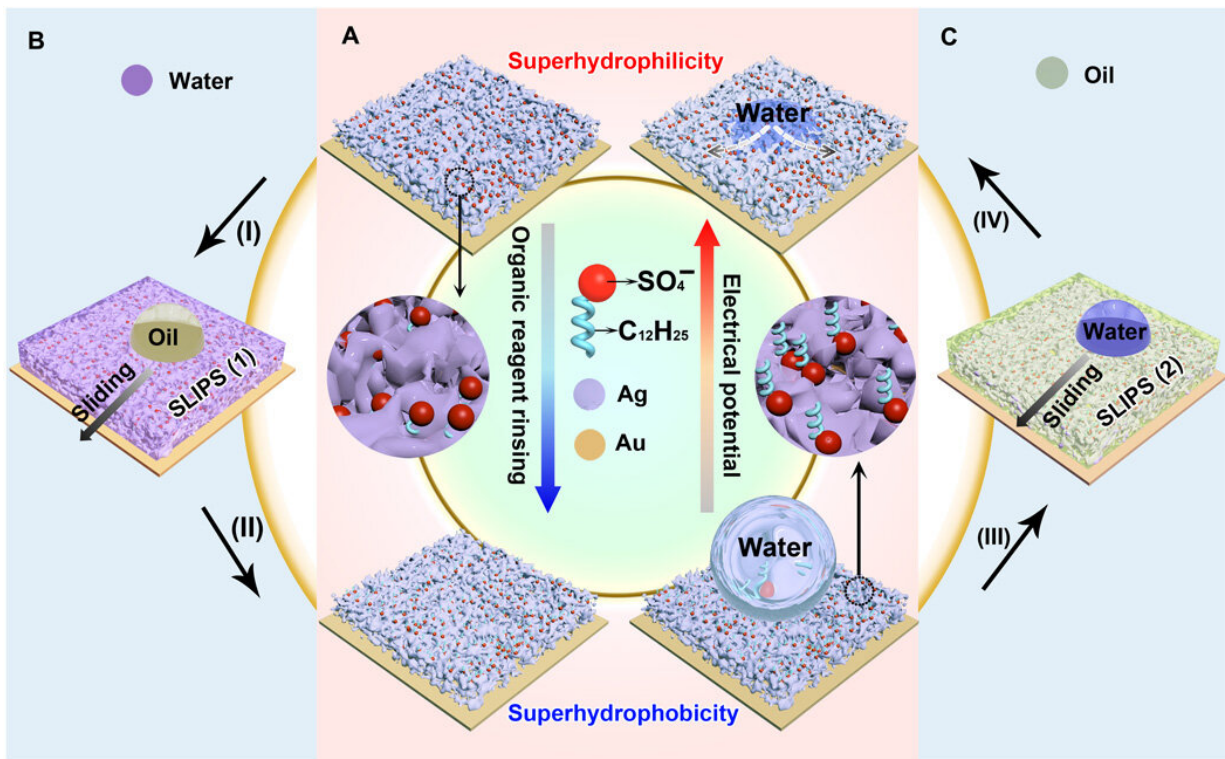


# Electrodeposited surfaces with reversibly switching interfacial properties

November 6 2019, by Thamarasee Jeewandara



Reversibly switching wettability and liquid repellency of the electrodeposited silver porous membranes. (A) Reversible wettability transition from superhydrophilic to superhydrophobic, enabled by the orientation change of the dodecyl sulfate ions. (B) SLIPS 1 is formed by infusing water into the superhydrophilic porous membrane (process I), which can repel oil. After rinsing with ethanol (process II), SLIPS 1 turns superhydrophobic. (C) Oil is infused into the superhydrophobic porous membrane (process III), forming SLIPS 2. Water will be repelled by SLIPS 2. The lubricating oil will be released from SLIPS 2 under an electrical potential (process IV), giving rise to a

superhydrophilic porous membrane. Credit: Science Advances, doi: 10.1126/sciadv.aax0380

