
Supplementary information

Mechanistic formulation of inorganic membranes at the air–liquid interface

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Supplementary Information for

Mechanistic formulation of inorganic membranes at the air-liquid interface

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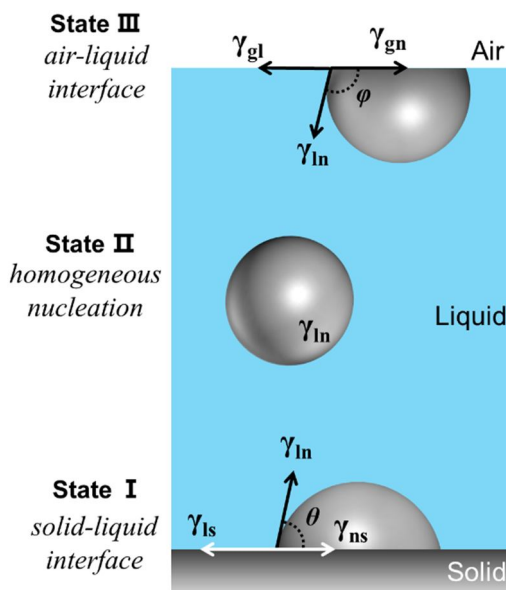
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Section S1. Development and Mechanism of SLIS Strategy.

S1.1 Discussion on the priority of spatial nucleation in aqueous solution



Supplementary Fig. 1. Schematic diagram of the three possible nucleation locations in an aqueous system held by an open vessel. These cases include the homogeneous nucleation in aqueous medium (State I), heterogeneous nucleation on the vessel wall (Solid-liquid interface) and the surface of the solution (air-liquid interface), respectively.

The initial birthplace of the nascent nucleus, driven by the chemical potential difference, directly determines the subsequent spatial location of the product particles. As illustrated in Supplementary Fig. 1, depending on the various spatial regions in an aqueous synthesis system held by a reaction vessel, the nucleation can possibly occur at the solid-liquid interface (heterogeneous nucleation, State I), in the aqueous medium (homogeneous nucleation, State II) and at the air-liquid interface (heterogeneous nucleation, State III). According to the classical nucleation theory, the total free energy change (ΔG) during the nucleation process expresses the sum of the changes in bulk free energy (ΔG_b) and interfacial free energy (ΔG_i)¹.

$$\Delta G = \Delta G_b + \Delta G_i \quad (1.1)$$

$$\Delta G_v = V\Delta g_b \quad (1.2)$$

where V is the critical volume of the nucleus, and Δg_b represents the difference in free energy per unit volume. Based on a rational hypothesis that the critical volumes of the nucleus in the aforementioned three cases are the same, which corresponds to an equal change in the bulk free

energy, the priority of spatial nucleation may be theoretically predicted by simply comparing the interfacial free energy changes in these three states. Namely, the original birth of the solid nucleus will preferentially occur at the location of lowest energy barrier.

In State I, the interfacial free energy change can be expressed as follows:

$$\Delta G_{i(\text{state I})} = S_{\text{ln}}\gamma_{\text{ln}} + S_{\text{ns}}(\gamma_{\text{ns}} - \gamma_{\text{ls}}) \quad (1.3)$$

where γ_{ln} is the interfacial tension between the nucleus and the aqueous solution, γ_{ns} is the interfacial tension between the nucleus and the solid inner wall of the vessel, and γ_{ls} is the interfacial tension between the aqueous solution and the solid inner wall of the vessel. S_{ln} is the superficial area of the interface between the nucleus and the aqueous solution, which can be calculated by:

$$S_{\text{ln}} = 2\pi R_1^2(1 - \cos\theta) \quad (1.4)$$

where R_1 is the radius of the spherical crown-corresponding sphere, θ is the contact angle of the nucleus on the solid inner wall of the vessel, whose range is between in 0 and π . S_{ns} is the superficial area of the interface between the nucleus and the solid inner wall of the vessel determined by:

$$S_{\text{ns}} = \pi R_1^2 \sin^2 \theta \quad (1.5)$$

According to the mechanical analysis on γ_{ln} , γ_{ns} and γ_{ls} , they should satisfy the following equation of static equilibrium:

$$\gamma_{\text{ln}} \cos\theta + \gamma_{\text{ns}} = \gamma_{\text{ls}} \quad (1.6)$$

In combination with the Equations (1.3) to (1.6), the interfacial free energy change can be determined as follows:

$$\Delta G_{i(\text{state I})} = \pi R_1^2 \gamma_{\text{ln}} (\cos\theta + 2)(1 - \cos\theta)^2 \quad \theta \in (0, \pi) \quad (1.7)$$

In state II, the shape of the nucleus in homogeneous nucleation is a sphere, thus the interfacial free energy change can be simply expressed as:

$$\Delta G_{i(\text{state II})} = 4\pi r^2 \gamma_{\text{ln}} \quad (1.8)$$

where r is the radius of the spherical nucleus in the aqueous solution.

In state III, the case is symmetrically similar to what occurs in state I, thus the interfacial

free energy change can be accordingly written as follows:

$$\Delta G_{i(\text{state III})} = \pi R_2^2 \gamma_{\text{ln}} (\cos \varphi + 2)(1 - \cos \varphi)^2 \quad \varphi \in (0, \pi) \quad (1.9)$$

where R_2 is the radius of the inverted spherical crown-corresponding sphere; φ is the contact angle of the nucleus on the interface between the aqueous solution and air.

Because the volume of the spherical nucleus in aqueous solution equals to that of the spherical crown-shaped nucleus on the interface between two phases, thus there is such an equation:

$$V = \frac{4}{3} \pi r^3 = \frac{1}{3} \pi R_1^3 (\cos \theta + 2)(1 - \cos \theta)^2 = \frac{1}{3} \pi R_2^3 (\cos \varphi + 2)(1 - \cos \varphi)^2 \quad (1.10)$$

Accordingly, the interfacial free energy change in the case of heterogeneous nucleation can be simply written as:

$$\Delta G_{i(\text{state I})} = 4\pi \gamma_{\text{ln}} \frac{r^3}{R_1} \quad (1.11)$$

$$\Delta G_{i(\text{state III})} = 4\pi \gamma_{\text{ln}} \frac{r^3}{R_2} \quad (1.12)$$

Consequently, the following inequalities are always true:

$$\frac{\Delta G_{i(\text{state I})}}{\Delta G_{i(\text{state II})}} = \frac{r}{R_1} < 1 \quad (1.13)$$

$$\frac{\Delta G_{i(\text{state III})}}{\Delta G_{i(\text{state II})}} = \frac{r}{R_2} < 1 \quad (1.14)$$

Due to the lower interfacial free energy change for the nucleation process, heterogeneous nucleation whether state I or state III always occurs in preference to the case of homogeneous nucleation in state II, which agrees with the experimental outcomes.

As a result, the spatial location of the nucleation will be determined by the comparison between $\Delta G_{i(\text{state I})}$ and $\Delta G_{i(\text{state III})}$. By combining Equations (1.7), (1.9) and (1.10), the $\Delta G_{i(\text{state I})}$ and $\Delta G_{i(\text{state III})}$ can be respectively simplified as:

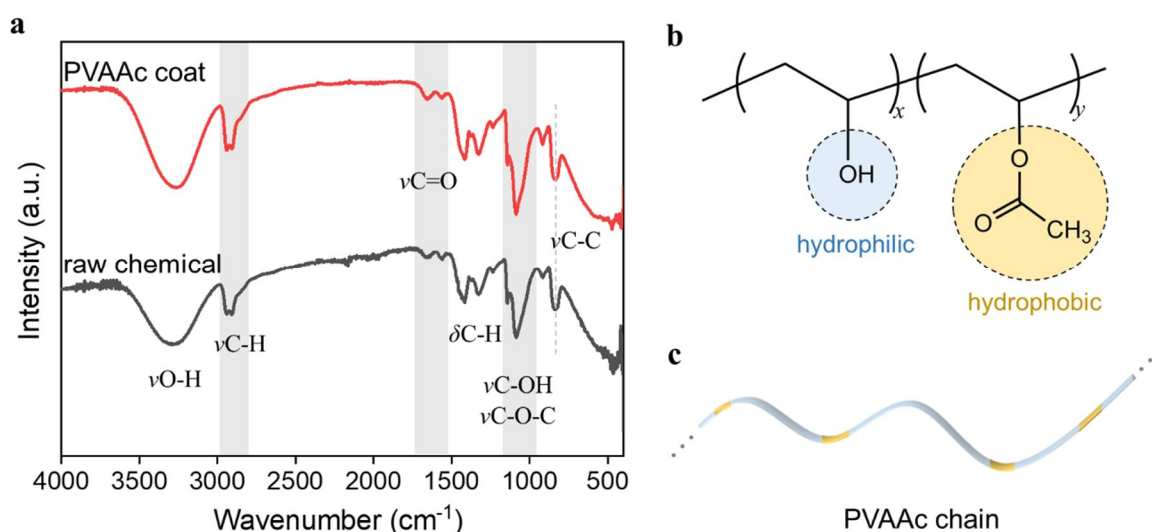
$$\Delta G_{i(\text{state I})} = (9\pi V^2)^{\frac{1}{3}} \gamma_{\text{ln}} (\cos \theta + 2)^{\frac{1}{3}} (1 - \cos \theta)^{\frac{2}{3}} \quad \theta \in (0, \pi) \quad (1.15)$$

$$\Delta G_{i(\text{state III})} = (9\pi V^2)^{\frac{1}{3}} \gamma_{\text{ln}} (\cos \varphi + 2)^{\frac{1}{3}} (1 - \cos \varphi)^{\frac{2}{3}} \quad \varphi \in (0, \pi) \quad (1.16)$$

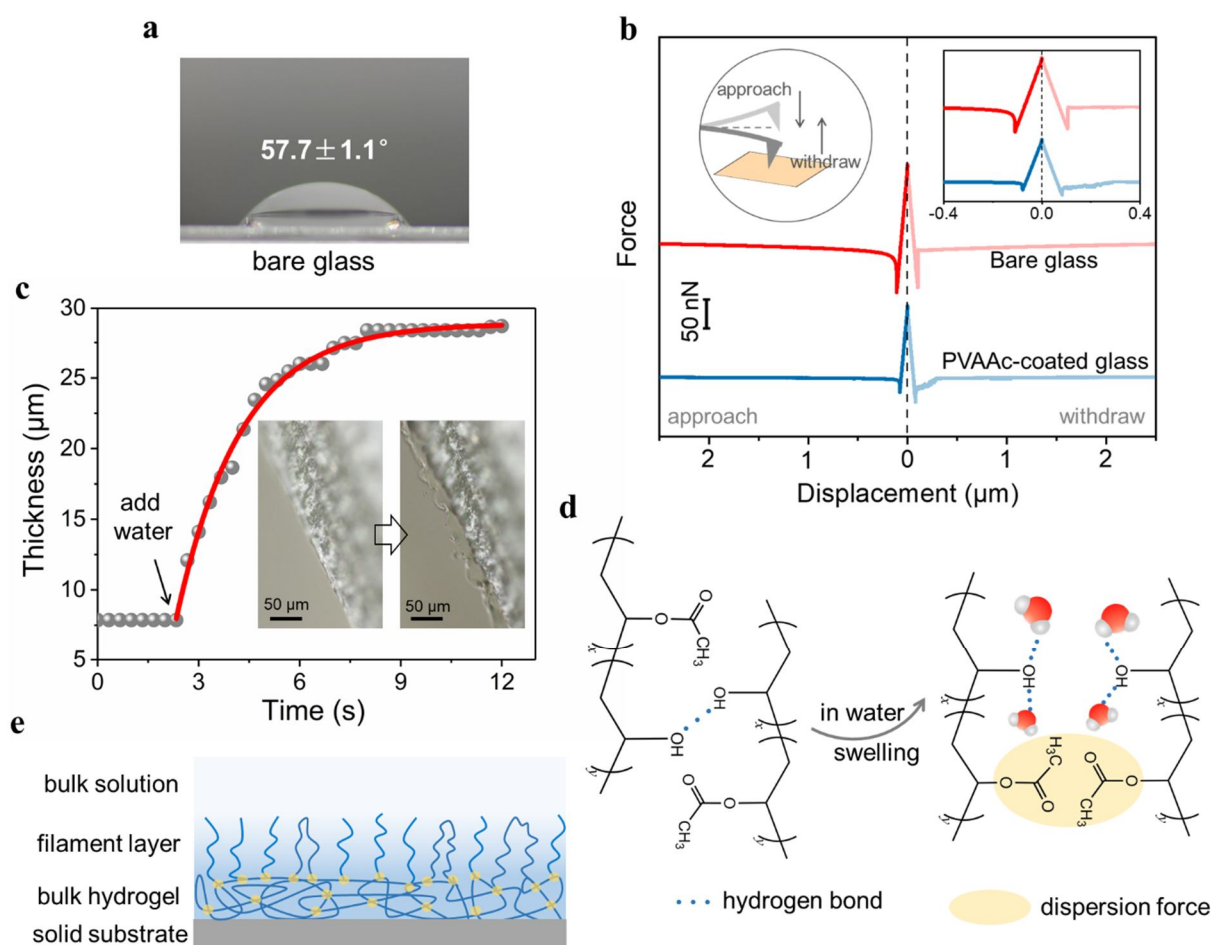
Generally, determined by the difference of the intermolecular interaction among different

phases, the interfacial tension between the gaseous and solid phase (γ_{gn}) should be much larger than that between the solid and solid phase (γ_{ns}), and the interfacial tension between the gaseous and liquid phase (γ_{gl}) is comparable to that between the liquid and solid phase (γ_{ls}). On this account, the contact angle φ should be larger than θ during general nucleation process, thus leading to the nucleation priority at the solid-liquid interface in common aqueous systems held by vessel. By further performing a numerical normalization to γ_{ln} , the Equations (1.8), (1.15) and (1.16) can then be visualized (Fig. 1a in the main text) to identify the specific interfacial free energy changes for various nucleation locations.

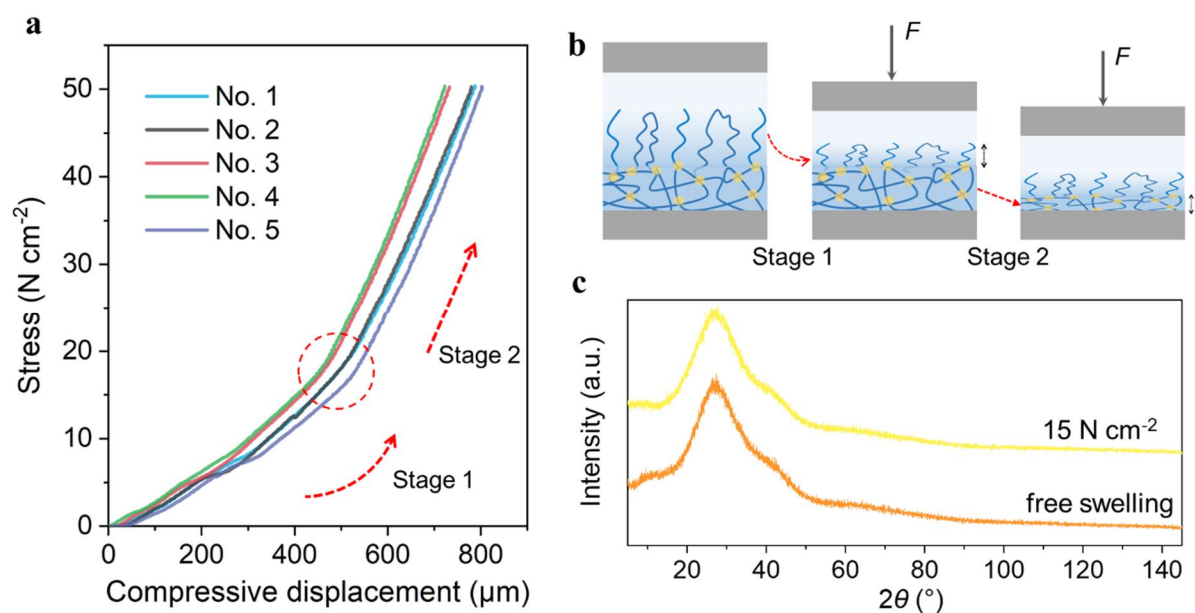
S1.2 Structure of the PVAAc hydrogel coat in aqueous solution



Supplementary Fig. 2. Molecular structure of the employed PVAAc coating. **a**, FTIR spectra of the raw chemical of PVAAc granules and the derived coat on the glass culture dish, revealing the well-remained partially acetylated/hydrolyzed structure in the as-prepared PVAAc coat. **b**, **c**, Molecular structure (**b**) and the schematic diagram (**c**) of a single PVAAc chain. The acetyl groups are hydrophobic and the hydroxyl groups are hydrophilic. They randomly distribute as the pendent groups in the polyethylene chain, forming the alternating hydrophilic and hydrophobic regions in the PVAAc chain. Respectively, the hydrophobic regions enable the insolubility of PVAAc and the hydrophilic regions endow its swelling ability in aqueous solution.



Supplementary Fig. 3. Structural transformation of the dry PVAAc coating after swelling into the wet hydrogel on the glass substrate. **a**, Contact angle image for a sessile water droplet on the bare glass substrate, showing its hydrophilic nature. **b**, AFM force-distance curves for the bare and dry PVAAc-coated glass surface measured in air. **c**, Time-course change in the thickness of the PVAAc coat ($\sim 4 \times 10^{-3}$ mg dry PVAAc per square millimeter) on the glass during the swelling process when it contacts with water. Note that the measured thickness of the wet hydrogel in water only contains the part with visible contrast instead of the whole hydrogel structure. The experiment was performed independently for three times, and the mean value was used for the scatter plot with the red best-fitting line. The insets are the cross-sectional microscopic photos in-situ recording the water-solid interface before and after the swelling process of the PVAAc film coat. **d**, Evolution of the molecular structure and interaction of the PVAAc coat during swelling in aqueous solution. **e**, Schematic diagram of the double-layer structure of the PVAAc hydrogel coat in water, including a compact bulk hydrogel layer adhering to the solid substrate and a filament layer extending towards the bulk solution.



Supplementary Fig. 4. Double-layer structure of the PVAAc hydrogel coating immersed in water. **a**, Compressive stress-strain curve of the PVAAc hydrogel ($\sim 1.6 \times 10^{-2}$ mg dry PVAAc per square millimeter) coated on a glass substrate (10×10 mm) measured under water. The measurement was performed independently for five times on independent samples. The dashed circle highlights the transition between a well-distinguished nonlinear (Stage 1) and linear region (Stage 2) for the elastic behavior. **b**, Schematic diagram showing the two-stage compression of the PVAAc hydrogel coat under water. The initial stage is mainly caused by the compression of the filament transition layer, whereas the compression of the bulk hydrogel becomes dominant in the later stage. **c**, XRD spectra of the wet PVAAc hydrogel coat at freely-swelling and compressive state with a load of 15 N cm^{-2} , showing its negligible change in the long-range order of the microstructure during the compression.

S1.3 Additional discussion on the proposed SLIS strategy

For the glass substrate of hydrophilic nature (Supplementary Fig. 3a), the coat of dry PVAAc film cannot directly generate the repulsion to remove the interfacial potential well (Supplementary Fig. 3b), which convincingly confirms the necessity of the derived wet hydrogel counterpart for achieving the desired SLIS strategy. Thanks to the alternating hydrophilic and hydrophobic regions in the PVAAc chain (Supplementary Fig. 2), the water molecules can quickly penetrate into the hydrophilic regions of the dry PVAAc coat, break the original intermolecular hydrogen bonds and form the new ones with the oxhydroxyl groups. Simultaneously, the insolubility is ensured by the dispersion forces between the hydrophobic acetyl parts. The rapid swelling behavior of PVAAc coat in water constitutes primarily of these two effects, featuring a large expansion in thickness by several times within several seconds once it contacts with water (Supplementary Fig. 3c and d). The subsequent bulk hydrogel layer enables the robust adhesion to the solid substrate. At the interface between the bulk hydrogel layer and the bulk aqueous solution, some terminal and/or middle hydrophilic chains freely stretch towards the bulk solution, forming an elastic filament transition layer (Supplementary Fig. 3e). This theoretically predicted double-layer structure of PVAAc hydrogel coat in water is convincingly confirmed by its compressive stress-strain curve, featuring a well-defined two-stage process comprising the initial nonlinear and later linear elasticity (Supplementary Fig. 4a and b), which correspond to the compression of the outer filament layer and the inner bulk hydrogel layer, respectively. In addition, this result further confirms that it is the water-permeated filament layer rather than the bulk hydrogel layer to serve as the elastic bed to repel the particles approaching from bulk solution. Therefore, the subsequent study focused on the structure change of the water-permeated filament layer to understand the origin of the interfacial repulsion. The X-ray scattering result reveals that the change in the long-range order of the microstructure is negligible after compression (Supplementary Fig. 4c), suggesting the change in short-range structure of the biphasic system may be the dominant cause to the SLIS strategy.

As shown in Extended Data Fig. 1, the well-defined potential well on the solid-water interface is ubiquitous for all the substrates that commonly used to fabricate the vessels for performing aqueous reactions, regardless of their compositions and hydrophilicity. This fact

implies that it is impossible to realize the desired SLIS by just changing the reaction vessels. The potential well originates from two comprehensive effects. Initial one is the positive work done by the interfacial attraction acting on the approaching particle, enabling the capture of the particle nearby in aqueous solution. The subsequent one is the permanent negative work provided by the interfacial force no matter which direction the trapped particle attempts to escape. Exhilaratingly, benefiting from the general applicability of the PVAAc hydrogel coat to different substrates with various chemical compositions, surface roughness and hydrophilicity, the SLIS strategy was accordingly revealed universal to various vessels, featuring a perpetual repulsion acting on the approaching particles that replaces the undesired interfacial potential well under water. Moreover, for all the investigated substrates, this endowed trampoline effect can only be observed on the water-infiltrated PVAAc hydrogel coat under water rather than on its dry film state in air, confirming the synergetic contribution of the PVAAc skeleton and the permeated water molecules in generating the entropic force when the particle approaches.

Section S2. Synthesis and Characterization of Various Membranes.

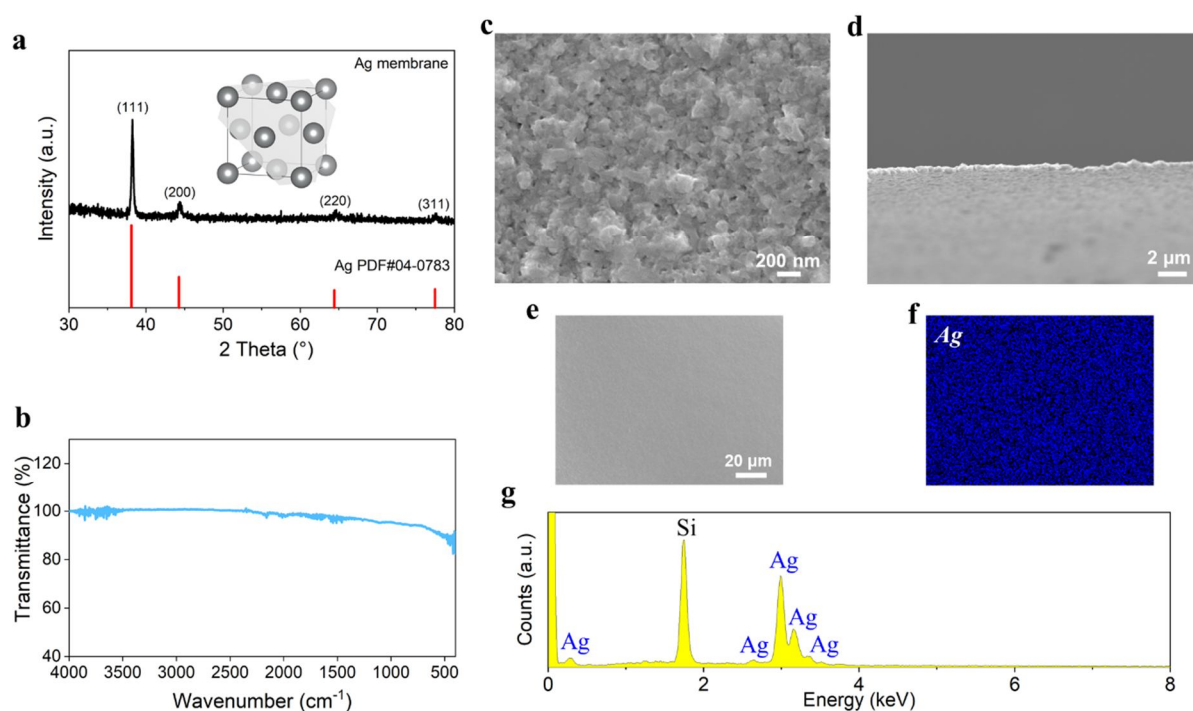
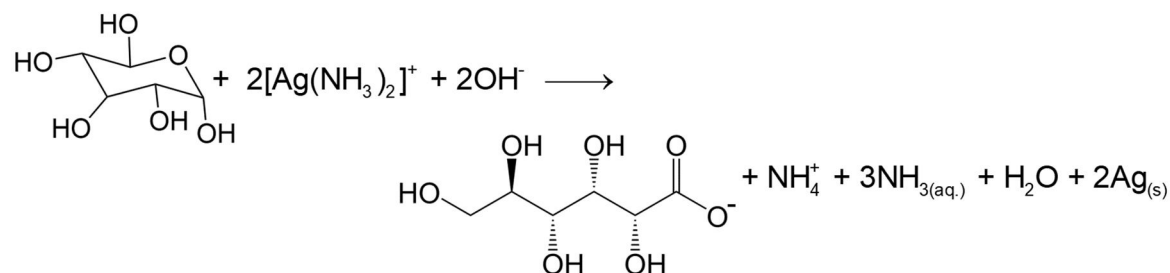
S2.1 Considerations for the construction of membrane library

The essential consideration for constructing the membrane library is to examine and illustrate the wide versatility of the developed SLIS strategy, which will be reflected in its feasibility for diverse inorganic materials and various types of aqueous reactions. Under normal conditions of mild temperature and atmospheric pressure, there are only three types of aqueous reactions for generating insoluble solid products, *i.e.*, precipitation reaction, redox reaction and hydrolysis reaction. To prevent unfavorable severe convection and mechanical disturbance, the employed synthesis process should have a homogeneous spatial temperature distribution and produce no gaseous products. In addition, the initial condition for the reaction should correspond to a mild chemical potential difference. The facile reaction driving force can essentially inhibit the instant precipitate (undesired homogeneous nucleation) caused by the excessive local reactant concentration in bulk solution during solution mixing process. From this perspective, the initially inert reaction but whose driving force can be drastically increased by changing the temperature should be the best candidate.

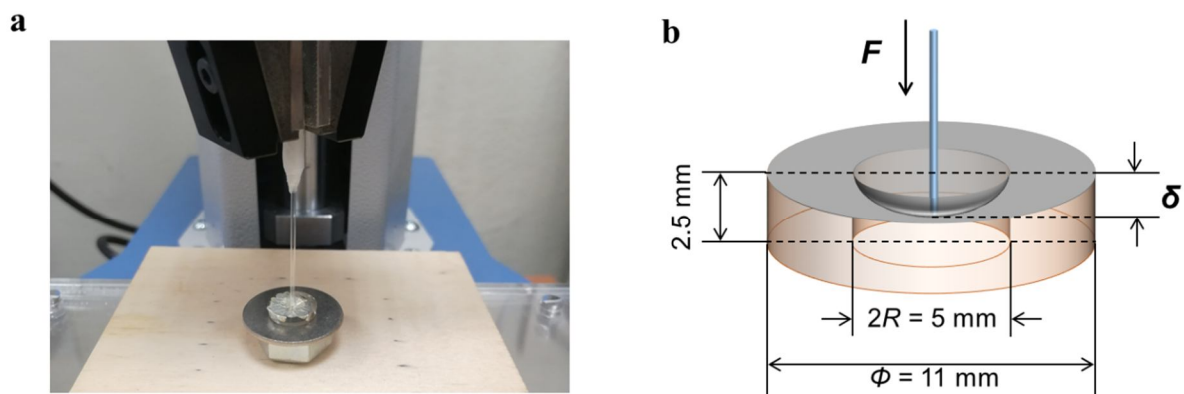
The selection principle of the representative membrane materials is to cover all the seventeen available element groups (except for the 18th group of the noble gases) and contain different available elements as many as possible in the periodic table (Extended Data Fig. 2a). These include the eight basic categories of chemical substances, including elementary substances, oxides, sulfides, halides, hydroxides, metallates, nonmetallates and coordination polymers. After determining the target membrane and the type of synthesis reaction, the raw reactants must have strong aqueous solubility and the least amount of unrelated ions/molecules, while also being easy to remove from the membrane product. Note that the membranes involved in the present library are obtained from the direct preparation from the employed reaction other than the indirect conversion of the precursor membrane. Out of the statistical comparability between different membrane syntheses by excluding other influences, the whole volume of the aqueous solutions for different membrane preparation were normalized to 3 mL. Without loss of generality of the proposed SLIS strategy, the reactions were performed in the consumable polystyrene dishes.

S2.2 Elementary substances

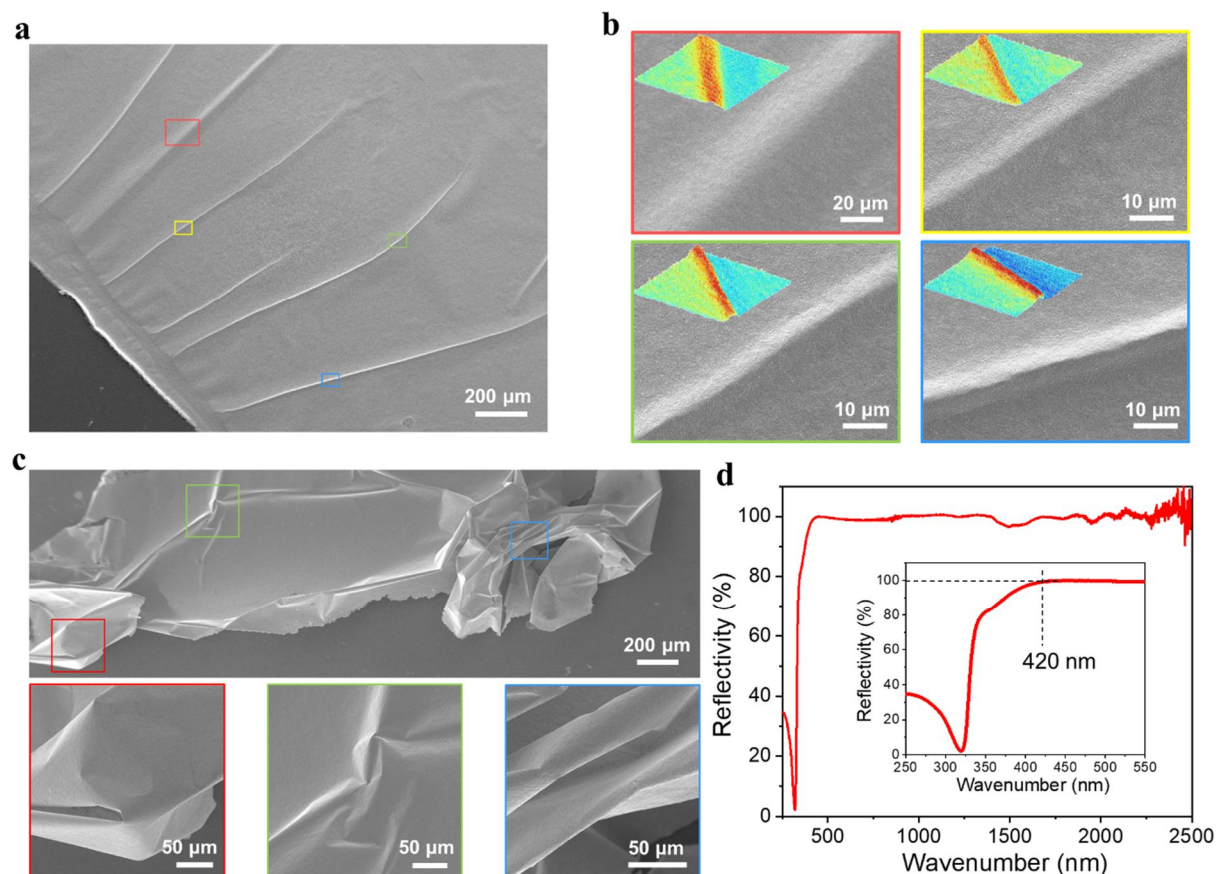
Ag membrane. The silver mirror reaction equation is presented as follows. The detailed procedure for the synthesis in the SLIS system is described in the Methods section of the main text.



Supplementary Fig. 5. Structure, morphology and composition of the as-synthesized Ag membrane. **a**, XRD spectrum of the single-layer Ag membrane supported on the PMMA substrate. The inset shows the crystal structure of the face-centered cubic Ag and highlights the preferred crystal orientation perpendicular to (111) plane. **b**, FTIR spectrum of the ground Ag membrane, confirming no other organic contaminants and residual reactants in the membrane. **c**, **d**, SEM images of the freestanding Ag membrane supplementary to Fig. 2d and 2e in the main text, showing its zoom-in surface topography (**c**) and overall cross section (**d**). **e**, **f**, **g**, SEM image of the silicon wafer-supported flat Ag membrane (**e**) and the corresponding elemental mapping image (**f**) and EDS spectrum (**g**), confirming the single element composition of the as-synthesized Ag membrane. Note that the Si in (**g**) is detected from the silicon wafer substrate, implying the Ag membrane's ultrathin thickness.

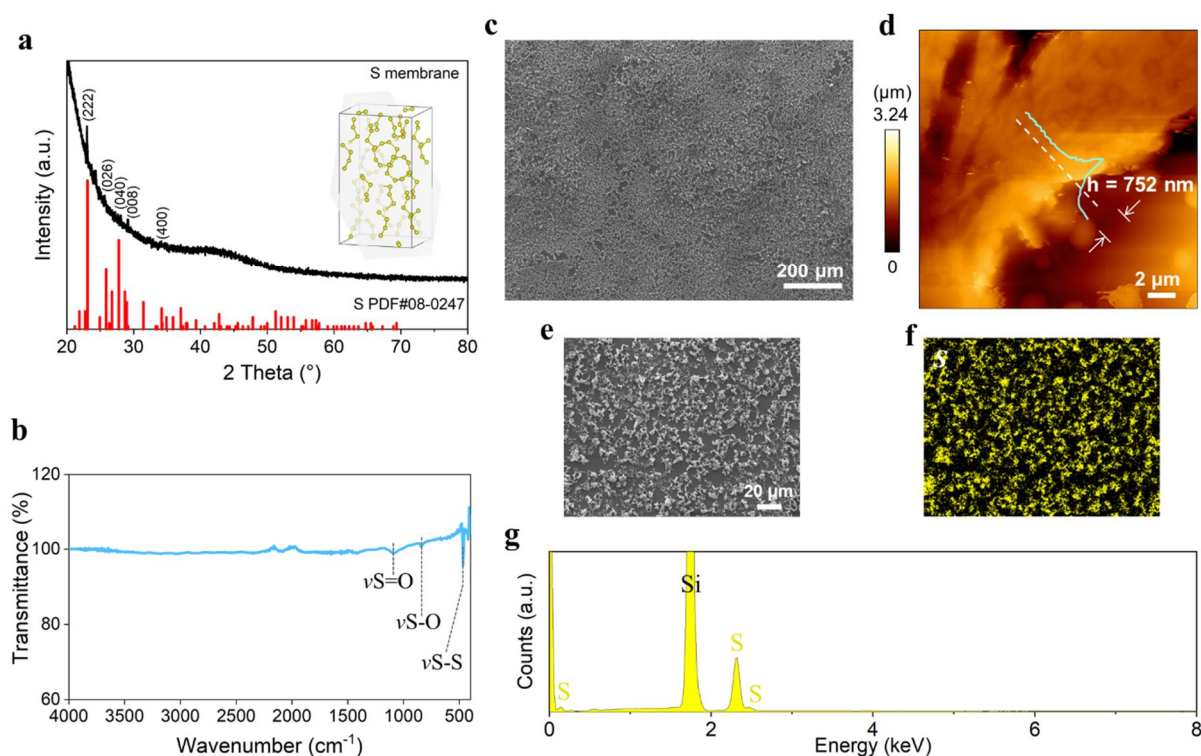
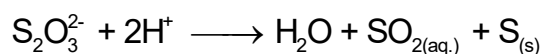


Supplementary Fig. 6. Experimental apparatus and sample preparation for the mechanical measurement of the as-prepared Ag membrane. **a**, Digital photo showing the setup and the ring-suspended Ag membrane used for the mechanical measurement. **b**, Schematic of the micro-indentation on the suspended Ag membrane with detailed dimension parameters.



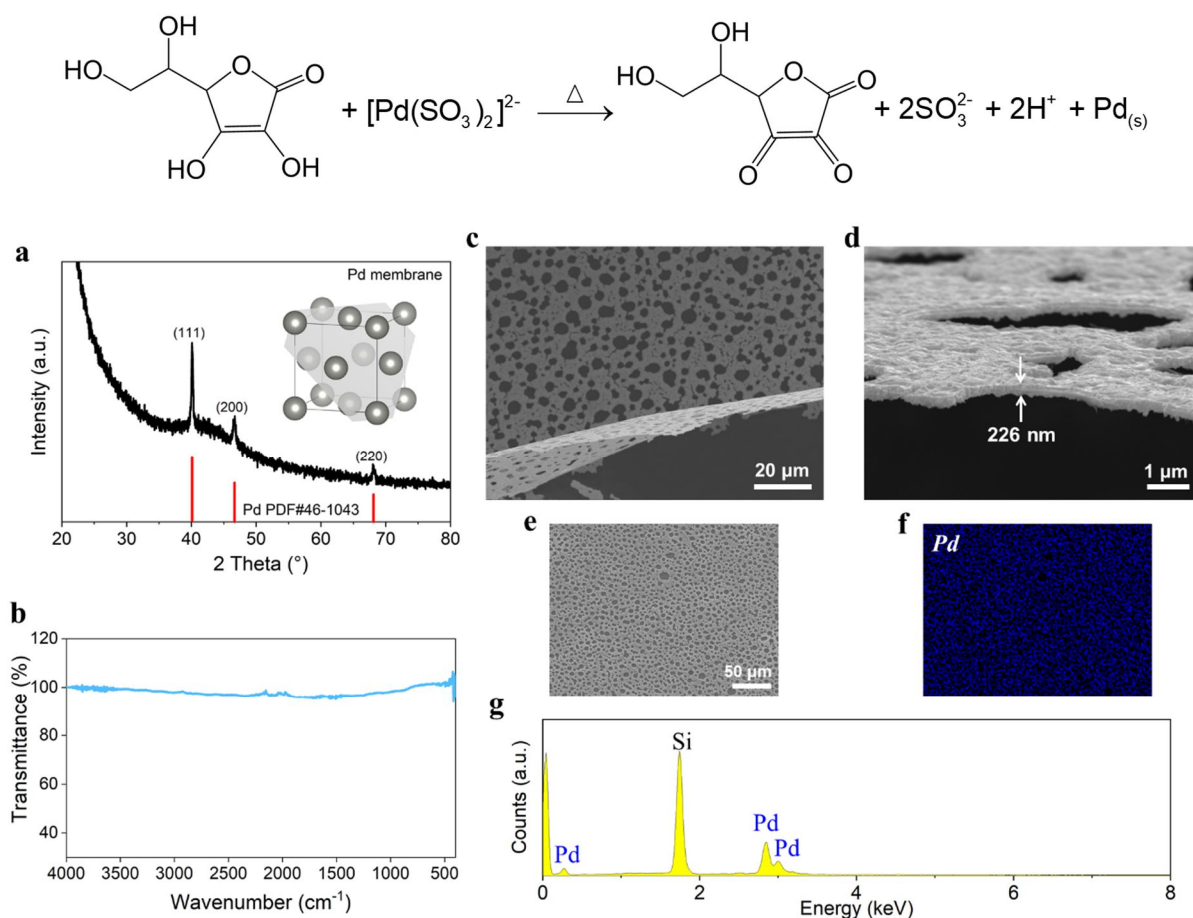
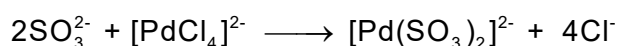
Supplementary Fig. 7. Mechanical flexibility and electromagnetic reflectivity of the as-prepared Ag membrane. **a**, Overall SEM image of the Ag membrane with ideal wrinkles (primary quasi-cylindrical wrinkles) supplementary for Fig. 2a in the main text. Note that the left-bottom edge of the membrane was stuck to the silicon substrate. **b**, Zoom-in SEM images of the regions of interest highlighted by the coloured rectangles in **(a)**. The insets are the corresponding microcrack analysis results of these quasi-cylindrical wrinkles based on the image contrast. Even a small bending radius of less than 5 μm , no microcracks were detected on these wrinkled regions of stress concentration. **c**, Overall SEM image (top row) of the Ag membrane rich of random wrinkles (non-cylindrical wrinkles with higher-order structure) and the zoom-in SEM images (bottom row) of the representative regions highlighted by the coloured rectangles. Beyond the simple quasi-cylindrical wrinkles **(a, b)**, the Ag membrane is of good mechanical flexibility to suffer from random and complicated wrinkles (red rectangle: multiple parasitic wrinkles, green rectangle: fractal wrinkles, blue rectangle: multilevel wrinkles). **d**, Reflectance spectrum of the as-synthesized Ag membrane, showing its outstanding optical reflectance with near-100 % reflectivity over a wide wavelength range. The inset zooms in the region between 250 and 550 nm, showing the characteristic absorption of the bulk silver in the ultraviolet region with a cut-off wavelength of 420 nm.

S membrane. 1 mL of H₂SO₄ aqueous solution (450 mM) was quickly added into a pretreated Petri dish containing 2 mL of Na₂S₂O₃ solution (1 M). The mixed solution was then allowed to stand still at room temperature for 4 h. During this process, the light yellow S membrane gradually formed on the solution surface according to the following redox reaction:



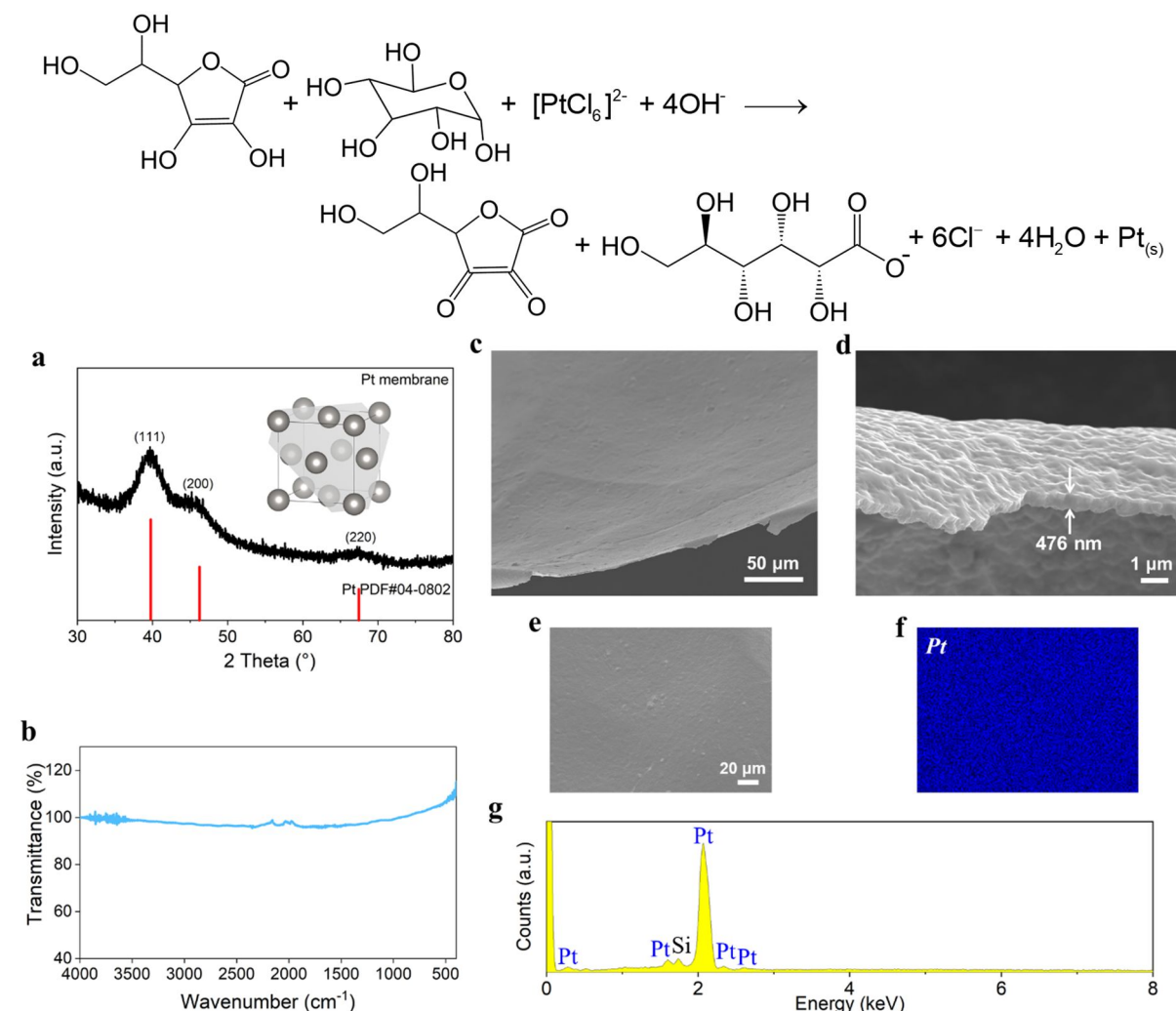
Supplementary Fig. 8. Structure, morphology and composition of the as-synthesized S membrane. **a**, XRD spectrum of the single-layer S membrane supported on the PMMA substrate. The inset shows the crystal structure of the orthorhombic S and highlights the preferred crystal orientation perpendicular to (111) plane. **b**, FTIR spectrum of the ground S membrane, confirming no other organic contaminants and residual reactants except for a little surface oxidation in the membrane. **c**, SEM images of the freestanding S membrane showing its network structure. **d**, AFM image of the S membrane supported on the silicon wafer showing its thickness. The blue line is the height profile measured along the white dashed line. **e**, **f**, **g**, SEM image of the silicon wafer-supported flat S membrane (**e**) and the corresponding elemental mapping image (**f**) and EDS spectrum (**g**), confirming the single element composition of the as-synthesized S membrane. Note that the Si in (**g**) is detected from the silicon wafer substrate. In addition, the SEM images for the sulfur is a little anamorphic due to its fast sublimation property under electron beam irradiation in the vacuum chamber. These SEM images were obtained at a low voltage of 2 keV as quickly as possible. And a necessary 15 keV was applied to obtain the EDS mapping image.

