

## Supplementary Information

# Interfacial Nanobubbles' Growth at the Initial Stage of Electrocatalytic Hydrogen Evolution

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## Contents

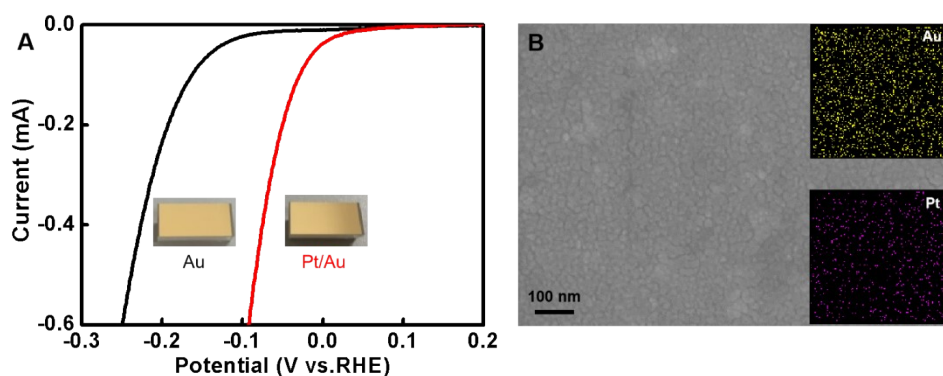
<b>Supplementary Tables.....</b>	<b>2</b>
<b>Supplementary Figures.....</b>	<b>3</b>

## Supplementary Tables

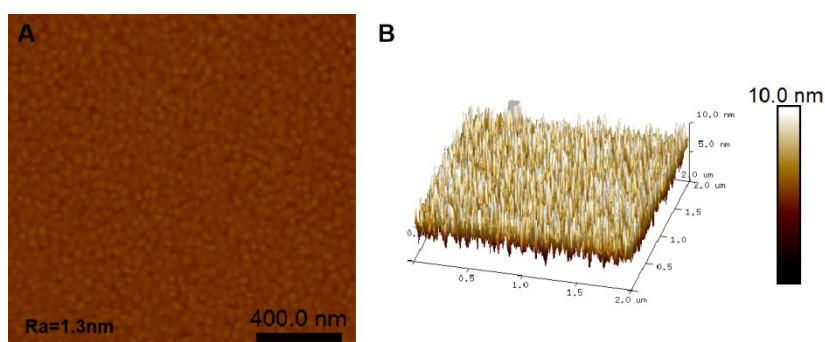
	H-H	W-W	E-E	A-A	H-E	H-A	W-E	W-A
$\mathcal{E}$ (kcal/mol)	0.022	0.155	5.29	5.29	0.334	0.115	0.453	0.906
$\sigma$ (Å)	2.683	3.169	2.951	2.951	2.817	2.817	2.937	3.292