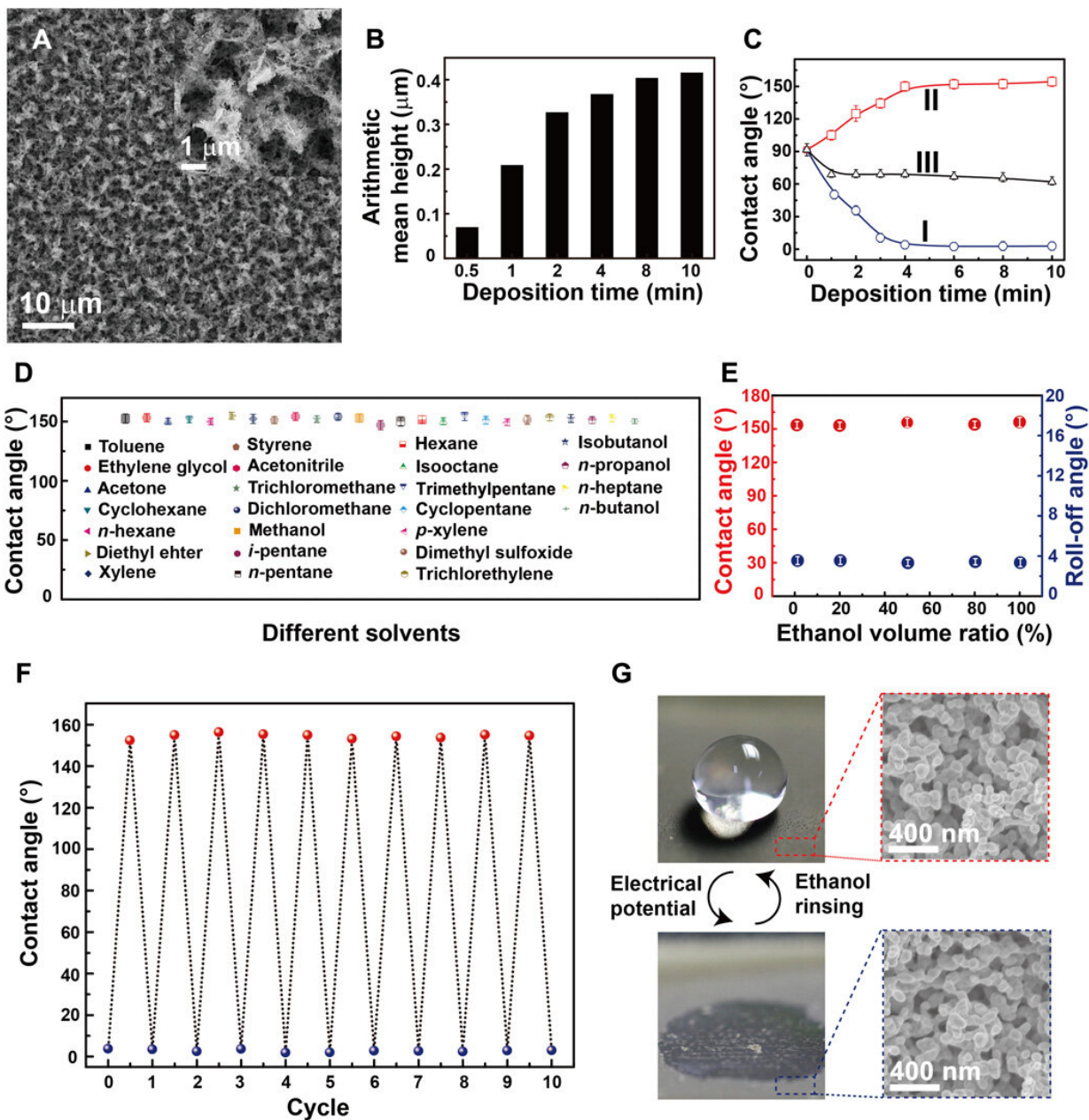
Materials engineering technologies aim to control [wettability](#) and [liquid repellence](#) of material surfaces for diverse applications in and beyond the field of [materials science](#). In a recent report on *Science Advances*, Yue Liu and a team of researchers in the departments of Materials Science and Engineering, and Chemistry and Molecular Engineering in China developed a general concept to develop metallic porous surfaces with exceptionally powerful, wettability-switch capabilities. To engineer the new surfaces, they used an extremely simple, one-step [electrochemical deposition](#) process. The team enabled the wettability switch and manipulated liquid repellent properties by changing the orientation of [dodecyl sulfate ions](#) that were ionically bonded to porous metallic membranes during electrodeposition. The resulting surfaces with adjustable wettability could trap diverse lubricants on demand in the pores to create liquid-infused porous surfaces customized for a variety of liquid-repellent properties. The research team demonstrated the applications of liquid-infused porous membranes for encryption, to control droplet transfer and for water-harvesting. Additionally, the materials scientists coated the silver porous membrane onto a copper mesh to engineer a smart, [antifouling liquid gate](#) to allow oil or water to pass through on request.

