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1 **An Electrochemical, Microtopographical and Ambient Pressure-**
2 **X-ray Photoelectron Spectroscopic Investigation of**
3 **Si/TiO₂/Ni/Electrolyte Interfaces**

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26 execution, and analysis of the experiment; EJC was critical in the design, building and testing of
27 the end station that allows atmospheric pressure XPS data collection on a solution under
28 potentiostatic control.

29

30 **Abstract**

31 The electrical and spectroscopic properties of the TiO₂/Ni protection layer system, which
32 enables stabilization of otherwise corroding photoanodes, have been investigated in contact with
33 electrolyte solutions by scanning-probe microscopy, electrochemistry and *in-situ* ambient
34 pressure X-ray photoelectron spectroscopy (AP-XPS). Specifically, the energy-band relations of
35 the p⁺-Si/ALD-TiO₂/Ni interface have been determined for a selected range of Ni thicknesses.
36 AP-XPS measurements using tender X-rays were performed in a three-electrode electrochemical
37 arrangement under potentiostatic control to obtain information from the semiconductor near-
38 surface region, the electrochemical double layer (ECDL) and the electrolyte beyond the ECDL.
39 The degree of conductivity depended on the chemical state of the Ni on the TiO₂ surface. At low
40 loadings of Ni, the Ni was present primarily as an oxide layer and the samples were not
41 conductive, although the TiO₂ XPS core levels nonetheless displayed behavior indicative of a
42 metal-electrolyte junction. In contrast, as the Ni thickness increased, the Ni phase was primarily
43 metallic and the electrochemical behavior became highly conductive, with the AP-XPS data
44 indicative of a metal-electrolyte junction. Electrochemical and microtopographical methods have
45 been employed to better define the nature of the TiO₂/Ni electrodes and to contextualize the AP-
46 XPS results.

47

48 **Introduction**

49 Photoelectron spectroscopy can be used to directly characterize the energy relations of
50 semiconductor/liquid junctions that underlie the operation of photoelectrochemical cells ¹,
51 provided that the kinetic energy of the emitted photoelectrons can elastically penetrate the water
52 film on the electrode surface. Conventional X-ray photoelectron spectroscopy (XPS) experiments
53 are performed in ultra-high vacuum (UHV) in the absence of electrolyte, and thus do not allow
54 for electrochemical control of an operating device during collection of XPS data. Recent
55 theoretical work has shown that the inclusion of structured solvation layers on electrodes can
56 alter the surface dipole by 0.5 – 0.7 eV (1.9 – 2.1 eV) for IrO₂ (WO₃) ². Established *in-system*
57 techniques that allow analyses of (photo)electrodes after electrochemical operation enable
58 assessment of aspects of the surface chemistry and of the associated energetic behavior ³⁻⁵.
59 However, such experiments are limited in scope and interpretation due to the rinsing, drying and
60 outgassing procedures required prior to insertion of the sample into the UHV analysis chamber.
61 In contrast, the use of tender X-rays having photon energies in the 2.3 – 5.2 keV energy range
62 allows generation of photoelectrons that have a substantially increased inelastic mean free path.
63 This approach allows “operando” XPS studies in conjunction with a classical three-electrode
64 potentiostatic arrangement and also facilitates investigation of the influence of the applied
65 potential on the band-edge energies of metal, semiconductor and hybrid electrodes at such
66 interfaces ^{6,7}. Band bending and band-edge shifts can thus be determined directly by this
67 spectroscopic technique ⁷.

68 We describe herein surface-sensitive analysis techniques for the characterization of
69 TiO₂/Ni/electrolyte interfaces. The protection and stabilization of photoanodes for water
70 oxidation to O₂(g) is of interest because high performance and stability can be achieved
71 simultaneously by protecting a variety of otherwise unstable semiconductor photoanodes ⁸⁻¹¹.

