

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

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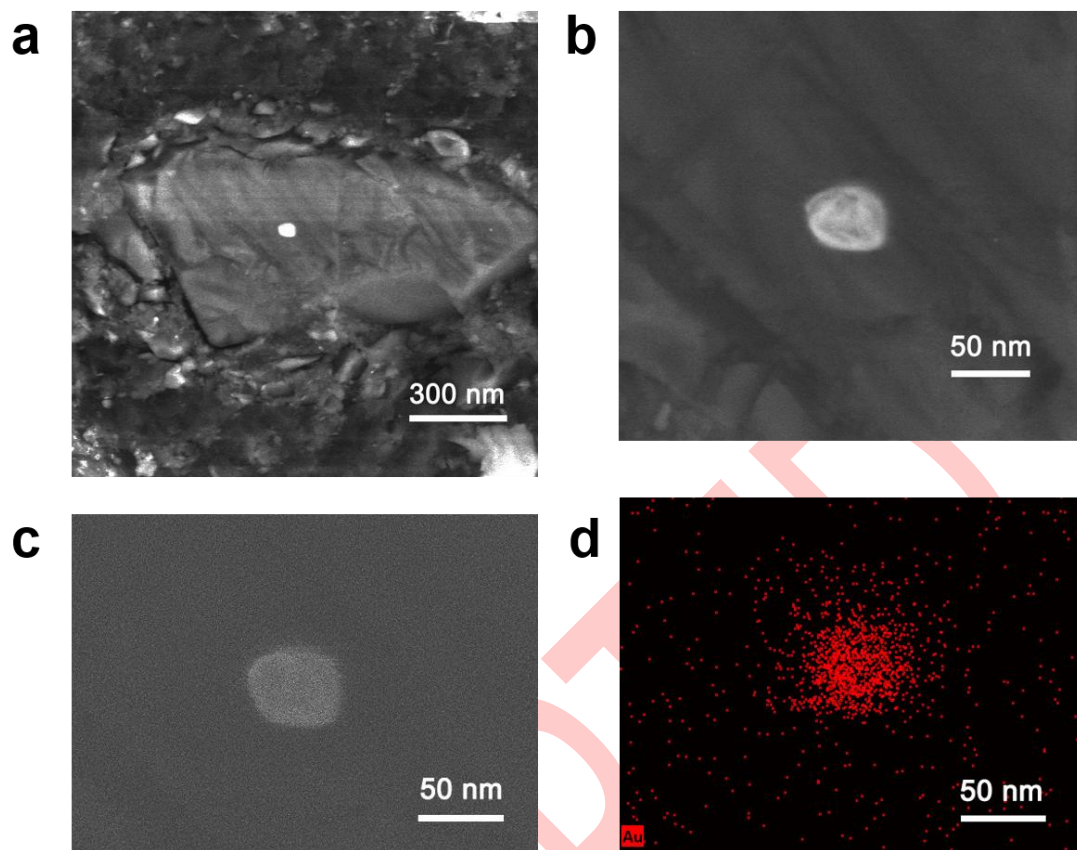
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**Table S1.** HER kinetic parameters ( $k^0$  and  $\alpha$ ) obtained from data fitting, bubble formation potentials ( $E_{\text{bubble}}$ ), NE Radii for Eight Au NEs (values are reported as mean  $\pm$  standard deviation).