**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.

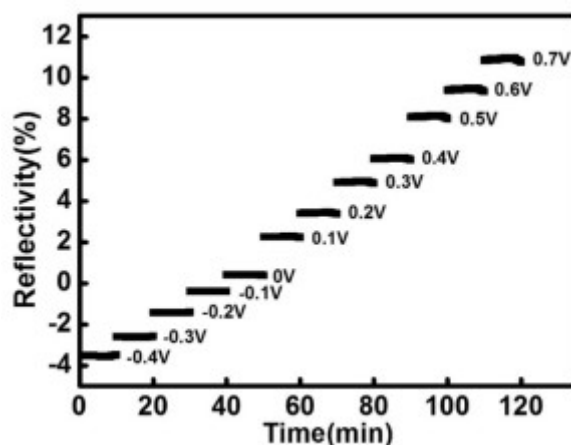
## Supplementary Figures



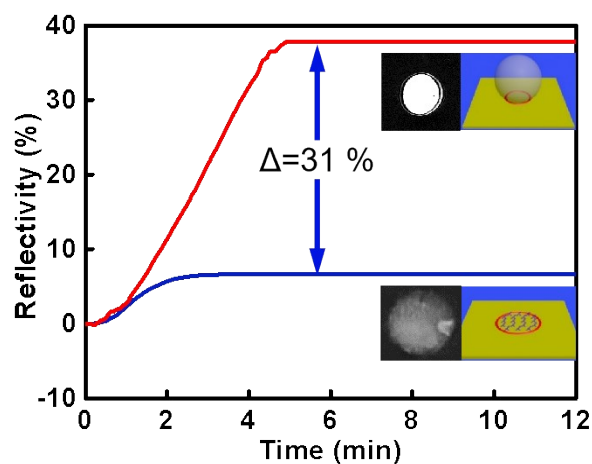
**Fig. S1** (A) Linear sweep voltammetry curve of hydrogen evolution reaction (HER) before and after platinum plating and (B) is the corresponding element distribution after platinum plating.



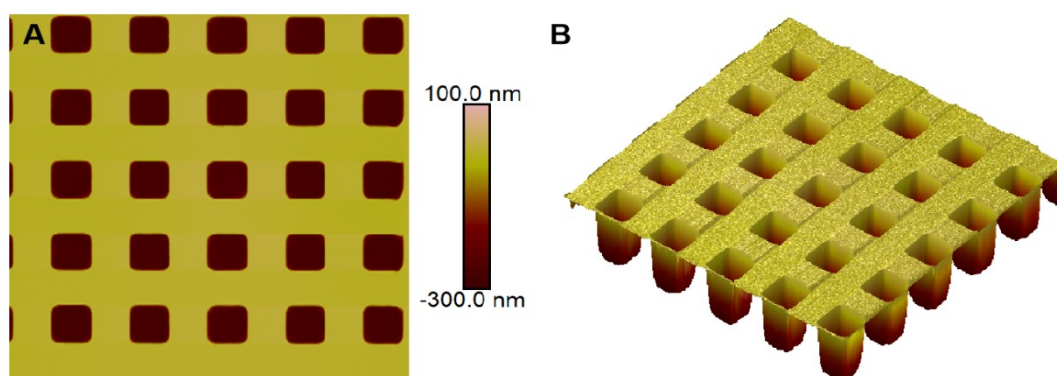
**Fig. S2** (A) AFM and (B) 3D view images of Au electrode after platinum plating.



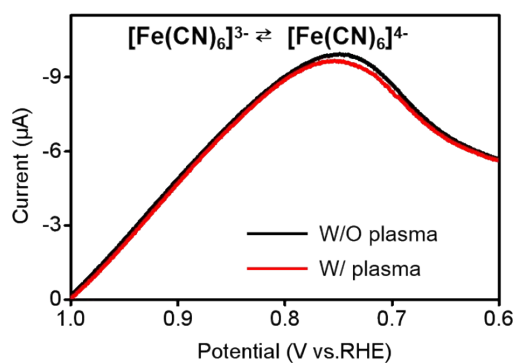
**Fig. S3** Variation of balanced reflectivity baselines of SPR curves at potentials from -0.4 V to 0.7 V.



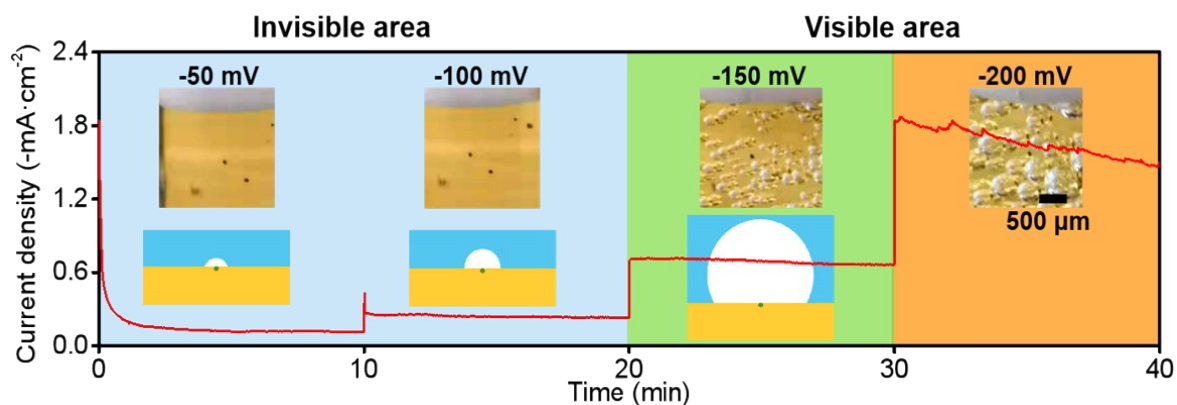
**Fig. S4** Time-dependent reflectivity curves of single bubble evolution (36%) and reference DNA molecules binding (7%), inset: differential images and the side-view schemes of the contact area of single bubble and the binding area of DNA molecules.



