Supporting Information

MoS_2-Modified Porous Gas Diffusion Layer with Air-Solid-Liquid Interface for Efficient Electrocatalytic Water Splitting

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ABSTRACT. The formation and adsorption of bubbles on electrodes always weaken the efficiency of gas evolution reactions such as hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) due to the barrier of proton-transfer and consuming of nucleation energy. Herein, a triphase electrode has been fabricated to address this limitation by immobilizing MoS_2 nanosheets on porous gas diffusion layer (GDL), which shows a superior HER and OER ratio, high current density and stable working state in electrocatalytic water splitting. Moreover, offering a lower pressure behind the GDL, we realized a further improvement of water-splitting speed (3 times higher current density than that of bare MoS_2 diphase electrode at -0.37 V for HER and 1.62 V for OER) and stability by extinguishing the appearance of bubbles even under a current density as high as 100 $mA \cdot cm^{-2}$. Our work manifests the significance of constructing a triphase system for water-splitting, which is also available for other gas evolution reactions.

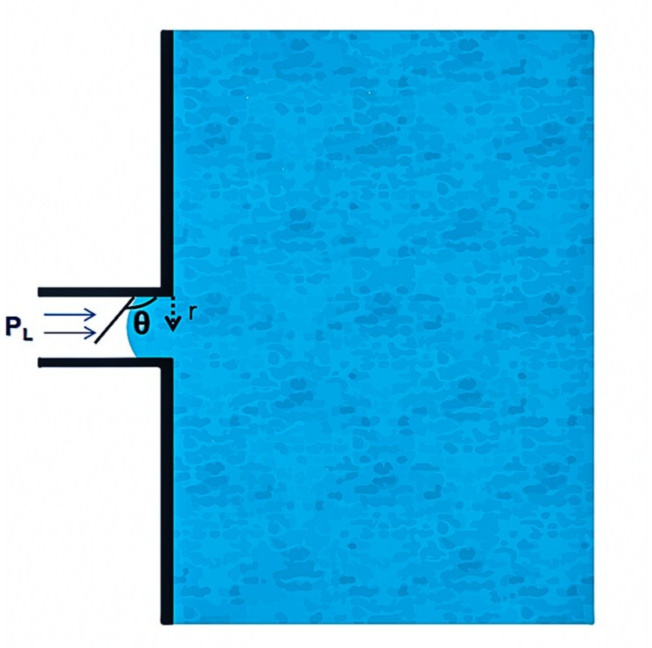

Figure S1. Capillarity model of the pore on carbon fiber paper.

According to Young-Laplace equation, the hydrophobic capillary that is immersed in water would form a meniscus, which has a Laplace pressure, and therefore support water behind porous film. The Laplace pressure can be calculated by the formula:

$$p_1 = \frac{2\alpha \cos\theta}{r}$$

where α is the surface tension coefficient of water and r is the radius of the pore of carbon fiber paper.

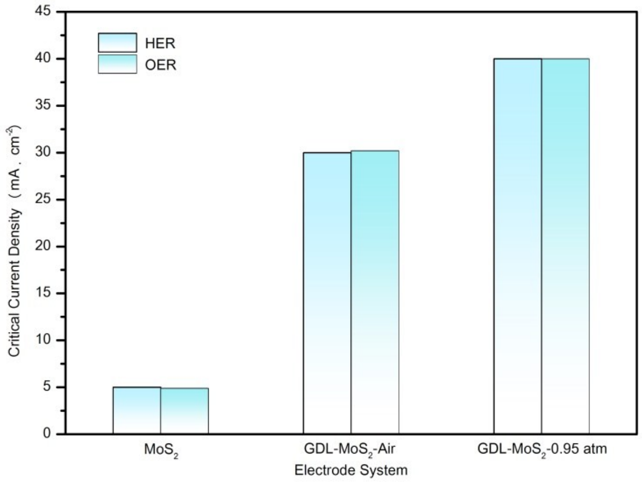

Figure S2. Critical current density for generating bubbles in different system.

