Supplementary Information

# Application of Reduced Graphene Oxide-Based Actuator for Real-time Chemical Sensing of Liquid and Vapour Phase Contaminants

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**Preparation of graphene oxide and reduced graphene oxide:**

Modified Hummers' method was followed for the synthesis of Graphene Oxide (GO). 2 g of graphite powder was added to 50 ml of concentrated sulphuric acid[1], maintaining a temperature below 5 °C. Under constant stirring, 6 g of potassium permanganate ($KMnO_4$) was slowly added and stirred for additional 2 hours at 35 °C. This step was followed by slow addition of 100 ml of deionised (DI) water, after which 10 ml of hydrogen peroxide ($H_2O_2$) was added under constant stirring. The yellow slurry formed was first washed with 10 % HCl solution and later with acetone until the filtrate's pH value increased above 5. For the preparation of reduced graphene oxide (r-GO), GO obtained by the above method was dispersed (0.5 mg/ml) in dimethylformamide (DMF) and refluxed at 153 °C for 2 hours.[2]

**Preparation of r-GO membranes:**

40 ml of the dispersion of r-GO in DMF was subjected to vacuum filtration through a polytetrafluoroethylene (PTFE) membrane of pore size 5 μm. This was followed by drying it at 70 °C for 2 hours. After air drying, reconstructed r-GO membranes could be peeled off easily from the PTFE membrane.

**Preparation of agar membranes**:

1 mg/ml mixture of agar in DI water was heated at 100 °C until we get a clear solution, which was then poured into a petri dish. The solution cooled down to room temperature and formed a gel-like substance which was then dried in an oven at 70 °C. A semi-transparent agar membrane could be peeled off easily from the petri dish.

**Preparation of r-GO/agar bilayer membrane:**

Firstly, 40 ml of r-GO (from 0.5 mg/ml GO dispersion) dispersion was vacuum filtered through a PTFE membrane resulting in a greyish-black membrane. After the r-GO membrane appeared to be dried, 20 ml of agar dispersion was filtered through it. Agar dispersion itself was prepared by mixing agar powder in DMF (1 mg/ml) under probe sonication (Labman, Model: PRO-650)

for 30 minutes (1 s on & 1 s off pulse). Thus prepared bilayer membrane of r-GO/agar could be easily peeled off from the PTFE membrane by heating in a hot air oven at 70 °C for 2 hours.

**Characterization:**

Atomic Force Microscope (AFM) (Make: Oxford; Model: Cypher) was used for characterizing nanosheets of GO and r-GO. Morphology and cross-section of the membranes were examined by Field Emission Scanning Electron Microscope (FESEM) (Make: Zeiss, Model: Sigma). Membranes of r-GO and GO were characterized by Raman Spectroscopy (Make: Horiba Jobin Vyon, Model: LabRam HR). Bruker D-205505 Cu-Kα radiation (λ = 1.5406 Å) was employed for X-ray diffraction studies. The shape transformations of the bilayer membranes was filmed using a digital camera, Nikon D 5200. The stress-strain curves were recorded in a 5kN Electromechanical Universal Testing Machine (Make: Zwick Roell : Z005TN).

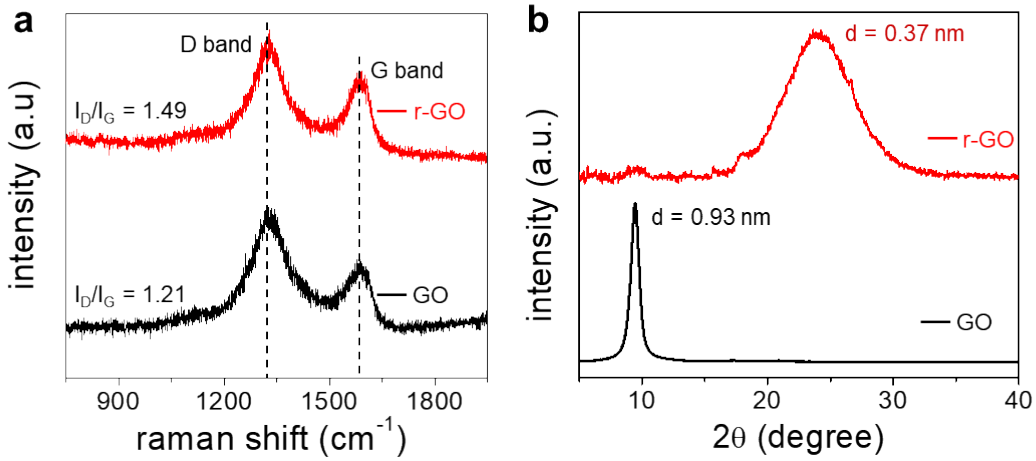


**Figure S1:** (a) Raman spectra and (b) XRD patterns of GO and r-GO membranes.

The G band in the Raman spectra signifies in-plane vibrations of $sp^2$ bonded carbon atoms whereas the D band denotes out of plane vibrations attributed to the presence of structural defects. $I_D/I_G$ is a measure of the defects present on the graphene structure. The peak of the D band for GO membrane was found at 1335 $cm^{-1}$ and the peak of the G band at 1592 $cm^{-1}$. For the r-GO sample, the peak of D band was found to be at same position (1335 $cm^{-1}$) while that of G band was shifted downwards to 1587 $cm^{-1}$.[3] The $I_D/I_G$ ratio was calculated for GO and r-GO to be 1.21 and 1.49 respectively,[4] where $I_D$ is the intensity of the D band and $I_G$ is the intensity of the G band. The increase in the $I_D/I_G$ value for r-GO confirms increasing defect concentrations during the reduction process of GO to r-GO.[5]

In case of XRD studies, the GO membrane showed a sharp diffraction peak at 2θ value of 9.4° corresponding to an interplanar spacing of 0.93 nm. A broad diffraction pattern with peak corresponding to an interplanar spacing of 0.37 nm (at 2θ value of 24°) appeared in the XRD pattern of r-GO membrane.

