Supplementary information for

Light and solvent-driven actuator of clay and vanadium pentoxide nanosheets

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Materials and methods:

1. Reagent

Vermiculite clay and vanadium pentoxide (V_2O_5) powder are purchased from Sigma Aldrich, and methanol, ethanol, 2-propanol, ethyl acetate, dichloromethane (DCM), acetone hydrogen peroxide (H_2O_2) and hydrochloride acid (HCl) were purchased from Merk. All the materials are used as received.

2. Preparation of vermiculite nanosheets membrane

1 g of bulk vermiculite crystals were magnetically stirred in a 100 mL dilute HCl solution (20 mL concentrated HCl in 80 mL water) for 18 hours at room temperature.[1] The adduct was washed with deionized (DI) water until the excess acids were removed and dried under an air atmosphere. The acid-treated vermiculite was further re-dispersed in DI water with 1mg/mL concentration and was used to prepare free-standing and flexible membranes.

3. Preparation of V_2O_5 nanosheets membrane (VO-M)

The V_2O_5 nanosheets were prepared by reaction of V_2O_5 powder with H_2O_2 in an aqueous medium following our previous reports.[2,3] In brief, 25 ml of 50 % H_2O_2 was added to 2.4 g of V_2O_5 powder previously poured in 25 mL of DI water under an ice-cold condition with constant stirring. Upon the addition of H_2O_2, the light brown-coloured solution started bubbling and yielded a dark brown gel. The gel was then sonicated in a bath sonicator for 30 minutes and diluted with DI water to maintain a concentration of 3 mg/mL, which was used to prepare the membrane.

4. Preparation of V_2O_5-vermiculite bilayer membrane

The bilayer actuator was fabricated by sequential filtration of the vermiculite and V_2O_5 nanosheets. At first, 12 mL of 1mg/mL vermiculite nanosheet dispersion was vacuum-filtered through a PTFE membrane (47 mm in diameter). Once the vermiculite membrane appears to form, 6 mL of 3 mg/mL V_2O_5 nanosheet dispersion was filtered through it and left for air drying. The bilayer membrane can be easily detached from the PTFE membrane, forming a flexible, and free-standing membrane. The two sides of the bilayer can be easily distinguished from the colour difference; colour grey-black for the V_2O_5 and yellow-brown for the vermiculite side. The thickness of the bilayer membrane was measured as ~ 15 μm.

Table S1: Comparison of thickness of vermiculite, V_2O_5, and V_2O_5-vermiculite bilayer membrane preaperd using different concentration and volume of the individual dispersions.

Vermiculite			V_2O_5			V_2O_5-vermiculite membrane		
volume (mL)	concentration (mg/mL)	thickness (μm)	volume (mL)	concentration (mg/mL)	thickness (μm)	Weight % Vermiculite	Weight % V_2O_5	thickness (μm)
12	1	6 ± 1	6	3	9 ± 1	40	60	15 ± 1
18	1	9 ± 1	9	3	13 ± 1	40	60	22 ± 1
24	1	13 ± 2	12	3	19 ± 2	40	60	32 ± 2

The thickness of the V_2O_5 and vermiculite in the bilayer strip is very difficult to distinguish in microscopic images. This is because both the components consist of 2D sheets. However, the individual thickness of the two layers can be estimated from the concentration and volume of the nanosheets dispersions used in the fabrication of the bilayer. We make different membranes of vermiculite and V_2O_5 individually using different volume of the respective dispersions and measured their thickness, compared in table S1. The thickness of the V_2O_5-vermiculite bilayer membrane for a particular composition is similar to the sum of the individual membranes' thickness.

5. Bending stiffness

The membranes' bending stiffness (S_B) was estimated using Lorentzen & Wettre two-point method. In brief, one end of a rectangular strip was fixed to a glass rod and placed horizontally. To the free end, a force was applied by placing a load of known weight. The S_B was calculated using the following equation:[4,5]

$$S_B = \frac{60 \times F \times l^2}{\pi \times \theta \times b}$$

Where, F is the bending force = weight of the load × acceleration due to gravity, l = distance between the two ends of the strip (shown in Figure 6a), θ = deflection, and b = width of the strip. For measuring the S_B of the VO-M, we used a load of 5.8 mg and the dimension of the strip, l = 25 mm, b = 4 mm, and thickness = 25 µm, and for vermiculite membrane, we used a load of 5.1 mg and the dimension of the strip, l = 25 mm, b = 4 mm, and thickness = 25 µm.

