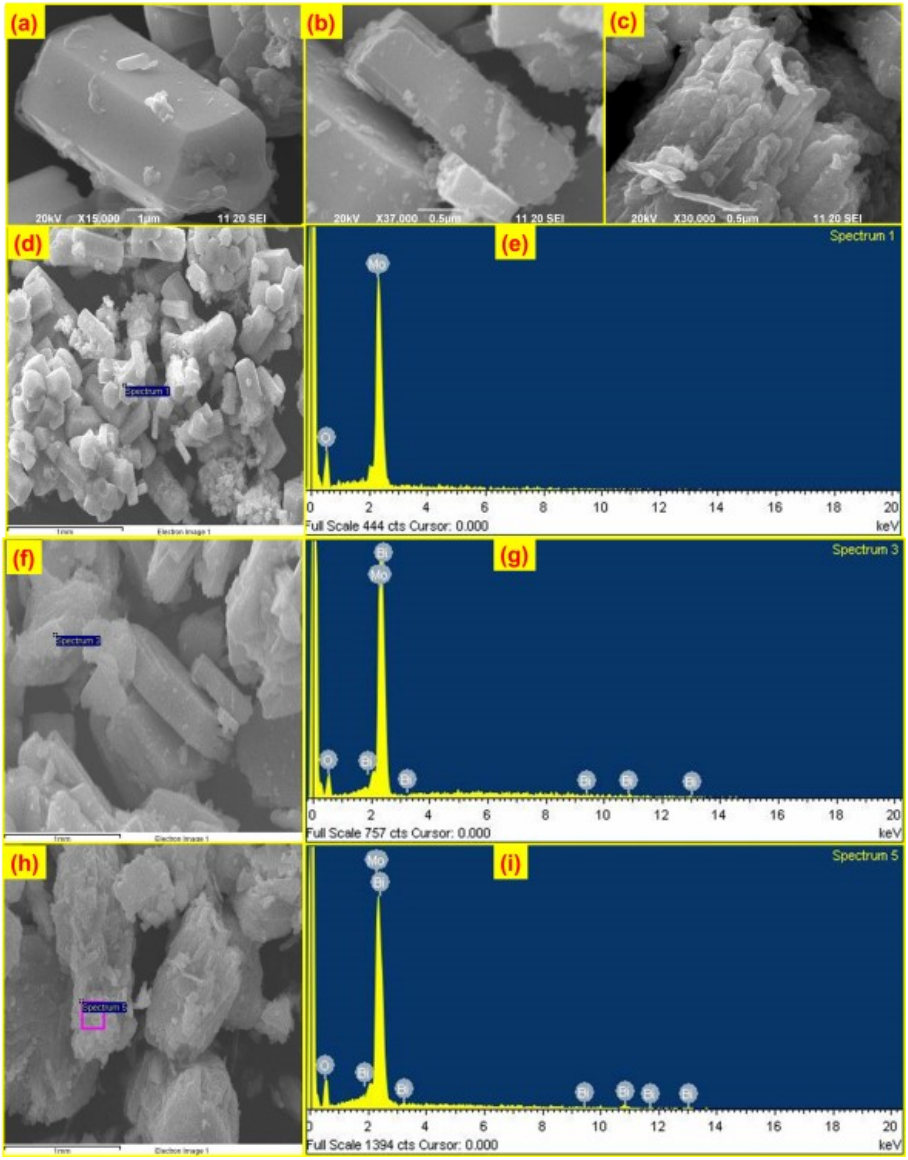

Fig. S1. SEM images at the scale of 5 µm of (a) MoO_3 (b) Bi_2MoO_6 (c) MoO_3/Bi_2MoO_6 (d) Image used for EDS scanning for MoO_3 (e) EDS spectrum of MoO_3 (f) Image used for EDS

scanning for Bi_2MoO_6 (g) EDS spectrum of Bi_2MoO_6 (h) Image used for EDS scanning for MoO_3/Bi_2MoO_6 (i) EDS spectrum of MoO_3/Bi_2MoO_6.

