

# Superwetting nanowire membranes for selective absorption

JIKANG YUAN<sup>1†</sup>, XIAOGANG LIU<sup>2,3†</sup>, OZGE AKBULUT<sup>2</sup>, JUNQING HU<sup>4</sup>, STEVEN L. SUIB<sup>5</sup>, JING KONG<sup>1\*</sup> AND FRANCESCO STELLACCI<sup>2\*</sup>

<sup>1</sup>Department of Electrical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

<sup>2</sup>Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

<sup>3</sup>Department of Chemistry, National University of Singapore, Singapore 117543

<sup>4</sup>International Center for Young Scientists, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan

<sup>5</sup>Department of Chemistry and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269-3060, USA

<sup>†</sup>These authors contributed equally to this work.

\*e-mail: frstella@mit.edu; jingkong@mit.edu

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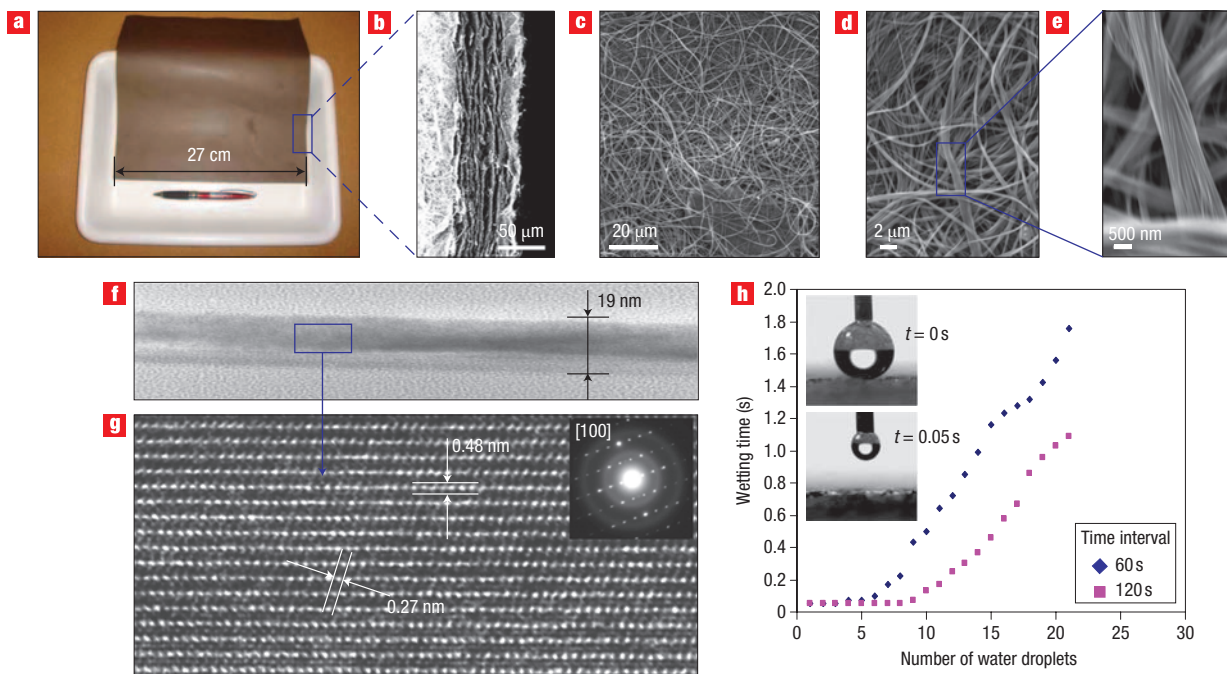
The construction of nanoporous membranes is of great technological importance for various applications, including catalyst supports, filters for biomolecule purification, environmental remediation and seawater desalination<sup>1–3</sup>. A major challenge is the scalable fabrication of membranes with the desirable combination of good thermal stability, high selectivity and excellent recyclability. Here we present a self-assembly method for constructing thermally stable, free-standing nanowire membranes that exhibit controlled wetting behaviour ranging from superhydrophilic to superhydrophobic. These membranes can selectively absorb oils up to 20 times the material's weight in preference to water, through a combination of superhydrophobicity and capillary action. Moreover, the nanowires that form the membrane structure can be re-suspended in solutions and subsequently re-form the original paper-like morphology over many cycles. Our results suggest an innovative material that should find practical applications in the removal of organics, particularly in the field of oil spill cleanup.