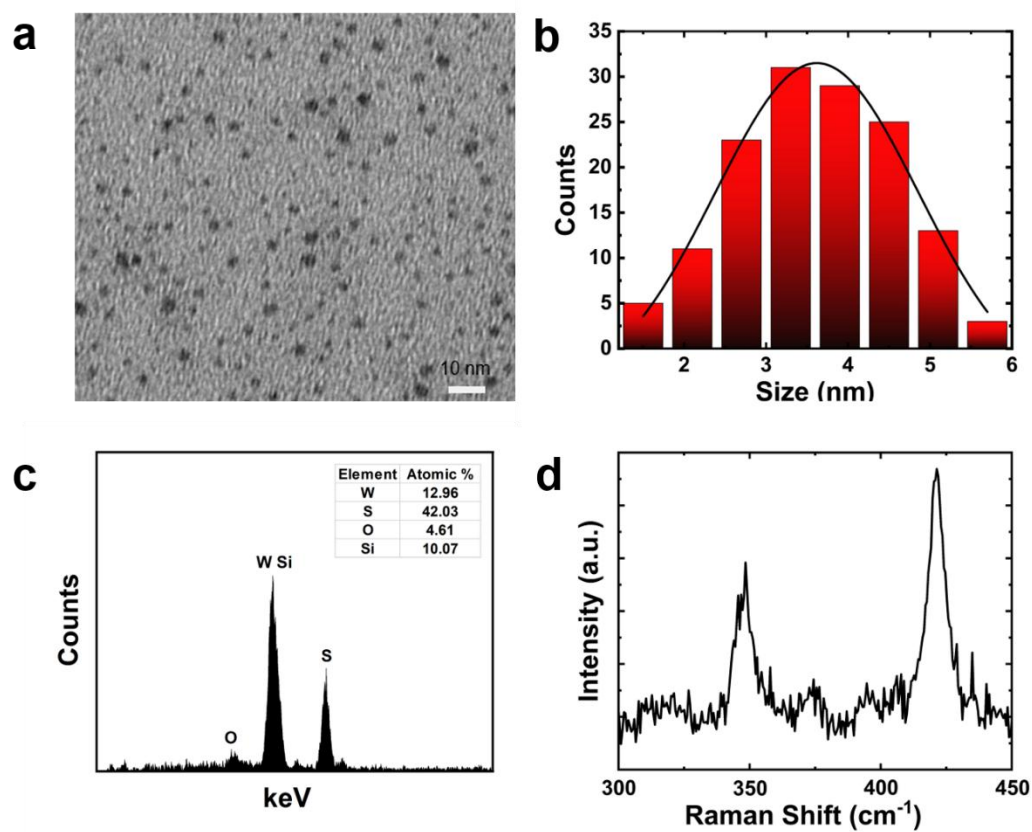
Au NE radius (nm)	$k^0$ (m/s)	$\alpha$	$E_{\text{bubble}}$ (V) vs Ag/AgCl
8	$5.1 \times 10^{-5}$	0.45	-0.812
17	$4.7 \times 10^{-5}$	0.38	-0.775
23	$2.3 \times 10^{-6}$	0.39	-0.806
30	$7.5 \times 10^{-6}$	0.41	-0.792
37	$4.2 \times 10^{-7}$	0.43	-0.821
average	$2.16 \times 10^{-5}$	0.41	

**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).

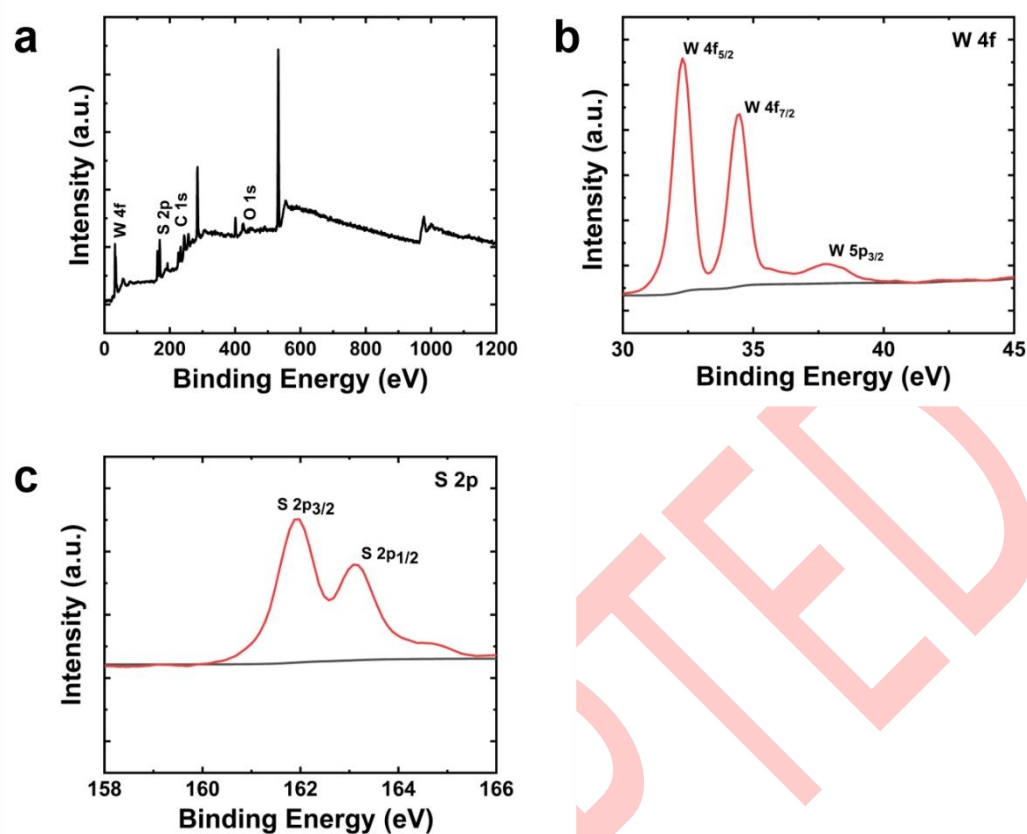
Au@WS <sub>2</sub> NE	$K^0$ (m/s)	$k^0$ (m/s)	$\alpha$	$E_{\text{bubble}}$ (V) vs	$\theta$
radius (nm)				Ag/AgCl	
10	$1.1 \times 10^{-5}$	1.5	0.54	-0.537	0.98
15	$1.0 \times 10^{-5}$	$2.7 \times 10^{-4}$	0.55	-0.516	0.99
26	$2.3 \times 10^{-5}$	$5.6 \times 10^{-4}$	0.52	-0.509	0.98
30	$1.5 \times 10^{-5}$	$7.1 \times 10^{-4}$	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



