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## Single Nanobubble Formation on Au Nanoelectrodes and Au@WS<sub>2</sub> Nanoelectrodes: Voltammetric Analysis and Electrocatalysis

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## ARTICLE

Single-Entity Electroanalysis

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## Abstract

Taking advantage of the extremely small size of the gold nanodisk electrode, the single hydrogen nanobubble generated on the surface of the nanoelectrode was studied to evaluate its hydrogen evolution performance. It was found that compared with the bare gold nanodisk electrode, the bubble formation potential of the gold nanodisk electrode modified with tungsten disulfide quantum dots (WS<sub>2</sub> QDs) on the surface was more positive, indicating that its hydrogen evolution activity was higher. Microdynamic model analysis shows that the average standard rate constant of the rate-determining step of the hydrogen evolution reaction of gold nanoelectrodes modified with WS<sub>2</sub> QDs is approximately 12 times larger than that of gold nanoelectrodes. This work based on the formation of nanobubbles provides new ideas for the design and performance evaluation of hydrogen evolution reaction catalysts.

**Keywords:** Nanoelectrode; Nanobubble; Electrocatalysis

## 1. Introduction

Today, solar energy, hydrogen energy, nuclear energy, etc. have attracted much attention, and the most important issue in the current development process of new energy sources is how to effectively realize the conversion, storage and utilization of these renewable energy sources. The production of clean energy hydrogen by electrolyzing water consists of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [1–4]. In the fuel cell, the hydrazine hydrate at the anode is oxidized to generate nitrogen [5,6]. In the chlor-alkali industry, an anodic oxidation produces chlorine, methanol oxidation reaction, etc. This series of gas evolution reactions form the basis of the electrochemical industry. Due to the extensive research and application of nanoparticles, clusters and even single atoms as catalysts for gas evolution chemical processes, the

study of gas nanobubbles on the surface of nanocatalysts, especially their formation, growth and detachment, has attracted more and more scientific researchers [7–11]. The electrochemistry of nanobubbles has only begun to receive attention in recent years, and nanoelectrodes have been developed as unique tools that enable the quantitative study of individual gas nanobubbles [12–18].

In this work, we explored the nucleation of single hydrogen nanobubbles on gold nanoelectrodes (Au NEs, radius <50 nm), and evaluated the hydrogen evolution reaction (HER) activities of gold nanoelectrodes (Au NEs) and gold@tungsten disulfide quantum dot nanoelectrodes (Au@WS<sub>2</sub> NEs) through microdynamic models. The results showed that the critically dissolved hydrogen concentration on the surface of Au NEs is approximately 0.4 mol · L<sup>-1</sup>. In addition, through the microdynamic analysis before the formation of a single nanobubble,

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it was found that the rate-determining steps of HER from the Au@WS<sub>2</sub> NEs and Au NEs are Heyrovsky step and Volmer step, respectively, and the standard rate constant ( $k^0$ ) of the rate-determining step of Au@WS<sub>2</sub> NEs is about 12 times that of Au NEs. This work demonstrates a basic research on nanobubble electrochemistry and provides new ideas for subsequent bubble-based applications.

## 2. Experimental section

### 2.1. Chemicals and materials

Sodium tungstate dihydrate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, >98%) and reduced glutathione (GSH, >98%) required for the synthesis of WS<sub>2</sub> QDs were provided by Shanghai Titan Scientific Co., Ltd. The ferrocene (Fc, 98%), acetonitrile (ACN, AR, >98%, GC), and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, AR, 95%–98%) required in the experiment were purchased from Sinopharm Chemical Reagent Co., Ltd. Alumino-silicate glasses (O.D.: 1.0 mm, I.D.: 0.64 mm, length: 10 cm) were purchased from Shutter Instrument Co., Ltd. (Novato, U.S.A.).

### 2.2. Instrumentation and measurements

The Au nanoelectrodes (Au NEs) were prepared from a laser-assisted puller (P-2000 mode, Sutter Instrument Co., USA), and the continuity of nanotips was checked by a biological optical microscope (BX53 + DP72, Olympus, Japan). The morphologies of WS<sub>2</sub> QDs were examined by a transmission electron microscope (TEM, HT7700 mode, Hitachi, Japan). The mapping and energy dispersive spectroscopic (EDS) analyses of the Au NEs and Au@WS<sub>2</sub> NEs were done by Regulus8100 microscope (Hitachi, Japan). An CHI660D model electrochemical workstation (Chenhua Instruments, Shanghai, China) was used to perform electrochemical test, which was equipped with a three-electrode system (Au NE as the working electrode, Pt wire and saturated Ag/AgCl as the counter electrode and the reference electrode, respectively).

### 2.3. Fabrication of Au NEs

The Au NEs were fabricated according to our previous method [19,20]. Put the gold wire into glass capillary and drew it using the P-2000 laser-assisted puller according to the following parameters:

Program 1: Heat = 365, Filament = 4, Velocity = 25, Delay = 225, Pull = 118

Program 2: Heat = 390, Filament = 1, Velocity = 30, Delay = 120, Pull = 120

Two electrodes were obtained with extremely fine tips, and the tips were examined under a light

microscope to ensure that the gold wire was continuous and not broken. The electrode was encapsulated to obtain a nanodisk electrode, and the electrode was polished with sandpaper of different mesh sizes (400–1200 mesh) until the gold wire was exposed.