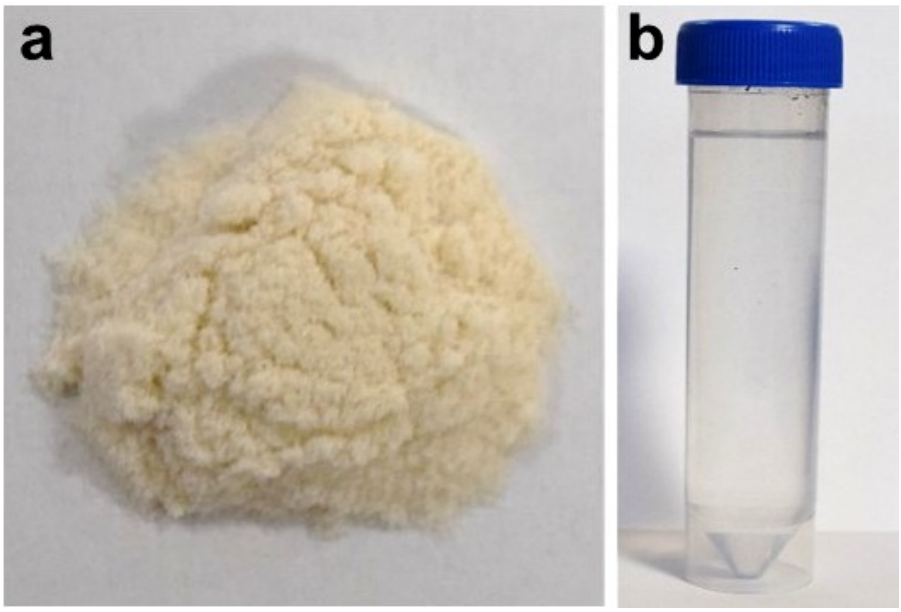


**Figure S2:** Digital photos of (a) agar powder and (b) agar dispersion in DMF.

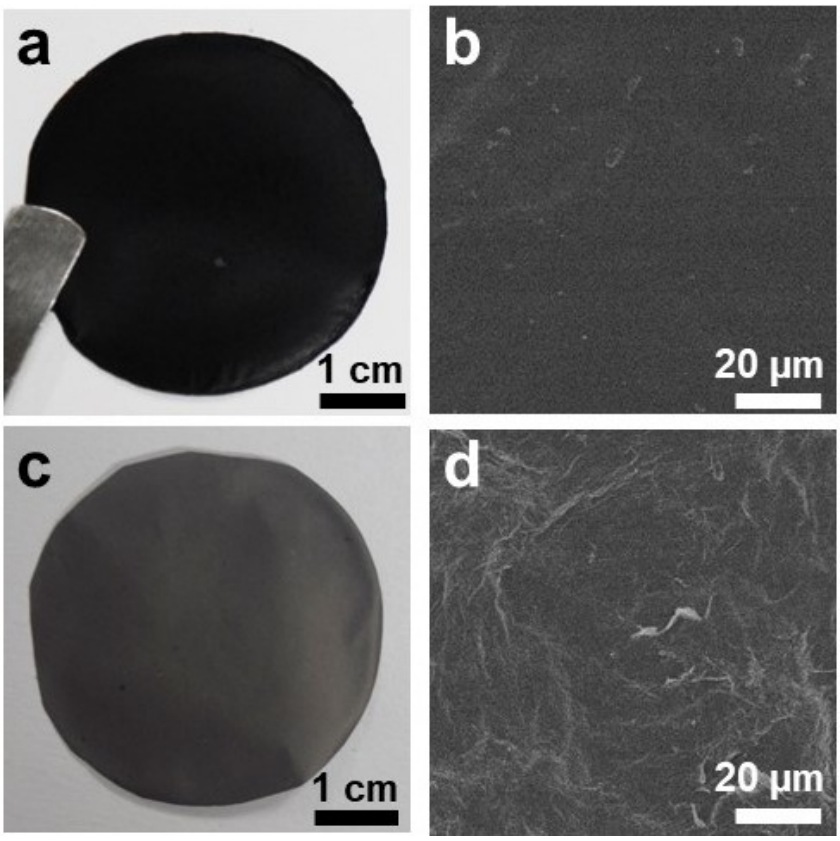


**Figure S3:** Digital photos of (a) agar side and (c) r-GO side of the bilayer membrane. FESEM images of (b) agar and (d) r-GO sides of the r-GO/agar bilayer membrane.

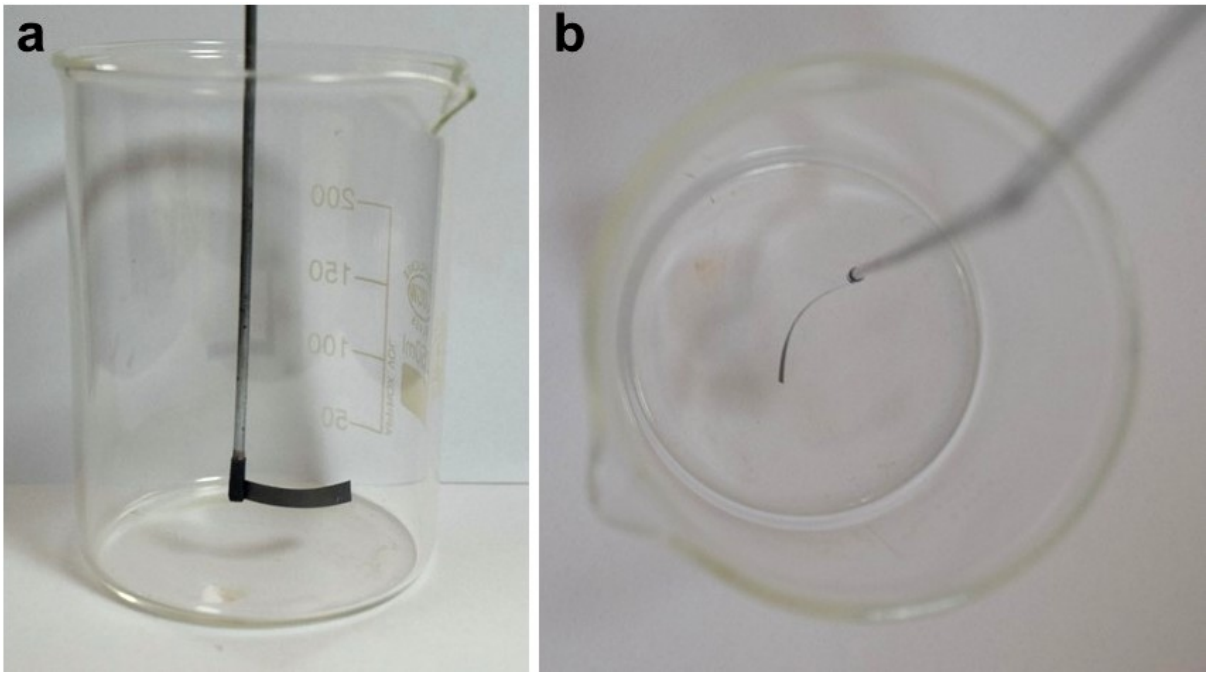


**Figure S4:** Digital photos showing the experimental setup used for studying the vapour induced shape alteration behaviour of the r-GO/agar bilayer strip (a) side view and (b) top view.

