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Supplementary Information

Preparation of Responsive Bilayer Membrane through Morphological Tuning of the Nano-scale Building Blocks

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Materials:

Hydrogen peroxide, vanadium pentoxide, methanol, ethanol, isopropanol, acetone, tetrahydrofuran, ethyl acetate and dichloromethane were purchased from Merck. Ammonium tetrathiomolybdate ($(NH_4)_3MoS_4$) was purchased from Sigma Aldrich. All the chemicals are used as received.

Preparation of V_2O_5 nanosheets and nanobelts:

In order to prepare V_2O_5 nanosheets, H_2O_2 was added to an aqueous solution of V_2O_5 in an ice cold condition.[1,2] 25 ml 50 % H_2O_2 was slowly added to 25 ml 0.5 M aqueous solution of V_2O_5 kept in an ice cool condition under continuous stirring. The light brown coloured solution started bubbling upon addition of H_2O_2, and yielded a dark brown gel. The as obtained gel was diluted to 400 ml with deionized (DI) water and sonicated for 30 minutes in a bath sonicator.

V_2O_5 nanobelts were prepared from the thus prepared nanosheets by hydrothermal treatment.[3,4] 15 ml of the above nanosheets dispersion was placed in a 25 ml autoclave at 250 °C for 18 hours, which yielded a yellow coloured adduct, which was characterised to be V_2O_5 nanobelts. The as prepared nanobelts were subjected to repeated washing with DI water and ethanol prior to further use.

Preparation of V_2O_5 nanosheets, nanobelts and bilayer membrane (V_2O_5-BS-BM):

Freestanding V_2O_5 nanosheets membrane (V_2O_5-NS-M) and V_2O_5 nanobelts membranes (V_2O_5-NB-M) were prepared through vacuum filtration of the 30 ml of the respective aqueous dispersion (3 mg/ml, and 1 mg/ml respectively) through polytetrafluoroethylene (PTFE) membranes. These membranes got detached from the filter papers upon air-drying. To prepare the V_2O_5-BS-BM, first 10 ml of 1 mg/ml V_2O_5 nanobelts dispersion was vacuum filtered through a cellulose nitrate membrane (diameter 47 mm). Once the membrane appeared to be dried, 10 ml of 3 mg/ml V_2O_5 sheets dispersion was filtered through it. The bilayer membrane

attached to cellulose nitrate membrane was air-dried at room atmosphere until they got detached by themselves. The two sides of the bilayer membrane can be distinguished from the colour differences, bluish-black for nanosheet side and yellow for nanobelts side.

Preparation of V_2O_5-BS-BM with varied dimensions of the nano-scale building blocks:

In order to prepare nanobelts of different sizes, 50 ml aqueous dispersions (1 mg/ml) of the as-prepared nanobelts were sonicated by using a probe sonicator (Labman, Model: PRO-650) in pulse mode (4 sec on and 4 sec off) for 1 and 2 hours respectively. These sonicated nano belts dispersions (for 1 and 2 hours) were used for the preparation of V_2O_5-BS-BM after appropriate characterization.

Similarly, V_2O_5-BS-BM with different nanosheet dimensions were prepared keeping the dimension of nanobelts unaltered. 50 ml aqueous dispersions (3 mg/ml) of as-prepared nanosheets were sonicated for 2 hours using a probe sonicator in pulse mode (4 sec on and 4 sec off). Upon sonication, the as-prepared nanosheets (labelled as *large sheets*) were broken down to smaller sheets and labelled as *small sheets*. A mixture of large and small nanosheets were prepared by adding them in a weight ratio of 1:1, and labelled as *mixture*. The concentration of all the nanosheets were maintained as 3 mg/ml, and used for the preparation of bilayer membranes.

Preparation of MoS_2 coated V_2O_5 nanosheets membranes (MoS_2@V_2O_5-NS-M):

A homogeneous aqueous dispersion (1mg/ml) of ammonium tetrathiomolybdate ($(NH_4)_3MoS_4$) and V_2O_5 nanosheets (1:1, w/w %) was subjected to microwave treatment in a domestic microwave (1150 W) for 120 seconds (at 4 steps, 30 second each). The as-obtained product was washed with DI water and ethanol repetitively to remove the excess MoS_2 precursor. The sample was air-dried prior to further use. MoS_2@V_2O_5-NS-M was prepared by vacuum

filtration of 90 ml 1mg/ml aqueous dispersion of $MoS_2@V_2O_5$ nanosheets through a PTFE membrane.

Preparation of $MoS_2@V_2O_5$ sheet and V_2O_5 nanobelts bilayer membranes ($MoS_2@V_2O_5$-BS-BM):

The $MoS_2@V_2O_5$-BS-BM was fabricated by sequential filtration of the V_2O_5 nanobelts followed by $MoS_2@V_2O_5$ nanosheets. At first 12 ml of 1 mg/ml V_2O_5 nanobelts was vacuum filtered through a cellulose nitrate membrane. Once the membrane appeared to be dried, 24 ml of 1 mg/ml $MoS_2@V_2O_5$ nanosheets dispersion was filtered through it. Thus prepared bilayer membranes got detached from the filter paper upon air-drying. Similarly, the $MoS_2@V_2O_5$-BS-BM with different percentages (weight %) of $MoS_2@V_2O_5$ nanosheets were also fabricated by varying the amount of dispersion used for the filtration process.

Chemical Sensing of freestanding membranes:

The sensing devices of V_2O_5-NS-M and V_2O_5-NB-M were fabricated by cutting rectangular strips of dimension ~ 17 × 5 × 0.03 mm^3 from the respective membranes. Either ends of the strips were connected to copper wires by applying conducting silver paste. Photos of the sensing devices of V_2O_5-NS-M and V_2O_5-NB-M are shown in Supplementary Figure S5a and S5b. A fixed bias of +5 V was applied across the devices and current values obtained in both the devices were simultaneously recorded as a function of time using two separate sourcemeter instruments (Keithley 2450). Both the devices were concurrently exposed to solvents vapours generated inside an open beaker (250 ml) by adding 10 ml of the desired solvent. Schematic representation of the experimental set-up used for chemical sensing are shown in Figure 2d. The response % was calculated employing the following equation:

$$response\ \% = \left| \frac{I_o - I_g}{I_o} \times 100 \right| \quad \text{..... S1}$$

Where, I_o and I_g are the current value of the device in absence and presence of the solvents gases, respectively.

Characterization:

Nanosheets and nanobelts of V_2O_5 were characterized by a Field Emission Transmission Electron Microscope (FETEM) (JEOL, Model: 2100F) and Atomic Force Microscope (AFM) (Make: Oxford; Model: Cypher). The morphology and the cross-sections of the membranes were studied by the Field Emission Scanning Electron Microscope (Make: Zeiss, Model: Sigma). X-ray diffraction studies were carried out by employing a Bruker D-205505 Cu-Kα radiation (λ = 1.5406 Å). UV-visible spectra were recorded using a UV-visible spectrometer (PerkinElmer, Model: Lambda 750). Tensile strength of the membranes were measurements in a 5 kN electromechanical universal testing machine (make: Zwick Roell: Z005TN). The shape transformations of the bilayer membranes in presence of different stimuli was filmed using a digital camera, Nikon D5200. The photo-thermal images of the membranes were captured using a High resolution Thermal Camera, Testo 872.