Owing to the increasing level of attention focused on the preservation of the environment, there is a growing need for membrane materials able to perform complex functions such as removing various forms of organic contaminants or oil spills from water<sup>4</sup>. The existing toolbox for the fabrication of membranes includes methods such as selective etching of solid or polymer templates, self-assembly of block co-polymers, layer-by-layer assembly, electrospinning of nanofibres, dry-state spinning of nanotube yarns, and replica moulding against porous templates<sup>5–10</sup>. Although widely implemented in research, these methods have limitations for practical use because of the need to withstand harsh conditions, the need for multistep procedures for implementation or limitations in substrate size. In addition, conventional polymeric membranes are unsuitable for high-temperature applications and lack substantial selectivity. New and recyclable membranes that overcome these fundamental limitations could significantly reduce materials waste and operating costs. Here, we present a thermally stable membrane material, based upon self-assembled, free-standing, paper-like structures of cryptomelane-type manganese oxide nanowires. The

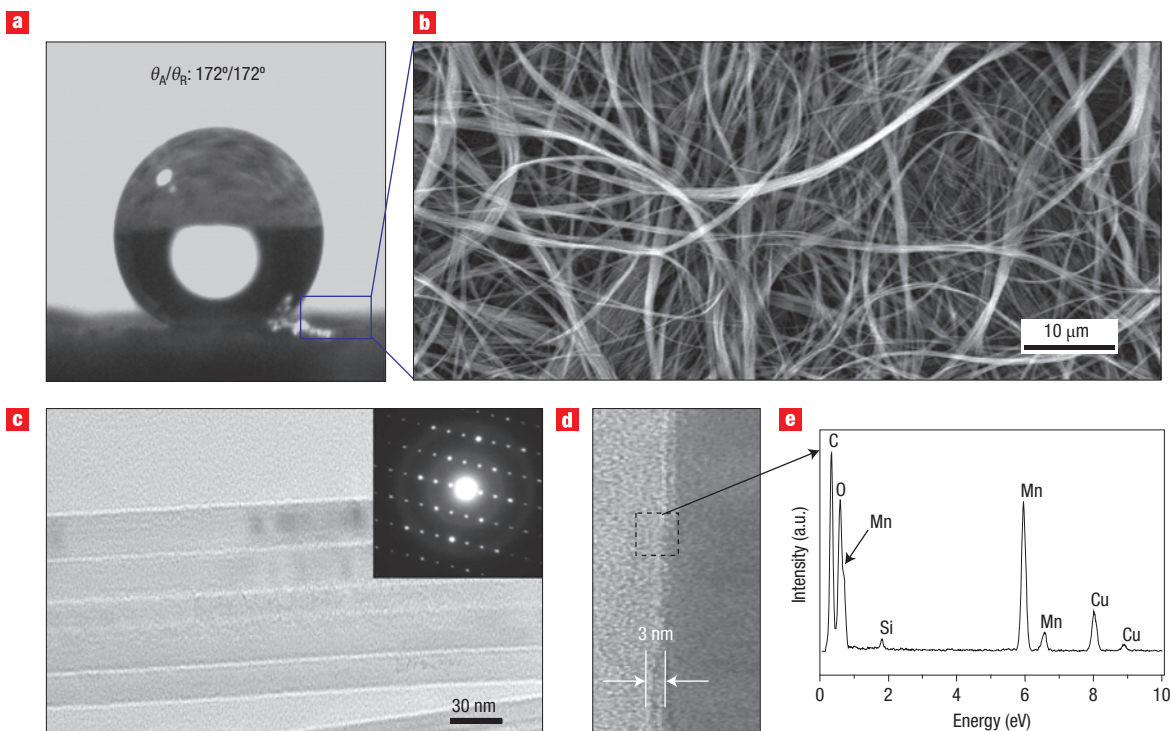
nanowire membrane, composed of three-dimensional porous nanostructures, exhibits a superhydrophilic character with a wetting time of 0.05 s. When coated with a thin layer of hydrophobic molecules, the membrane becomes superhydrophobic, as is made evident by its high water contact angle ( $\theta > 170^\circ$ ). These two extreme wetting characteristics are completely switchable upon coating with or removal of the hydrophobic molecules at elevated temperatures. We demonstrate the efficient absorption and high level of selectivity of this superwetting nanowire membrane for a broad range of organic solvents and oil.