Pd membrane. 0.4 mmol of PdCl₂ was firstly dissolved in 20 mL of dilute hydrochloric acid solution (~ 25 mM) to prepare H₂PdCl₄ stock solution of 20 mM. Then, 200 μL of fresh Na₂SO₃ solution (1 M) and 400 μL of L-ascorbic acid solution (1 M) were successively added into 2.4 mL of H₂PdCl₄ stock solution. The mixed solution was transferred into a pretreated Petri dish and kept at 55 °C for 5 h with the cover. During this process, the reflective and argenteous Pd membrane gradually formed on the solution surface according to the following redox reactions:



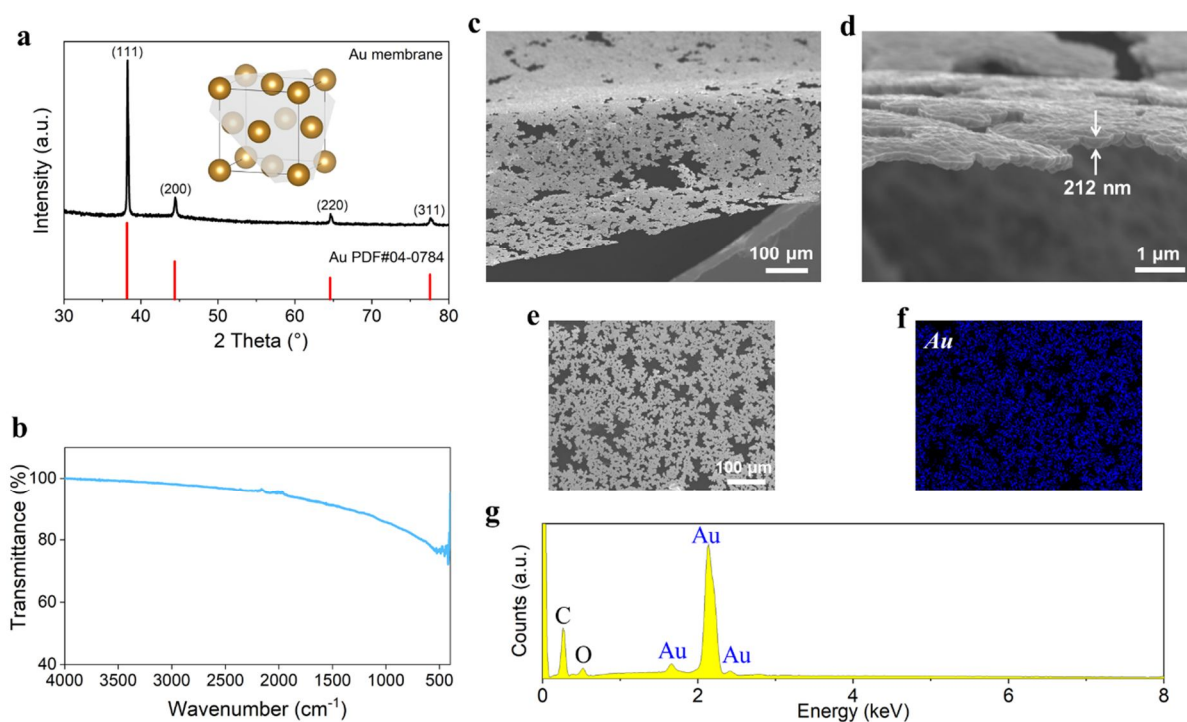
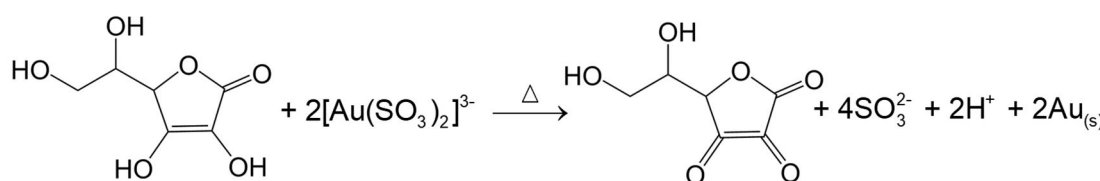
Supplementary Fig. 9. Structure, morphology and composition of the as-synthesized Pd membrane. **a**, XRD spectrum of the single-layer Pd membrane supported on the PMMA substrate. The inset shows the crystal structure of the face-centered cubic Pd and highlights the preferred crystal orientation perpendicular to (111) plane. **b**, FTIR spectrum of the ground Pd membrane, confirming no other organic contaminants and residual reactants in the membrane. **c**, **d**, SEM images of the freestanding Pd membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, SEM image of the silicon wafer-supported flat Pd membrane (**e**) and the corresponding elemental mapping image (**f**) and EDS spectrum (**g**), confirming the single element composition of the as-synthesized Pd membrane. Note that the Si in (**g**) is detected from the silicon wafer substrate.

Pt membrane. The mixture of 1 mL of H_2PtCl_6 solution (120 mM) and 1 mL of NaOH (4 M) was firstly kept at 55 °C for 30 min and transferred into a pretreated Petri dish. After a further addition of 1 mL fresh solution mixed of isometric L-ascorbic acid solution (1 M) and D(+)-glucose (0.5 M), the mixed solution was then kept at 55 °C for 1 h. During this process, the reflective and argenteous Pt membrane gradually formed on the solution surface according to the following redox reaction:



Supplementary Fig. 10. Structure, morphology and composition of the as-synthesized Pt membrane. **a**, XRD spectrum of the single-layer Pt membrane supported on the PMMA substrate. The inset shows the crystal structure of the face-centered cubic Pt and highlights the preferred crystal orientation perpendicular to (111) plane. **b**, FTIR spectrum of the ground Pt membrane, confirming no organic contaminants and residual reactants in the membrane. **c**, **d**, SEM images of the freestanding Pt membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, SEM image of the silicon wafer-supported flat Pt membrane (**e**) and the corresponding elemental mapping image (**f**) and EDS spectrum (**g**), confirming the single element composition of the as-synthesized Pt membrane. Note that the Si in (**g**) is detected from the silicon wafer substrate.

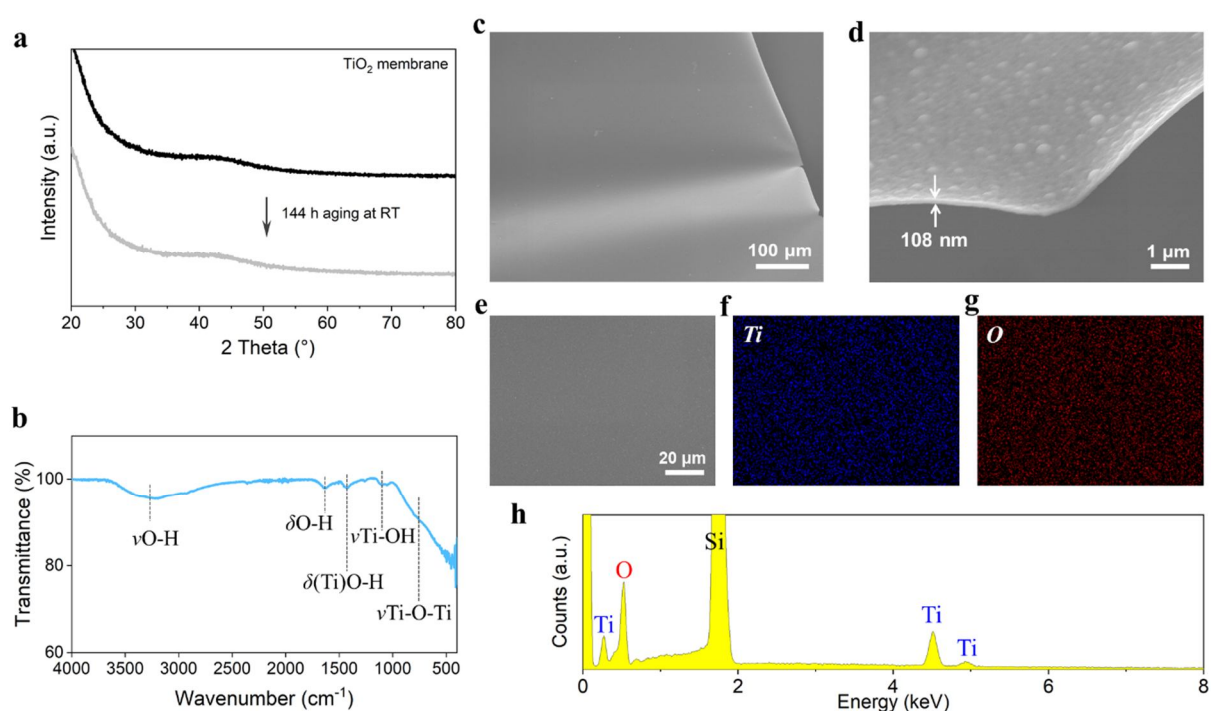
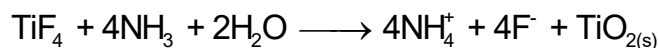
Au membrane. 0.9 mL of fresh Na₂SO₃ solution (850 mM) was firstly mixed with 1.1 mL of HAuCl₄ solution (160 mM). The mixture was quickly added into a pretreated Petri dish containing 1 mL of L-ascorbic acid solution (1 M), then further allowed to stand still at 50 °C for 6 h. During this process, the clinquant Au membrane gradually formed on the solution surface according to the following redox reactions:



Supplementary Fig. 11. Structure, morphology and composition of the as-synthesized Au membrane. **a**, XRD spectrum of the single-layer Au membrane supported on the PMMA substrate. The inset shows the crystal structure of the face-centered cubic Au and highlights the preferred crystal orientation perpendicular to (111) plane. **b**, FTIR spectrum of the ground Au membrane, confirming no organic contaminants and residual reactants in the membrane. **c**, **d**, SEM images of the freestanding Au membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, SEM image of the conductive carbon tape-supported flat Au membrane (**e**) and the corresponding elemental mapping image (**f**) and EDS spectrum (**g**), confirming the single element composition of the as-synthesized Au membrane. Note that the C and O in (**g**) are detected from the conductive carbon tape.

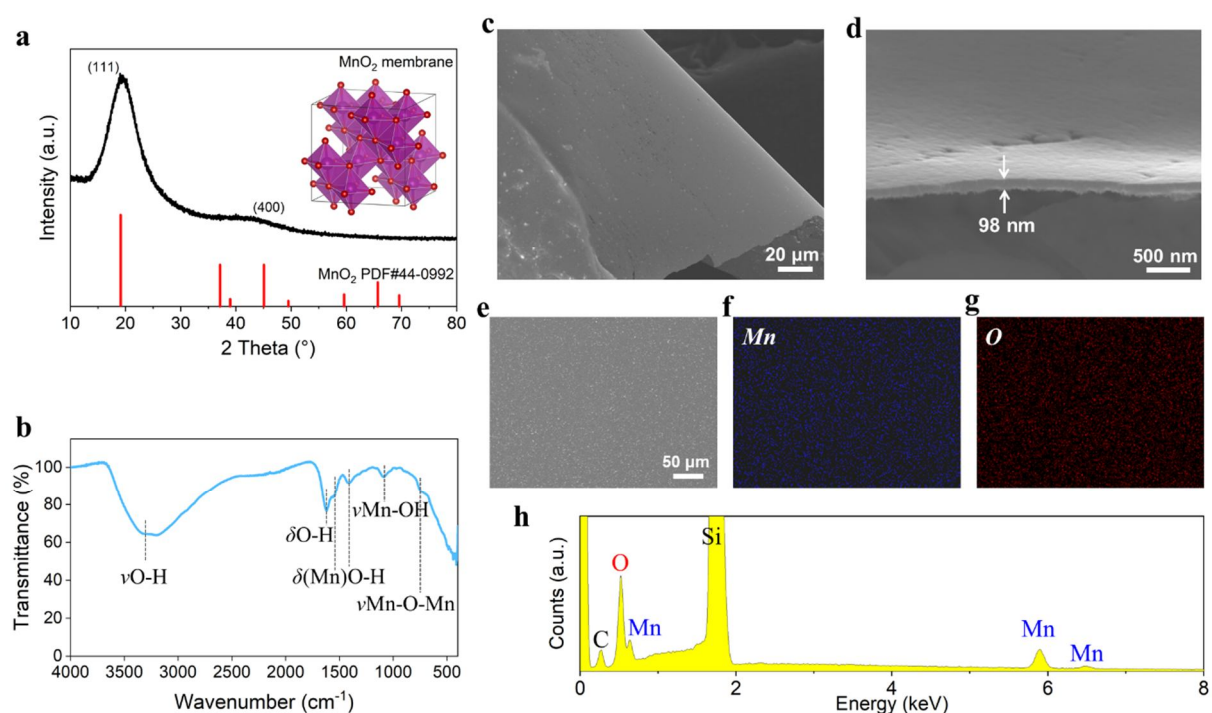
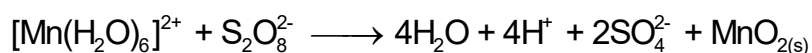
S2.3 Oxides

TiO₂ membrane. 2.88 mL of TiF₄ aqueous solution (15 mM) was firstly added into a pretreated Petri dish. After a quick addition of 120 μ L of dilute ammonium hydroxide solution ($\sim$ 10 wt%), the mixed solution was then allowed to stand still with cover at room temperature for 1 h. During this process, the colourless and transparent TiO₂ membrane gradually formed on the solution surface according to the following hydrolysis reaction:



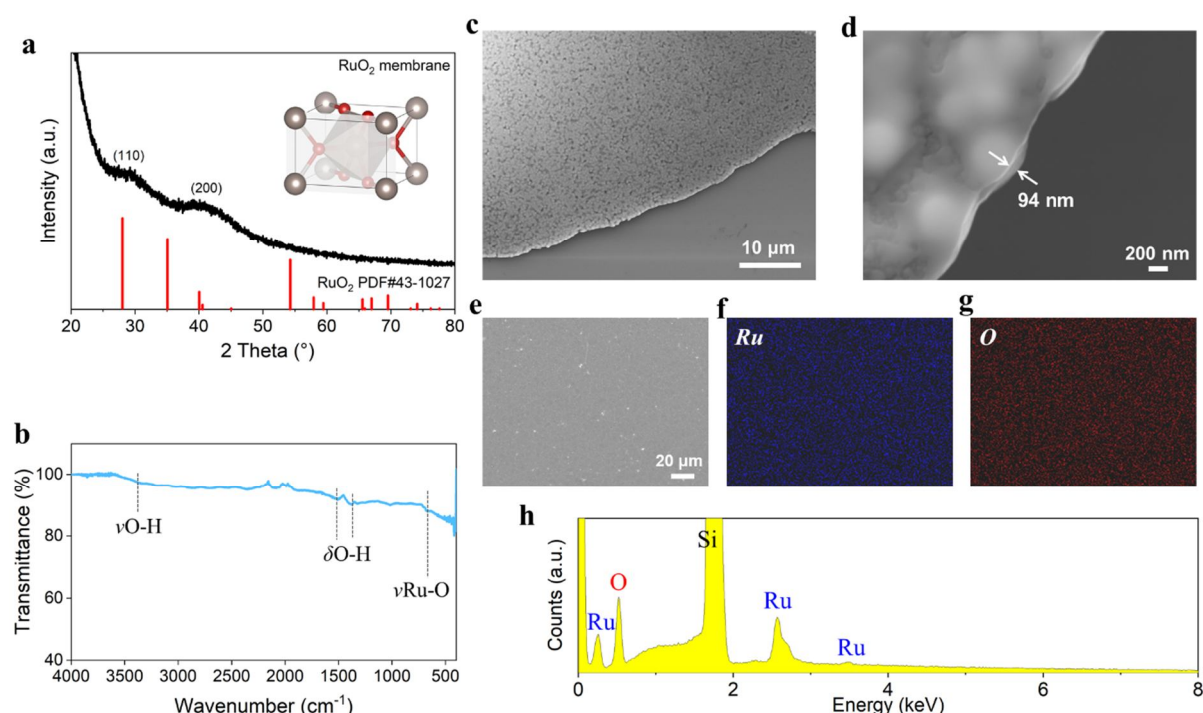
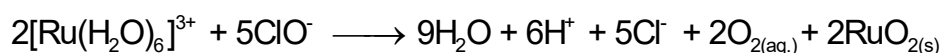
Supplementary Fig. 12. Structure, morphology and composition of the as-synthesized TiO₂ membrane. **a**, XRD spectra of the PMMA substrate-supported seven-layered TiO₂ membrane and the counterpart after 144-hour aging in dry air at room temperature, showing its amorphous nature. **b**, FTIR spectrum of the ground TiO₂ membrane, confirming no other organic contaminants and residual reactants except for a few adsorbed water in the membrane. **c**, **d**, SEM images of the freestanding TiO₂ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat TiO₂ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized TiO₂ membrane. Note that the Si in (**h**) is detected from the silicon wafer substrate.

MnO₂ membrane. 2.47 mL of Mn(CH₃COO)₂ solution (0.2 M) was firstly acidized by adding 30 μ L H₂SO₄ (4 M), which was then mixed with 0.5 mL of fresh (NH₄)₂S₂O₈ solution (1 M). The mixed solution was further transferred into a pretreated Petri dish and kept at room temperature for 1.5 h. During this process, the brown and transparent MnO₂ membrane gradually formed on the solution surface according to the following redox reaction:



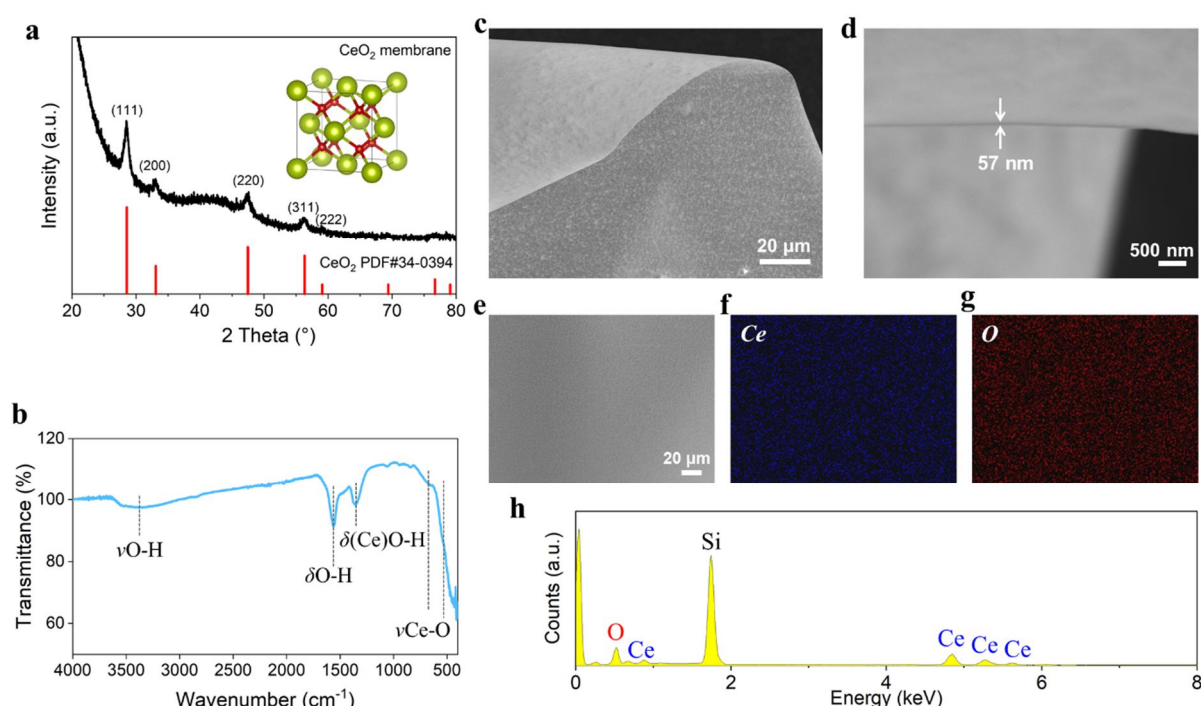
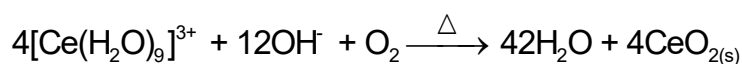
Supplementary Fig. 13. Structure, morphology and composition of the as-synthesized MnO₂ membrane. **a**, XRD spectrum of the five-layered MnO₂ membrane supported on the PMMA substrate. The inset shows the crystal structure of the cubic MnO₂. **b**, FTIR spectrum of the ground MnO₂ membrane, revealing no other organic contaminants and residual reactants except for a few adsorbed water in the membrane. **c**, **d**, SEM images of the freestanding MnO₂ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat MnO₂ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized MnO₂ membrane. Note that the Si in (**h**) is detected from the silicon wafer substrate.

RuO₂ membrane. 1 mL of fresh NaClO solution which was precooled at 5 °C for 30 min and then quickly added into a pretreated Petri dish containing 2 mL of RuCl₃ solution (10 mM). Subsequently, the mixed solution was allowed to stand still at room temperature with cover for 12 h. During this process, the black membrane with metallic lustre gradually formed on the solution surface according to the following redox reaction:



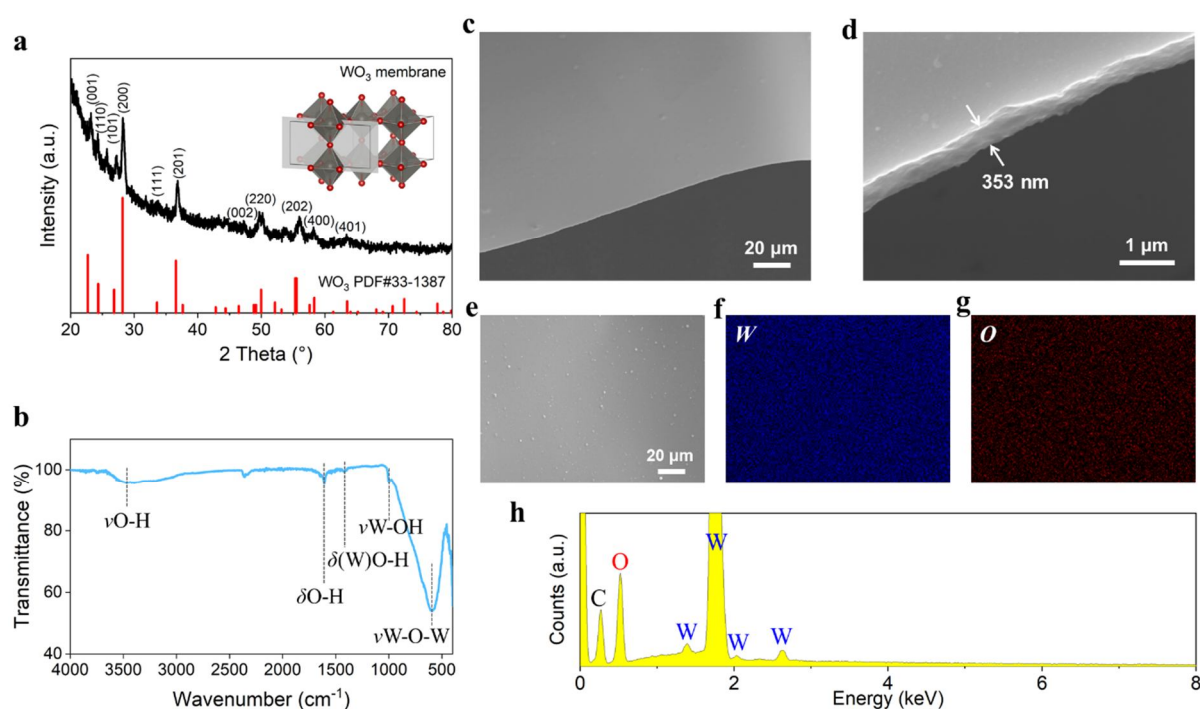
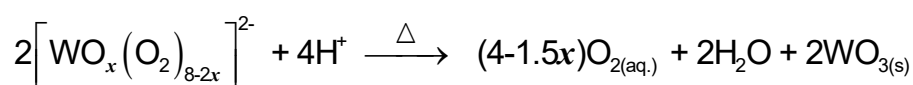
Supplementary Fig. 14. Structure, morphology and composition of the as-synthesized RuO₂ membrane. **a**, XRD spectrum of the single-layer RuO₂ membrane supported on the PMMA substrate. The inset shows the crystal structure of the tetragonal RuO₂ and highlights the preferred crystal orientation perpendicular to (100) plane. **b**, FTIR spectrum of the ground RuO₂ membrane, revealing no other organic contaminants and residual reactants except for a few adsorbed water in the membrane. **c**, **d**, SEM images of the freestanding RuO₂ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat RuO₂ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized RuO₂ membrane. Note that the Si in (**h**) is detected from the silicon wafer substrate.

CeO₂ membrane. 1 mL of Ce(NO₃)₃ solution (250 mM) was firstly mixed with 2 mL of hexamethylenetetramine aqueous solution (1 M). The mixture was then transferred into a pretreated Petri dish and kept at 50 °C for 2.5 h. During this process, the light yellow and transparent CeO₂ membrane gradually formed on the solution surface according to the following redox reaction:



Supplementary Fig. 15. Structure, morphology and composition of the as-synthesized CeO₂ membrane. **a**, XRD spectrum of the single-layer CeO₂ membrane supported on the PMMA substrate. The inset shows the crystal structure of the cubic CeO₂. **b**, FTIR spectrum of the ground CeO₂ membrane, revealing no other organic contaminants and residual reactants except for a few adsorbed water in the membrane. **c**, **d**, SEM images of the freestanding CeO₂ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat CeO₂ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized CeO₂ membrane. Note that the Si in (**h**) is detected from the silicon wafer substrate.

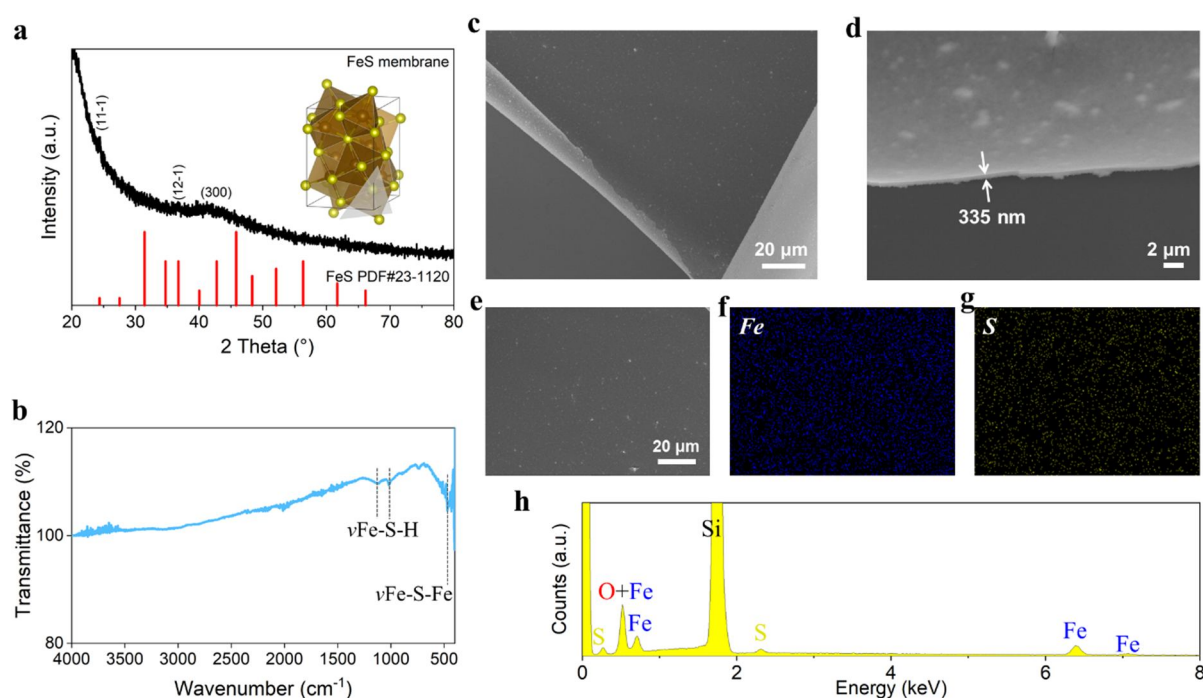
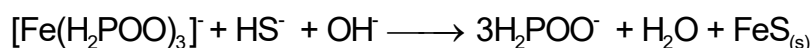
WO₃ membrane. To obtain the precursor solution of peroxo tungsten complexe (WO_x(O₂)_{4-x}, $x = 0, 1, 2$ and 3), 0.3 g of tungsten powder was allowed to fully dissolve in 5 mL of H₂O₂ solution (30-32%) by stirring the suspension solution continuously at room temperature for 48 h. After a centrifugal treatment (10,000 r.p.m for 15 min) to remove the potential solid impurities, 0.6 mL of this fresh peroxo tungsten complexe solution was mixed with 2.4 mL of HCl solution (0.15 M) in a pretreated Petri dish. Then, the mixed solution was kept at 55 °C with cover for 10 h. During this process, the yellowy and transparent WO₃ membrane gradually formed on the solution surface according to the following redox reaction:



Supplementary Fig. 16. Structure, morphology and composition of the as-synthesized WO₃ membrane. **a**, XRD spectrum of the single-layer WO₃ membrane supported on the PMMA substrate. The inset shows the crystal structure of the hexagonal WO₃ and highlights the preferred crystal orientation perpendicular to (100) plane. **b**, FTIR spectrum of the ground WO₃ membrane, revealing no other organic contaminants and residual reactants except for a few adsorbed water in the membrane. **c**, **d**, SEM images of the freestanding WO₃ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, SEM image of the conductive carbon tape-supported flat WO₃ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized WO₃ membrane. Note that the C in (**h**) is detected from the conductive carbon tape.

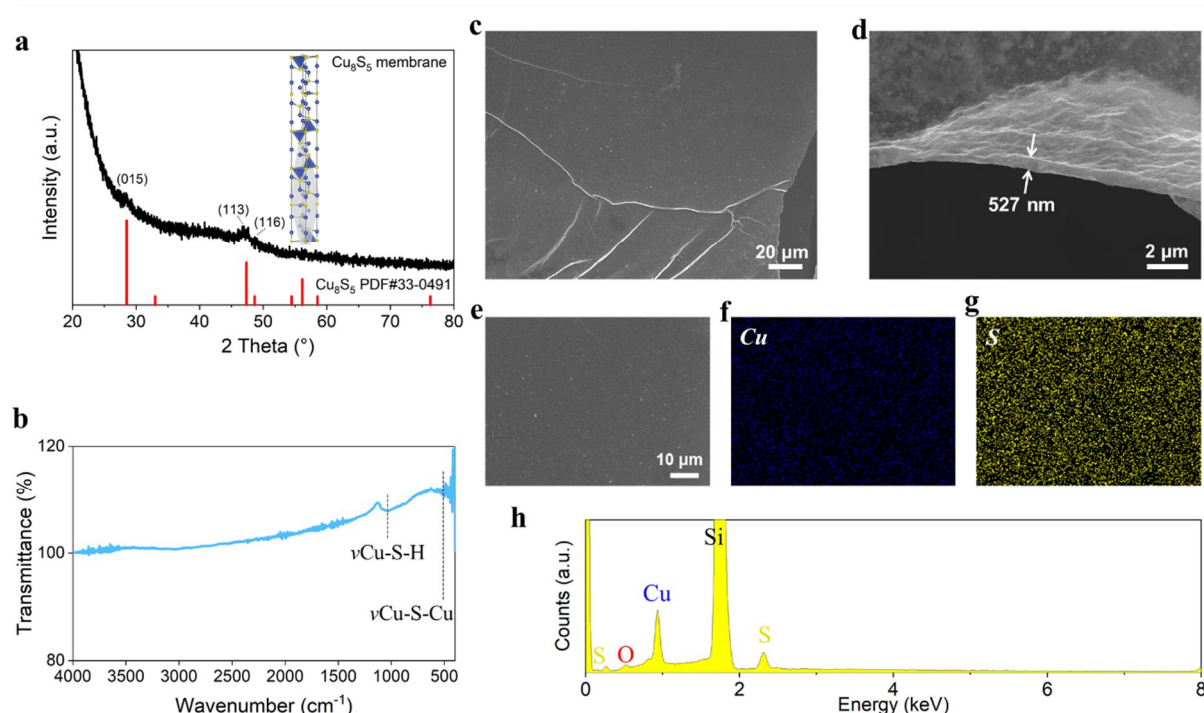
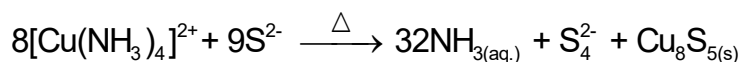
S2.4 Sulfides

FeS membrane. 250 μL of NaOH solution (4 M) was firstly added into 2.47 mL of fresh FeSO_4 solution (25 mM) with additional 120 μL of H_3PO_2 solution (50 wt%) as the antioxidant and chelating agent. This mixed solution was then transferred into a pretreated Petri dish after a further addition of 60 μL of Na_2S solution (0.6 M). Finally, 100 μL of dilute ammonium hydroxide (~ 5 wt%) was quickly added into the Petri dish, which was allowed to stand still with cover at room temperature for 1 h. During this process, the gray and transparent FeS membrane gradually formed on the solution surface according to the following precipitation reaction. Note that the as-synthesized FeS membrane is easy to be oxidized in air, thus it should be preserved in dry N_2 or Ar atmosphere to prevent oxidization.



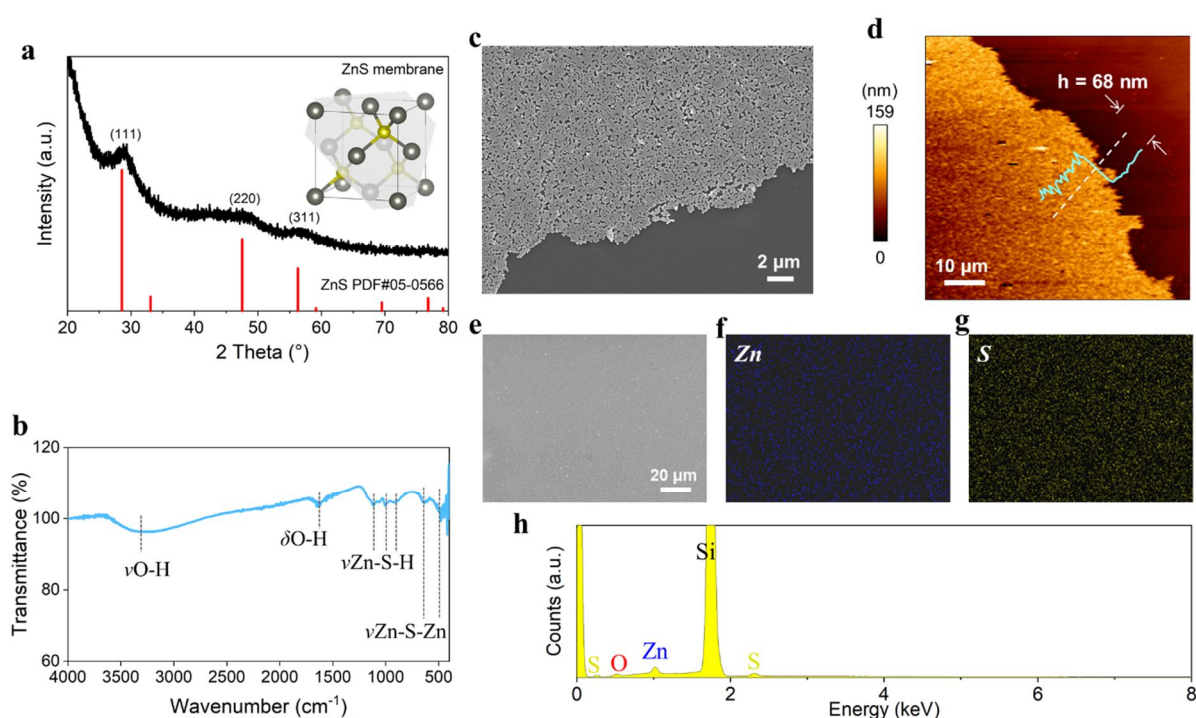
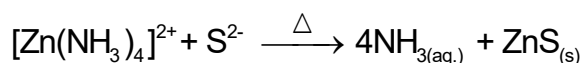
Supplementary Fig. 17. Structure, morphology and composition of the as-synthesized FeS membrane. **a**, XRD spectrum of the single-layer FeS membrane supported on the PMMA substrate. The inset shows the crystal structure of the monoclinic FeS and highlights the preferred crystal orientation perpendicular to (11-1) plane. **b**, FTIR spectrum of the ground FeS membrane, revealing no organic contaminants and residual reactants in the membrane. **c**, **d**, SEM images of the freestanding FeS membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat FeS membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the membrane. Note that the Si in (**h**) is detected from the silicon substrate. The detected little O shows a slight oxidation of the membrane surface.

Cu₈S₅ membrane. 30 μ L of CuSO₄ solution (1.2 M) was firstly dissolved into 1.97 mL of ammonium hydroxide (28-30 %). The obtained [Cu(NH₃)₄]²⁺ solution was then mixed with 1 mL of freshly-prepared Na₂S solution (18 μ M), transferred into a pretreated Petri dish and allowed at 45 °C for 25 min. During this process, the brown and transparent Cu₈S₅ membrane gradually formed on the solution surface according to the following precipitation reaction:



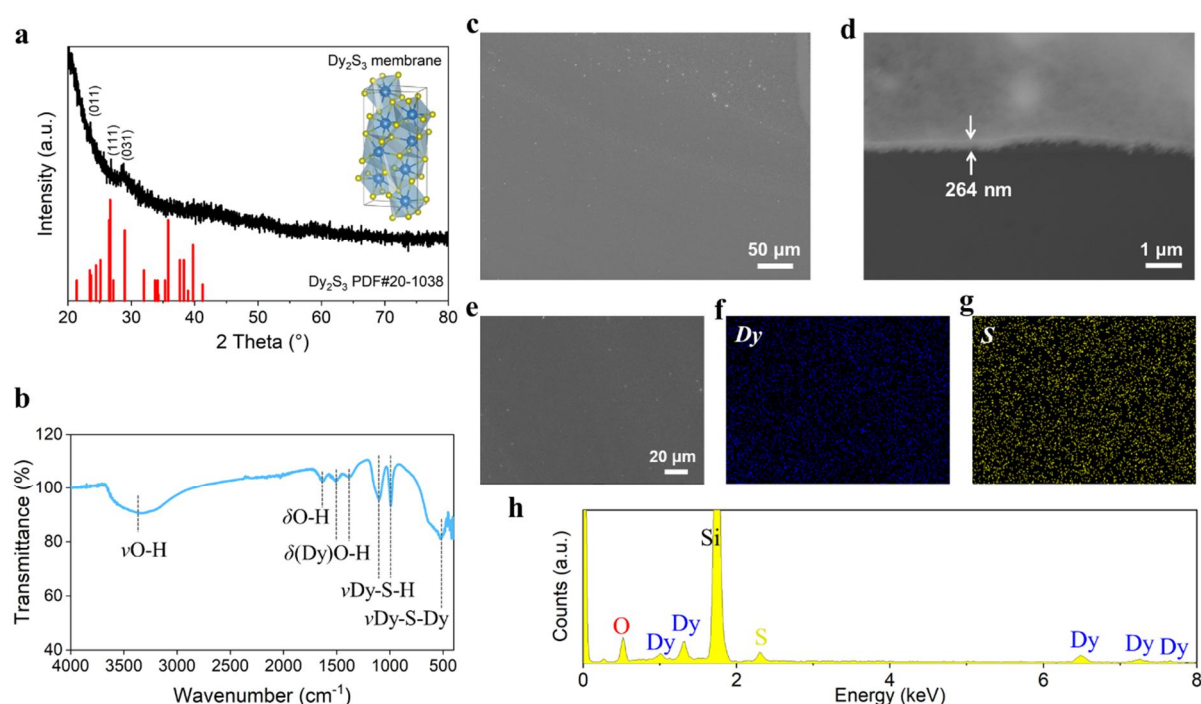
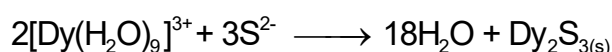
Supplementary Fig. 18. Structure, morphology and composition of the as-synthesized Cu₈S₅ membrane. **a**, XRD spectrum of the single-layer Cu₈S₅ membrane supported on the PMMA substrate. The inset shows the crystal structure of the hexagonal Cu₈S₅ and highlights the preferred crystal orientation perpendicular to (116) plane. **b**, FTIR spectrum of the ground Cu₈S₅ membrane, revealing no organic contaminants and residual reactants in the membrane. **c**, **d**, SEM images of the freestanding Cu₈S₅ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat Cu₈S₅ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized Cu₈S₅ membrane. Note that the Si in (**h**) is detected from the silicon wafer substrate. The detected little O indicates the slight oxidation of the membrane surface.

ZnS membrane. 100 μL of ZnSO_4 solution (3.5 M) was firstly dissolved into 1.4 mL of ammonium hydroxide solution (28-30 wt%). The obtained $[\text{Zn}(\text{NH}_3)_4]^{2+}$ solution was then mixed with 1.5 mL of freshly-prepared Na_2S solution (40 mM), transferred into a pretreated Petri dish and allowed to stand still at 40 $^\circ\text{C}$ for 20 min. During this process, the colourless and transparent ZnS membrane gradually formed on the solution surface according to the following precipitation reaction:



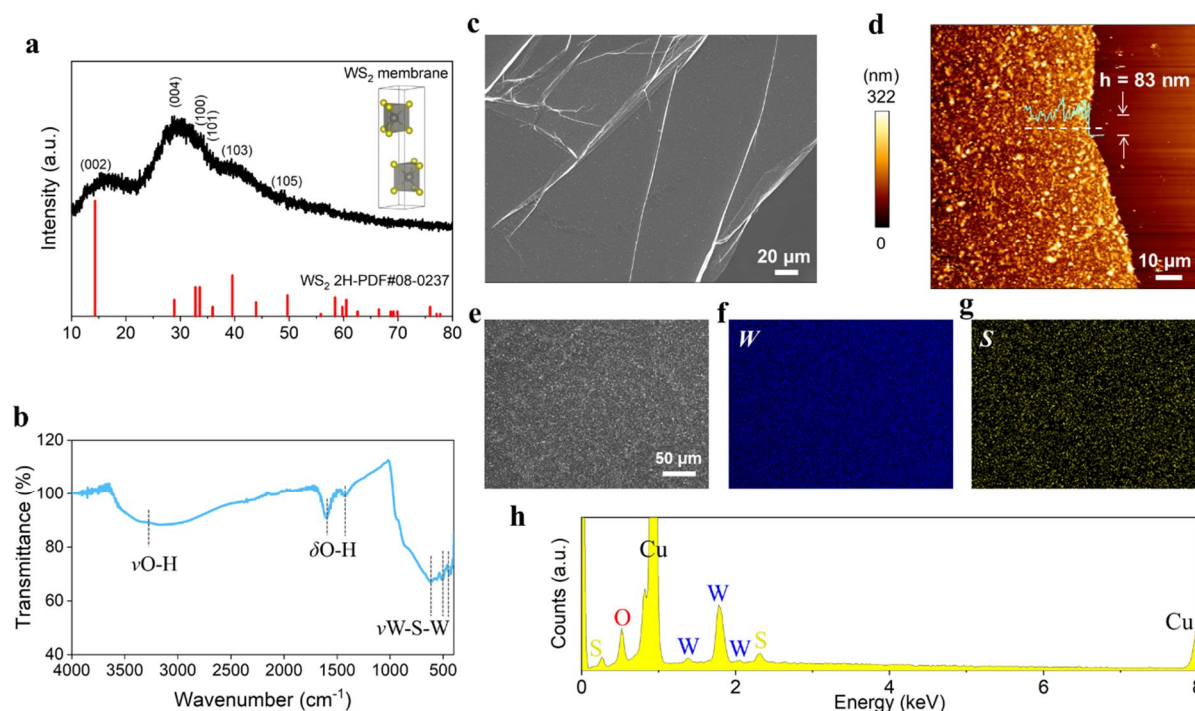
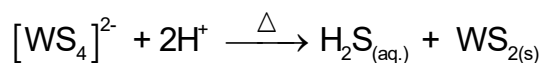
Supplementary Fig. 19. Structure, morphology and composition of the as-synthesized ZnS membrane. **a**, XRD spectrum of the single-layer ZnS membrane supported on the PMMA substrate. The inset shows the crystal structure of the cubic ZnS and highlights the preferred crystal orientation perpendicular to (111) plane. **b**, FTIR spectrum of the ground ZnS membrane, revealing no other organic contaminants and residual reactants except for a few adsorbed water molecules in the membrane. **c**, SEM image of the freestanding ZnS membrane showing its holey structure. **d**, AFM image of the ZnS membrane supported on the silicon wafer showing its uniformities in morphology and thickness. The blue line is the height profile measured along the white dashed line. **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat ZnS membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized ZnS membrane. Note that the Si in (**h**) is detected from the silicon wafer substrate.

