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Supporting information

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

Xianzhun Luo, Xiaohu Chen, Yongxin Li\*

Anhui Province Key Laboratory of Biomedical Materials and Chemical Measurement,  
Key Laboratory of Functional Molecular Solids, Ministry of Education, College of  
Chemistry and Materials Science, Anhui Normal University, Wuhu, 241000, P.R.  
China.

\*corresponding author. Email: [yongli@mail.ahnu.edu.cn](mailto:yongli@mail.ahnu.edu.cn)

Phone: 86-553-386-9302; Fax: 86-553-386-9303

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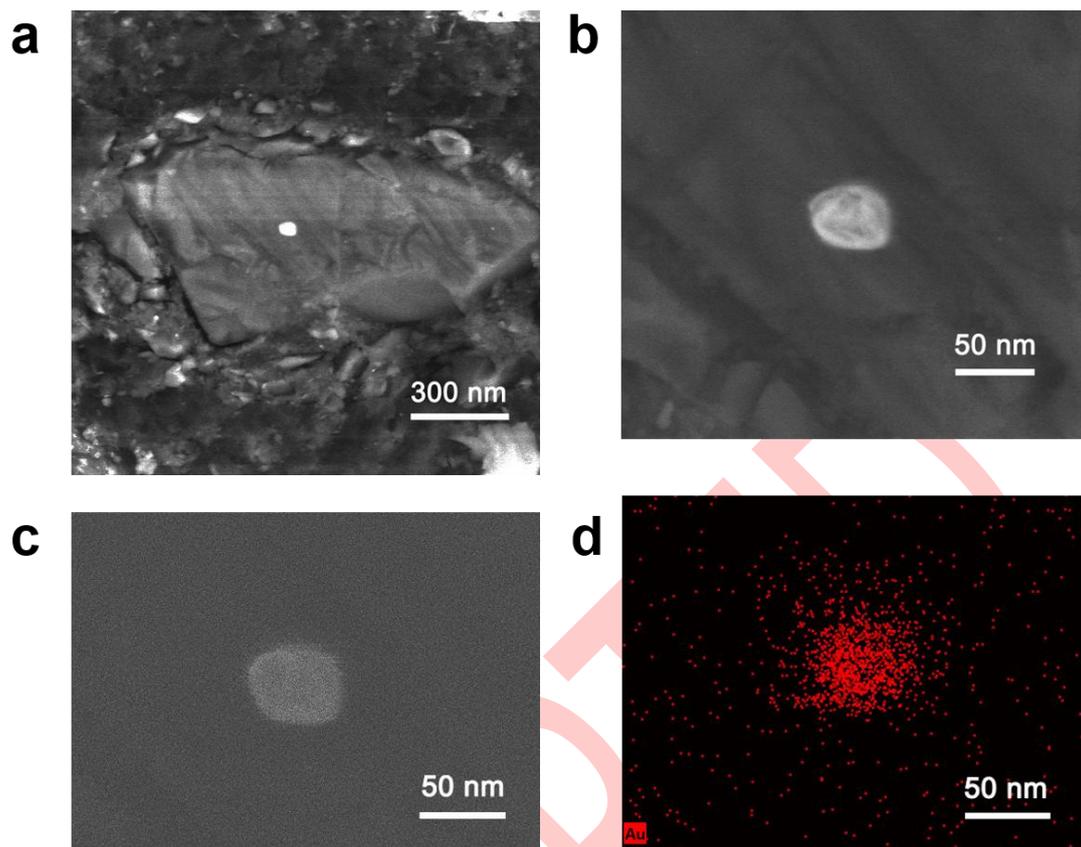
Figure S9. Experimental cyclic voltammograms and their corresponding best fits.

**Table S1.** HER kinetic parameters ( $k^0$  and  $\alpha$ ) obtained from data fitting, bubble formation potentials ( $E_{\text{bubble}}$ ), NE Radii for Eight Au NEs (values are reported as mean  $\pm$  standard deviation).