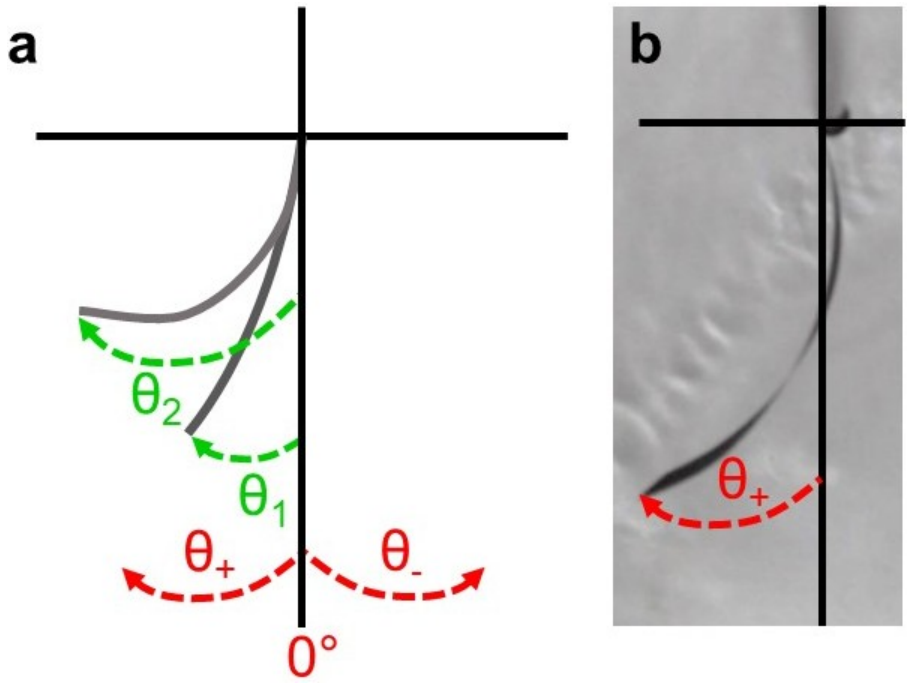


**Figure S5:** (a) Schematic diagram of the design employed for bending angle measurements, and (b) bending angle measured for the r-GO/agar bilayer strips in response to solvent vapours.

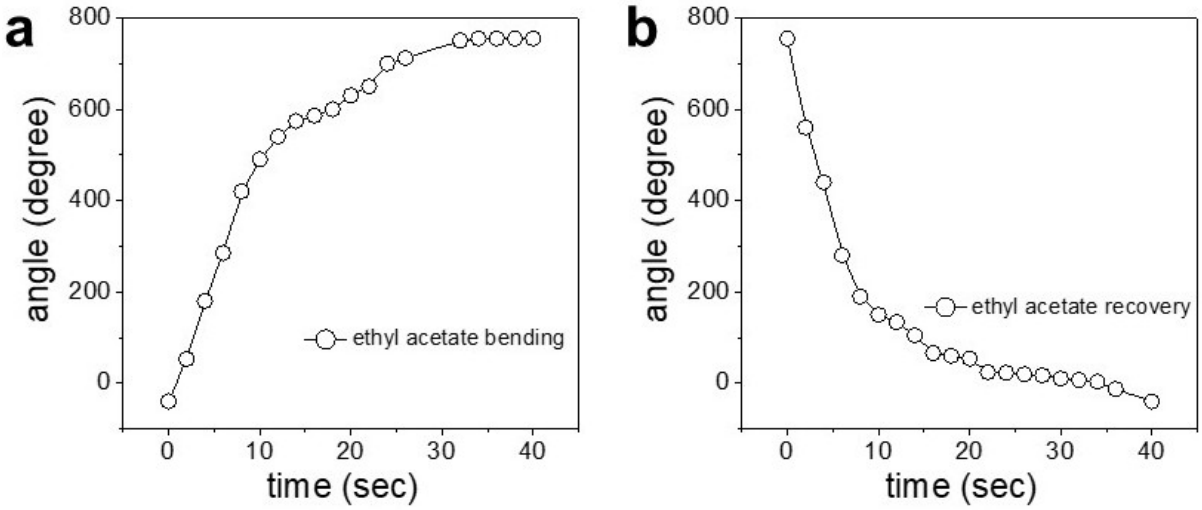


**Figure S6:** Plots showing the bending movements of the r-GO/agar bilayer strip (a) in ethyl acetate environment and (b) in open atmosphere