The design of suitable membranes for selective absorption of organics requires a material composed of superhydrophobic or oleophilic fibres that form a net of open superwetting capillaries. When combined with capillary action, for example in the case of non-woven poly(propylene) fibres, absorption efficiency is significantly improved<sup>11</sup>. Surface energy, and consequently contact angle, is a materials property that depends critically on surface morphology<sup>12,13</sup>. Surface roughness and the fraction of air trapped on a surface, as well as material composition, determine the wetting property of the surface<sup>14–25</sup>. To this end we synthesized a material composed of manganese oxide nanowires that assemble into free-standing membranes according to a modified procedure available in the literature<sup>26</sup>.

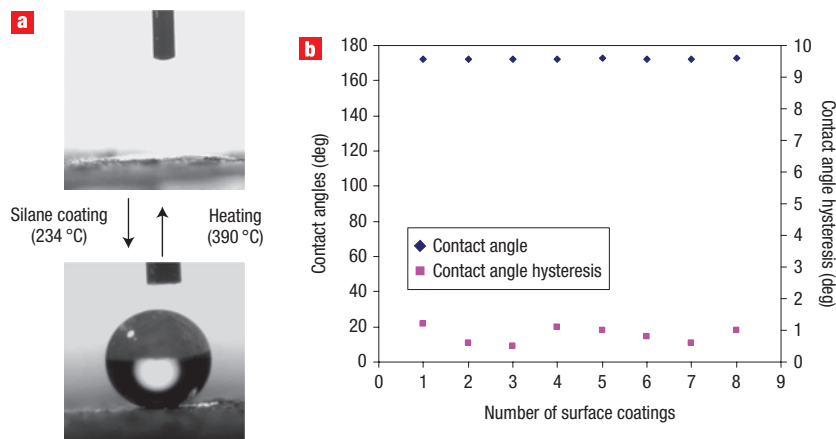
In a typical experiment, nanowires were first synthesized at 250 °C in an autoclave in the presence of stoichiometric mixtures of potassium sulphate (19.1 mmol), potassium persulphate and manganese sulphate monohydrate in a ratio of 1:2:1 in 80 ml of deionized water. This hydrothermal treatment yielded a wool-like suspension after dispersion in deionized water. The water was subsequently removed by casting the suspension on a Teflon<sup>®</sup> substrate placed in an oven, leading to the formation of self-assembled nanowire membranes. Free-standing nanowire membranes of arbitrary size exhibiting a uniform surface morphology could be readily synthesized with this approach in almost quantitative yield. A typical sample of the nanowire paper with a 27-cm edge length is shown in Fig. 1a. A scanning electron microscopy (SEM) image (Fig. 1b) shows a cross-sectional view of the nanowire membrane (~50 µm thick)



**Figure 1** Characterization of the as-synthesized nanowire membrane. **a**, Optical image of the cryptomelane membrane. **b**, SEM image of cross-sectional area of the membrane, showing a layered structure. **c**, Low-magnification SEM image showing surface morphology of the membrane. **d**, SEM image of the interpenetrating nanowire networks. **e**, High-magnification SEM image of a nanowire bundle. **f**, TEM image of a single cryptomelane nanowire. **g**, High-magnification TEM image of the nanowire shown in **f**. Inset: the corresponding selected-area electron pattern. **h**, Wetting time values as a function of the number of water droplets sequentially deposited at time intervals of 60 s and 120 s, respectively. Inset: video snapshots of the wetting of a water droplet on the membrane.



**Figure 2** Characterization of the silicone-coated nanowire membrane. **a**, Water contact angle measurements of the silicone-coated cryptomelane membrane. Note that  $\theta_A$  and  $\theta_R$  refer to advancing and receding angles, respectively. **b**, SEM image of the silicone-coated nanowires. **c**, TEM image of as-modified nanowires. Inset: the corresponding SAED pattern. **d**, High-magnification TEM image showing a conformal sheath on the surface of the nanowire. **e**, EDS spectrum taken from a selected area marked in **d**.