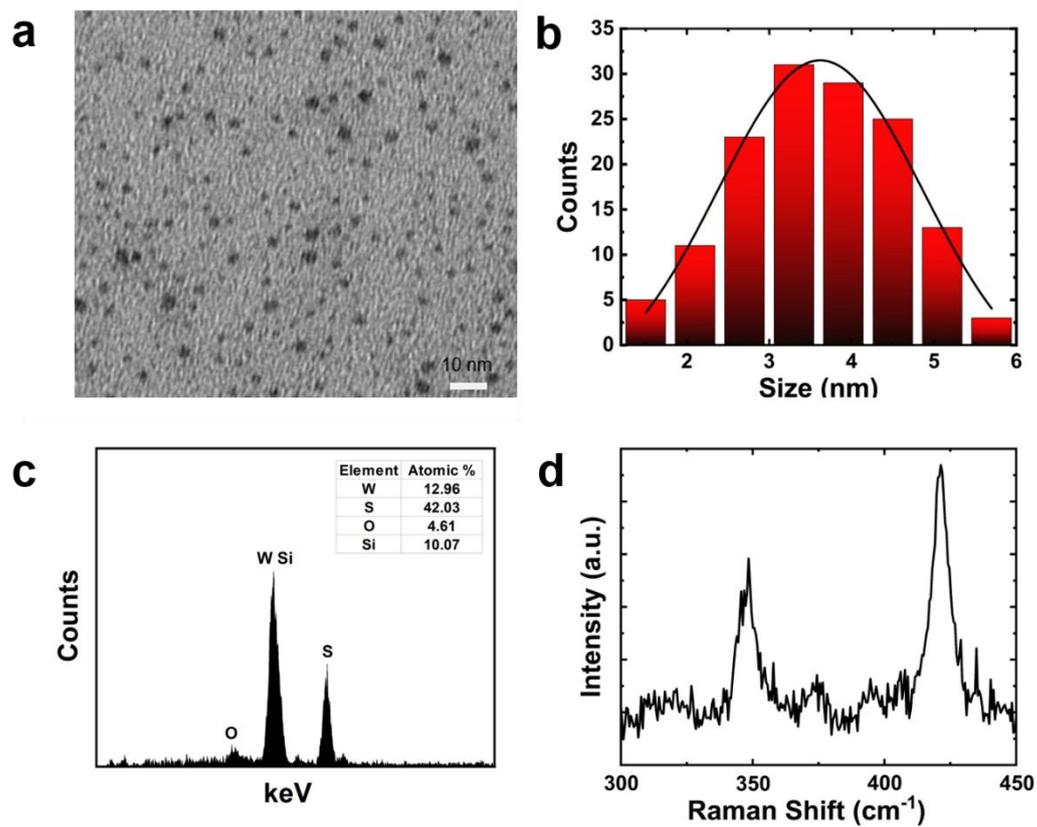
| Au NE radius (nm) | $k^0$ (m/s)           | $\alpha$ | $E_{\text{bubble}}$ (V) vs Ag/AgCl |
|-------------------|-----------------------|----------|------------------------------------|
| 8                 | $5.1 \times 10^{-5}$  | 0.45     | -0.812                             |
| 17                | $4.7 \times 10^{-5}$  | 0.38     | -0.775                             |
| 23                | $2.3 \times 10^{-6}$  | 0.39     | -0.806                             |
| 30                | $7.5 \times 10^{-6}$  | 0.41     | -0.792                             |
| 37                | $4.2 \times 10^{-7}$  | 0.43     | -0.821                             |
| average           | $2.16 \times 10^{-5}$ | 0.41     |                                    |

**Table S2.** HER kinetic parameters ( $K^0$ ,  $k^0$ , and  $\alpha$ ) obtained from data fitting, bubble formation potentials ( $E_{\text{bubble}}$ ), NE radius, and surface coverage of adsorbed H ( $\theta$ ) at  $E_{\text{bubble}}$  for eight Au@WS<sub>2</sub> NEs (values are reported as mean  $\pm$  standard deviation).