### 2.4. Synthesis of WS<sub>2</sub> QDs

The WS<sub>2</sub> QDs were synthesized by referring to the method reported by Duan et al. [21,22] An amount of 0.0625 g Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O was dissolved in 12.5 mL ultrapure water, and the pH of the solution was adjusted to 6.0 with 0.1 mol·L<sup>-1</sup> HCl. Then, 0.8625 g GSH and 50 mL ultrapure water were added to the above solution, and followed by ultrasonic dissolution. After complete dissolution, the above reactants were transferred to a 100 mL polytetrafluoroethylene autoclave, heated at 200 °C for 9 h, and then centrifuged after natural cooling. The supernatant was WS<sub>2</sub> QDs. The obtained WS<sub>2</sub> QDs were stored at 4 °C for subsequent use.

### 2.5. Fabrication of Au@WS<sub>2</sub> NEs

In order to obtain WS<sub>2</sub> QDs-modified Au NEs, the pre-prepared Au NEs were inserted into the WS<sub>2</sub> QDs aqueous solution and incubated in an atmosphere of N<sub>2</sub> flow for 1 h. The WS<sub>2</sub> QDs could be self-assembled onto the Au NEs surface through Au–S covalent bonds [23], thereby obtaining the Au@WS<sub>2</sub> QDs NEs.

## 3. Results and discussion

### 3.1. Characterization of Au NEs

We drew the nanoelectrodes, encapsulated and polished them according to the method previously reported by our group, and fabricated single Au NEs with different radii [19,20]. Fig. 1A shows the cyclic voltammetric behavior of gold nanoelectrodes with different radii in 5 mmol·L<sup>-1</sup> Fc-ACN solution (containing 0.1 mol·L<sup>-1</sup> TBAPF<sub>6</sub>). It can be clearly observed that all cyclic voltammetric curves always maintain a good steady-state “S” curve and the charging current is small, showing that single Au NEs with different radii are prepared successfully [24]. Based on the steady-state limiting current, the radius of the electrode can be calculated from Eq. 1 [25].

$$i_d = 4nFDC_b a \quad (1)$$

Where  $i_d$  is the steady-state limiting current of the nanoelectrode,  $n$  is the number of electron transfer,  $F$  is the Faraday constant,  $D$  and  $C_b$  are the diffusion coefficient ( $2.4 \times 10^{-9}$  m<sup>2</sup>·s<sup>-1</sup>) and

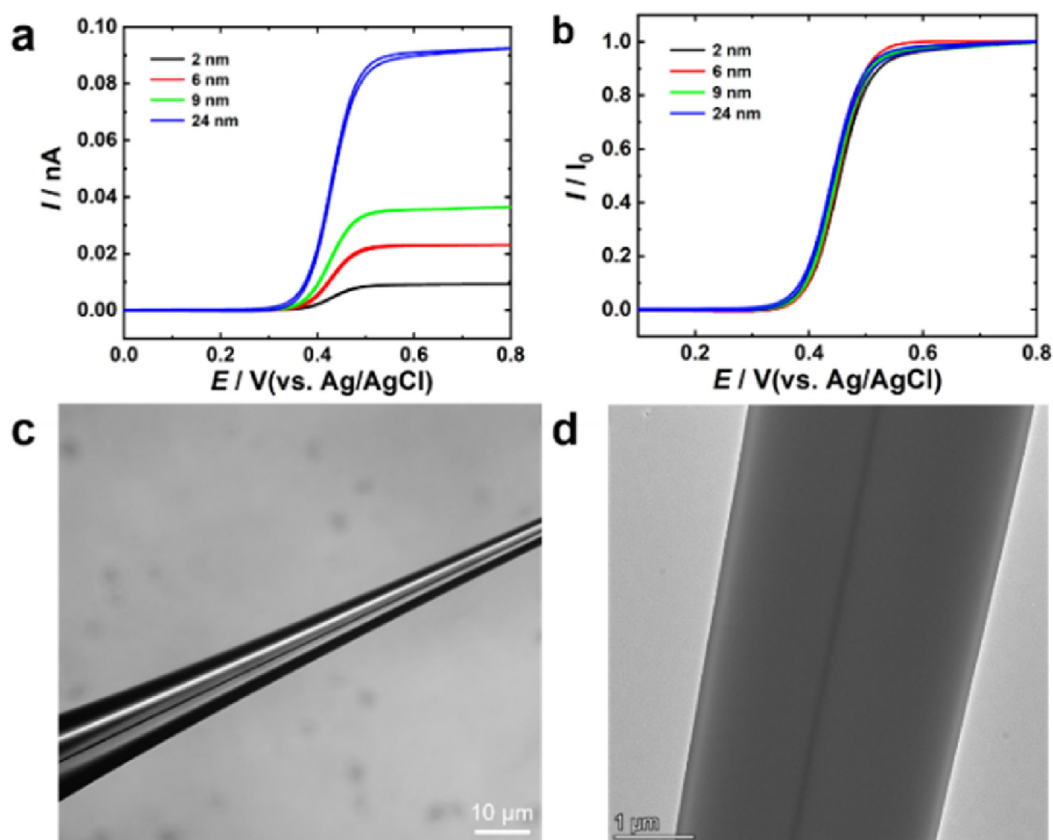


Fig. 1. (a) Voltammetric responses of single Au NEs with different sizes in a  $5 \text{ mmol}\cdot\text{L}^{-1}$  Fc-ACN solution containing  $0.1 \text{ mol}\cdot\text{L}^{-1}$  TBAPF<sub>6</sub>. (b) Normalized current to the limiting value of the voltammetric responses of Au NEs in  $5 \text{ mmol}\cdot\text{L}^{-1}$  Fc-ACN solution containing  $0.1 \text{ mol}\cdot\text{L}^{-1}$  TBAPF<sub>6</sub>. (c) Optical micrograph of the Au NE. (d) HRTEM image of the Au NE.