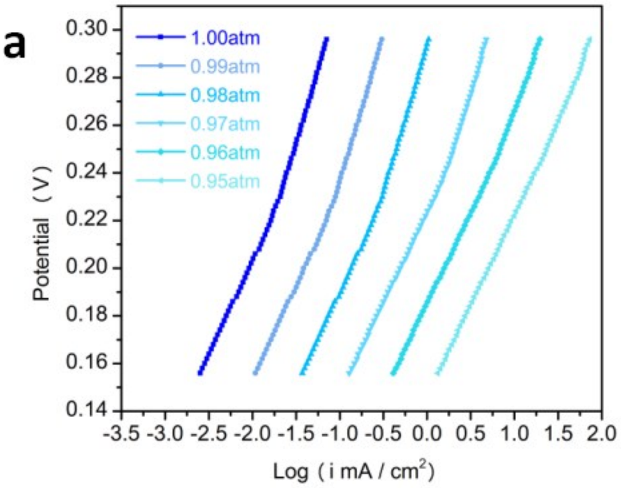

Figure S3. (a) and (b) are Tafel plots of lengthening potential range for HER and OER at different pressure, respectively.

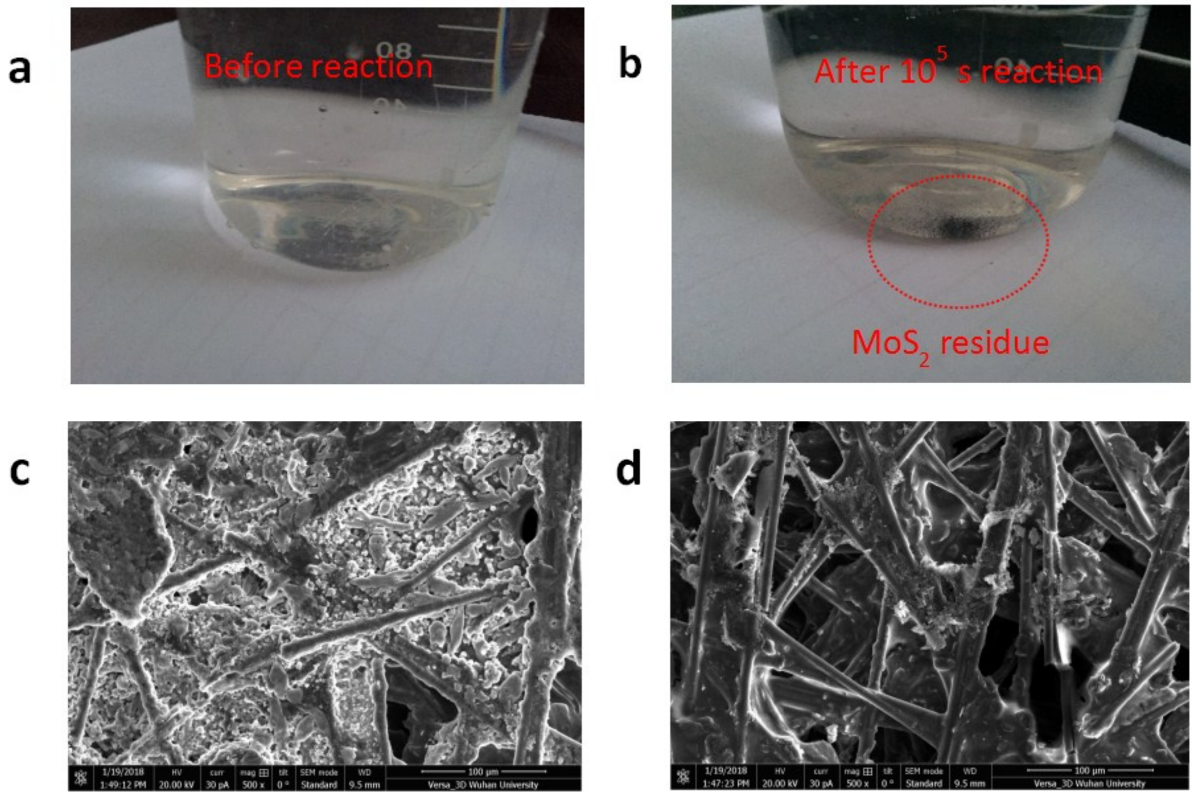

Figure S4. (a, b) Digital images for traditional diphase electrode before and after high current reaction, respectively. (c, d) SEM images for traditional diphase electrode before and after high current reaction, respectively. After working at high current condition for 10^5 s, a lot of MoS_2 nanosheets were taken off from surface of electrode by rapidly emerging bubbles and thus form the black residue.