72 Specifically, TiO₂ has been used as a protection layer for photoelectrodes in either alkaline or
73 acidic media ^{7,12-17}. Some work indicates that annealing the TiO₂ allows for charge conduction
74 with minimal band bending, with unannealed TiO₂ preferred for photocathodes. However, the
75 role of the metallization layer in determining the charge-conduction properties of the films has
76 not been well elucidated ¹⁸. A thin layer of TiO₂ can protect Si and allows for water oxidation
77 with an Ir oxygen-evolution catalyst, but in such systems increases beyond 2 nm in the thickness
78 of the TiO₂ film led to a substantial increase in resistance, such that a 10 nm film was nearly
79 nonconductive even when contacted with Ir ¹¹. In contrast, TiO₂ has been found to be a nearly
80 ideal protection layer from the viewpoint of the band-edge alignment when used on p-InP or p-Si
81 photocathodes ^{19,20}. Thus, while the band positions of the TiO₂ films appear to be inherently
82 conducive to photocathode protection, the nature of the TiO₂/(metal)/electrolyte contact requires
83 further investigation. Specifically, when contacted with Ni metal, TiO₂ films allow for the
84 sustained use of highly efficient semiconductor materials (Si, III-V, II-VI) for water splitting and
85 in other oxidizing environments, especially in alkaline media where efficient, intrinsically safe
86 solar-driven water-splitting systems can be built ^{12,13}.

87 We describe herein the use of a three-electrode photoelectrochemical cell that contains a
88 meniscus-based ~ 13 nm thick electrolyte on the working electrodes formed from p⁺-Si/TiO₂/Ni
89 interfaces, which allows XPS measurements under electrochemical control through the solution
90 ^{6,7}. Combined electrochemistry-photoelectron spectroscopic data that extend the previous
91 characterization of this system ⁷ have been collected in this work.

92 Degenerately doped Si was used as a back contact for the TiO₂ to ensure that the changes
93 in the observed binding energies originated from electric fields (or their absence) in the TiO₂ and
94 not in the underlying Si. (Photo)electrochemical and microtopographical characterization using
95 scanning probe microscopy have additionally been performed to assess the nature of the electrode

96 surfaces and their conductivity properties as a function of the amount of metal deposited onto the
97 TiO₂-coated photoanode surface. Recent work¹⁵ in addition to work from our labs^{7,12,13,17}
98 suggests that the presence or absence of band bending is a key factor for facilitating charge
99 conduction through these films. The experiments reported herein demonstrate that the degree of
100 band-bending in a semiconductor (photo)electrode is not the only parameter that allows for
101 charge conduction. The data also indicate that metallization that decreases the band bending is
102 necessary for conduction. Hence multiple parameters must be optimized to obtain a functional
103 protected photoelectrode.

104

105 **Experimental**

106 Films of TiO₂ were produced by atomic-layer deposition (ALD)^{12,13,21,22} on degenerately
107 doped p-type silicon (“p⁺-Si”) substrates. (100)-oriented boron doped Si wafers with a resistivity
108 $\rho < 0.005 \Omega\text{-cm}$ were first cleaned *via* an oxidizing etch, with the Si soaked for 2 min in a 3:1 (by
109 volume) “piranha” solution of concentrated H₂SO₄ (98 %) to 30 % H₂O₂(aq), followed by an etch
110 for 10 s in a 10 % (by volume) solution of HF(aq). The wafers were then immediately etched in a
111 5:1:1 (by volume) solution of H₂O, 36 % hydrochloric acid, and 30 % hydrogen peroxide for
112 10 min at 75 °C before being moved into the ALD chamber. The TiO₂ was deposited from a
113 tetrakis(dimethylamido)titanium (TDMAT) precursor in a Cambridge Nanotech Savannah ALD
114 reactor. In an ALD cycle, a 0.1 s pulse of TDMAT was followed by a 15 s purge of N₂ at
115 20 sccm, followed by a 0.015 s pulse of H₂O before another 15 s purge with N₂. This process was
116 repeated for 1500 cycles to provide films ~ 70 nm in thickness. Where desired, Ni was deposited
117 at a rate of ~ 2 nm per min by use of a RF sputtering power of 150 W for 20 s – 300 s in an AJA-
118 International sputtering system. The time used to sputter the Ni is denoted herein as t_{sp} .