Dy₂S₃ membrane. A pretreated Petri dish containing 2 mL of Dy(NO₃)₃ solution (20 mM) was firstly kept at 40 °C for 30 min. After a quick addition of 1 mL of Na₂S solution (36 mM) of room temperature, the mixed solution was further allowed to stand still at room temperature for 1.5 h. During this period, the light yellow and transparent Dy₂S₃ membrane gradually formed on the solution surface according to the following precipitation reaction:



Supplementary Fig. 20. Structure, morphology and composition of the as-synthesized Dy₂S₃ membrane. **a**, XRD spectrum of the four-layered Dy₂S₃ membrane supported on the PMMA substrate. The inset shows the crystal structure of the orthorhombic Dy₂S₃ and highlights the preferred crystal orientation perpendicular to (031) plane. **b**, FTIR spectrum of the ground Dy₂S₃ membrane, revealing no other organic contaminants and residual reactants except for a few adsorbed water molecules in the membrane. **c**, **d**, SEM images of the freestanding Dy₂S₃ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat Dy₂S₃ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized Dy₂S₃ membrane. Note that the Si in (**h**) is detected from the silicon wafer substrate. The detected little O indicates the slight oxidation of the membrane surface.

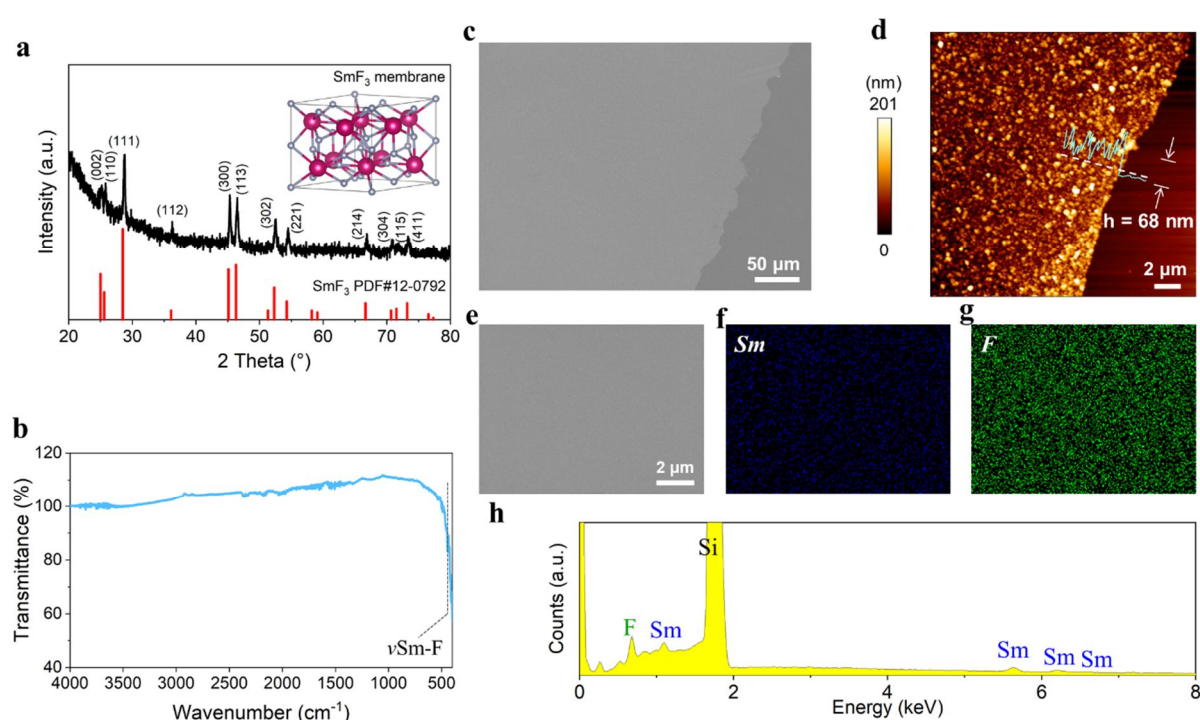
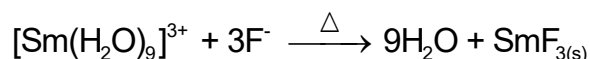
WS₂ membrane. 0.4 mL of H₂SO₄ solution (4 M) was mixed with 2.6 mL of (NH₄)₂WS₄ solution (20 mM) in a pretreated Petri dish. Then the mixed solution was kept at 55 °C for 5 h. During this process, the light brown WS₂ membrane gradually formed on the solution surface according to the following redox reaction:



Supplementary Fig. 21. Structure, morphology and composition of the as-synthesized WS₂ membrane. **a**, XRD spectrum of the six-layered WS₂ membrane supported on the PMMA substrate. The inset shows the crystal structure of the hexagonal WS₂. **b**, FTIR spectrum of the ground WS₂ membrane, revealing no other organic contaminants and residual reactants except for a few adsorbed water molecules in the membrane. **c**, SEM image of the freestanding WS₂ membrane highlighting its wrinkled morphology. **d**, AFM image of the WS₂ membrane supported on the silicon wafer showing its uniformities in morphology and thickness. The blue line is the height profile measured along the white dashed line. **e**, **f**, **g**, **h**, SEM image of the polished copper foil-supported flat WS₂ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized WS₂ membrane. Note that the Cu in (**h**) is detected from the copper foil substrate. The detected little O indicates the slight oxidation of the membrane surface.

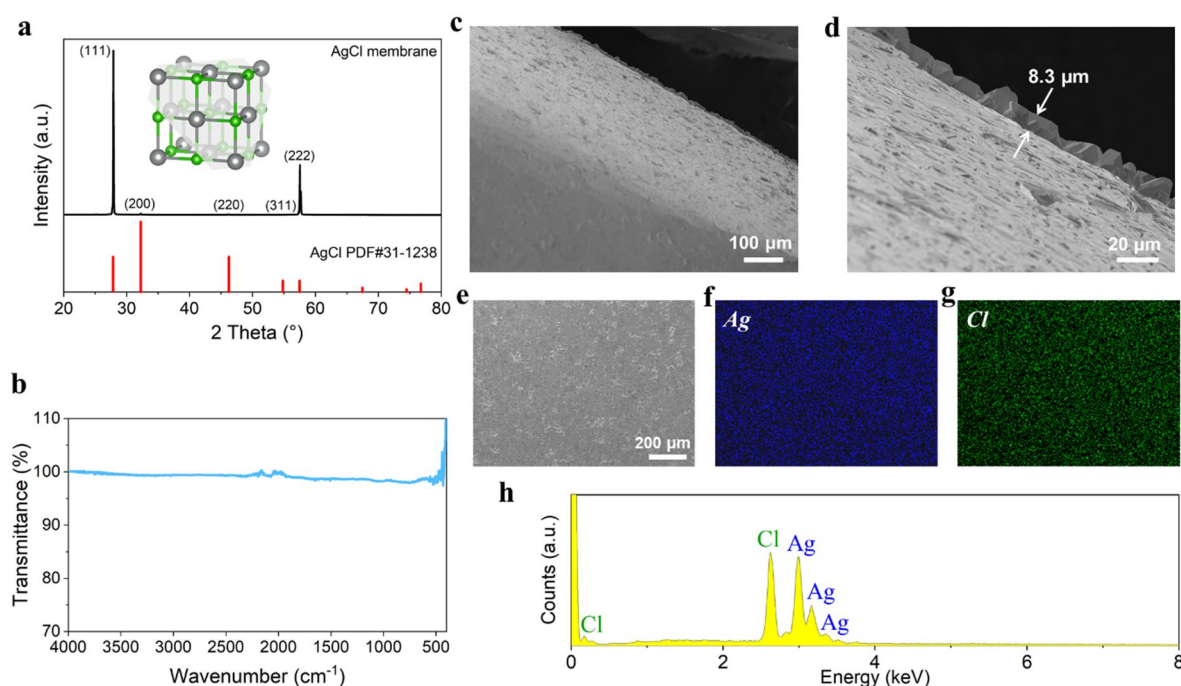
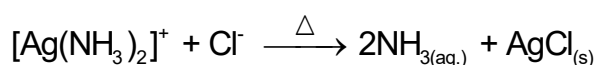
S2.5 Halides

SmF₃ membrane: 1.5 mL of Sm(NO₃)₃ solution (120 mM) was firstly added into a pretreated Petri dish and kept at 55 °C for 20 min. Subsequently, after a quick addition of 1.5 mL of NH₄F solution (260 mM), the mixed solution with some suspended gelatinoids was further kept at 55 °C for 20 h. During this process, the transparent SmF₃ membrane gradually formed on the solution surface according to the following precipitation reaction:



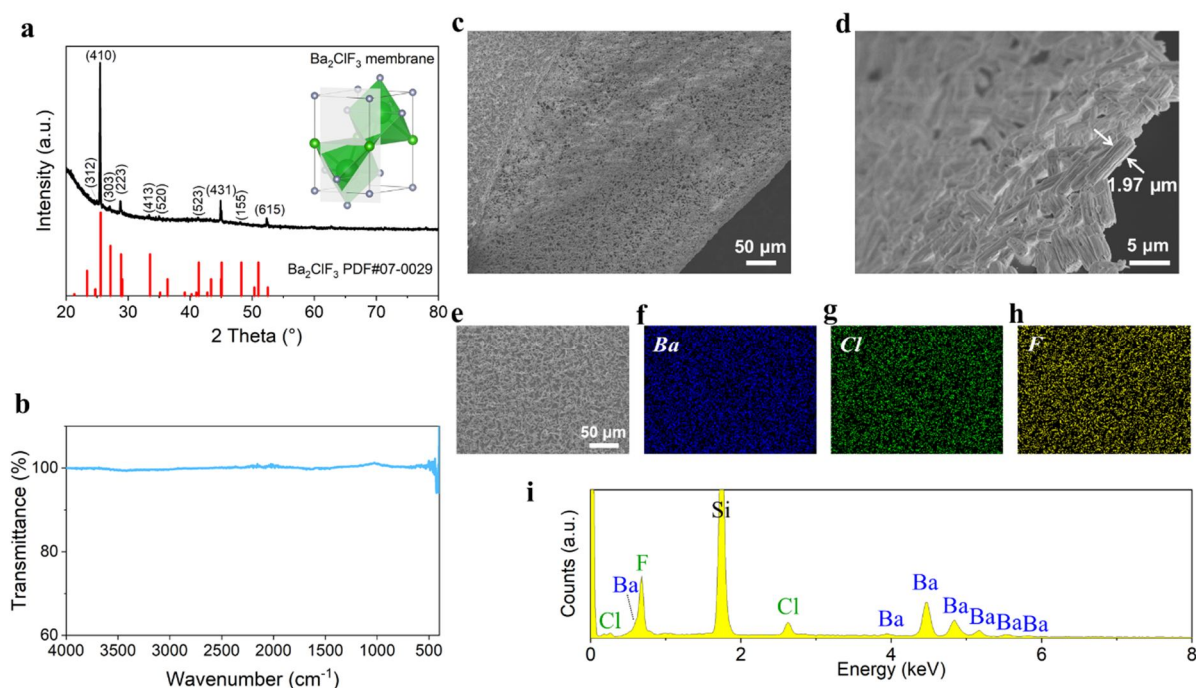
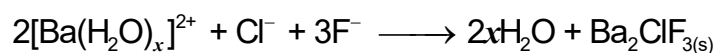
Supplementary Fig. 22. Structure, morphology and composition of the as-synthesized SmF₃ membrane. **a**, XRD spectrum of the five-layered SmF₃ membrane supported on the PMMA substrate. The inset shows the crystal structure of the hexagonal SmF₃. **b**, FTIR spectrum of the ground SmF₃ membrane, revealing no organic contaminants and residual reactants in the membrane. **c**, Overlooked SEM image of the freestanding SmF₃ membrane. **d**, AFM image of the SmF₃ membrane supported on the silicon wafer showing its uniformities in morphology and thickness. The blue line is the height profile measured along the white dashed line. **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat SmF₃ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized SmF₃ membrane. Note that the Si in (**h**) is detected from the silicon wafer substrate.

AgCl membrane. Fresh AgCl was firstly prepared from the precipitation reaction between 3 mL of AgNO₃ solution (250 mM) and 1 mL of NaCl solution (1 M). After a further centrifugal collection, the AgCl was dissolved in 3 mL of dilute ammonium hydroxide (~10 wt%) assisted by ultrasonic treatment. Subsequently, the fresh [Ag(NH₃)₂]⁺ solution was transferred into a pretreated Petri dish and kept at 35 °C for 40 min. The transparent AgCl membrane gradually formed on the solution surface according to the following precipitation reaction during this period. Note that the AgCl is extremely sensitive to the light irradiation. Thus, the aluminum foil was used to seal the reaction vessels away from the light throughout the preparation process.



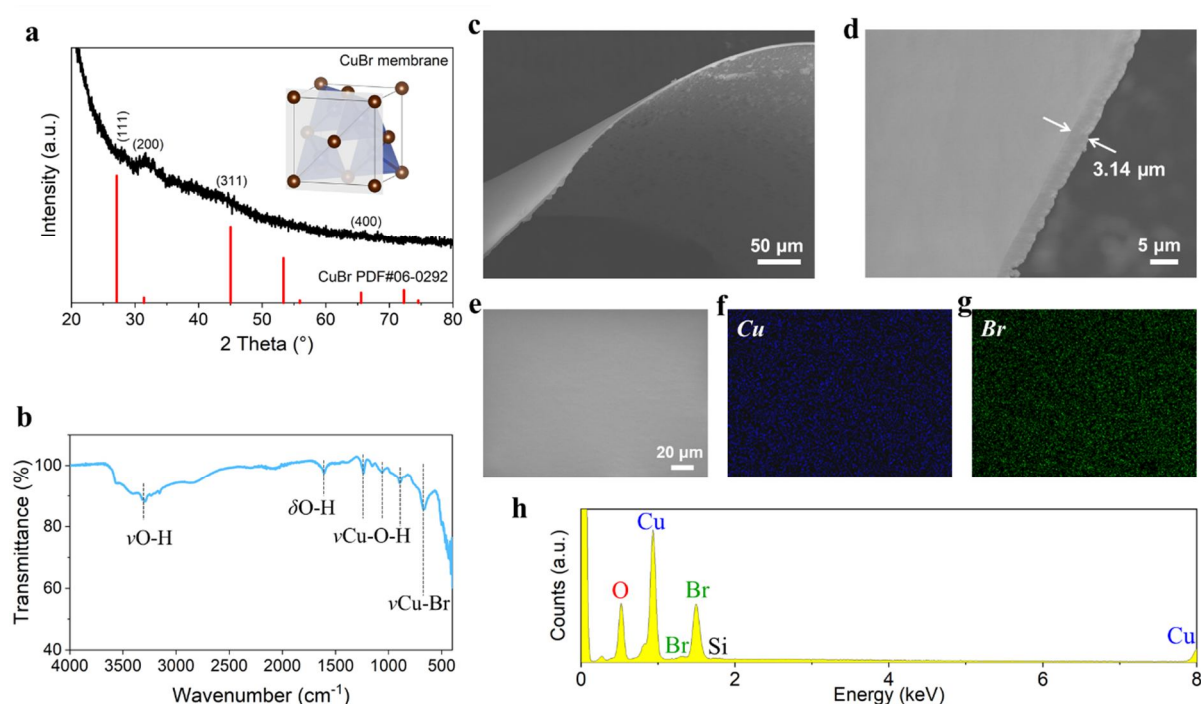
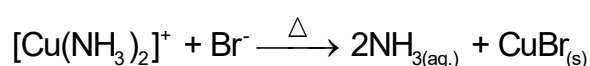
Supplementary Fig. 23. Structure, morphology and composition of the as-synthesized AgCl membrane. **a**, XRD spectrum of the single-layer AgCl membrane supported on the PMMA substrate. The inset shows the crystal structure of the cubic AgCl and highlights the preferred crystal orientation perpendicular to (111) plane. **b**, FTIR spectrum of the ground AgCl membrane, revealing no organic contaminants and residual reactants in the membrane. It's worth noting that the AgCl membrane is completely transparent to infrared light in the measuring range. **c**, **d**, SEM images of the freestanding AgCl membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat AgCl membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized AgCl membrane.

Ba₂ClF₃ membrane. 1.6 mL of BaCl₂ solution (150 mM) was quickly added into a pretreated Petri dish containing 1.4 mL of NH₄F solution (0.4 M). The mixed solution was then allowed to stand still at room temperature for 4 h. During this process, the white and subtranslucent Ba₂ClF₃ membrane gradually formed on the solution surface according to the following precipitation reaction:



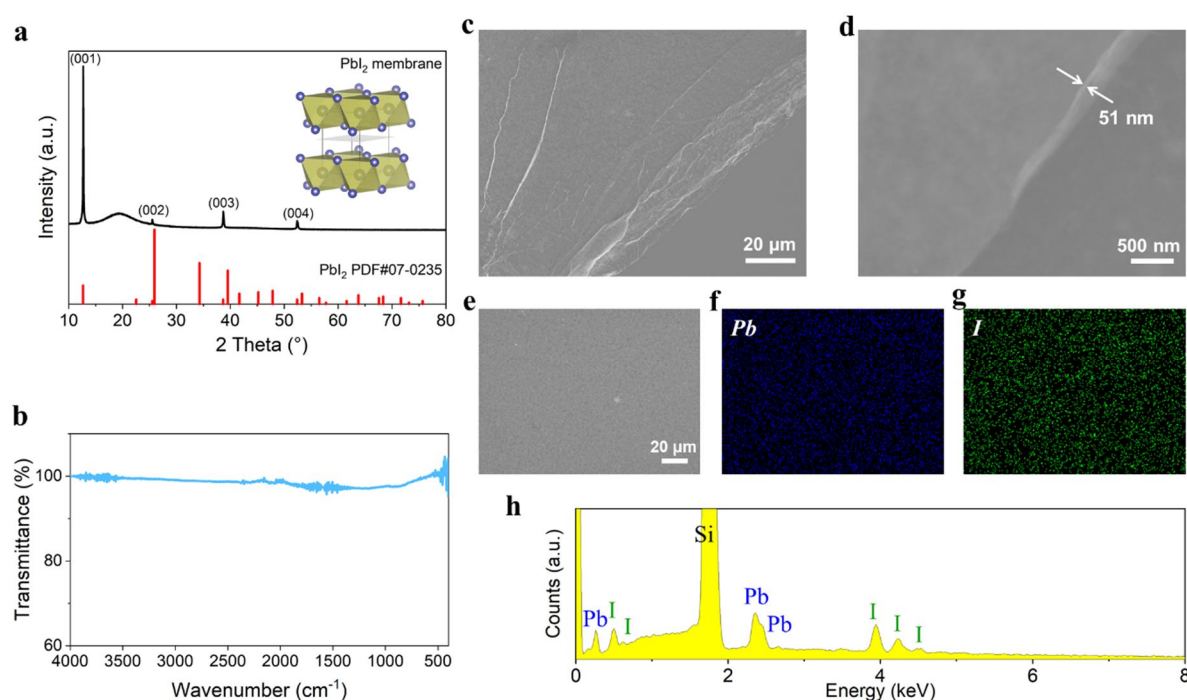
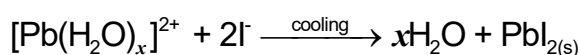
Supplementary Fig. 24. Structure, morphology and composition of the as-synthesized Ba₂ClF₃ membrane. **a**, XRD spectrum of the single-layer Ba₂ClF₃ membrane supported on the PMMA substrate. The inset shows the crystal structure of the hexagonal Ba₂ClF₃ and highlights the preferred crystal orientation perpendicular to (410) plane. **b**, FTIR spectrum of the ground Ba₂ClF₃ membrane, revealing no organic contaminants and residual reactants in the membrane. It's worth noting that the Ba₂ClF₃ membrane is completely transparent to infrared light in the measuring range. **c**, **d**, SEM images of the freestanding Ba₂ClF₃ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). The membrane presents well-defined holey structure. **e**, **f**, **g**, **h**, **i**, SEM image of the silicon wafer-supported flat Ba₂ClF₃ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**, **h**) and EDS spectrum (**i**), confirming the element composition of the as-synthesized Ba₂ClF₃ membrane. Note that the Si in (**i**) is detected from the silicon wafer substrate.

CuBr membrane. 0.3 g of CuBr powder was firstly dissolved in 6 mL of ammonium hydroxide (28-30 wt%) under the ultrasonic treatment, followed by removing the insoluble precipitate by centrifugation (9,000 r.p.m. for 10 min). 100 uL of diluted N₂H₄ solution (~1 wt%) was further added to slow down the undesirable oxidation of the fresh [Cu(NH₃)₂]⁺ that was exposed to the air. Subsequently, 1.5 mL of the [Cu(NH₃)₂]⁺ solution was mixed with equivoluminal DI water, transferred into a pretreated Petri dish and kept at 40 °C for 40 min. During this process, the virescent and transparent CuBr membrane gradually formed on the solution surface according the following precipitation reaction. Note that the as-synthesized CuBr membrane is easy to be oxidized in air, thus it should be preserved in dry N₂ or Ar atmosphere to prevent oxidation.



Supplementary Fig. 25. Structure, morphology and composition of the as-synthesized CuBr membrane. **a**, XRD spectrum of the single-layer CuBr membrane supported on the PMMA substrate. The inset shows the crystal structure of the cubic CuBr and highlights the preferred crystal orientation perpendicular to (100) plane. **b**, FTIR spectrum of the ground CuBr membrane, revealing no other organic contaminants and residual reactants except for a few species of oxidation in the membrane. **c**, **d**, SEM images of the freestanding CuBr membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat CuBr membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized CuBr membrane. Note that the Si in (**h**) is detected from the silicon wafer substrate. The detected little O indicates the slight oxidation of the membrane surface.

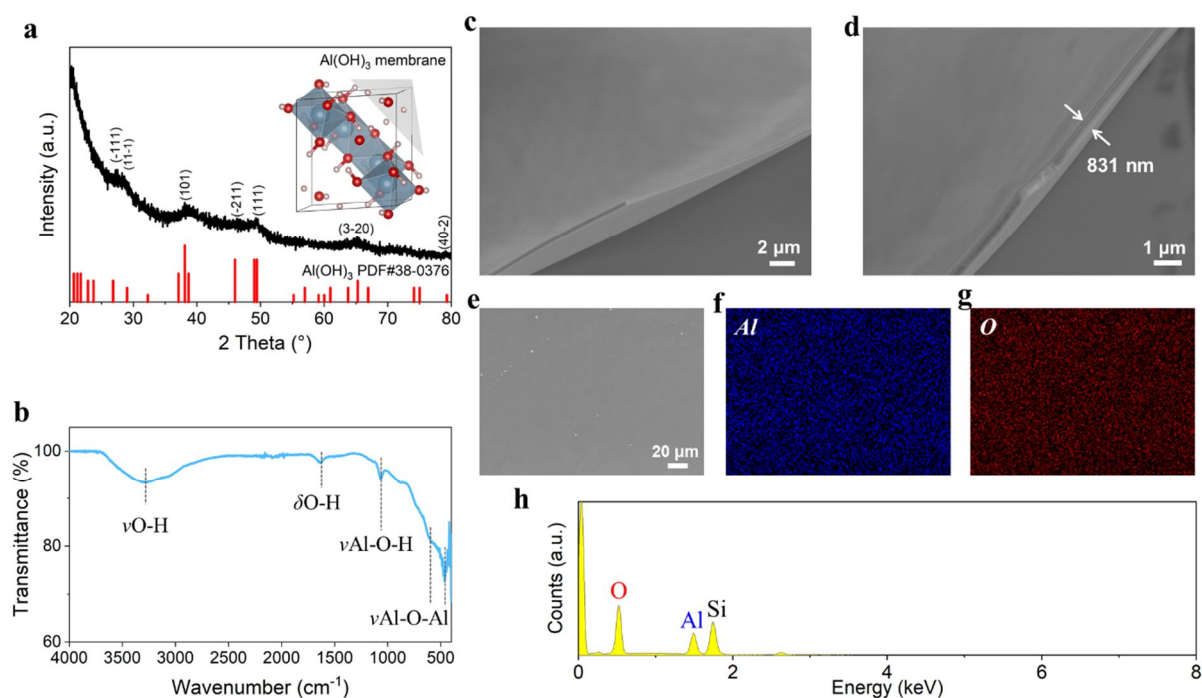
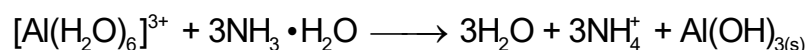
PbI₂ membrane. To prepare the fresh PbI₂, 1 mL of Pb (NO₃)₂ solution (20 mM) was dropwise added into 2 mL of NaI solution (20 mM) under the ultrasonic treatment. The yellow precipitate was collected by centrifugation (8,000 r.p.m. for 10 min) and washed with precooled deionized water of 5 °C for three times. Colorless PbI₂ solution was then prepared by dissolving all the collected precipitate in 4 mL of deionized water at 80 °C for 3 h. The solution was then let cool down at room temperature without any vibration to obtain the oversaturated solution, 3mL of which was transferred into a pretreated Petri dish and kept at 5 °C in a fridge for 2 h. During this process, the light yellow PbI₂ membrane gradually formed on the solution surface according to the following precipitation reaction. Note that the PbI₂ membrane should be avoided to contact with abundant water to avoid dissolution.



Supplementary Fig. 26. Structure, morphology and composition of the as-synthesized PbI₂ membrane. **a**, XRD spectrum of the single-layer PbI₂ membrane supported on the PMMA substrate. The inset shows the crystal structure of the hexagonal PbI₂ and highlights the preferred crystal orientation perpendicular to (001) plane. **b**, FTIR spectrum of the ground PbI₂ membrane, revealing no organic contaminants and residual reactants in the membrane. **c**, **d**, SEM images of the freestanding PbI₂ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat PbI₂ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized PbI₂ membrane. Note that the Si in (**h**) is detected from the silicon wafer substrate.

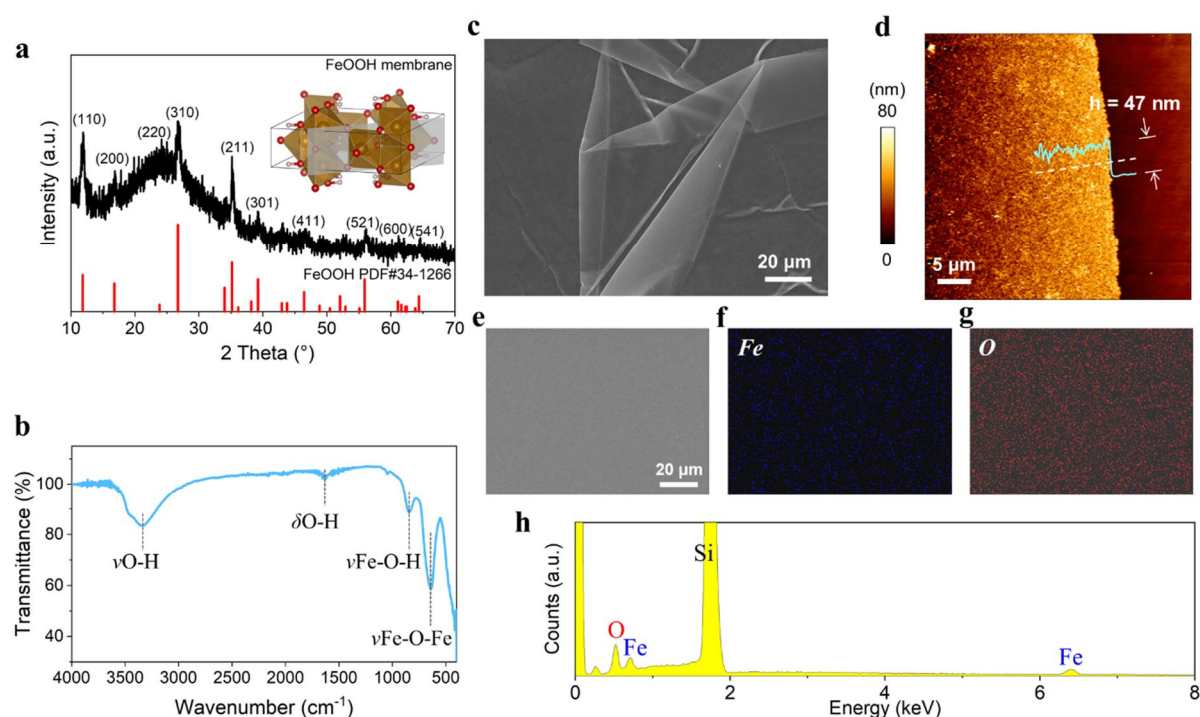
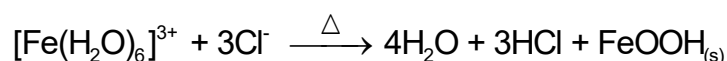
S2.6 Hydroxides

Al(OH)₃ membrane. 2.9 mL of fresh AlCl₃ solution (80 mM) was added into a pretreated Petri dish and then kept at 50 °C with cover for 20 min. After being shifted to room temperature with a quick addition of 100 μL of dilute ammonium hydroxide (~10 wt%), the system was allowed to stand still at room temperature for 20 min. During this process, the colorless and transparent Al(OH)₃ membrane gradually formed on the solution surface according to the following hydrolysis reaction:



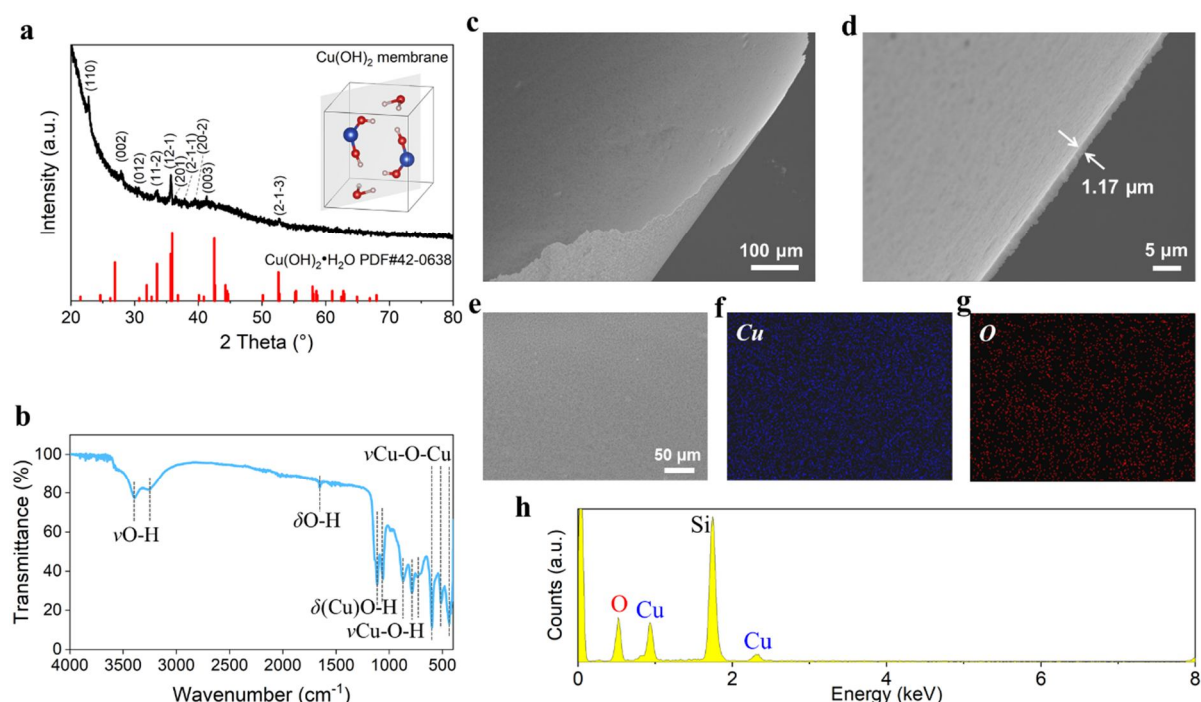
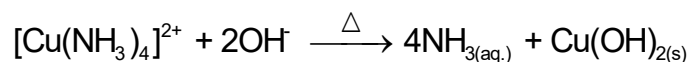
Supplementary Fig. 27. Structure, morphology and composition of the as-synthesized Al(OH)₃ membrane. **a**, XRD spectrum of the single-layer Al(OH)₃ membrane supported on the PMMA substrate. The inset shows the crystal structure of the triclinic Al(OH)₃ and highlights the preferred crystal orientation perpendicular to (-111) plane. **b**, FTIR spectrum of the ground Al(OH)₃ membrane, revealing no organic contaminants and residual reactants in the membrane. **c**, **d**, SEM images of the freestanding Al(OH)₃ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat Al(OH)₃ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized Al(OH)₃ membrane. Note that the Si in (**h**) is detected from the silicon wafer substrate.

FeOOH membrane. A pretreated Petri dish containing 3 mL of freshly-prepared FeCl₃ solution (50 mM) was kept at 65 °C with cover for 3 h and then allowed to cool down to the room temperature in the oven. During this process, the orange-yellow and transparent FeOOH membrane gradually formed on the solution surface according to the following hydrolysis reaction:



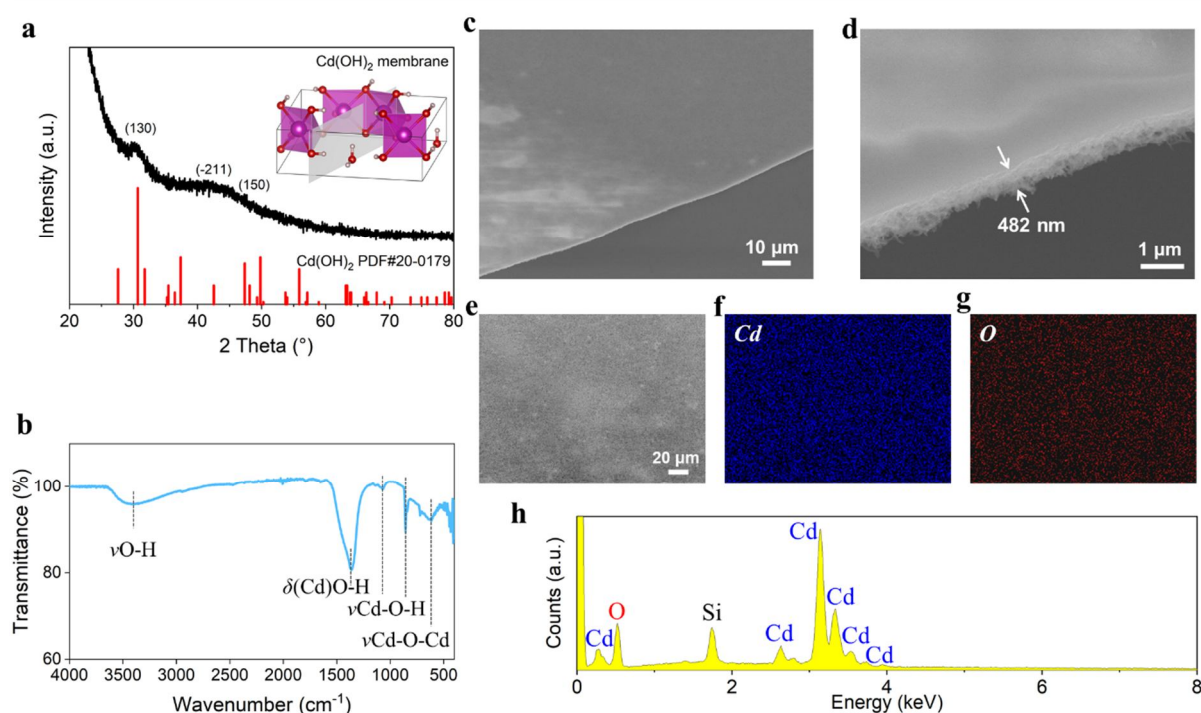
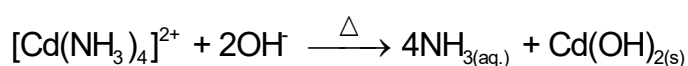
Supplementary Fig. 28. Structure, morphology and composition of the as-synthesized FeOOH membrane. **a**, XRD spectrum of the five-layered FeOOH membrane supported on the glass substrate. The inset shows the crystal structure of the tetragonal FeOOH and highlights the preferred crystal orientation perpendicular to (110) plane. **b**, FTIR spectrum of the ground FeOOH membrane, revealing no other organic contaminants and residual reactants except for a few adsorbed water molecules in the membrane. **c**, SEM image of the freestanding and wrinkled FeOOH membrane. **d**, AFM image of the FeOOH membrane supported on the silicon wafer showing its uniformities in morphology and thickness. The blue line is the height profile measured along the white dashed line. **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat FeOOH membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized FeOOH membrane. Note that the Si in (**h**) is detected from the silicon wafer substrate.

Cu(OH)₂ membrane. 180 μL of ammonium hydroxide (28-30 wt%) was firstly added into 2.82 mL of CuSO₄ solution (0.2 M) to prepare fresh [Cu(NH₃)₄](OH)₂ solution. The mixed solution was transferred into a pretreated Petri dish and then kept at 45 °C for 1.5 h. During this process, the light blue and transparent Cu(OH)₂ membrane gradually formed on the solution surface according to the following precipitation reaction:



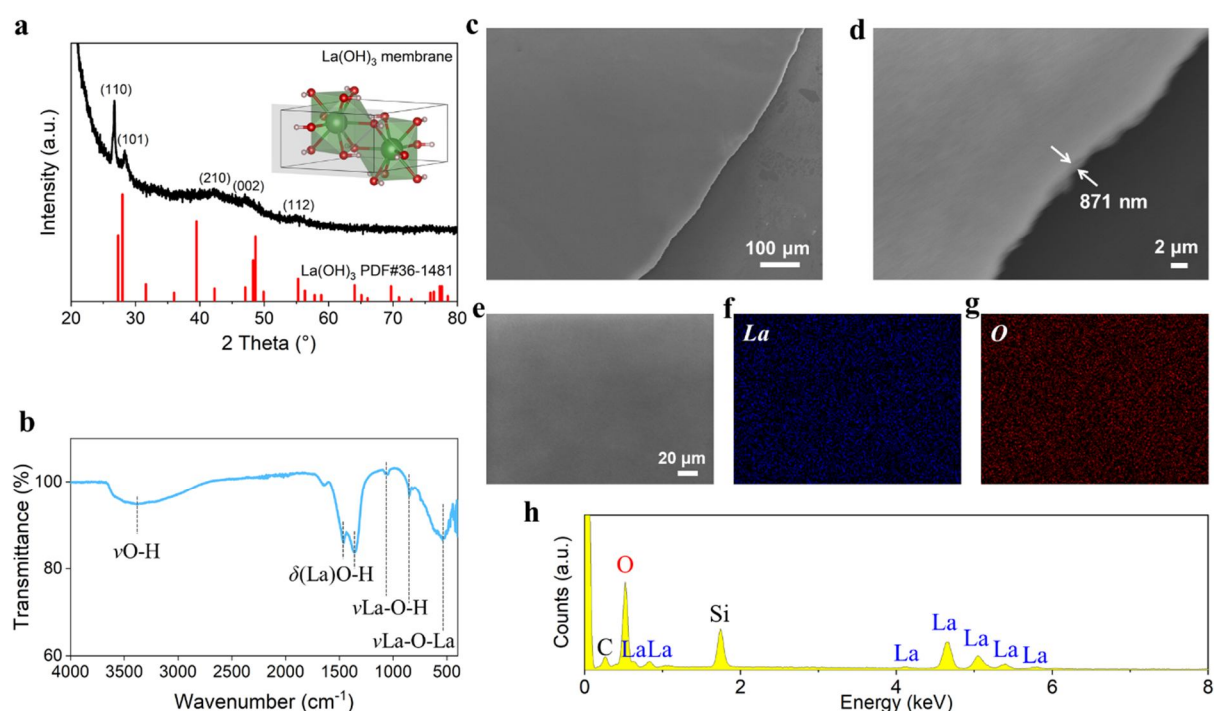
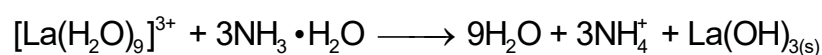
Supplementary Fig. 29. Structure, morphology and composition of the as-synthesized Cu(OH)₂ membrane. **a**, XRD spectrum of the four-layered Cu(OH)₂ membrane supported on the PMMA substrate. The inset shows the crystal structure of the triclinic monohydrate Cu(OH)₂ and highlights the preferred crystal orientation perpendicular to (12-1) plane. **b**, FTIR spectrum of the ground Cu(OH)₂ membrane, revealing no organic contaminants and residual reactants in the membrane. **c**, **d**, SEM images of the freestanding Cu(OH)₂ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat Cu(OH)₂ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized Cu(OH)₂ membrane. Note that the Si in (**h**) is detected from the silicon wafer substrate.

Cd(OH)₂ membrane. 0.6 mL of dilute ammonium hydroxide (~10 wt%) was firstly mixed with 2.4 mL of CdCl₂ solution (30 mM) to form a clear and transparent solution, which was further transferred into a pretreated Petri dish and then kept at 50 °C for 20 min. During this period, the colorless and transparent Cd(OH)₂ membrane gradually formed on the solution surface according to the following hydrolysis reaction. Note that the as-synthesized Cd(OH)₂ membrane can efficiently adsorb atmospheric CO₂, thus it should be preserved in dry N₂ or Ar atmosphere before characterization to isolate the air.



Supplementary Fig. 30. Structure, morphology and composition of the as-synthesized Cd(OH)₂ membrane. **a**, XRD spectrum of the single-layer Cd(OH)₂ membrane supported on the PMMA substrate. The inset shows the crystal structure of the monoclinic Cd(OH)₂ and highlights the preferred crystal orientation perpendicular to (130) plane. **b**, FTIR spectrum of the ground Cd(OH)₂ membrane, revealing no organic contaminants and residual reactants in the membrane. **c**, **d**, SEM images of the freestanding Cd(OH)₂ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat Cd(OH)₂ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized Cd(OH)₂ membrane. Note that the Si in (**h**) is detected from the silicon wafer substrate.