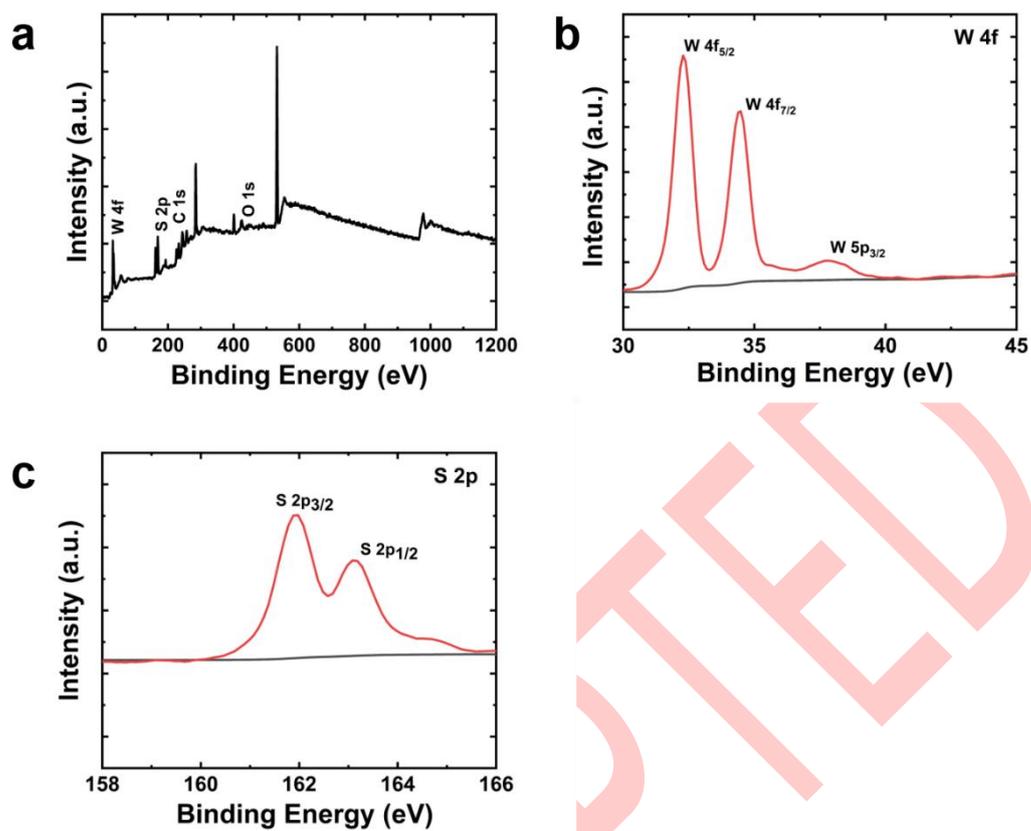
| Au@WS <sub>2</sub> NE<br>radius (nm) | $K^0$ (m/s)          | $k^0$ (m/s)          | $\alpha$ | $E_{\text{bubble}}$ (V) vs<br>Ag/AgCl | $\theta$ |
|--------------------------------------|----------------------|----------------------|----------|---------------------------------------|----------|
| 10                                   | $1.1 \times 10^{-5}$ | 1.5                  | 0.54     | -0.537                                | 0.98     |
| 15                                   | $1.0 \times 10^{-5}$ | $2.7 \times 10^{-4}$ | 0.55     | -0.516                                | 0.99     |
| 26                                   | $2.3 \times 10^{-5}$ | $5.6 \times 10^{-4}$ | 0.52     | -0.509                                | 0.98     |
| 30                                   | $1.5 \times 10^{-5}$ | $7.1 \times 10^{-4}$ | 0.55     | -0.525                                | 0.99     |
| 39                                   | $4.2 \times 10^{-5}$ | $3.4 \times 10^{-5}$ | 0.51     | -0.518                                | 0.99     |
| 44                                   | $3.7 \times 10^{-5}$ | $9.2 \times 10^{-5}$ | 0.49     | -0.573                                | 0.96     |
| 49                                   | $1.9 \times 10^{-5}$ | $1.2 \times 10^{-6}$ | 0.57     | -0.567                                | 0.97     |
| average                              | $2.2 \times 10^{-5}$ | $2.6 \times 10^{-4}$ | 0.53     |                                       | 0.98     |



**Figure S1.** (a) The SEM image of Au NE surface. (b) A magnification of the surface of the NE in Figure S1A. (c, d) EDS element mapping characterization of Au NE surface.