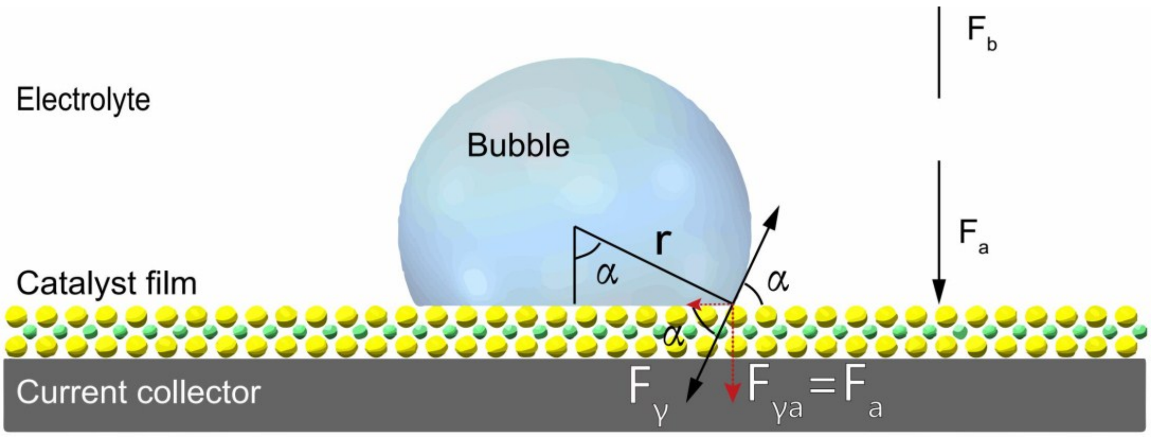

Figure S5. Nucleation is the first step in the formation of either a new thermodynamic phase or a new structure via self-assembly or self-organization. (i) The direct diffusion from the back to the air does not require nucleation, and does not consume energy; (ii) In the liquid it needs to form bubbles and take off, resulting the consumption of energy, and reduction of the rate.

So, let's suppose that a certain amount of hydrogen of 1.0 atmospheres and then we compress it into the bubble of radius "*r*" isothermally, and calculate the nucleation energy consumed by this process. We have,

$$p = p_0 + p_1 + 2\sigma / r = p_0 + \mathrm{rg}h + 2\sigma / r$$

p is the pressure of gas inside the bubble, p_0 is the atmospheric pressure, p_1 is the liquid pressure, and σ is the surface tension coefficient of water. Then, work done to increase surface area of bubble,

$$A_1 = \sigma \cdot 4\pi r^2$$

Bubble expands isothermolly, p_0 increase to p, using Carno formular,

$$A_2 = pV \ln(p / p_0) = (p_0 + \rho g h + 2\sigma / r) \cdot (4/3) r^3 \pi \cdot \ln(1 + \rho g h / p_0 + 2\sigma / r p_0)$$

Using Taylor expansion and approximation, the total work of bubble expansion,

$$A = A_1 + A_2 = 4\sigma\pi r^2 + (4/3) r^3 \pi (\rho g h + 2\sigma / r)$$

F_a is the adhesion force between substrate and bubble, F_b is buoyancy, in order to release， F_a=F_b,

$$F_a = \gamma 2\pi(\gamma \sin\beta)\sin\beta$$
$$F_b = \rho g \frac{4}{3}\pi r^3$$

where γ is the surface tension coefficient of the substrate, β is the contact angle between the bubbles and the base.

When $F_a = F_b$,

$$r = \sin\alpha\sqrt{\frac{3\gamma}{2\rho g}}$$

Finally, we can calculate the work which bubble inflates to the volume required to release,

$$A = 6\pi\sin^3\alpha(3\gamma/2\rho g)^{1/2}\left[\rho g h + 2\sigma(2\rho g/3\gamma)^{1/2}\right]$$

This is the nucleation energy that a bubble needs to cost in order to release in the liquid.

According to relation between current and radius, [1]

$$r = (3i\mathrm{R}T/8f_0\mathrm{F}p_0)^{1/3}$$

where i is current, f_0 is the frequency of bubble produce, F is Faraday's Constant. Thus, the critical current for generating a bubble which could release,