In [materials engineering](#), researchers aim to develop reversibly switchable interfacial properties for diverse applications from [microfluidics systems](#), to [water harvesting and transportation](#), as well as [separators](#), [sensors](#) and [drug delivery systems](#). Materials scientists have extensively studied such switchable-wettability surfaces controlled via external stimuli including [light](#), [pH value](#), [thermal and electrochemical treatment](#), [counterions](#) and [electrical potentials](#). In the present work, Liu

et al. reported an extremely simple, one-step electrodeposition approach to engineer porous metallic surfaces with robust wettability switching capacities coupled to outstanding liquid-repellant properties that differed from [previously reported mechanisms](#) to engineer a new wettability switch.

## **Engineering reversible wettability on electrodeposited porous surfaces**

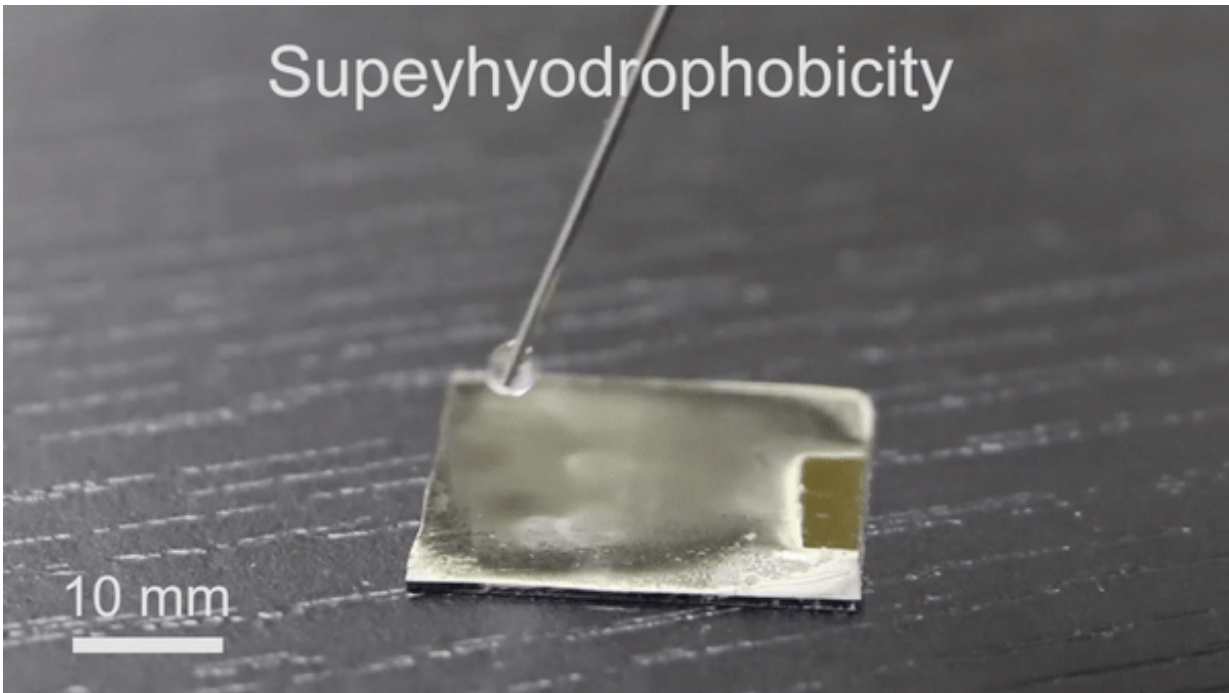
Liu et al. modulated the orientation of dodecyl sulfate ions that ionically bonded to the porous [membrane](#) during electrodeposition to establish reversibly tunable surface wettability. For instance, when the dodecyl chains pointed outward, the membrane retained superhydrophobicity ([water](#) hating nature). Then the researchers used electric potentials to transition the wettability from [superhydrophobic](#) (water hating) to the [superhydrophilic](#) (water loving) state. They confirmed ionic surface orientation changes using [surface-enhanced Raman scattering](#) (SERS) measurements. Based on the ionic orientation-induced evolution of electrodeposited porous surfaces, the research team firmly trapped diverse lubricants within the pores to form different "slippery liquid-infused porous surfaces (SLIPS)" for multiple applications.



