Electronic Supplementary Material (ESI) for Energy and Environmental Science

Electronic Supplementary Information for: Evaluation of Pt, Ni, and Ni–Mo Electrocatalysts for Hydrogen Evolution on Crystalline Si Electrodes

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CATALYST REMOVAL

The Cu growth catalyst was removed from the tops of the Si microwires before subsequent deposition with catalyst, using the following procedure. First, samples were etched in buffered HF for 10 s, rinsed with >18 MΩ water and dried. The samples were then submerged for 15 min in an RCA2 etching solution (6:1:1 H_2O:HCl:H_2O_2) at 70 °C, rinsed, and dried. The process was then repeated, followed by a third 10 s buffered HF etch. Finally, the samples were treated with 30 wt% KOH(aq) at room temperature for 30 s, rinsed and dried a final time.

TEM DATA

Transmission electron micrograph images, electron diffraction data, and EDS composition data for Ni–Mo and Ni samples, deposited as noted in the main text, are shown in Figure S1.

FIGURES OF MERIT

Figures of merit for all electrodes tested for this study are set out in Tables S1 and S2.

DEPOSITION CURRENT EFFICIENCIES

Deposition current efficiency (DCE) values for Ni–Mo and Ni from the sulfamate bath were determined by a modified anodic stripping voltammetry technique. First, catalysts were deposited using the conditions noted in the main text onto glass electrodes that had been coated with fluorine doped tin oxide (FTO). The result was a partially or completely opaque black coating. These electrodes were then rinsed, dried, immersed in 1 M H_2SO_4(aq), and the potential was swept from −0.25 V to +0.90 V vs. SCE at 50 mV s^{-1}, to strip the catalyst from the electrode surface. $J - t$ and $J - E$ data for the deposition and stripping processes, respectively, are shown in Figure S2.

Complete or near complete removal of the catalyst was evidenced by the FTO-coated glass electrodes becoming transparent again after the anodic sweep. By integrating the total charge passed during the deposition and stripping processes, the DCE was estimated by use of Eq. (S1).