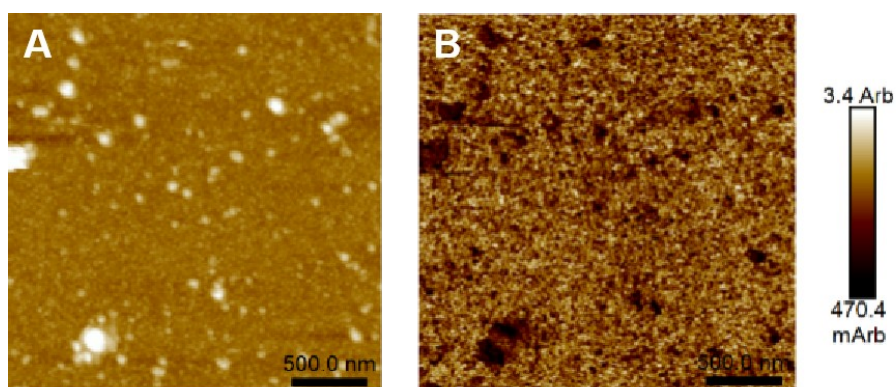
**Fig. S5** Tip correction of AFM.



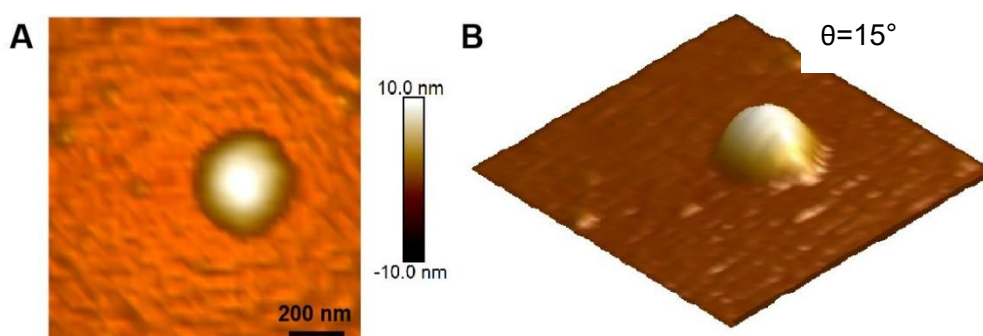
**Fig. S6** The LSV oxidation curves of  $[\text{Fe}(\text{CN})_6]^{3-} \leftrightarrow [\text{Fe}(\text{CN})_6]^{4-}$  recorded on electrodes with (the red line) and without (the black line) oxygen plasma treatment.



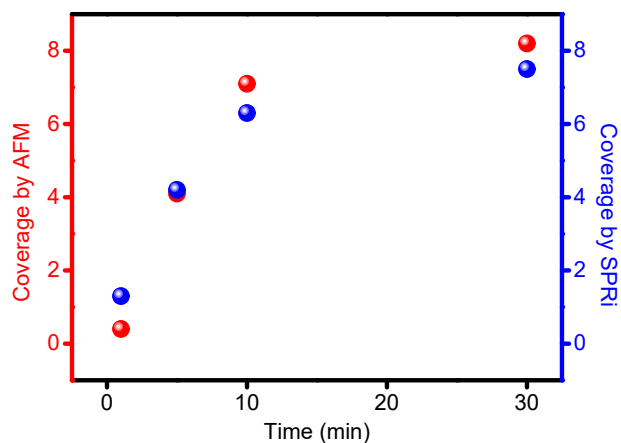
**Fig. S7** Overpotential-dependent current steps before ( $V \leq 100\text{mV}$ ) and after ( $V \geq 150\text{mV}$ ) formation of macroscopic bubbles, and the corresponding bubbles' images on electrodes.