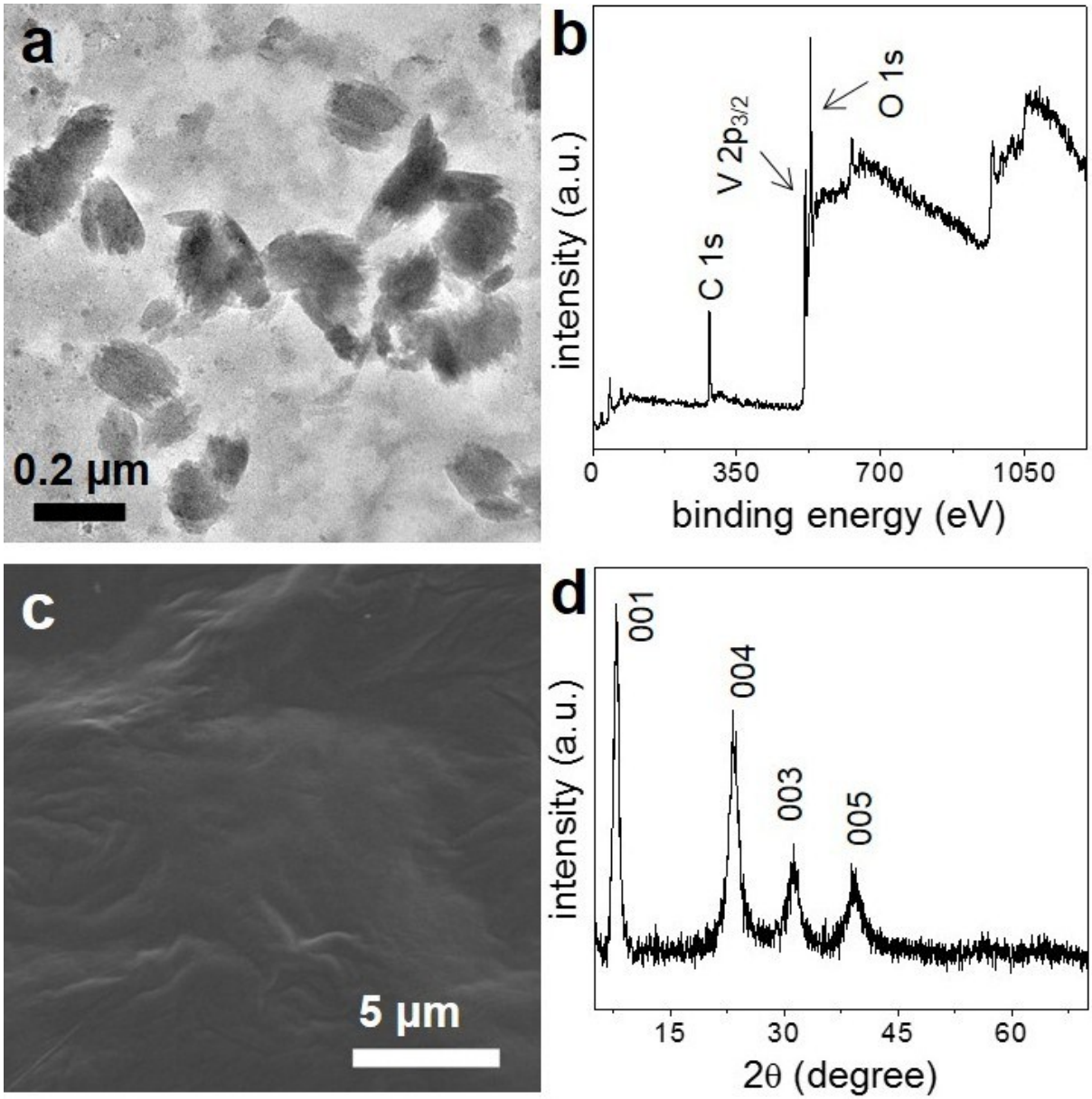

Figure S1. Characterization of V_2O_5 nanosheet membranes (V_2O_5-NS-M): (a) FETEM image of V_2O_5 nanosheets used for the fabrication of V_2O_5-NS-M. (b) Wide scan XPS spectra, (c) FESEM images of the surface, and (d) XRD patterns of V_2O_5-NS-M.

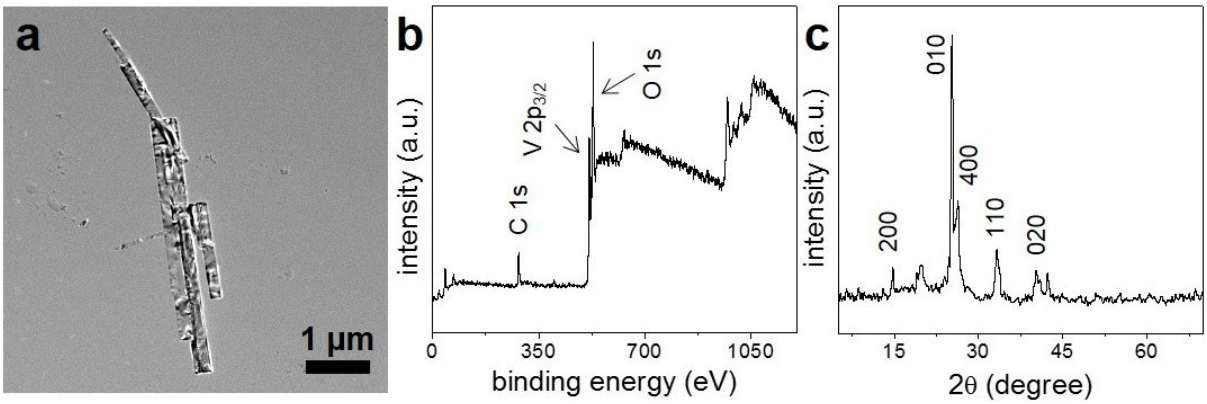

Figure S2. Characterization of V_2O_5 nanobelt membranes (V_2O_5-NB-M): (a) FETEM image of V_2O_5 nanobelts used for the fabrication of V_2O_5-NB-M. (b) Wide scan XPS spectra, and (c) XRD patterns of V_2O_5-NB-M.

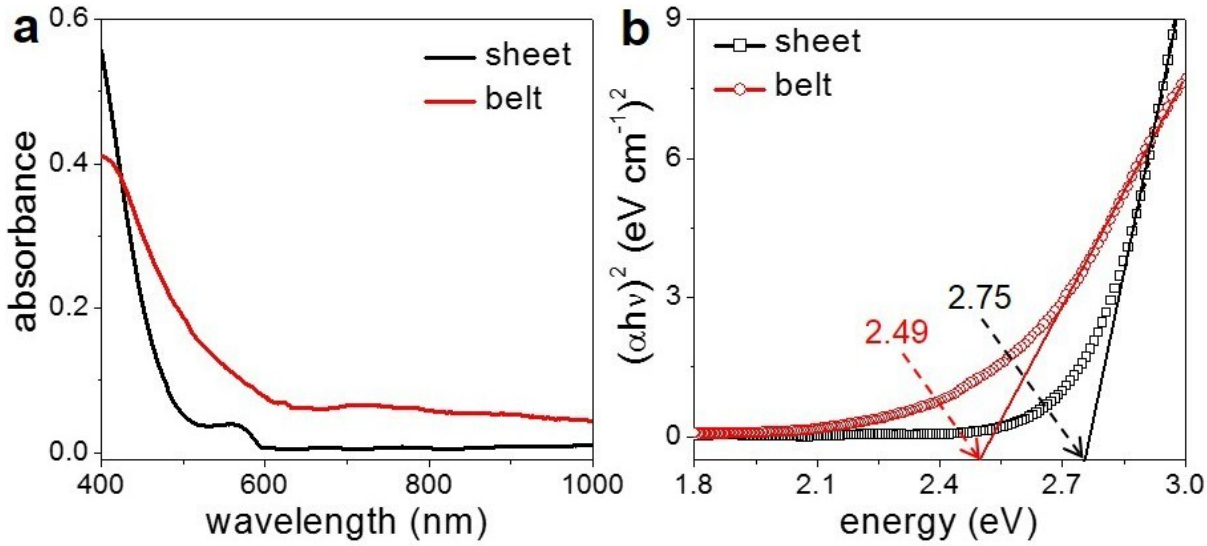

Figure S3. Calculation of bandgaps: (a) UV-vis spectra of the aqueous dispersion V_2O_5 nanosheets and nanobelts along with the (b) corresponding Tauc-plots.