119 Atomic-force microscopy (AFM) data were collected using a Bruker Dimension Icon
120 AFM, using Peakforce Quantitative Nanomechanical parameters, to provide information on the
121 height, adhesion and deformation of the sample surface. ScanAsyst mode was used to optimize
122 the tapping frequency and other experimental parameters, e.g. the gain, set point, and cantilever
123 tuning. ScanAsyst-Air tips (silicon nitride) were used, with a nominal tip radius of 2 nm and a
124 rotated (symmetric) geometry.

125 Electrochemical characterization was performed at a scan rate of 50 mV s^{-1} in either
126 1.0 M KOH(aq) or $50/350 \text{ mM Fe(CN)}_6^{3-/4-}(\text{aq})$, using Biologic SP-200 and SP-300 potentiostats.
127 In KOH, a leak-free Ag/AgCl reference electrode (eDAQ) and a platinum counter electrode were
128 used. For measurements in $\text{Fe(CN)}_6^{3-/4-}(\text{aq})$, the reference and counter electrodes were each Pt
129 mesh electrodes.

130 *Operando* AP-XPS experiments were performed at the Advanced Light Source, Berkeley
131 at the tender X-ray beamline 9.3.1^{6,7}. Fig. 1 presents schematically the geometry of the end
132 station. Potentials were applied between the reference electrode, E_{REF} , and the Fermi energy, E_{F} ,
133 of the working electrode. X-rays at an energy of 4 keV were selected from a range of 2.3 keV –
134 5.2 keV with an energy resolution of $E/\Delta E = 3000\text{-}7200$. The X-ray beam spot size at the beam
135 line was $1 \text{ mm} \times 2 \text{ mm}$ ⁶. The photoelectron collection cone was aligned to the beam line X-ray
136 spot at a distance of $\sim 300 \mu\text{m}$ (Fig. 1). The experiments were performed using an
137 electrochemical cell with a hanging meniscus “emersion” configuration. Negligible steady-state
138 faradaic current was passed at the potentials used in the experiments described herein. We
139 designate this condition as “*operando*” because the observed region of the working electrode was
140 under potential control and the working electrode itself comprised an isopotential surface. The
141 pressure in the sample chamber was between 20 and 27 mbar, which is considered ambient
142 pressure in the context of X-ray spectroscopy. To prepare electrodes for *operando* AP-XPS, strips

143 of the p^+ -Si/TiO₂/(Ni) wafers were cut into 1 cm x 3.5 cm rectangles. Highly doped p^+ -Si was
144 used simultaneously as a support material as well as to provide an effective back contact to the
145 ALD-TiO₂. The ohmic contact at the back of the semiconductor was connected to the
146 photoelectron analyzer to provide a high conductivity ground for the sample. To make ohmic
147 contact to the sample, an In/Ga eutectic was scribed into the back of the Si wafer, and Ag paint
148 was used to contact the electrode to a strip of Cu tape that was supported on a 0.8 cm x 3 cm
149 glass slide.

150

151 **Results**

152 TiO₂/Ni/electrolyte structures having varying thicknesses of Ni were analyzed in detail.
153 The Ni thickness is referred to by the sputter deposition time, t_{sp} , as described in the experimental
154 section. For short deposition times, the Ni films were incomplete and non-uniform. Thus, the
155 deposition time is more informative than a calculated thickness, and hence t_{sp} has been quoted
156 herein as the independent variable that was varied experimentally to produce the different
157 interfaces under study.

158

159 **Electrochemical Characterization**

160 Deposition of Ni onto relatively thick (44 nm to 150 nm) ALD-grown TiO₂ enables
161 charge conduction through the TiO₂^{12,13}. In previous photoelectrochemical analyses^{12,13}, Ni
162 deposits consisted either of large islands (3 x 7 micron grid) or of thin, $t_{sp} \sim 120$ s, sputtered Ni
163 films. Herein we investigate the characteristics of interfaces formed by deposition of a variety of
164 Ni layer thicknesses.