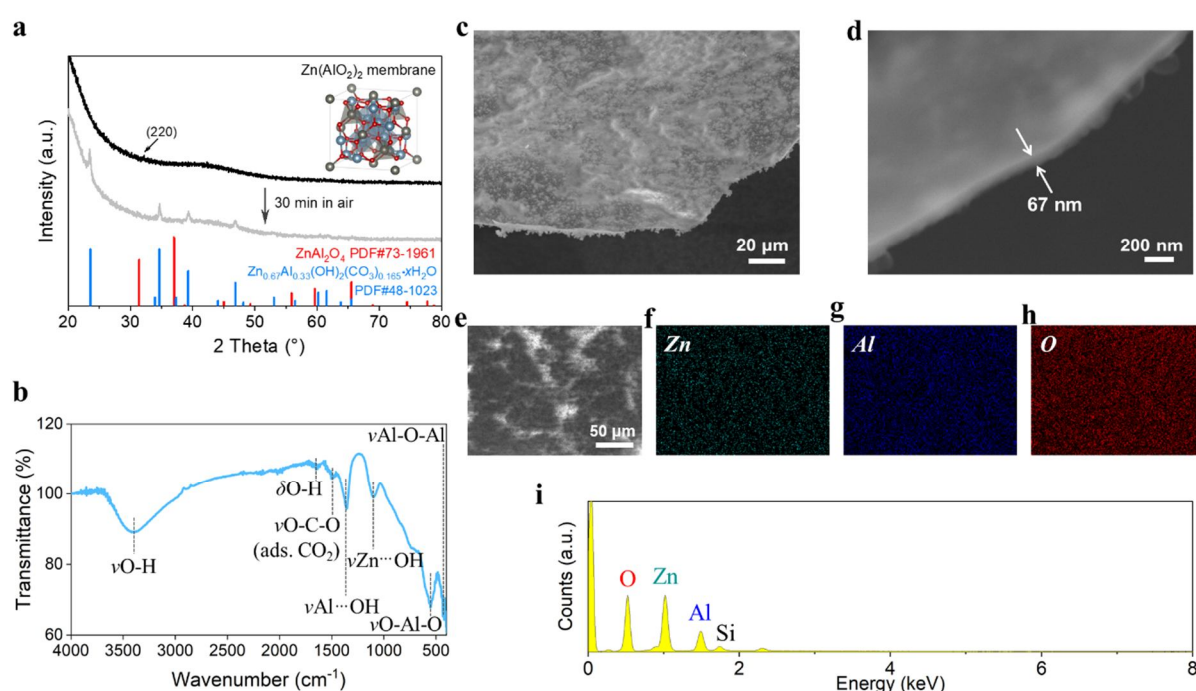
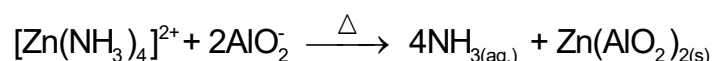
La(OH)₃ membrane. 100 μ L of dilute ammonium hydroxide ($\sim$ 5 wt%) was added into a pretreated Petri dish containing 2.9 mL of La(NO₃)₃ solution (0.1 M). Then let the mixture stand still at room temperature for 35 min. During this process, a colorless and transparent La(OH)₃ membrane gradually formed on the solution surface according to the following hydrolysis reaction:



Supplementary Fig. 31. Structure, morphology and composition of the as-synthesized La(OH)₃ membrane. **a**, XRD spectrum of the single-layer La(OH)₃ membrane supported on the PMMA substrate. The inset shows the crystal structure of the hexagonal La(OH)₃ and highlights the preferred crystal orientation perpendicular to (110) plane. **b**, FTIR spectrum of the ground La(OH)₃ membrane, revealing no organic contaminants and residual reactants in the membrane. **c**, **d**, SEM images of the freestanding La(OH)₃ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat La(OH)₃ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized La(OH)₃ membrane. Note that the Si in (**h**) is detected from the silicon wafer substrate and the slight C comes from the CO₂ adsorption by La(OH)₃ from the air.

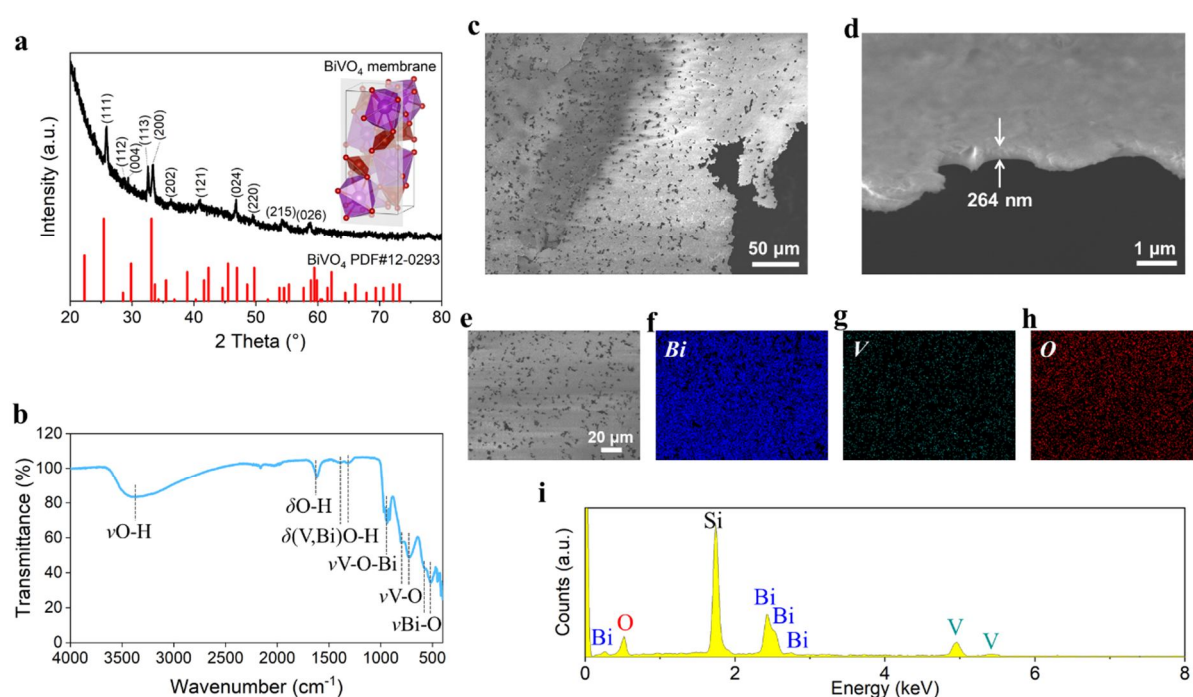
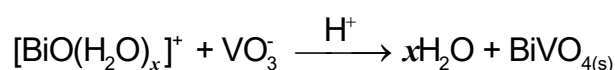
S2.7 Metallates

Zn(AlO₂)₂ membrane. 150 μL of ZnSO₄ solution (3.5 M) was first added into 850 μL of ammonium hydroxide (28-30 wt%) to produce fresh [Zn(NH₃)₄]²⁺ solution, which was further mixed with 2 mL of freshly-prepared NaAlO₂ solution (250 mM). Then, the mixture was quickly transferred into a pretreated Petri dish and kept at 45 °C for 20 min. During this process, the colorless and transparent Zn(AlO₂)₂ membrane gradually formed on the solution surface according to the following precipitation reaction:



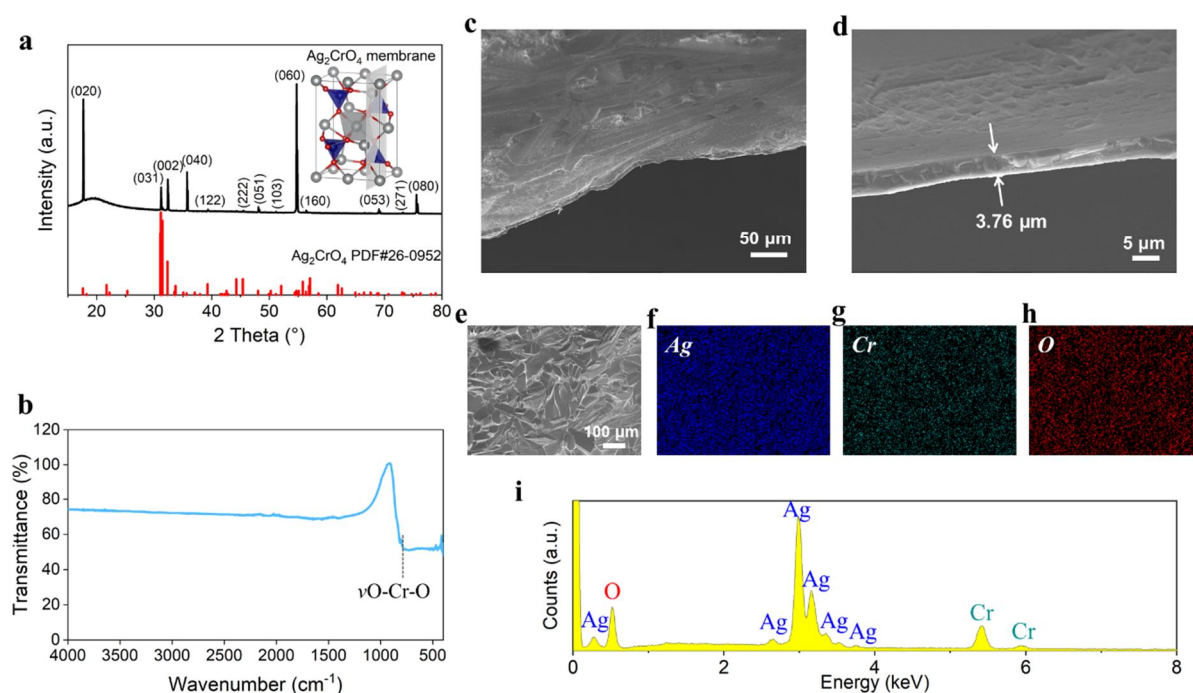
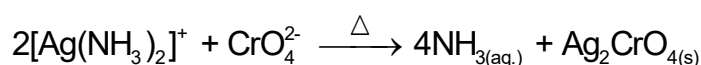
Supplementary Fig. 32. Structure, morphology and composition of the as-synthesized Zn(AlO₂)₂ membrane. **a**, XRD spectra of the freshly-prepared single-layer Zn(AlO₂)₂ membrane supported on the PMMA substrate and the counterpart exposed to air for 30 min. The inset shows the crystal structure of the hexagonal Zn(AlO₂)₂. Note that the humid Zn(AlO₂)₂ membrane with weak crystallization is capable of adsorbing CO₂ from air and transforming into the carbonate hydroxide hydrate. **b**, FTIR spectrum of the ground Zn(AlO₂)₂ membrane, revealing no organic contaminants and residual reactants in the membrane. The detected slight carbonate comes from the inevitable CO₂ adsorption by Zn(AlO₂)₂ from the air during measurement. **c**, **d**, SEM images of the freestanding Zn(AlO₂)₂ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, SEM image of the silicon wafer-supported flat Zn(AlO₂)₂ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**) and EDS spectrum (**h**), confirming the element composition of the as-synthesized Zn(AlO₂)₂ membrane. Note that the Si in (**h**) is detected from the silicon wafer substrate.

BiVO₄ membrane. 1.425 g of solid bismuth (III) nitrate pentahydrate was dissolved into 10 mL of HNO₃ solution (2.9 M) to obtain clarified Bi(NO₃)₃ solution (0.5 M). Subsequently, 0.7 mL of the freshly-prepared Bi(NO₃)₃ solution was mixed with 30 μ L of HCl solution (4 M) and transferred into a pretreated Petri dish. After a further addition of 2.15 mL of saturated NH₄VO₃ solution (~170 mM) obtained at 50 °C containing 120 μ L of HCl solution (4 M), the mixed solution was then allowed to stand still at room temperature for 5 h. During this process, the bright yellow BiVO₄ membrane gradually formed on the solution surface according to the following precipitation reaction:



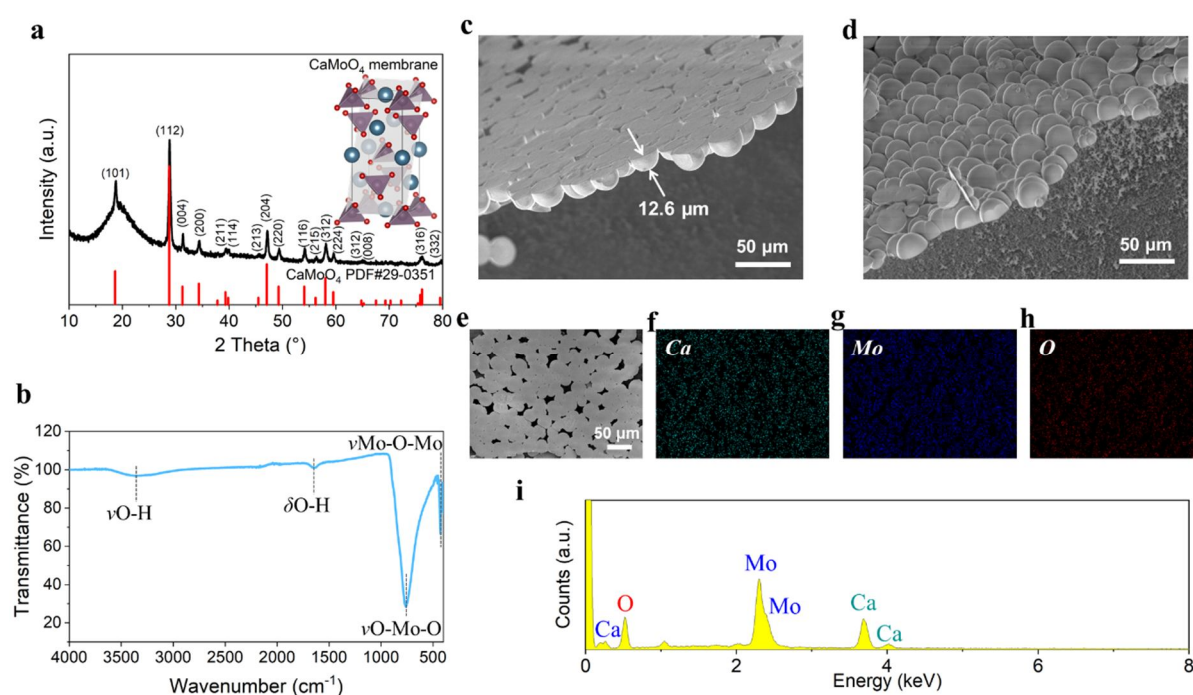
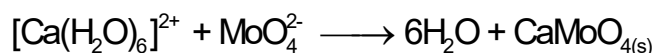
Supplementary Fig. 33. Structure, morphology and composition of the as-synthesized BiVO₄ membrane. **a**, XRD spectrum of the single-layer BiVO₄ membrane supported on the PMMA substrate. The inset shows the crystal structure of the orthorhombic BiVO₄ and highlights the preferred crystal orientation perpendicular to (100) plane. **b**, FTIR spectrum of the ground BiVO₄ membrane, revealing no other organic contaminants and residual reactants except for a few adsorbed water molecules in the membrane. **c**, **d**, SEM images of the freestanding BiVO₄ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, **i**, SEM image of the silicon wafer-supported flat BiVO₄ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**, **h**) and EDS spectrum (**i**), confirming the element composition of the as-synthesized BiVO₄ membrane. Note that the Si in (**i**) is detected from the silicon wafer substrate.

Ag₂CrO₄ membrane. The fresh Ag₂CrO₄ precipitate was firstly prepared by mixing 500 μ L of K₂CrO₄ (1 M) with 2 mL of AgNO₃ (250 mM) in a Eppendorf tube, then collected by centrifugation at 3000 rpm for 5 min and washed with DI water for three times. Subsequently, the as-prepared precipitate was dissolved in 2.5 mL of dilute ammonium hydroxide (~2 wt%) assisted by ultrasonic treatment. After a further addition of 150 μ L of K₂CrO₄ (1 M), the mixed solution was transferred into a pretreated Petri dish and kept at 55 °C for 30 min. During this period, the dark red crystalline Ag₂CrO₄ membrane gradually formed on the solution surface according to the following precipitation reaction:



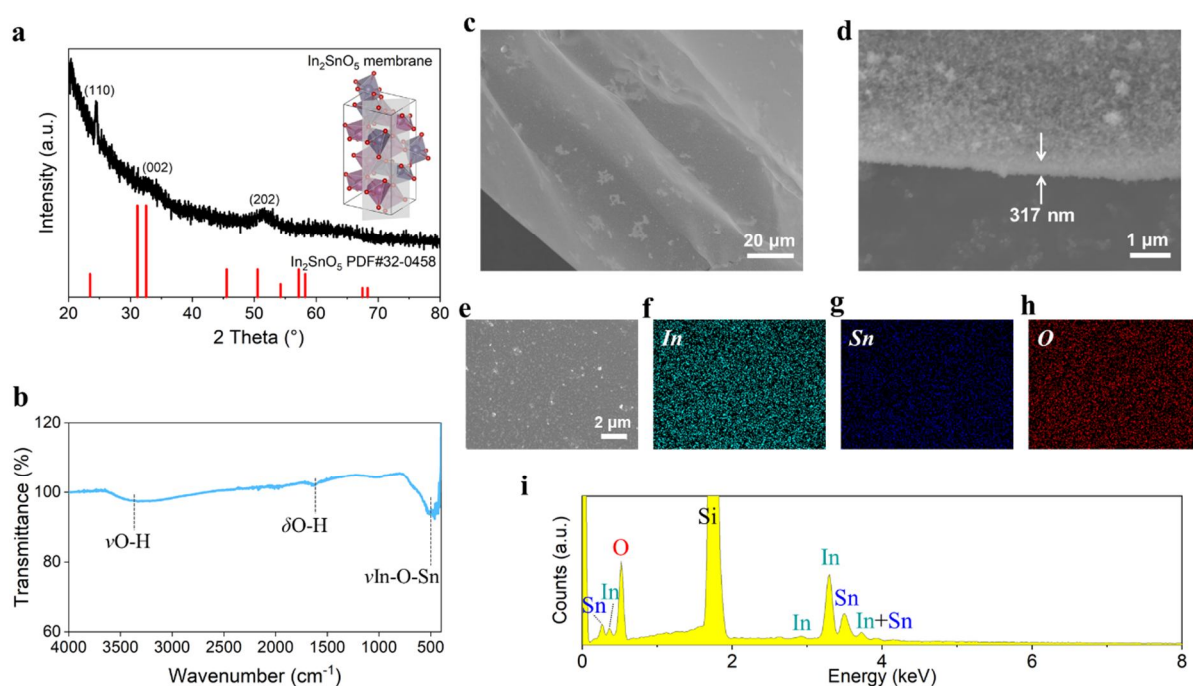
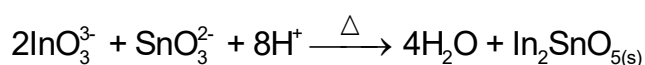
Supplementary Fig. 34. Structure, morphology and composition of the as-synthesized Ag₂CrO₄ membrane. **a**, XRD spectrum of the single-layer Ag₂CrO₄ membrane supported on the PMMA substrate. The inset shows the crystal structure of the orthorhombic Ag₂CrO₄ and highlights the preferred crystal orientation perpendicular to (010) plane. **b**, FTIR spectrum of the ground Ag₂CrO₄ membrane, revealing no organic contaminants and residual reactants in the membrane. **c**, **d**, SEM images of the freestanding Ag₂CrO₄ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, **i**, SEM image of the silicon wafer-supported flat Ag₂CrO₄ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**, **h**) and EDS spectrum (**i**), confirming the element composition of the as-synthesized Ag₂CrO₄ membrane.

CaMoO₄ membrane. 1 mL of CaCl₂ solution (650 mM) was quickly added into a pretreated Petri dish containing 2 mL of Na₂MoO₄ solution (1 M). After a gentle shake to fully mix the solution, the solution was allowed to stand still at room temperature for 3 h. During this process, the white CaMoO₄ membrane gradually formed on the solution surface according to the following precipitation reaction:



Supplementary Fig. 35. Structure, morphology and composition of the as-synthesized CaMoO₄ membrane. **a**, XRD spectrum of the single-layer CaMoO₄ membrane supported on the PMMA substrate. The inset shows the crystal structure of the tetragonal CaMoO₄ and highlights the preferred crystal orientation perpendicular to (112) plane. **b**, FTIR spectrum of the ground CaMoO₄ membrane, revealing no other organic contaminants and residual reactants except for a few adsorbed water molecules in the membrane. **c**, **d**, SEM images of the freestanding CaMoO₄ membrane showing the morphology viewed from the front side (**c**) and the reverse side (**d**), respectively. The membrane presents well-defined holey structure composed of the hemispherical particles. **e**, **f**, **g**, **h**, **i**, SEM image of the silicon wafer-supported flat CaMoO₄ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**, **h**) and EDS spectrum (**i**), confirming the element composition of the as-synthesized CaMoO₄ membrane.

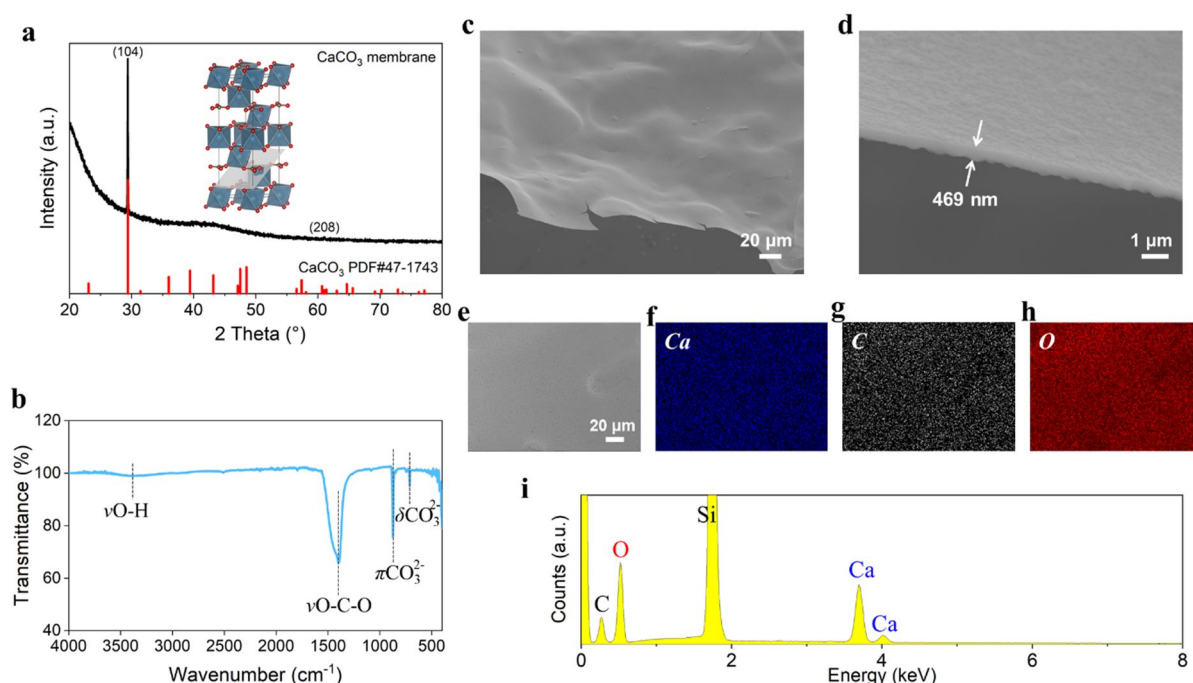
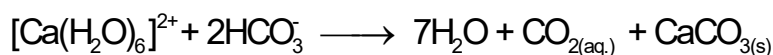
In₂SnO₅ membrane. The mixed solution containing 1.93 mL of fresh K₂SnO₃ solution (13.5 mM) and 70 μ L of dilute ammonium hydroxide (~10 wt%) was firstly transferred into a pretreated Petri dish and kept at 50 °C for 15 min. After a further addition of another mixed solution containing 920 μ L of InCl₃ solution (250 mM) and 60 μ L of NaOH solution (4 M), the solution was further kept at 50 °C for 30 min. Subsequently, 50 μ L of HCl solution (4 M) was added into the system, followed by letting it stand still at 50 °C for 2 h. During this process, the white and transparent In₂SnO₅ membrane gradually formed on the solution surface according to the following precipitation reaction:



Supplementary Fig. 36. Structure, morphology and composition of the as-synthesized In₂SnO₅ membrane. **a**, XRD spectrum of the three-layered In₂SnO₅ membrane supported on the PMMA substrate. The inset shows the crystal structure of the cubic In₂SnO₅ and highlights the preferred crystal orientation perpendicular to (110) plane. **b**, FTIR spectrum of the ground In₂SnO₅ membrane, revealing no other organic contaminants and residual reactants except for a few adsorbed water molecules in the membrane. **c**, **d**, SEM images of the freestanding In₂SnO₅ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, **i**, SEM image of the silicon wafer-supported flat In₂SnO₅ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**, **h**) and EDS spectrum (**i**), confirming the element composition of the as-synthesized In₂SnO₅ membrane. Note that the Si in (**i**) is detected from the silicon wafer substrate.

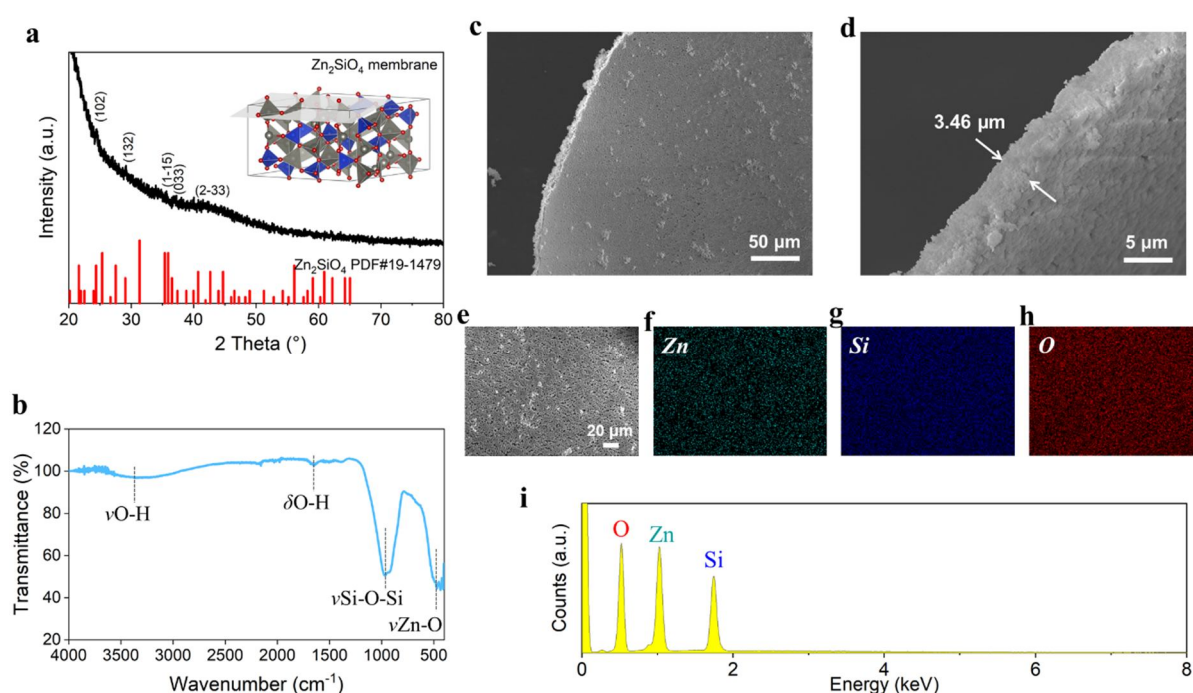
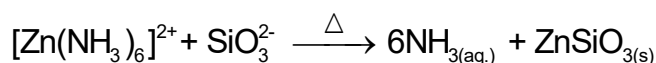
S2.8 Nonmetallates

CaCO₃ membrane. 0.5 mL of KHCO₃ solution (1 M) and 2.5 mL of CaCl₂ solution (0.4 M) were firstly cooled at 5 °C in a fridge for 1 h. Then, they were quickly mixed with each other in a pretreated Petri dish. The mixed solution was further allowed to stand still at room temperature for 2 h. During this process, the transparent CaCO₃ membrane gradually formed on the solution surface according to the following precipitation reaction:



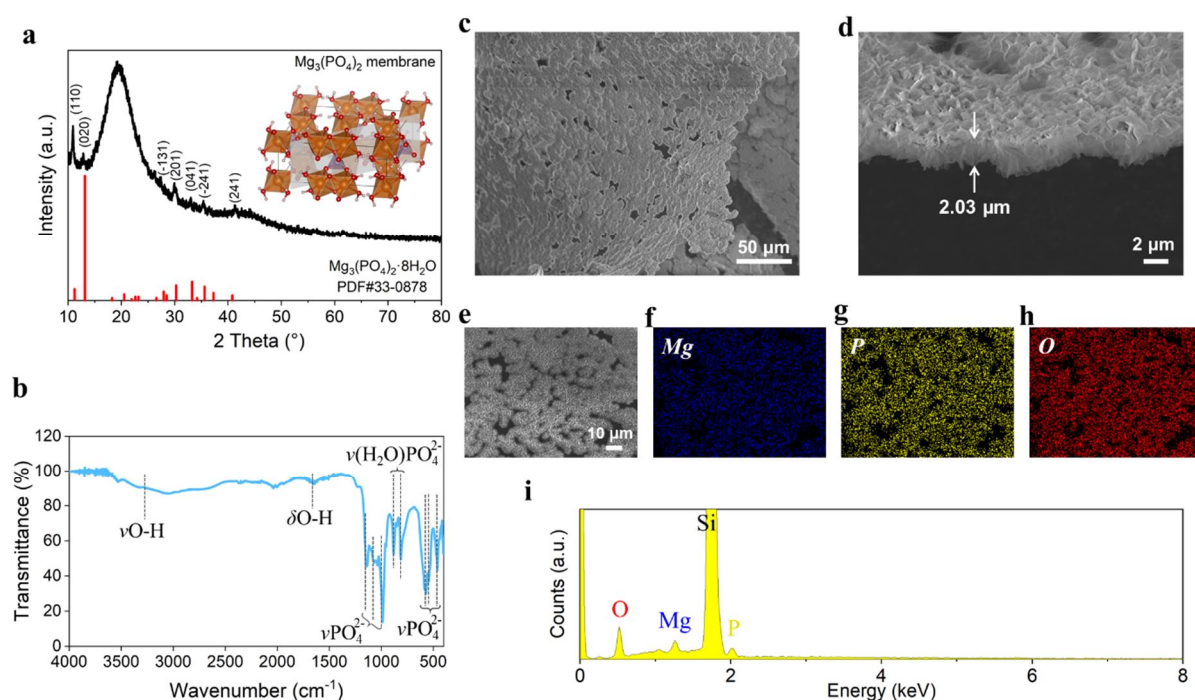
Supplementary Fig. 37. Structure, morphology and composition of the as-synthesized CaCO₃ membrane. **a**, XRD spectrum of the single-layer CaCO₃ membrane supported on the PMMA substrate. The inset shows the crystal structure of the hexagonal CaCO₃ and highlights the preferred crystal orientation perpendicular to (104) plane. **b**, FTIR spectrum of the ground CaCO₃ membrane, revealing no other organic contaminants and residual reactants except for a few adsorbed water molecules in the membrane. **c**, **d**, SEM images of the freestanding CaCO₃ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, **i**, SEM image of the silicon wafer-supported flat CaCO₃ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**, **h**) and EDS spectrum (**i**), confirming the element composition of the as-synthesized CaCO₃ membrane. Note that the Si in (**i**) is detected from the silicon wafer substrate.

Zn₂SiO₄ membrane. 80 μ L of ZnSO₄ solution (3.5 M) was firstly added into 9.2 mL of ammonium hydroxide (28-30 wt%) to produce [Zn(NH₃)₄]²⁺ solution, which was further mixed with 2 mL of Na₂SiO₃ solution (0.2 M). The mixture was then transferred into a pretreated Petri dish and then kept at 45 °C for 25 min. During this process, the colorless and transparent Zn₂SiO₄ membrane gradually formed on the solution surface according to the following precipitation reaction:



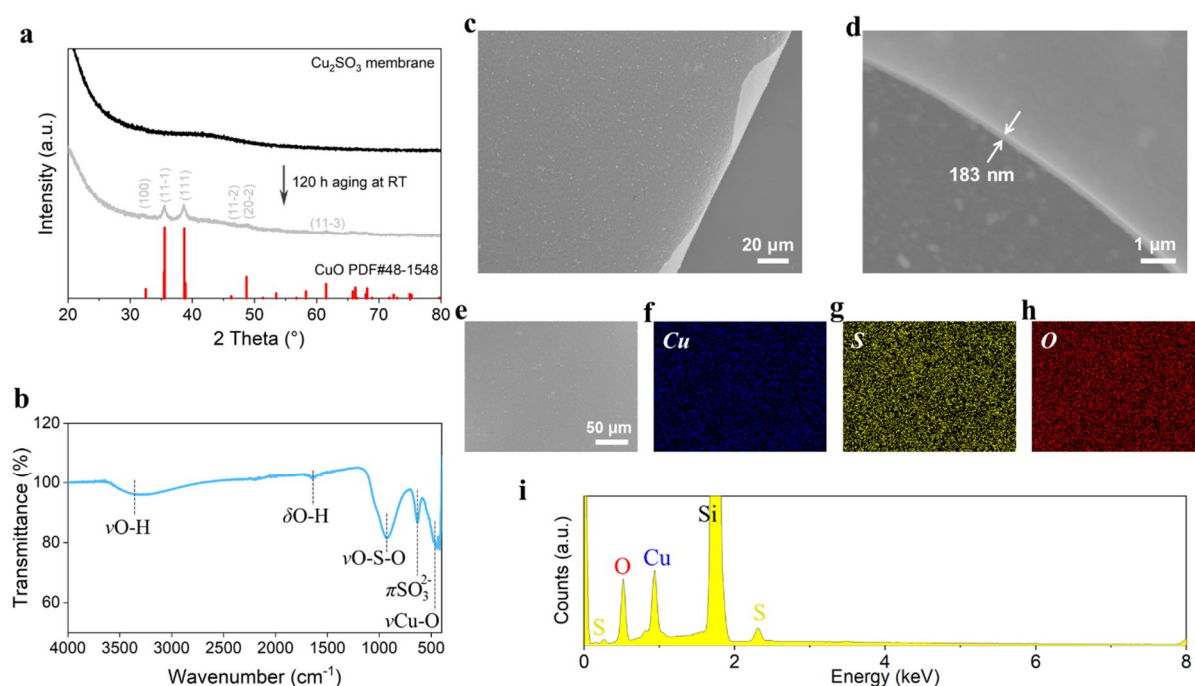
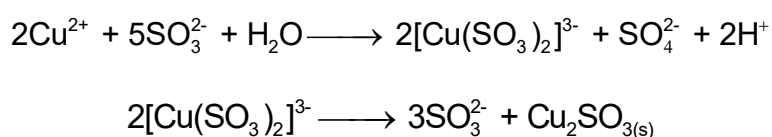
Supplementary Fig. 38. Structure, morphology and composition of the as-synthesized Zn₂SiO₄ membrane. **a**, XRD spectrum of the single-layer Zn₂SiO₄ membrane supported on the PMMA substrate. The inset shows the crystal structure of the triclinic Zn₂SiO₄ and highlights the preferred crystal orientation perpendicular to (102) plane. **b**, FTIR spectrum of the ground Zn₂SiO₄ membrane, revealing no other organic contaminants and residual reactants except for a few adsorbed water molecules in the membrane. **c**, **d**, SEM images of the freestanding Zn₂SiO₄ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, **i**, SEM image of the conductive carbon tape-supported flat Zn₂SiO₄ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**, **h**) and EDS spectrum (**i**), confirming the element composition of the as-synthesized Zn₂SiO₄ membrane.

Mg₃(PO₄)₂ membrane. 2.1 mL of Mg(NO₃)₂ solution (50 mM) was firstly added into a pretreated Petri dish and kept at 45 °C for 25 min. After a quick addition of mixed solution including 740 μL of fresh Na₃PO₄ solution (0.8 M) and 160 μL of H₃PO₄ solution (4 M), the Petri dish was further kept at 45 °C for 3 h. During this process, the colorless and transparent Mg₃(PO₄)₂ membrane gradually formed on the solution surface according to the following precipitation reaction:



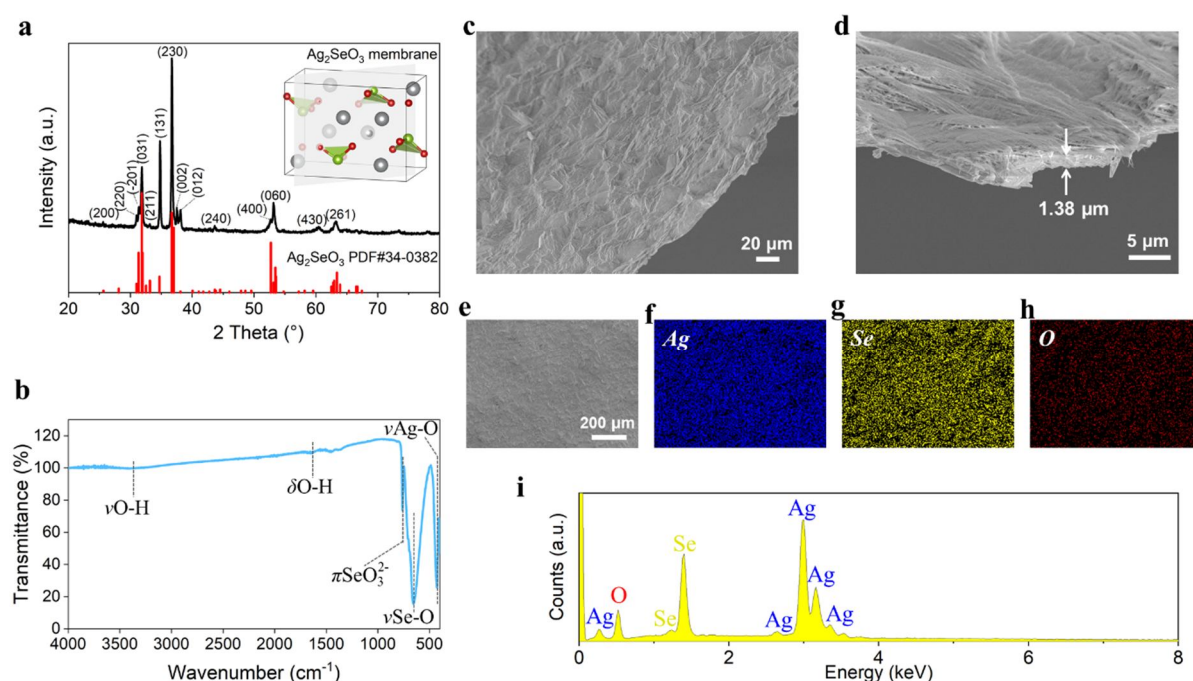
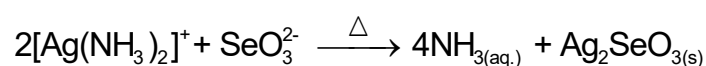
Supplementary Fig. 39. Structure, morphology and composition of the as-synthesized Mg₃(PO₄)₃ membrane. **a**, XRD spectrum of the single-layer Mg₃(PO₄)₃ membrane supported on the PMMA substrate. The inset shows the crystal structure of the monoclinic octahydrate Mg₃(PO₄)₃ and highlights the preferred crystal orientation perpendicular to (110) plane. **b**, FTIR spectrum of the ground Mg₃(PO₄)₃ membrane, revealing no other organic contaminants and residual reactants except for a few adsorbed water molecules in the membrane. **c**, **d**, SEM images of the freestanding Mg₃(PO₄)₃ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, **i**, SEM image of the silicon wafer-supported flat Mg₃(PO₄)₃ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**, **h**) and EDS spectrum (**i**), confirming the element composition of the as-synthesized Mg₃(PO₄)₃ membrane. Note that the Si in (**i**) is detected from the silicon wafer substrate.

Cu₂SO₃ membrane. 100 μL of CuCl₂ solution (1 M) was firstly mixed with 2.9 mL of fresh Na₂SO₃ solution (0.6 M). The mixed solution was then quickly transferred into a pretreated Petri dish and left to stand still at room temperature for 1 h. During this process, the colorless (the membrane will present a little green due to the partial oxidation if it is exposed to the air for more than five hours) and transparent Cu₂SO₃ membrane gradually formed on the solution surface according to the following redox reactions. Note that the moist Cu₂SO₃ membrane is very easy to be oxidized in air and can gradually convert into well-crystalline CuO membrane.



Supplementary Fig. 40. Structure, morphology and composition of the as-synthesized Cu₂SO₃ membrane. **a**, XRD spectra of the PMMA substrate-supported five-layered amorphous Cu₂SO₃ membrane and the derived CuO membrane after 120-hour aging in the reaction system at room temperature. **b**, FTIR spectrum of the ground Cu₂SO₃ membrane, revealing no other organic contaminants and residual reactants except for a few adsorbed water molecules in the membrane. **c**, **d**, SEM images of the freestanding Cu₂SO₃ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, **i**, SEM image of the silicon wafer-supported flat Cu₂SO₃ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**, **h**) and EDS spectrum (**i**), confirming the element composition of the as-synthesized Cu₂SO₃ membrane. Note that the Si in (**i**) is detected from the silicon wafer substrate.

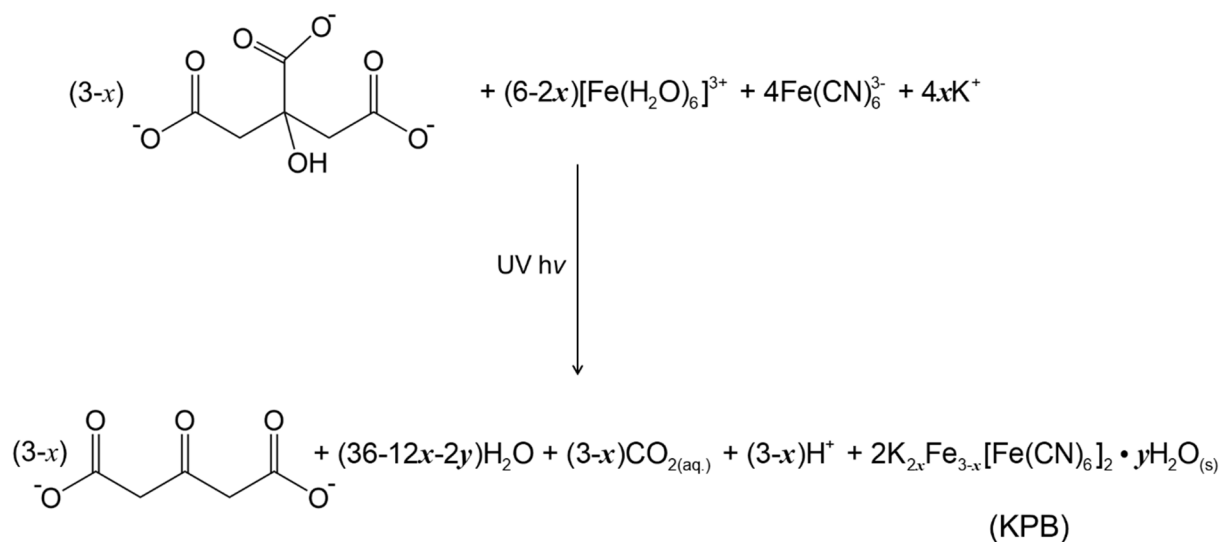
Ag₂SeO₃ membrane. 2 mL of freshly-prepared Na₂SeO₃ solution (0.5 M) was intensively mixed with 2 mL of AgNO₃ solution (250 mM) to produce Ag₂SeO₃ precipitate, which was centrifugally collected, cleaned by DI water for three times and then dissolved into 600 μ L of dilute ammonium hydroxide (~10 wt%). After a further addition of 2.4 mL of Na₂SeO₃ solution (65 mM), the mixed solution was transferred into a pretreated Petri dish and kept 40 °C for 40 min. During this process, the white Ag₂SeO₃ membrane gradually formed on the solution surface according the following precipitation reaction:

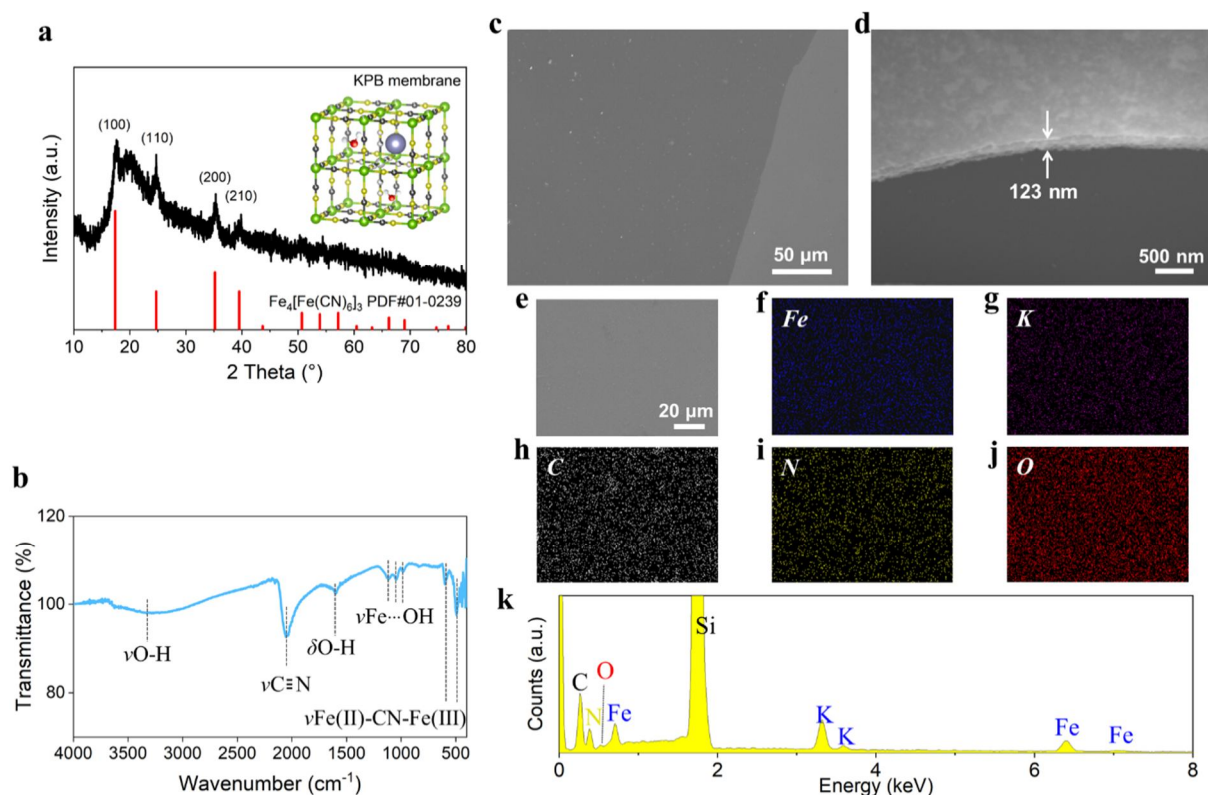


Supplementary Fig. 41. Structure, morphology and composition of the as-synthesized Ag₂SeO₃ membrane. **a**, XRD spectrum of the single-layer Ag₂SeO₃ membrane supported on the PMMA substrate. The inset shows the crystal structure of the monoclinic Ag₂SeO₃ and highlights the preferred crystal orientation perpendicular to (230) plane. **b**, FTIR spectrum of the ground Ag₂SeO₃ membrane, revealing no other organic contaminants and residual reactants except for a few adsorbed water molecules in the membrane. **c**, **d**, SEM images of the freestanding Ag₂SeO₃ membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, **i**, SEM image of the silicon wafer-supported flat Ag₂SeO₃ membrane (**e**) and the corresponding elemental mapping images (**f**, **g**, **h**) and EDS spectrum (**i**), confirming the element composition of the as-synthesized Ag₂SeO₃ membrane.