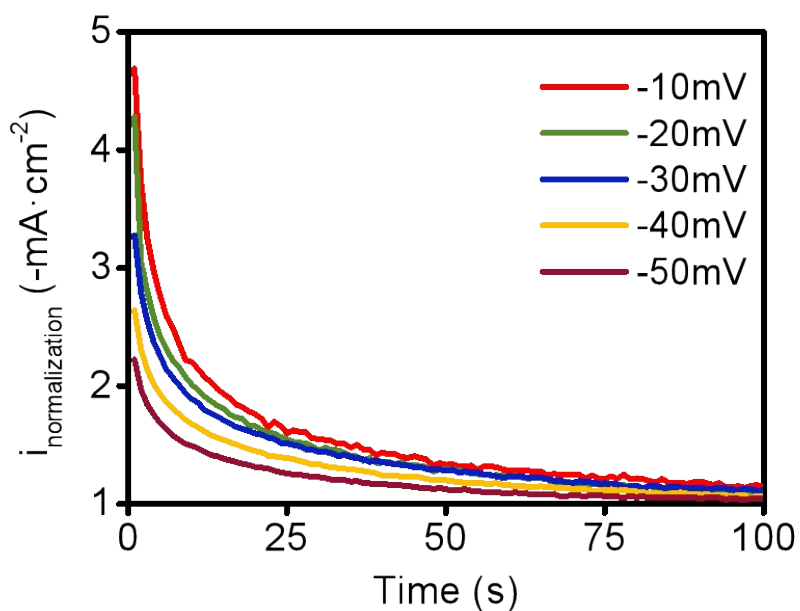
**Fig. S8** (A) AFM image of nanobubbles and (B) DMT Modulus (contact force) test.



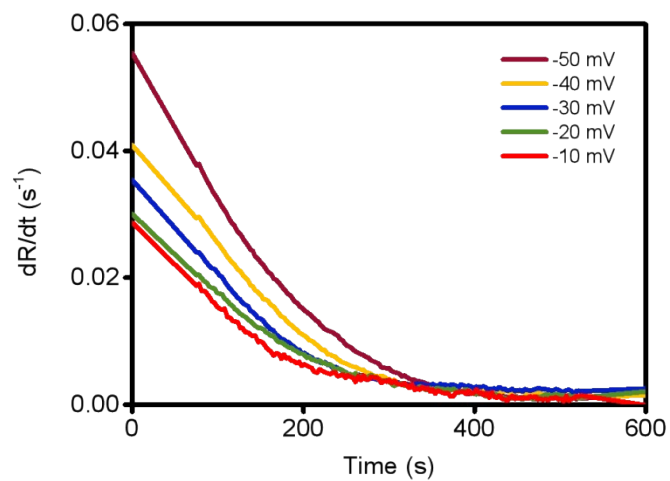
**Fig. S9** AFM and 3D view images of nanobubble pancake appeared on the electrode surface after 10 minutes of HER.



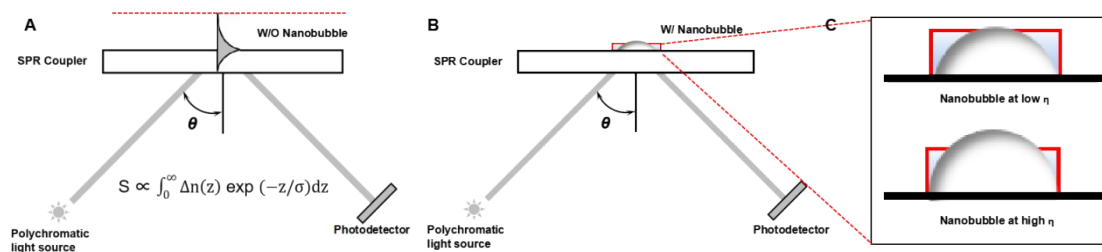
**Fig. S10** Comparison of time-dependent variations of nanobubble coverage by AFM and SPR.