Fabrication and characterization of the silver porous membranes. (A) Scanning electron microscope image of the electrodeposited silver porous membrane. Inset: Magnified image. (B) The arithmetical average roughness height of the silver membranes electrodeposited at 1.5 V for different times. (C) Curves I and II are the water contact angles on the as-prepared and the ethanol-treated silver porous membranes prepared at 1.5 V for different times, respectively. Curve III is the water contact angles on the ethanol-treated silver nanoparticle film electrodeposited in pure silver nitrate aqueous solutions. (D) The wettability

transition from superhydrophilic to superhydrophobic can be completed by treatment with 25 commonly used organic reagents. (E) Contact angles and roll-off angles of the superhydrophilic silver porous membrane after being treated by a mixture of water and ethanol at different volume ratios. (F) The wettability transition from superhydrophilic to superhydrophobic and back to superhydrophilic for 10 cycles. (G) The morphology of the porous membrane is unchanged after 10 cycles of wettability transition. The error bars in (C) to (F) are obtained on the basis of at least five independent measurements. Credit: Science Advances, doi: 10.1126/sciadv.aax0380

The new technique will have significant potential in diverse thermochemical applications due to its engineering [simplicity, versatility and low-cost](#). To form the reversible wettability switch, the researchers first electrodeposited a silver porous membrane onto a gold-covered silicon wafer in an electrolyte solution containing silver nitrate and sodium dodecyl sulfate (SDS). As the timeline of electrodeposition increased, the membrane roughness gradually increased, after four minutes, the resulting membrane was superhydrophilic. With the assistance of organic liquids as well as with water containing a minute amount of ethanol (one percent in volume), the scientists could induce the transition of wettability from superhydrophilic (or superoleophilic; water loving) to superhydrophobic (water hating). The instant transition indicated high sensitivity of the membrane toward organic reagents. The water contact angle also increased (hydrophobic character) when they simply exposed the silver porous membrane to an ethanol atmosphere (i.e organic reagent).