Supplementary Figures

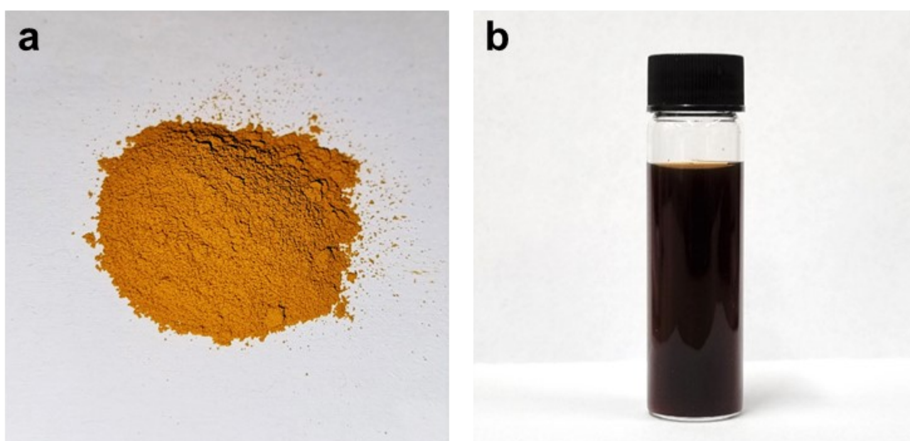

Figure S1: Digital photo of (a) bulk powder of V_2O_5 and (b) an aqueous dispersion (3 mg/ml) of V_2O_5 nanosheets.

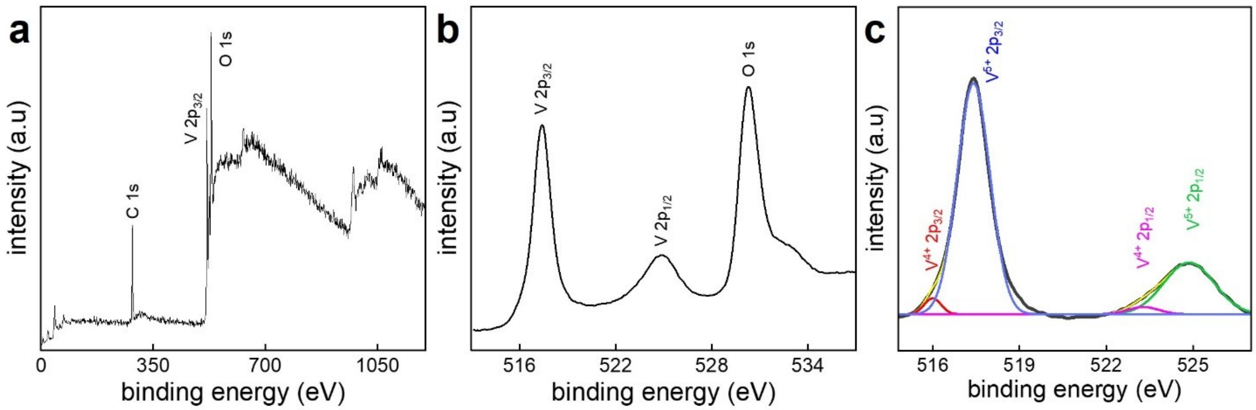

Figure S2: XPS of V_2O_5 nanosheets. XPS spectra presenting the (a) wide scan, (b) V 2p and O 1s region and (c) different oxidation states of V in the V_2O_5 nanosheets.