5. XRD

Table S2: XRD analysis for MoO_3, Bi_2MoO_6, MoO_3/Bi_2MoO_6

MoO_3			Bi_2MoO_6			MoO_3/Bi_2MoO_6		
2θ (°)	**FWHM**	**Braggs planes**	**2θ (°)**	**FWHM**	**Braggs planes**	**2θ (°)**	**FWHM**	**Bragg's planes**
12.7767	0.1791	020	12.8246	0.0964	020	12.787	0.202	020
23.3685	0.3194	110	23.40853	0.2984	120	23.409	0.202	110
25.755	0.2535	120	25.74045	0.289	111	23.649	0.313	120
27.3344	0.1342	021	27.33393	0.144	131	25.821	0.387	111
27.9558	0.1331	130	33.20259	0.2376	200	27.239	0.156	021
33.1657	0.2883	101	33.805	0.2371	210	33.167	0.802	101
33.7434	0.2883	111	35.57337	0.2276	201	33.774	0.238	111
35.4966	0.3218	041	39.12955	0.3261	240	35.431	0.166	041
39.0124	0.5768	131	45.81438	0.3978	202	39.021	0.161	131
45.7586	0.2894	200	46.49452	0.3978	260	46.422	0.249	210
46.3564	0.29	210	49.31226	0.6115	320	49.275	0.157	320
49.2555	0.1869	002	55.29752	0.2697	331	52.81	0.393	211
52.5833	0.5747	211	56.44404	0.33	082	55.258	0.277	331
54.1125	0.5833	221	64.70292	0.47	282	56.4	0.8	082
55.2997	0.5901	112	69.59995	0.2797	420	58.867	0.46	081
58.8749	1.5246	081	76.61514	0.5593	211	64.813	0.394	282
64.5705	0.6715	152	78.94707	0.5593	214	69.526	0.146	212
69.6008	0.7693	212				79.044	0.146	214

Table S3: Size of each element estimated by Scherrer's formula

Sample	**Size (nm)**
MoO_3	34.264
Bi_2MoO_6	31.595
MoO_3/Bi_2MoO_6	37.003

6. XPS Table Atomic weight percentage

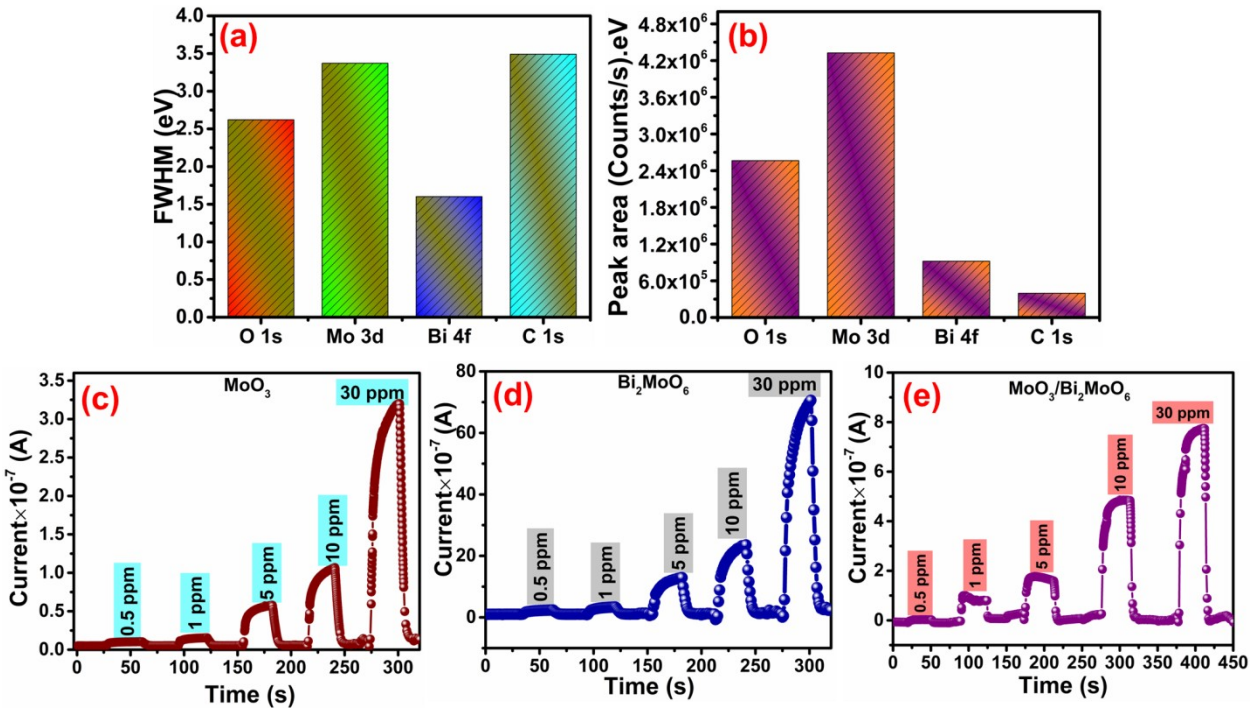

Fig. S2. (a) FWHM of each element presents in XPS spectrum (b) Peak area of each element in XPS. Acetone sensing characteristics for (c) MoO_3 (d) Bi_2MoO_6 and (e) MoO_3/Bi_2MoO_6 in the range of 0.5-30 ppm.