S2.9 Coordination polymers

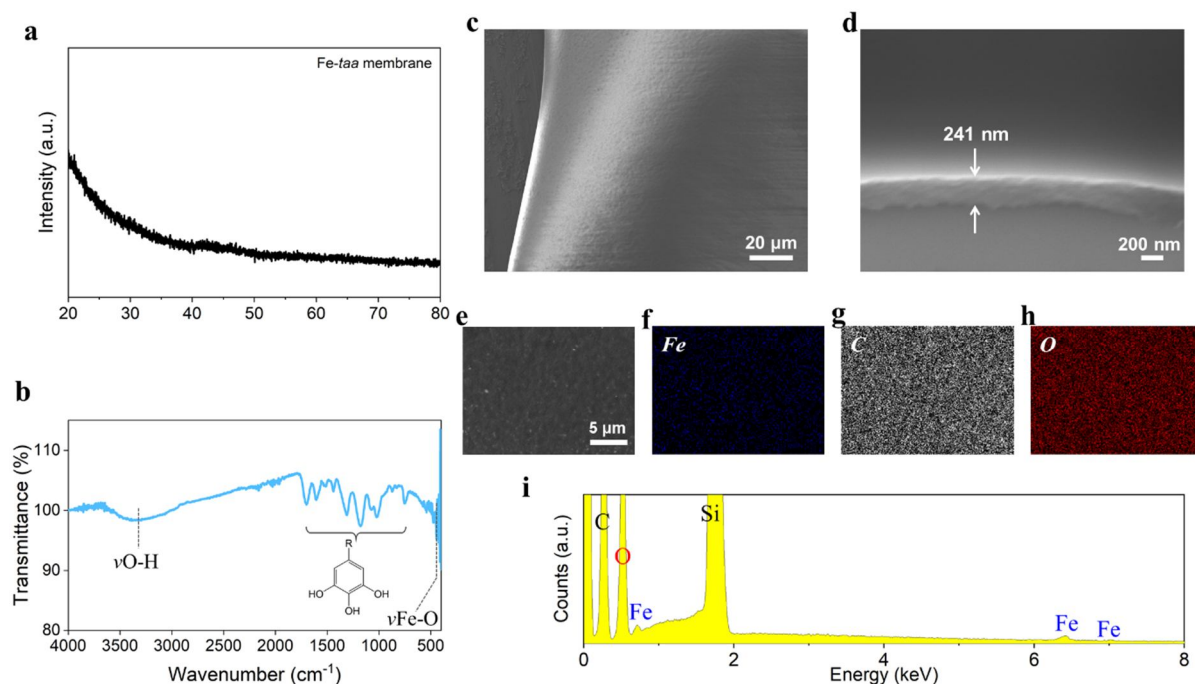
$K_{2x}Fe_{3-x}[Fe(CN)_6]_2 \cdot yH_2O$ (KPB) membrane. A pretreated Petri dish containing 3 mL mixed solution of ferric ammonium citrate $(NH_4)_xFe_yC_6H_5O_7$, 0.1 M) and potassium ferricyanide $(K_3[Fe(CN)_6])$, 0.2 M) was exposed to the Xenon light (CEL-PUV300-T8, Beijing China Education Au-light Technology Co., Ltd) with the energy density of 1000 w m^{-2} at room temperature for 15 min. During this process, the transparent and glaucous KPB membrane gradually formed on the solution surface according to the following precipitation reaction:





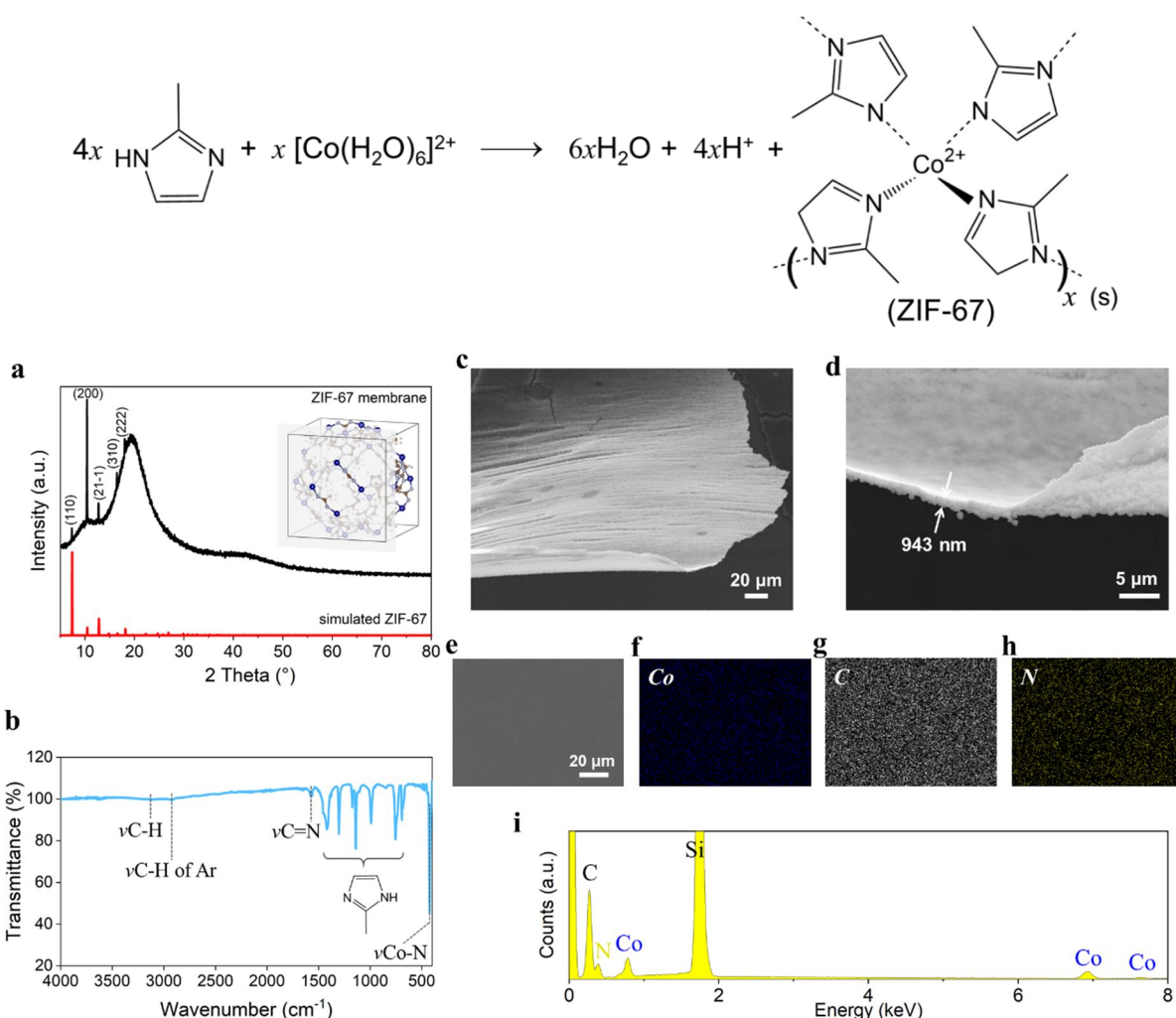
Supplementary Fig. 42. Structure, morphology and composition of the as-synthesized KPB membrane. **a**, XRD spectrum of the five-layered KPB membrane supported on the PMMA substrate. The inset shows the crystal structure of the cubic KPB. **b**, FTIR spectrum of the ground KPB membrane, revealing no other organic contaminants and residual reactants in the membrane. **c**, **d**, SEM images of the freestanding KPB membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, **i**, **j**, **k**, SEM image of the silicon wafer-supported flat KPB membrane (**e**) and the corresponding elemental mapping images (**f**, **g**, **h**, **i**, **j**) and EDS spectrum (**k**), confirming the element composition of the as-synthesized KPB membrane. Note that the Si in (**k**) is detected from the silicon wafer substrate.

[illegible]



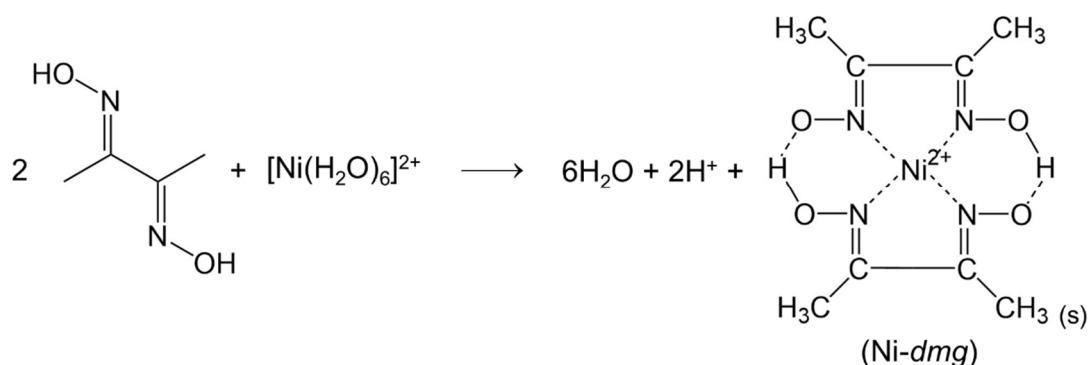
Supplementary Fig. 43. Structure, morphology and composition of the as-synthesized Fe-*taa* membrane. **a**, XRD spectrum of the seven-layered Fe-*taa* membrane supported on the PMMA substrate, showing its amorphous nature. **b**, FTIR spectrum of the ground Fe-*taa* membrane, revealing no other organic contaminants and residual reactants in the membrane. **c**, **d**, SEM images of the freestanding Fe-*taa* membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, **i**, SEM image of the silicon wafer-supported flat Fe-*taa* membrane (**e**) and the corresponding elemental mapping images (**f**, **g**, **h**) and EDS spectrum (**i**), confirming the element composition of the as-synthesized Fe-*taa* membrane. Note that the Si in (**i**) is detected from the silicon wafer substrate.

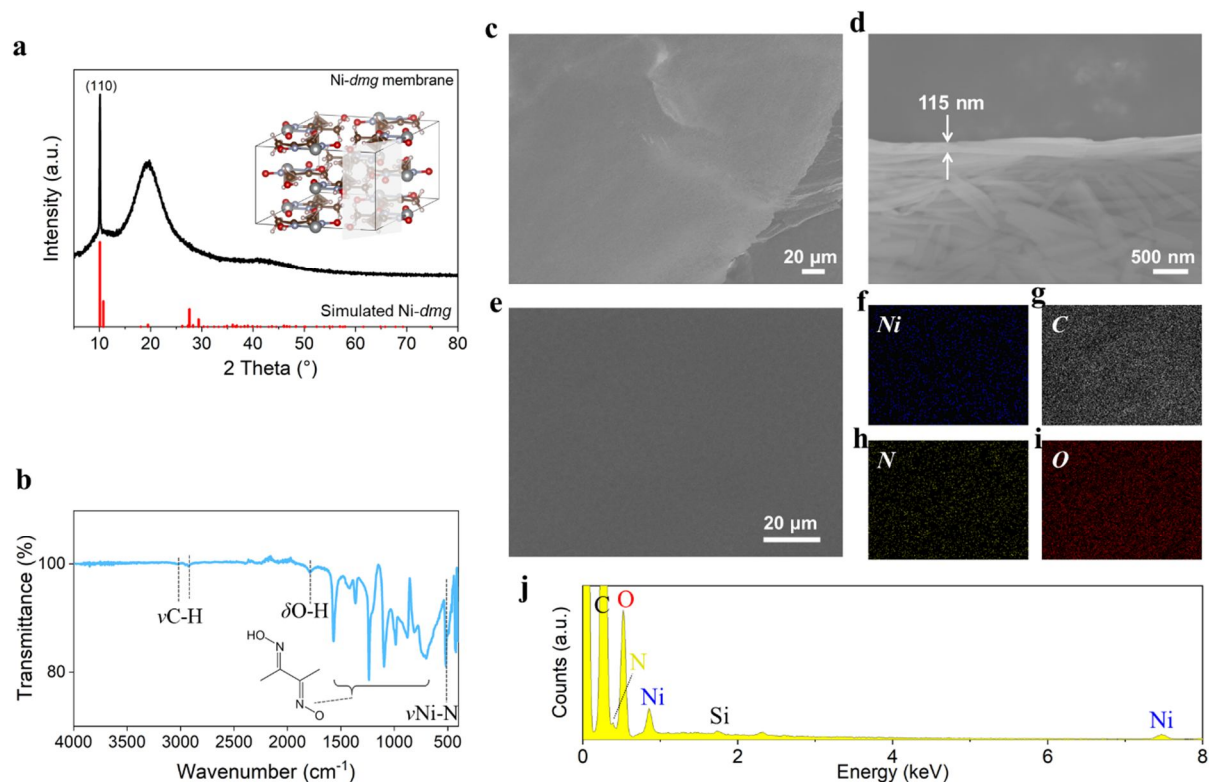
ZIF-67 membrane. A pretreated Petri dish containing 2 mL of 2-methylimidazole aqueous solution (1 M) was firstly cooled at 5 °C for 30 min. After a quick addition of 1 mL of cobalt acetate aqueous solution (250 mM) that was also precooled at 5 °C for 30 min, the mixed solution was further left to stand still at room temperature for 1 h. During this process, the transparent purple ZIF-67 membrane gradually formed on the solution surface according to the precipitation reaction:



Supplementary Fig. 44. Structure, morphology and composition of the as-synthesized ZIF-67 membrane. **a**, XRD spectrum of the single-layer ZIF-67 membrane supported on the PMMA substrate. The inset shows the crystal structure of the cubic ZIF-67 and highlights the preferred crystal orientation perpendicular to (100) plane. **b**, FTIR spectrum of the ground ZIF-67 membrane, revealing no other organic contaminants and residual reactants in the membrane. **c**, **d**, SEM images of the freestanding ZIF-67 membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, **i**, SEM image of the silicon wafer-supported flat ZIF-67 membrane (**e**) and the corresponding elemental mapping images (**f**, **g**, **h**) and EDS spectrum (**i**), confirming the element composition of the as-synthesized ZIF-67 membrane. Note that the Si in (**i**) is detected from the silicon wafer substrate.

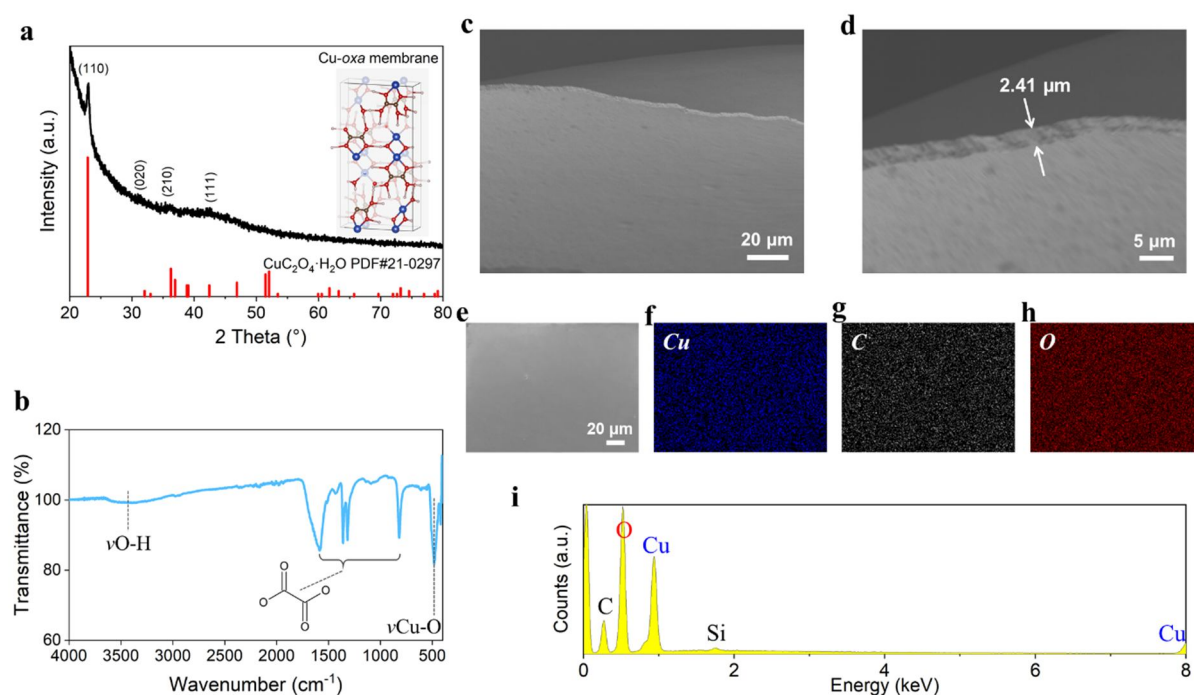
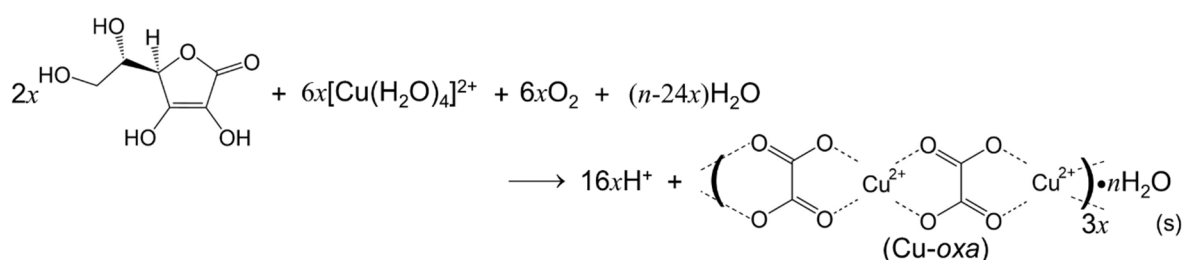
Ni(II)-dimethylglyoxime complex (Ni-*dmg*) membrane. Firstly, 20 mL of DI water and 0.2 g of dimethylglyoxime powder were mixed and kept at 50 °C for 4 hour. The mixture was further filtered to obtain the saturated dimethylglyoxime aqueous solution (~15 mM at 50 °C) by removing the suspended solids. Subsequently, 2 mL of the as-prepared dimethylglyoxime solution was transferred into a pretreated Petri dish while it was still hot. After an instant addition of 1 mL of NiCl₂ solution (70 mM), the mixed solution was allowed to stand still at room temperature for 1 h. During this process, the pink red Ni-*dmg* membrane gradually formed on the solution surface according to the following precipitation reaction:





Supplementary Fig. 45. Structure, morphology and composition of the as-synthesized Ni-*dmg* membrane. **a**, XRD spectrum of the single-layer Ni-*dmg* membrane supported on the PMMA substrate. The inset shows the crystal structure of the orthorhombic Ni-*dmg* and highlights the preferred crystal orientation perpendicular to (110) plane. **b**, FTIR spectrum of the ground Ni-*dmg* membrane, revealing no other organic contaminants and residual reactants in the membrane. **c**, **d**, SEM images of the freestanding Ni-*dmg* membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, **i**, **j**, SEM image of the silicon wafer-supported flat Ni-*dmg* membrane (**e**) and the corresponding elemental mapping images (**f**, **g**, **h**, **i**) and EDS spectrum (**j**), confirming the element composition of the as-synthesized Ni-*dmg* membrane. Note that the Si in (**j**) is detected from the silicon wafer substrate.

Cu(II)-oxalic acid complex (Cu-oxa) membrane. 0.8 mL of L-ascorbic acid solution (1 M) was dropwise added into 2.2 mL of CuCl₂ solution (0.1 M) in a pretreated Petri dish, then the mixed solution was allowed to stand still at room temperature for 80 h. During this process, the absinthe-green Cu-oxa membrane gradually formed on the solution surface according to the following precipitation reaction:



Supplementary Fig. 46. Structure, morphology and composition of the as-synthesized Cu-oxa membrane. **a**, XRD spectrum of the single-layer Cu-oxa membrane supported on the PMMA substrate. The inset shows the crystal structure of the orthorhombic Cu-oxa and highlights the preferred crystal orientation perpendicular to (110) plane. **b**, FTIR spectrum of the ground Cu-oxa membrane, revealing no other organic contaminants and residual reactants in the membrane. **c**, **d**, SEM images of the freestanding Cu-oxa membrane showing the overall morphology (**c**) and the zoom-in cross section (**d**). **e**, **f**, **g**, **h**, **i**, SEM image of the silicon wafer-supported flat Cu-oxa membrane (**e**) and the corresponding elemental mapping images (**f**, **g**, **h**) and EDS spectrum (**i**), confirming the element composition of the as-synthesized Cu-oxa membrane. Note that the Si in (**i**) is detected from the silicon wafer substrate.

S2.10 Summary of the membrane library constructed by SLIS strategy

Supplementary Table 1. Parameter summary for preparing various membranes through SLIS strategy.

No.	materials	Reaction type	T (°C)	Particle Size (nm)	t_{criti} (min) ^a	t_{termi} (h) ^b	Thickness (nm) ^c	H (%) ^d	η_{conv} (%) ^e
1	Ag	redox	20	56	5 ± 0.5	0.5	189 ± 3	0.68	9.76
2	Pt	redox	55	47	15 ± 1	1	476 ± 9	0.24	41.86
3	Au	redox	50	104	40 ± 3	6	212 ± 11	35.77	7.29
4	Pd	redox	55	119	145 ± 15	5	226 ± 6	33.86	33.84
5	S	redox	20	700	55 ± 5	4	752 ± 24	31.30	1.60
6	CeO ₂	redox	50	43	45 ± 2	2.5	57 ± 3	0.76	0.91
7	MnO ₂	redox	20	24	5 ± 0.5	1.5	98 ± 4	2.31	1.08
8	RuO ₂	redox	20	87	480 ± 50	12	94 ± 8	11.36	20.99
9	WO ₃	redox	55	49	210 ± 30	10	353 ± 13	< 0.05	5.36
10	WS ₂	redox	55	52	180 ± 30	5	83 ± 5	15.77	3.91
11	Cu ₂ SO ₃	redox	20	96	40 ± 5	1	183 ± 17	5.83	5.71
12	KPB	redox	20	34	4 ± 0.5	0.25	123 ± 12	1.05	0.24
13	TiO ₂	hydrolysis	20	73	5 ± 0.5	1	108 ± 8	< 0.05	12.74
14	FeOOH	hydrolysis	65	31	115 ± 15	3	47 ± 4	4.17	1.38
15	Al(OH) ₃	hydrolysis	20	148	10 ± 1	0.33	831 ± 12	< 0.05	10.69
16	La(OH) ₃	hydrolysis	20	389	15 ± 3	0.58	871 ± 23	0.70	6.47
17	Cd(OH) ₂	hydrolysis	50	104	5 ± 0.5	0.33	482 ± 19	10.71	18.81
18	In ₂ SnO ₅	hydrolysis	50	75	70 ± 15	2	317 ± 42	17.65	7.63
19	ZnS	precipitation	40	137	5 ± 0.5	0.33	68 ± 3	28.16	0.56
20	FeS	precipitation	20	181	35 ± 5	1	335 ± 7	1.08	28.42
21	Cu ₈ S ₅	precipitation	45	93	2 ± 0.3	0.42	527 ± 26	1.42	10.86
22	Dy ₂ S ₃	precipitation	20	62	10 ± 1	1.5	264 ± 8	1.93	17.98
23	Cu(OH) ₂	precipitation	45	466	35 ± 5	1.5	1170 ± 55	17.4	5.69
24	AgCl	precipitation	35	10237	10 ± 1.5	0.67	8300 ± 126	0.71	43.63
25	CuBr	precipitation	40	721	10 ± 1	0.67	3140 ± 51	< 0.05	19.45
26	PbI ₂	precipitation	5	153	35 ± 10	2	51 ± 5	2.05	4.28
27	Ba ₂ ClF ₃	precipitation	20	3989	200 ± 30	4	1970 ± 87	33.26	13.32
28	SmF ₃	precipitation	55	60	670 ± 30	20	68 ± 6	3.71	1.11
29	Zn(AlO ₂) ₂	precipitation	45	51	10 ± 1	0.33	67 ± 8	8.04	0.49
30	CaMoO ₄	precipitation	20	15233	125 ± 5	3	12600 ± 366	4.19	26.04
31	Ag ₂ CrO ₄	precipitation	55	83428	10 ± 1	0.5	3760 ± 97	< 0.05	20.46
32	BiVO ₄	precipitation	20	439	12 ± 3	5	264 ± 39	8.39	1.23
33	CaCO ₃	precipitation	20	617	20 ± 3	2	469 ± 32	5.17	1.05
34	Zn ₂ SiO ₄	precipitation	45	224	15 ± 3	0.42	3460 ± 126	13.33	39.30
35	Ag ₂ SeO ₃	precipitation	40	4142	15 ± 3	0.67	1380 ± 103	< 0.05	9.78
36	Mg ₃ (PO ₄) ₂	precipitation	45	3855	130 ± 20	3	2030 ± 249	10.25	41.91
37	Fe- <i>taa</i>	precipitation	20	388	50 ± 5	3	241 ± 18	0.77	0.20

38	ZIF-67	precipitation	5	638	10 ± 1	1	943 ± 187	3.38	1.49
39	Cu-oxa	precipitation	20	360	4020 ± 300	80	2410 ± 144	< 0.05	13.24
40	Ni-dmg	precipitation	20	573	10 ± 1	1	115 ± 13	10.24	0.83

^a t_{criti} is the critical time once the formation of the quasi-biocontinuous network. The value is based on the continuous monitoring (interval observation instead for these long-term reactions) on three independent reaction systems and presented as mean $\pm$ SD. ^b t_{termi} is the terminal time for the reaction adopted in the study. ^c Thickness value is based on the measurements on three dependent samples and presented as mean $\pm$ SD. ^d Through-hole ratio (H) denotes the ratio of the whole projected area of through holes and that of the membrane, which is analyzed from the representative SEM image. The membrane is regarded to be compact when the calculated H value is less than 0.05 %. ^e Calculation of the convert ratio (η_{conv}) is based on the metal element, namely the ratio of its content in the as-prepared membrane and the initial amount in the precursor. The weighted average value is adopted for these membranes with more than one kind of metal element.

Section S3. Examples of Innovative Utility of the SLIS-mediated Inorganic Membranes.

The as-established SLIS-mediated membrane library has provided a diversity of potential 2D mediators for various energy coupling and/or conversion (Extended Data Fig. 2c, Supplementary Tab. 2), thus laying the foundation for unique applications from the perspective of the generalized notion of membrane. Beyond the conventional role as a selective barrier to the matter flows (gas, fluid and solute), the concept of membrane can also extend to mediate a selective resistance/resonance to a certain energy flow that is passing through/transporting into it, typically including mechanical wave, photon stream, magnetic field, electric field and thermal radiation. Therefore, in contrast to the traditional matter flow-oriented membranes with well-known applications in particulate sieving, ionic filtration and gas separation, we provide two intriguing examples of innovative utility to demonstrate the energy flow-oriented membranes, *i.e.*, the holey Ag membrane as a selective barrier for photon streams and the dense AgCl membrane as a thermal-transparent acoustic damping. They may help to understand the practical value of developing a general synthetic methodology towards those unrevealed energy-responsive inorganic membranes.

Example 1. Holey Ag membrane as a selective barrier for photon streams

As shown in Supplementary Fig. 47, due to the interaction of the light with electronic resonances at the surface of the metallic Ag matrix (Supplementary Fig. 47a), the prepared holey Ag membrane with subwavelength through holes have been confirmed to selectively allow the light to pass through. Only these photons of high frequency can penetrate through the holey membrane with negligible obstruction, and most cutoff light that is of long wavelength will be reflected through the efficient specular reflection (Supplementary Fig. 47b and c). Moreover, the cutoff wavelength can be flexibly adjusted by tuning the through-hole parameters (Supplementary Fig. 47d-g). Realistically, the continuous tunability has been well demonstrated in Fig. 3a and Supplementary Section S8.2. As the reaction goes on, the hole size continues to reduce with continuously-sharpened size distribution. One can predictably terminate the reaction once the evolving holey membrane presents the desired optical property. This example demonstrates a generalized membrane that can sieve the photons based on their energy. For the researchers in the fields of optics and electromagnetics, such a developed holey membrane may

inspire the membrane-based advanced optical filters, wavelength splitters, display, anti-counterfeiting, waveguide and so on.

Example 2. Dense AgCl membrane as a thermal-transparent acoustic damping

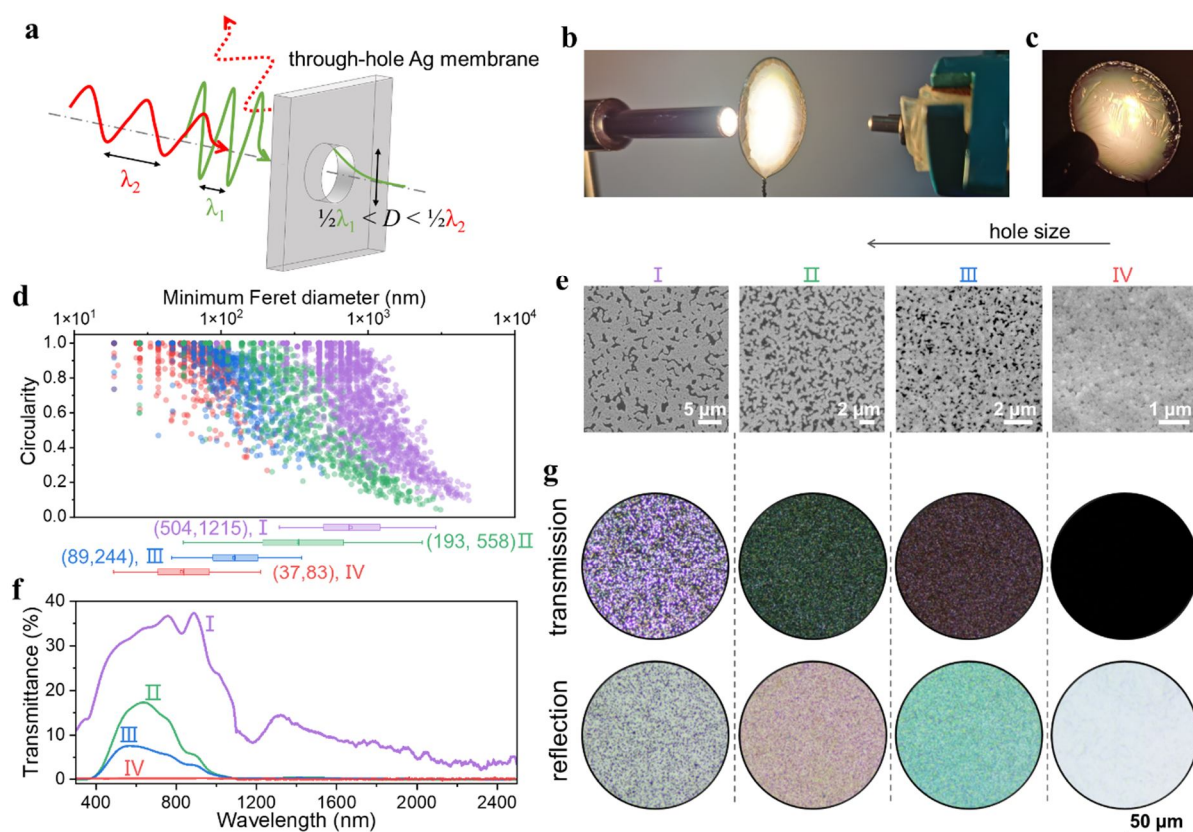
The matrix of AgCl is a kind of superplastic inorganic with plenty of active slip planes at room temperature (Supplementary Fig. 48a and b). Such a property indicates the potential consumption of the mechanical/acoustic vibration through the internal slipping. On the other hand, AgCl is also a good candidate to infrared window as its complete transmittance in a wide infrared region (Supplementary Fig. 23b). Supplementary Fig. 48c-f demonstrates the plastic AgCl membrane serving as a 2D high-frequency (megahertz-level) acoustic damping for infrared window. Most of the vibration energy that is transmitted through the AgCl membrane is well consumed compared to that in the blank case (Supplementary Fig. 48c). More intriguingly, the as-prepared AgCl membrane is further proven to be flexibly rasterized/patterned by the short-wave laser, which depends on the localized Ag particles deposition through the fast photochemical decomposition of the raw AgCl matrix (Supplementary Fig. 48d and e). The rasterized AgCl membrane is further revealed to a programmable 2D mediator enabling selective control the permeation of the thermal radiation (Supplementary Fig. 48f). This example demonstrates a generalized membrane that can selectively interact with the mechanical wave and thermal radiation, which is of great value for manufacturing customized infrared grating with resistance to mechanical interference.

Based on the above practical examples of the generalized membranes, it is easy to explain the different standards of the energy flow-oriented membranes in contrast to that of the traditional matter flow-oriented ones, which necessitate the well-defined porous structures with high controllability. Notably, as demonstrated in example 1, it is important to emphasize that the application involving the near-infrared band sieving necessitates the macroscopic holes instead of the micropores that are used for the traditional gas or ion filtering. In addition, the holey network with irregular through holes (samples I and II), that may be regarded as the low structural quality for the traditional matter flow-oriented membranes, is also useful in these photon flow-oriented applications. As demonstrated example 2, even the completely dense membrane without any pores is useful in selectively interacting with some specific energy flows.

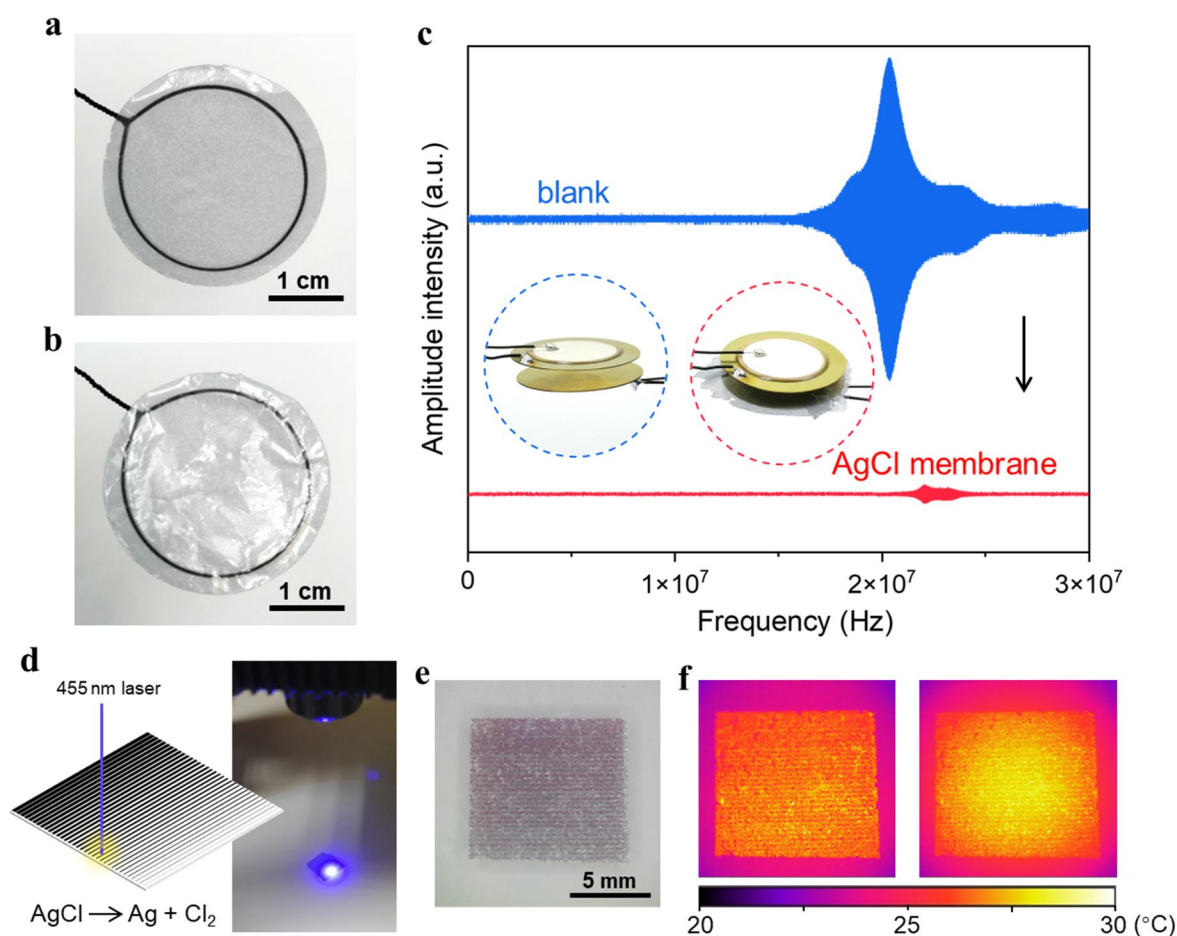
Taken together, for most energy flows, the assessment of the membrane quality does not conform to the standards of the pore quality/parameters, but primarily to consider the intrinsic coupling ability of the 2D mediator with a specific energy. Despite the fact that the abundant inorganic materials can offer a variety of options for different energy couplings, there are not many accessible inorganic membranes, which severely hindered the practical applications of the “energy flow-oriented membranes”. This perspective underpins the essential motivation of this work, that is to develop a general synthetic methodology to various energy-responsive inorganic membranes.

Supplementary Table 2. Potential conversion pathways between various energy types mediated by these functional membranes presented in the library.

Output Input	Mechanical	Electromagnetic	Thermal	Electrical	Magnetic	Chemical
Mechanical		ZnS	AgCl	ZnS, WS ₂ , Zn ₂ SiO ₄		
Electromagnetic		S, TiO ₂ , CeO ₂ , WO ₃ , ZnS, Dy ₂ S ₃ , SmF ₃ , Zn(AlO ₂) ₂ , CaMoO ₄ , ZnSiO ₄	MnO ₂ , RuO ₂ , FeS, Cu ₈ S ₅ , WS ₂ , Cu(OH) ₂ , KPB, Fe- <i>taa</i>	TiO ₂ , CeO ₂ , WO ₃ , Ba ₂ ClF ₃ , PbI ₂ , BiVO ₄	KPB	TiO ₂ , CeO ₂ , WO ₃ , FeS, ZnS, BiVO ₄ , CaMoO ₄ , In ₂ SnO ₅ , Ag ₂ SeO ₃
Thermal	Pd, Ag, Pt, Au	ZnS, Zn(AlO ₂) ₂ , CaMoO ₄		FeS, Cu ₈ S ₅		Pd, Ag, Pt, Au, MnO ₂ , CeO ₂ , WO ₃ , FeS, Cu ₈ S ₅
Electrical		CeO ₂ , ZnS	Pd, Ag, Pt, Au		Pd, Ag, Pt, Au	Pd, Ag, Pt, Au, RuO ₂ , FeOOH, KPB, ZIF- 67, Ni- <i>dmg</i> , Cu- <i>oxa</i>
Magnetic	FeS, Dy ₂ S ₃ , FeOOH		FeS, Dy ₂ S ₃	Pd, Ag, Pt, Au		
Chemical		RuO ₂				Pd, Pt, Au, MnO ₂ , RuO ₂ , CuBr, Ag ₂ CrO ₄ , Cu ₂ SO ₃



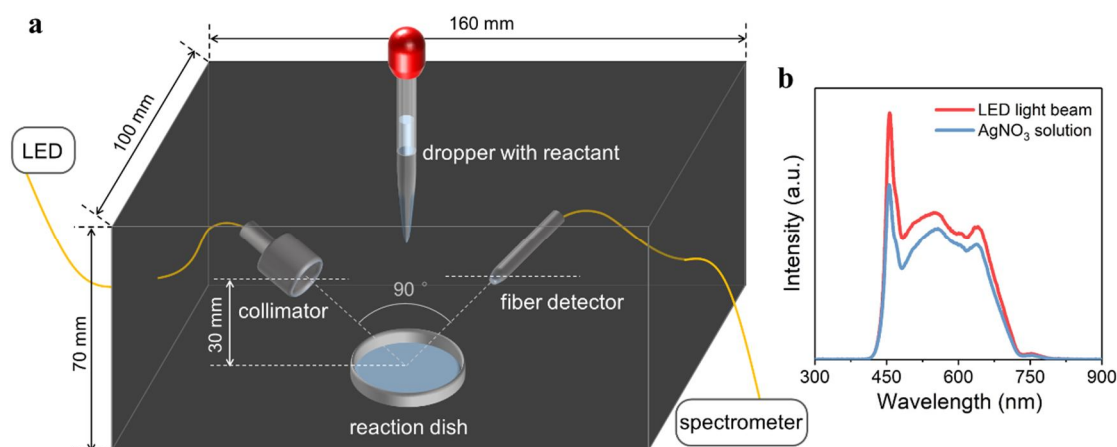
Supplementary Fig. 47. Holey Ag membrane as a selective barrier for photon streams. **a**, Schematic diagram of the unusual transmission of light through a subwavelength hole in a thin Ag membrane. The cutoff wavelength of the transmission light is dependent on the through-hole size, which is approximately twice the diameter of the hole. **b**, **c**, Digital photographs of a holey Ag membrane illuminated with white light taken from the front side (transmission, **b**) and the back side (reflection, **c**), respectively. The light emits from the left optical fiber, selectively passes through the holey Ag membrane (the membrane corresponds to sample II in **e**) into the right optical detectors (Maya2000 and NIRQuest⁺ spectrometers, Ocean Optics). Most of the cutoff light with long wavelength is reflected through specular reflection. Notably, the membrane looks light green from the transmission view, but complementary yellow red from the reflected view. **d**, **e**, Hole parameters (**d**) of the four representative holey Ag membranes, their structures are illustrated by the SEM images in (**e**). The bottom box chart in (**d**) shows the statistical result of the minimum Feret diameters of the through holes in different membranes. The caps indicate the $1.5\times$ interquartile range. The box shows 25-75 percentiles with the marked median (transverse inside) and mean (box inside). **f**, Transmission spectra for the four holey Ag membranes. **g**, Optical micrographs of the holey Ag membranes illuminated with white light source obtained under the transmission mode (first row) and reflectance mode (second row), respectively.



Supplementary Fig. 48. Dense AgCl membrane as an acoustic damping for infrared window. **a, b**, Digital photographs of the as-prepared dense AgCl membrane before **(a)** and after mechanical plastic deformation at room temperature **(b)**. **c**, Frequency-dependent acoustic amplitudes for the two cases as shown in the inset, demonstrating the high-frequency acoustic damping of the dense AgCl membrane. Two piezo buzzers of 20 mm in diameter are placed facing one another with a gap of 6 mm. The bottom one serves as the generator of acoustic wave, and the top one serves as the vibration transducer. In contrast to the blank case with the air in between, a piece of AgCl membrane is placed in between the two buzzers. **d, e**, Digital photograph of the process **(d)** for producing rasterized AgCl membrane **(e)** through a 455 nm laser (K6-promax laser engraver, WAINLUX). The left schematic diagram illustrates the patterned mechanism. The region scanned by the laser beam will be deposited with the Ag particles through the photochemical decomposition of the raw AgCl. **f**, Infrared images of the as-prepared rasterized AgCl membrane before and under the illustration of a fiber optic halogen illuminator (Techniquip FOI-150) from the back side, respectively. The two images share the same bottom temperature bar.

Section S4. Methods and Additional Data for Revealing Ag Membrane Evolution.