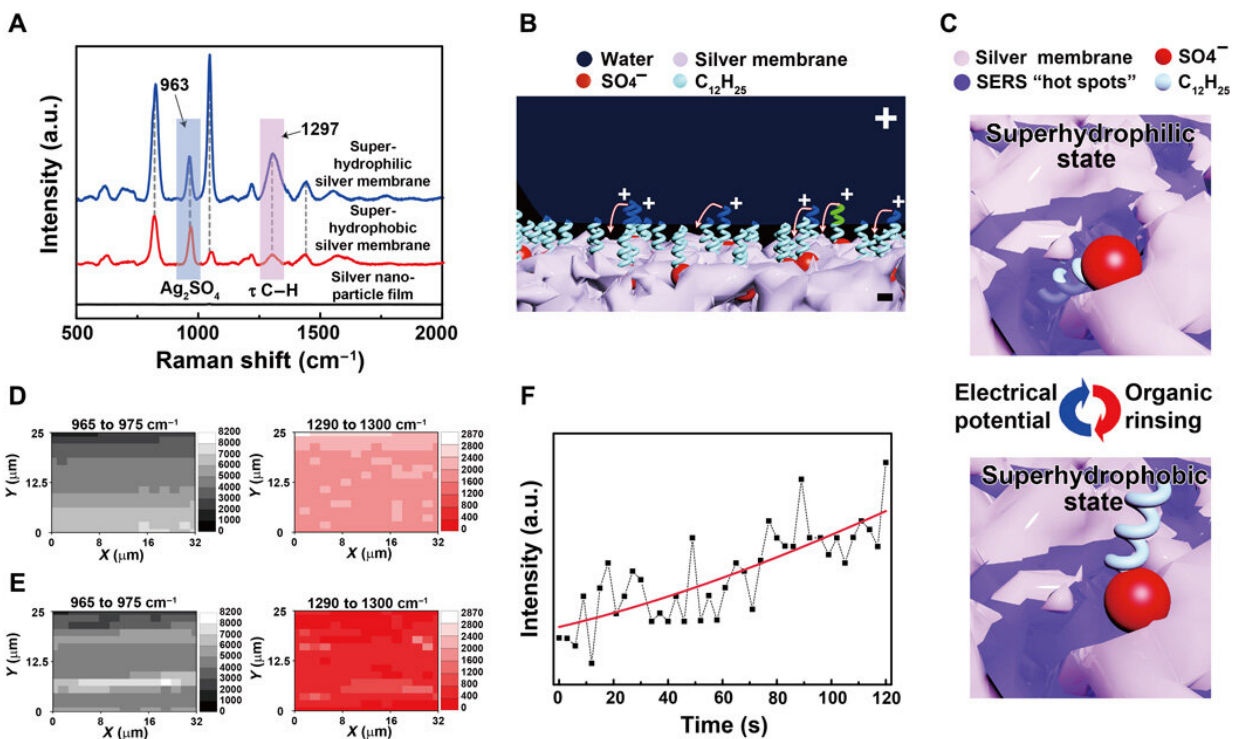


The superhydrophobicity of the organic reagent-treated silver porous membrane. Credit: Science Advances, doi: 10.1126/sciadv.aax0380

### **Understanding the mechanism of wettability transition**

The research team conducted systematic studies to reveal the underlying mechanisms of wettability transition, first by using [Fourier transform infrared spectroscopy](#) (FTIR) and [X-ray photoelectron spectroscopy](#) (XPS) for surface analysis. They proved the existence of SDS ions within the silver porous membrane to form a monolayer structure similar to a previously [well-studied surface](#). Liu et al. hypothesized that hydrophobic dodecyl chain tails hid inside the pores of the freshly prepared silver porous membrane—prompting the silver membrane to initially demonstrate hydrophilicity due to the exposed, hydrophilic sulfate heads.

When the superhydrophilic surface then encountered organic reagents such as ethanol, the hidden dodecyl chain tails changed orientation to face the organic liquids due to their mutually strong affinity. Due to challenges of proving the changing orientation of the dodecyl chains on the rough porous membranes using conventional scanning tunneling microscopy or atomic force microscopy, the team used SERS. The SERS intensity, which mapped the interactions between dodecyl ionic chains and silver sulfate surface, confirmed the transition that facilitated the membrane wettability switch. When they removed the dodecyl ions using oxygen plasma treatment, they eliminated the wettability switch from the silver porous membrane.