The peaks corresponding to the binding energies of V $2p_{3/2}$, V $2p_{1/2}$ and O 1s electrons at 517.4, 525 and 530.4 eV, respectively and with a O/V ratio of ~2.7 (calculated from the areas under the peaks V $2p_{3/2}$, and O 1s) confirm the stoichiometry of the nanosheets as V_2O_5. In the nanosheets, the percentage of the V^{+5} and V^{+4} are found to be 96.5% and 3.5%, respectively (calculated from the areas under the peaks V $2p_{3/2}$)

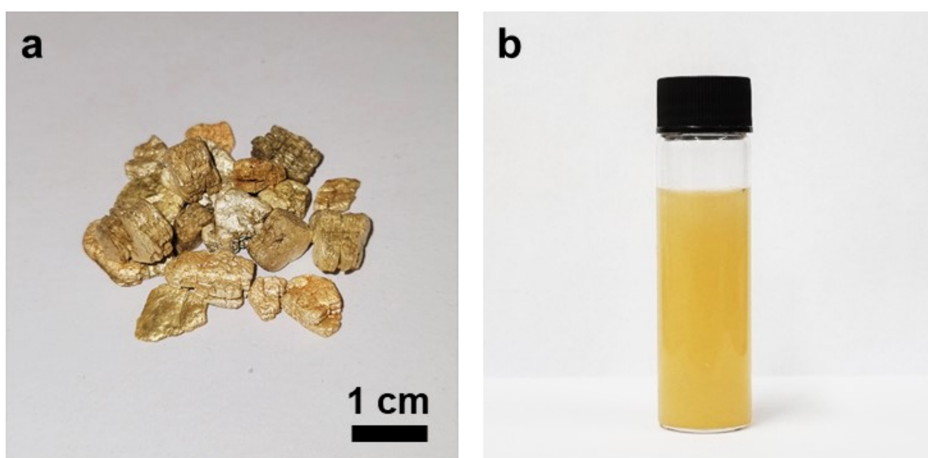

Figure S3: Digital photo of (a) bulk crystal of vermiculite and (b) an aqueous dispersion (1 mg/ml) of vermiculite nanosheets.

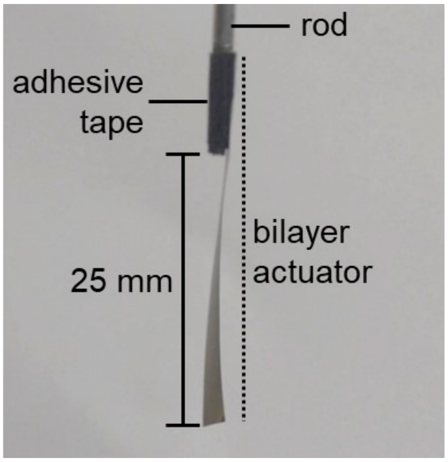

Figure S4: Photo of a strip attached to a glass rod for the light experiment.

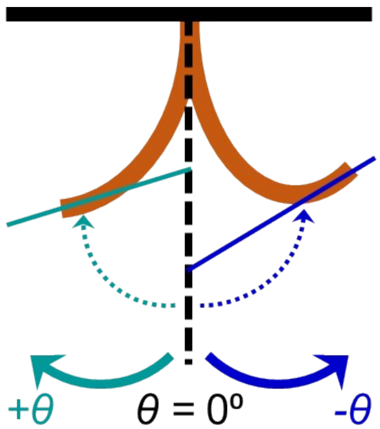

Figure S5: Schematic description of the bending angle measurement of the actuator.