Table S4: Peak binding energy, FWHM, peak area and atomic percentage of each element estimated by XPS spectra

Element	**Peak BE**	**FWHM (eV)**	**Peak Area (CPS.eV)**	**Atomic (%)**
O 1s	530.83	2.62	2.56236E6	57.03
Mo 3d	233.16	3.37	4.32426E6	20.48
Bi 4f	159.38	1.6	918665.15	1.2
C 1s	285.12	3.49	395459.69	21.3

6. UV-Visible absorption peaks and optical band gap energy

Tauc equation

$$\alpha h\upsilon = A(h\upsilon - E_g)^n \quad \text{(S2)}$$

Where A is a constant, υ is the band transition frequency, and exponent n describes the band transition's characteristics. n=1/2 and 3/2, respectively, for direct allowed and direct forbidden transitions. Indirect allowed transitions have n=2 and indirect forbidden transitions have n=3 respectively.

Table S5: Absorption peaks and band gaps of the materials by UV-visible absorption analysis

Sample	Peaks (at nm)	Optical band gap energy (eV)
MoO_3	233, 300	3.37
Bi_2MoO_6	232	2.93
MoO_3/Bi_2MoO_6	227, 300	3.20

8. Acetone sensing studies

Table S6: Sensor response of MoO_3, Bi_2MoO_6, and MoO_3/Bi_2MoO_6 with respect to the acetone concentration

Concentration (ppm)	MoO_3	Bi_2MoO_6	MoO_3/Bi_2MoO_6
0.5	1.003	1.285	1.431
1	2.004	2.249	4.965
5	8.680	11.780	8.793
10	20.299	22.440	24.265
30	31.490	34.795	38.745
50	53.310	44.200	80.972
100	64.927	53.540	104.153
200	95.455	67.250	162.346
500	104.780	84.400	184.678
1000	108.744	94.150	302.062
1500	113.714	155.250	460.387

Limit of detection (LOD) analysis for MoO_3, Bi_2MoO_6, and MoO_3/Bi_2MoO_6

Limit of detection formula

$$LOD = \frac{3\sigma}{s} \quad \text{(S3)}$$

Where σ is the standard deviation and s is the slope of the linearly fitted graph between sensor response and concentration.

Table S7: LOD of each device in different concentration ranges and in logarithmic scale

Total	MoO_3 (ppm)	Bi_2MoO_6 (ppm)	MoO_3/Bi_2MoO_6 (ppm)
In 0.5-1500 ppm range	60.755	61.965	0.560
In Logarithmic scale	0.594	0.559	0.168
In 1-30 ppm range	8.100	8.451	0.287
In 50-1500 range	872.822	312.515	0.224

Table S8: Sensor response at different temperature for MoO_3, Bi_2MoO_6, and MoO_3/Bi_2MoO_6

Temperature (°C)	MoO_3	Bi_2MoO_6	MoO_3/Bi_2MoO_6
27	5.585	10.490	9.605
50	10.631	16.020	18.385
100	20.299	22.440	24.265
150	35.988	30.730	34.425
200	40.080	26.040	54.115
250	47.106	23.850	39.940

300	63.054	22.330	22.280
350	72.236	21.920	14.000
400	42.275	19.510	10.710

Table S9: Selectivity studies for MoO_3, Bi_2MoO_6, and MoO_3/Bi_2MoO_6

Analytes	**MoO_3**	**Bi_2MoO6**	**MoO_3/Bi_2MoO_6**
Acetone	20.299	22.44	24.265
Methanol	10.469	20.964	12.896
Ethanol	9.21	19.559	10.452
Ammonia	15.921	20.915	6.349
Aniline	8.6	15.981	5.211
Xylene	5.217	13.91	4.921
Formaldehyde	4.321	12.056	4.265
Water	2.395	11.459	2.526

Response and recovery times formula

$$I(t) = I_a\left(e^{-t/t_{response}}\right) \quad \text{(S4)}$$

$$I(t) = I_a\left(1 - e^{-t/t_{recovery}}\right) \quad \text{(S5)}$$

Table S10: Response and recovery times

Material	**Response time (s)**	**Recovery times (s)**
MoO_3	4.76	6.57
Bi_2MoO_6	6.88	6.26
MoO_3/Bi_2MoO_6	6.86	4.64

9. DFT studies

Formulae used for calculating electronic properties

$$HOMO - LUMO\ gap\ (\Delta E) = E_{LUMO} - E_{HOMO} \quad \text{(S6)}$$

$$Electron\ affinity\ (EA) = -E_{LUMO} \quad \text{(S7)}$$

$$Ionization\ potential\ (IP) = -E_{HOMO} \quad \text{(S8)}$$

$$Electronegativity\ (\mu) = -\left(\frac{E_{HOMO} + E_{LUMO}}{2}\right) \quad \text{(S9)}$$

$$Chemical\ potential\ (\chi) = \left(\frac{E_{HOMO} + E_{LUMO}}{2}\right) \quad \text{(S10)}$$

$$Chemical\ hardness\ (\eta) = \left(\frac{E_{LUMO} - E_{HOMO}}{2}\right) \quad \text{(S11)}$$