Mechanism of the reversibly switching interfacial properties. (A) SERS spectra of the silver porous membrane at superhydrophilic state and superhydrophobic state and the electrodeposited silver nanoparticle film in pure silver nitrate aqueous solutions. The SERS peaks located at 963 and 1297 cm<sup>-1</sup> are assigned

to silver sulfate and the torsional vibration mode ( $\tau$ ) of C—H in the dodecyl chains, respectively. a.u., arbitrary units. (B) Schematic illustration of the orientation change of the dodecyl chains under an electrical potential. Positive charges will accumulate at the tips of the dodecyl chains contacting water, rotating them toward the negatively charged silver porous membrane. (C) Schematic illustration of the SERS intensity evolution of the dodecyl chains at different wetting states. At hydrophilic state, dodecyl chains are exposed to the SERS “hot spots” existing within the pores of the silver membrane, resulting in strong SERS signals. At hydrophobic state, the dodecyl chains are far away from the SERS hot spots, demonstrating weak SERS signals. (D and E) The SERS mapping results of silver sulfate and the dodecyl chains when the porous membrane is superhydrophilic and superhydrophobic, respectively. (F) The intensity evolution of the 1297-cm<sup>-1</sup> SERS peak from dodecyl chains at a specific location as the electrical potential was applied to the superhydrophobic silver porous membrane (photo credit: Yue Liu, Zhejiang University). Credit: Science Advances, doi: 10.1126/sciadv.aax0380

## **Applications of the technique—encryption and liquid transfer**

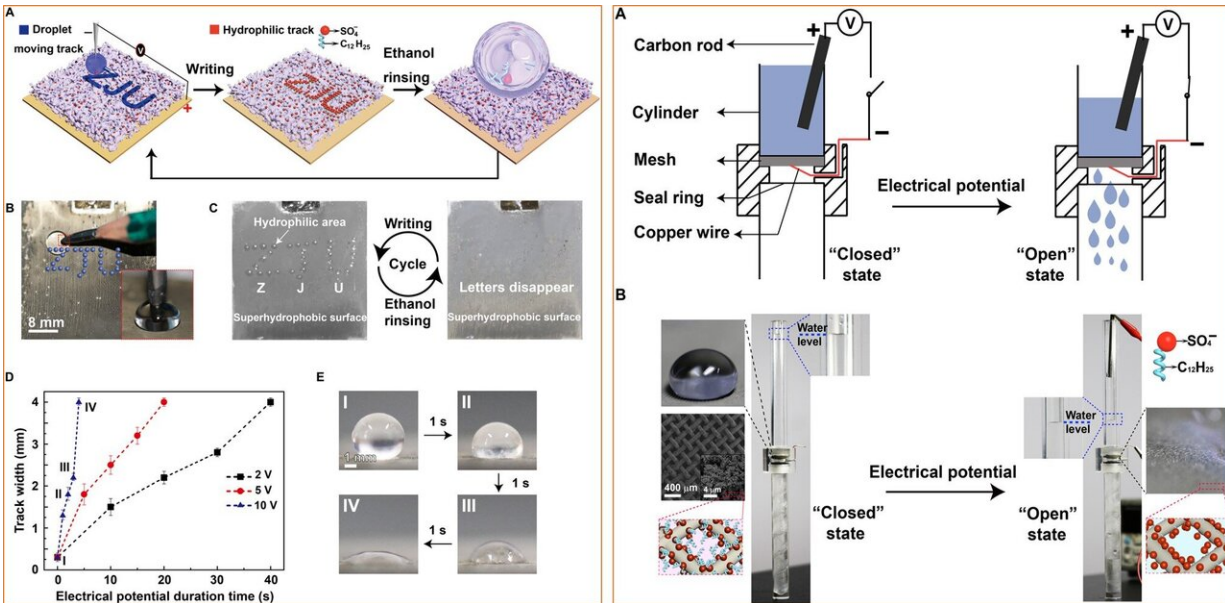
Having developed a new concept to engineer reversible wettability, the research team developed a variety of applications such as information encryption, droplet transfer, liquid-repellence, fog harvesting, and smart liquid gate as well as oil/water separation. For information encryption, Liu et al. dragged a pencil that behaved as a cathode electrode immersed in a droplet, upon the superhydrophobic surface connected to the positive pole of the power supply to write the letters "ZJU." The surface then transformed to maintain hydrophilicity and when the scientists exposed the surface to water or steam, the encrypted invisible words were revealed due to surface attachment of water droplets. They could change the speed of encryption and remove the hydrophilic track using ethanol to recycle the surface multiple times for reuse. By changing surface properties, they could also induce conditions of hydrophobic



encryption. The research team then made use of strong surface adhesion to transfer water droplets across from superhydrophilic surfaces using ethanol-treated silver porous membranes, where droplets adhered on top of the silver membrane for easy transfer.