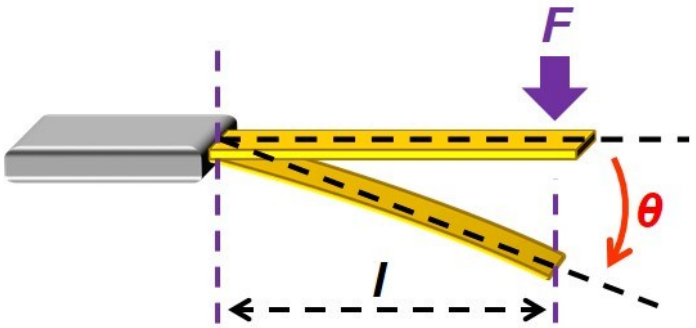

Figure S4. Bending stiffness: Schematic representation of the experimental setup used in measuring bending stiffness.

The bending stiffness of the membranes were recorded employing Lorentzen and Wetter's 2-point method using a custom made device, schematic diagram is shown in Figure S4. Strips of known dimensions were cut from the membranes and fixed to glass slides with one end, leaving the other end to bend freely. To the free end of the strip force was applied, in form of a load perpendicularly to the plane of the strip which results in bending. The bending stiffness (S_b), was calculated by using equation (S2).[5-7]

$$\text{Bending stiffness } (S_b) = \frac{60\ x\ F\ x\ l^2}{\pi\ x\ \theta\ x\ b} \quad \ldots\ldots\ldots\ldots\ldots \text{(S2)}$$

Where, F is bending force (weight of the load x gravitational constant), l is the distance between the two end, θ is the deflection and b is the width of the strip.

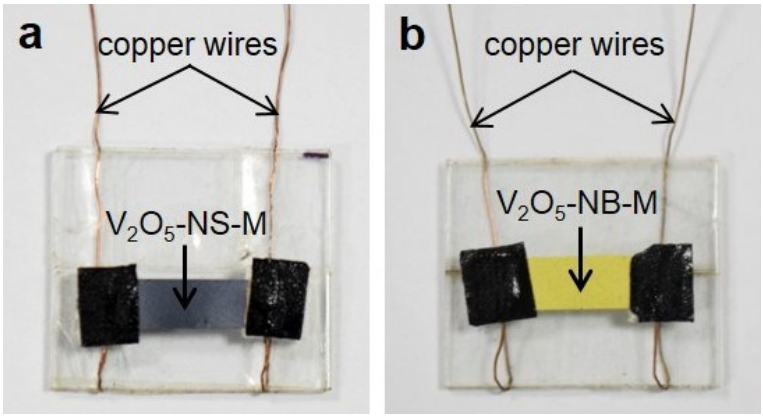

Figure S5. Photos of (a) V_2O_5-NS-M and (b) V_2O_5-NB-M devices used for the study of electrical conductivity and chemical sensing.

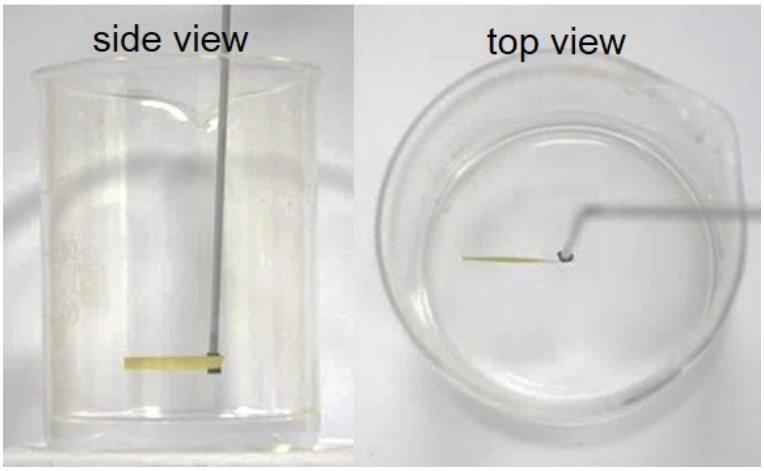

Figure S6. Experimental Setup: Photos showing the side and top view of the experimental setup used for the study of vapor induced responsiveness of the bilayer membranes.

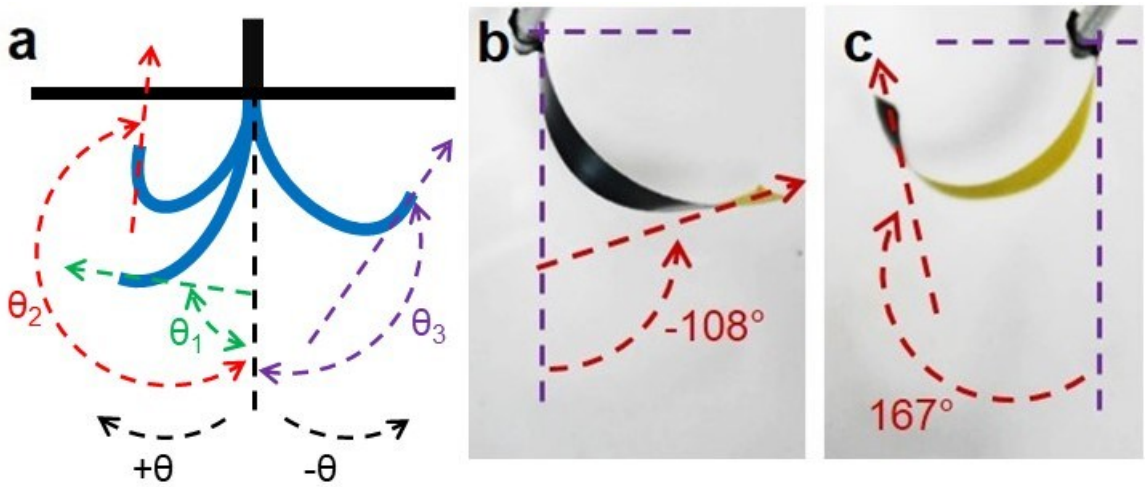

Figure S7. Bending angle measurement: (a) Schematic representation of the measurements of the bending angles of the bilayer strips. Photos showing the bending angles of strips moving in (b) anticlockwise and (c) clockwise directions.