$$i_c = (8f_0\mathrm{F}p_0\sin 3\alpha/3\mathrm{R}T)(3\gamma/2\rho g)^{3/2}$$

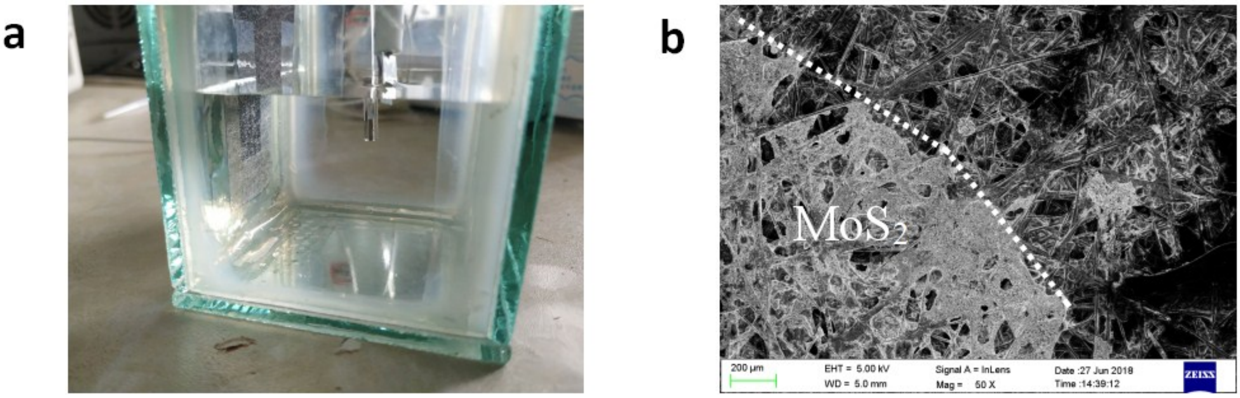

Figure S6. Characterization of of triphase system after stability testing 10^4 s under 100 mA/cm^2. Almost no MoS$_2$ nanosheets were taken off from substrate. (a) Digital image of triphase system. (b) SEM image of GDL-MoS$_2$.

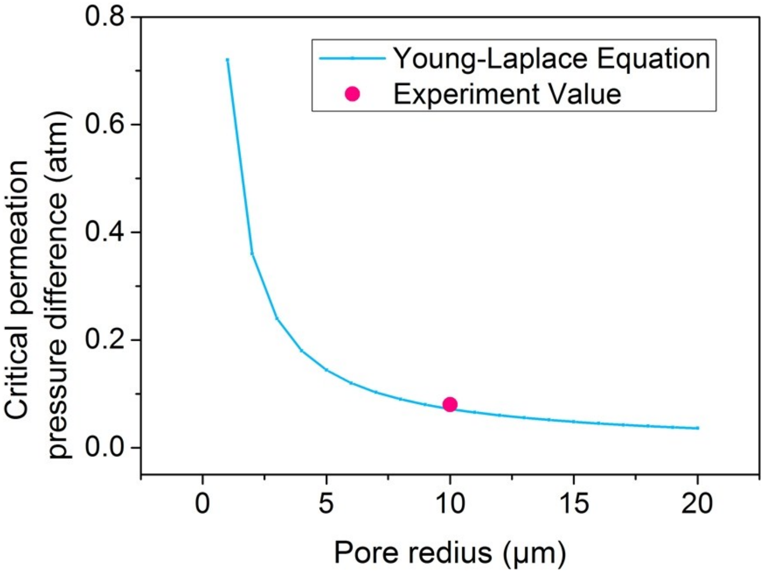

Figure S7. The theoretical (obtained from Young-Laplace equation) and experimental relation between critical permeation pressure. This demonstrated the critical permeation pressure of the triphase system is reasonable and such triphase system does exist as long as the permeation pressure on the air side is higher than 0.92 atm.