## **Harnessing the liquid-repellent properties for additional applications**

Thereafter, the research team designed silver [porous membranes](#) to change from superhydrophilic SLIPS1 (slippery liquid-infused porous surfaces) to superhydrophobic SLIPS2 to form a repeatable cycle between SLIP1 and SLIP2 surfaces for a desired timeframe. The work described here were a first in study to engineer such complex wetting and liquid-repellent properties with potential for dynamic adjustment to match diverse lubricants. Additionally, bioinspired by the [Namib desert beetle](#) that used patterned hydrophilic and hydrophobic [elytra](#) (hardened forewing) to retain or remove water droplets, Liu et al. patterned stripes of SLIP2 for excellent water repellence. They engineered surfaces to adhere water molecules for [nucleation](#) on hydrophilic surfaces upon exposure to water mist for outstanding fog harvesting efficiency.



LEFT: Application in encryption. (A) Schematic of the information encryption process. A water droplet is dragged by a pencil connected to the negative pole of a power supply to write letters ZJU on the superhydrophobic surface connected to the positive pole of the power supply. The track turns hydrophilic. When the porous membrane is immersed in water or exposed to water steam, the ZJU letters will appear. Ethanol rinsing can turn the hydrophilic track superhydrophobic, allowing for repeatable usage. (B) The setup for the encryption application. Inset: A pencil behaving as a cathode immersed in a droplet sitting on the superhydrophobic surface. (C) Reusable usage of the silver porous membrane in encryption applications. (D) The track width as a function of the duration time at 2, 5, and 10 V. The error bars are obtained on the basis of five independent measurements. (E) Photographs of the track created at 10 V for different times (photo credit: Yue Liu, Zhejiang University).

RIGHT: Application as a smart liquid gate. (A) Schematic of the setup of the smart liquid gate. (B) At the beginning, the mesh is at the “closed” state because the silver-coated copper mesh is superhydrophobic. Once the mesh is triggered by an electrical potential, it turns to the “open” state, and water starts to pass through the mesh. Inset: The image of a water droplet on and the orientation of the dodecyl sulfate ions on the silver-coated copper mesh at the closed and the open state, as well as the microstructure of the silver-coated copper mesh (photo credit: Yue Liu, Zhejiang University). Credit: Science Advances, doi: 10.1126/sciadv.aax0380

Next, the scientists electrochemically coated the silver porous membrane onto a copper mesh for applications as a smart liquid gate. While the original superhydrophobicity prohibited the passage of water, when they applied a negative electric potential to the copper mesh, the surfaces became superhydrophilic for the immediate passage of water. The surface property could be interchangeably engineered by exposure to ethanol vapor, for reuse. Liu et al. similarly engineered silver-coated copper meshes for selective water/oil separation, which differed from existing prototypes for efficient oil and water isolation and transfer.

In this way, Yue Liu and colleagues developed a general concept to engineer metallic coatings with switchable wettability liquid repellence using a simple, one-step electrodeposition method. They harnessed the changing orientation of dodecyl sulfate ions ionically bonded to the electrodeposited porous metallic membrane, with organic reagent treatment or an external electric potential to facilitate the wettability switch. They recycled the wettability transition more than 10 times in the study, while forming diverse SLIPS for a variety of applications. The extremely simple and cost-effective materials engineering approach to form switchable [wettability](#) and liquid-repellant materials surfaces will have promising applications in liquid/thermal-related fields within and beyond materials science.

**More information:** Electrodeposited surfaces with reversibly switching interfacial properties  
[advances.sciencemag.org/content/5/11/eaax0380/](https://advances.sciencemag.org/content/5/11/eaax0380/) Yue Liu et al. 01 November 2019, *Science Advances*.

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Nature-inspired superwettability systems

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