**Figure S2.** (a) The TEM image of WS<sub>2</sub> QDs. (b) The size distribution of WS<sub>2</sub> QDs. (c) EDS elemental analysis of WS<sub>2</sub> QDs. (d) Raman spectrum of WS<sub>2</sub> QDs.



**Figure S3.** (a) XPS spectrum of WS<sub>2</sub> QDs. (b) Narrow-band XPS spectrum of W 4f. (c) Narrow-band XPS spectrum of S 2p.

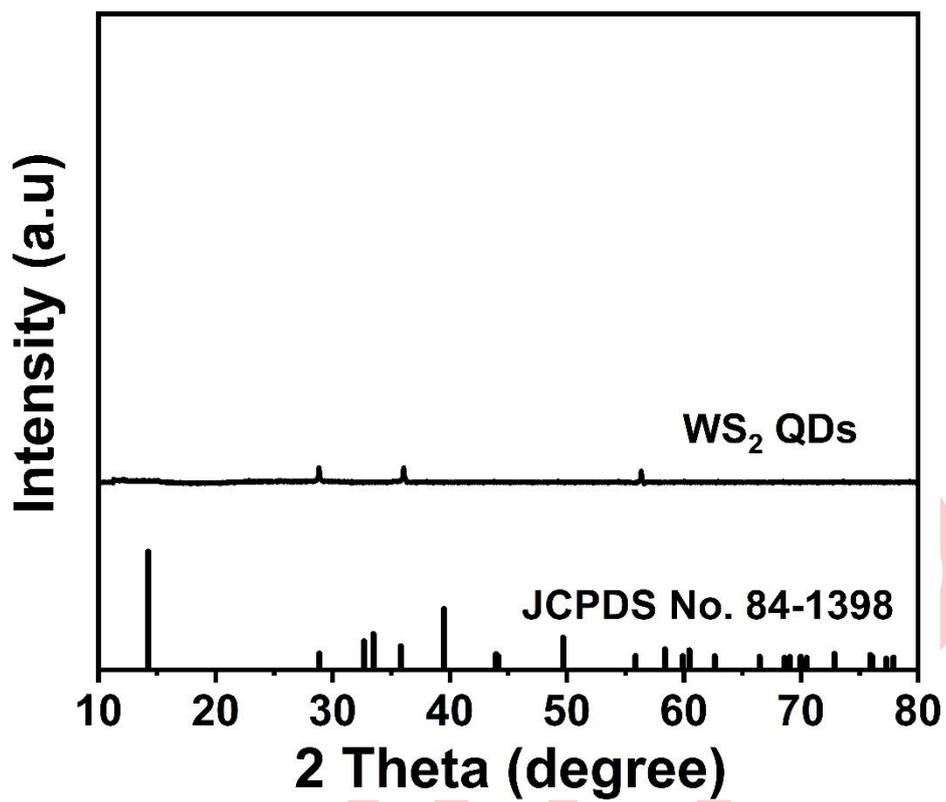
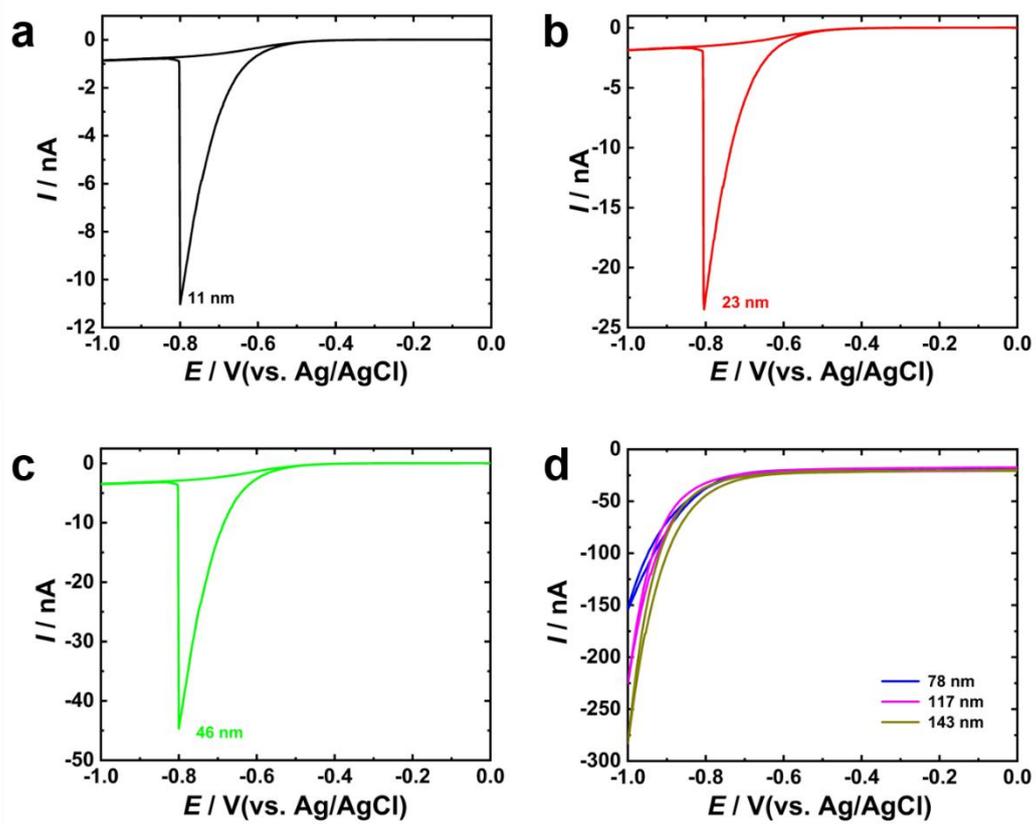