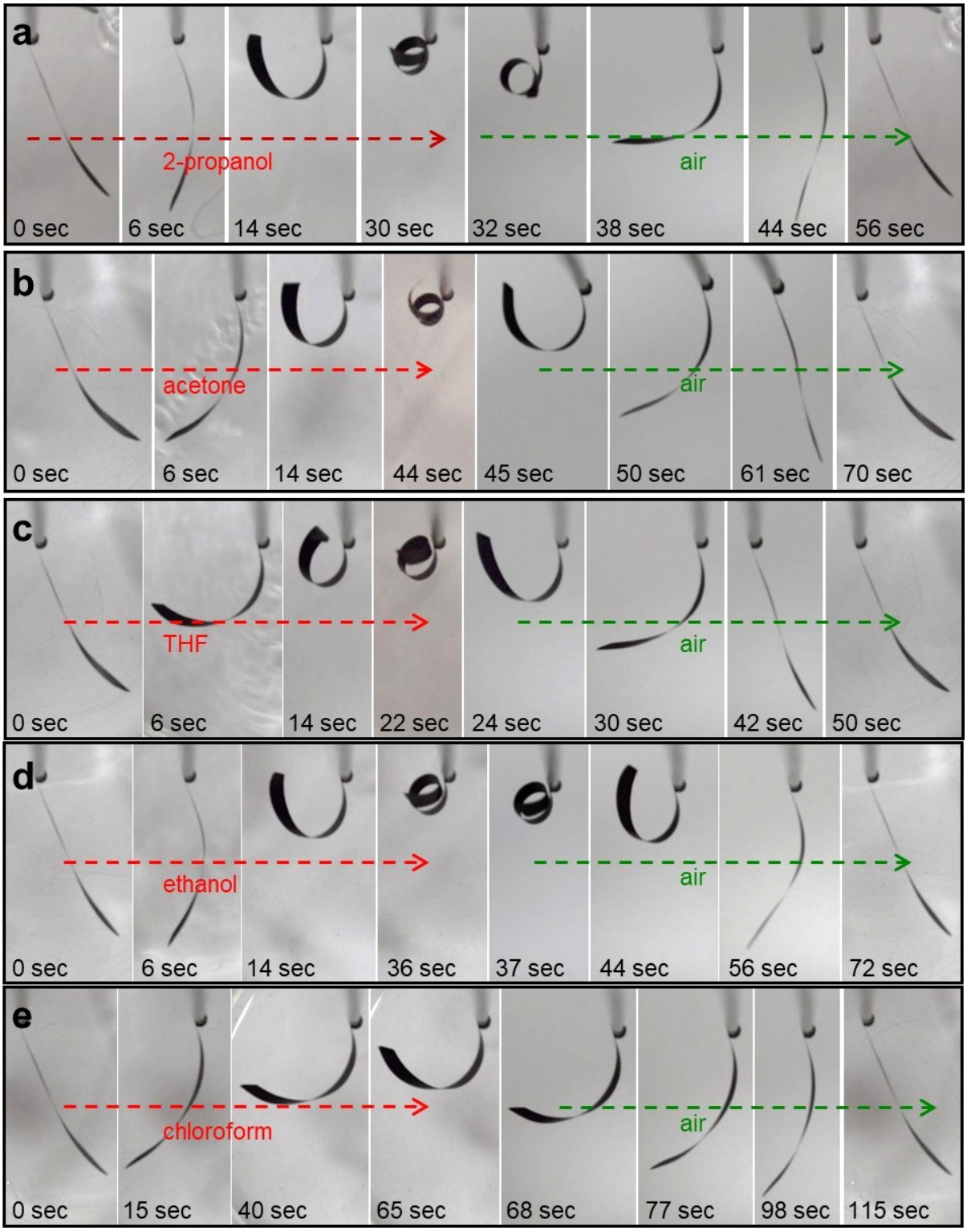


**Figure S7: Vapour induced responsiveness of the r-GO/agar bilayer membrane:** Snapshots showing the bending and recovery movements of a bilayer strip of r-GO/agar bilayer strip in presence of (a) 2-propanol, (b) acetone, (c) THF, (d) ethanol and (e) chloroform vapours.

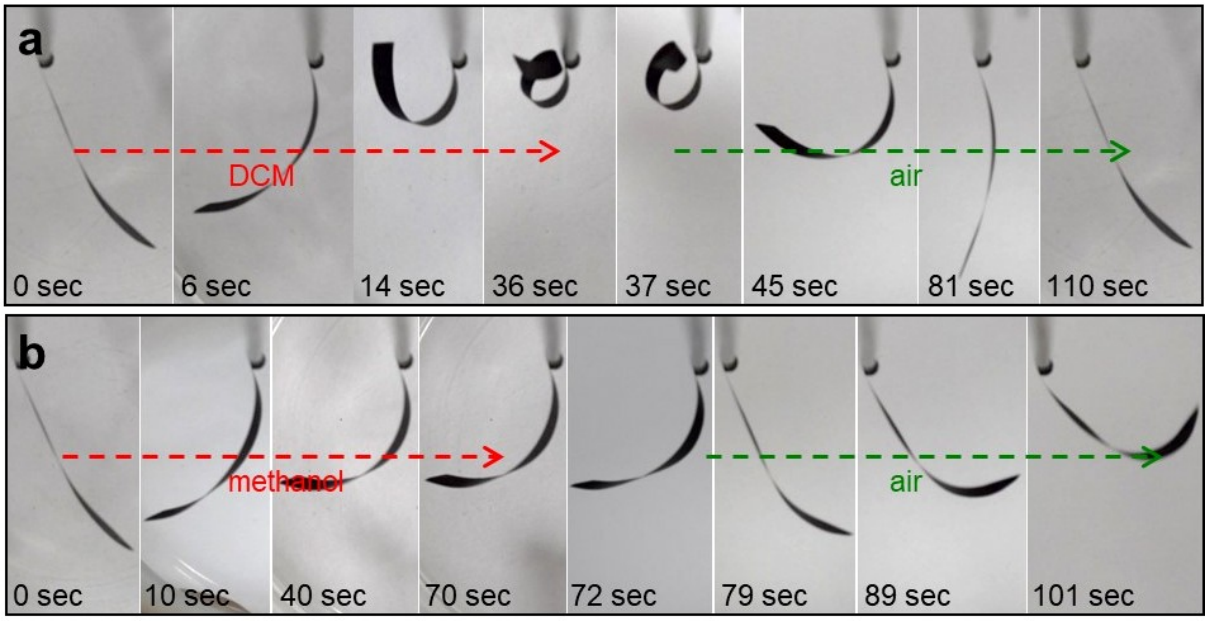


**Figure S8:** Snapshots showing the bending and recovery movements of a bilayer strip of r-GO/agar bilayer membrane in presence of (a) DCM and (b) methanol vapours.

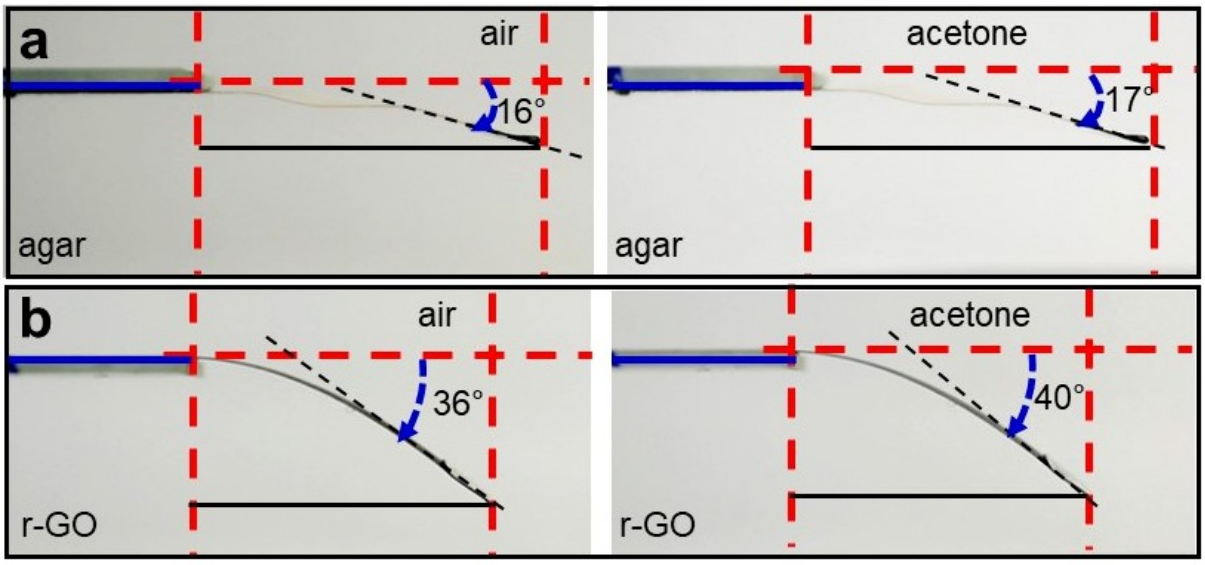


**Figure S9:** Measurement of solvent vapour induced bending stiffness alteration of the bilayer membrane. Snapshots of (a) agar and (b) r-GO strips with load applied on one end in open atmosphere and on exposing to vapours of acetone.