concentration of Fc-ACN, respectively, and  $a$  is the radius of the nanodisk electrode. According to the above equation, the radius values of the Au nanoelectrodes determined from the voltammetric curves shown in Fig. 1a are 2 nm (black curve), 6 nm (red curve), 9 nm (green curve), and 24 nm (blue curve). When the voltammetric current in Fig. 1a is normalized by dividing it by the corresponding limit diffusion current, the result is shown in Fig. 1b. It can be observed that with the decrease of Au NE radius, the voltammetric half-wave potential  $E_{1/2}$  gradually shifts to the positive potential, indicating that the shorter the nanoelectrode radius, the faster the mass transport rate can be obtained, which is in good agreement with the results of Pt NE [25,26]. The prepared Au nanoelectrode was placed under an OLYMPUS bio-optical microscope to observe the integrity of the continuous and uniform state of the gold wire. The optical microscope image of the middle part is shown in Fig. 1c. It can be clearly seen from the image that the gold wire and the outer glass can be perfectly integrated, extending all the way to the middle, becoming even and thin, and the tip is complete and continuous without any fusion. Further through HRTEM (Fig. 1d), it can be

observed that a single gold nanowire is sealed inside the glass tube with no obvious gap and a diameter of approximately 40 nm.

In addition, SEM characterization was also performed on the nanoelectrode surface. Fig. S1a is the surface of the polished Au NE, and Fig. S1b is the enlarged view of Au NE surface, where a flat, disc-shaped geometric surface can be observed, and the radius is about 25 nm. According to the results of EDS element mapping characterization (Fig. S1c, S1d), Au NEs were successfully prepared.

### 3.2. Characterization of WS<sub>2</sub> QDs

We characterized the morphology and size of the synthesized WS<sub>2</sub> QDs by TEM. Results from Fig. S2a show that the synthesized WS<sub>2</sub> QDs are spherical and well dispersed. Particle size statistics were performed on the WS<sub>2</sub> QDs in Fig. S2a, and the results are shown in Fig. S2b. Size distribution analysis shows that the average particle size of WS<sub>2</sub> QDs is 3.62 nm. We further performed EDS elemental analysis on WS<sub>2</sub> QDs, and the results are shown in Fig. S2c. The analysis results show that the quantum dots contain a large amount of W and S elements, the W/S atomic ratio is nearly

1:2, which agrees with the element composition of WS<sub>2</sub> [27,28]. The EDS spectrum also proves the successful synthesis of WS<sub>2</sub> QDs. Fig. S2d provides the Raman spectrum of WS<sub>2</sub> QDs. The characteristic peaks of E<sub>2g</sub> and A<sub>1g</sub> of WS<sub>2</sub> QDs located at 350.89 and 421.8 cm<sup>-1</sup>, respectively, can be observed, which are assigned to the in-plane motion of the W/S atoms and the out-of-plane vibrations of the S atoms, respectively [27,29]. Fig. S3 shows the XPS spectra of WS<sub>2</sub> QDs, which was used to confirm the chemical state and elemental composition of the quantum dots. As shown in Fig. S3a, except for W and S elements, other elements show their original chemical states. The appearance of C and O is attributed to the oxidation of W element and the adsorption of CO<sub>2</sub> in the air on the quantum dot surface [27,30]. The bands at 32.28 and 34.48 eV (about 2.2 eV) are assigned to W 4f<sub>7/2</sub> and W 4f<sub>5/2</sub>, respectively, and the W 5p<sub>3/2</sub> peak can be seen at 37.88 eV (Fig. S3b), indicating that the W element of WS<sub>2</sub> QDs mainly exists in the +4 valence form, and the existence of W<sup>6+</sup> may be due to the oxidation of the W edge during ultrasonic exfoliation and hydrothermal processes [31,32]. The bands of 161.98 and

163.08 eV belong to S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub>, respectively (Fig. S3c), which is caused by the -2 valence state of the S atom [33]. The results shown above are in good agreement with literature reported previously for 2H-WS<sub>2</sub> and demonstrate the successful synthesis of WS<sub>2</sub> QDs [33,34]. The XRD pattern of WS<sub>2</sub> QDs is provided in Fig. S4. For WS<sub>2</sub> QDs, there are only three very weak characteristic peaks corresponding to (004), (006), and (008), which is similar to the single-layer TMD quantum dots reported previously [27], revealing that the WS<sub>2</sub> quantum dots synthesized have the nanostructure of quantum dots.

