Supplementary Information

Interfacial Nanobubbles’ Growth at the Initial Stage of Electrocatalytic Hydrogen Evolution

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### Supplementary Tables

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<td>$\varepsilon$(kcal/mol)</td>
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<td>5.29</td>
<td>0.334</td>
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<td>$\sigma$ (Å)</td>
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<td>3.169</td>
<td>2.951</td>
<td>2.951</td>
<td>2.817</td>
<td>2.817</td>
<td>2.937</td>
<td>3.292</td>
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</table>

**Table S1.** Interaction parameters between atoms. H represents the atom of a hydrogen molecule; W represents the O atom of a water molecule while the interaction parameters of the H atom in the water molecule are both 0; E the atom of electrode; A the atoms of the hydrophilic layer surrounding the electrode.
Supplementary Figures

Fig. S1 (A) Linear sweep voltammetry curve of hydrogen evolution reaction (HER) before and after platinum plating and (B) is the corresponding element distribution after platinum plating.

Fig. S2 (A) AFM and (B) 3D view images of Au electrode after platinum plating.

Fig. S3 Variation of balanced reflectivity baselines of SPR curves at potentials from -0.4V to 0.7 V.
**Fig. S4** Time-dependent reflectivity curves of single bubble evolution (36%) and reference DNA molecules binding (7%), inset: differential images and the side-view schemes of the contact area of single bubble and the binding area of DNA molecules.

**Fig. S5** Tip correction of AFM.

**Fig. S6** The LSV oxidation curves of $[\text{Fe(CN)}_6]^{3-} \leftrightarrow [\text{Fe(CN)}_6]^{4+}$ recorded on electrodes with (the red line) and without (the black line) oxygen plasma treatment.
Fig. S7 Overpotential-dependent current steps before ($V \leq 100\text{mV}$) and after ($V \geq 150\text{mV}$) formation of macroscopic bubbles, and the corresponding bubbles’ images on electrodes.

Fig. S8 (A) AFM image of nanobubbles and (B) DMT Modulus (contact force) test.

Fig. S9 AFM and 3D view images of nanobubble pancake appeared on the electrode surface after 10 minutes of HER.
**Fig. S10** Comparison of time-dependent variations of nanobubble coverage by AFM and SPR.

**Fig. S11** Normalized time-dependent current variations at different overpotentials.
**Fig. S12** Differential curves of reflectivity at different overpotentials.

![Differential curves of reflectivity at different overpotentials](image1)

**Fig. S13** Longitudinal variation of the evanescent wave on the electrode surface: A) without nanobubbles; B) with nanobubbles; C) nanobubbles with different geometries.

![Longitudinal variation of the evanescent wave](image2)

S \propto \int_{-\infty}^{\infty} \Delta n(x) \exp \left(-\frac{x}{\sigma}\right) dx
Fig. S14 Size distribution of nanobubbles at (A) 1 min, (B) 5 min, (C) 10 min and (D) 30 min.
**Fig. S15** Size distribution of nanobubbles under different overpotentials.

**Fig. S16** Distribution range of nanobubbles at different overpotentials
Fig. S17 Under 50 mV overpotential, the nanobubbles generated (A) and reflectivity (B) in the electrode after different plasma treatment time.

Fig. S18 Coverage of nanobubbles under different overpotentials.

Fig. S19 Variation curve of ln(r) and ln(i) with overpotential.
Fig. S20 The variation of contact angle and curvature radius of nanobubbles.

Fig. S21 Simulated contact angles of equilibrium nanobubble at different sized electrodes.

Fig. S22 Snapshots of nanobubbles with different driving force $F$. 
Fig. S23 Simulated variation of pressures of nanobubbles and the molar fractions with different driving forces.