Lorentzen & Wettre 2-point method was employed to calculate the bending stiffness of the individual strips. Known loads were used to apply a force at one end while keeping the other end of the strip fixed to a glass slide. The weight and dimensions of the agar strip used for the experiment was 5.2 mg and 20 mm x 4 mm x 50 µm respectively. Likewise, r-GO strip was handled a load of 2.5 mg having dimensions 20 mm x 4 mm x 42 µm. Bending stiffness ($S_b$) was calculated using the following equation:

$$S_b = \frac{60 \times F \times l2}{\pi \times \theta \times b}$$

Where, bending force ($F$) = weight × gravitational constant, $l$ = distance between the fixed end and the load, $\theta$ = deflection, $b$ = width of the strip. At first bending angle was calculated in open atmosphere after which strips were exposed to acetone vapours causing further bending.

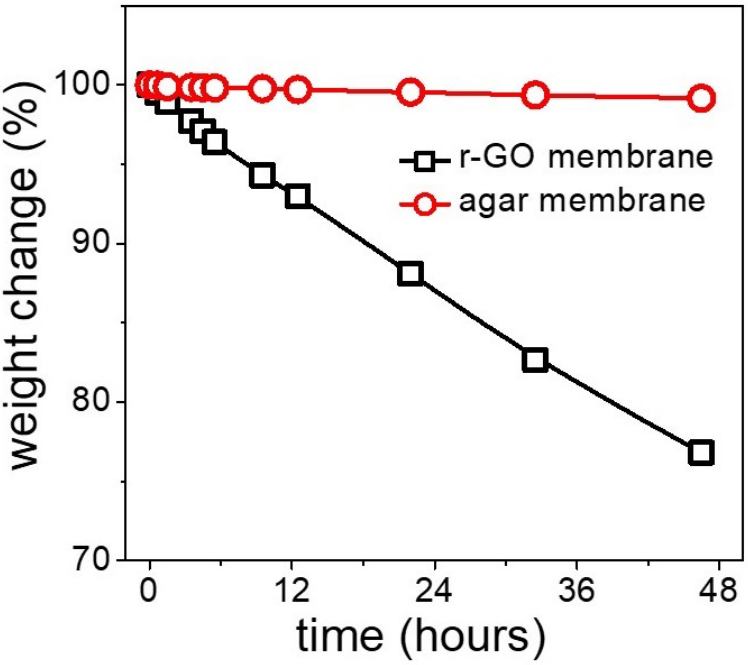


**Figure S10:** Change in weight % of the vials as a result of evaporation of acetone through the individual membranes. Significant weight loss was found in case of the vial covered with r-GO membrane as compared to that covered with agar membrane.

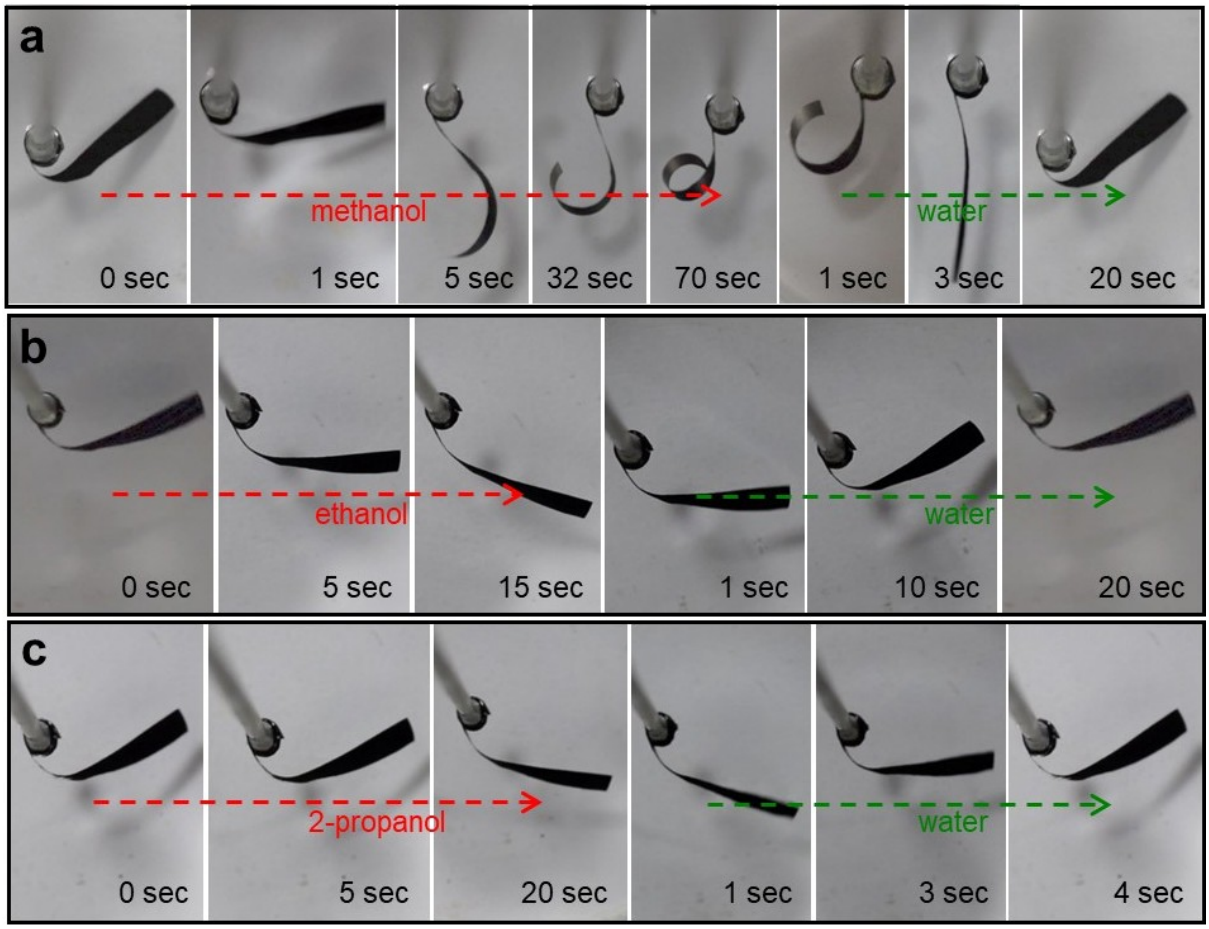


**Figure S11: Solvent induced responsiveness of r-GO/agar bilayer membrane:** Snapshots showing the bending of a bilayer strip of r-GO/agar bilayer membrane in (a) methanol, (b) ethanol and (c) 2-propanol solvents and its corresponding recovery in water.