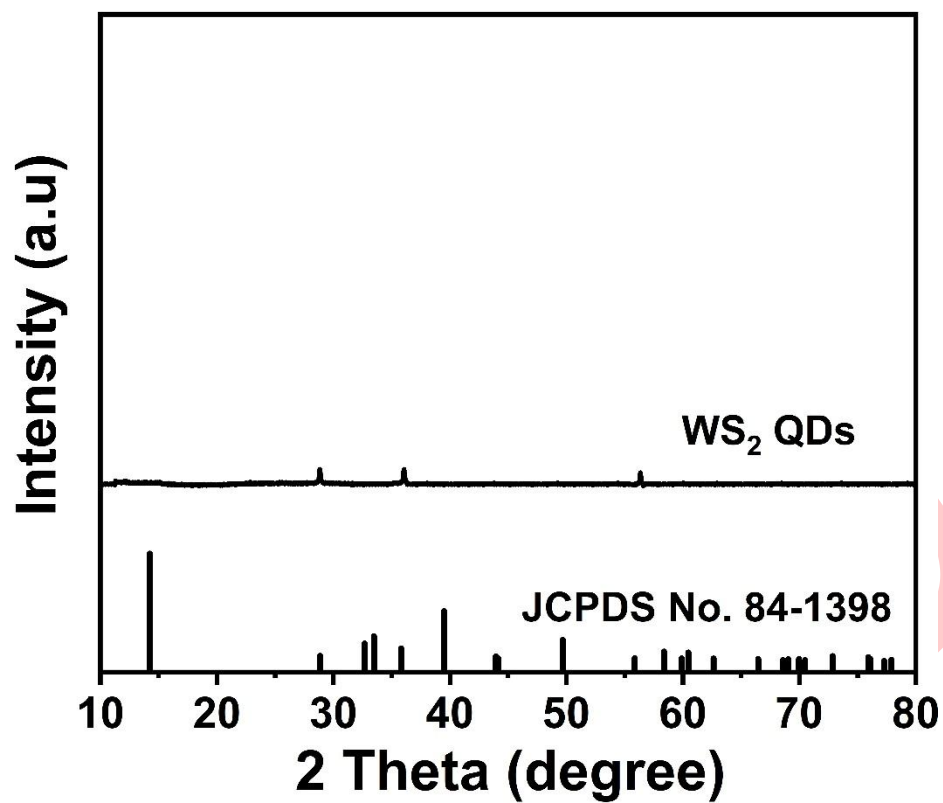
**Figure S1.** (a) The SEM image of Au NE surface. (b) A magnification of the surface of the NE in Figure S1A. (c, d) EDS element mapping characterization of Au NE surface.