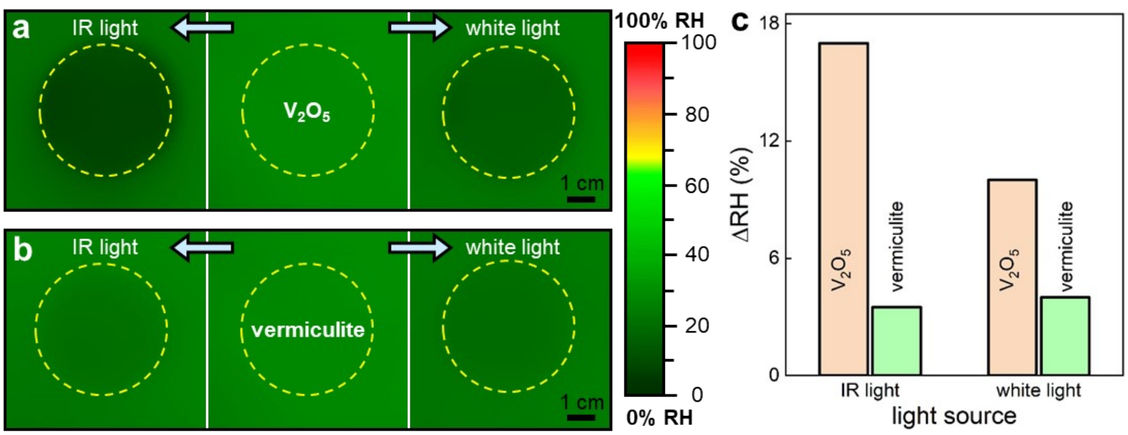

Figure S6: Images showing the water content of the individual (a) VO-M and (b) vermiculite membranes upon exposure to IR light (left side) and white light (right side). (c) Bar diagram comparing the change in RH (ΔRH) of V_2O_5 and vermiculite membranes upon exposure to light sources.

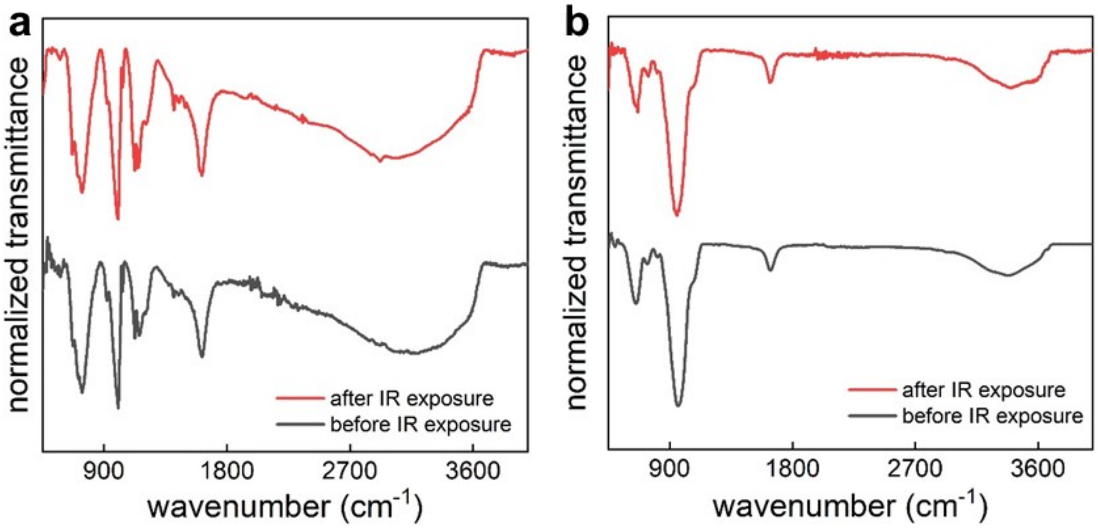

Figure S7: Comparison of the IR spectra of (a) V_2O_5 and (b) vermiculite membranes before and after exposure to IR light.