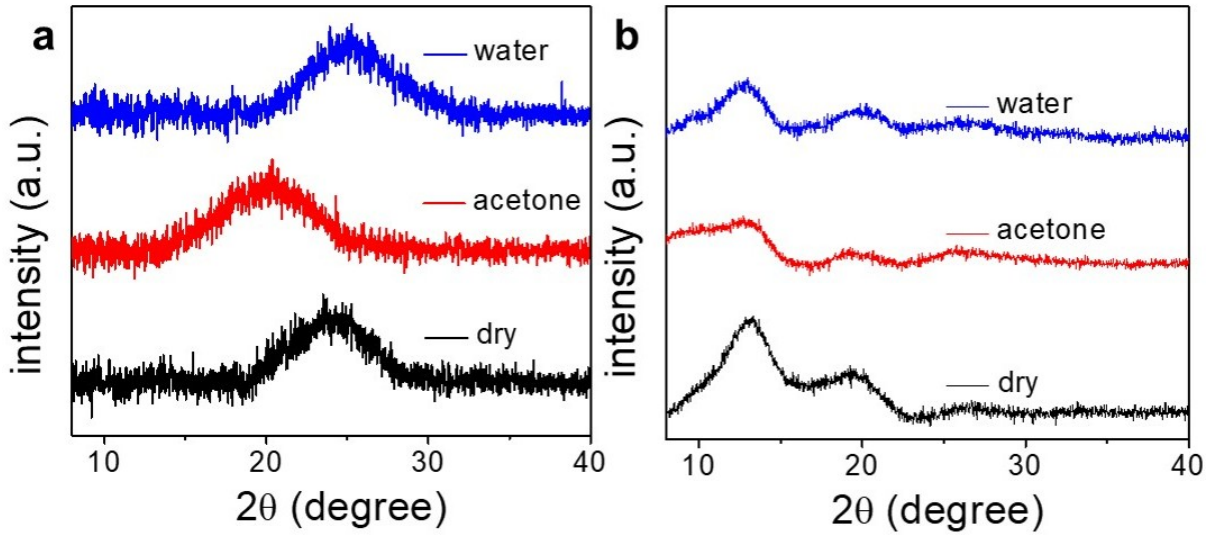


**Figure S12: Solvent induced variations in interlayer spacing's of individual membranes:** (a) r-GO membrane and (b) agar membrane. Significant variation in d-spacing's was seen in the case of the r-GO membrane but no such definite changes were observed for the agar membrane.

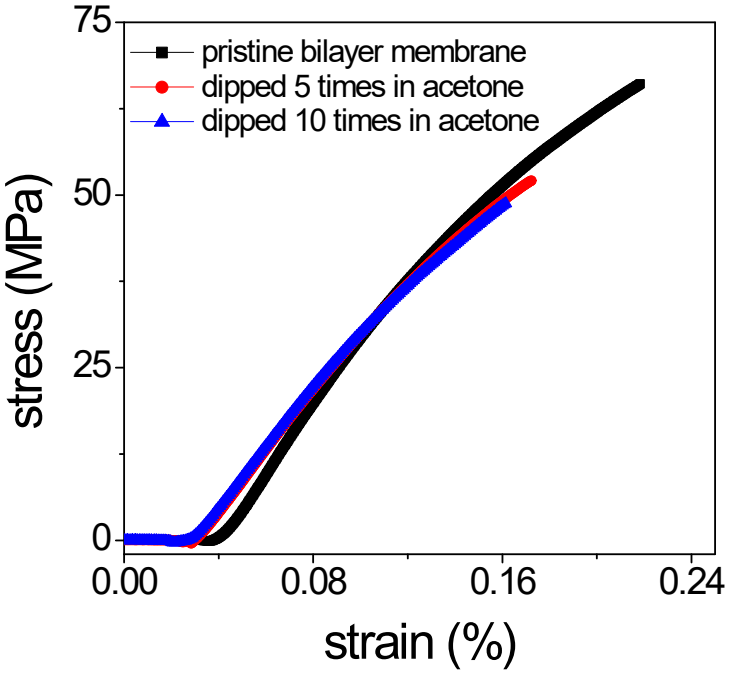


**Figure S13: Stress-strain curve:** Stress-strain curve of a strip of pristine bilayer membrane is compared with the ones dipped and taken out of acetone for 5 and 10 times respectively.

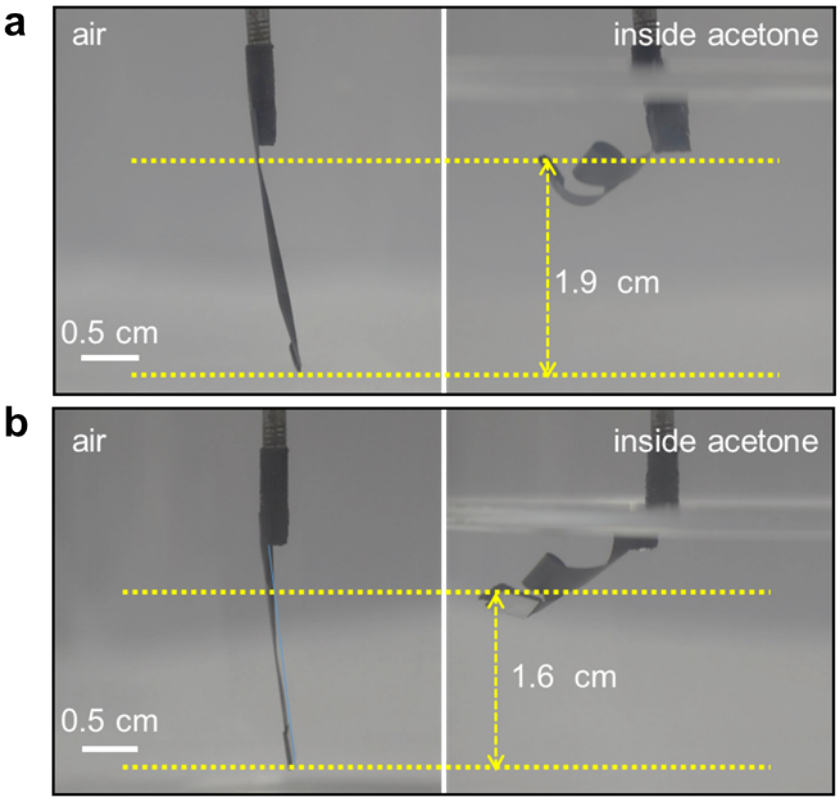


**Figure S14: Work done by the bilayer strip of r-GO/agar:** Snapshots showing lifting of weights by the bilayer strip upon dipping in liquid acetone. A strip weighing 2 mg (of dimensions 20 × 3 × 0.023 $mm^3$) could lift a weight of (a) 3 mg up to 1.9 cm and (b) 10 mg up to 1.6 cm inside acetone.