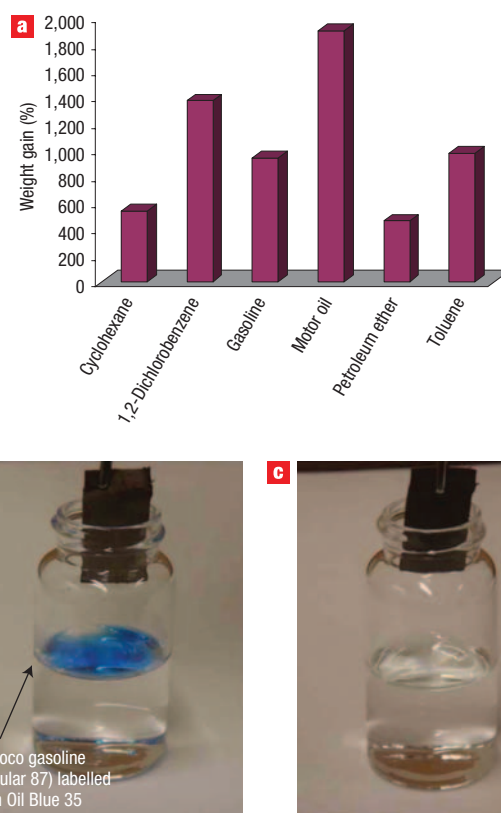


**Figure 3** Surface wetting switchability of the nanowire membrane. **a**, Representation of the reversible transition between superhydrophilic (top) and superhydrophobic (bottom) states of the nanowire membrane. **b**, A series of contact angle and hysteresis measurements taken after each transition cycle.

consisting of nanowires assembled over multiple length scales. A large portion of the nanowires assemble in bundles over a length scale longer than several hundreds of micrometres, forming an open porous network (Fig. 1c–e). Figure 1f shows a transmission electron microscopy (TEM) image of a single nanowire with a uniform diameter ( $\sim 19$  nm). Selected-area electron diffraction (SAED) patterns (upper right inset, Fig. 1g) of the nanowire can be indexed in accordance with the [100] zone axis of a cryptomelane-M type ( $K_{2-x}Mn_8O_{16}$ ) crystal (Joint Committee on Powder Diffraction Standards file no. 44-1386;  $a = 9.942$  Å,  $b = 2.866$  Å,  $c = 9.709$  Å). The high-magnification TEM image of the nanowire shown in Fig. 1g reveals lattice fringes of the {002} and {011} with a  $d$ -spacing of 0.48 nm and 0.27 nm, respectively, typical for monoclinic  $K_{2-x}Mn_8O_{16}$ . Within this nanowire, the [001] crystallographic direction is essentially parallel to the long axis direction of the nanowire.

The self-assembled cryptomelane nanowire membrane has a pore size distribution centred at 10 nm and a surface area of  $44 \text{ m}^2 \text{ g}^{-1}$ . To examine the wettability of the membrane, a video contact angle instrument was used and operated in dynamic mode at a capture speed of 60 frames per second (inset, Fig. 1h). The wetting time for a water droplet ( $\sim 2 \mu\text{l}$ ) added to the surface was found to be 0.05 s. Interestingly, further additions of water droplets to the same location at time intervals of 60 s and 120 s show a constant wetting time of 0.05 s until a saturation point is reached (Fig. 1h), indicating that water penetrates in the bulk of the material.