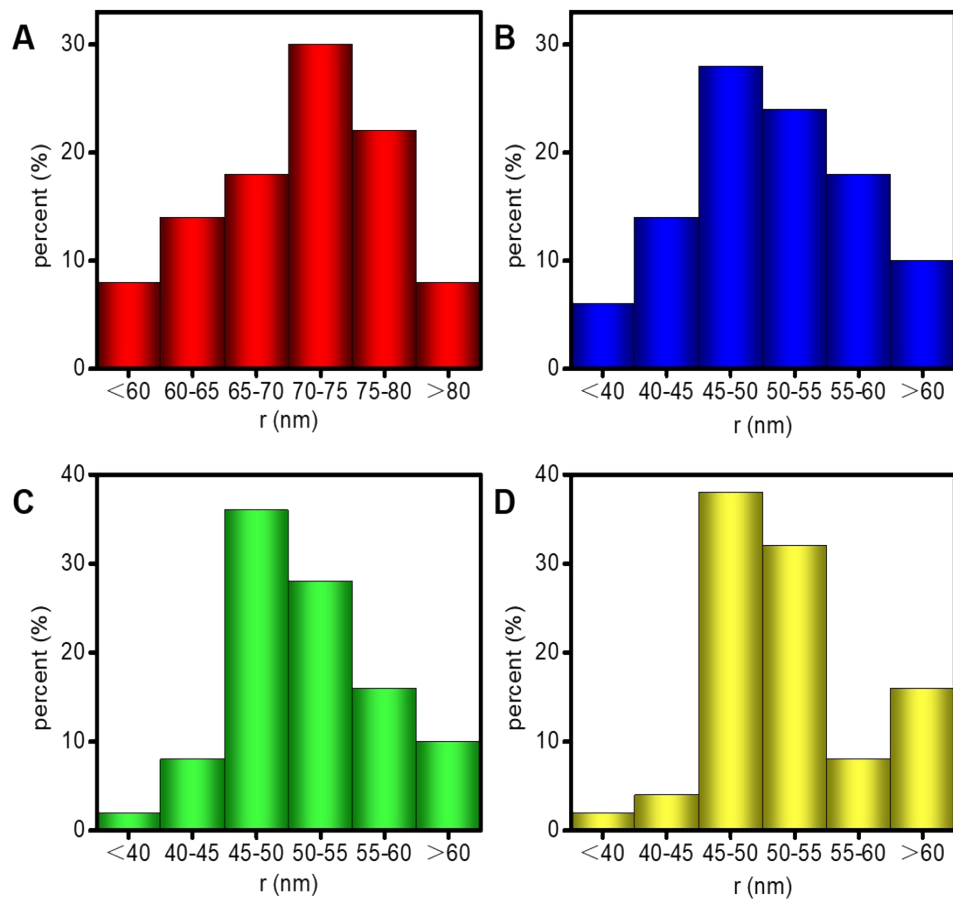
**Fig. S11** Normalized time-dependent current variations at different overpotentials.