### 3.3. Formation of single nanobubbles on Au NEs

Fig. 2a shows a typical cyclic voltammogram (CV) recorded on an Au NEs with a radius of 18 nm in H<sub>2</sub>SO<sub>4</sub> solution. When the scan voltage is more negative than -0.5 V, the current increases rapidly, corresponding to the thermodynamic potential of proton reduction ( $E(\text{H}^+/\text{H}_2)_0$ ), until it reaches a peak value ( $i_{\text{nb}}^{\text{p}}$  is about 20.23 nA), at which the voltage is approximately -0.82 V relative to Ag/AgCl. Within the range of 0 ~ -0.5 V, the  $i$ - $V$  curve

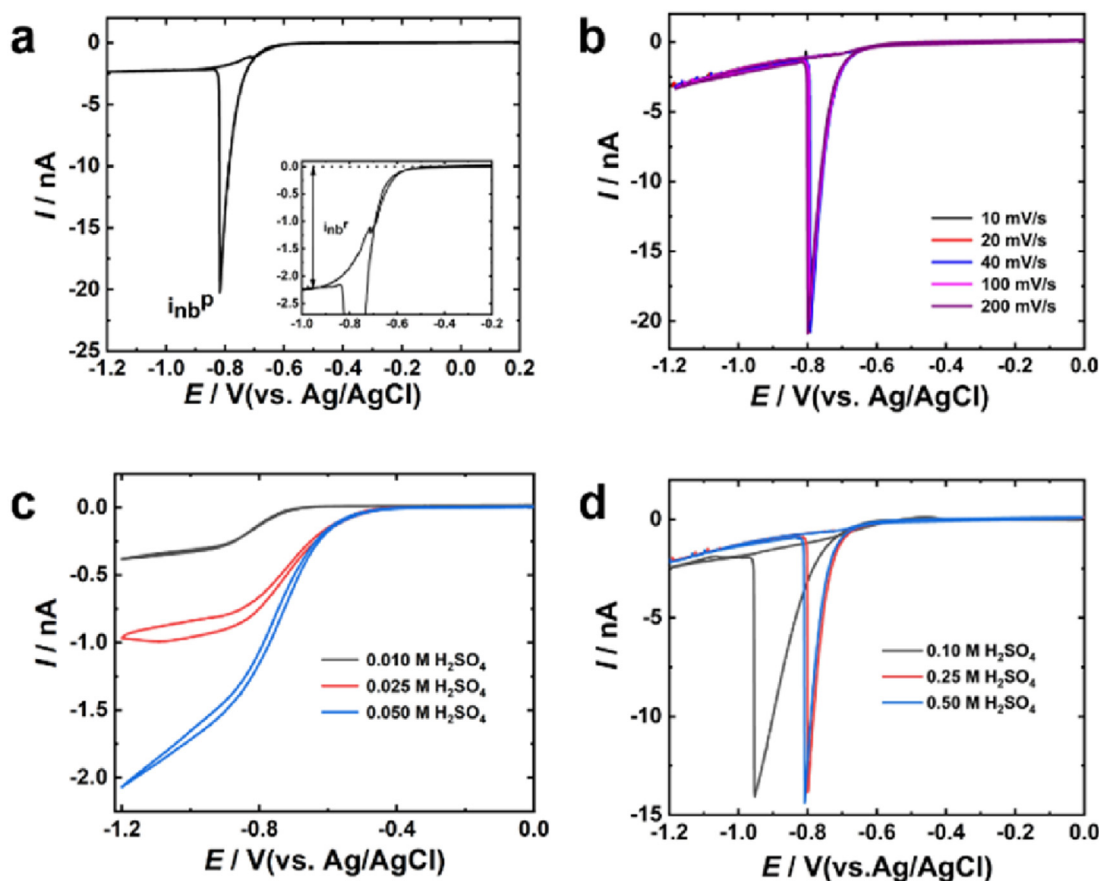


Fig. 2. (a) Cyclic voltammogram for the Au NE (20 nm radius) immersed in a N<sub>2</sub>-purged 0.5 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 10 mV·s<sup>-1</sup>. (b) Cyclic voltammograms of the same electrode recorded at different scan rates ranging from 10 to 200 mV·s<sup>-1</sup>. (c, d) Cyclic voltammetric responses of Au NE (15 nm radius) as a function of H<sub>2</sub>SO<sub>4</sub> solution concentration.



is smooth and continuous, meaning that no bubble was formed. After the peak current at  $\sim -0.82$  V, the current decreases sharply to a residual current value  $i_{nb}^r$  of  $\sim -2.2$  nA. According to previous results, this voltammetric response was due to the formation of a single nanobubble on Au NE, which blocks large area of the active surface of Au NE (>95%) [12,35]. The inset in Fig. 2a shows a magnified view of the residual current after nanobubble formation. The H reduction  $i_{nb}^r$  remains basically unchanged, indicating that the nanobubbles at NE are in a dynamic steady state [12]. In the reverse voltammetric scan from  $-1.0$  V to positive potential, no anodic peak  $H_2$  nanobubbles, corresponding to the oxidation at the positive potential  $E(H^+/H_2)_0$ , was observed, indicating that  $H_2$  bubbles dissolve rapidly on the voltammetric time scale once H can no longer be reduced. Fig. 2b shows the CV responses of Au NEs at different scan rates in the range of  $10\text{--}200\text{ mV}\cdot\text{s}^{-1}$ , which is independent of the scan rate. Before nanobubble formation, the current is limited by  $H^+$  transport and reduction kinetics at NE [12]. When the current reaches a critical value of  $\sim -21$  nA, the current decreases rapidly, and nanobubbles are formed very quickly and are not affected by the scanning speed.