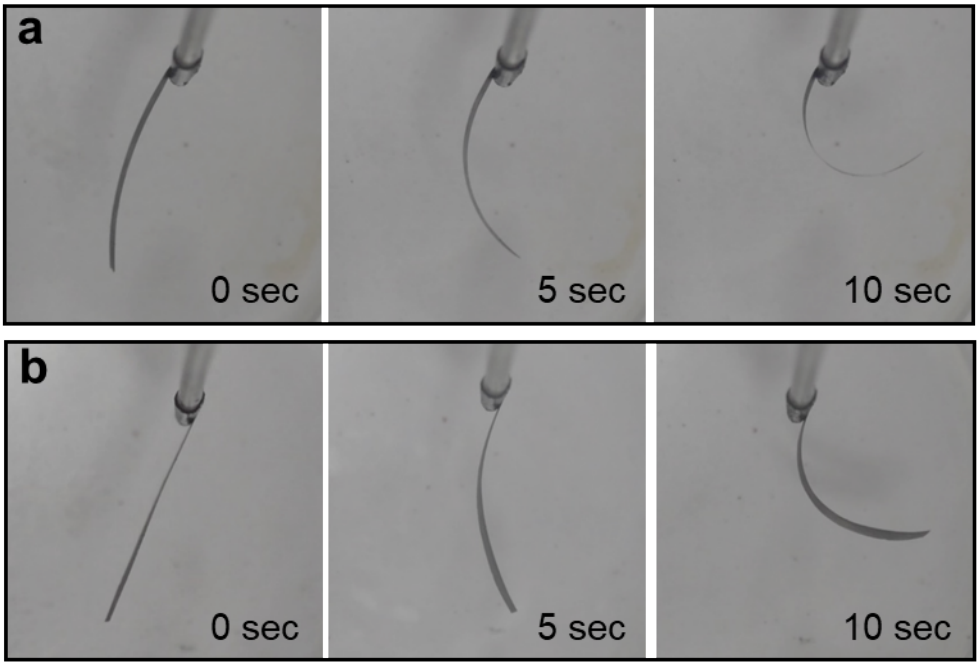

**Figure S15: Robustness of the r-GO/agar bilayer membrane:** Strips of the bilayer membrane were found to show responsive even after subjecting to extreme conditions. Photos showing acetone vapour induced bending movements of a bilayer strip after exposing to (a) concentrated HCl vapours and (b) $NH_3$ vapours for 6 hours.

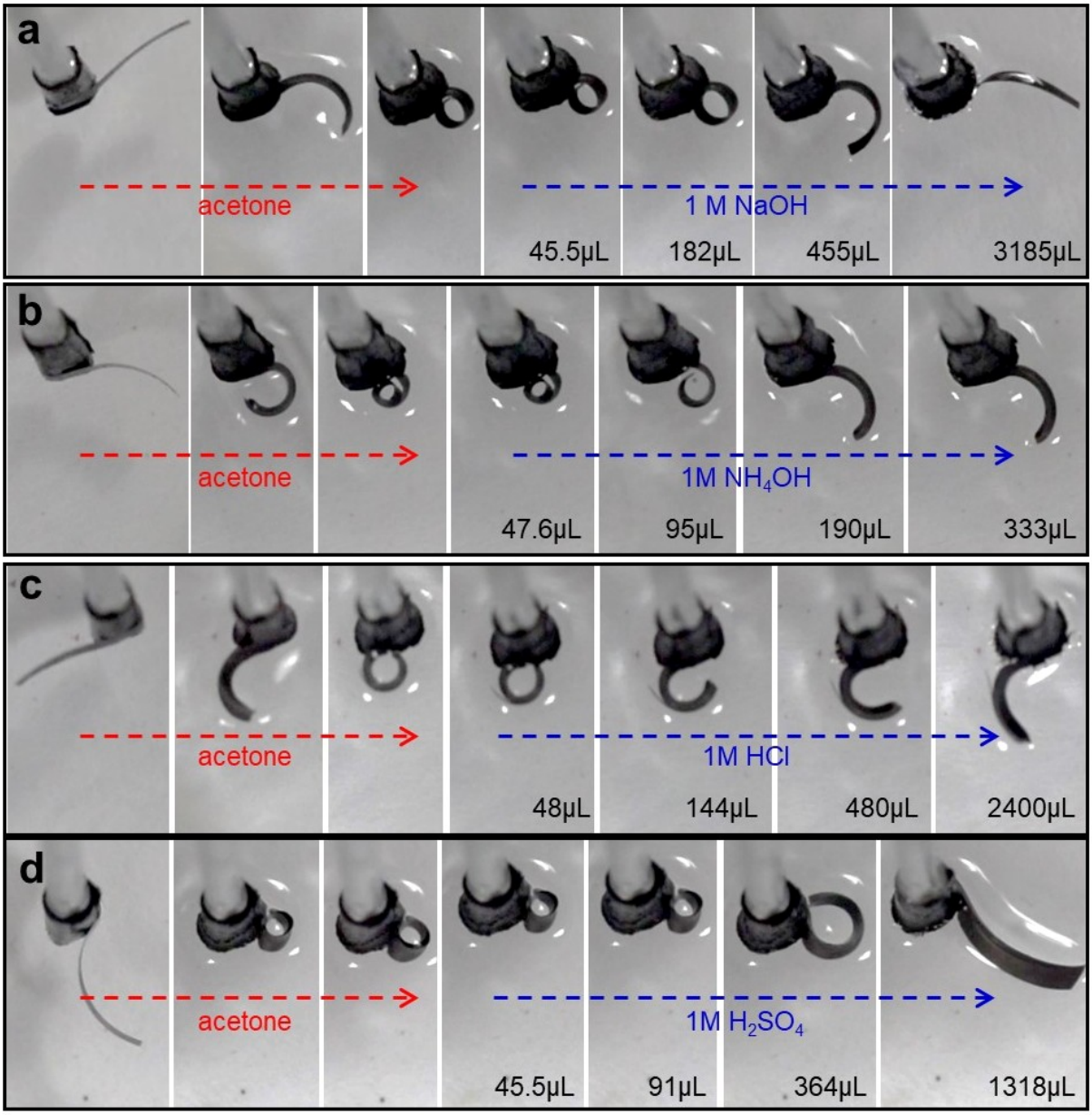


**Figure S16:** Snapshots showing the detection of trace amounts of aqueous impurities inside acetone by the r-GO/agar bilayer strips: (a) 1M NaOH, (b) 1M $NH_4OH$, (c) 1M HCl and (d) 1M $H_2SO_4$.