**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.

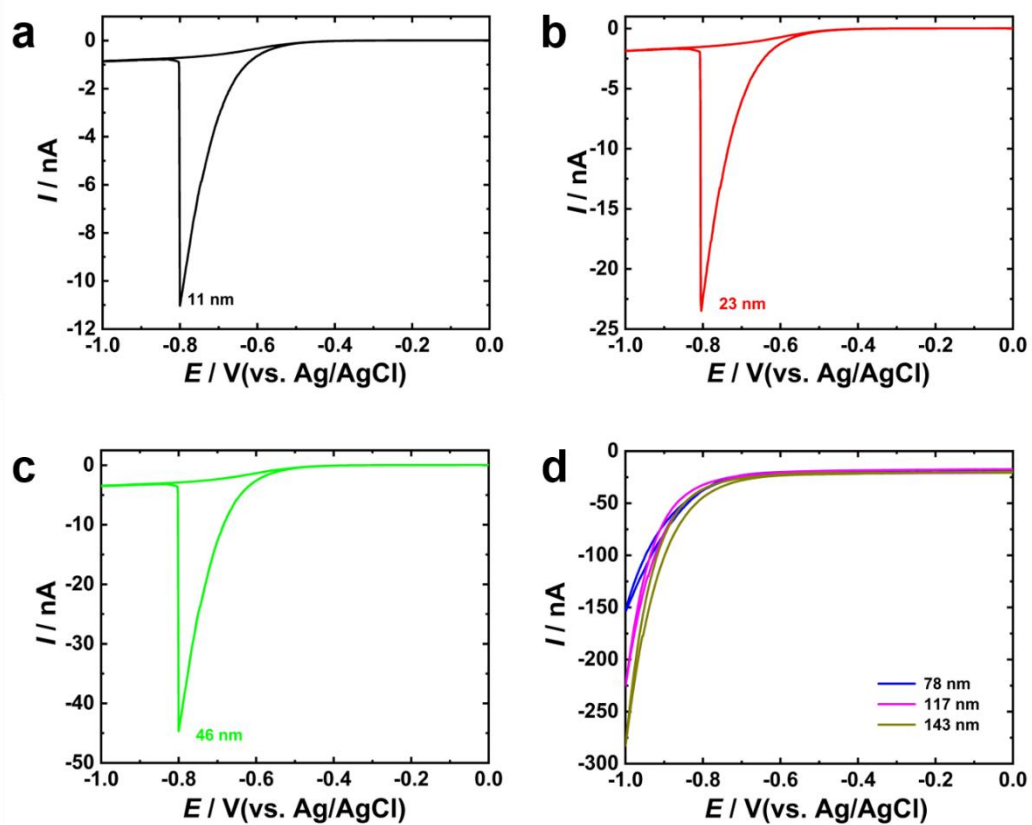


**Figure S3.** (a) XPS spectrum of WS<sub>2</sub> QDs. (b) Narrow-band XPS spectrum of W 4f.  
(c) Narrow-band XPS spectrum of S 2p.