**Fig. S12** Differential curves of reflectivity at different overpotentials.

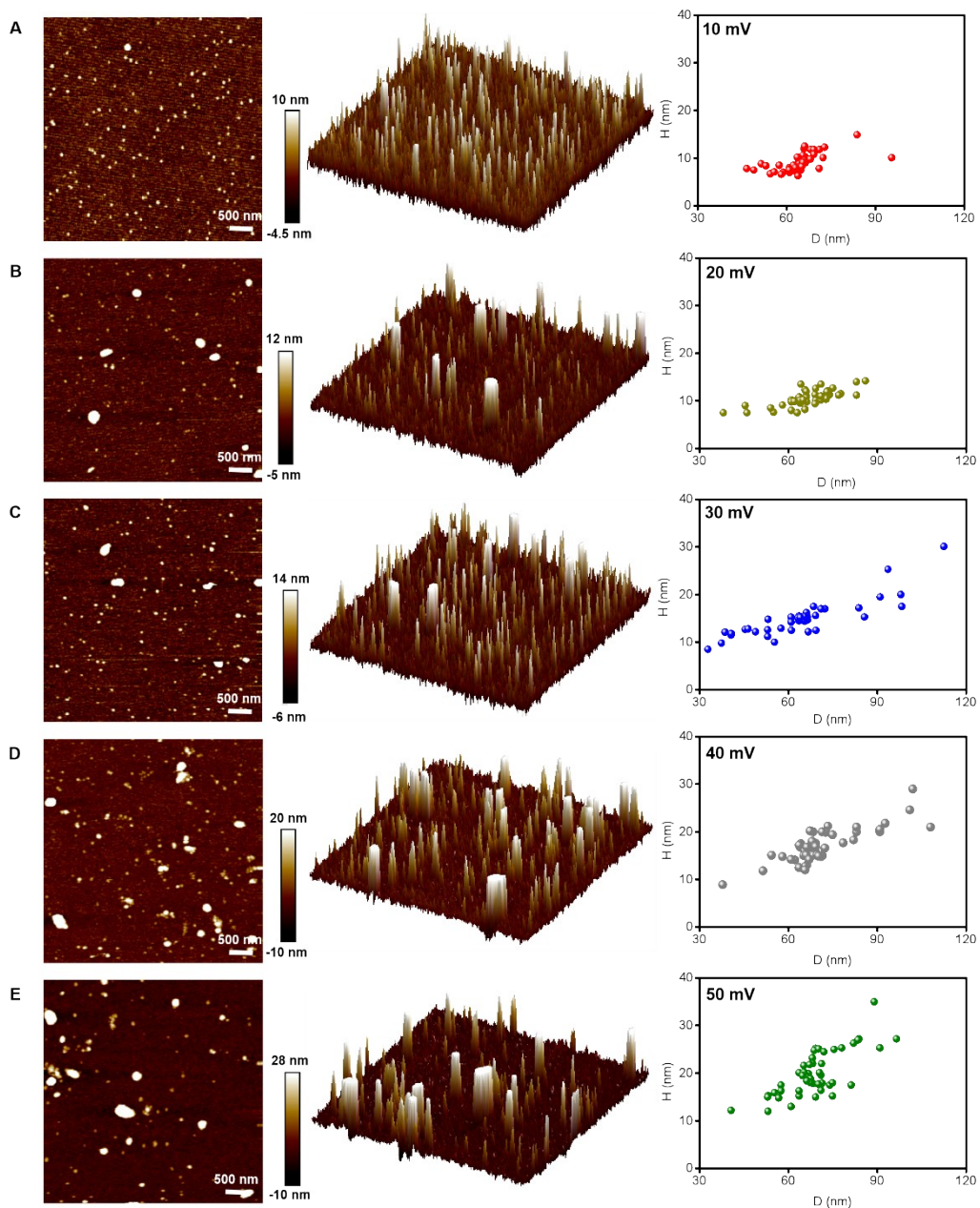


**Fig. S13** Longitudinal variation of the evanescent wave on the electrode surface: A) without nanobubbles; B) with nanobubbles; C) nanobubbles with different geometries.