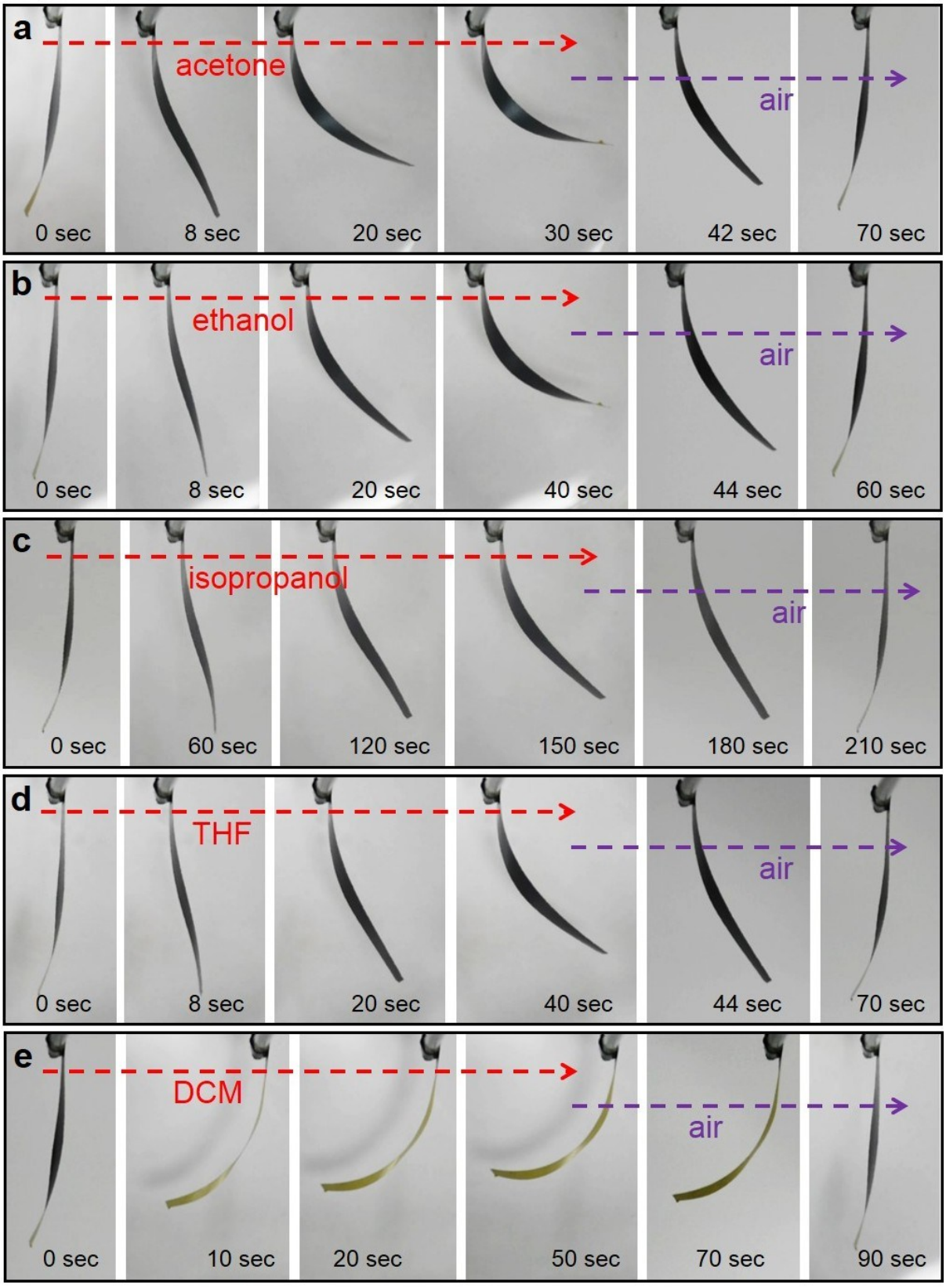

Figure S8. Vapor assisted bending of V_2O_5-BS-BM: Snapshots showing the bending and recovery movements of bilayer strip of V_2O_5-BS-BM in presence of (a) acetone, (b) ethanol, (c) isopropanol, (d) THF and (e) DCM.

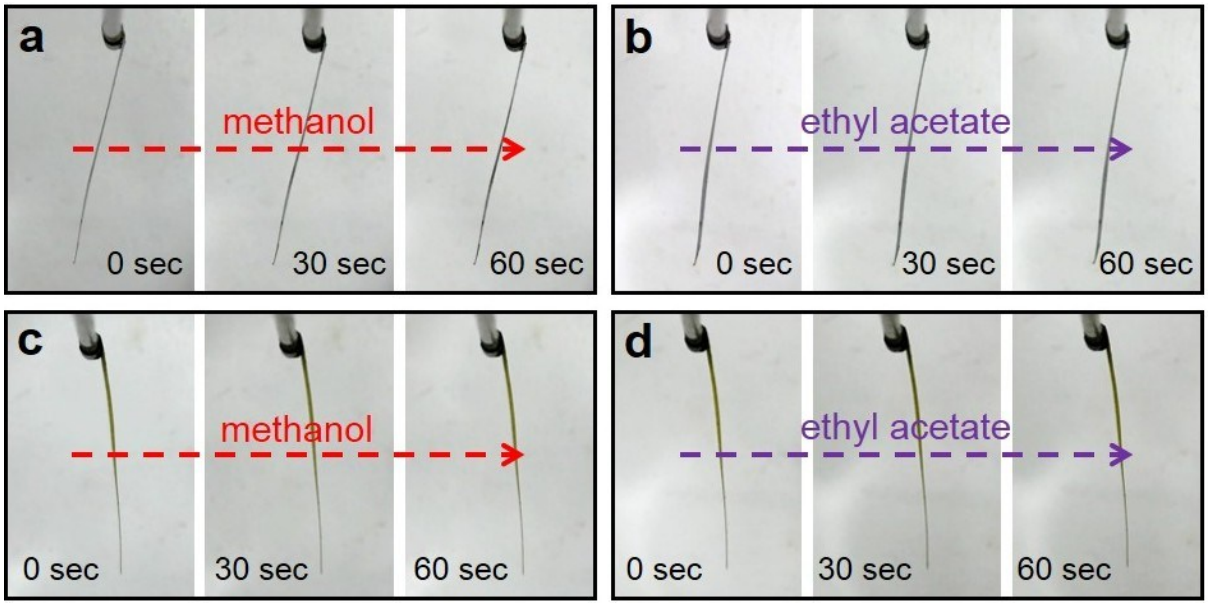

Figure S9. Snapshot showing the time laps images of V_2O_5-NS-M strip (dimensions ~ 25 × 2 × 0.02 mm^3) in presence of (a) methanol, and (b) ethyl acetate vapours. Photos of V_2O_5-NB-M strip (dimensions ~ 25 × 2 × 0.02 mm^3) in presence of (c) methanol and (d) ethyl acetate vapours**.**

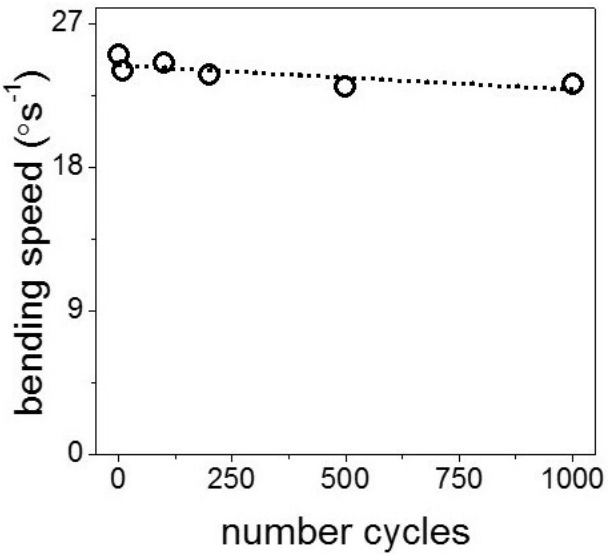

Figure S10. Plot comparing the bending speeds of a V_2O_5-BS-BM strip for 1000 cycles of exposure to methanol vapors.