165 Fig. 2a shows the current density vs. potential (J - U) characteristics of TiO₂/Ni electrodes
166 in 1.0 M KOH formed using Ni deposition times of 0 s, 20 s, 60 s, or 300 s. The J - U sweeps were

167 initiated in the positive direction from the open-circuit potential, U_{OC} . The data were recorded
168 after completion of the AP-XPS measurements, to establish the interrelation of the
169 voltammograms with the photoelectron spectra. Five main features were observed in the
170 voltammetric data for TiO₂/Ni (60 s) and TiO₂/Ni (300 s) interfaces. For $t_{sp} = 60$ s, the onset of
171 hydrogen evolution (HER) occurred at -1.1 V vs. Ag/AgCl, and an anodic peak, wave A, was
172 observed at $U = -0.7$ V vs. Ag/AgCl, attributable to the oxidation of metallic Ni(0) to Ni(II)²³.
173 The related cathodic peak associated with the reduction of Ni(II) to Ni(0) was not observed. At
174 positive potentials, the $J-U$ data exhibited an oxidative transformation at $U = +0.39$ V (wave B;
175 anodic current) ascribable to Ni(II) to Ni(III), prior to the onset of the oxygen-evolution reaction
176 (OER) at +0.52 V vs. Ag/AgCl. A reductive peak at $U = +0.23$ V vs. Ag/AgCl (wave C; cathodic
177 current) was observed on the return sweep. For $t_{sp} = 300$ s, the anodic and cathodic waves at
178 +0.34 V and +0.28 V vs. Ag/AgCl, respectively, exhibited less separation, and the catalytic OER
179 current was observed at 0.49 V vs. Ag/AgCl. The samples that had lower catalyst loadings, e.g.
180 $t_{sp} = 20$ s, did not display the Ni(0)/Ni(II) and Ni(II)/Ni(III) redox peaks.

181 Fig. 2b shows the electrochemical data obtained when the electrodes were in contact with
182 Fe(CN)₆^{3-/4-}(aq). An analogous trend was observed, and only electrodes with Ni thicknesses of
183 > 2 nm (sputter times ≥ 60 s) exhibited substantial current flow, even in the presence of an
184 electrochemically reversible one-electron redox couple.

185

186 **Surface Microtopography**

187 Tapping mode AFM data were obtained to determine the coverage and structure of the Ni
188 overlayer (Fig. 3). Only minor differences (~ 4 %) in roughness between bare TiO₂ and TiO₂ with
189 $t_{sp} = 20$ s or 60 s of Ni deposition (Table 1) were observed in the sample height data obtained
190 using peak force quantitative nanomechanical measurements (Fig. 3a). However, a local

191 minimum in deformation was observed for the electrode that had been coated with Ni for 20 s.
192 For increased sputter times, i.e. for the sample with $t_s = 300$ s, much higher roughness ($\sim 30\%$)
193 and deformations ($\sim 160\%$) were observed. Electrodes having $t_{sp} = 60$ s generally were very
194 similar to the behavior observed for bare TiO_2 .

195

196 **Junction Energy Relations: AP-XPS**

197 $\text{TiO}_2/(\text{Ni})$ electrodes were examined by AP-XPS in a manner analogous to that described
198 previously ⁷, with Ni deposited for $t_{sp} = 0$ s, 20 s, 60 s, or 300 s, respectively. The binding energy,
199 E_B , of a core level can be calculated as $E_B = h\nu - E_{K,VAC} - \phi_{\text{sample}}$ where $E_{K,VAC}$ is the kinetic
200 energy of the photoelectron with respect to the vacuum energy level (E_{VAC}), ϕ_{sample} is the work
201 function of the sample, and $h\nu$ is the X-ray energy. E_B is measured relative to the Fermi energy,
202 E_F , of the analyzer (or of the sample, which are equal, because the two components are in
203 electrical contact). However ϕ_{sample} is unknown during the XPS measurements, and the kinetic
204 energy is referenced to the Fermi energy, E_F , if not otherwise noted, i.e. $E_K = E_{K,VAC} + \phi_{\text{sample}}$
205 (where ϕ_{sample} is the energetic difference between the E_{VAC} and the Fermi level of the sample).
206 This approach provides binding energies that are referenced to the analyzer. To provide a
207 description from an electrochemical perspective, we define E_B' as the core-level binding energy
208 referenced to the solution potential instead of referenced to E_F of the working electrode/analyzer.
209 Because the potentials are set at the working electrode with respect to the reference electrode, E_B'
210 can be defined by equation (1)