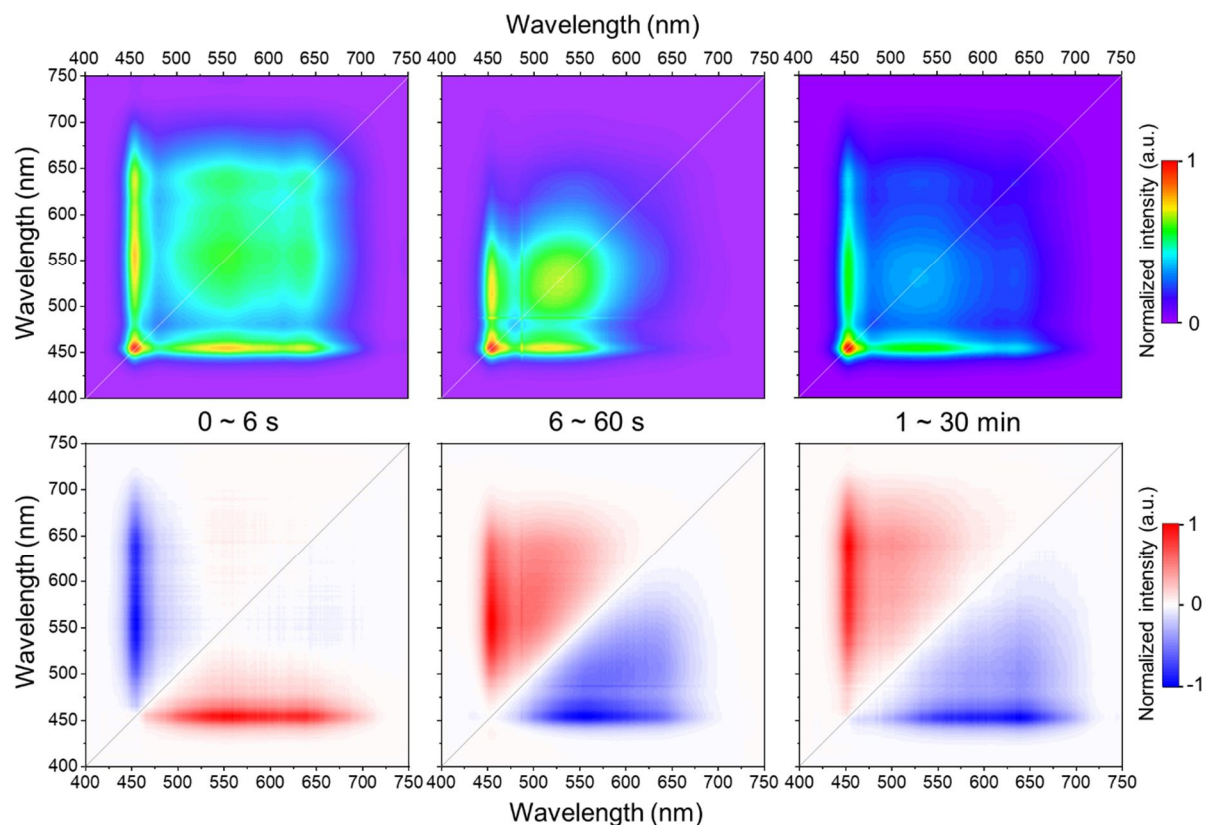
S4.1 In-situ reflectance spectra recording Ag membrane formation



Supplementary Fig. 49. Apparatus for recording the in-situ reflectance spectra. a, Schematic diagram of the setup for collecting the in-situ reflectance spectra of the air-liquid interface during the preparation of Ag membrane. The reaction was performed in an opaque chamber. By quickly adding 1.5 mL of the reductant solution containing D(+)-glucose (250 mM) and NaOH (50 mM) in the dropper, the silver mirror reaction was instantly ignited. The incident light source was set at the height of 30 mm above the on-going reaction solution surface with a tilted angle of 45° to the horizontal plane. A right angle was fixed between the incident light source and the fiber detector. The time-resolved reflectance spectra of the solution surface throughout the Ag membrane formation can thus be recorded by the spectrometer. The drastic variations in the reflectance, which is comprehensively resulted from the size-dependent surface plasmon resonance absorption of Ag particles and the linkage geometry-related specular reflection of Ag patches, help to identify the critical moments associated with the structural evolutions of floating silver solids. These floating solids at the critical moments can be accordingly collected for further analyses. **b,** Spectrum of the employed LED light source and the reflectance spectrum of the aqueous AgNO₃ solution before adding the reductant solution.

2D correlation analysis of the segmented reflectance spectra (0 to 6 s, 6 to 60 s and 1 to 30 min) between 400 to 750 nm, including the generation of the synchronous and asynchronous 2D correlation maps (Supplementary Fig. 48), was performed in Matlab by using the previously-reported algorithm^{2,3}. Notably, all the cross-peaks/bands in the three synchronous 2D correlation maps that correspond to different time periods are positive, suggesting that these correlated signals present the same variation trend over time. For the initial period of 0 to 6 s,

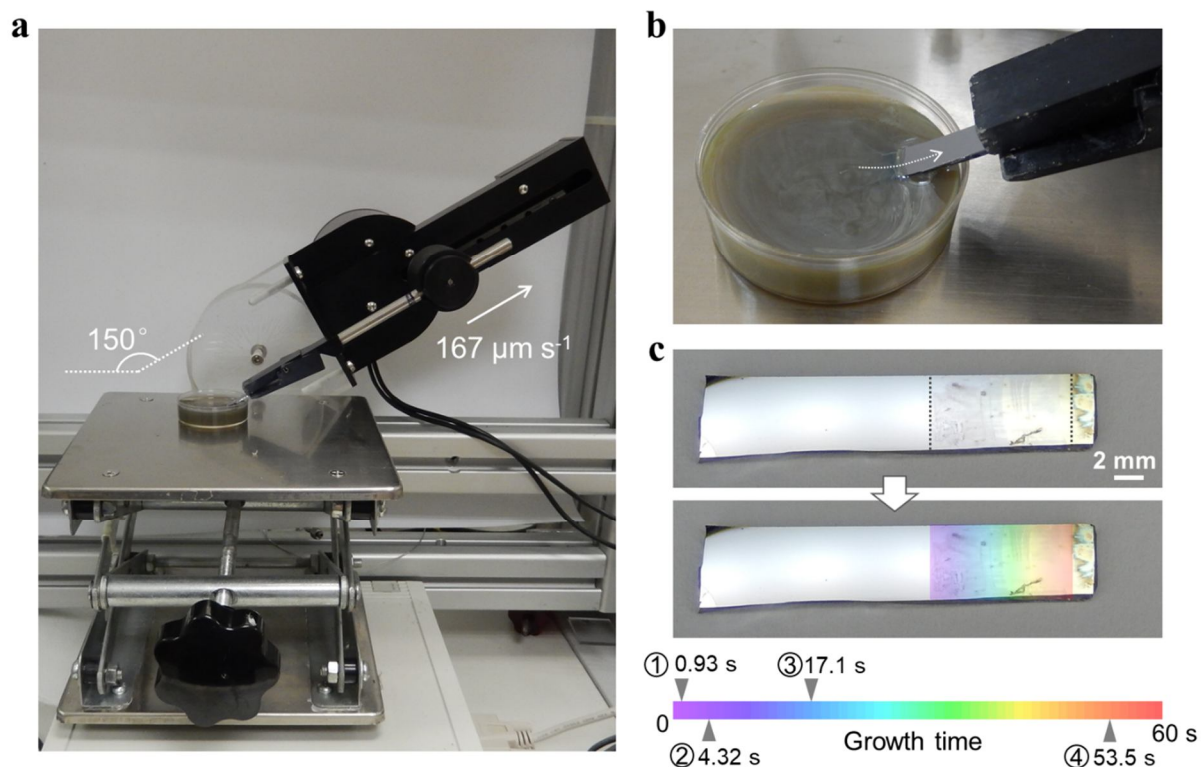
the asynchronous spectrum reveals three cross-peaks, respectively centered at [556-455 nm (+)], [637-455 nm (+)] and [637-556 nm (-)]. During 6 to 60 s of the reaction process, the asynchronous spectrum reveals two cross-peaks, respectively centered at [559-455 nm (-)] and [571-494 nm (-)]. For the long-term period of 1 to 30 min, two cross-peaks, which are respectively centered at [556-455 nm (-)], [637-455 nm (-)] and [637-528 nm (-)], are identified in the asynchronous spectrum. By using Noda's rules²⁻⁴, we can then extract the information of the event order according to the signs of the corresponding cross-peaks in the synchronous and asynchronous spectrum. During the first 6 s, the decrease of the reflection intensity at 556 nm occurs prior to that at 637 nm and the reference wavelength of 455 nm. This period is dominated by an explosive formation of numerous floating Ag nanoparticles, which have a wide wavelength absorption in visible region of a peak at about 556 nm. During the middle period of 6s to 60 s that corresponds to the Brownian clusters formation and their aggregations, only the reflection between 450 and ~620 nm is found to gradually increase. The intensity increase for the characteristic peak at around 556 nm occurs behind that of the referenced peak of 455 nm. This result confirms the continuous supply of isolated nanoparticles with maintained size to the aqueous surface during the Brownian clusters formation and their aggregations. Furthermore, the size of the Brownian clusters/their initial aggregation at this period is limited to enable a full spectrum reflection. The later period of the reaction is mainly dominated by the reflection behavior of the growing Ag slices/membrane, which become large enough to expend the reflection range to longer wavelength. The lagged increase in the reflection intensity at ~556 nm behind that at 637 nm and the reference wavelength of 455 nm suggests the supplying Ag nanoparticles. Compared to the synchronous 2D correction map of the middle period, the normalized intensity of the cross-peak of [556-455 nm (+)] is significantly reduced. These findings are in line with the theoretical prediction, namely that the newborn Ag nanoparticles will be instantly captured by the solid network.



Supplementary Fig. 50. Segmented synchronous (top) and asynchronous (bottom) 2D correlation maps of the dynamic reflectance spectra. These maps were obtained over the periods between 0 to 6 s (first column), 6 to 60 s (second column) and 1 to 30 min (third column), respectively.

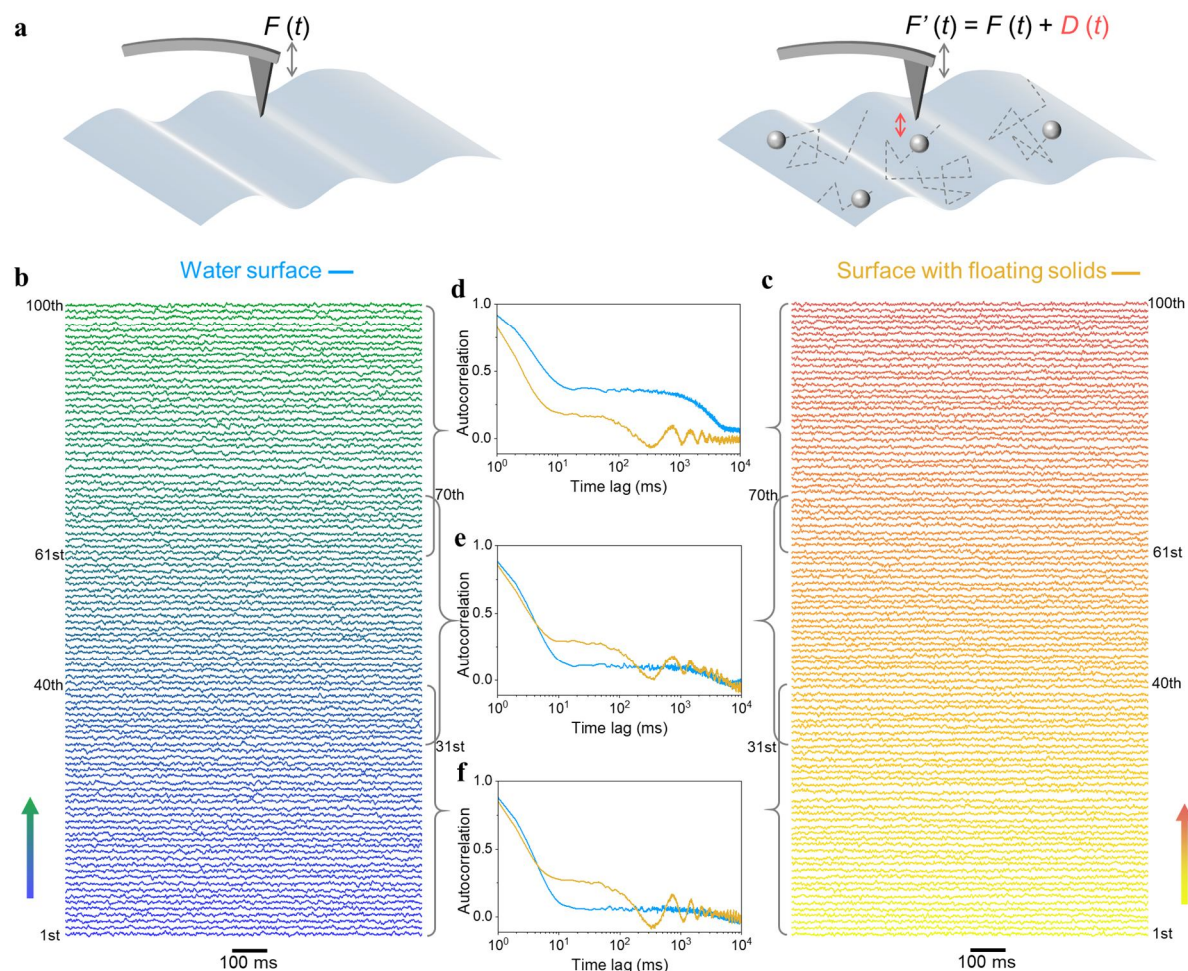
Based on the time-course reflectance spectra, nine critical time nodes (numbered from ① to ⑨ as indicated in Fig. 3a in the main text) were identified during the Ag membrane growth, which correspond to the moments of substantial changes during the membrane evolution. For these time nodes on large time scale of minutes (time nodes after 1 min), it is easy to directly collect the floating solid on the solution surface by using the silicon substrate because the operation time is ample. However, this method is unpractical for these time nodes on tiny time scale within 1 min (identified time nodes at 0.93 s, 4.32 s, 17.1 s and 53.5 s). We developed a continuous strategy to realize the accurate collection of the floating solid on tiny time scale during Ag membrane growth. Briefly, a piece of clean silicon slice (28×5 mm in dimension) was firstly pretreated by immersing it in the ethanol solution of oleamide (100 mg L^{-1}) for 10 min, taking it out at a constant rate of 5 mm min^{-1} , and then allowing it to drain at 80°C for 40

min. Such a treatment can decrease the hydrophilicity of the silicon slice surface and prevent the direct deposition of silver particles on the surface from the reaction solution. By using a digital controlled dip coater system (NIMA IU4 micro-processor interface module) that was tilted and fixed at an angle of 30° with the horizontal plane (Supplementary Fig. 49), the clamped silicon slice was raised up at a constant rate ($167 \mu\text{m s}^{-1}$ along the axle of the dip coater) once the silver mirror reaction was triggered. Because the convection flow is negligible in such a slow-moving system, this method can enable a continuous collection of the floating solid from the solution surface, with negligible influence on the floating solid pattern. Finally, the silicon slice was quickly taken out of the solution at a rate of 5 mm s^{-1} after 60 s, which created an identifiable dividing line on the silicon slice surface. Through a linear interpolation on the section in-between the initial dividing line (0 s) and the last one (60 s), a pseudo-colour coding with a time-scaled colour bar was created to localize the region of interest. Accordingly, the floating solid collected at critical time nodes can then be easily addressed and focused for further characterizations.

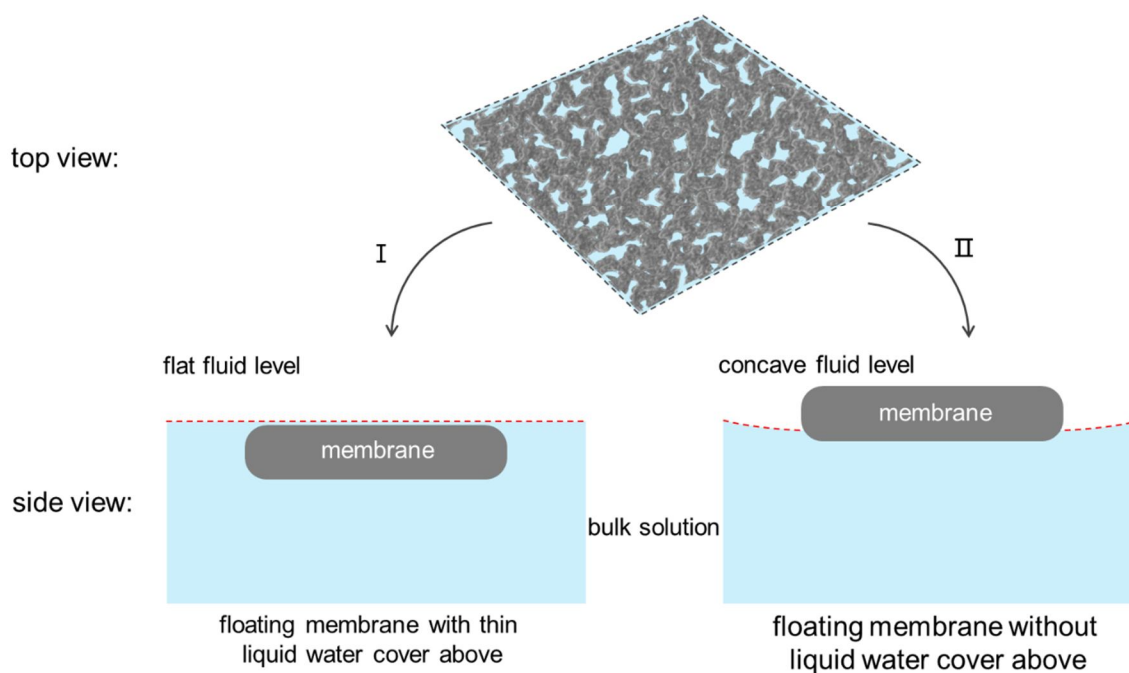


Supplementary Fig. 51. Strategy for accurately collecting the floating solid on tiny time scale during Ag membrane growth. **a, b,** Digital photos of the overviewed apparatus (**a**) and the typical snapshot (**b**) showing the rising silicon slice partially-immersed in the reaction medium. **c,** Digital photo of the silicon slice after time-course sample collection and the counterpart with pseudo colour marked on the region of interest (region in-between the dashed lines in the original photo). The pseudo colour denotes a liner time evolution as indicated in the bottom colour bar. The arrows indicate the locations corresponding to these identified critical time nodes on the tiny time scale based on the analysis result of the in-situ reflectance spectra.

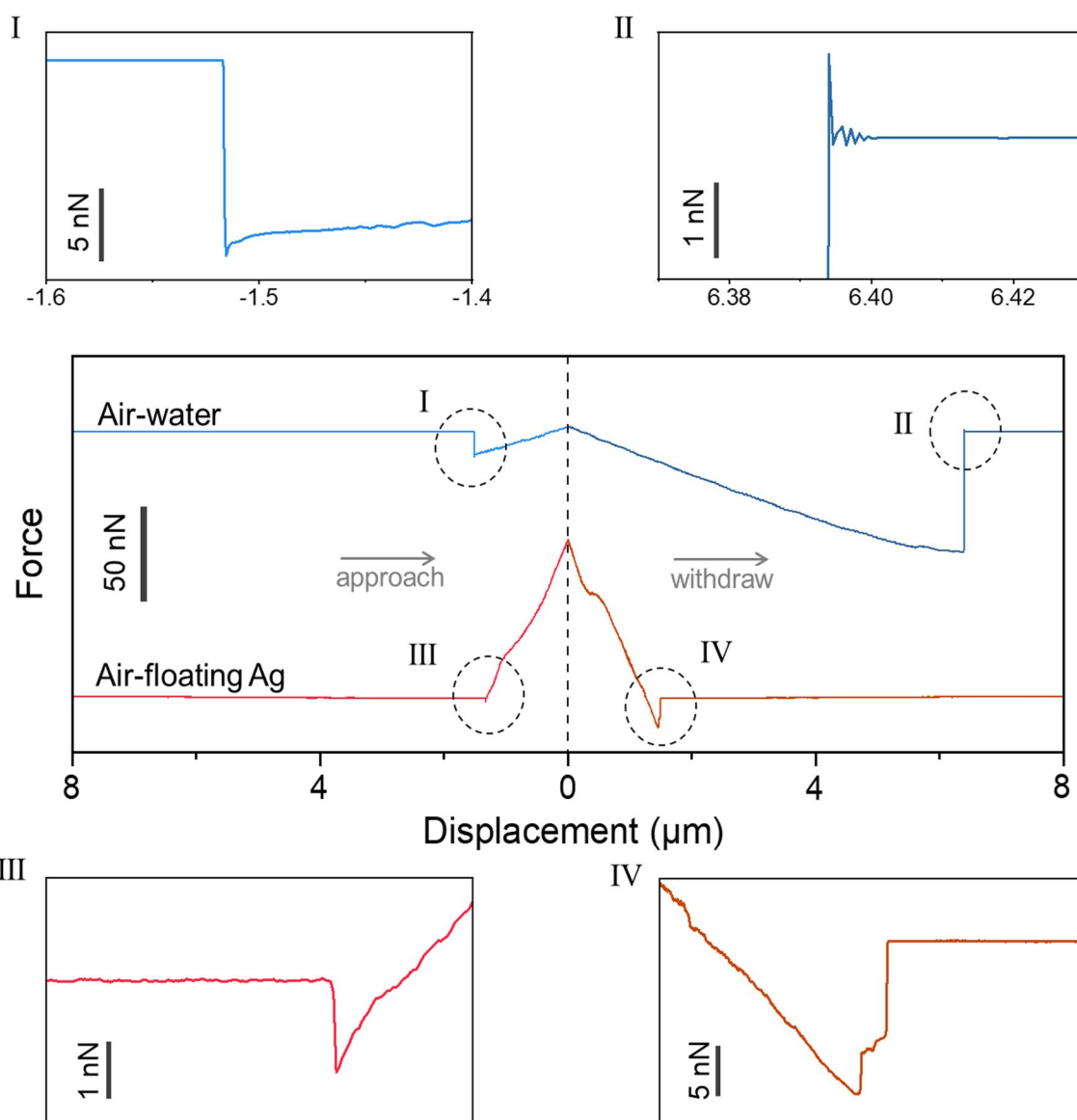
S4.2 Investigations on the actual position and kinematic of Ag solids on aqueous surface



Supplementary Fig. 52. Indirect confirmation of the Brownian motion for the floating Ag particles. **a**, Schematic diagram of the collections of the time series of force by AFM tip in two different cases, namely the pure water surface with intrinsic fluctuation and the aqueous surface with floating solid particles. In contrast to the case of pure water surface, additional disturbance $D(t)$ will be recorded in the collected time series $F(t)$ that is essentially caused by the Brownian motion of the floating solids. **b**, **c**, Raw time series $F(t)$ collected in 100 seconds for water surface (**b**) and the aqueous surface obtained in 1 s after initiating the silver mirror reaction in the SLIS system (**c**). **d-f**, Autocorrelation analyses for the two cases by using different time series segments, namely 1 - 40 s (**d**), 31 - 70 s (**e**) and 61 - 100 s (**f**).

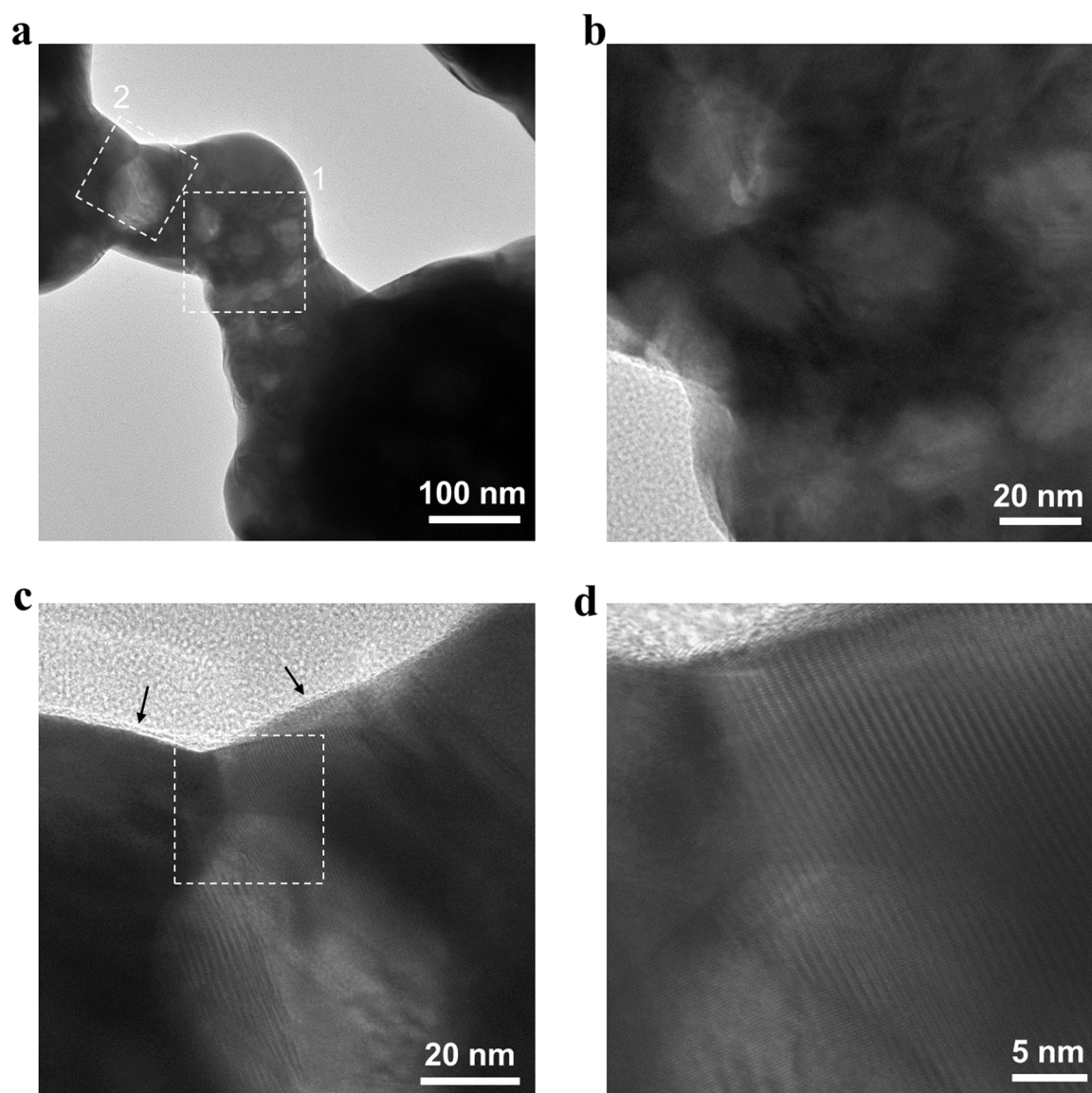


Supplementary Fig. 53. Two possible locations of the as-prepared Ag membrane floating on the aqueous surface. Traditional imaging techniques can only provide a top-view observation and /or characterization on the floating Ag membrane as shown in the schematic diagram. However, it is impossible to distinguish its detailed location on the solution surface, namely to confirm if there is liquid water layer covering above the membrane (possibility I) or not (possibility II). For the former case, the fluid level is flat, which is concave for the later possibility. The experimental identification of the actual position of the as-prepared floating Ag membrane is the essential basis for subsequent theoretical analysis of the Cheerios effect-related kinematics.

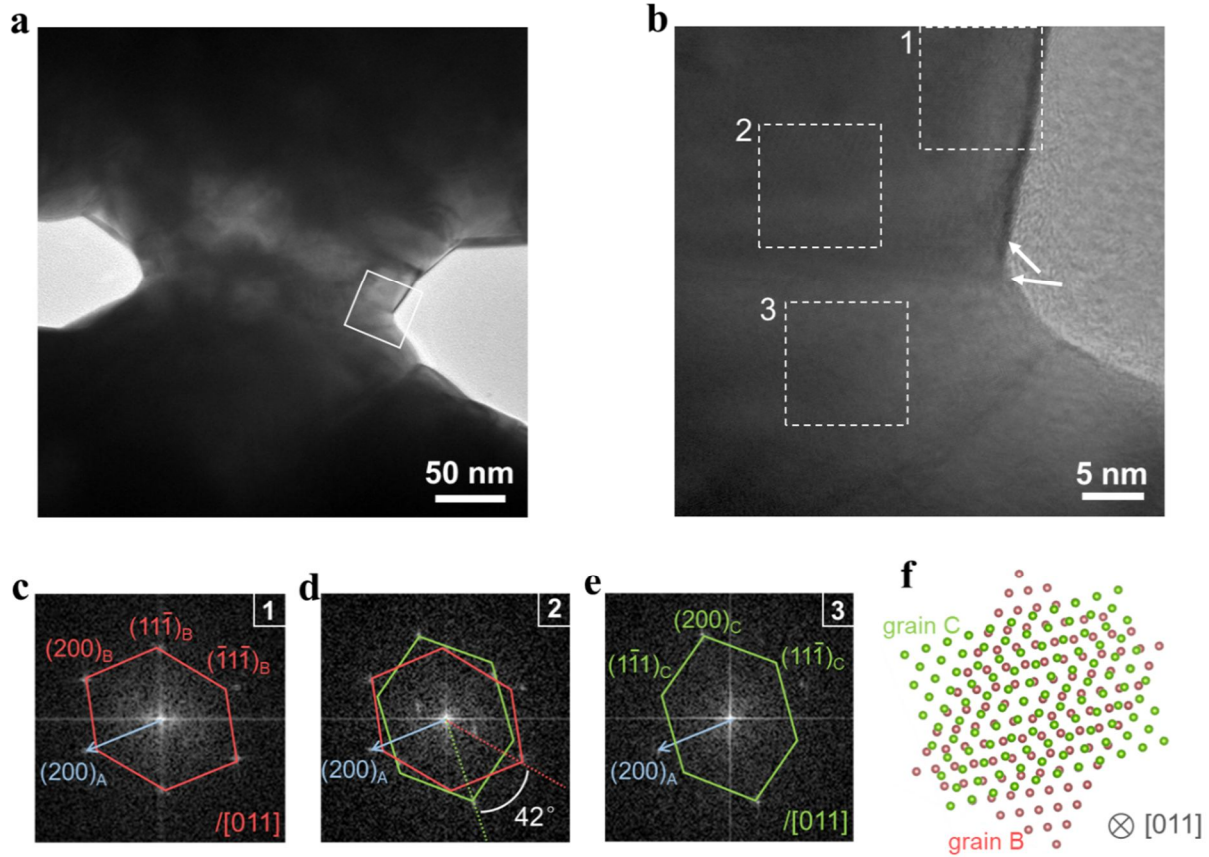


Supplementary Fig. 54. Detailed location of the as-prepared floating Ag membrane on the aqueous surface. Representative force-distance curves obtained from the AFM indentation measurements performed on the air-DI water interface and the interface between air and the on-site floating Ag membrane (30 min after igniting the silver mirror reaction in SLIS system), respectively. The characteristics of the force-distance curves were highlighted in the corresponding zoom-in figures as indicated by the dashed cycles (I and II in the curve for air-DI water interface, III and IV in the curve for the air-floating Ag membrane interface). Notably, in contrast to the case of the well-defined air-water interface, the detected interfacial stiffness is much larger for the air-Ag membrane interface, in which case, both of the adhesion force and rupture distance are much smaller. Due to the strong polarity of water molecules, the AFM tip will detect an enormous snap-in force when it approaches to the air-water interface (I). In addition, resulting of the fluid adhesion, the typical oscillation of the elastic cantilever is observed after the pull-off point (II). The presented characteristics of the force-distance curve implies a well-defined stiff solid surface for the measured air-Ag membrane interface, evidently confirming that the as-prepared Ag membrane float on the aqueous surface without liquid water cover above.

S4.3 Microscopic study on the grain boundaries in the Ag membrane



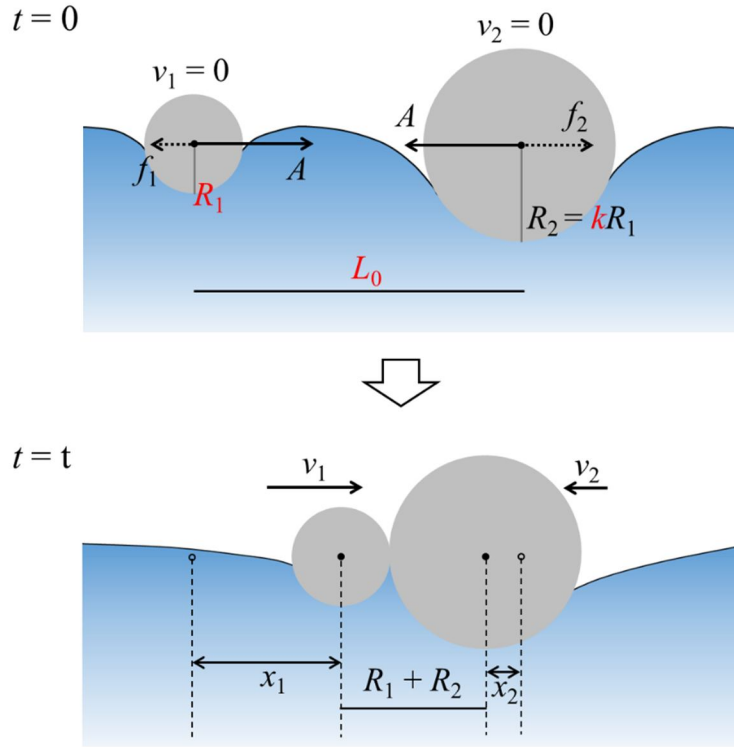
Supplementary Fig. 55. Polycrystalline structure in the as-prepared (quasi)-bicontinuous Ag membrane. **a**, TEM image of a typical wall in the network of the (quasi)-bicontinuous Ag membrane. **b**, **c**, Zoom-in TEM images of the region 1 and region 2 of interest marked in (**a**), respectively. Note that the image contrast in small area is resulted from the crystal orientation difference between different grains instead of the thickness difference. These grains with larger degree of deviation from the standard Bragg diffraction correspond to a higher gray-scale value (relatively white in colour). This can be confirmed by the achieved contrast inversion by rotating the sample. This fact enables the direct distinguishing of the grains in the TEM image at low magnification according to the diffraction contrast. Accordingly, the polycrystalline (quasi)-bicontinuous Ag membrane is thus revealed to be comprised of numerous tiny grains of tens of nanometers in size (Extended Data Fig. 5). The black arrows in (**c**) indicate the surface amorphous layer. **d**, HRTEM image of the marked region rich of boundaries in (**c**), which is the original image used for further crystallographic analysis presented in Fig. 3g of the main text.



Supplementary Fig. 56. Typical twist boundary in the (quasi)-bicontinuous Ag membrane viewed from a direction perpendicular to the boundary. **a, b**, TEM image of the network in the (quasi)-bicontinuous Ag membrane (**a**), showing a marked region of large curvature that is highlighted in the HRTEM image (**b**). The two white arrows indicate the boundaries constructed by the image contrast. **c, d, e, f**, FFT images of the marked region 1 (**c**), 2 (**d**) and 3 (**e**) in (**b**). A, B and C denote three grains with different orientations. Grain B and grain C are viewed along $[011]$, and grain A deviates significantly from the zone axis orientation. Region 2 is composed of the overlapped grain B and grain C with the twist boundary that perpendicular to the $[011]$ as visually illustrated in (**f**), featuring a twisted angle of about 42° . Note that the unindexed dots corresponding to the small length of the reciprocal vectors in (**d**) come from the periodic Moire fringes.

Section S5. Detailed Kinematic Mechanism during Membrane Growth.

S5.1 Kinematics of capillary attraction-driven two floating particles



Supplementary Fig. 57. Schematic illustration of the analytical kinematics for a pair of mutually attracted floating objects. The radii of the smaller object and bigger one is R_1 and R_2 , respectively, with a liner diversity factor of k ($R_2 = kR_1$). At the initial state ($t = 0$), the two floating spheres are relatively stationary ($v_1 = 0$ and $v_2 = 0$) with an initial distance of L_0 , and then begin to move towards each other driven by the combined interaction of the capillary attraction (A) dominated by the Cheerios effect and the contrary friction force (f_i) caused by the viscous effect from the fluid medium. At the final state ($t = t$), the two spheres are just touching each other at the critical distance of $R_1 + R_2$ with final velocities of v_1 and v_2 , respectively. During this process, the respective displacements for the two objects are x_1 and x_2 . In such a simplified system, the deterministic parameters controlling the kinematic behavior are R_1 , L_0 and k as highlighted in red.

In a simplified model of two mutually attracted floating spheres in the absence of hydromechanics as illustrated in Supplementary Fig. 55, their kinematics are simply driven by the combined interaction (F_i) of the capillary attraction (A) dominated by the Cheerios effect

and the contrary friction force (f_i) caused by the viscous effect from the fluid medium, which can be mathematically described by Newton's second law:

$$F_i = A - f_i = m_i a_i = m_i \frac{dv_i}{dt} \quad (5.1)$$

where m_i , a_i and v_i are the mass, accelerated velocity and velocity for sphere 1 or sphere 2, respectively. Without loss of generality, the smaller sphere is defined as the left sphere 1 with the radius of R_1 . The radius of the right bigger one is R_2 with a linear diversity factor of k compared to the small one, namely $R_2 = kR_1$. The capillary attraction can be derived from the interaction potential $E(L)$ between two floating objects with masses m_1 and m_2 at a distance of L ^{5,6}:

$$E(L) = m_1 m_2 \frac{(\rho g)^2}{2\pi\gamma\rho_m^2} K_0(L/a) \quad (5.2)$$

$$A = -\frac{\delta E(L)}{\delta L} = \frac{m_1 m_2}{a} \frac{(\rho g)^2}{2\pi\gamma\rho_m^2} K_1(L/a) \quad (5.3)$$

$$a = \sqrt{\frac{\gamma}{\rho_m g}}, \quad K_0(x) = \int_0^\infty \frac{\cos(xt)}{\sqrt{t^2 + 1}} dt, \quad K_1(x) = \frac{\sqrt{\pi}}{2(\frac{1}{2})!} x \int_1^\infty e^{-xt} (t^2 - 1)^{\frac{1}{2}} dt$$

where the length scale a is the capillary length of the aqueous medium, g is the gravitational acceleration constant (10 m s^{-2}), ρ is the density of the floating object, γ and ρ_m are the surface tension (simply regarded as a constant of 72 mN m^{-1} when the temperature does not significantly deviate from room temperature) and the density (nearly a constant of 10^3 kg m^{-3} for pure water with negligible temperature influence) of the aqueous medium, respectively. The functions $K_0(x)$ and $K_1(x)$ are the zeroth-order and first-order modified Bessel functions of the second kind, respectively. In the actual situation, the floating objects are of irregular shapes, such as Brownian clusters instead of ideal sphere. Therefore, the original capillary attraction is corrected by multiplying a factor of ε ($0 < \varepsilon \leq 1$) to reflect the actual efficiency of the capillary attraction action. The friction force can be simply expressed as⁷:

$$f_i = 6\pi\eta R_i v_i = 6\pi\eta R_i \frac{dx_i}{dt} \quad (i=1, 2) \quad (5.4)$$

where η is the viscosity of the medium and x_i is the respective displacement for object 1 or object 2.

Furthermore, by using the relationship between m_i and R_i (Equation (5.5)), we can further obtain the differential equation group to describe the kinematics of the mutually-attracted floating objects as shown in Equation (5.6), which is determined by the key parameters of R_1 , k and L_0 with the initial boundary conditions of Equation (5.7).

$$m_1 = \frac{4}{3}\pi\rho R_1^3, \quad m_2 = \frac{4}{3}\pi\rho k^3 R_1^3 \quad (5.5)$$

$$\begin{cases} \frac{d^2 x_1}{dt^2} = \frac{F_1}{m_1} = \frac{2\varepsilon\rho^3 g^2 k^3 R_2^3}{3a\gamma\rho_m^2} K_1(L/a) - \frac{9\eta}{2\rho R_1^2} \frac{dx_1}{dt} \\ \frac{d^2 x_2}{dt^2} = \frac{F_2}{m_2} = \frac{2\varepsilon\rho^3 g^2 R_1^3}{3a\gamma\rho_m^2} K_1(L/a) - \frac{9\eta}{2\rho k^2 R_1^2} \frac{dx_2}{dt} \\ \int_{L_0}^L dL = -\int_0^t (v_1 + v_2) dt \end{cases} \quad (5.6)$$

$$\begin{cases} \left. \frac{d x_1}{dt} \right|_{t=0} = 0, \quad \left. \frac{d^2 x_1}{dt^2} \right|_{t=0} = 0 \\ \left. \frac{d x_2}{dt} \right|_{t=0} = 0, \quad \left. \frac{d^2 x_2}{dt^2} \right|_{t=0} = 0 \\ L \big|_{t=t} = R_1 + R_2 \end{cases} \quad (5.7)$$

It is not available to directly obtain the analytical solutions of this high-order differential equation group. By controlling the variables, the numerical solutions under some typical conditions were alternatively in Matlab, which were employed to alternatively discuss the influences of these key parameters of R_1 , L_0 and k on the kinematics (Extended Data Fig. 7).

For the estimation of the collision energy ($E_{\text{collision}}$) between the two floating silver Brownian clusters, which are respectively composed of n_1 and n_2 silver nanoparticles, the nanoparticles serving as the building block for the Brownian clusters are reasonably simplified to be uniform spheres with a radius r of 28 nm as indicated by the statistical result (Extended Data Fig. 6b). The equivalent R_i and m_i can be regarded as:

$$R_i = r\sqrt{n_i} \quad (i=1, 2) \quad (5.8)$$

$$m_i = \frac{4}{3}\pi r^3 \rho n_i \quad (i=1, 2) \quad (5.9)$$

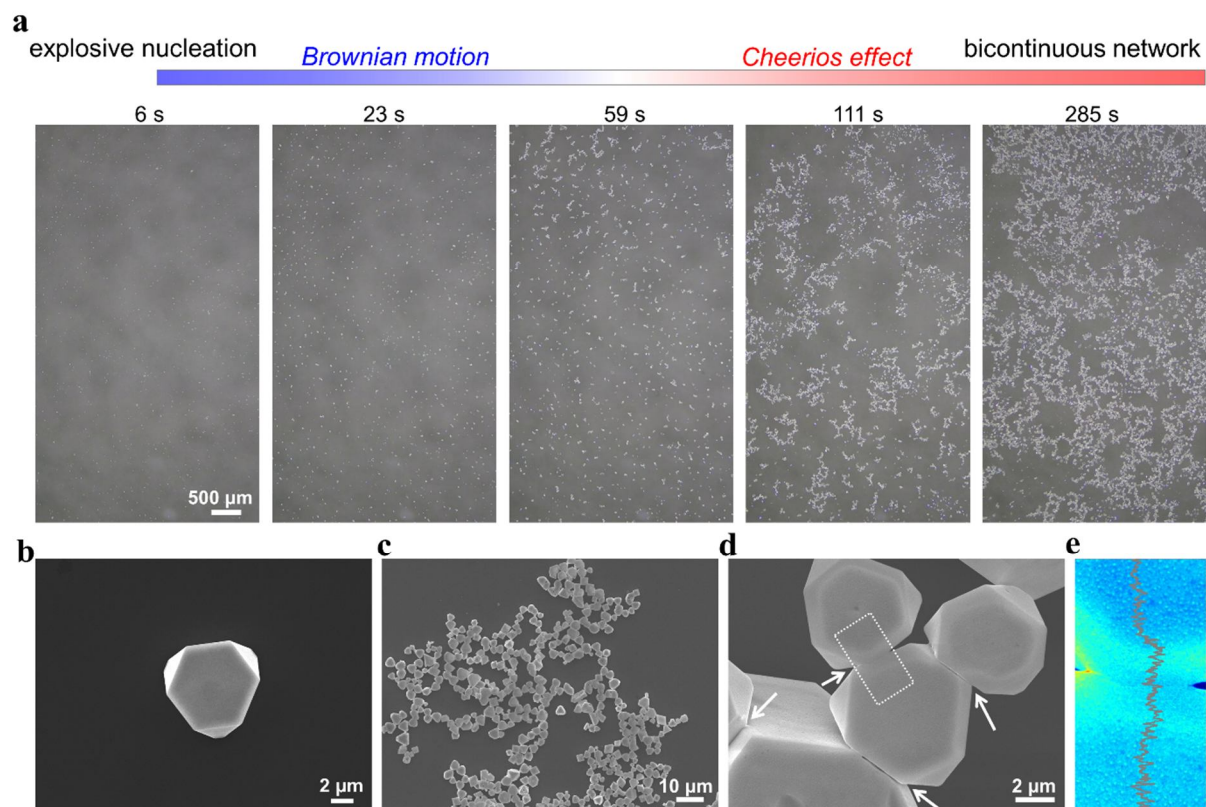
where the density of metallic silver ρ is 10490 kg m⁻³. According to the preliminary analysis (Extended Data Fig. 7e-h), the initial distance does not influence the terminal velocities of the

moving Brownian clusters. Without loss of generality, the initial distance L_0 of 50 μm were then plugged into Equation (5.6) to solve the terminal velocities (v_{t1} and v_{t2}) of the moving Brownian clusters once they touch each other. The collision energy is regarded as the sum of the kinetic energy of the two moving Brownian clusters and can then be easily obtained by:

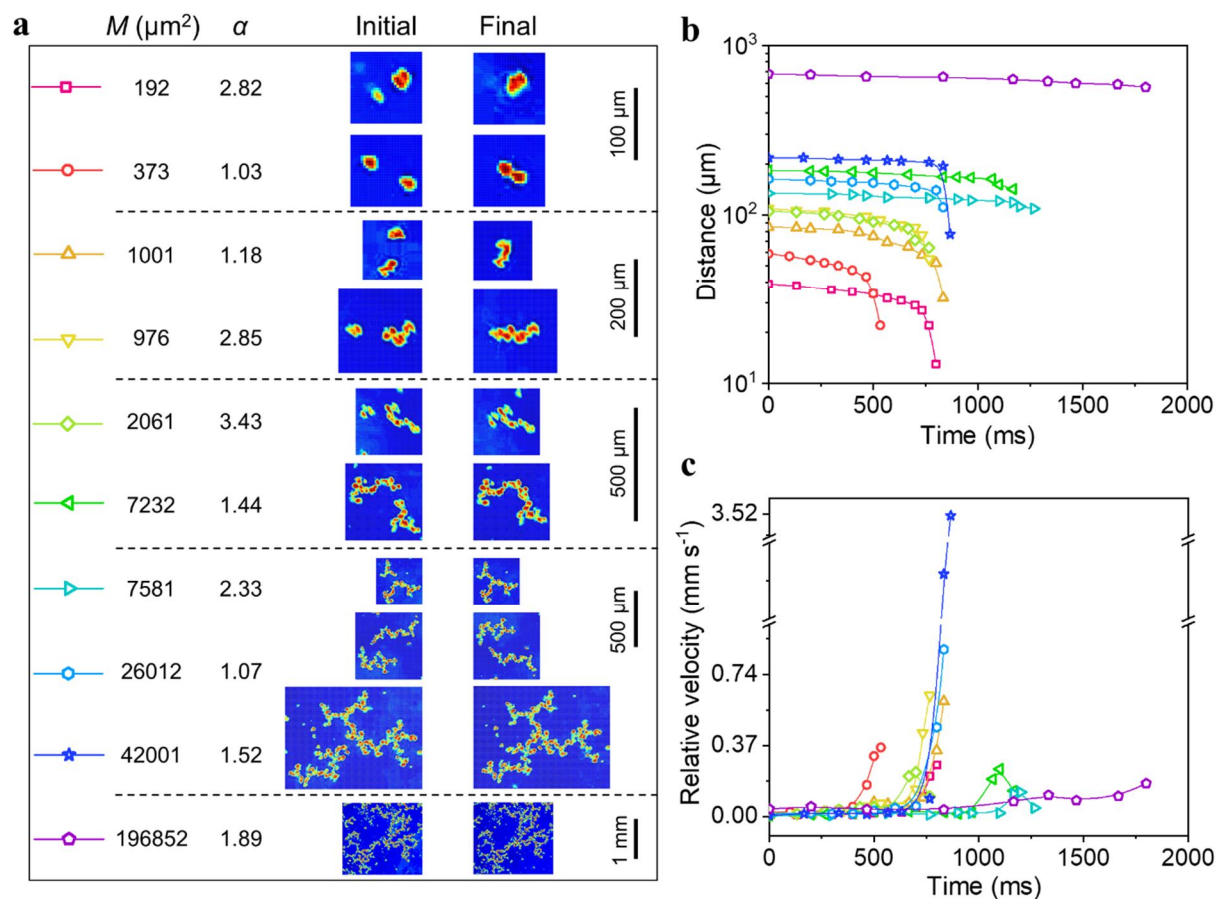
$$E_{\text{collision}} = \sum_{i=1}^2 \frac{2}{3} \pi r^3 \rho v_{ti}^2 n_i \quad (5.10)$$

The numerical solutions for Equation (5.6) and the visualization of Equation (5.10) regarding the collision energy $E_{\text{collision}}$ and the Ag nanoparticle numbers n_1 and n_2 in the mutually-attracted floating Brownian clusters were realized by using customized Matlab codes (see Supplementary Section S10.1 and S10.2).