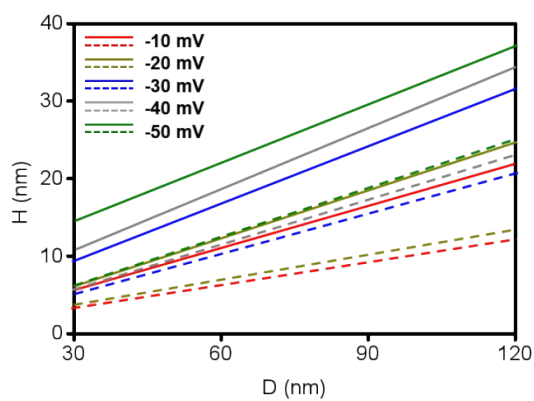


**Fig. S14** Size distribution of nanobubbles at (A) 1 min, (B) 5 min, (C) 10 min and (D) 30 min.

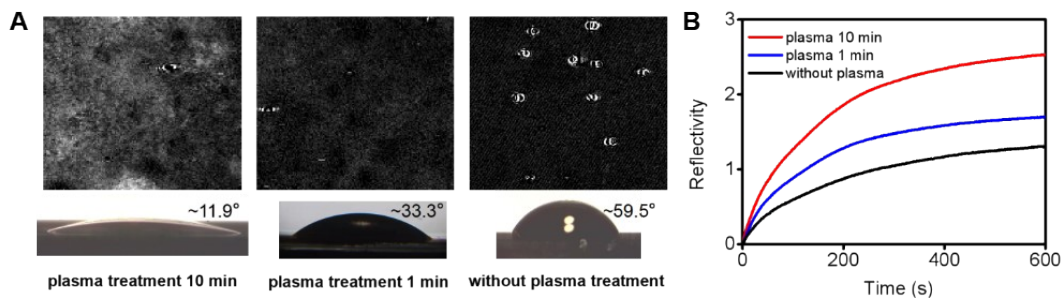




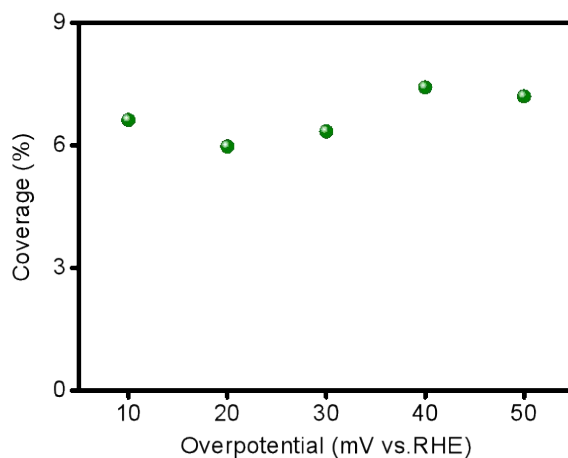
**Fig. S15** Size distribution of nanobubbles under different overpotentials.



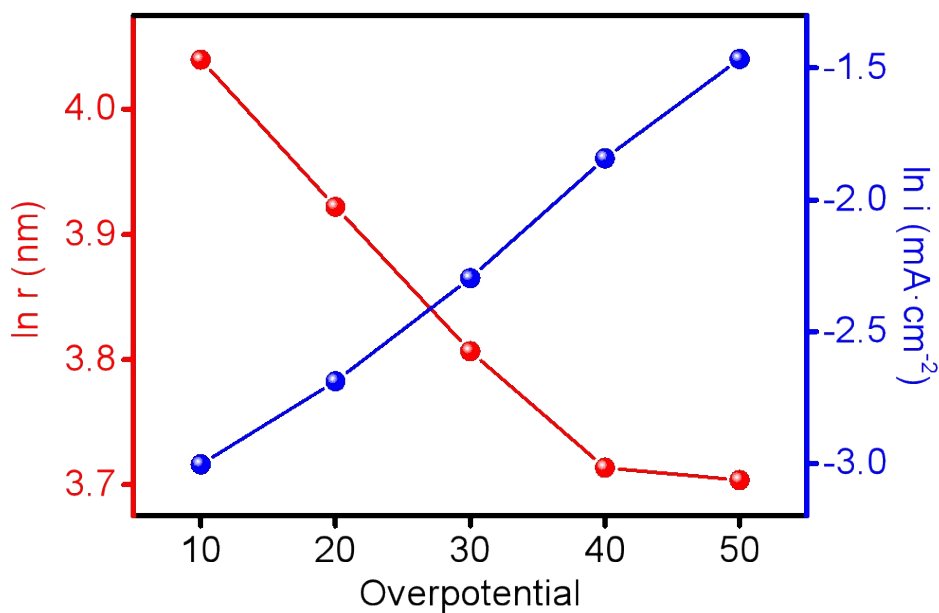
**Fig. S16** Distribution range of nanobubbles at different overpotentials