We also studied the electrochemical behaviors of Au NEs in different concentrations of  $H_2SO_4$ , and we can see that the shape of the CV curve gradually changes from “S-type” to “peak-type” as the concentration of  $H_2SO_4$  increases (Fig. 2c, d). According to the mechanism of proton electroreduction to form nanobubbles on Pt NEs proposed by White et al. [12], reaching critical  $H_2$  supersaturation on the NEs surface is important for the generation of single nanobubbles, which is related to the value of  $i_{nb}^p$ . When the concentration of  $H_2SO_4$  is in the range of  $0.01\text{ mol}\cdot\text{L}^{-1}$  to  $0.05\text{ mol}\cdot\text{L}^{-1}$ , it cannot reach critical  $H_2$  supersaturation, and the maximum current is limited by the proton diffusion flux. Therefore, an S-shaped curve without nanobubble formation was obtained in Fig. 2c. However, when the concentration is larger than  $0.1\text{ mol}\cdot\text{L}^{-1}$ , a peak-shaped curve with concentration-independent  $i_{nb}^p$  can be observed in Fig. 2d, indicating that  $H_2$  reaches critical supersaturation on the electrode surface and single nanobubbles are generated.

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was formed. After the peak current at  $\sim -0.82$  V, the current decreases sharply to a residual current value  $i_{nb}^r$  of  $\sim -2.2$  nA. According to previous results, this voltammetric response was due to the formation of a single nanobubble on Au NE, which blocks large area of the active surface of Au NE (>95%) [12,35]. The inset in Fig. 2a shows a magnified view of the residual current after nanobubble formation. The H reduction  $i_{nb}^r$  remains basically unchanged, indicating that the nanobubbles at NE are in a dynamic steady state [12]. In the reverse voltammetric scan from  $-1.0$  V to positive potential, no anodic peak  $H_2$  nanobubbles, corresponding to the oxidation at the positive potential  $E(H^+/H_2)_0$ , was observed, indicating that  $H_2$  bubbles dissolve rapidly on the voltammetric time scale once H can no longer be reduced. Fig. 2b shows the CV responses of Au NEs at different scan rates in the range of  $10$ – $200$   $mV \cdot s^{-1}$ , which is independent of the scan rate. Before nanobubble formation, the current is limited by  $H^+$  transport and reduction kinetics at NE [12]. When the current reaches a critical value of  $\sim -21$  nA, the current decreases rapidly, and nanobubbles are formed very quickly and are not affected by the scanning speed.

We also studied the electrochemical behaviors of Au NEs in different concentrations of  $H_2SO_4$ , and we can see that the shape of the CV curve gradually changes from “S-type” to “peak-type” as the concentration of  $H_2SO_4$  increases (Fig. 2c, d). According to the mechanism of proton electroreduction to form nanobubbles on Pt NEs proposed by White et al. [12], reaching critical  $H_2$  supersaturation on the NEs surface is important for the generation of single nanobubbles, which is related to the value of  $i_{nb}^p$ . When the concentration of  $H_2SO_4$  is in the range of  $0.01$   $mol \cdot L^{-1}$  to  $0.05$   $mol \cdot L^{-1}$ , it cannot reach critical  $H_2$  supersaturation, and the maximum current is limited by the proton diffusion flux. Therefore, an S-shaped curve without nanobubble formation was obtained in Fig. 2c. However, when the concentration is larger than  $0.1$   $mol \cdot L^{-1}$ , a peak-shaped curve with concentration-independent  $i_{nb}^p$  can be observed in Fig. 2d, indicating that  $H_2$  reaches critical supersaturation on the electrode surface and single nanobubbles are generated.

We compared the cyclic voltammetric curves of Au NEs obtained with different radii in  $H_2SO_4$  solution ( $0.5$   $mol \cdot L^{-1}$ ). For the NEs with  $r < 60$  nm, a “peak-type” cyclic voltammetric response can be obtained (Fig. S5a, S5b, S5c), while for the NEs with  $r > 60$  nm, an “S-type” cyclic voltammetric response can be obtained, but there is obvious hysteresis in forward and reverse scans (Fig. S5d). The value of  $i_{nb}^p$  increases as the radius of NEs

increases. However, for Au NEs with a radius larger than  $60$  nm, the maximum current approaches the diffusion-limited current. Taking the Au NE with a radius of  $143$  nm as an example, the maximum current observed from Fig. S5d is about  $-283$  nA, which is close to the calculated  $\sim -295$  nA according to Eq. 1. The appearance of “S-type” on larger-sized electrodes may be caused by insufficient nanobubbles generated covering the entire electrode surface [12].