$$Chemical\ softness\ (\sigma) = \frac{1}{\eta} \tag{S12}$$

$$Nucleophilic\ index\ (\omega) = -\frac{\mu^2}{2\eta} \tag{S13}$$

$$Charge\ transfer\ (\Delta N_{max}) = -\left(\frac{\mu}{\eta}\right) \tag{S14}$$

$$SR = \frac{E_{HLG\ (air)} - E_{HLG\ (analyte)}}{E_{HLG\ (air)}} \tag{S15}$$

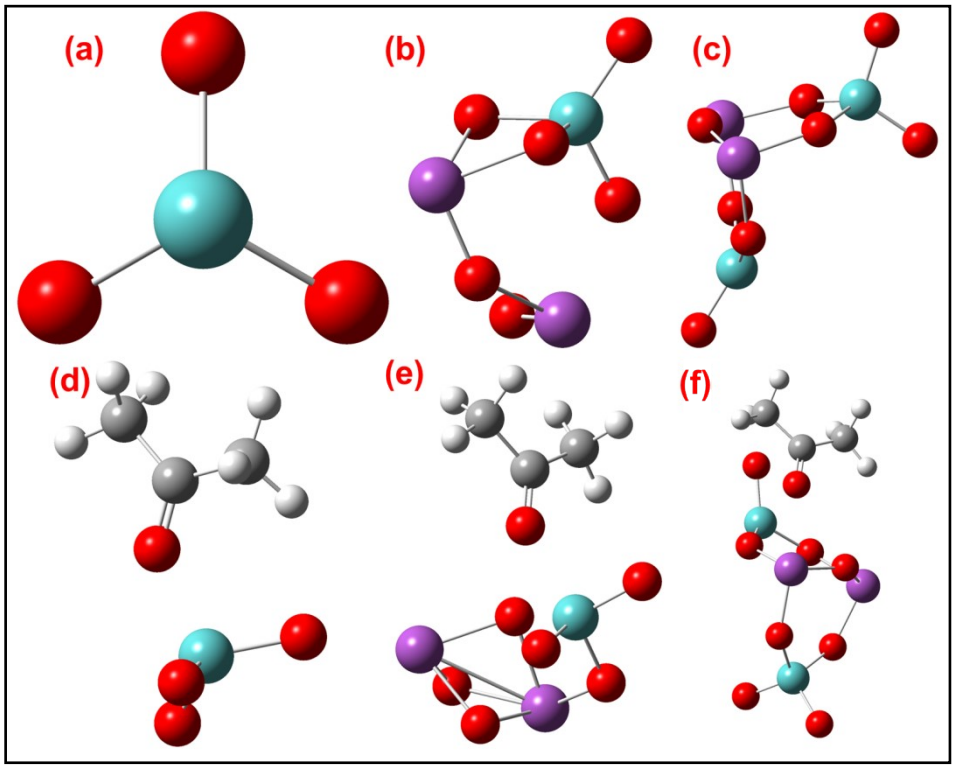

Fig. S3. Optimized structures for (a) MoO_3 (b) Bi_2MoO_6 (c) MoO_3/Bi_2MoO_6 (d) MoO_3-acetone (e) Bi_2MoO_6-acetone (f) MoO_3/Bi_2MoO_6-acetone species.