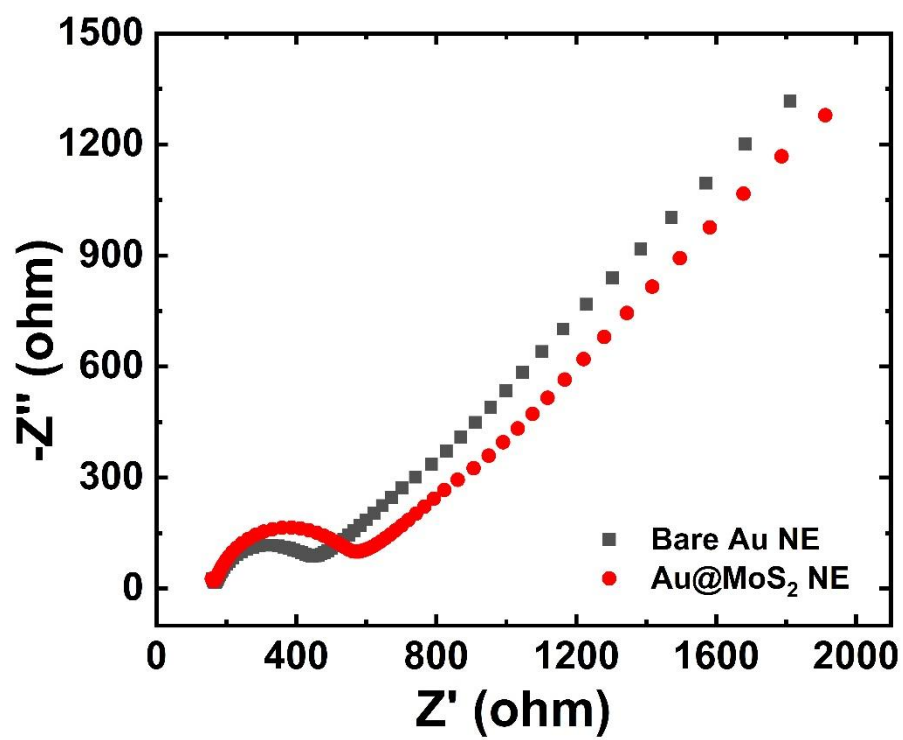


**Figure S4.** The XRD patterns of  $\text{WS}_2$  QDs.

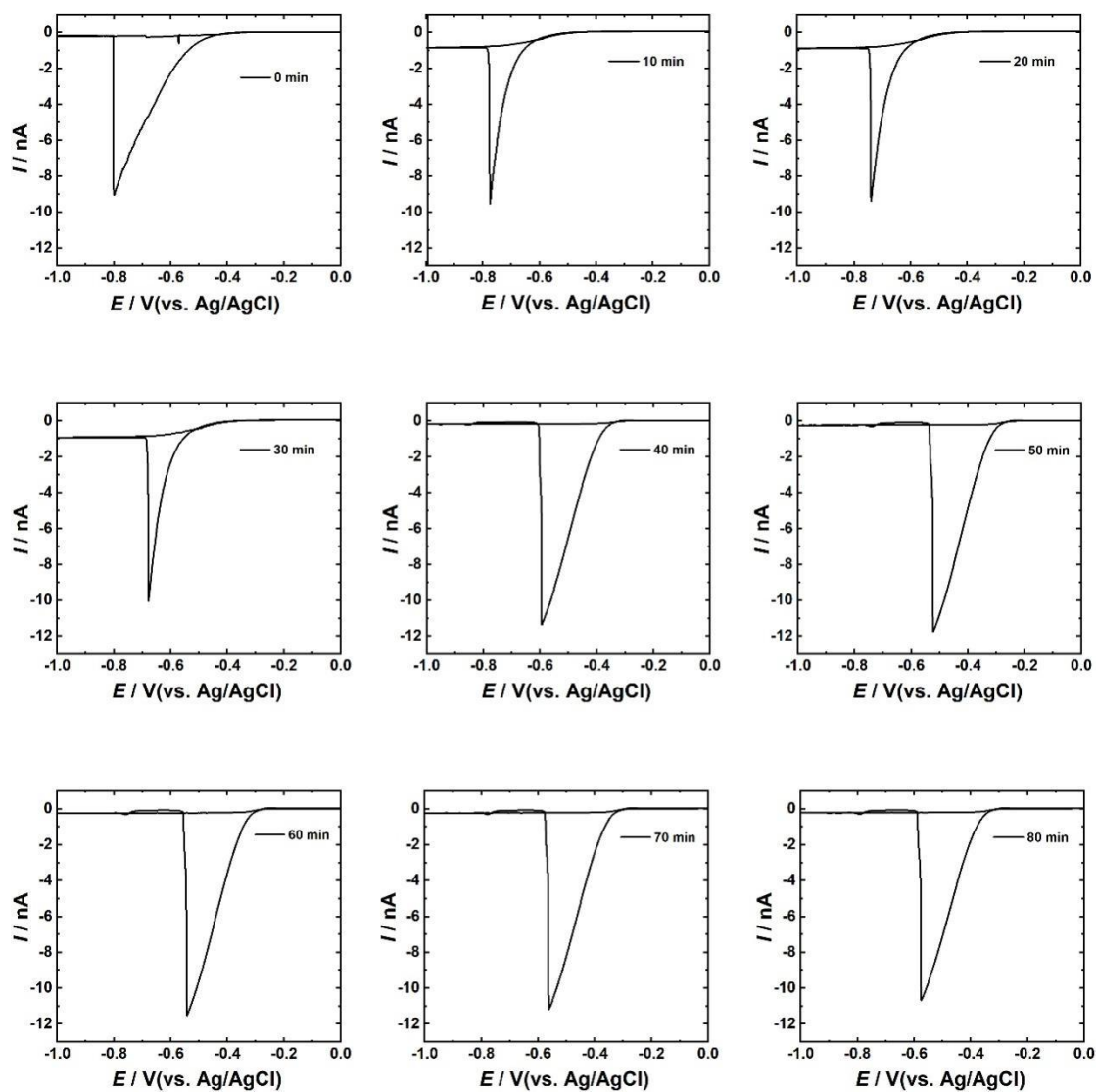




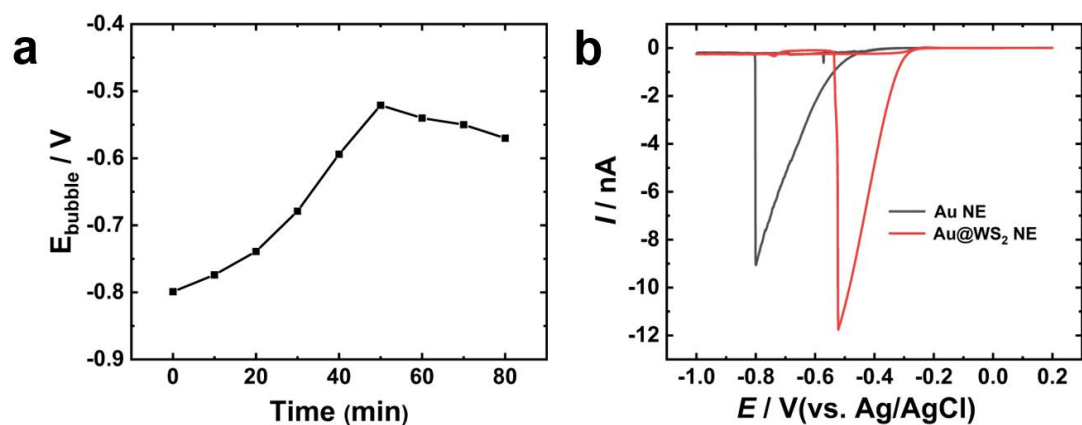
**Figure S5.** Cyclic voltammetric responses as a function of the radius of the Au NE in a 0.5 M  $\text{H}_2\text{SO}_4$  solution with a scan rate of 10 mV/s.



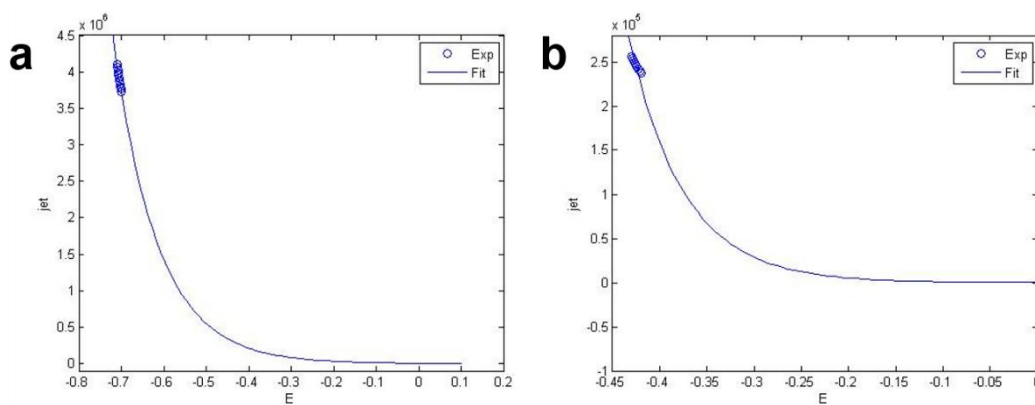
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**Figure S8.** (a) The potential of nanobubble formation as a function of the time of that Au NEs were immersed in 2 mg/mL WS<sub>2</sub> QDs solution, radius, 30 nm. (b) Cyclic voltammograms of a 30 nm radius Au and Au@WS<sub>2</sub> NE in N<sub>2</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<sup>2</sup> and V (vs Ag/AgCl).