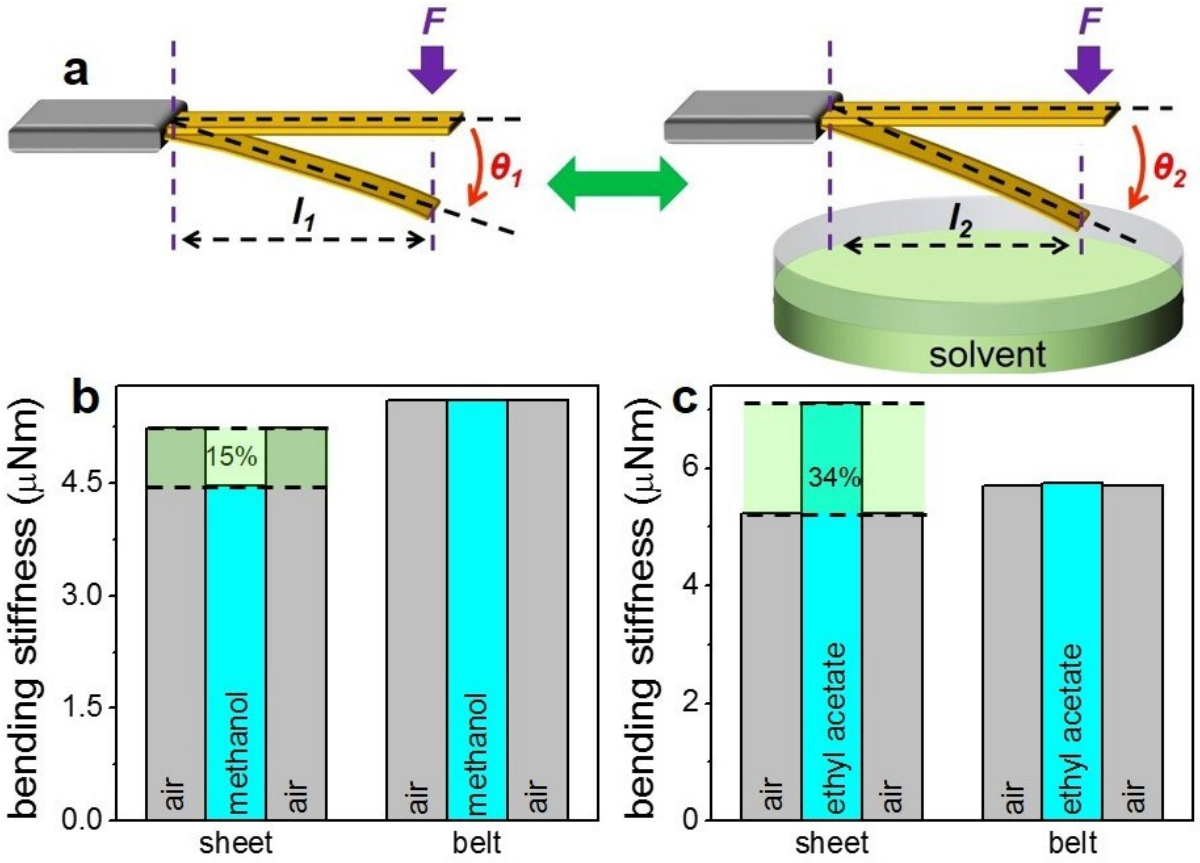

Figure S11. Mechanism of responsiveness: (a) Schematic representation of the bending stiffness measurements of strips in different environmental conditions using Lorentzen and Wettre 2-points method. Bar diagrams comparing the bending stiffness of V_2O_5 nanosheets and nanobelt membranes in presence of (b) methanol and (c) ethyl acetate vapors.

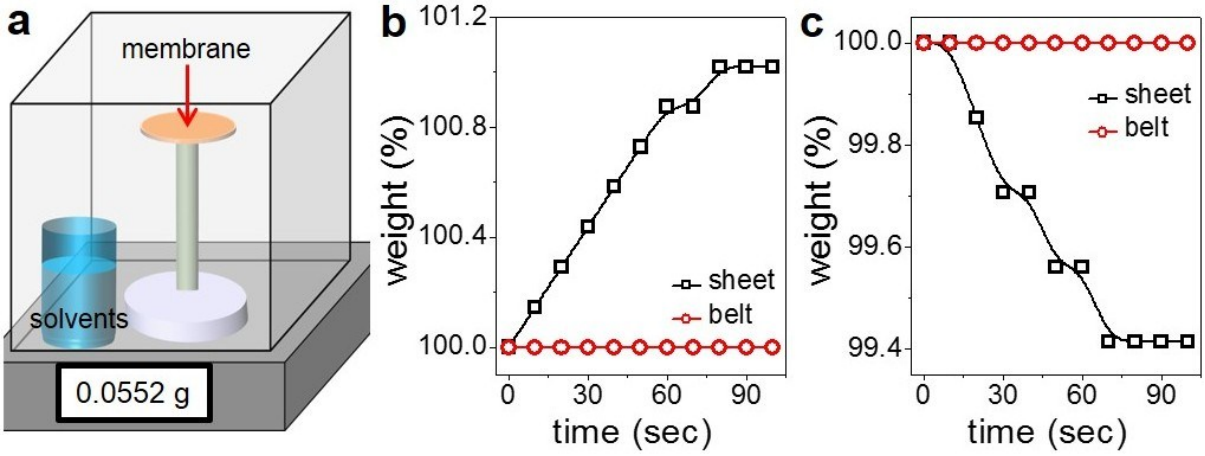

Figure S12. (a) Schematic representation of the experimental set-up used for the measurement of weight changes of V_2O_5-NS-M and V_2O_5-BS-M upon exposure to solvent vapors. Plots comparing the weight of V_2O_5-NS-M (black curve) and V_2O_5-BS-M (red curve) in presence of (b) methanol and (c) ethyl acetate vapors.

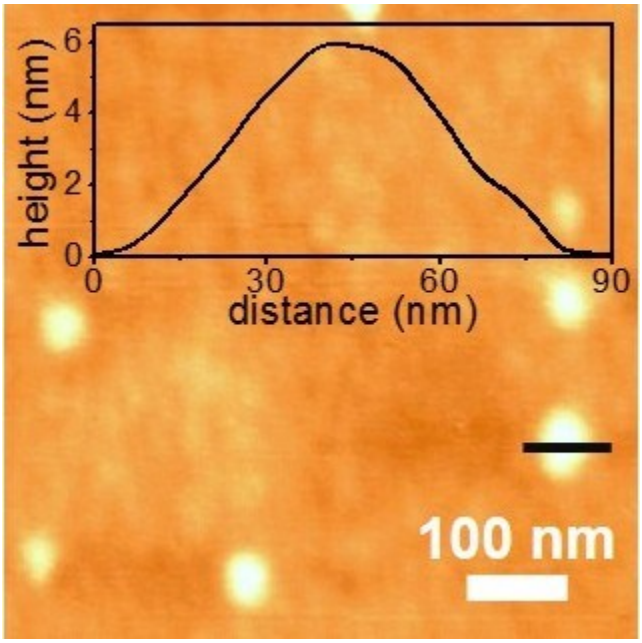

Figure S13. AFM image of smaller V_2O_5 nanosheets prepared through sonication of the as prepared nanosheets dispersion for 2 hours using a probe sonicator in a pulse mode (4 sec on and 4 sec off).