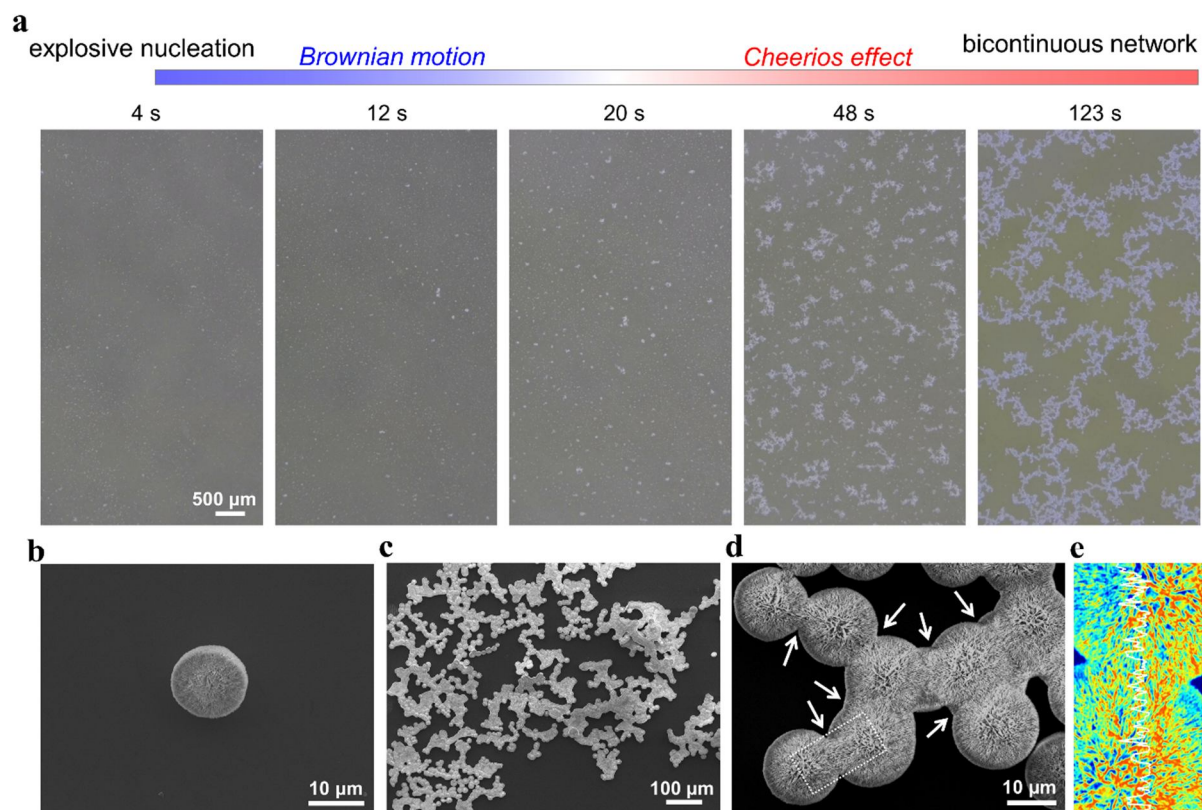
S5.2 In-situ observation of kinematic-dominated membrane formation



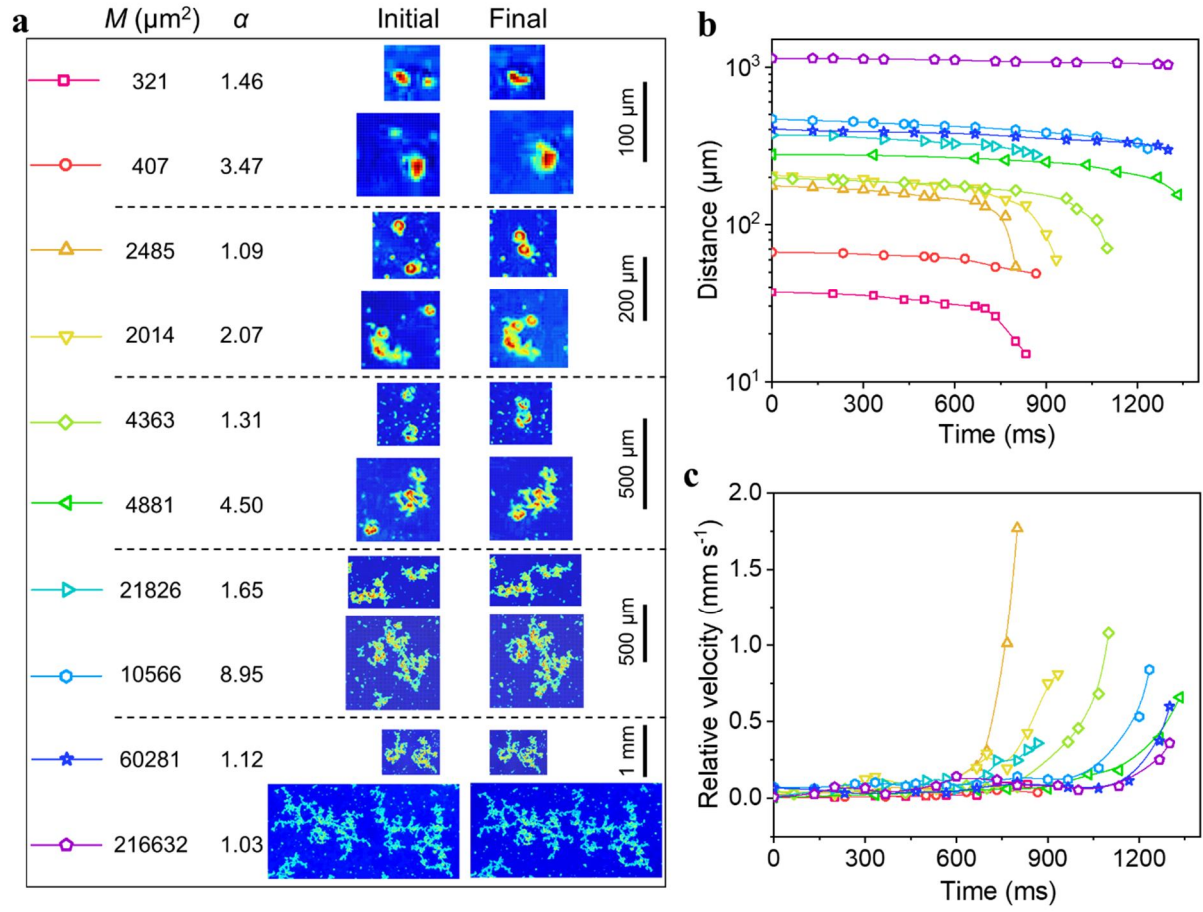
Supplementary Fig. 58. Visualized kinematics and connectivity of the AgCl particles/Brownian clusters until the formation of bicontinuous network. **a**, Time-lapse microscopic images recording the surface evolution of the reaction solution for preparing AgCl membrane (also see **Supplementary Video 2**). The top colour bar marks the temporal regimes that are respectively dominated by Brownian motion and Cheerios effect from the initial explosive nucleation to the moment of forming (quasi)-bicontinuous network. **b**, SEM image of a representative AgCl particle collected at 6 s after igniting the reaction, highlighting its discal structure. **c**, **d**, SEM images of the representative AgCl network collected at 285 s after igniting the reaction. The arrows in (**d**) indicate these tight joints between AgCl particles. **e**, Contrast analysis of the marked cross-boundary region in (**d**). The curve is the contrast line profile along the center vertical line of the picture. Note that these visible particles on the AgCl particles are Ag nanoparticles, which derive from the AgCl decomposition under long-term electron beam irradiation in SEM chamber.



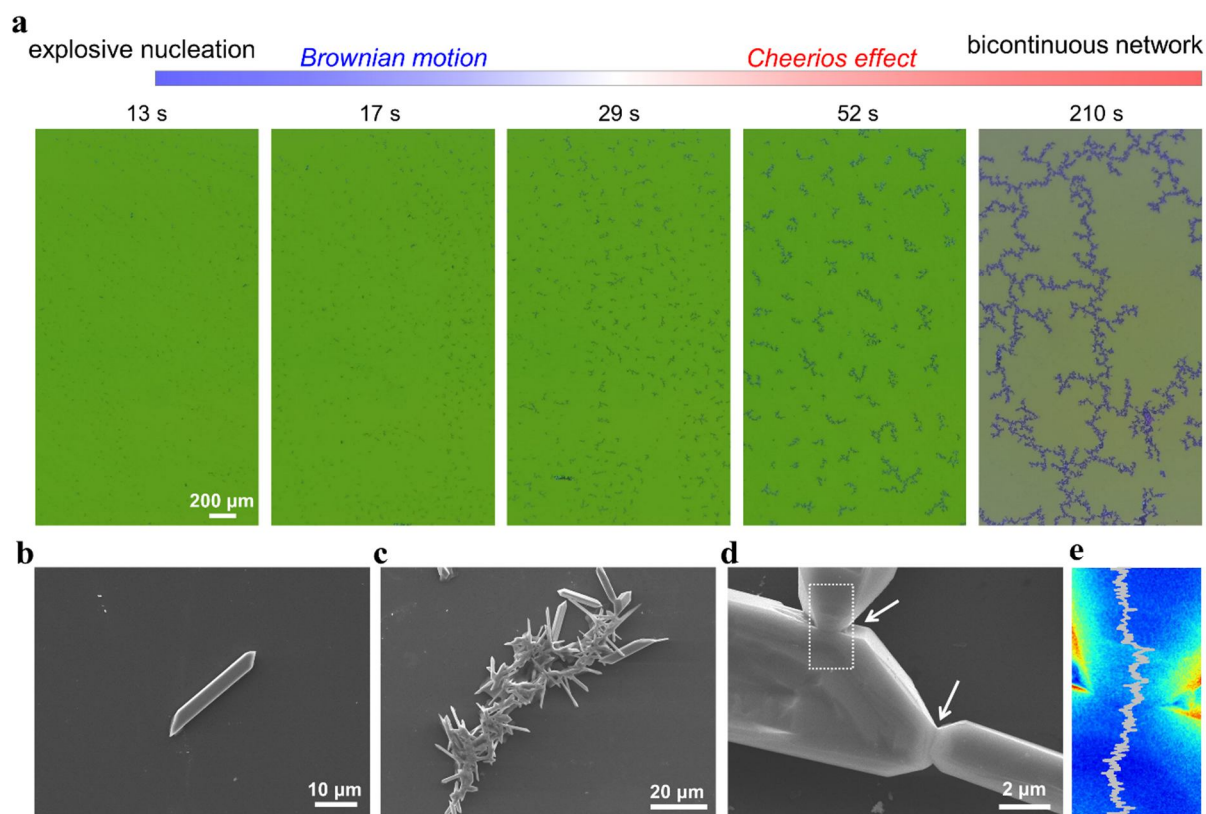
Supplementary Fig. 59. Kinematic analyses of the AgCl particles/Brownian clusters during the formation of (quasi)-bicontinuous network. **a**, Images of ten representative pairs of AgCl particles/Brownian clusters with different geometric parameters (the projected area of the smaller-area part M and the ratio of projected area α), visually presenting their startup state (Initial) and just-touching state (Final). The microscopic images were intentionally colorized to enhance the contrast. **b**, The corresponding time-dependent distance changes between the two capillary-attractive AgCl particles/Brownian clusters as presented in (a). **c**, The corresponding time-dependent velocities of the smaller-area AgCl particles/Brownian clusters relative to the bigger ones.



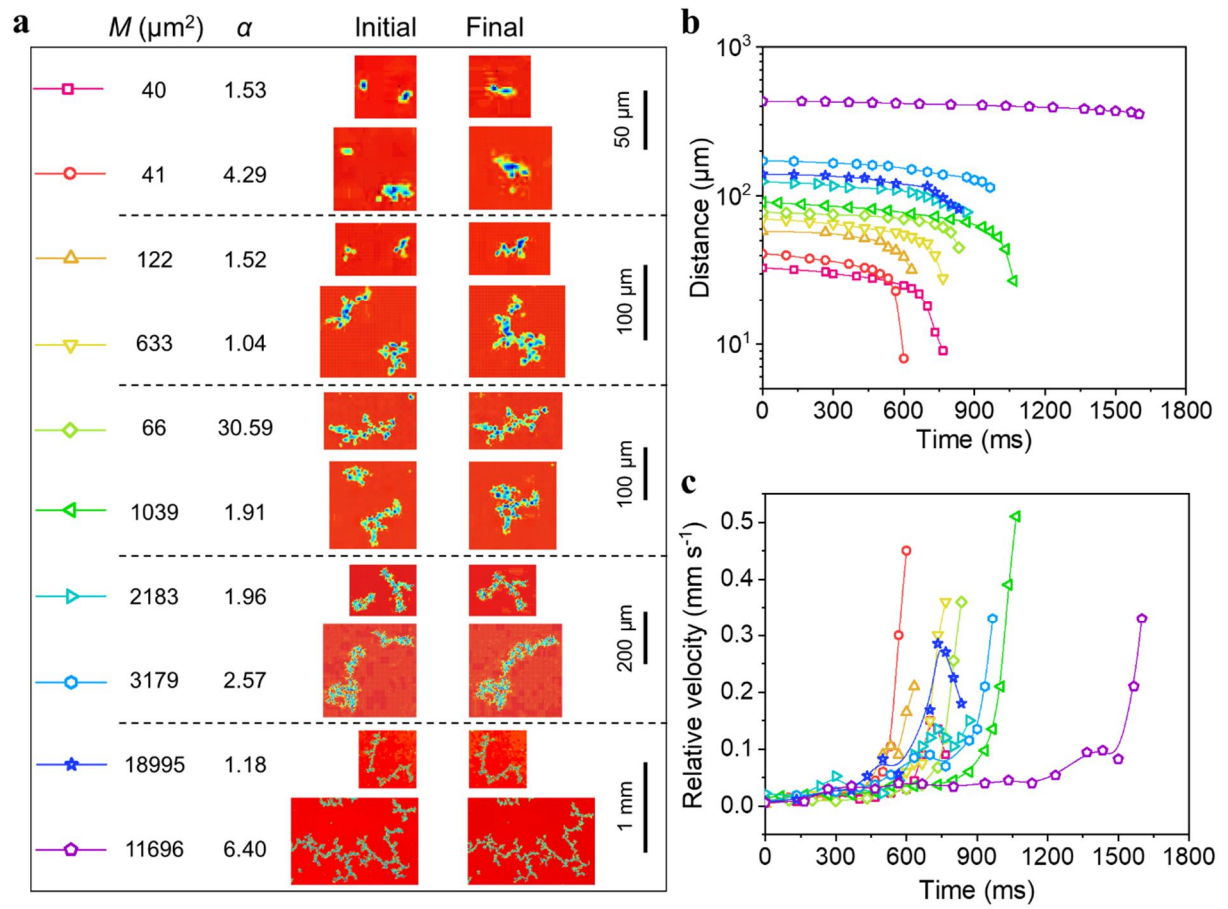
Supplementary Fig. 60. Visualized kinematics and connectivity of the BiVO_4 particles/Brownian clusters until the formation of (quasi)-bicontinuous network. **a**, Time-lapse microscopic images recording the surface evolution of the reaction solution for preparing BiVO_4 membrane (also see **Supplementary Video 2**). The top colour bar marks the temporal regimes that are respectively dominated by Brownian motion and Cheerios effect from the initial explosive nucleation to the moment of forming (quasi)-bicontinuous structure. **b**, SEM image of a representative BiVO_4 particle collected at 4 s after igniting the reaction, highlighting its hemispherical structure. **c**, **d**, SEM images of the representative BiVO_4 network collected at 123 s after igniting the reaction. The arrows in (**d**) indicate these tight joints between BiVO_4 particles. **e**, Contrast analysis of the marked cross-boundary region in (**d**). The curve is the contrast line profile along the center vertical line of the picture.



Supplementary Fig. 61. Kinematic analyses of the BiVO_4 particles/Brownian clusters during the formation of (quasi)-bicontinuous network. **a**, Images of ten representative pairs of BiVO_4 particles/Brownian clusters with different geometric parameters (the projected area of the smaller-area part M and the ratio of projected area α), visually presenting their startup state (Initial) and just-touching state (Final). The microscopic images were intentionally colorized to enhance the contrast. **b**, The corresponding time-dependent distance changes between the two capillary-attractive BiVO_4 particles/Brownian clusters as presented in **(a)**. **c**, The corresponding time-dependent velocities of the smaller-area BiVO_4 particles/Brownian clusters relative to the bigger ones.



Supplementary Fig. 62. Visualized kinematics and connectivity of the Ag_2CrO_4 particles/Brownian clusters before the formation of (quasi)-bicontinuous network. **a**, Time-lapse microscopic images recording the surface evolution of the reaction solution for preparing Ag_2CrO_4 membrane (also see **Supplementary Video 2**). The top colour bar marks the temporal regimes that are respectively dominated by Brownian motion and Cheerios effect from the initial explosive nucleation to the moment of forming (quasi)-bicontinuous structure. **b**, SEM image of a representative Ag_2CrO_4 particle collected at 13 s after igniting the reaction, highlighting its claviform structure. **c**, **d**, SEM images of the representative Ag_2CrO_4 network collected at 210 s after igniting the reaction. The arrows in (**d**) indicate these tight joints between Ag_2CrO_4 particles. **e**, Contrast analysis of the marked cross-boundary region in (**d**). The curve is the contrast line profile along the center vertical line of the picture.



Supplementary Fig. 63. Kinematic analyses of the Ag_2CrO_4 particles/Brownian clusters during the formation of (quasi)-bicontinuous network. **a**, Images of ten representative pairs of Ag_2CrO_4 particles/Brownian clusters with different geometric parameters (the projected area of the smaller-area part M and the ratio of projected area α), visually presenting their startup state (Initial) and just-touching state (Final). The microscopic images were intentionally colorized to enhance the contrast. **b**, The corresponding time-dependent distance changes between the two capillary-attractive Ag_2CrO_4 particles/Brownian clusters as presented in (a). **c**, The corresponding time-dependent velocities of the smaller-area Ag_2CrO_4 particles/Brownian clusters relative to the bigger ones.

S5.3 Further evolution after the formation of critical bicontinuous network

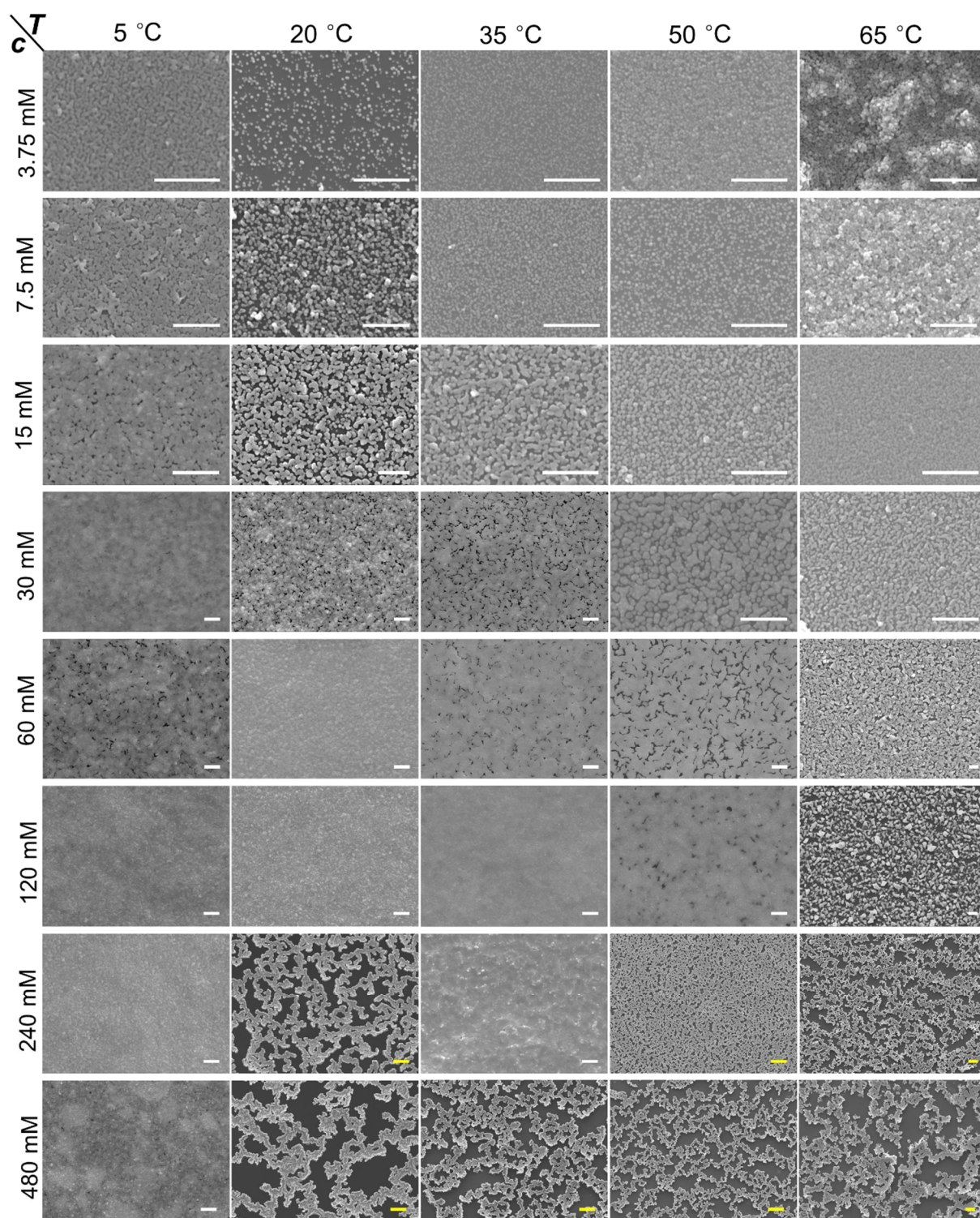
The subsequent evolution after the construction of the essential (quasi)-bicontinuous network are quite smooth visually. Due to the extremely large size difference between the newborn particles and the (quasi)-bicontinuous network, these particles generated outside the network were found to be continuously attracted and stuck to the network margin, resulting in an extensional extension of the network (Extended Data Fig. 8a-c, Supplementary Video 3). This effect ensures that the as-prepared membrane size can be considerable to the employed vessel diameter as long as abundant building blocks are supplied onto the aqueous surface.

For these particles that generated inside the holey region of the network, they were observed to be directly trapped by the hole boundary, namely the wall of the network (Extended Data Fig. 8d and e, Supplementary Video 4). The process is very quick due to the large attractive interaction between the particle and the huge network caused by the Cheerios effect, which thus does not allow the particles to aggregate with each other to form the new Brownian cluster inside the holey region. The trapped probability of the particles to the network wall is almost equal, which accounts for the reserved geometrical similarity of the holes during evolution (Extended Data Fig. 9). However, the hole boundary of high curvature and low Feret diameter corresponds to a higher relatively shrink rate that is oriented to the center of curvature. This fact allows to preferentially eliminate these boundaries of high curvature and divide the irregular hole into small pieces through the “neck” regions of low Feret diameter, simultaneously diminish the hole connectivity and the geometrical similarity along with the decreasing hole area. Notably, such a continuous and monotonic process is the practical basis to continuously adjust the membrane through-hole ratio by simply controlling the evolution time after the formation of critical network.

Section S6. Graph Theory Method for Various Structures of Floating Ag Solids

S6.1 Various structures of the floating Ag solids emerging from different conditions

The orthogonal experiments related to the initial concentration (c) of $[\text{Ag}(\text{NH}_3)_2]^+$ and reaction temperature (T) were performed. Briefly, 1.5 mL of the freshly-prepared Tollens' reagent solutions of various concentrations (7.5, 15, 30, 60, 120, 240, 480 and 960 mM) were respectively transferred into the pretreated Petri dishes. These Tollens' reagent solution-holding Petri dishes, along with the reductant solution containing D(+)-glucose (250 mM) and NaOH (50 mM), were then kept at the designed temperature (5, 20, 35, 50 and 65 °C, note that the temperature of 5 °C was obtained in a fridge and other conditions were obtained in oven) for 20 min. Subsequently, each Petri dish was quickly added of 1.5 mL of the precooled/preheated reductant solution, and then allowed to stand still at the designed temperature for long enough time until almost all of the $[\text{Ag}(\text{NH}_3)_2]^+$ in the system was reduced into solid Ag species. The reaction time durations were set at 80, 5, 3, 1 and 0.6 h for the reactions performed at 5, 20, 35, 50 and 65 °C, respectively. After the reaction finished, the corresponding Ag solids floating on the surface of the solution were then carefully collected by the silicon slice for further SEM observation. To accurately identify the geometrical connectivity in the structures of the floating Ag solids, an appropriate contrast enhancement was then performed to these representative SEM images (Supplementary Fig. 62) by using a customized Matlab code. Based on a further graph theory analysis, the phase diagram about the geometrical description of the structures of floating Ag solids evolving from different reaction temperatures (T) and initial concentrations of $[\text{Ag}(\text{NH}_3)_2]^+$ ($\log_2 c$) was subsequently constructed.



Supplementary Fig. 64. Structural diversity of the floating Ag solids evolving from various initial conditions. Representative SEM images of the floating Ag solids prepared from various systems of different initial concentrations (c) of $[\text{Ag}(\text{NH}_3)_2]^+$ and reaction temperatures (T). Scale bars in white, 1 μm. Scale bars in yellow, 10 μm.

S6.2 Detailed discussion of the Graph theory analysis

Due to the significant differences in the size and dynamic density of the Ag particles acting as the building blocks, the dimensions of their assembled network/pattern evolving from different initial conditions vary widely (Supplementary Fig. 62). This fact prevents the direct comparison among various structures of these floating Ag solids simply from the geometrical view. To describe the structural diversity of the floating Ag solids evolving from different initial conditions, we employed the mathematical method of graph theory (GT), which is scale-free and can provide an abstract classification by taking full considerations of the geometrical connectivity and physiochemical bonding strength. Accordingly, we can then establish initial condition (concentration and temperature)-framework structure relationships for the assemblies of the floating solids based on their topological equivalences.

The observed floating Ag solids (Supplementary Fig. 62) were simplified as the well-defined assemblies of single-layered particles and then discretized into simple building blocks, namely the particles, whose centers of mass serve as nodes in graph. When these floating particles get moving that controlled by the Brownian motion and/or Cheerios effect, their kinematic behavior leads to particle-to-particle connectivity and thus results in a more complex assemblies than the basic particles, namely cliques, clusters and networks. Following the discretization rules⁸, if the nodes share interfaces in geometry with considerable physiochemical bonding strength, they are regarded to be connected with an edge in graph. Because the existence of steric hindrance for the practical building blocks of definite projected area in two-dimensional (2D) space, the number of linkages connecting to one node cannot be infinite. Moreover, the well-known finite GT-model, quotient graph, that commonly employed to describe the semi-infinite structures rich in translationally equivalent nodes is inapplicable here by reason of no distinct periodic structures. Thus, these finite graph segments retaining the essential characteristics of the semi-infinite assemblies were extracted from the 2D geometries in the SEM images, and then represented as the minimal topological contracts (MTCs).

Based on the above considerations for the discretization methods, four kinds of well-defined structural multigraphs can be identified among all the observed SEM results, which thus inductively correspond to four established GT-models, *i.e.*, node islands, clique islands,

open network and closed network. Taking the representative SEM images as presented in Supplementary Tab. 3 for instance, these images were firstly enhanced in contrast by using a customized Matlab code to further identify the geometrical connectivity of the structures. For these isolated particles with no interconnections, there are no static or fixed bonding patterns between them, but they would have dynamic collision or contact on a certain long-range view due to the persistent Brownian motion. Thus, the GT-model of the pattern named node islands, will be represented as a cyclic graph with a subgraph inside to depict the MTCs of the randomly distributed particles, the simplest example of which is expressed as a loop with one node encircling finite unconnected nodes inside. Consistent with the fact, there is no specific order and weight between the nodes. Moreover, the limited number of the nodes depends on the collision probability, that directly determines the minimum range of observation to ensure the presence of one dynamic binding in the pattern. This content will not be further discussed here.

Similarly, these isolated Brownian clusters with no static interconnections will be represented as a loop with one node encircling finite unconnected K_3 complete graphs inside, namely clique islands. Because these unconnected Brownian clusters in this case are only composed of several particles, resulting in a large fractal dimension. The structure of the Brownian clusters is thus approximate to 2D sheets in geometry, whose MTC is K_3 complete graph on account of a minimum of three points to define a plane. For the (quasi)-bicontinuous network without any isolated particles/Brownian clusters and any closed holes, its highly-branched structure assembled from large particles corresponds to a small fractal dimension. Such graph will be simply represented as one node linked with three independent chains that consists finite nodes, namely open network. In spite of much smaller building particles, from the view of assembled evolution and the as-revealed growth kinetics of the membrane, the pattern of the continuous plane with completely-enclosed holes or dense surface can be regarded as the progressive counterpart of the open network, which owns more linkages to connect the nodes and thus can significantly break the (quasi)-bicontinuous structure (the breakup of the continuity of the gaseous phase). Accordingly, the minimal representation of such closed network in GT-model will be expressed as one node linked with three dependent chains that consist finite nodes, namely each three of the equative nodes located in the chains

are further linked into a triangle built on the GT-model of the open network. Note that only when the closed network evolves into well-defined dense membrane without any holes through it, it is meaningful to use complete graph to represent its GT-model. This case is not general for the closed network. Thus, the proposed noncomplete-graph GT-model with diminished graph density is more reasonable to describe the closed network.

Based on the established GT-models above, these related multiple GT indexes can then be calculated. Here, we focus on two general indexes, namely the graph density (*GD*) and the complexity index (*CI*). Graph density represents the ratio between the edges present in a graph and the maximum number of edges that the graph can contain, which conceptually provides an intuitive insight of how dense a graph is in terms of its edge connectivity⁹. For a simple undirected graph, *GD* value can be directly obtained according to the following formula:

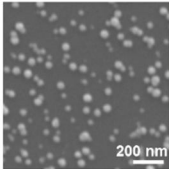
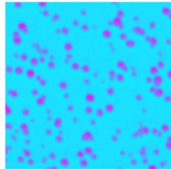
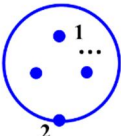
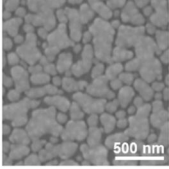
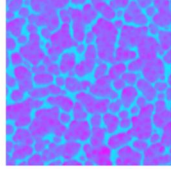
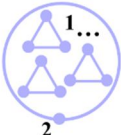
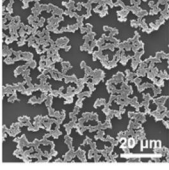
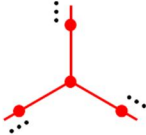
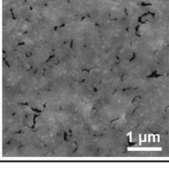
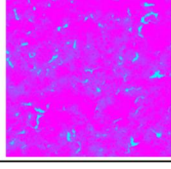
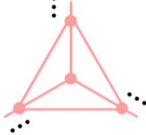
$$GD \text{ value} = \frac{E}{C_v^2} = \frac{2E}{V(V-1)} \quad (6.1)$$

where E is the number of edges present in the graph, V is the number of vertices (nodes) in the graph. C is the combination notation. Beyond the graph density, the complexity index was further employed to estimate the structural complexity of the multigraphs by giving sufficient consideration to the connectivity patterns of nodes, whose value can be mathematically calculated through the reported augmented valence complexity (AVC) algorithm based on the augmented valence of an individual nodes (AVV)¹⁰. Note that the contribution to the *CI* value only lays in the amount of the non-repetitive information within the GT-model, namely correlating with these different classes of nodes instead of these nodes with different locations. In the AVC method, the *CI* value is the sum of the augmented vertex valence for all non-equivalent vertexes. In addition, the summation components of *CI* decay as $(1/2)^k$ where k is the distance in edges away from the node of interest¹⁰. After all the nodes are grouped into classes of symmetrically equivalent nodes, the *CI* value can be obtained through:

$$CI \text{ value} = AVC = \sum_{i=1}^n (AVV)_i = \sum_{i=1}^n \left(\sum_{j=1}^N \left(\frac{1}{2} \right)^{j-1} a_j \right)_i \quad (6.2)$$

where n is the number of the non-equivalent classes, N is the number of the nodes belonging to a specific equivalence class and a_j is the augmented valence for the node of interest.

Supplementary Table 3. GT representations and indices for different structures of floating Ag solids.

Condition reference (<i>T</i> , <i>c</i>)	SEM image	Contrast enhancement	Description	GT-model	<i>CI</i> value	<i>GD</i> value	Model name
(20 °C, 3.75 mM)			Isolated particles with no static interconnections		$\begin{aligned} N1 &= 0 \\ N2 &= 2 \\ CI &= 0+2 = 2 \end{aligned}$	$\frac{2}{n(n+1)}$	Node islands
(50 °C, 30 mM)			Isolated Brownian clusters with no static interconnections		$\begin{aligned} N1 &= 2+(2*2)/2 = 4 \\ N2 &= 2 \\ CI &= 4+2 = 6 \end{aligned}$	$\frac{2}{n+1}$	Clique islands
(35 °C, 480 mM)			(Quasi)-Bicontinuous framework composed of large particles		$CI = 3 + \sum_{n=1}^{\infty} \frac{2*3}{2^n} = 9$	$\frac{2}{n}$	Open network
(5 °C, 60 mM)			Continuous plane with completely-enclosed holes or dense structure		$CI = 3 + \sum_{n=1}^{\infty} \frac{4*3}{2^n} = 15$	$\frac{4}{n}$	Closed network

Section S7. Theoretical Criterion for Unimpeded Membrane Growth.

S7.1 Criterion for the Brownian motion-dominated formation of Brownian cluster

The criterion is based on the mathematical evaluation on the collision probability of the isolated particles in Brownian motion. Simply, the randomly-moving particles that float on the aqueous surface can be approximately abstracted to mobile discs with specific radius r in a plane of Euclidean space, whose motor patterns are all governed by the two-dimensional Brownian motion. The mean squared displacement (Δx^2) in two-dimensional Brownian motion during time t is¹¹:

$$\Delta x^2 = 4Dt \quad (7.1)$$

where D is the diffusion coefficient, which can be obtained from Stokes-Einstein equation¹²:

$$D = \frac{k_B T}{6\pi\eta r} \quad (7.2)$$

where k_B is Boltzmann's constant of $1.3806 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$, T is the absolute temperature, η is the dynamic viscosity of $8.9 \times 10^{-4} \text{ Pa}\cdot\text{s}$ for water at 25°C and r is the radius of the disc.

Accordingly, the critical area A that a Brownian disc may attain per unit of time can be expressed as follows:

$$A = \frac{\Delta x^2}{t} = \frac{2k_B T}{3\pi\eta r} \quad (7.3)$$

Given the density of particle floating on the aqueous surface is n , the total number of particles N in a critical area can be determined to be:

$$N = nA \quad (7.4)$$

Without loss of generality, the critical area is simplified into a orthohexagonal region, which can satisfy the seamless cover on a specific plane. For the closest-packed pattern in two-dimensional space (Supplementary Fig. 63), the maximal amount M of the discs that can be contained in the orthohexagonal region is:

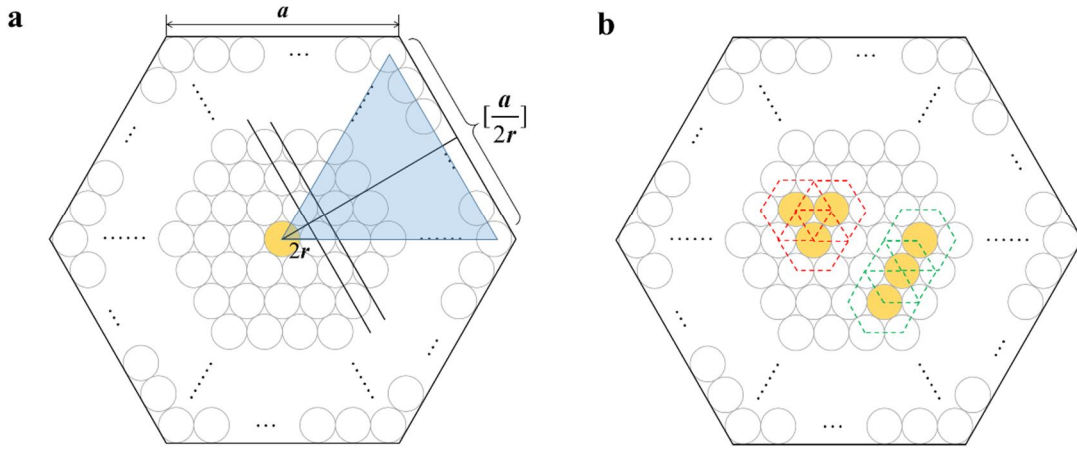
$$M = 6 \times \left(\frac{1}{6} + \sum_{i=1}^{n^*} i \right) \quad (7.5)$$

$$n^* = \left[\frac{a}{2r} \right] \quad ([] \text{ denotes rounding function}) \quad (7.6)$$

$$A = \frac{3\sqrt{3}a^2}{2} \quad (7.7)$$

where n^* is the amount of the disc along the outer side of the orthohexagonal region, whose side length is a . With this geometric consideration, it should be noted that the upper limit of the surface density of particle n is dependent on the particle radius r according to the following inequation:

$$n \leq \frac{M}{A} \quad (7.8)$$



Supplementary Fig. 65. Geometrical model of the disc packing in two-dimensional space.

a, Schematic diagram of the closest-packed discs inside the orthohexagonal region with geometric auxiliary lines helps to calculate the maximum number of discs that may be housed. The blue triangle marks the symmetrically equivalent structure in the orthohexagon, visually showing one-sixth amount of discs may be contained. **b**, Schematic diagram of the disc packing patterns in two extreme cases, showing different coordination numbers for the densest-packed case (encircled by red dashed line) and the loosest-packed case (encircled by green dashed line).

Thus, collision probability for the homogeneous collision (namely a mobile disc collides with another mobile one, whose subsequent aggregation determines the formation rate of the initial immobile seeds for Brownian cluster) P_{homo} can be expressed as follows:

$$P_{\text{homo}} = C_N^2 \times \frac{1}{M^2} \times M \quad (7.9)$$

For the case of heterogeneous collision, namely a mobile disc collides with a relatively-static aggregate consisted of k discs, we should firstly obtain the number of the adjacent vacancies n_a for a specific aggregate. The number of the adjacent vacancies gets the minimum

value ($n_a = k+6$) when the disc aggregate adopts the densest packing (red dashed highlighted region in Supplementary Fig. 63b), and gets the maximum value ($n_a = 2k+4$) when the disc in aggregate arrange in line (green dashed highlighted region in Supplementary Fig. 63b). Thus, collision probability for the heterogeneous collision P_{hetero} that determines the growth rate of the Brownian cluster can be expressed as follows:

$$P_{\text{hetero}} = \frac{n_a}{M - n_a} \times N \quad n_a \in [k+6, 2k+4] \quad (k \geq 2) \quad (7.10)$$

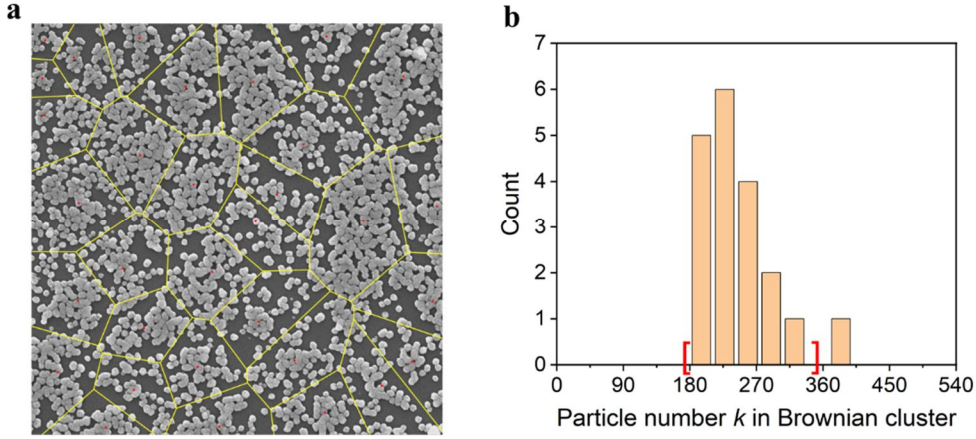
It can be mathematically noted that the homogeneous collision overwhelmingly dominates during the initial period, and the heterogeneous collision will gradually become dominant after the critical period that meets the criterion:

$$\frac{P_{\text{hetero}}}{P_{\text{homo}}} = \frac{2Mn_a}{(M - n_a)(N - 1)} \geq 1 \quad n_a \in [k+6, 2k+4] \quad (k \geq 2) \quad (7.11)$$

With a further simplification, the criterion can be expressed as follows:

$$\left\{ \begin{array}{l} n_a \geq \frac{M(N-1)}{(2M+N-1)} \\ n \leq \frac{M}{A} \\ k_{\min} \geq \frac{1}{2}n_a - 2 \end{array} \right. \quad n_a \in [k+6, 2k+4] \quad (k \geq 2) \quad (7.12)$$

By combining all the critical equations, the visualization of the relationship between r , n and $k_{\min}$ was realized in Matlab. Based on this mathematical derivation, we can then estimate the critical cluster size k related to the transformation from the “seed formation dominating state” to “cluster growth dominating state” of the Brownian cluster in a specific SLIS system. The example of the standard SLIS system for Ag membrane growth (Supplementary Fig. 64) at $T = 298.15$ K was selected to test the theoretical reliability. With the essential parameters were statistically determined from the SEM images as $r = 28$ nm and $n = 21 \mu\text{m}^{-2}$, thus n_a was determined to be 357. The calculated range of the critical cluster size k should be in-between 177 and 351, which is highly consistent with the experimental result of cluster size distribution (Supplementary Fig. 64b) when the seed growth is found to become the dominant instead of new-seed formation.