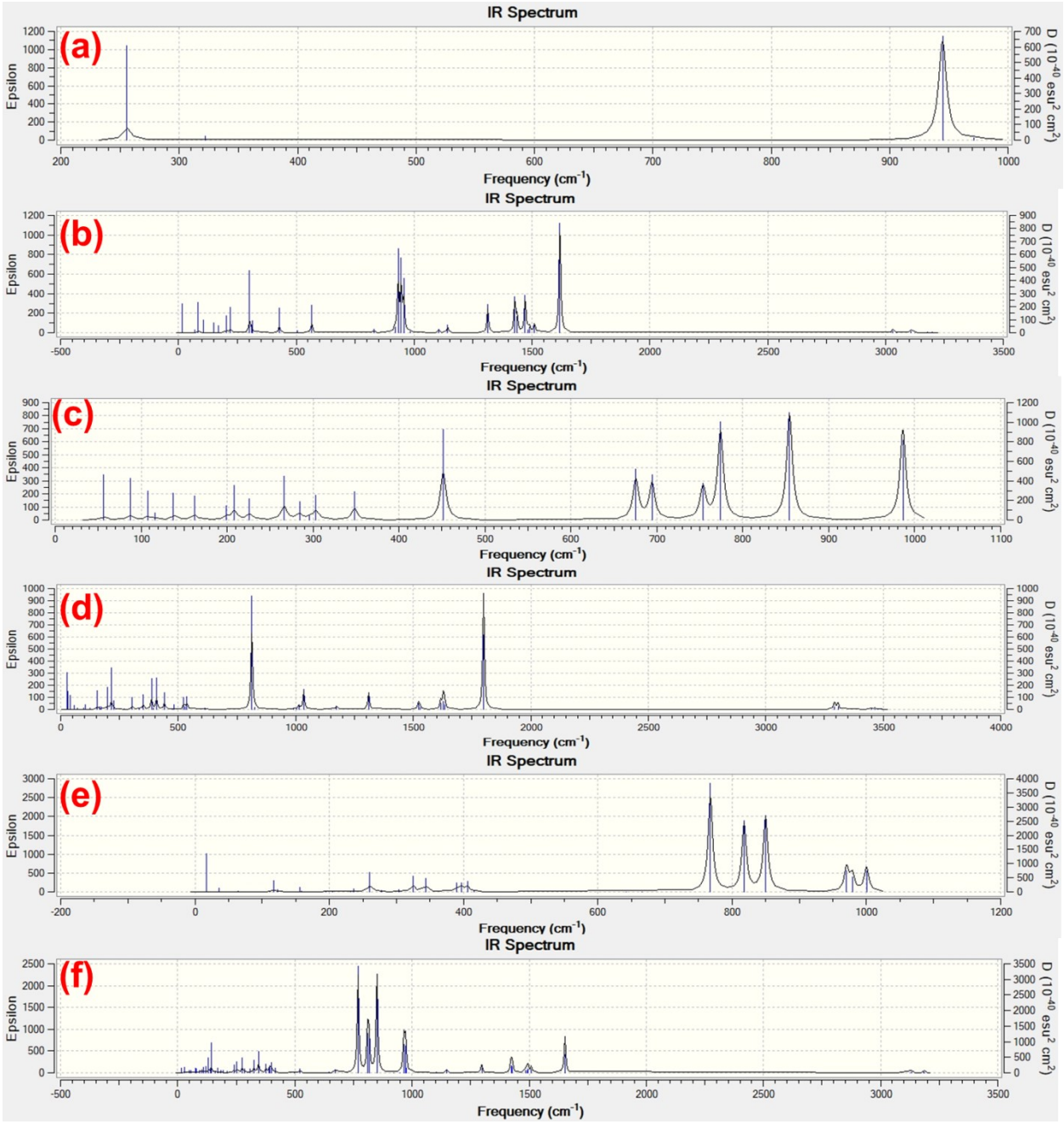

Fig. S4. Infrared spectrum based on DFT studies for (a) MoO_3 (b) Bi_2MoO_6 (c) MoO_3/Bi_2MoO_6 (d) MoO_3-acetone (e) Bi_2MoO_6-acetone (f) MoO_3/Bi_2MoO_6-acetone.