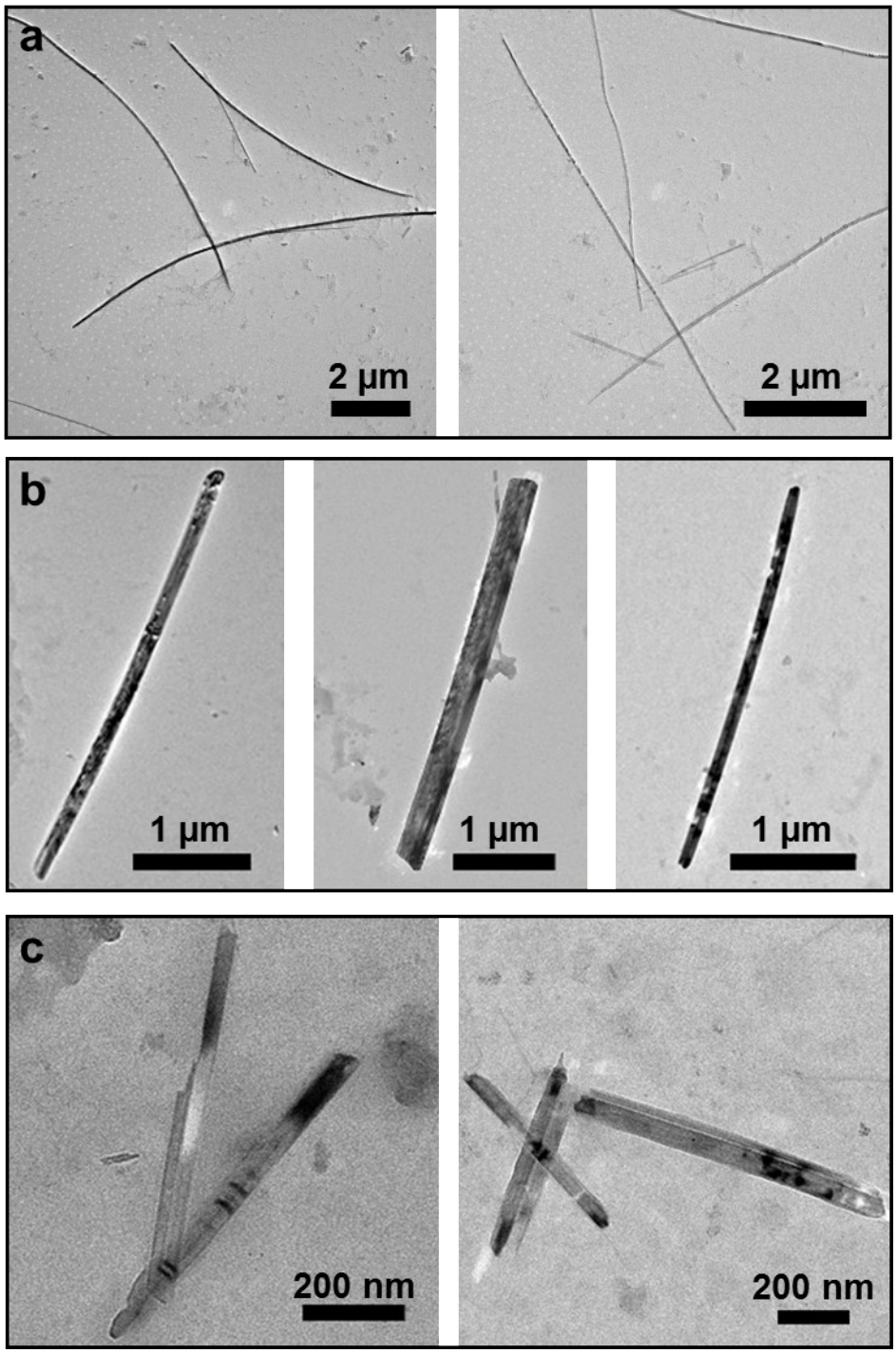

Figure S14. FETEM images of V_2O_5 nanobelts samples: (a) as prepared, sonicated for (b) 1 hour and (c) 2 hours. The as prepared V_2O_5 nanobelts are sonicated using a probe sonicator to break them into smaller dimensions.

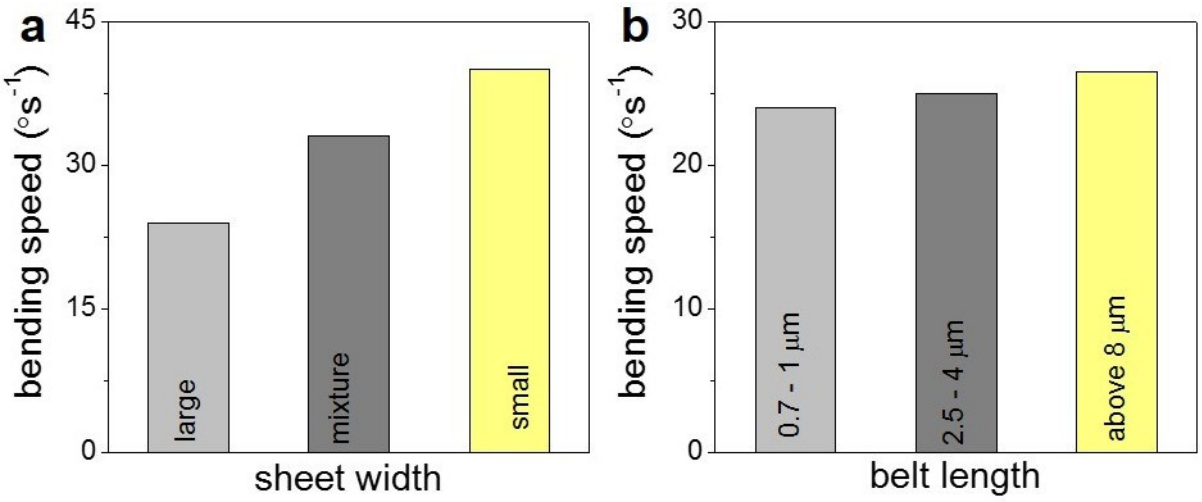

Figure S15. Bar diagrams comparing methanol vapour induced bending speeds of V_2O_5-BS-BM strips (a) with varying dimensions nanosheets by keeping the length of the nanobelts (~8 μm) unaltered, and (b) with varying dimensions nanobelts by keeping the dimension of the nanosheets (~140 nm) unaltered.

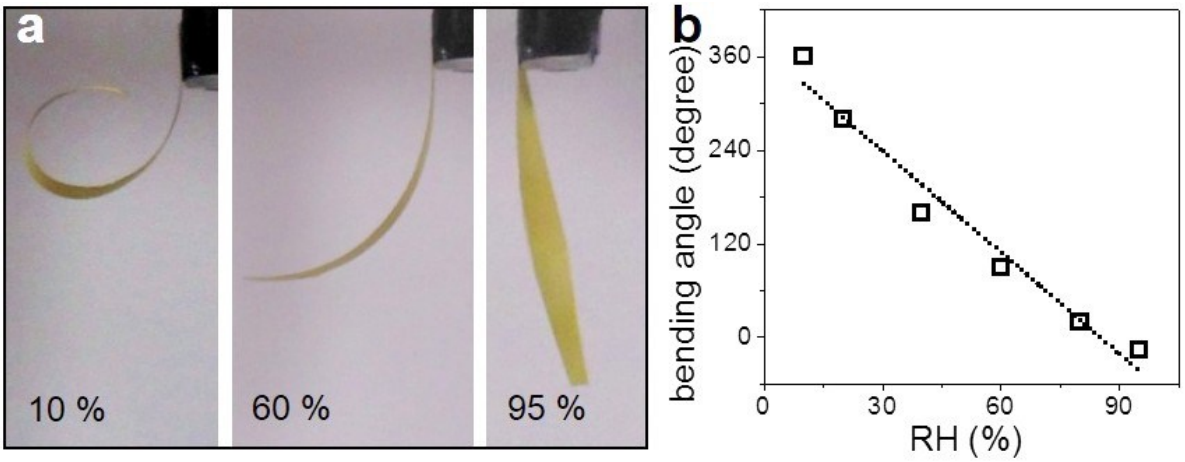

Figure S16. Humidity induced bending of V_2O_5-BS-BM: (a) Photo showing the bending of a strip of V_2O_5-BS-BM at 10 %, 60 % and 95 % relative humidity. (b) Plot of bending angle of a bilayer strip against relative humidity (RH).

