†Electronic Supplementary Information

Unidirectional Bubble Transportation on Slippery Micro-Cone Array Electrodes Enables Spontaneous 99.99% Gas Separation in a Membrane-less Water Electrolysis

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Experimental procedures

Chemical Reagents

The photosensitive resin for 3D printing (BMF Materials Technology Co., Ltd., Shenzhen, China) contains methacrylate zwitterion, lauryl methacrylate, and 2,4,6-trimethyl benzoyl diphenyl phosphine oxide (TPO) as a photoinitiator for 405 nm UV light. Chemicals except for SnCl₂ (AR, Sinopharm), NaH₂PO₂-H₂O (AR, Macklin), and PdCl₂ (AR, Aladdin) were purchased from Beijing InnoChem Science & Technology Co., Ltd. All chemicals were used directly, without further treatment.

Preparation of Tilted Array Electrodes

Initially, the design of the electrodes was accomplished through the utilization of computer-aided design software. The electrodes were created as a comprehensive structure of 1×1 cm². Each individual cone inside the structure possessed dimensions of 300 µm and a pitch of 200 µm. The inclination angle of the cones, in relation to the horizontal plane, was varied to construct the array electrodes. Specifically, the angles chosen for adjustment were 0°, 10°, 20°, 30°, 40°, 50° and 60°. Subsequently, the 3D sample files were transferred to proprietary software and fabricated using a UV stereolithography 3D printer, namely the BMF nanoArch P140 model, which used a 405 nm light-cured UV photosensitive resin. Ultimately, the unhealed resin was thoroughly eliminated using a triple washing process employing ultrasonic ethanol.

Preparation of 3D Cu-Pt Working electrodes

A typical chemical deposition method was used to synthesize a nickel-phosphorus metal layer on the surface of the previous resin to make it conductive. First, the 3D array electrodes were immersed for 15 min at 50 °C in a sensitization solution (10 g·L⁻¹ SnCl₂, 0.12 M HCl) and then rinsed three times with deionized (DI) water. Second, the previously treated samples were soaked in activation solution (0.1 g·L⁻¹ PdCl₂, 0.03 M HCl) for 25 mins at 50°C and rinsed three times with deionized water. Finally, the samples were immersed in ammonia in a chemical deposition solution (13 g·L⁻¹ NiSO₄·6H₂O, 21 g·L⁻¹ C₆H₈O₇·H₂O, 10.6 g·L⁻¹ NaH₂PO₂·H₂O) at pH 10.0 for 30 mins at 80 °C. The samples were then rinsed three times with deionized water. In order to grow secondary structures on the electrode surface, copper electrodes were synthesized by electrodeposition in a solution consisting of CuSO₄·5H₂O and H₂SO₄ at pH = 2.0 while enhancing their electrical conductivity in this way. Specifically, platinum wires were used as counter electrodes and Ag/AgCl as reference electrodes, which were deposited at a constant voltage of 1 washed three times with deionized water, and freeze-dried (YB-FD-1) for 12 hr. Finally, we prepared the TMCA electrode for the HER reaction by electrodepositing platinum on its surface to enhance its catalytic performance.H₂PtCl₆ solution (3 mM, Aladdin) with KNO₃ (100 mM, Aladdin) was used as the electrolyte in the electrodeposition process with a deposition potential of -0.3 V versus Ag/AgCl, while a platinum wire was used as the counter electrode.

Characterization

The morphology and composition of the samples were characterized using a scanning electron microscope (SEM, Z Nyquist curve s SUPRA 55). In the range 0-100°, x-ray diffraction (XRD, Siemens D-5000) with Cu (K = 0.15418 nm) was used at a scan rate of 10° min⁻¹. In-situ microscopy was done with a high-speed camera (i-speed 3). Adhesion experiments were performed using an adhesion tester (DCAT 21). Characterization of the wettability of the electrode

surface using an optical contact angle tester (CA100D). An in-situ gas chromatograph (Shimadzu-GC-2014) was used to determine the purity of the H₂ produced.