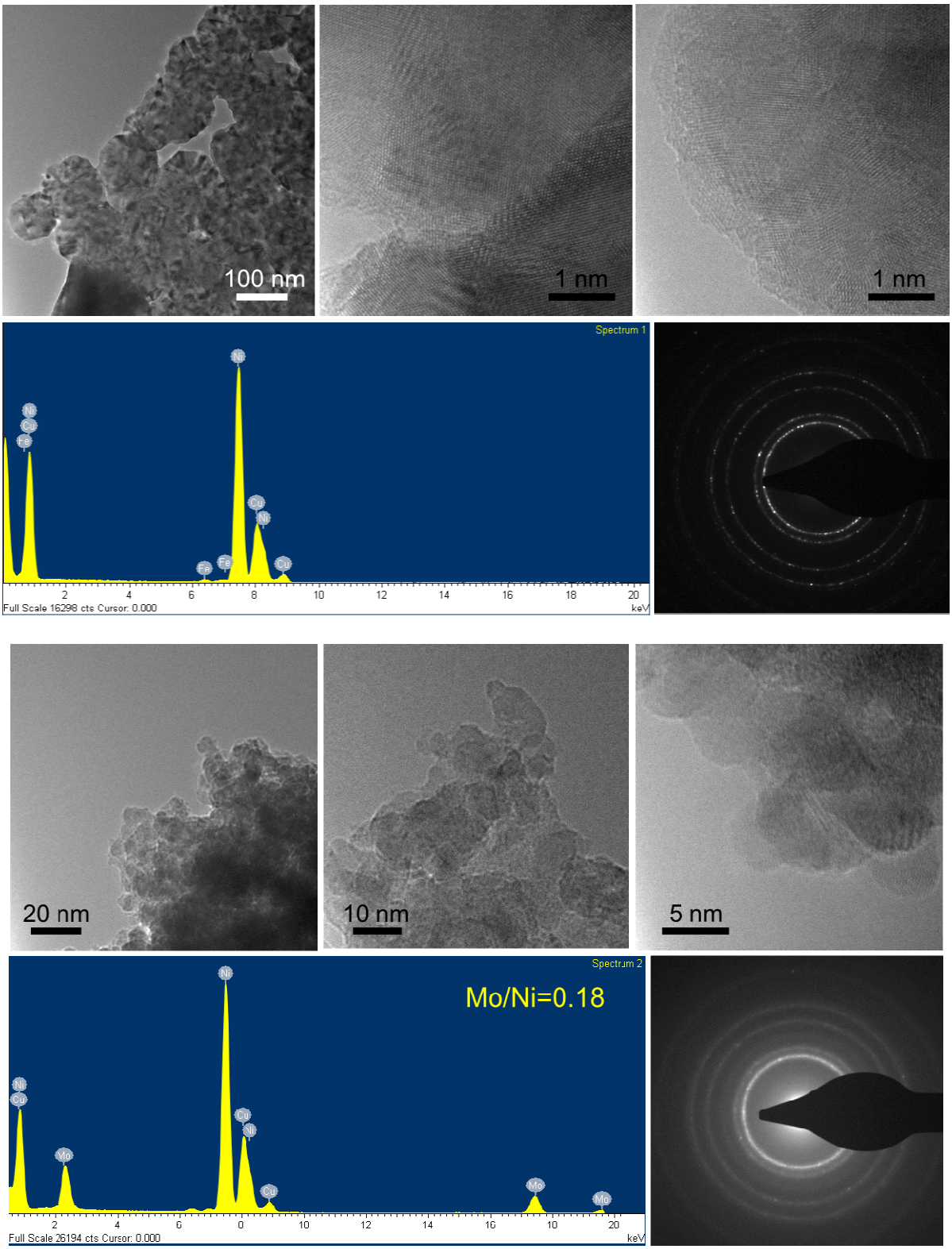

Figure S1: TEM (above), EDS data (below left), and electron diffraction data (below right) for electrodeposited films of Ni (top) and Ni–Mo alloy (bottom). Scale bars are as noted.

Table S1: Figures of merit for all p^+-Si dark electrodes

Electrode	Geometry	Catalyst	Dep. Time (s)	$J_{dark,\ 100}$ (mA cm^{-2})
15a	planar	none	0	0.01
14a	planar	Ni	0.5	0.05
14b	planar	Ni	5.5	0.11
15b	planar	Ni	5	0.12
16	planar	Ni	5	0.12
17	planar	Ni	5	0.12
18a	planar	Ni–Mo	30	1.8
18b	planar	Ni–Mo	90	6.1
19	planar	Ni–Mo	90	7.2
20a	planar	Ni–Mo	30	2.3
20b	planar	Ni–Mo	90	6.3
21a	planar	Ni–Mo	30	1.8
21b	planar	Ni–Mo	90	6.2
22	planar	Ni–Mo	30	1.6
26a	planar	electroless Pt	120	0.8
26b	planar	electroless Pt	240	6.6
26c	planar	electroless Pt	360	4.5
27a	planar	electroless Pt	120	1.3
27b	planar	electroless Pt	240	2.6
27c	planar	electroless Pt	360	4.4
23	planar	e-beam Pt	N/A	25.3
24	planar	e-beam Pt	N/A	27.7
42a	wires	no catalyst	0	0.02
39	wires	Ni	0.5	0.2
39b	wires	Ni	1	0.24
39c	wires	Ni	5	0.36
41a	wires	Ni	1	0.46
41b	wires	Ni	5	0.56
259-3	wires	Ni–Mo	60	10.4
249-4	wires	Ni–Mo	180	26.5
259-5	wires	Ni–Mo	15	5.7
35a	wires	Ni–Mo	30	6.7
35b	wires	Ni–Mo	60	11.5
35c	wires	Ni–Mo	180	20.8
37	wires	Ni–Mo	30	6.6
38	wires	Ni–Mo	90	14.3
41a	wires	electroless Pt	120	1.4
41b	wires	electroless Pt	240	6.9
41c	wires	electroless Pt	360	12.2
41d	wires	electroless Pt	480	15.7
42b	wires	electroless Pt	120	1.7
42c	wires	electroless Pt	240	5.5
42d	wires	electroless Pt	360	11.2
54	wires	e-beam Pt	N/A	35.0
55	wires	e-beam Pt	N/A	36.8