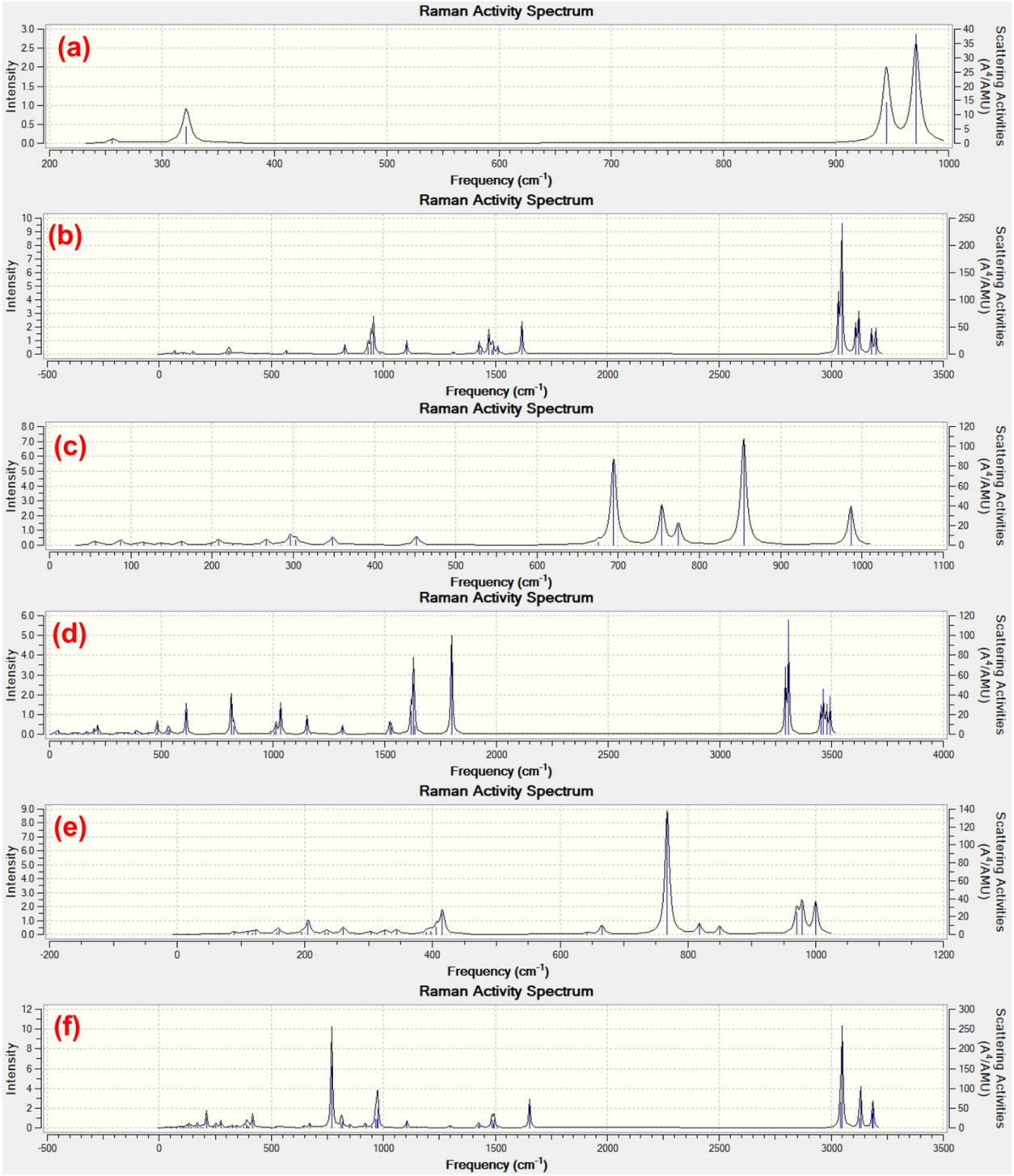

Fig. S5. Raman spectrum based on DFT studies for (a) MoO_3 (b) Bi_2MoO_6 (c) MoO_3/Bi_2MoO_6 (d) MoO_3-acetone (e) Bi_2MoO_6-acetone (f) MoO_3/Bi_2MoO_6-acetone.

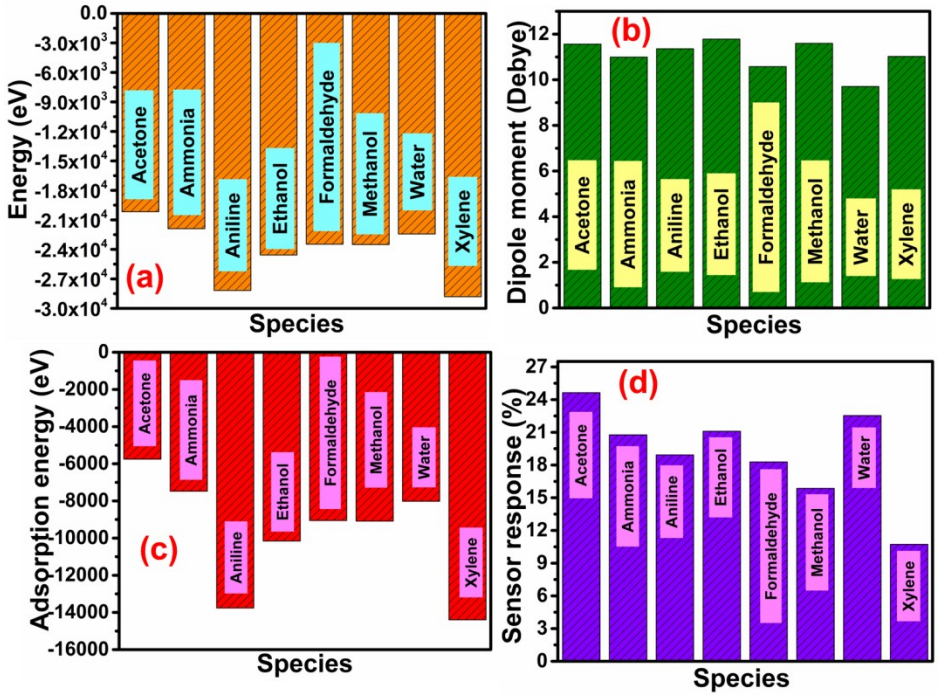

Fig. S6. Electronic parameters calculated by the DFT studies of MoO_3/Bi_2MoO_6 interaction with different VOCs (a) Total energy (b) Dipole moment (c) Adsorption energy (d) Sensor response.