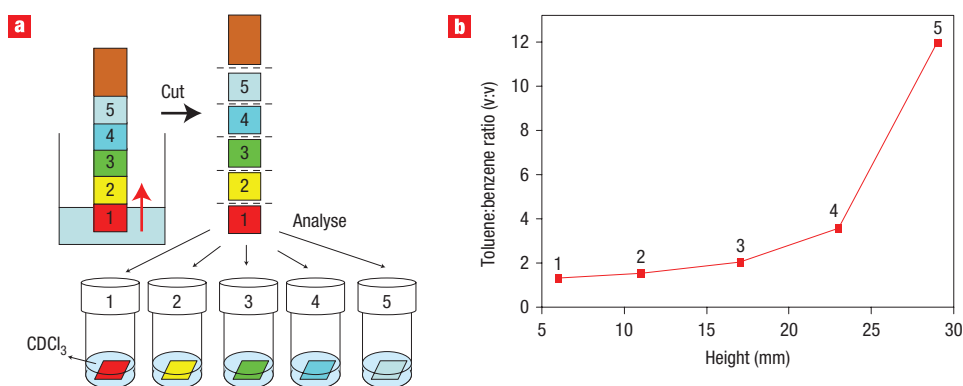
To obtain superhydrophobic surfaces, we coated the membrane using a vapour deposition technique that provides a coating over the entire surface of the porous material. The nanowire membrane was placed together with a polydimethylsiloxane (PDMS) film in a covered glass container and heated at  $234$  °C for 30 min. Upon heat treatment, we suspect that volatile silicone molecules in the form of short PDMS chains form a conformal layer on the metal oxide substrate and subsequently crosslink, to result in the formation of a silicone coating. As anticipated, the modified membrane becomes superhydrophobic, as is made evident by its water contact angle of  $172 \pm 1^\circ$  (Fig. 2a) with a negligible hysteresis between the advancing and receding angle. Notably, the superhydrophobicity of the silicone-coated membrane remains unaltered after being immersed in water at ambient temperature for more than three months. The silicone-coated nanowires maintain their typical morphology (Fig. 2b), remain single crystalline (Fig. 2c), and are conformally coated with a sheath ( $\sim 3$  nm thick, Fig. 2d). Compositional analysis of



**Figure 4** Oil uptake studies of the silicone-coated nanowire membrane. **a**, Absorption capacities of the membrane for a selection of organic solvents and oils in terms of its weight gain. **b,c**, A layer of gasoline can be removed by addition of the self-supporting membrane to the gasoline followed by the removal of the paper. The gasoline was labelled with Oil Blue 35 dye for clear presentation.

the sheath by energy-dispersive X-ray spectroscopy (EDS) reveals the presence of silicon (Fig. 2e). Etching of the inorganic nanowires leaves silicone ‘nanotubes’ that are mostly composed of silicon and oxygen (see Supplementary Information, Fig. S1). Fourier transform infrared (FTIR) spectroscopy on a potassium





**Figure 5 Solvent-separation studies.** **a**, Schematic showing a typical procedure for separation of mixed solvents of very similar hydrophobicity. A piece of superhydrophobic nanowire membrane was immersed in a mixture of toluene and benzene for 3 min, the membrane was then removed from the solvent, cut into equally sized pieces, and subsequently placed into separated vials containing deuterated solvents. **b**, Calculated molar ratios of the solvents absorbed on five pieces cut from the nanowire membrane according to the scheme shown in **a**.

bromide pellet coated with the silicone by the same procedure as for the nanowires shows the presence of short chains of PDMS (see Supplementary Information, Fig. S10). Importantly, this hydrophobic coating can be easily removed by heating the nanowire membrane to elevated temperatures (390 °C), resulting in switchable wetting behaviour between its superhydrophilic and superhydrophobic states (Fig. 3a). Only subtle changes in water contact angles and hysteresis were observed in each switching cycle (eight times for the study shown in Fig. 3b), indicating a high degree of switchability in the wetting behaviour. The free-standing silicone-coated nanowire membrane exhibits a considerable degree of mechanical robustness, as is shown by its resistance to repeated ultrasonic treatment. Control experiments on manganese oxide nanoparticle films exposed to the same silicone coating treatment produced a surface with a contact angle of 141°, confirming that the coating itself is not the sole cause of the superhydrophobic behaviour (see Supplementary Information, Fig. S2). Furthermore, by ion exchange of  $K^+$  with  $NH_4^+$  and heating the membrane at 600 °C in a furnace for 2 h, we induced a transformation into bixbyite-type manganese oxide with a further nanostructuring of the surface features while keeping the self-standing structure intact (see Supplementary Information, Fig. S3). A conformal silicone coating of this structure could also be obtained, as proven by high-resolution TEM imaging and by a water contact angle of 177°.