Table S2: Figures of merit for all p-Si photoelectrodes

Electrode	Geometry	Catalyst	Dep. Time (s)	V_{oc} (mV)	$J_{light,100}$ (mA cm^{-2})	J_{sc} (mA cm^{-2})	J_{ph} (mA cm^{-2})[a]	*ff*	η_{H_2} (%)
45a	planar	no catalyst	N/A	25	0.16	0.82	N/A	0.17	0.03
298-4	planar	Ni	0.5	340	0.28	10	19.0	0.11	0.4
298-7	planar	Ni	1	320	0.20	3.1	19.7	0.11	0.1
298-8	planar	Ni	1	325	0.32	6.6	19.4	0.11	0.2
298-9	planar	Ni	0.5	345	0.11	3.5	21.6	0.09	0.1
45b	planar	Ni–Mo	30	120	6.7	8.6	14.7	0.21	0.2
46	planar	Ni–Mo	30	140	7.3	9.3	11.0	0.27	0.4
47	planar	Ni–Mo	30	120	7.3	8.7	11.0	0.25	0.3
48	planar	Ni–Mo	20	155	7.6	11.8	14.0	0.24	0.4
49	planar	Ni–Mo	20	140	7.9	11.6	15.6	0.22	0.4
50	planar	Ni–Mo	20	160	8.2	14.0	18.8	0.23	0.5
7a	planar	electroless Pt	60	210	1.6	8.0	23.5	0.14	0.2
7b	planar	electroless Pt	120	230	4.0	17.4	21.6	0.18	0.7
7c	planar	electroless Pt	180	245	2.4	16.8	19.0	0.17	0.7
7d	planar	electroless Pt	240	240	1.1	13.9	21.4	0.13	0.4
7e	planar	electroless Pt	360	155	2.2	5.4	24.0	0.14	0.1
7f	planar	electroless Pt	600	170	0.3	1.4	25.5	0.10	0.02
8a	planar	electroless Pt	120	210	2.5	11.5	32.7	0.14	0.3
8b	planar	electroless Pt	240	250	5.2	23.5	24.7	0.22	1.3
8c	planar	electroless Pt	300	250	4.9	21.5	25.1	0.22	1.1
9a	planar	electroless Pt	120	205	2.7	10.7	27.7	0.15	0.3
9b	planar	electroless Pt	240	230	6.2	21.8	23.4	0.22	1.1
9c	planar	electroless Pt	300	230	4.0	17.7	27.2	0.18	0.7
10a	planar	electroless Pt	120	210	1.5	9.8	25.8	0.12	0.2
10b	planar	electroless Pt	240	220	2.7	16.5	21.4	0.15	0.5
10c	planar	electroless Pt	360	240	2.4	18.1	25.6	0.16	0.7
10c	planar	electroless Pt	480	210	1.5	10.1	27.2	0.12	0.3
11	planar	e-beam Pt	N/A	0	30.7	0	N/A	0.0	0.0
12	planar	e-beam Pt	N/A	0	23.3	0	N/A	0.0	0.0
317-E0	wires	no catalyst	N/A	34	0.01	0.005	N/A	0.43	0.0
137-E1	wires	Ni	0.5	190	3.4	7.3	10.6	0.24	0.3
317-E2	wires	Ni	1	195	3.6	6.9	11.1	0.24	0.3
317-F1	wires	Ni	0.5	210	2.5	6.9	12.2	0.20	0.3
317-F2	wires	Ni	1	210	3.2	8.0	12.0	0.22	0.4
3170C1	wires	Ni–Mo	20	145	6.0	7.4	9.2	0.31	0.3
317-C2	wires	Ni–Mo	40	145	6.0	7.0	8.6	0.35	0.4
317-D1	wires	Ni–Mo	5	160	5.3	7.0	9.4	0.31	0.3
317-D2	wires	Ni–Mo	20	145	5.7	6.8	8.3	0.33	0.3
317-G	wires	electroless Pt	120	265	5.0	11.7	13.1	0.31	1.0

[a] J_{ph} is the light-limited photocurrent density.

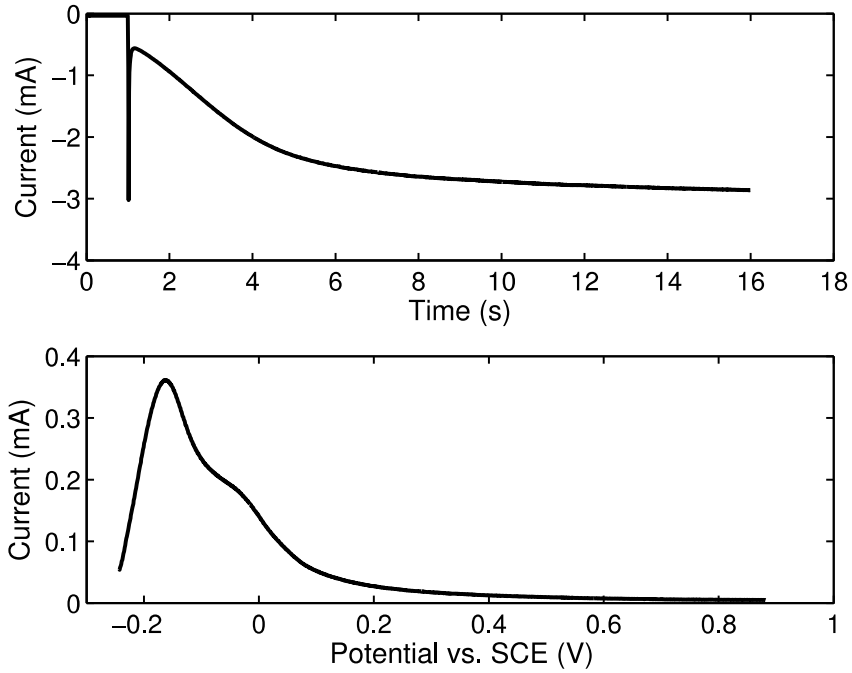

Figure S2: Example of $J - t$ data for deposition (top) and $J - E$ data for stripping (bottom) of Ni–Mo alloy using a FTO glass electrode.

$$\mathrm{DCE} = \frac{\int I_{\mathrm{strip}} \mathrm{d}t}{\int I_{\mathrm{dep}} \mathrm{d}t} \qquad \text{(S1)}$$

I_{strip} is the current passed during the course of catalyst stripping and I_{dep} is the current passed during catalyst deposition.