$$211 \quad E_B' = E_B + qU_{\text{eff}} \quad (1)$$

212 where q is the absolute charge of an electron and U_{eff} tracks the difference in the electrochemical
213 potentials between the solution and the working electrode. U_{eff} is given by $U_{\text{eff}} = U - U_{\text{fb}}$ where U

214 is the applied potential and U_{fb} is the flat-band potential for the bare TiO_2 electrode (for details
 215 see Ref. ⁷). Hence the solution-corrected core-level binding energy, E_B' , measures the binding
 216 energy of a level relative to the solution potential. In this approach, the solution-corrected binding
 217 energies E_B' of core levels of materials in solution, such as the O 1s level of solution (bulk) water,
 218 should remain constant as the potential at the working electrode is varied (the effect of water in
 219 the double layer is negligible at the ionic strengths used). Semiconductors that have “fixed” band
 220 edges in a semiconductor/liquid junction should show no change in E_B' at the interface with a
 221 change in U_{eff} , because in this picture, the band edges are fixed relative to the solution energetics.
 222 However, for cases in which the band edges of the semiconductor shift, such as in the case of
 223 accumulation or Fermi-level pinning due to defect states ⁷, the solution-corrected binding energy
 224 would be expected to shift with respect to the solution potential. Thus when the binding energy is
 225 referenced to the solution potential or to the potential of the reference electrode, the E_B' of the
 226 water O 1s level and of the semiconductor/liquid junction semiconductor core levels would be
 227 expected to be independent of the solution potential, and should exhibit a shift parameter
 228 $\Delta' \equiv \partial E_B' / \partial U_{eff} = 0 \text{ eV V}^{-1}$. However, for cases where the band edges shift with respect to the
 229 solution, as may result from Fermi level pinning, a change in the solution-corrected binding
 230 energies with solution potential is expected. This situation can be contrasted with the results
 231 expected when the binding energies are determined with respect to the analyzer ⁷, because when
 232 referencing binding energies to the analyzer (E_B), the water O 1s and pure (without metallization)
 233 semiconductor/liquid junction semiconductor core levels are expected to show a shift
 234 $\Delta \equiv \partial E_B / \partial U_{eff} = \Delta = -1 \text{ eV V}^{-1}$ with respect to the applied voltage ⁷.

235 Fig. 4 plots solution-corrected XPS spectra for the O 1s and Ti 2p core levels for a bare
 236 TiO_2 electrode, in which the photoemission intensities are plotted against E_B' , and Fig. 5 plots the
 237 solution-corrected XPS spectra for the Ni 2p, O 1s and Ti 2p core levels of the TiO_2/Ni (20 s)

238 electrode vs E_B' . The bare TiO_2 XPS peaks showed less band-edge shifting whereas electrodes
239 with Ni showed a larger shift. Fig. 6a displays the full width at half maximum (FWHM) of the
240 liquid water O 1s core level, as well as of the TiO_2 O 1s peak, for the bare TiO_2 electrode. The
241 FWHM data are expected to reach a minimum at the flat-band potential ⁷. Fig 6a shows that for
242 the bare TiO_2 electrode, the FWHM for the TiO_2 O 1s peak reaches a minimum at -0.9 V vs.
243 Ag/AgCl. Fig. 6b shows the solution-corrected core level shift for the Ti $2p_{3/2}$ core levels across a
244 range of potentials for the three different $\text{TiO}_2/(\text{Ni})$ electrodes. The slopes, Δ'_{Ti} , of the fitted lines
245 show that the solution-referenced binding energy E_B' of the Ti $2p_{3/2}$ core level shifted with a slope
246 of $1.0 \pm 0.08 \text{ eV V}^{-1}$ for TiO_2/Ni (20 s), $0.9 \pm 0.10 \text{ eV V}^{-1}$ for TiO_2/Ni (60 s), and
247 $1.0 \pm 0.07 \text{ eV V}^{-1}$ for TiO_2/Ni (300 s). Fig. 6c shows that the relative peak shift, Δ'_{Ni} , of E_B' for
248 the Ni $2p_{3/2}$ core level for TiO_2/Ni (20 s) was $0.7 \pm 0.07 \text{ eV V}^{-1}$; that for TiO_2/Ni (60 s) was
249 $0.9 \pm 0.08 \text{ eV V}^{-1}$; and the value for TiO_2/Ni (300 s) was $1.0 \pm 0.08 \text{ eV V}^{-1}$. The errors associated
250 with these slopes result primarily from the resolution of, and uncertainty inherent to, the
251 measurement.