### 3.6. Bubble nucleation conditions of Au NEs

According to the cyclic voltammogram, changes in voltammetric current are produced by proton reduction. Before bubble nucleation, the system is in a steady-state, and the steady-state dissolved  $H_2$  concentration ( $C_{H_2}$ ) on the electrode surface can be estimated from the peak current by Eq. 2 [12,35].

$$i_{nb}^p = 4nFD_{H_2}C_{H_2, critical}^s a \quad (2)$$

where  $n$  is the number of electrons transferred per molecule of  $H_2$  generated ( $n = 2$ ),  $F$  is Faraday's constant ( $96,485 C \cdot mol^{-1}$ ),  $D_{H_2}$  is the diffusion coefficient of  $H_2$  ( $4.5 \times 10^{-5} cm^2 \cdot s^{-1}$ ), and  $C_{H_2, critical}^s$  is the concentration of  $H_2$  on the NE surface. It can be seen from Eq. 2 that  $i_{nb}^p$  is related to the radius of the electrode ( $a$ ) and the  $C_{H_2, critical}^s$ . According to our measurements of Au NEs with different radii in  $H_2SO_4$ ,  $i_{nb}^p$  is proportional to the radius of nanoelectrode (Fig. 3a). The slope ( $i_{nb}^p/a$ ) that can be derived from the linear relationship between  $i_{nb}^p$  and  $a$  is  $\sim 0.12$ . And according to Eq. 2,  $C_{H_2, critical}^s$  is calculated to be approximately  $0.4$   $mol \cdot L^{-1}$ , which is similar to the results reported in the literature [36]. Fig. 3b shows that the  $C_{H_2, critical}^s$  for the formation of  $H_2$  nanobubbles on the surface of NEs is relatively constant for Au NEs with different radii, indicating that the critical concentration of dissolved  $H_2$  for bubble nucleation/formation at the NE is not related to electrode size [37].

### 3.7. Formation of single nanobubbles on $WS_2@Au$ NEs

To obtain  $WS_2$  QDs coated Au NEs ( $WS_2@Au$  NEs), we soaked the Au NE with a radius of  $9$  nm into  $WS_2$  QDs solution ( $2$   $mg \cdot mL^{-1}$ ) for  $1$  h. Then,  $WS_2$  QDs would be attached on the surface of Au NE through Au–S bonds to obtain the  $WS_2@Au$  NE [23]. In order to prove that the  $WS_2$  QDs were successfully self-assembled onto the Au NE surface, we conducted EIS tests on the Au NE and  $WS_2@Au$  NE, respectively, and the results are shown in Fig. S6. The charge transfer resistance ( $R_c$ ) of Au NE (black curve) is  $445 \Omega$ . After self-assembly of

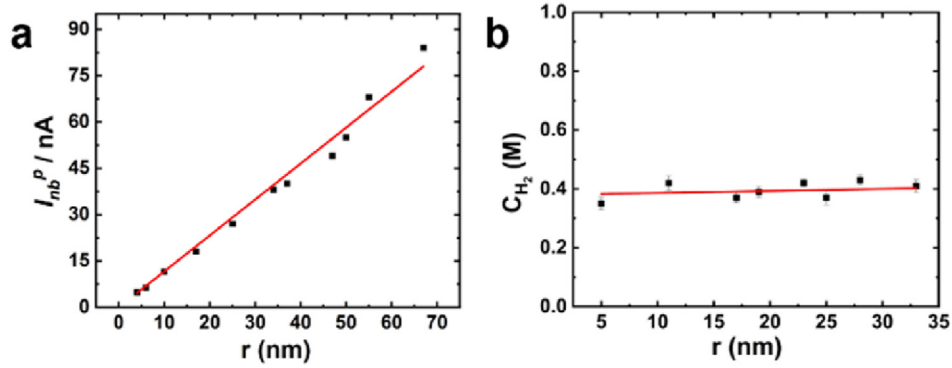
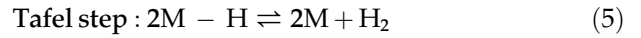
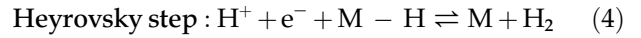
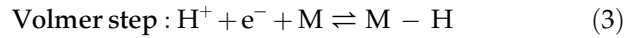


Fig. 3. (a) H<sub>2</sub> nanobubble peak current  $i_{nb}^P$  as a function of NE radius for H<sub>2</sub> bubble nucleation in 0.5 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. (b) The concentration of dissolved H<sub>2</sub> at the NE surface that is required for bubble nucleation and formation,  $C_{H_2, critical}^S$  as a function of NE radius. The linear data-fitted lines are included.

WS<sub>2</sub> QDs onto the Au NE surface, the  $R_{ct}$  value of WS<sub>2</sub>@Au NE increased significantly (578 Ω, red curve). This result proved that the WS<sub>2</sub> QDs were successfully assembled onto the Au NE surface. In order to explore the optimal conditions for generating H<sub>2</sub> bubbles, we optimized the incubation time for the self-assembly of WS<sub>2</sub> QDs onto the Au NE surface. Cyclic voltammetric tests were performed on Au NEs soaked in WS<sub>2</sub> QDs for different time, and the test results are shown in Fig. S7. We found that as the soaking time increases (from 0 to 60 min), the potential corresponding to  $i_{nb}^P$  moves positively, while at 60 and 80 min of soaking, the potential appears moving negative slightly. According to the different soaking time of Au NE and the corresponding potentials of  $i_{nb}^P$ , we drew a broken line (Fig. S8a). We found that a soaking time of 60 min produced a potential correction of H<sub>2</sub>, so 60 min were selected as the optimal soaking time, and used for all the subsequent related experiments. Fig. S8b compares typical voltammetric responses of Au NE and WS<sub>2</sub>@Au NE in H<sub>2</sub>SO<sub>4</sub> solution, and the nanobubble formation potential of WS<sub>2</sub>@Au NE (−0.522 V) is corrected relative to that of Au NE (−0.8 V), indicating the enhanced HER activity with the modification of WS<sub>2</sub>, and further proving the successful modification of WS<sub>2</sub> QDs [36]. However, when the WS<sub>2</sub> QDs are assembled on the Au NE, the larger peak current is required to form H<sub>2</sub> bubbles in the WS<sub>2</sub>@Au NE compared to the Au NE, which may be due to the increased surface area [38].