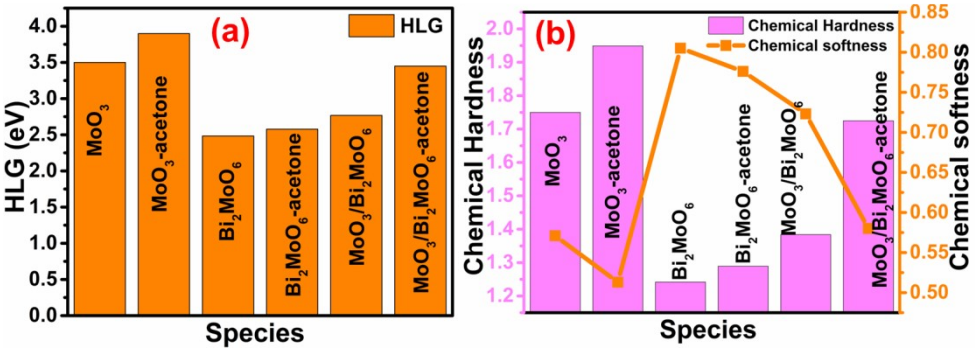

Fig. S7. (a) HOMO-LUMO gap (HLG) (b) Chemical hardness and softness.

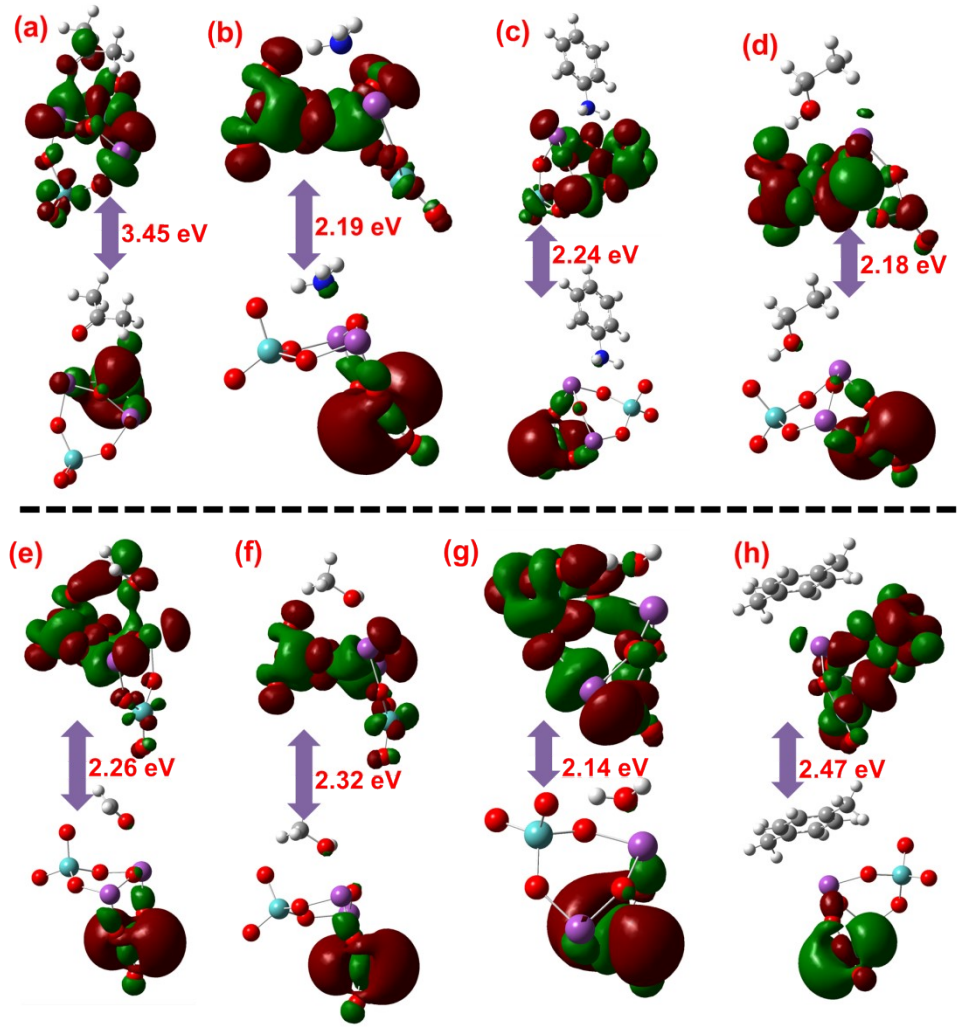

Fig. S8. HOMO-LUMO representation and their HLG energy for MoO_3/Bi_2MoO_6 interaction with different VOCs (a) Acetone (b) Ammonia (c) Aniline (d) Ethanol (e) Formaldehyde (f) Methanol (g) Water (h) Xylene.

Table S11: Electronic parameters for MoO_3, Bi_2MoO_6, MoO_3/ Bi_2MoO_6 and interaction of these with acetone.