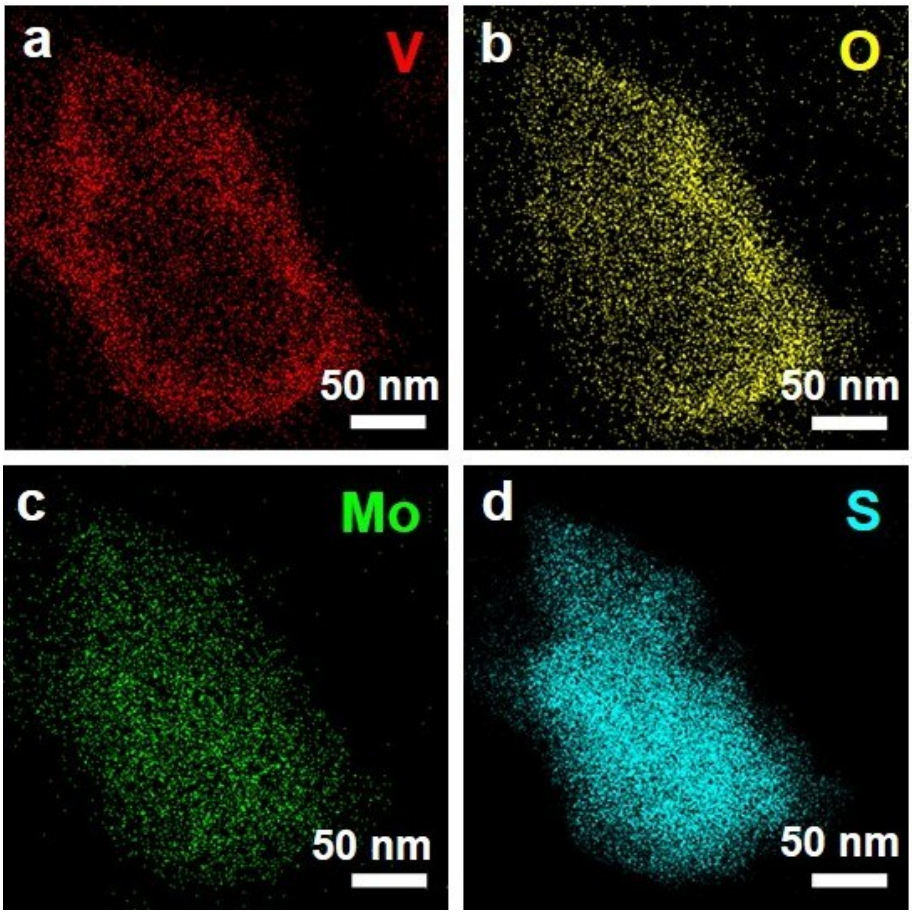

Figure S17. Elemental mapping of MoS_2@V_2O_5 nanosheets: TEM EDX mapping showing the distribution of the (a) vanadium (red colour), (b) oxygen (yellow colour), (c) molybdenum (green colour) and (d) sulphur (blue colour) atoms in a MoS_2@V_2O_5 nanosheet.

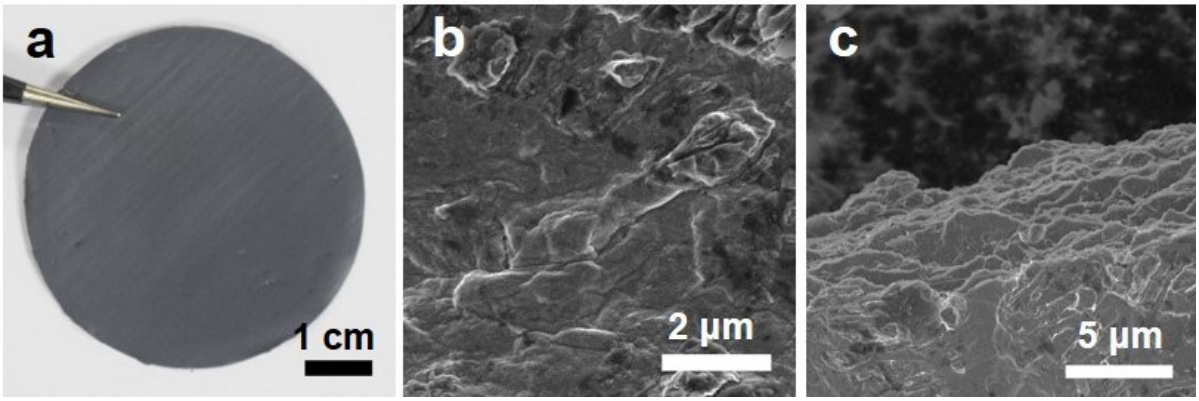

Figure S18. Characterization of $MoS_2@V_2O_5$ nanosheet membrane ($MoS_2@V_2O_5$-NS-M): (a) Photos showing freestanding $MoS_2@V_2O_5$-NS-M fabricated through vacuum assisted self-assembly process. FESEM images showing the (b) surface and (c) cross-section of $MoS_2@V_2O_5$-NS-M.

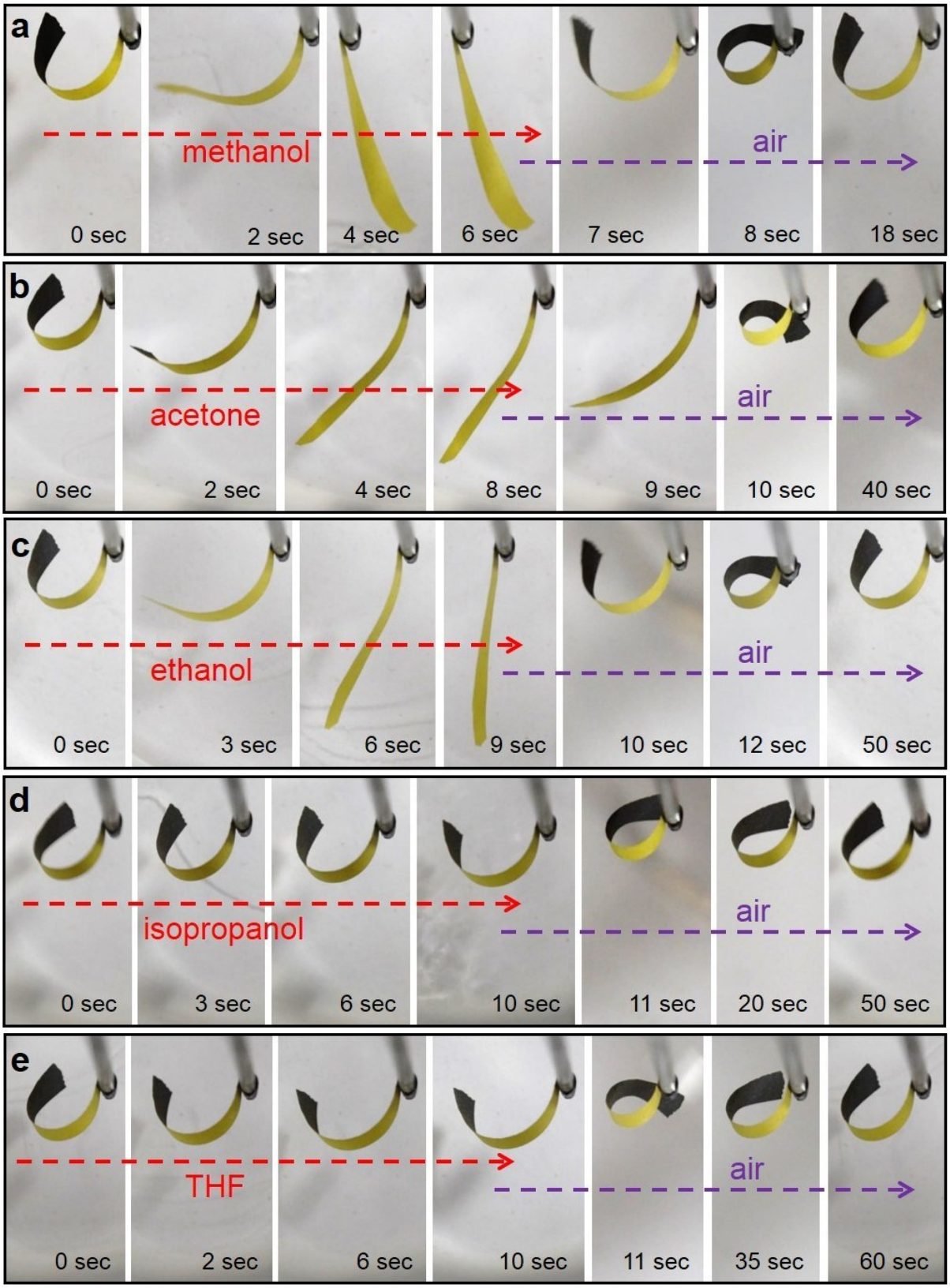

Figure S19. Vapor induced responsiveness of MoS_2@V_2O_5-BS-BM: Snapshots showing the bending and recovery movements of bilayer strip of MoS_2@V_2O_5-BS-BM in presence of (a) methanol, (b) acetone, (c) ethanol, (d) isopropanol, and (e) THF vapors.