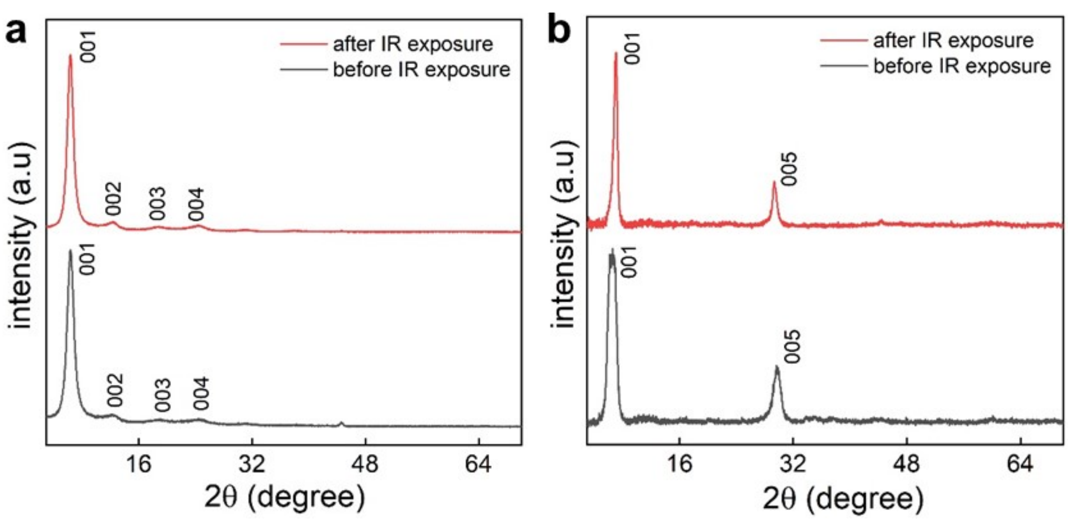

Figure S8: Comparison of the XRD-spectra of (a) V_2O_5 and (b) vermiculite membranes before and after exposure of IR light.

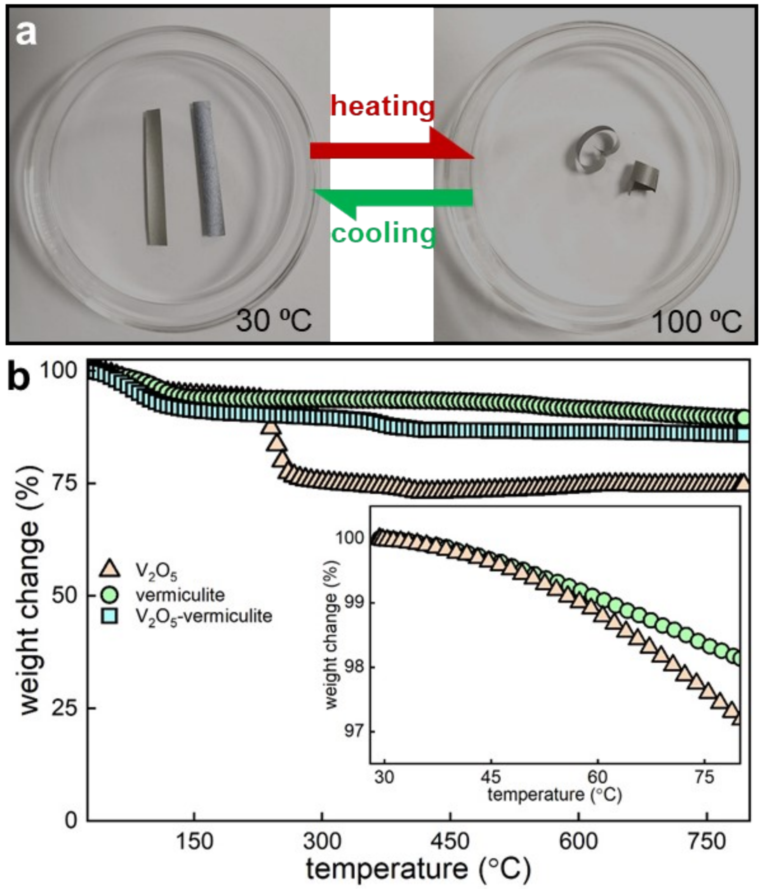

Figure S9: Thermal stability: (a) Photos showing the stability of the V_2O_5-vermiculite bilayer actuator after heating at 100 ºC for 30 minutes in an air atmosphere. (b) Graphs comparing weight changes of vermiculite, VO-M and V_2O_5-vermiculite bilayer membranes as a function of temperature changes. In the inset of (b), the graphs are zoomed to the range of 30 to 100 ºC for clarity.

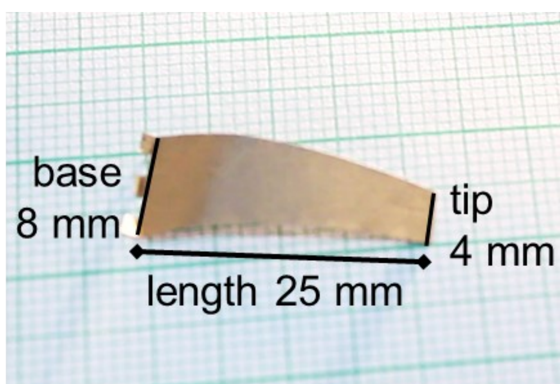

Figure S10: Photo of the strip used to demonstrate worm-like walking.