Species	HOMO (eV)	LUMO (eV)	HOMO-LUMO gap, HLG (eV)	Electron affinity (eV)	Ionization potential (eV)	Electronegativity (eV)	Chemical potential (eV)	Chemical hardness (eV)	Chemical softness (eV)	Nucleophilicity index	N max	E (eV)	Dipole moment (Debye)
MoO_3	-8.891	-5.391	3.500	5.391	8.891	7.141	-7.141	1.750	0.571	-14.571	4.081	-7979.040	5.241
MoO_3-acetone	-7.642	-3.744	3.898	3.744	7.642	5.693	-5.693	1.949	0.513	-8.315	2.921	-13236.540	11.378

Bi_2MoO_6	-5.813	-3.329	2.484	3.329	5.813	4.571	-4.571	1.242	0.805	-8.412	3.681	-20356.954	7.597
Bi_2MoO_6-acetone	-5.506	-2.928	2.578	2.928	5.506	4.217	-4.217	1.289	0.776	-6.898	3.271	-25612.930	7.978
MoO_3/ Bi_2MoO_6	-6.993	-4.226	2.768	4.226	6.993	5.609	-5.609	1.384	0.723	-11.369	4.054	-14420.233	8.091
MoO_3/ Bi_2MoO_6-acetone	-4.638	-1.188	3.450	1.188	4.638	2.913	-2.913	1.725	0.580	-2.460	1.689	-20169.931	11.564

Table S12: Adsorption energies and sensor response for MoO_3, Bi_2MoO_6, MoO_3/ Bi_2MoO_6

Species	Adsorption Energy (eV)	Sensor response (%)
MoO_3	-5257.499	10.210
Bi_2MoO_6	-5255.976	3.784
MoO_3/ Bi_2MoO_6-	-5749.698	24.638

Table S13: Selectivity studies for MoO_3/Bi_2MoO_6 based on DFT studies

Species	Energy (eV)	Dipole moment (Debye)	Adsorption energy (eV)
MoO_3/Bi_2MoO_6-acetone	-0169.9313	11.5643	-5749.698
MoO_3/ Bi_2MoO_6-ammonia	-21896.5715	10.995	-7476.338
MoO_3/ Bi_2MoO_6-aniline	-28182.605	11.361	-13762.372
MoO_3/ Bi_2MoO_6-ethanol	-24576.125	11.784	-10155.892
MoO_3/ Bi_2MoO_6-formaldehyde	-23472.7874	10.577	-9052.554
MoO_3/ Bi_2MoO_6-methanol	-23506.2573	11.5987	-9086.024
MoO_3/ Bi_2MoO_6-water	-22437.1897	9.7084	-8016.956
MoO_3/ Bi_2MoO_6-xylene	-28815.5567	11.0252	-14395.323

Table S14: Electronic parameters for MoO_3/Bi_2MoO_6 after interaction with different VOCs

Species	HOMO (eV)	LUMO (eV)	Band gap (eV)	Electron affinity (eV)	Ionization potential (eV)	Electro negativity (eV)	Chemical potential (eV)	Chemical hardness	Chemical Softness	Nucleo philicity index	Charge transfer (N_{max})
MoO_3/Bi_2MoO_6-acetone	-4.638	-1.188	3.450	1.188	4.638	2.913	-2.913	1.725	0.580	-2.460	1.689
MoO_3/ Bi_2MoO_6—ammonia	-5.338	-3.145	2.193	3.145	5.338	4.241	-4.241	1.096	0.912	-8.202	3.868
MoO_3/ Bi_2MoO_6—aniline	-5.396	-3.152	2.244	3.152	5.396	4.274	-4.274	1.122	0.891	-8.142	3.810
MoO_3/ Bi_2MoO_6—ethanol	-5.418	-3.234	2.184	3.234	5.418	4.326	-4.326	1.092	0.916	-8.567	3.961
MoO_3/ Bi_2MoO_6--formaldehyde	-5.558	-3.296	2.262	3.296	5.558	4.427	-4.427	1.131	0.884	-8.663	3.914
MoO_3/ Bi_2MoO_6-methanol	-5.430	-3.101	2.329	3.101	5.430	4.265	-4.265	1.164	0.859	-7.813	3.663
MoO_3/ Bi_2MoO_6--water	-5.437	-3.293	2.144	3.293	5.437	4.365	-4.365	1.072	0.933	-8.885	4.071
MoO_3/ Bi_2MoO_6—xylene	-5.561	-3.090	2.471	3.090	5.561	4.325	-4.325	1.236	0.809	-7.570	3.500

Table S15: Sensor responses calculated by using DFT results

Species	Sensor response (%)
MoO_3/Bi_2MoO_6-acetone	24.638
MoO_3/ Bi_2MoO_6-ammonia	20.773
MoO_3/ Bi_2MoO_6-aniline	18.930
MoO_3/ Bi_2MoO_6-ethanol	21.098
MoO_3/ Bi_2MoO_6-formaldehyde	18.280
MoO_3/ Bi_2MoO_6-methanol	15.859
MoO_3/ Bi_2MoO_6-water	22.543
MoO_3/ Bi_2MoO_6-xylene	10.729