Supplementary Fig. 66. Examination of the validity of the established criterion for the unimpeded growth of Brownian cluster. **a**, Voronoi texture-meshed typical SEM images of the floating Ag solids collected at 55 s (also presented in Fig. 3e in the main text). The red dot indicates the center of each Brownian cluster. **b**, Statistical distribution of the sizes (namely number of particle) of these Brownian clusters presented in **a**. The red bracket indicates the range of the critical size of the Brownian cluster derived from the established theoretical criterion.

S7.2 Criterion for the Cheerios effect-driven aggregation of Brownian clusters/particles

In the absence of external force fields, the two isolated Brownian clusters or particles floating on the aqueous surface are generally subjected to three kinds of forces. The first is the friction force (f) caused by the interaction with the fluid medium for the moving object, which is proportional to the velocity of the Brownian cluster/particle^{7,13}:

$$f = \beta \frac{dx}{dt} = 6\pi\eta R \frac{dx}{dt} \quad (7.13)$$

where the friction coefficient β is given by Stokes law, $\beta = 6\pi\eta R$ (η , viscosity of the medium; R , radius of cluster/particle). The second is the random fluctuation force (F) resulted from the occasional impacts of the Brownian particle with the surrounding fluid molecules. Its distribution over the time of any observation satisfies¹⁴:

$$\langle F(t) \rangle = 0 \quad (7.14)$$

$$\langle F(t_1)F(t_2) \rangle = 12\pi\eta R k_B T \delta(t_1 - t_2) \quad (7.15)$$

in which $\langle \dots \rangle$ is an average with respect to the distribution of the realizations of the stochastic variable $F(t)$, k_B is Boltzmann's constant, T is the absolute temperature and $\delta(t)$ is the Dirac

delta function. The last force is the mutual attraction (A) between the clusters/particles resulting from the Cheerios effect. Under ideal conditions, it can be derived from the interaction potential $E(d)$ between two floating objects with masses m_1 and m_2 at a distance d ^{5,6}:

$$E(d) = m_1 m_2 \frac{(\rho g)^2}{2\pi\gamma\rho_m^2} K_0(d/a) \quad (7.16)$$

$$A = -\frac{\delta E(d)}{\delta d} = \frac{m_1 m_2}{a} \frac{(\rho g)^2}{2\pi\gamma\rho_m^2} K_1(d/a) \quad (7.17)$$

$$a = \sqrt{\frac{\gamma}{\rho_m g}}, \quad K_0(x) = \int_0^\infty \frac{\cos(xt)}{\sqrt{t^2 + 1}} dt, \quad K_1(x) = \frac{\sqrt{\pi}}{2(\frac{1}{2})!} x \int_1^\infty e^{-xt} (t^2 - 1)^{\frac{1}{2}} dt$$

where the lengthscale a is the capillary length of the aqueous medium, g is the gravitational acceleration constant (10 m s^{-2}), ρ is the density of the floating object, γ and ρ_m are the surface tension (simply regarded as a constant of 72 mN m^{-1} when the temperature does not fluctuate significantly from room temperature) and density (nearly a constant of 10^3 kg m^{-3} for pure water with negligible temperature influence) of the aqueous medium, respectively. The functions $K_0(x)$ and $K_1(x)$ are the zeroth-order and first-order modified Bessel function of the second kind, respectively.

Intuitively, the smooth aggregating process for the two Brownian clusters/particles originally isolated at a certain distance depends on two conditions. Firstly, the mutual attraction between them should be larger than the fluctuation force, which means that the Cheerios effect becomes dominant at current moment rather than the Brownian motion at previous stage. Secondly, the Cheerios effect-determined attraction should keep dominant against the friction force during the clusters/particles approaching each other, which ensures that the isolated two clusters/particles can continuously get close to each other until the absolute aggregation once the attractive interaction works (as described in the first condition). However, the second condition turns out to be unnecessary when we take the actual formulas of these forces into consideration. During the mutual approaching process, the work done by the fluctuation force will be zero because $\langle xF(t) \rangle = \langle x \rangle \langle F(t) \rangle = \langle x \rangle 0 = 0$. The attraction increases exponentially with the decreased distance and the friction force increases linearly from zero with the increased velocity. If the attraction is always larger than the friction force, the two floating Brownian

clusters/particles should smoothly approach to each other with an increasing accelerated velocity and velocity. If the attraction is smaller than the friction force at a certain moment before the absolute aggregation of the two floating Brownian clusters/particles, they will experience a deceleration process to keep approaching to each other until the accordingly-decreased friction force gets smaller than the attraction, then resulting in a new round of acceleration process. Taken together, the criterion for the Cheerios effect-dominated aggregation of Brownian clusters/particles only need to identify the critical condition that the attractive interaction can compete with the fluctuation force, that is:

$$A \geq F(t) = \sqrt{\langle F^2(t) \rangle} \quad (7.18)$$

In terms of the symmetry and reciprocity in the whole system of the two attractive objects, the criterion should be further modified as:

$$2A \geq F(t)_{\text{obj1}} + F(t)_{\text{obj2}} \quad (7.19)$$

For simplicity, we assume that it is the spherical particles with the radius of r to consist the two isolated Brownian clusters with the amount of n_1 and n_2 , respectively. Then, the corresponding parameters in A and $F(t)$ can be expressed as:

$$m_i = \frac{4}{3}\pi r^3 \rho n_i \quad (i=1, 2) \quad (7.20)$$

$$R_i \cong r\sqrt{n_i} \quad (i=1, 2) \quad (7.21)$$

By combining all the equations and performing a further organization, the criterion becomes:

$$\left(\frac{64\pi g^5}{243\eta k_B \gamma^3 \rho_m^3}\right)^{\frac{1}{2}} \frac{n_1 n_2}{\sqrt[4]{n_1} + \sqrt[4]{n_2}} K_1\left(\frac{d}{a}\right) \geq \left(\frac{T}{r^{11} \rho^8}\right)^{\frac{1}{2}} \quad (7.22)$$

with the boundary condition that $d \geq (R_1 + R_2)$. From the geometric perspective, the left equation of the inequality is a family of three-dimensional curved surface (denoted as Ω), which depends on n_1 and n_2 at given distance d . Similarly, the right equation represents a plane (denoted as Ψ) that can be simply determined by these determined parameters (T , r and ρ) in a certain reaction system. As a result, the critical condition for the Cheerios effect-dominated aggregation of Brownian clusters/particles is located at the region that locates in the curved surface Ω but above the plane Ψ for a special initial distance d .

S7.3 Tradeoff between the density and size of the floating particles

In the actual reaction system, the supply of building-block particles from the bulk solution to aqueous surface should not be infinite, resulting in the inevitable competition between the density and size of the floating particles in consuming the finite precursor. The whole process, including the incipient nuclei formation and growth on the air-liquid interface along with their further floating onto the liquid surface, may be generally associated to a unique phase transformation process, which can then be described by the Johnson-Mehl-Avrami-Kolmogorov (JMAK) kinetic model^{15,16}.

As shown in Supplementary Fig. 65, once growth of these incipient nuclei with negligible initial size occurs, their radius r can be expressed as:

$$r(t) = Gt \quad (7.23)$$

where G is the radial velocity of the particle growth. Note that these particles are approximately regarded as hemispheric on the ideal air-liquid interface. Furthermore, the density of particles N (number of nuclei/per volume or per area) at time t will be given by:

$$N(t) = N[1 - f(t)] \quad (7.24)$$

where $f(t)$ denotes the extent of consumption of the precursor. After time dt , the radical of the particles below the liquid level grow and lead to the increase in the extent of consumption of the precursor by:

$$df(t) = 2\pi N[1 - f(t)]r^2 dr \quad (7.25)$$

By combining the following equation that is derived from Equation (7.23):

$$dr = Gdt \quad (7.26)$$

Equation (7.25) can be further arranged and simplified into:

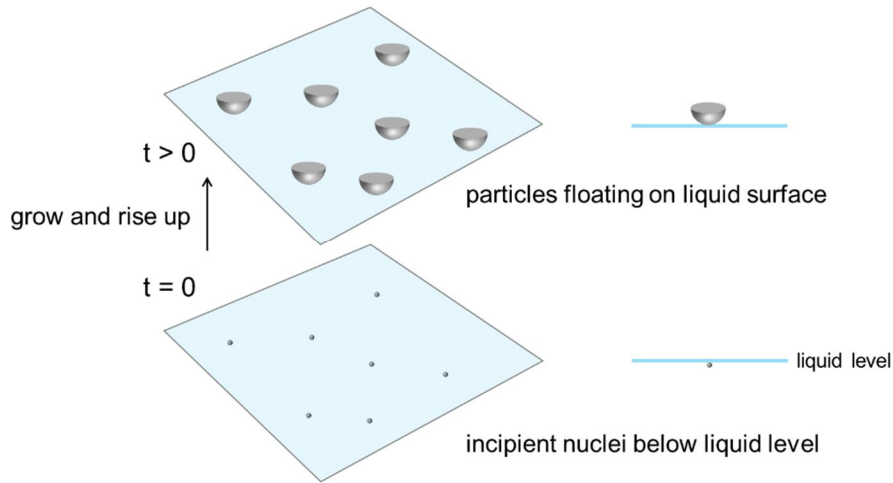
$$\int \frac{df(t)}{1 - f(t)} = \int 2\pi NG^3 t^2 dt \quad (7.27)$$

Based on the initial condition of $f(0) = 0$, the consumption extent of the precursor against time can then be expressed as:

$$f(t) = 1 - \exp\left[-\frac{2}{3}\pi NG^3 t^3\right] \quad (7.28)$$

In reality, due to the finite precursor limit, the particle density and size cannot be extremely big at the same time. Equivalently, an alternative consideration is the evolution time in Equation (7.28) is set to be finite with a simple constraint condition:

$$t \leq t_{critical} \quad (7.29)$$



Supplementary Fig. 67. Schematic diagram of the equivalent phase transformation occurring near the liquid level. The incipient nuclei with negligible initial size form underwater and grow on the air-liquid interface. At a critical moment, these hemispheric particles rise up to float on the liquid level. Thereout, the whole equivalent phase transformation is completed.

Section S8. Foolproof Synthetic Guidance and Membrane Tunability.

S8.1 General synthetic guidance to an unexplored inorganic membrane

On the basis of this figure, the following specific instructions are provided: First, a target inorganic membrane is chosen whose substance is of thermodynamic possibility to produce in an aqueous environment (*S1*). Then one selects the most appropriate among the three reactions, namely precipitation, redox, and hydrolysis, as well as the suitable raw chemicals accordingly (*S2*). The reaction follows the principles of mild temperature, no instant precipitate and no gaseous product. Under the empirical reference of Extended Data Fig. 10b, one can choose the arbitrary initial reaction conditions, including the initial reactant concentration C_{0i} and the reaction temperature T (*S3*). This specified aqueous reaction is then performed in the SLIS system (*S4*), which can constrain the distribution of solid products on aqueous surface.

After a sufficient time that ensures most reactants have been consumed ($t \rightarrow \infty$), one can evaluate the structure attribute of the floating solids in the GT phases through some microscopic characterizations (*S5*). If the well-defined continuous membrane has been observed, proceed to *S7*. If not, one can assuredly adjust the reaction conditions of a new synthesis following the offered guideline oriented to the geometric continuity (*S6*). Generally, if there is no detected floating solid on the aqueous surface, one may increase the reaction driven force by raising the C_{0i} and temperature change ΔT (increasing the temperature for most chemical reactions and these physical crystallizations corresponding to retrograde solubility, but reducing the temperature for physical crystallizations of positive-temperature-dependent solubility to overcome the supercooling, unique example case for the preparation of PbI_2 membrane). Opposite operations should be performed to address the observed case of instant precipitate, which is mainly caused by the excessive local reactant concentration in bulk solution during solution mixing process. If the observed structure of the floating solid belongs to the *NI* phase, namely numerous isolated particles, this suggests that the kinematic process does not pass through the barrier for the initial formation of the Brownian clusters (Fig. 4b, Supplementary Section S7.1). It theoretically results from the too small size of the building units, essentially originating from the fact of extremely high nucleation rate but extremely low radial growth velocity (Fig. 4d, Supplementary Section S7.3). One can appropriately increase C_{0i} and T to

balance the reactant consumptions in nucleation and growth. If the *CI* phase is observed, namely numerous isolated particle clusters, this implies they cannot go over the obstacle that prevents effective aggregation (Fig. 4c, Supplementary Section S7.2). It is primarily caused by the fact that the capillary force between particle clusters is insufficient to counteract their individual random Brownian motion. Thus, one can appropriately raise C_{0i} that generally helps to increase the size of particle clusters and subsequent capillary attraction, as well as decreasing T to weaken the activity of Brownian motion.

For the obtained continuous structure from *S5*, the further evaluation is to judge if it is well-defined *CN* phase (*S7*), based on which, one may further adjust the membrane thickness and through-hole parameters according to requirement (*S9*). Respectively, through finely tuning the reaction conditions, one can regulate the building unit size (vertical dimension) which positively correlates to the membrane thickness (Extended Data Fig. 10g, see Supplementary Section S8.2). By identifying the critical time t_c of bicontinuous network formation, one can then adjust the through-hole parameters, including the through-hole ratio, size distribution and shapes. Generally, the through-hole ratio and size are inversely proportional to the subsequent reaction time after t_c . And the through-hole circularity and geometrical convexity have the opposite trend (Extended Data Fig. 3b-e, Extended Data Fig. 9).

Notably, the *ON* phase may be identified in *S7* instead of *CN* phase. The *ON* phase is an extreme case that is opposite to that of *NI* phase, namely resulted from the fact of extremely high radial growth velocity but extremely low nucleation rate (Fig. 4d). It corresponds to a drastic aggregation of large floating particles directly driven by capillary attraction, thus trending to produce thick membrane featuring less tunability in membrane structure (Supplementary Fig. 66). This thick but continuous membrane can be straightly output for applications (*S10*) if one pays no attention to the membrane structure. If the preparation is oriented to a more compact membrane of much thinner thickness, the intermediate state of *CN* phase is necessary. Accordingly, one may slightly reduce the reaction temperature to decrease the radial growth velocity (*S8*), which contributes to turn down the size of building units. After a foolproof repetition of the prescribed experimental loop, the target membrane with desired thickness and through-hole parameters is produced (*S10*).

S8.2 Discussion on the tunability of the membrane structure

The tunability in membrane thickness and through-hole parameters should correspond to the particular scale, despite the fact that all membranes have the same growth mechanism from the perspective of graph theory, which is scale-free and concentrates on geometrical connection. Since we are unable to do either the precise theoretical prediction or brute experimental exhaustion, it is therefore extremely challenging to provide a universal discussion of the concrete tunability of thickness and pore characteristics for different membranes. Alternatively, on basis of the sufficient data collected along with the as-revealed membrane growth mechanism, we performed some statistical analysis to uncover the hidden patterns and trends, which may provide some prospective insights into the tunability on the structural characteristics of the SLIS-mediated membranes.

Theoretically, the membrane thickness should be positively correlated with the vertical dimension of the building units since their in-plane assembly essentially dictates the membrane formation. Because the aqueous surface fluctuation and the geometric anisotropy of the building units, it is challenging to achieve the perfect aggregation of the single-layer particles in practice, thus leading to the deviation of the thickness compared to the unit size. Based on the statistical results from the various membranes in the as-established library, the SLIS-mediated membrane thickness is empirically revealed to be about 1.06 ~ 5.94 times of the vertical dimension of the building units (Extended Data Figs. 10g). Additionally, this empirical coefficient is found to be almost independent of the reaction time scale, which is the terminal reaction time normalized to the critical time. Based on the determined deviation coefficient, for a certain membrane derived from a specific aqueous reaction, the concerned tuning range in membrane thickness can then be empirically predicted through the tuning range of the building unit size, and the control accuracy in thickness can also be semi-quantitatively estimated based on the unit size distribution (the vertical dimension distribution).

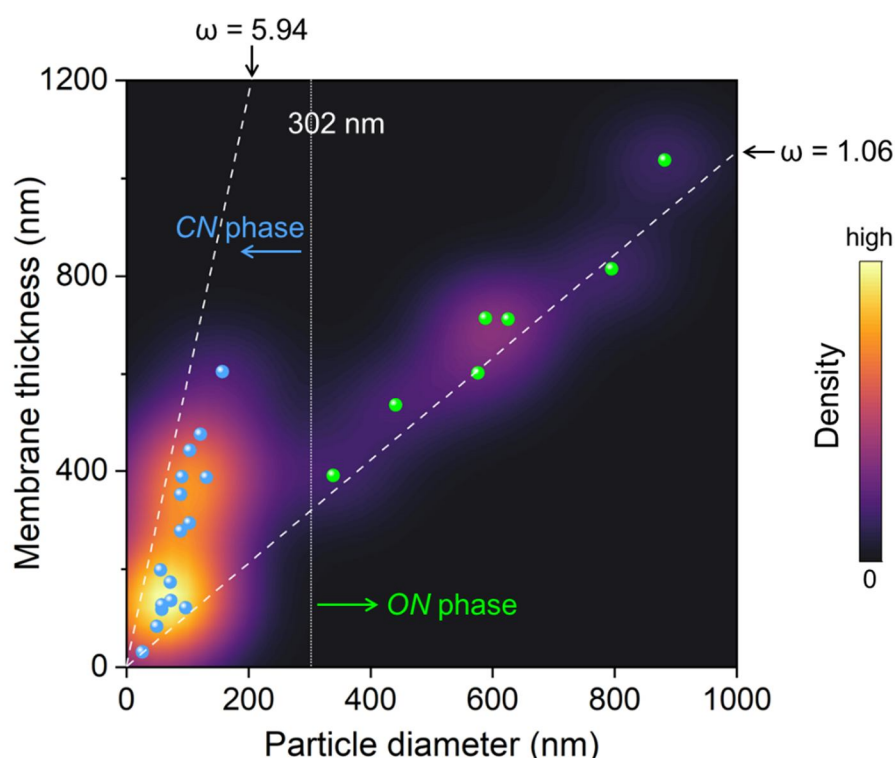
Beyond the empirical law obtained from the statistical summary of various membranes, we have also specifically ascertained the boundary of tunability for the Ag membrane through an orthogonal experimental traversal on the available reaction conditions (Fig. 4a). Notably, the thickness range of the Ag membrane prepared from the SLIS system can widely range across

three orders of magnitude, from 30 nm to ~ 1 μm . Additionally, the membrane thickness continuously increases when the initial reactant concentration rises. Therefore, on the basis of the provided reactant concentrations and the revealed thickness, one can flexibly tune the Ag membrane thickness as required by purposeful interpolation between the gap of the given reactant concentrations. In particular, the minimal thickness difference between the two Ag membranes, which are obtained from the two similar reactant concentrations, may be used to indirectly estimate the tuning precision in the thickness. In the current experiment based on the dichotomized concentration, the tuning precision has reached 35 nm, which may be further reduced by performing more refined interpolation in the given reactant concentrations. Significantly, a further in-depth investigation (Supplementary Fig. 66) reveals that the Ag membrane thickness obtained under various reaction conditions also complies with the empirical rule, which states that it is between 1.06 and 5.94 times the size of the building particle. However, the cases are quite different for the *CN*-phase and *ON*-phase membranes. The *CN* phase completely dominates the region of thin membrane (30 nm to ~ 600 nm) with a relatively high deviation coefficient. In contrast, the region of thicker membrane (~ 400 nm to ~ 1 μm) is absolutely occupied by the *ON* phase, whose deviation coefficient is very close to 1, implying an approximate ideal aggregation of single-layer particles. Retrospectively, this result is easy to understand, it is the floating particle size that essentially determines the kinematic process towards the successful membrane formation. If the particles are large enough (the critical diameter is determined to be about 302 nm for Ag nanoparticles as shown in Supplementary Fig. 66) to result in an overwhelmingly capillary attraction compared to the random Brownian motion, these floating particles will skip the complex kinematic processes and directly aggregate towards the *ON* phase. Although it tends to produce thick membrane, such an effective process is less susceptible to the aqueous surface fluctuation, thus leading to a much lower deviation coefficient for the subsequent membrane thickness in comparison to the *CN* case. Generally, if the critical particle size (the vertical dimension) for the interphase boundary is determined, the tuning range of the membrane thickness can then be empirically estimated. Briefly, the lower boundary is determined through multiplying the smallest available particle size by 5.94, and the upper one through multiplying the largest available particle size by 1.06.

As for the through-hole parameters, including the hole ratio, hole size distribution and hole shape, they are just a concomitant result during the membrane growth to some extent, which can simultaneously evolve over time but not be independently tuned. Notably, once the rigid structure foundation is established, namely the critical bicontinuous network (the least criterion to define a membrane in geometry, as such a structure simultaneously satisfies the 2D matter distribution and the geometric continuity), the through-hole structure will then unimpededly undergo a continuous evolution concomitant with the further floating particle trapping (Extended Data Figs. 7 and 8). This evolves from the initial highly-connected network to a low-circularity closed hole structure, then to a high-circularity closed hole structure and an eventual compact structure (Extended Data Fig. 3). During this process, the through holes are exponentially reduced in the projected area accompanied by the continuously-narrowed size distribution and increased geometrical convexity. From a deeper insight into the hole shape evolution (see Supplementary Section S5.3), the hole boundary of high curvature and low Feret diameter corresponds to a higher relatively shrink rate that is oriented to the center of curvature (Extended Data Fig. 9). This fact allows to preferentially eliminate these boundaries of high curvature and divide the irregular hole into small pieces through the “neck” regions of low Feret diameter, simultaneously diminish the hole connectivity and the geometrical similarity along with the decreasing hole area. Such a continuous process is the practical basis to continuously adjust the membrane through-hole ratio and hole size by simply controlling the evolution time after the formation of critical network. Therefore, if the critical time t_c for the formation of bicontinuous structure is determined, one can accordingly terminate the reaction at the appropriate juncture to obtain the membrane of desired through-hole ratio and hole size distribution. To our best knowledge, this is the first report to realize the continuous adjustment on the inorganic membrane through-hole ratio and through-hole size distribution through a template-free approach.

Honestly, the through-hole shapes cannot be desirably tuned in the SLIS system since their evolution are discontinuous in the geometrical shape parameters. Fortunately, due to the distinctive hole structure in the as-prepared (quasi)-bicontinuous membrane with relative linear open space, their stacking operation has been proven to be an effective post-approach for

modifying the through-hole shape parameters. As illustrated in Extended Data Fig. 5f-j and Supplementary Video 1, in contrast to the mother one-layer membrane, the well-defined closed through holes can be directly created in the stacked counterpart with significantly diminished through-hole size and narrowed size distribution. Additionally, almost every through hole in the stacked membrane may achieve a high circularity of greater than 0.5. It is worth mentioning that such a flexible stacking strategy to modify the through-hole parameters is unique to the (quasi)-bicontinuous membrane.



Supplementary Fig. 68. Tunability of the SLIS-mediated Ag membrane thickness. 2D KDE map of the locations of the Ag membranes derived from various reaction conditions (Supplementary Fig. 62, Fig. 4a) in a customized space, which consists of the particle diameter and the membrane thickness. The particle diameter is the mean value determined by performing Gaussian fitting to the randomly-measured 100 particles in SEM image. The two oblique dash lines indicate the locations that correspond to $\omega = 1.06$ and $\omega = 5.94$, respectively. The dots are coloured in blue and green to distinguish the *CN* and *ON* phases, which are governed by the particle size. The interphase boundary is mathematically determined to be 302 nm (white vertical dot line) through the dot density gradient. The dot density is indicated by the right colour bar.

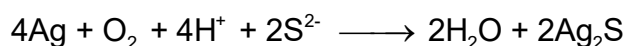
S8.3 Advantages and limitations of the SLIS-mediated membrane synthesis

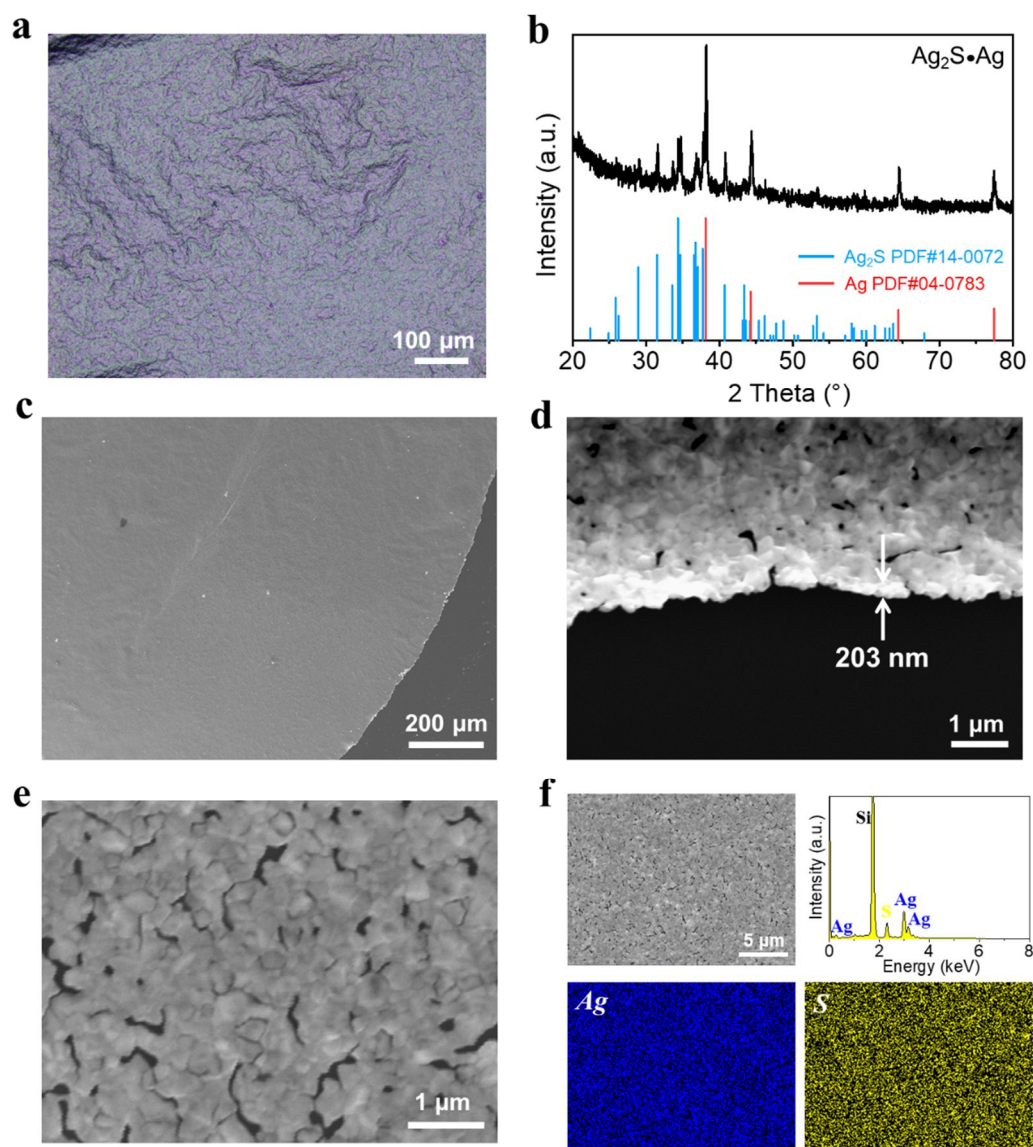
Notably, the universality towards the foolproof synthesis of diverse inorganic membranes, even to those inaccessible and inconceivable ones, without demanding any professional equipment, is the greatest advantage of the SLIS strategy compared to other approaches. This means that one can readily and economically obtain the desired inorganic membrane of intended function from the guided SLIS synthesis.

Someone may argue that the sacrificial substrate-based strategy by separating the pre-deposited films may provide a better controllability with down to atomic-level accuracy^{17,18}, when facing of a certain developed membrane. However, even ignoring the need of professional equipment for high-quality film deposition, this method is only applicable to prepare several specific membranes, rather than a versatile approach. Such a limitation comes from: firstly, the mother film-forming ability highly depends on the interfacial wettability between the targeted membrane and the sacrificial substrate. It is of extreme difficulty to experimentally overcome the undesired Volmer-Weber growth mode (namely island growth mode) for most film-deposition systems¹⁹. In fact, it is challenging to immediately identify the ideal sacrificial substrate and the appropriate film forming conditions for the underdeveloped inorganic membranes. Secondly, the extensional single crystalline is more limited, as it lies on the perfect lattice matching between the targeted membrane and the sacrificial substrate. Thirdly, the size of the as-prepared freestanding membrane is only confined to millimeter level. Because inevitable stress concentration may be induced during the rigid substrate removal. To some extent, our SLIS technique is of a significant complement to the existing substrate-based sacrificial strategies as opposed to competing with them. By relying on the former, one may readily achieve the desired functional membranes with minimal effort and expense, and then explore their possibility for novel applications. Only after the pilot success that validates the worth of future efforts input, one may then pursue these extremely high-quality membranes towards the state-of-the-art performance through the latter strategy, which necessitates the additional input of professional equipment and significant research resources.

Section S9. Extension of Topological Complexity from Simplex Membranes

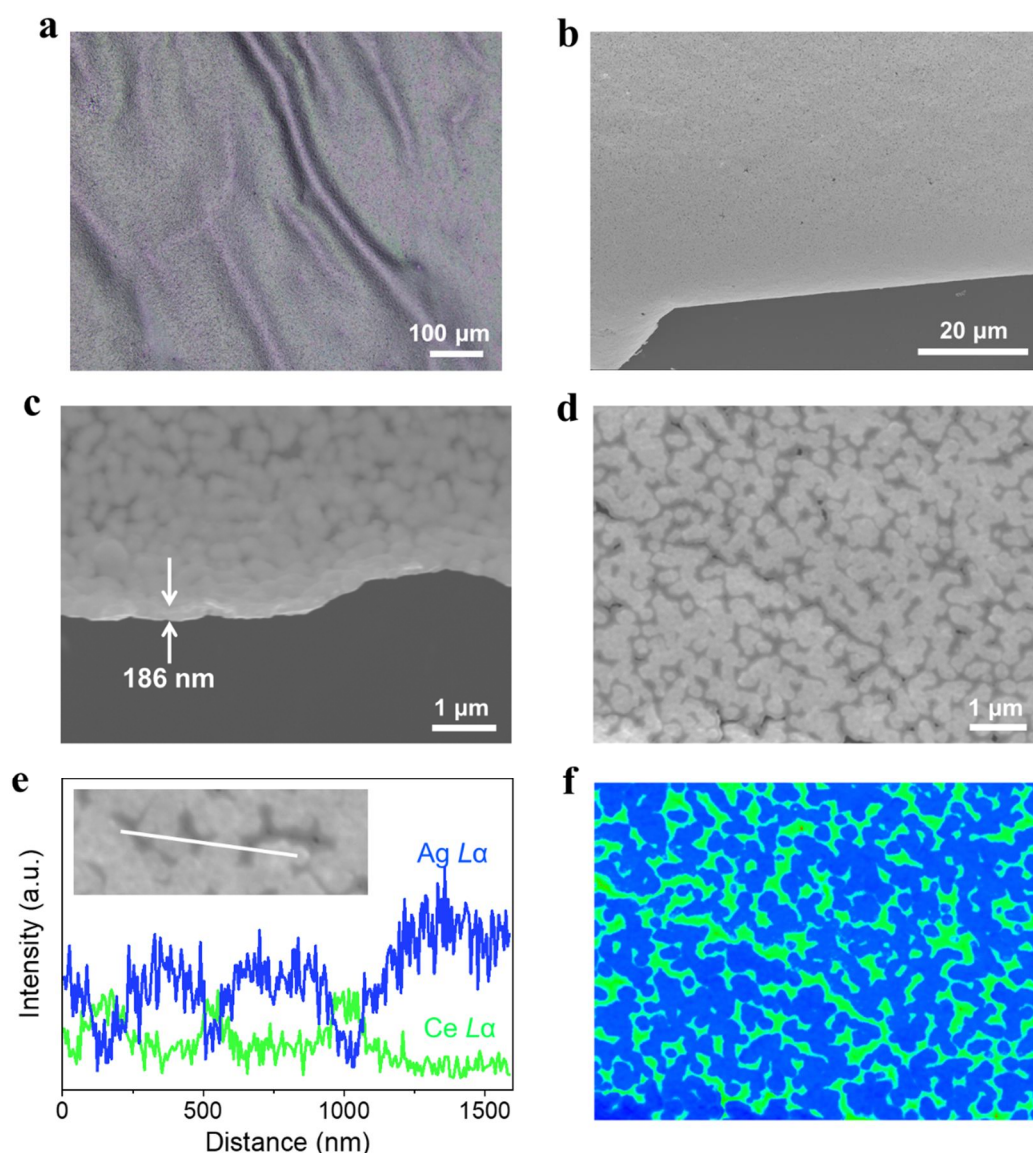
Ag₂S·Ag mixed membrane obtained through chemical conversion. 60 μ L of ammonium hydroxide solution (28-30 wt%) was added into 1.5 mL of AgNO₃ solution (120 mM) to produce fresh Tollens' reagent, and the solution was then transferred into a pretreated Petri dish. Subsequently, 1.5 mL of mixed solution containing D(+)-glucose (250 mM) and NaOH (50 mM) was quickly added and let stand for 20 minutes at room temperature. The aqueous solution was then removed by using a plastic dropper. An alternate addition and removal of 4 mL of DI water was further performed for three times to remove the residual reactants. Finally, after the addition of 3 mL of fresh Na₂S aqueous solution (150 mM) with saturated dissolved oxygen to re-float the Ag membrane, the system was allowed to stand still at room temperature for 12 h. During this process, the original Ag membrane was partially converted into black Ag₂S (Supplementary Fig. 67) with the assistance of dissolved oxygen according to the following redox reaction:





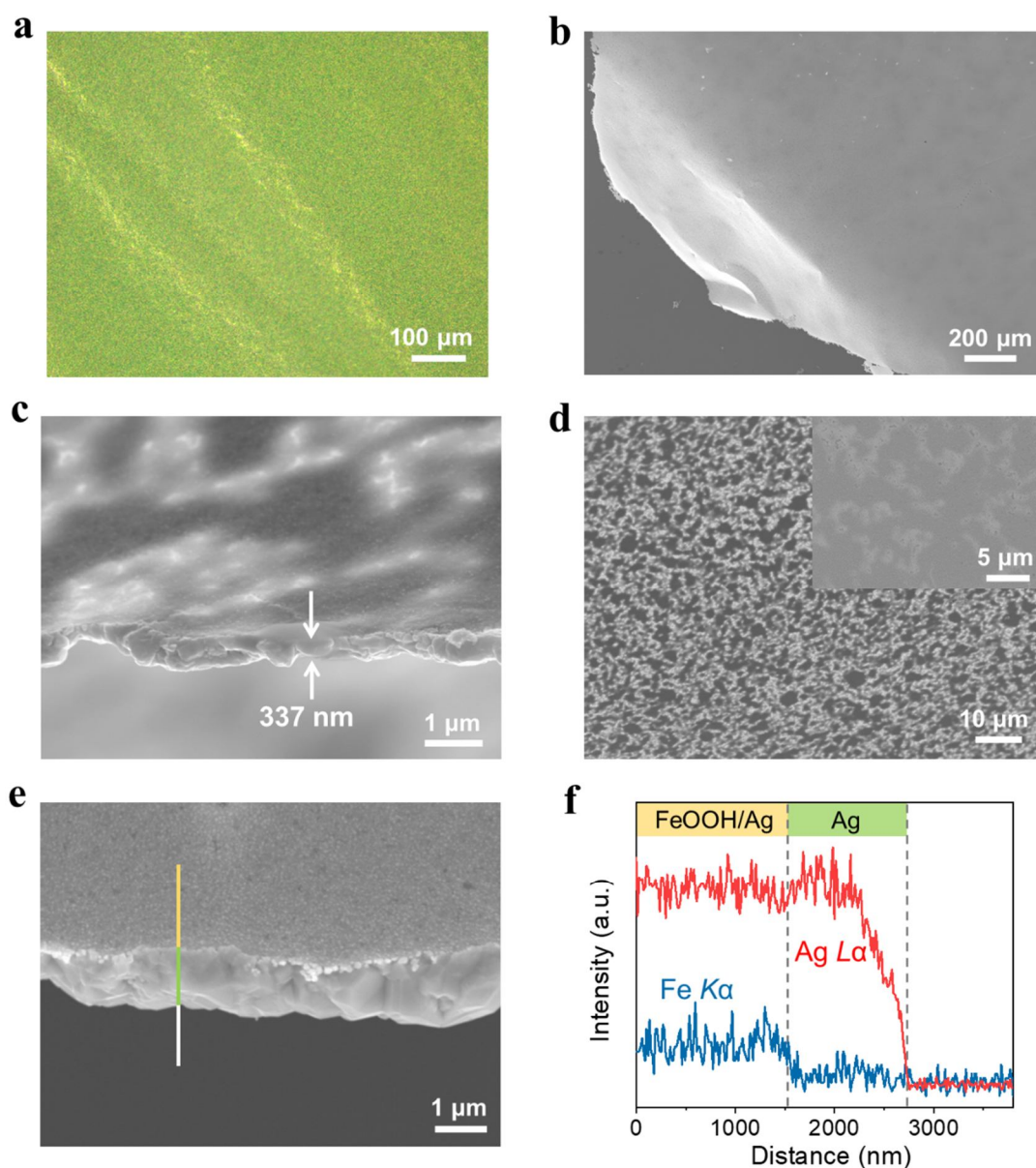
Supplementary Fig. 69. Structure, morphology and composition of the $\text{Ag}_2\text{S}\cdot\text{Ag}$ mixed membrane. **a, b, c**, Optical micrograph (**a**), XRD spectrum (**b**) and overall SEM image (**c**) of the as-synthesized $\text{Ag}_2\text{S}\cdot\text{Ag}$ mixed membrane. **d, e**, Zoom-in SEM images of the cross section (**d**) and the surface (**e**) of the $\text{Ag}_2\text{S}\cdot\text{Ag}$ membrane. **f**, SEM image of the representative surface region of the as-prepared membrane and the corresponding EDS spectrum and element mapping images, confirming the well-defined mixed structure consisted of Ag_2S and Ag in the membrane.

CeO₂~Ag bicontinuous membrane obtained through topological hybridization. 60 μ L of ammonium hydroxide solution (28-30 wt%) was added into 1.5 mL of AgNO₃ solution (120 mM) to produce the fresh Tollens' reagent, and the solution was then transferred into a pretreated Petri dish. Subsequently, 1.5 mL of mixed solution containing D(+)-glucose (250 mM) and NaOH (50 mM) was quickly added and let stand for 10 minutes at room temperature. The aqueous solution was then removed by using a plastic dropper. An alternate addition and removal of 4 mL of DI water was further performed for three times to remove the residual reactants. Finally, after a further addition of fresh mixture of 1 mL of Ce(NO₃)₃ solution (250 mM) and 2 mL of hexamethylenetetramine aqueous solution (1 M) to re-float the Ag membrane, the system was allowed to stand still at 50 °C for 2.5 h. During this process, the single-layer CeO₂~Ag hybrid membrane, featuring a shiny and yellowy appearance with a mutually interlaced network structure (Supplementary Fig. 68), gradually formed on the solution surface when the produced CeO₂ filled inside the pores of the original Ag network.



Supplementary Fig. 70. Structure, morphology and composition of the CeO₂-Ag bicontinuous membrane. **a, b, c,** Optical micrograph (**a**) and overall SEM image (**b**) of the as-synthesized CeO₂-Ag bicontinuous membrane. **c, d,** Zoom-in SEM images of the cross section (**c**) and the surface (**d**) of the CeO₂-Ag membrane. **e,** EDS line scan profile along the white line in the inset SEM image showing the chemical compositions of the bicontinuous regions. The result confirms the observed bi-phase structure is composed of CeO₂ and Ag in a single layer. **f,** Contrast-enhanced image of (**d**) with pseudo colors to highlight the bicontinuous structure in the as-prepared CeO₂-Ag membrane.

FeOOH/Ag stacked membrane obtained through physical stacking. A pretreated Petri dish containing 3 mL of freshly-prepared FeCl_3 solution (50 mM) was kept at 65 °C with a cover for 3 h and then allowed to cool down to the room temperature in the oven. The aqueous solution was then carefully removed by using a plastic dropper. An alternate addition and removal of 4 mL of DI water was further performed for three times to fully remove the residual reactants. Subsequently, 60 μL of ammonium hydroxide solution (28-30 wt%) was added into 1.5 mL of AgNO_3 solution (120 mM) to produce the fresh Tollens' reagent, which was then transferred into the pretreated Petri dish to re-float the as-prepared FeOOH membrane. After a further addition of 1.5 mL of mixed solution containing D(+)-glucose (250 mM) and NaOH (10 mM), the system was kept at 50 °C for 30 min. During this process, the FeOOH/Ag stacked membrane with a golden appearance (Supplementary Fig. 69) gradually formed on the solution surface.



Supplementary Fig. 71. Structure, morphology and composition of the FeOOH/Ag stacked membrane. **a, b, c,** Optical micrograph (**a**) and overall SEM image (**b**) of the as-synthesized FeOOH/Ag stacked membrane. **c, d,** Zoom-in SEM images of the cross section (**c**) and the surface (**d**) of the FeOOH/Ag membrane. **e,** Top-view SEM image of the marginal region of the FeOOH/Ag membrane with a partially-destroyed upper layer, highlighting the well-defined double-layer structure. **f,** EDS line scan profile along the line in (**e**) showing the chemical compositions of the upper and bottom layers and confirming the double-layered structure composed of FeOOH and Ag.

Section S10. Calculation and Simulation.

S10.1 Numerical solution of the capillary attraction-driven kinematic equation

Available Code: S10.1.m

After specific values of $L_0(x)$, $R_1(r_1)$, $k(K)$, and $\rho(p)$ were assigned to the program according to Extended Data Fig. 7, the numerical solutions in these conditions can be obtained.

For Extended Data Fig. 7a-d,

Constants: $x = 400 \mu\text{m}$, $K = 3$, $p = 8000 \text{ kg m}^{-3}$ and $\varepsilon = 0.05$

Variable r_1 : from 10 to 99.99 μm

For Extended Data Fig. 7e-h,

Constants: $x = 20 \mu\text{m}$, $K = 3$, $p = 8000 \text{ kg m}^{-3}$ and $\varepsilon = 0.05$

Variable x : from 100 to 1000 μm

For Extended Data Fig. 7i-l,

Constants: $x = 500 \mu\text{m}$, $r_1 = 40\text{E-}6$, $p = 8000 \text{ kg m}^{-3}$ and $\varepsilon = 0.05$

Variable K : from 1 to 10

S10.2 Collision energy of two Ag Brownian clusters driven by capillary attraction

Available Code: S10.2.m

The values of $x_0 = 50\text{E-}6$, $t = 200$, $dt = 0.0001$, $r = 0.028\text{E-}6$ (experimental value) and $K = 1000$ were employed to calculate the collision energy against the sizes of the Ag Brownian clusters, corresponding to Fig. 3h in the main text.

S10.3 Simulation of dynamic evolutions for four GT-phases

Available Code: S10.3.py

For the simulation of dynamic evolutions for four different GT-phases (Supplementary Video 5, Extended Data Fig. 10c-f), the initial parameters employed are presented as follows:

For *NI* phase (Extended Data Fig. 10e),

Typical parameters: num_points = 100, num_increase = 50, num_fixed = 1, stick_dis = 0.001, scale = 0.01, size = 50, ce = 5e8, a = 1e-7, interval = 0.1 and obs_time = 200

For *CI* phase (Extended Data Fig. 10f),

Typical parameters: num_points = 600, num_increase = 15, num_fixed = 250, stick_dis = 0.01, scale = 0.01, size = 50, ce = 6e8, a = 1e-7, interval = 0.1 and obs_time = 200

For *CN* phase (Extended Data Fig. 10c),

Typical parameters: num_points = 600, num_increase = 35, num_fixed = 20, stick_dis = 0.02, scale = 0.01, size = 200, ce = 5e8, a = 2e-7, interval = 0.1 and obs_time = 200

For *ON* phase (Extended Data Fig. 10d),

Typical parameters: num_points = 20, num_increase = 1, num_fixed = 4, stick_dis = 0.07, scale = 0.01, size = 1400, ce = 2e7, a = 3e-6, interval = 0.1 and obs_time = 200

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