A trapezoidal strip was cut from a V_2O_5-vermiculite bilayer membrane (thickness 15 µm) with length = 25 mm, base = 8 mm and tip = 4 mm.

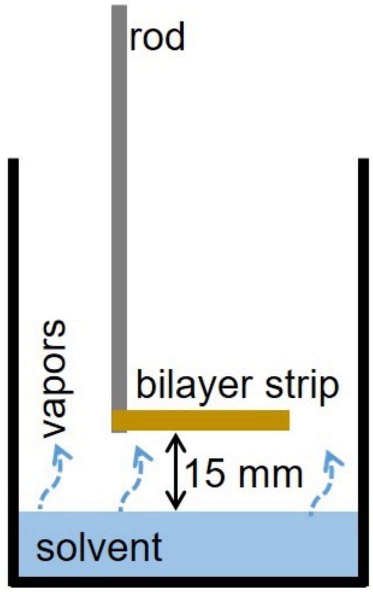

Figure S11: Schematic of the experimental set-up used to study the solvent-induced responsiveness of the bilayer actuator.

To study the solvent-induced responsiveness, a rectangular strip (dimensions, 25 mm × 2 mm × 15 µm), fixed to a rod with one end, was exposed to solvent vapor generated by pouring 10 mL of the solvent in a beaker (250 mL volume) without any lid. The strip was placed parallel to the liquid solvent maintaining a distance of 15 mm between the strip and the solvent surface. This configuration of the experimental setup is used for all the solvent-induced responsiveness experiments, except when mentioned when it is different.