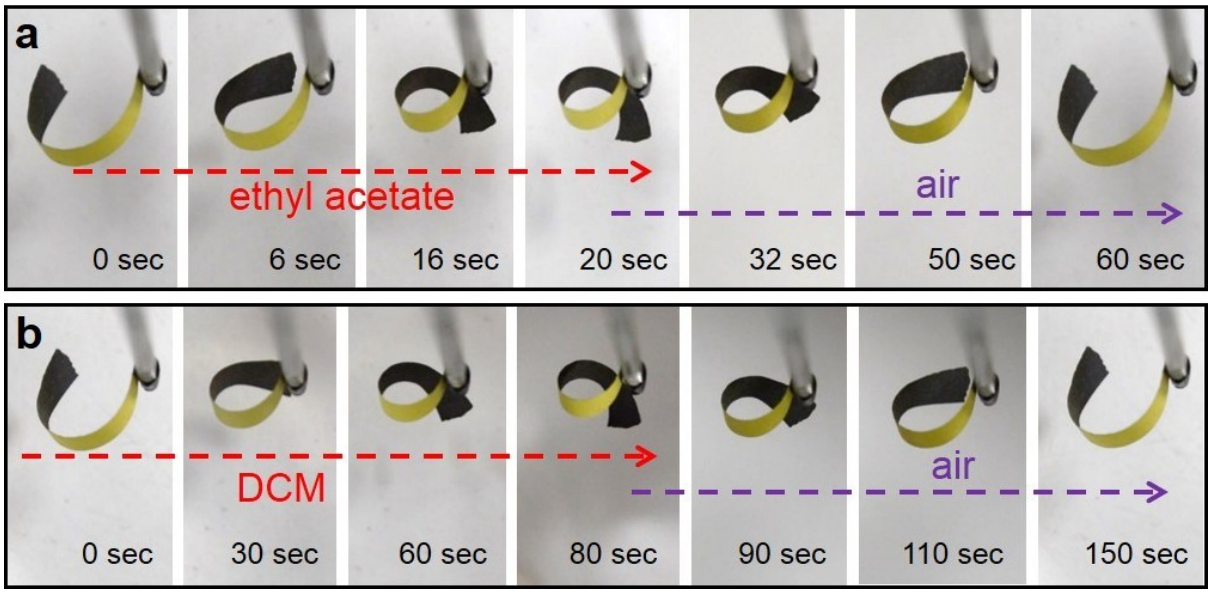

Figure S20. Snapshots showing the bending and recovery movements of bilayer strip of $MoS_2@V_2O_5$-BS-BM in presence of (a) ethyl acetate, (b) DCM vapors.

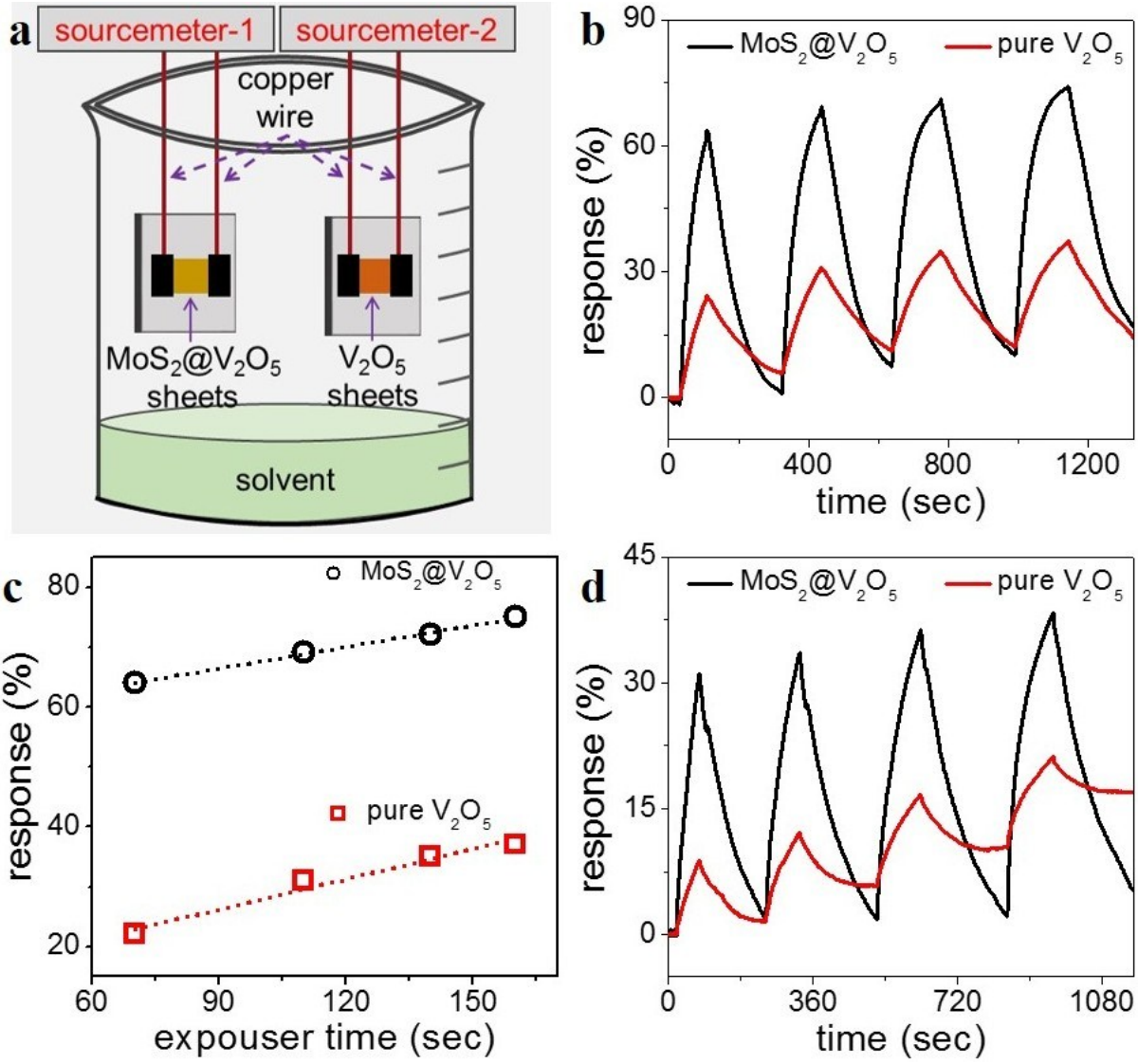

Figure S21. Sensing of chemical vapors by $MoS_2@V_2O_5$-NS-M: (a) Schematic illustration of the experimental setup used for the study of chemical-sensitivity of the V_2O_5 membranes. Comparison of responsive curves obtained with $MoS_2@V_2O_5$ nanosheets, with that of pure V_2O_5 nanosheets membranes towards (b) methanol and (d) ethyl acetate vapors. (c) Comparison of response % of the $MoS_2@V_2O_5$ nanosheets and pure V_2O_5 nanosheets membranes as a function of exposure time.

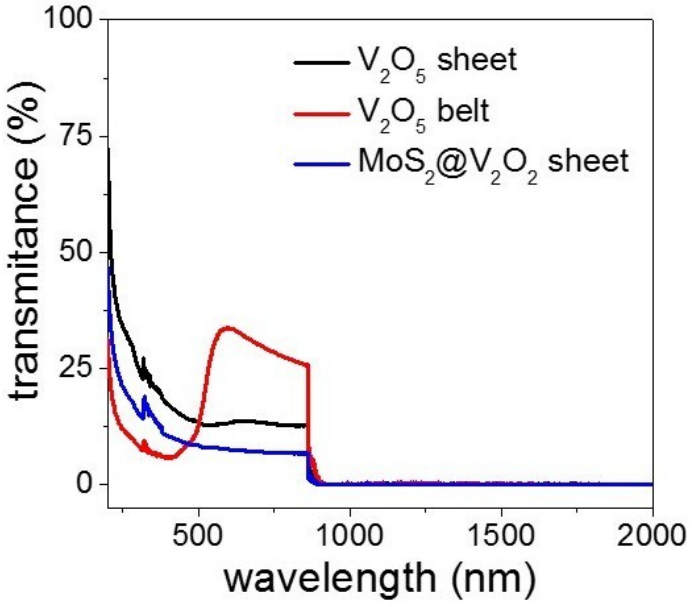

Figure S22. UV-vis spectra of V_2O_5 nanosheets, nanobelts and $MoS_2@V_2O_5$ nanosheets membranes.

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