As expected, the membrane combined its superwetting behaviour (that is, superhydrophobicity) with good capillary action, an overall property that we call selective superabsorbance. When brought into contact with a layer of oil on a water surface, the membrane, with a calculated density of  $0.286 \text{ g cm}^{-3}$  (in contrast to  $4.36 \text{ g cm}^{-3}$  in bulk cryptomelane mineral), quickly absorbed the oil while repelling the water (see Supplementary Information, Movie M1). As shown in Fig. 4, the membrane ( $1.5 \times 3 \text{ cm}$ ) showed uptake capacities up to 20 times its weight for a collection of organic solvents and oil. Specifically, the membrane absorbs on average  $14 \text{ t m}^{-3}$  of motor oil, making this membrane an ideal candidate as an oil absorbent. As control experiments, using  $^1\text{H}$  NMR, we compared the solvent selectivity of the membrane (see Supplementary Information, Fig. S11) with that of porous polypropylene and silicone-coated glass fabric membranes with water contact angles of 142 and 128°, respectively (see Supplementary Information, Fig. S4). The polypropylene and glass fabric membranes were found to absorb

both water and toluene, whereas only toluene was absorbed by the superhydrophobic nanowire membrane, confirming the important role of the superwetting surfaces for selective absorption. More importantly, the membrane can selectively absorb emulsified oil suspensions in water with a remarkable uptake capacity of  $\sim 9 \text{ t m}^{-3}$  (see Supplementary Information, Fig. S5). As confirmed by dynamic light scattering studies, the nanowire membrane readily takes up toluene droplets of different sizes, but the glass fabric counterpart does not show any notable selectivity of the toluene droplets over water (see Supplementary Information, Fig. S6). Another major advantage of the nanowire membrane is its thermal stability for temperatures up to 380 °C. The membrane can be regenerated after each use by ultrasonic washing and autoclaving ( $\sim 130 \text{ °C}$  for 20 min), making recycling schemes for both the membrane and the absorbed liquid possible.

An intriguing property of the superwetting membrane is the possibility of separating one solvent from a mixture of solvents of very similar polarity. By eluting the solvents against the membrane by means of a technique similar to thin layer chromatography, the subtle adhesion difference between the solvent and the membrane in these two systems can be amplified through capillary force and enormous surface areas in the membrane. As a result, the elution method leads to an increased variation in the ratio of the solvents absorbed as the solvent mixture rises from the bottom to the top of the material. As a proof-of-concept experiment, a superhydrophobic membrane was placed into a 1:1 (v:v) mixture of toluene and benzene (Fig. 5a). Despite very similar dielectric constant values for toluene (2.4) and benzene (2.3), we were able to retrieve a solvent ratio of 12:1 (v:v) at 3 cm above the solvent level 3 min after the immersion of the membrane (Fig. 5b). A more immediate application for these membrane materials will be in the removal of hydrophobic contaminants from water (for example, sea water or industrial discharge). Given the global scale of severe water pollution arising from oil spills and industrial organic pollutants, this study may prove particularly useful in the design of recyclable absorbents with significant environmental impact.

## METHODS

### MATERIALS

Potassium sulphate, potassium persulphate and manganese sulphate monohydrate were used as received. A sample of motor oil was purchased from

Citgo. For all experiments, deionized water (Milli-Q) was used. Muscovite mica (V-1 grade) substrates were purchased from Structure Probe. Silicon oxide wafers were cut into  $0.5 \times 0.5 \text{ cm}^2$  slides and sonicated sequentially in dichloromethane, methanol and deionized water for 10 min. The wafers were then immersed in a freshly mixed ammonia peroxide solution ( $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{NH}_3\cdot\text{H}_2\text{O}(\text{v}:\text{v}:\text{v}) = 5:1:1$ ) for 1 h at  $\sim 90^\circ\text{C}$ , after which they were rinsed with deionized water followed by ethanol.