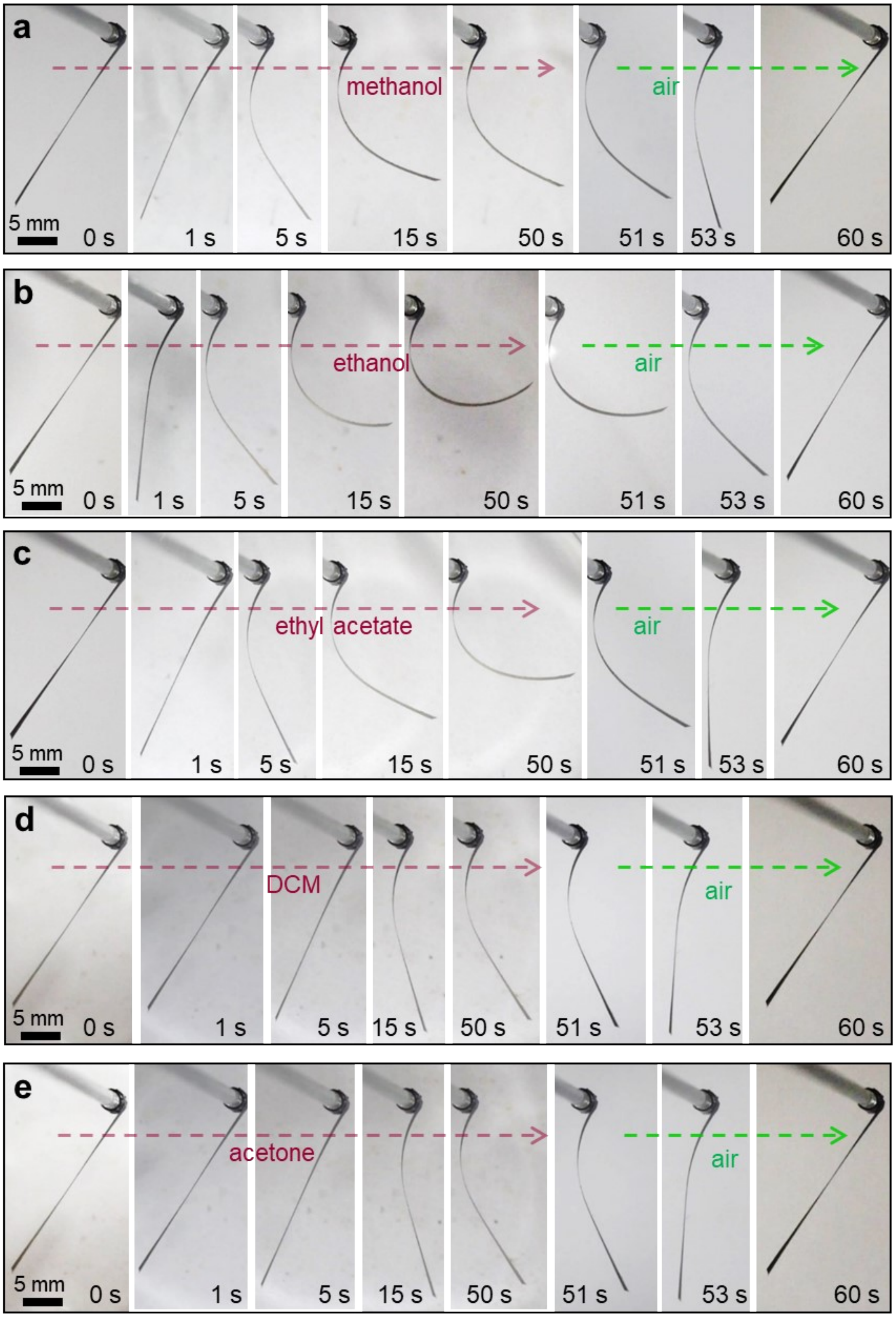

Figure S12: Solvent-induced responsiveness: Snapshots showing the bending and the recovery moment of V_2O_5-vermiculite bilayer strip (25 mm × 2 mm, thickness 15 μm) upon exposure to (a) methanol, (b) ethanol, (c) ethyl acetate, (d) DCM and (e) acetone vapours.

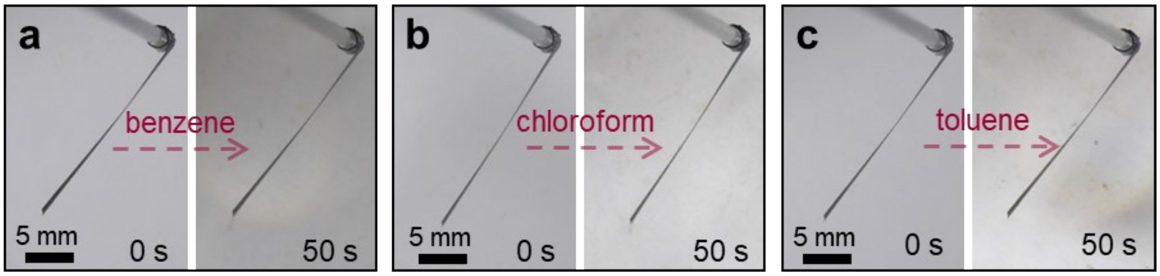

Figure S13: Snapshots of V_2O_5-vermiculite bilayer strip (25mm × 2mm, thickness 15 µm) upon exposure to (a) benzene, (b) chloroform, and (c) toluene vapours. In the presence of these vapours, no bending was observed.

References:

(1) R. K. Gogoi, K. Saha, J. Deka, D. Brahma and K. Raidongia, *J. Mater. Chem. A*, 2017, **5**, 3523-3533.

(2) Y. Li, C. Liu, Z. Xie, J. Yao and G. Cao, *J. Mater. Chem. A*, 2017, **5**, 16590-16594.

(3) R. K. Gogoi, A. B. Neog, T. J. Konch, N. Sarmah and K. Raidongia, *J. Mater. Chem. A*, 2019, **7**, 10552-10560.

(4) R. E. Mark, C. C. Habeger, J. Borch and M. B. Lyen, *Handbook of Physical Testing of Paper*, 2001, vol. 1.

(5) R. K. Gogoi and K. Raidongia, *Adv. Mater.*, 2017, **29**, 1701164.