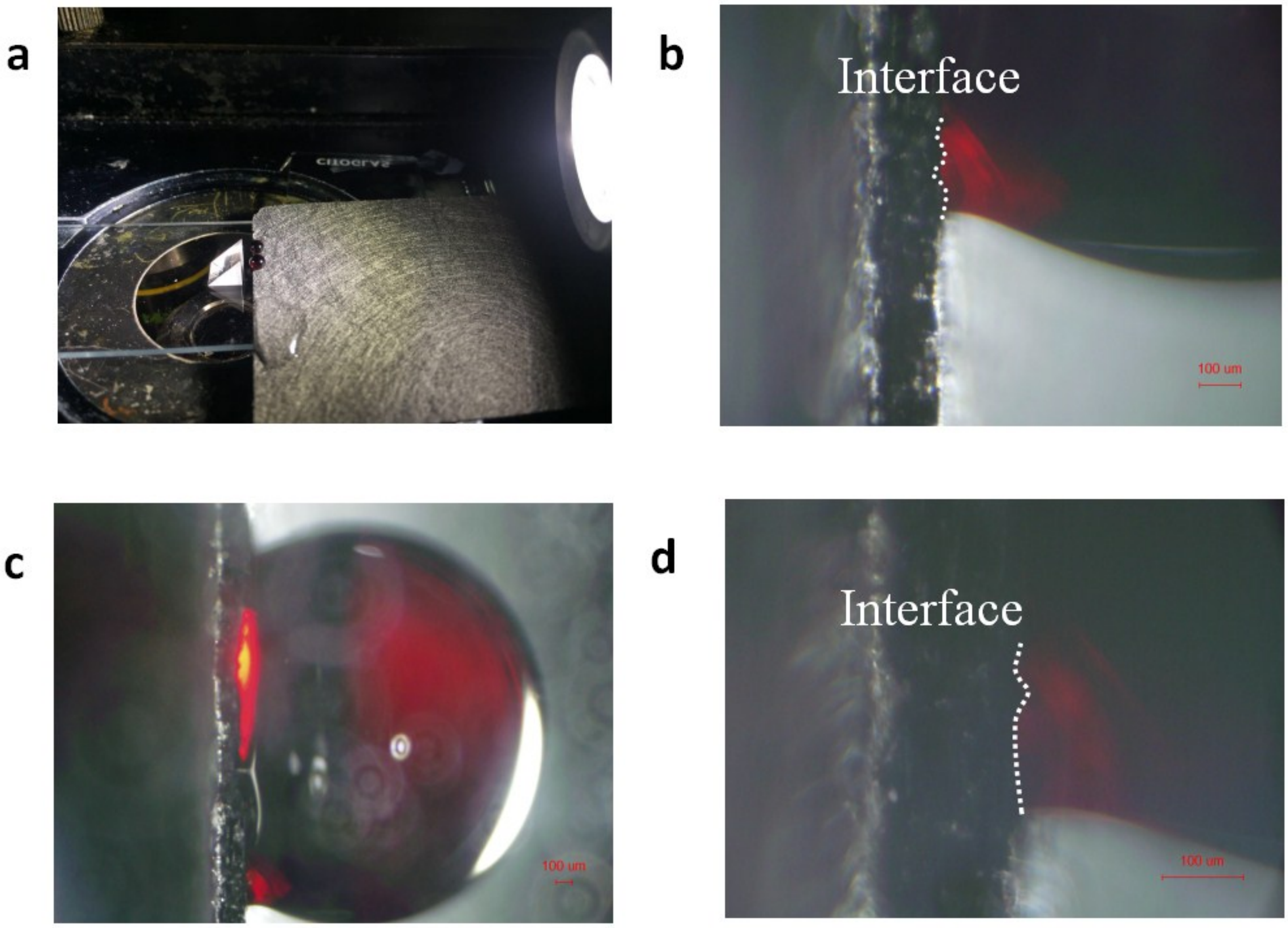

Figure S8. Digital characterization of triphase interface. (a) Experimental setup. (b, c, d) Cross section of carbon paper and infiltration of water at the interface under different scales. It can be seen that only a small part of the water droplets have entered the voids on the cross-section of the carbon paper, and the water can no longer seep through the pore due to Laplace pressure. At the same time, because these pores are connected to the air on the other side, a triphase interface is formed. In the figure, the white dashed line represents the interface where the water droplet enters the pore.

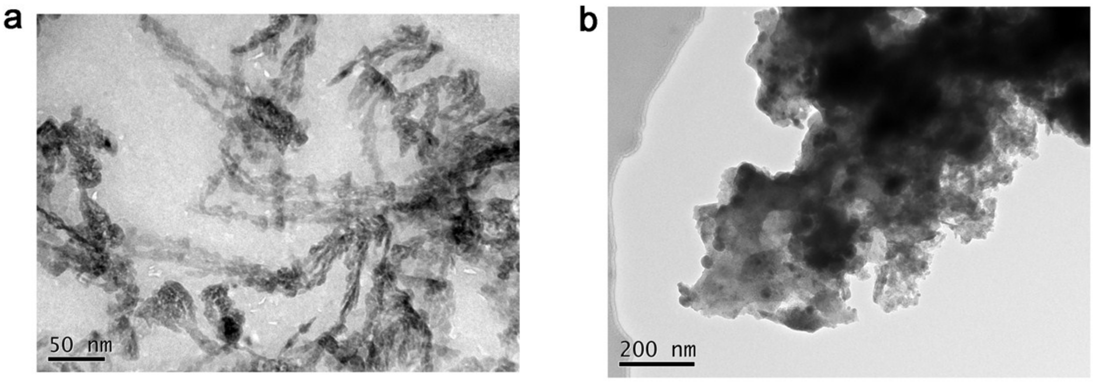

Figure S9. TEM image for MoS_2 samples (a) before and (b) after OER reaction.

Reference

[1] Q. Chen, L. Luo, H. Faraji, S. W. Feldberg, H. S. White, *J. Phys. Chem. Lett.*, 2014, 5, 3539-3544.