Electrochemical Measurements

Three-electrode experiments were conducted in a single-chamber quartz reactor utilizing 0.5 M H_2SO_4 as the electrolyte, including a platinum wire counter electrode, a saturated calomel reference electrode (with saturated KCl as the internal reference solution), and a Cu-Pt working electrode. The three-electrode experiments were carried out in a single-compartment quartz reactor using 0.5 M H_2SO_4 as the electrolyte, consisting of a platinum wire counter electrode, a saturated mercuric glycol reference electrode (with saturated KCl as the internal reference solution), and a copper-platinum working electrode. For the accuracy of the measurement data, a salt bridge is used to reduce the solution resistance between the working electrode and the reference electrode to within 1 Ω . The L-type salt bridge is inserted into the reference electrode after adding saturated KCl, and the reference needs to be calibrated before use.

Electrochemical linear polarization curve (LSV) and hydrogen evolution reactions were conducted using an electrochemical workstation (CHI 660e). EIS experiments were carried out in the galvanostatic mode across frequencies ranging from 0.1 to 10 kHz, employing the same workstation. It's worth noting that all results obtained from the three-electrode tests were presented without iR correction, unless explicitly stated otherwise.

The interaction force between the gas bubbles and electrode interfaces can be assessed by a high-sensitivity microelectromechanical balance system (Dataphysics DCAT21, Germany). An optical microscope lens and a charge-coupled device camera system were used to take photographs at the rate of one frame per second. The electrode surface was placed in a square quartz cell (50 mm × 50 mm × 50 mm) filled with 0.5 M H₂SO₄ (electrolyte), and the cell was fixed to the plate of the balance system. Gas bubble ($\approx 2 \mu$ L) was suspended on a metal ring in the 0.5 M H₂SO₄, and the force of this balance system was initially set to zero. The electrodes were moved downward at a constant speed of 0.1 mm·s⁻¹ until their surfaces contacted the air bubble. The force was increased gradually until it reached its maximum and the shape of the air bubble changed from spherical to elliptical. Subsequently, when the electrode moved up then, the contact was sharply reduced to near zero and the shape of the air bubble changed back to spherical.

In the membrane-less water electrolysis device, two tilted array electrodes served as the cathode and anode for the water electrolysis reaction (Ir electrodeposited on the anode side as a catalyst), with 0.5 M H_2SO_4 acid as the electrolyte. The distance between the two electrodes is regulated by use of shims of different thicknesses during assembly. The shims are placed symmetrically, with an ultra-thin shim in the middle (the center window is smaller than the reaction area of the thicker shims on both sides) to achieve the non-crossing of hydrogen and oxygen in area of the gas chamber at the upper end of the electrolyte. Outlet ports are provided above both cathode and anode, and then the produced hydrogen was directly transported in a gas chromatograph for in situ purity measurement.

Contact Angle Measurement Methods

The contact angles of bubbles on solid substrates were characterized by the captive bubble method using a Dataphysics OCA20 system. The advancing and receding contact angles of underwater gas bubbles on the solid surfaces were measured by pinning an initial 4.0 μ L gas bubble first on the solid surface and then increasing or decreasing the volume of the bubble with a 0.1 μ L s⁻¹ dosing rate. The values of the contact angles were obtained as the three-phase contact lines of bubbles moved with the varied bubble volumes.

Note 1

The forces acting on the bubble include bubble buoyancy F_B , hysteresis resistance F_H , Laplace pressure F_L , water resistance F_D , lifting force F_{Lift} and adhesion force F_A .

The buoyancy force F_B is determined by the effective part of the upper and lower surfaces, which can be expressed as

$$F_B = V(\rho_l - \rho_g)g \tag{1}$$

where V is volume of liquid occupied by the bubble, ρ_l is the density of water (10³ kg/m³), ρ_g is the density of hydrogen (0.0899 kg/m³), g is the acceleration of gravity (9.80 m/s²).