We attempted to account for capacitive charging of the electrode in calculations of DCE, but found that the corrections were small compared to the error implicit in the standard deviations of the measured efficiencies. Measured DCE values and their standard deviations are set out in Table S3. In spite of relatively large standard deviations, it is clear that the DCE for Ni deposition from sulfamate bath was at least an order of magnitude larger than for Ni–Mo from an otherwise identical bath.

Table 3: DCE values for Ni and Ni–Mo deposition on FTO glass electrodes

Electrode	Catalyst	Dep charge (mC)	Strip charge (mC)	DCE (%)
5-1	Ni	83	88	106
6-1	Ni	16	12	75
7-1	Ni	12	10	83
8-1	Ni	17	17	100
9-1	Ni	12	14	117
average	Ni	n/a	n/a	96 ± 17 (1σ)
5-4	Ni–Mo	127	4	3.2
6-4	Ni–Mo	25	1.3	5.1
7-4	Ni–Mo	323	8.1	2.5
8-4	Ni–Mo	22	0.8	3.6
9-4	Ni–Mo	181	5.5	3.0
10-4	Ni–Mo	39	0.7	1.8
11-4	Ni–Mo	675	13	1.9
average	Ni–Mo	n/a	n/a	3.0 ± 1.1 (1σ)

EXTERNAL QUANTUM YIELDS

Approximate external quantum yield (EQY) values for photoelectrodes were calculated by determination of the spectral photon flux from an ELH-type bulb at AM1.5 via its measured emission spectrum. That photon flux was used to calculate an upper bound current density of 44 mA cm^{-2} for a Si electrode absorbing all photons above its bandgap (1.1 eV) and collecting all of those photons as current (EQY = 100%). $J - E$ data for Si photoelectrodes were then normalized to this upper bound value to determine the EQY as a function of applied potential. Representative EQY – E data for a planar p-Si electrode and a p-Si microwire electrode, both deposited with Ni, are shown in Figure S3.

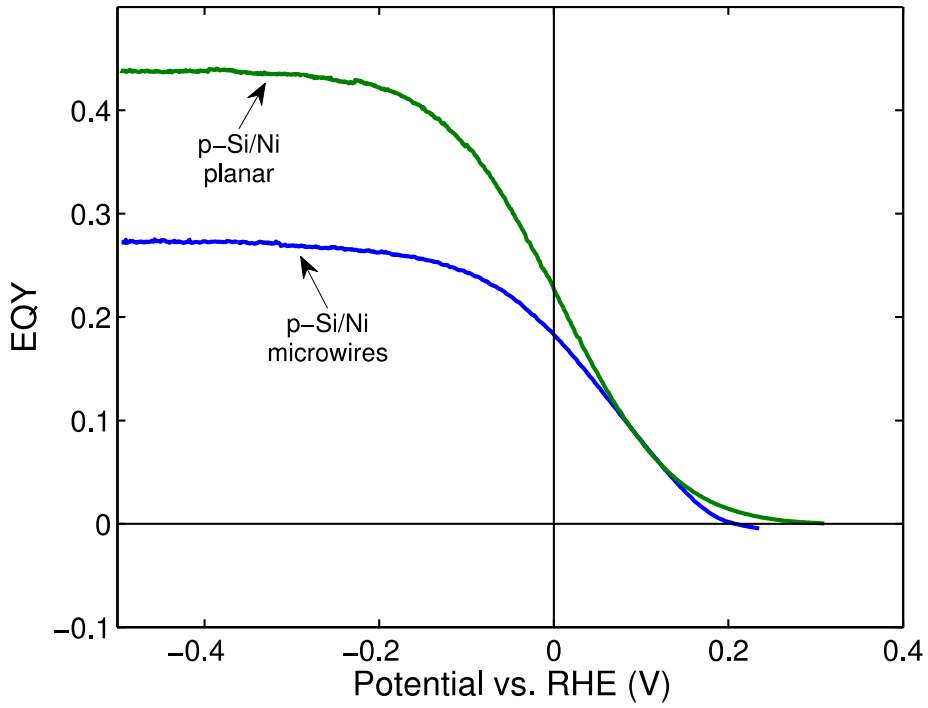

Figure S3: EQY – *E* curves for planar and microwire p-Si electrodes deposited with Ni catalyst.