Figure S4. The XRD patterns of WS<sub>2</sub> QDs.



**Figure S5.** Cyclic voltammetric responses as a function of the radius of the Au NE in a 0.5 M  $H_2SO_4$  solution with a scan rate of 10 mV/s.

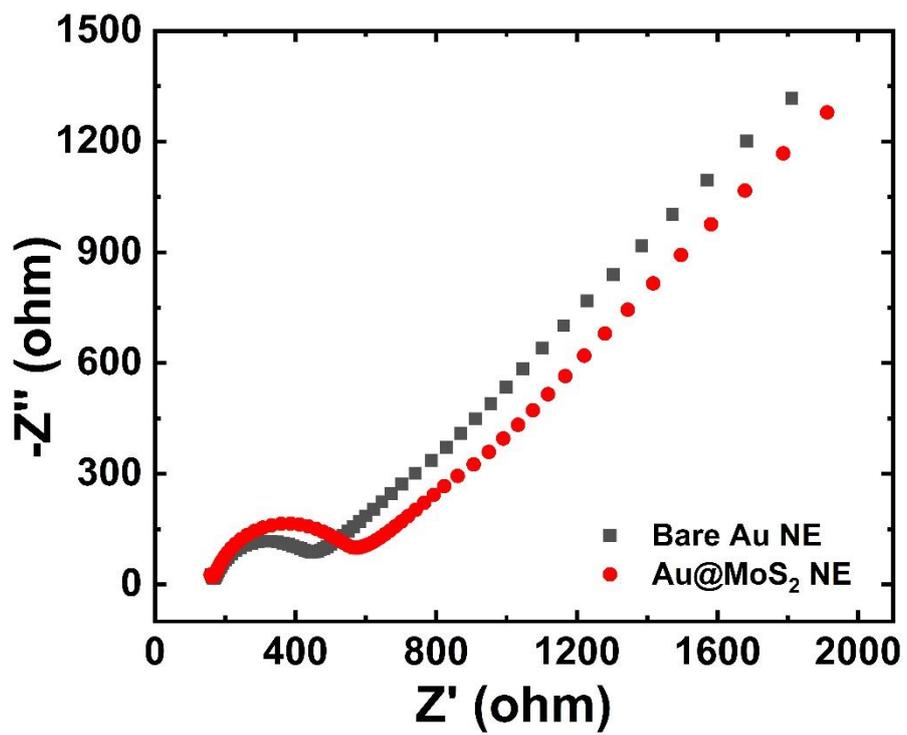
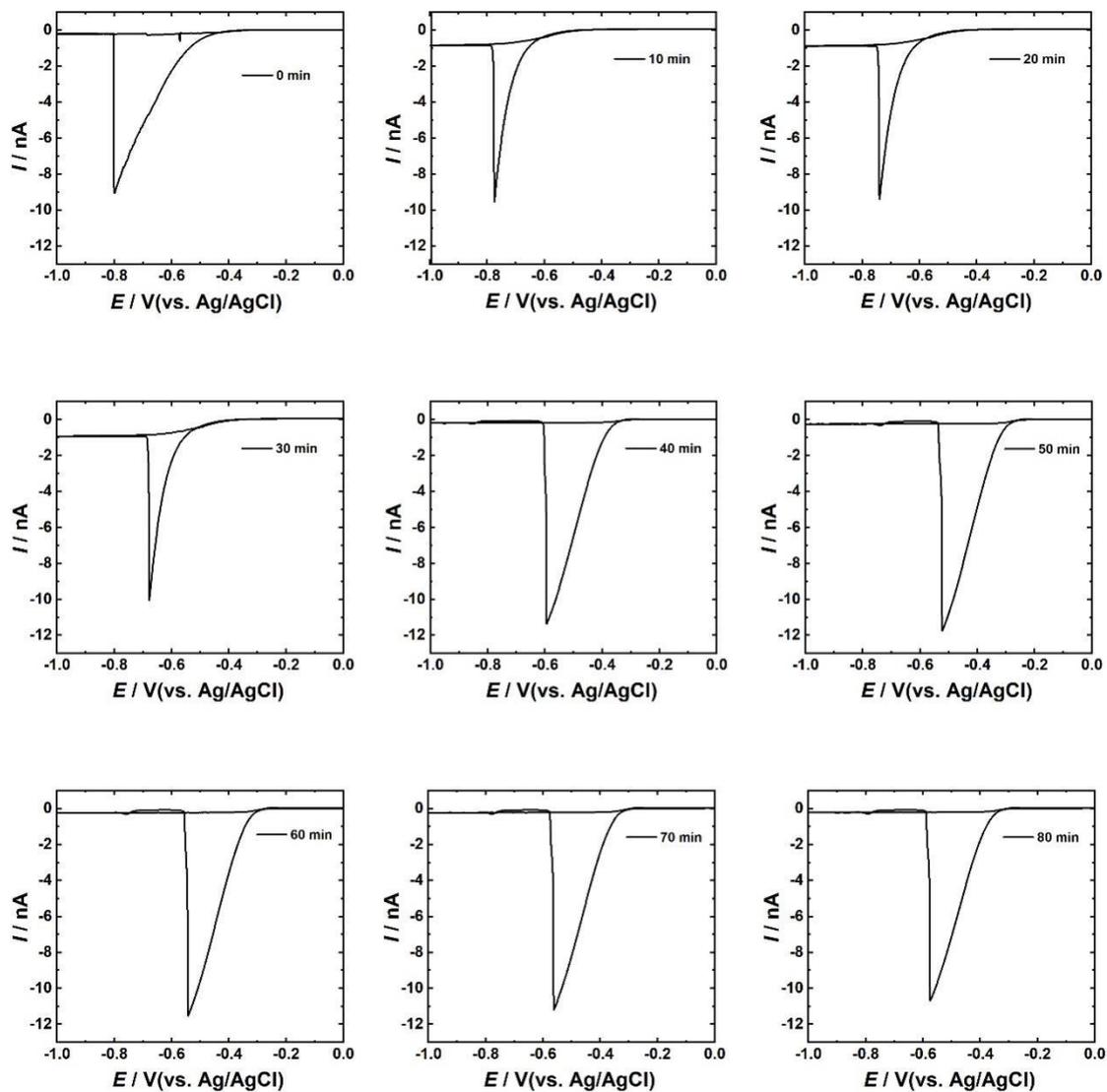
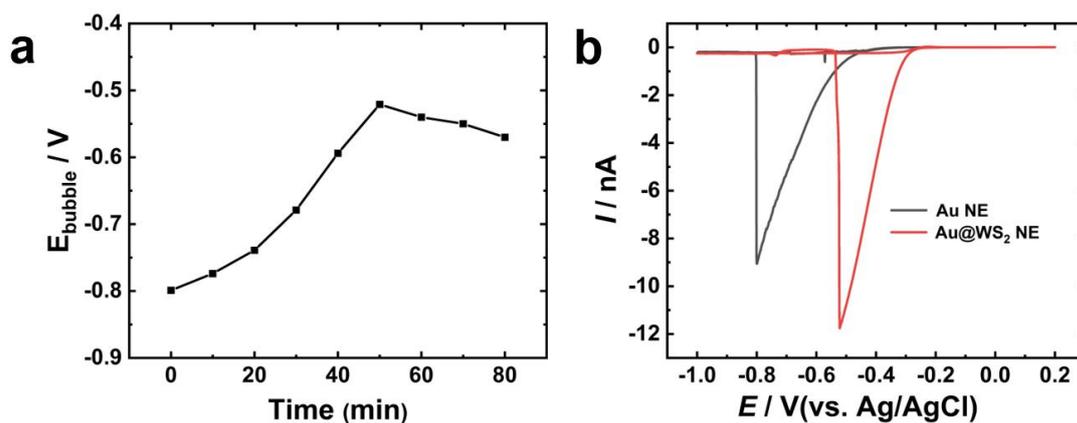