As $f_{\rm H}$ is basically determined by the contact angle and the contact angle hysteresis (δ , namely " $\vartheta_a - \vartheta_r$ "), expressed as $f_a = 2\gamma sin\left(\theta_{ms} + \frac{\delta}{4}\right) sin\left(\frac{\delta}{4}\right)_{\rm Or} f_r = 2\gamma sin\left(\theta_{ms} - \frac{\delta}{4}\right) sin\left(\frac{\delta}{4}\right)_{\rm or}$, where γ is the surface tension of water, ϑ_r and ϑ_a are the receding

and advancing angles and ϑ_{ms} are the mean value of ϑ_{r} and ϑ_{a} , respectively.

The Laplace pressure F_L is the axial component of the Laplace pressure driving the automatic movement of the bubble towards the bottom of the cone, which can be expressed as

$$F_L = 2\gamma \left(\frac{1}{r_1} - \frac{1}{r_2}\right) Ssin\beta \tag{3}$$

where r_1 , r_2 are the local radii of the bubbles on opposite sides, S is the bottom area of the bubble in contact with the vertebrae and B is the half-vertex angle of the cone. As the cone is prepared by controlling the constant radius of the cone base and height, as the tilting angle becomes larger, the cone's apex angle will gradually become smaller, resulting in r_1 , r_2 becoming smaller. Combined with the asymmetric deformation of the bubble that occurs in the tilted case (*S* becomes larger) and the smaller cone curvature, it is reasonable to assume that the F_L will remain constant as the tilting angle becomes larger, which is consistent with the calculations.

The water resistance F_D is the resistance of water to the bubble's movement and can be expressed as

$$F_D = \frac{1}{2} C_D \rho_l v^2 A \tag{4}$$

where C_D is the drag coefficient of the water, which can be estimated as 1.22, v is the transport speed of the bubbles and A is the cross-sectional area of the bubble (2560.358 μ m² at R_0 = 30 μ m).

The lifting force F_{Lift} is the lifting force due to fluid movement. It is generated by the suction on an adhering body of a uniform flow over the body (Bernoulli suction),

$$F_{Lift} = \frac{1}{4} C_L \frac{w}{R_0} \rho A v^2 \tag{5}$$

where C_L can be calculated using Bernoulli's equation and potential flow theory and can be estimated as 1.375.

The adhesion force F_A can be presented as

$$F_A = \gamma 2\pi (R_0 \sin \theta) \sin \theta \tag{6}$$

where ϑ is the intrinsic contact angle (130°) on smooth surface.

For the force analysis of Figure 4, we fix the curvature radius of the contact line r_1 to be 30 µm, then with the increase of the bubble and the change of the tilting angle, the curvature radius of the contact line r_2 , the contact width w and the bottom area of the bubble *S* change as shown in the table below:

α (°)	r₂ (μm)								
R₀ (µm)	10	20	30	40	50	60			
5	33	31	28	23	16	10			
10	35	34	30	24	17	10			
15	38	36	32	26	19	11			
20	40	39	35	28	20	12			
25	43	41	37	30	21	13			
30	45	44	39	31	22	13			
35	48	46	41	33	24	14			
40	50	48	43	35	25	15			
45	53	51	45	37	26	15			
50	55	53	48	38	27	16			
55	58	56	50	40	29	17			
60	60	58	52	42	30	18			

r₁=30 µm

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Table S1. As the radius of the bubble increases and the tilting angle changes, r_2 numeric table.

R₀ (µm)	5	10	15	20	25	30	35	40	45	50	55	60
w (µm)	7.15	14.30	21.45	28.60	35.75	42.90	50.05	57.20	64.35	71.50	78.65	85.8
S (μm²)	40.2	160.6	361.4	642.4	1003.7	1445.5	1967.4	2569.7	3252.3	4015.2	4858.3	5781.8
r ₁ =30 µm												

Table S2. As the radius of the bubble increases and the tilting angle changes, w, S numeric table.