### 3.8. Microdynamic analysis

We performed microkinetic analysis of the HER processes of Au NEs and Au@WS<sub>2</sub> NEs to evaluate the HER activity. The HER process generally consists of two possible steps, the Volmer step (Eq. 3) and the Heyrovsky or Tafel step (Eq. 4 and Eq. 5), as shown below [37,39,40].



where M denotes the surface empty site. The overall rate can be determined by each step, and their corresponding kinetic current expressions can be expressed as [41].

$$i_{et} = nFAk^0 a_{H^+} \exp(-\alpha f \eta) \quad (6)$$

$$i_{et} = nFA \frac{k^0 K^0 a_{H^+}^2 \exp(-\alpha f \eta)}{\exp(f \eta) + K^0 a_{H^+}} \quad (7)$$

$$i_{et} = nFAk^0 \left[ \frac{K^0 a_{H^+}^2}{\exp(f \eta) + K^0 a_{H^+}} \right]^2 \quad (8)$$

where  $i_{et}$  and  $F$  are the current flowing under the kinetic limit and the Faraday constant, respectively, and  $A$  and  $k^0$  are the electrode surface area and the standard rate constant of the HER rate-determining step, respectively.  $K^0$  and  $a_{H^+}$  are the equilibrium constant and proton activity of the Volmer step, respectively.  $f$  is equal to  $F/RT$  and  $\eta$  is the overpotential, and  $\alpha$  is the conversion coefficient of the rate-determining step.

Before data fitting,  $i_{et}$  could be obtained by subtracting the contribution of mass transfer from the Koutecký–Levich equation (Eq. 9) [37,42].

$$\frac{1}{i_{et}} = \frac{1}{i} - \frac{1}{i_{mt}} = \frac{1}{i} - \frac{1}{4FD_{H^+}C_{H^+}r} \quad (9)$$

Where  $i$  represents the experimentally measured overall current,  $i_{mt}$  and  $D_{H^+}$  are the limiting current controlled solely by mass transfer of H<sup>+</sup> and diffusion coefficient of H<sup>+</sup> ( $7.8 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ ), respectively.  $r$  is the radius of the NE. By fitting the experimental data using the



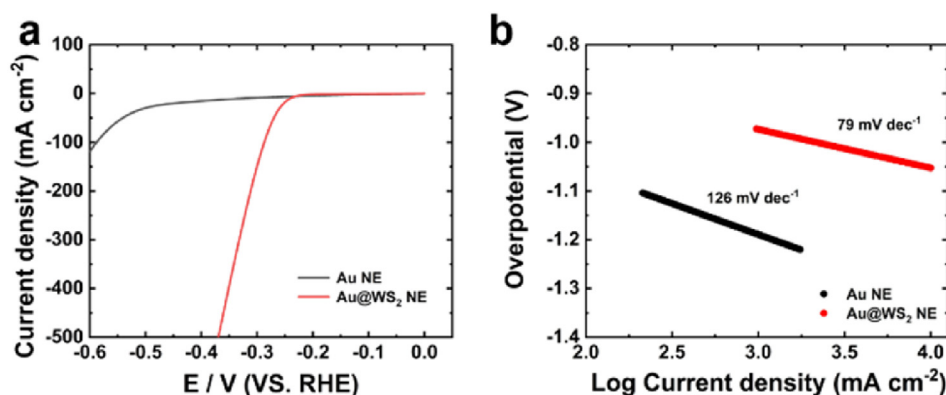


Fig. 4. (a) Polarization curves and (b) the corresponding Tafel plots of Au NE and Au@WS<sub>2</sub> NE (both with 30 nm radius) in a 0.5 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution.

three rate-determining formulas provided above, and the correct kinetic model by finding the best result between fit and experiment can be obtained.

After the nonlinear fitting of Eqs. 6–8, the best fit was obtained using Eq. 6 for the Au NE (Fig. S9a), which suggests that the rate-determining step should be the Volmer step in the HER process of Au NE. On the other hand, the Heyrovsky step is the rate-determining step in the HER process of Au@WS<sub>2</sub> NE (Fig. S9b). As reported previously, the Volmer step on the Pt surface is very fast [43], and the rate-determining step of our fitted Au NEs may contradict this. Therefore, in order to further verify the accuracy of the simulation results, the polarization curves and Tafel slopes of Au NE and Au@WS<sub>2</sub> NE with a radius of 30 nm were obtained, as shown in Fig. 4. Tafel slope is used to distinguish different mechanistic pathways in HER. Generally, there are three main reaction steps for HER in acidic electrolytes, including an initial discharge step (Volmer step, Tafel slope of ~120 mV·dec<sup>-1</sup>), followed by an electrochemical desorption step (Heyrovsky reaction, Tafel slope of ~40 mV·dec<sup>-1</sup>) or the recombination step where hydrogen is adsorbed on the catalyst surface (Tafel reaction, Tafel slope ~30 mV·dec<sup>-1</sup>). For the HER process, the H<sub>2</sub> generation mechanism step is either a combination of Volmer-Tafel steps or a combination of Volmer-Heyrovsky steps. In Fig. 4b, the Tafel slopes of Au NE and Au@WS<sub>2</sub> NE are 126 mV·dec<sup>-1</sup> and 79 mV·dec<sup>-1</sup>, respectively, which are in agreement with the theoretical values, indicating that during HER, the Volmer-Heyrovsky process exists on the Au NE and Au@WS<sub>2</sub> NE. Based on the consistency between experimental results and simulation results, the surface coverage of adsorbed H on the Au@WS<sub>2</sub> NE can be calculated by Eq. 10:

$$\theta = \frac{K^0 a_{\text{H}^+}}{\exp(f\eta) + K^0 a_{\text{H}^+}} \quad (10)$$

The values of  $\alpha$ ,  $k^0$ ,  $K^0$  and  $\theta$  for the Au NEs and Au@WS<sub>2</sub> NEs are shown in Table S1 and Table S2. At the bubble formation potential, the value of  $\theta$  is about 0.98, indicating that the adsorbed H protons almost completely cover the Au@WS<sub>2</sub> NEs when the bubbles are formed. In addition, the average  $k^0$  of Au@WS<sub>2</sub> NEs is approximately 12 times that of Au NEs, indicating that Au@WS<sub>2</sub> NEs have higher HER activity. Compared with  $\alpha$ ,  $K^0$  and  $\theta$ ,  $k^0$  of different NEs showed larger changes, indicating the activity heterogeneity of NEs. This heterogeneity may not only be due to size effects but also result from the structural dispersion observed at the nanoscale [44–47].

#### 4. Conclusions

We have studied the behaviors of single hydrogen bubbles formed on Au NEs and Au@WS<sub>2</sub> NEs based on voltammetry, providing help for understanding the basic research on nanobubble electrochemistry and the evaluation of HER activity. Microkinetic analysis of the voltammetric response showed that the average  $k^0$  of Au@WS<sub>2</sub> NEs was approximately 12 times that of Au NEs, indicating that Au@WS<sub>2</sub> NEs had higher HER activity. As the HER activity increased, the bubble formation potential shifted to a more positive potential. This work can help us design and screen new nanomaterials for the application in fundamental electrochemistry, electrocatalysis and energy-related field, especially at a single entity level.

#### Supporting information

Additional information as noted in the text. This material is available free of charge via the internet at <https://jelectrochem.xmu.edu.cn/journal/>.

HER kinetic parameters of Au NEs; HER kinetic parameters of Au@WS<sub>2</sub> NEs; Characterization of a single Au NE; Characterization of WS<sub>2</sub> QDs; XPS spectrum of WS<sub>2</sub> QDs; XRD patterns of WS<sub>2</sub> QDs; CVs of the Au NE with different radius; EIS characterization of Au NE and Au@WS<sub>2</sub> NE; CVs for Au NE in WS<sub>2</sub> QDs after various immersion times; The relationship between Au@WS<sub>2</sub> NEs different soaking time and the voltage of bubble generation; and experimental CVs and their corresponding best fits.

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## Conflict of interest

The authors declare no competing interests.

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# 纳米电极上单纳米气泡的伏安分析和电催化

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## 摘要

利用金纳米盘电极的极小尺寸 (Au NEs, 半径小于 50 nm), 研究了在纳米电极表面产生的单个氢纳米气泡, 以评价其析氢性能。我们研究了 Au NEs 在不同浓度硫酸中的电化学行为, 结果表明 CV 的形状随着硫酸浓度的增加从 S 型波逐渐变为峰型波。根据纳米气泡的形成机理, 得出了产生单个纳米气泡的最小硫酸浓度, 表明此时氢气在电极表面达到了临界过饱和, 产生了单个纳米气泡和电化学峰型响应。并通过微动力学模型评价了金纳米电极和金@二硫化钨量子点纳米电极 (Au@WS<sub>2</sub> NEs) 的析氢反应 (HER) 活性。结果表明, 在 Au NEs 表面的临界溶解氢气浓度约为 0.4 mol·L<sup>-1</sup>, 相当于室温和大气压下溶于水中的氢气过饱和度的 500 倍。此外, 通过对单个纳米气泡形成前的电流强度的微动力学分析, 发现 Au@WS<sub>2</sub> NEs 和 Au NEs 析氢反应的决速步骤分别为 Heyrovsky step 和 Volmer step, Au@WS<sub>2</sub> NEs 决速步骤的标准速率常数 ( $k^0$ ) 约为 Au NEs 的 12 倍, 表明 Au@WS<sub>2</sub> NEs 具有更高的 HER 活性。随着 HER 活性的增加, 气泡形成电位转向更正的电位。这项工作利用极小尺寸的纳米电极甚至包括分子尺寸的纳米电极对其表面产生的单个氢纳米气泡进行研究, 为纳米气泡电化学研究提供了基础, 并为后续基于气泡的应用提供了新的思路, 可以帮助我们设计和筛选应用于基础电化学、电催化和能源相关领域的新型纳米材料, 特别是在单个实体水平上。

**关键字:** 纳米电极; 纳米气泡; 电催化