#### SYNTHESIS

The precursor to cryptomelane nanowire membranes was synthesized using a hydrothermal method. The starting materials were composed of 19.1 mmol of potassium sulphate ( $\text{K}_2\text{SO}_4$ ), potassium persulphate ( $\text{K}_2\text{S}_2\text{O}_8$ ) and manganese sulphate monohydrate ( $\text{MnSO}_4\cdot\text{H}_2\text{O}$ ) in a ratio of 1:2:1 in 80 ml of deionized (DI) water. The mixture was transferred to a Teflon vessel held in a stainless steel vessel. The sealed vessel was placed in an oven and heated at  $250^\circ\text{C}$  for 4 days. The resulting solid was then resuspended in 800 ml of deionized water and stirred vigorously overnight to yield a homogeneous suspension. The suspension was filtered and washed a couple of times until all soluble impurities were removed from the solid. The nanowire membrane was produced by dispersing the precursor, casting the suspension on a Teflon substrate placed in an oven, and subsequently heating at  $85^\circ\text{C}$  for 24 h.

The bixbyite nanowires were synthesized according to the following procedure. The cryptomelane-type nanowires were first placed in a solution of  $\text{NH}_4\text{Cl}$ , resulting in ion exchange of  $\text{K}^+$  within the crystalline tunnel of the nanowires with  $\text{NH}_4^+$  cations. Heating of the  $\text{NH}_4^+$ -doped nanowires at  $600^\circ\text{C}$  leads to the oxidation  $\text{NH}_4^+$  and subsequent conversion to  $\text{N}_2$  gas. The oxidation process was confirmed by a temperature-programmed desorption method.

#### SILICONE COATING PROCEDURE

The silicone coatings of the substrates were achieved using a vapour deposition technique. In a typical experiment, a PDMS stamp and the nanowire membrane were placed in a sealed glass container heated at  $234^\circ\text{C}$  for 30 min. The thermal degradation of PDMS through heterolytic cleavage of the Si–O bonds leads to a mixture of volatile, low-molecular-weight products that form a conformal layer on the surface of the substrates. The coated nanowire membrane exhibited a water contact angle of more than  $170^\circ$  throughout both sides of the membrane, which is indicative of full surface coverage.

#### CHARACTERIZATION

The crystallographic phase of the bixbyite nanowires was determined by powder XRD (Rigaku RU300,  $\text{CuK}\alpha$  radiation). TEM images were recorded on a field-emission JEM-3000F high-resolution transmission electron microscope operated at 300 kV and equipped with an energy-dispersive X-ray spectrometer. Surface morphology of the nanowire membrane was observed using a JEOL-5910 scanning electron microscope. Sessile drop contact angle measurements were performed by adding water to the sample surface with a motor-driven syringe. Unless otherwise noted, all contact angle measurements were carried out under ambient laboratory conditions at temperature of  $\sim 20^\circ\text{C}$ . The advancing ( $\theta_A$ ) and receding ( $\theta_R$ ) angles were obtained by extending and contracting the volume of the drop, respectively. The surface area for the cryptomelane nanowire membrane was measured by a three-point BET method (nitrogen gas as adsorbate). Nitrogen desorption and adsorption studies using Quantachrome Corp Autosorb-1 equipment were used to determine the pore size distribution.

The separation of toluene from benzene was performed by using a  $6 \times 40 \text{ mm}$  hydrophobic membrane soaked into a 1:1 (v:v) mixture of toluene and benzene (molar ratio of toluene/benzene: 0.84) for 3 min. The nanowire membrane was then removed from the solvent mixture and subsequently cut into six pieces, as shown in Fig. 5. The first five pieces were immediately placed into five individual vials containing deuterated chloroform. Molar ratios of the solvents absorbed on these five pieces were determined by  $^1\text{H}$  NMR analysis (Bruker DPX 400). The integrated areas of  $^1\text{H}$  NMR resonance signals at

2.36 p.p.m. for toluene ( $\text{C}_6\text{H}_5\text{CH}_3$ ) and 7.36 p.p.m. for benzene ( $\text{C}_6\text{H}_6$ ) were used to calculate the molar ratio.

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#### Author contributions

J.Y. and X.L. conceived and designed the experiments. J.Y., X.L. and O.A. performed the experiments. J.H. performed the TEM characterization. J.Y. analysed the data together with S.L.S., J.K. and E.S. X.L. and E.S. co-wrote the paper. All authors discussed the results and commented on the manuscript.

#### Author information

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