Therefore, based on equations (1-3), we can find out the forces on the bubble in different cases as shown below:

<u>α (°)</u>		F _L (μN)						E (NI)	E (11NI)
R₀ (µm)	10	20	30	40	50	60	г _в (µм)	г _н (µм)	Γ _Α (μΝ)
5	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.033	1.342
10	0.019	0.019	0.019	0.019	0.020	0.020	0.021	0.066	2.685
15	0.061	0.061	0.061	0.061	0.062	0.062	0.069	0.099	4.027
20	0.135	0.135	0.136	0.136	0.137	0.137	0.165	0.132	5.369
25	0.249	0.249	0.250	0.251	0.252	0.252	0.322	0.164	6.711
30	0.406	0.406	0.408	0.409	0.411	0.412	0.556	0.197	8.054
35	0.611	0.611	0.613	0.616	0.618	0.619	0.882	0.230	9.396
40	0.866	0.867	0.870	0.873	0.876	0.878	1.317	0.263	10.738
45	1.175	1.176	1.179	1.184	1.188	1.191	1.875	0.296	12.080
50	1.538	1.540	1.544	1.550	1.556	1.560	2.573	0.329	13.423
55	1.958	1.960	1.966	1.973	1.981	1.986	3.424	0.362	14.765
60	2.436	2.439	2.446	2.455	2.465	2.471	4.446	0.395	16.107

r₁=30 μm

Table S3. As the radius of the bubble increases and the tilting angle changes, Laplace pressure F_L , bubble buoyancy F_B , hysteresis resistance F_H and adhesion force F_A numeric table.

	Aerophilic	Superaerophobic	Slippery aerophobic
Bubble contact angle	32°	165°	130°
Advancing angle (θ_a)	50°	167°	135°
Receding angle (θ_r)	23°	162°	127°

 Table S4. The receding and advancing angles of aerophilic, superaerophobic and slippery aerophobic electrode surfaces.



Figure S1. (a) Digital photographs of 3D printing of Resin template, Ni-P conductive layer, electrodeposited Copper layer, Pt nanoparticle layer. (b) The schematic diagram of the PµSL 3D printer. (c) XRD pattern of 3D Cu nanowire and the illustration shows SEM of an enlarged inclined platinum array electrode.



Figure S2. Schematic diagram of a tilted micro-cone array (TMCA) electrode design.



Figure S3. (a-e) SEM images of electrodeposited Cu layer for different times (0 s, 60 s, 120 s, 300 s, 600 s) and Cu layer after electrodeposition of Pt epidermal layer. (g) Corresponding elemental mapping of Cu layer after electrodeposition of Pt skin layer. (h-i) Adhesion curves and data of Cu layer after electrodeposition of Cu layer for different times (0 s, 60 s, 120 s, 300 s, 600 s) and electrodeposition of Pt skin layer.



Figure S4. Cross-section SEM image of Cu electrodeposited layer.



Figure S5. Nyquist curve of the TMCA electrode with tilting angle of 50°.



Figure S6. Bubble transport behaviors on electrodes with tilting degree of (a) 30° and (b) 60°.



Figure S7. Bubble images at different tilting angles of (a) 10° (b) 40° and (c) 50° with front view.



Figure S8. Statistics of detached bubble size on electrodes with different tilting angles and smooth electrode as the reference.



Figure S9. Bubble transport behaviors at different tilting angles of (a) 50° and (b) 60° from front view.



Figure S10. Drag force (F_L , $F_B \sin \alpha$ and F_H) analysis curve for a given bubble (R_0 =30 µm) rolling on cones with different tilting angles.



Figure S11. (a-f) Cyclic voltammetry curves of TMCA electrodes with different tilting angles at different scan rates.



Figure S12. (a) Plots of scanning speed versus current for array electrodes with different tilting angles. (b) Tafel plots from LSV curves with different tilting angles.



Figure S13. LSV curves of TMCA electrodes (50° tilting angle) with different inter-cone spacing R₇₅D₂₀₀, R₃₀₀D₂₀₀, R₁₅₀D₄₀₀.



Figure S14. (a-c) Bubble transport behaviors on TMCA electrodes (50° tilting angle) with different inter-cone spacing $R_{75}D_{200}$, $R_{300}D_{200}$, $R_{150}D_{400}$.



Figure S15. Stability test of TMCA electrode at 100 mA·cm⁻².



Figure S16. (a-b) Design diagram and actual photo of membrane-free water electrolysis device



Figure S17. (a) Inter-electrode distance-dependent current density variation. (b) Gas purity chromatography testing in close proximity.