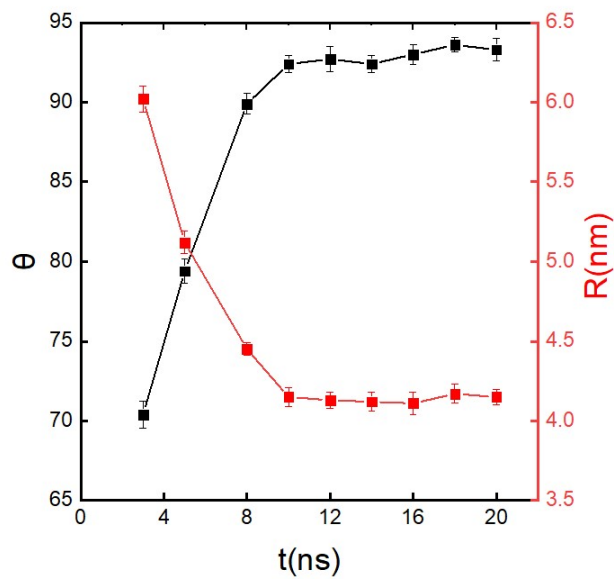
**Fig. S17** Under 50 mV overpotential, the nanobubbles generated(A) and reflectivity (B) in the electrode after different plasma treatment time.



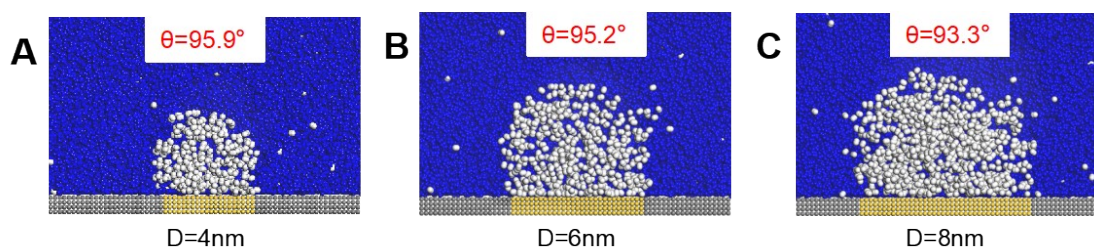
**Fig. S18** Coverage of nanobubbles under different overpotentials.



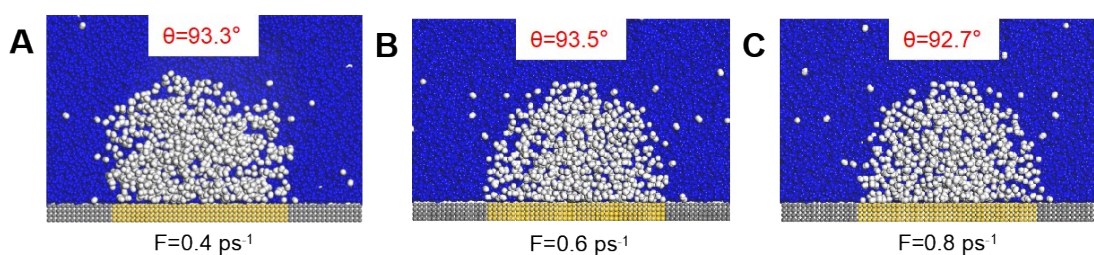
**Fig. S19** Variation curve of  $\ln(r)$  and  $\ln(i)$  with overpotential.



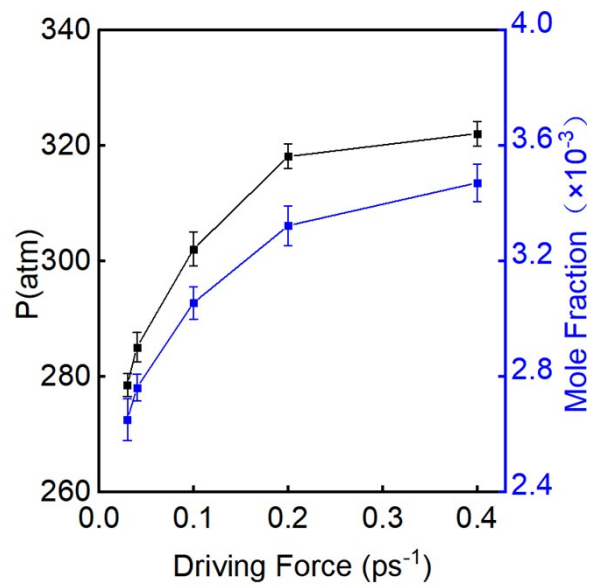
**Fig. S20** The variation of contact angle and curvature radius of nanobubbles.



**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.