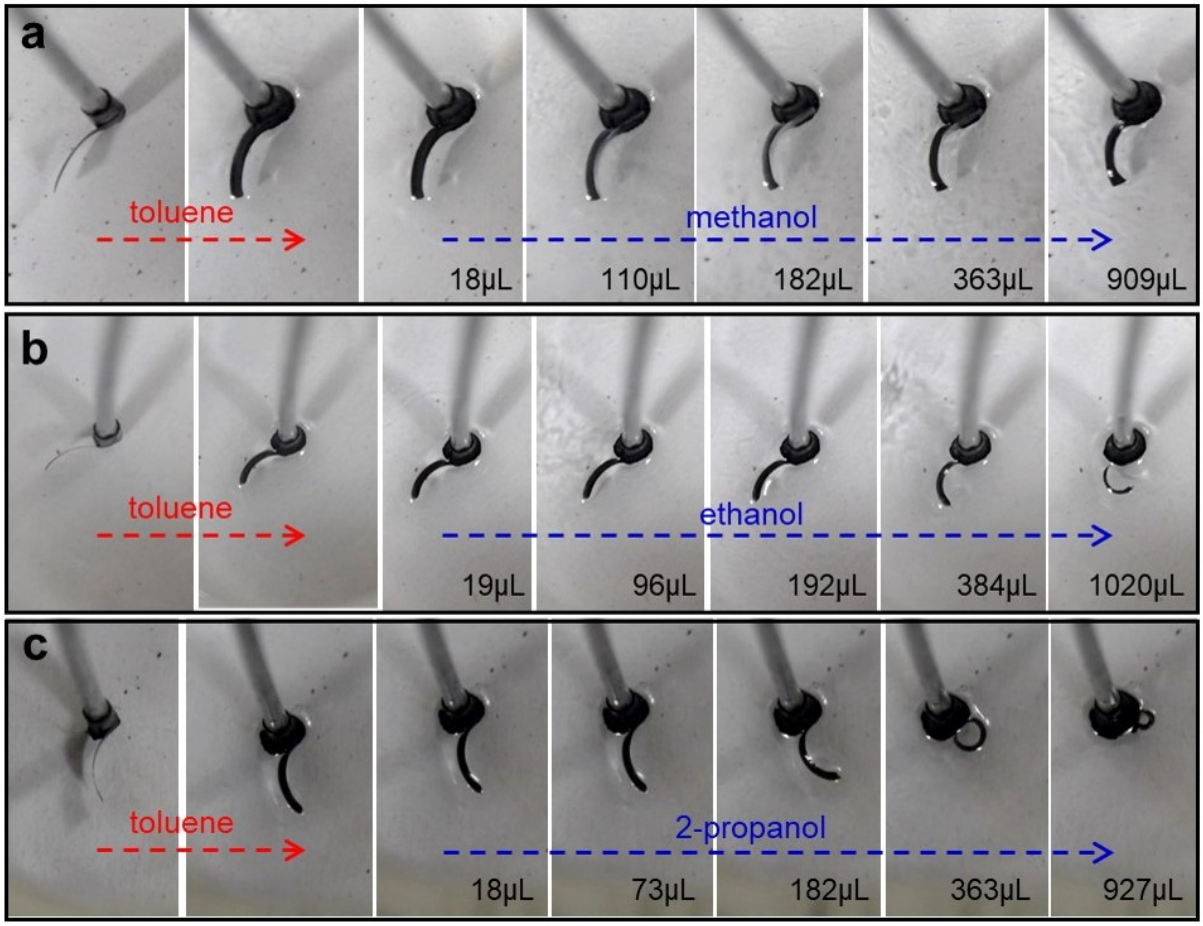


**Figure S17:** Snapshots showing the detection of trace amounts of alcohol impurities inside toluene by the r-GO/agar bilayer strips: (a) methanol, (b) ethanol and (c) 2-propanol.

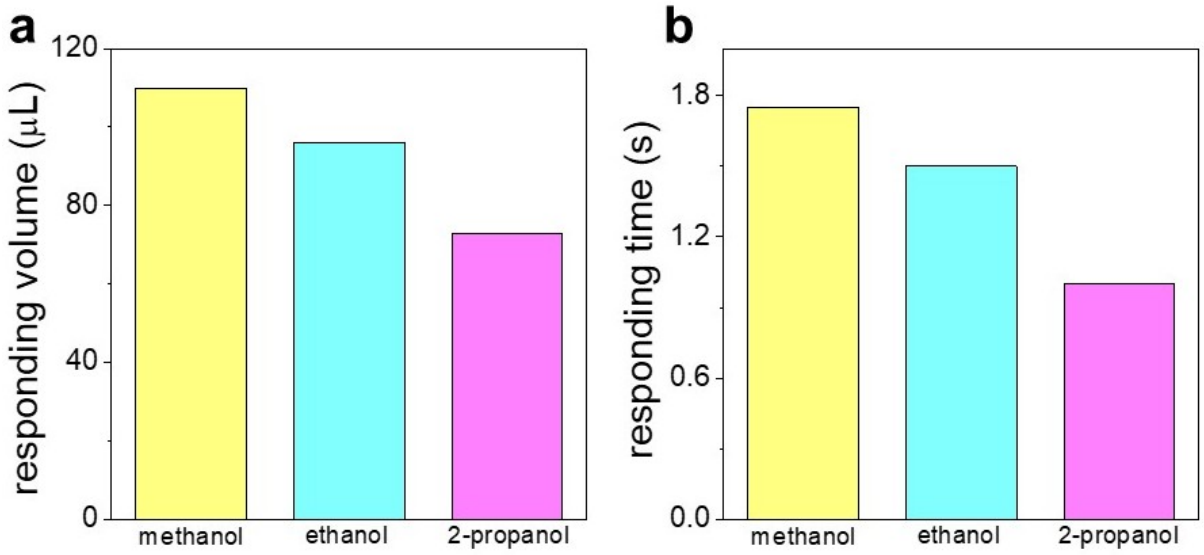


**Figure S18:** Bar diagrams showing (a) minimum responding volume and (b) minimum responding time of the r-GO/agar bilayer strips in the presence of trace amounts of alcohol impurities inside toluene.

**References:**


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(5) T. N. Lin, M. R. Inciong, S. R. M. S. Santiago, T. W. Yeh, W. Y. Yang, C. T. Yuan, J. L. Shen, H. C. Kuo and C. H. Chiu, Photo-induced Doping in GaN Epilayers with Graphene Quantum Dots, *Sci. Rep.*, 2016, **6**, 23260.