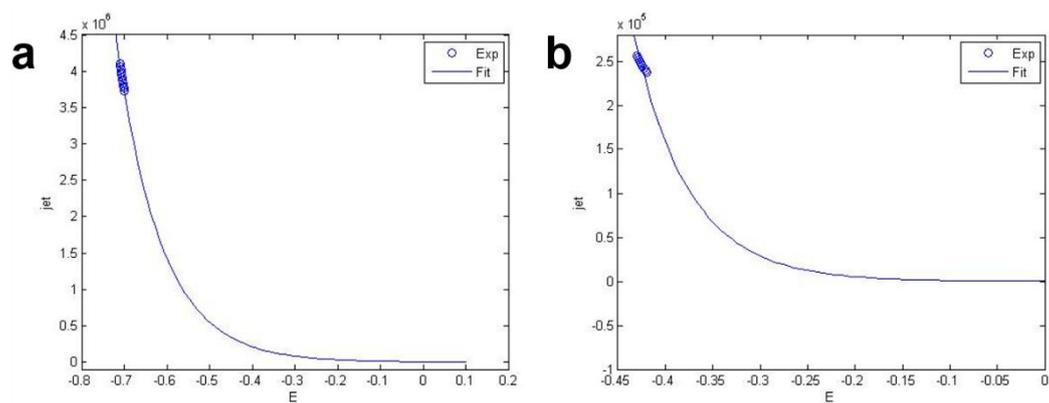
Figure S6. EIS characterization of Au NE and Au@WS<sub>2</sub> NE.



**Figure S7.** Cyclic voltammograms at 10 mV/s for a 30 nm radius Au NE in 2 mg/mL WS<sub>2</sub> QDs solution after various immersion times.



**Figure S8.** (a) The potential of nanobubble formation as a function of the time of that Au NEs were immersed in 2 mg/mL WS<sub>2</sub> QDs solution, radius, 30 nm. (b) Cyclic voltammograms of a 30 nm radius Au and Au@WS<sub>2</sub> NE in N<sub>2</sub> purged 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 20 mV/s, immerse time, 60 min.



**Figure S9.** Experimental cyclic voltammograms (black dot) and their corresponding best fits (blue line) for a (a) 20 nm radius Au NE and (b) 30 nm radius Au@WS<sub>2</sub> NE. The unit of  $j_{et}$  and  $E$  is  $A/m^2$  and  $V$  (vs Ag/AgCl).