252 Fig. 7 displays XPS data showing the Ni $2p_{3/2}$ core level for samples prepared with
253 $t_{\text{sp}} = 20 \text{ s}$, 60 s and 300 s . The electrode was maintained at a potential of -1.0 V vs. Ag/AgCl, and
254 the Ni(0), Ni(II), and Ni(III) peaks as well as the satellite peaks are labeled. A clear lack of a
255 metallic Ni phase was observed for the $t_{\text{sp}} = 20 \text{ s}$ sample at potentials positive of flat-band, and
256 only a very small amount of metallic Ni (6 %, Ni $2p_{3/2}$ peak area) was visible under reducing
257 conditions at $U = -1.0 \text{ V}$ vs. Ag/AgCl. In contrast, the $t_{\text{sp}} = 60 \text{ s}$ sample had a significant peak
258 area fraction (40%) of metallic Ni and the sample prepared using $t_{\text{sp}} = 60 \text{ s}$ showed a large
259 fraction (51 %) of metallic Ni. The Ni(III) content was 94 % for $t_{\text{sp}} = 20 \text{ s}$, 47 % for $t_{\text{sp}} = 60 \text{ s}$ and
260 22 % for $t_{\text{sp}} = 300 \text{ s}$, based on peak areas in the Ni $2p_{3/2}$ peak.

261

262 **Discussion**

263 **Electrochemistry**

264 For lower Ni coverage, the electrode exhibited resistive behavior with very low currents
265 in both the KOH electrolyte and the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox solution (Fig. 2). However, currents
266 become substantial for the electrode that had $t_{\text{sp}}=60$ s (~ 2 nm) of Ni. The typical electrochemical
267 signatures of Ni oxidation and reduction as well as HER and OER were observed, with the
268 Ni(II)/(III) redox reaction showing irreversible behavior with a peak separation of 0.16 V.
269 Increasing t_{sp} to 300 s decreased this peak separation to 0.06 V, indicating that the conductivity of
270 the sample improved. Starting at the open-circuit potential and scanning toward more positive
271 potentials, the electrodes became covered with NiO, and then NiOOH, as evidenced by the
272 observation of a partial reduction of Ni(III) to Ni(II) (peak C, Fig. 2) in the cathodic branch of the
273 voltammetry. After several cycles in which the potential scan was stopped in the anodic waves,
274 the initially existing Ni metal had been partially oxidized. The corresponding current for Ni
275 oxidation was small because the successfully oxidized Ni overlayers inhibited further oxidation
276 of Ni metal. Prior XPS data on these 2 nm thick Ni films ⁷ support this conclusion by showing a
277 decrease in the Ni(0) signal with a concomitant increase in the Ni(II) signal. The increase in
278 sample conductivity for thicker Ni coverages is evident in Fig. 2b, where current densities
279 $> 10 \text{ mA cm}^{-2}$ are evident at +0.1 V vs. Ag/AgCl. Thus, the data show a distinct difference in the
280 sample conductivity depending on the amount of Ni deposited and on the anodization procedure
281 ¹².

282

283 **AFM Microtopography**

284 Microtopography data indicated that for small t_{sp} values, the sample exhibited surface
285 roughness and a deformation of the bare TiO_2 /solution interface. The dip in the deformation data

286 for the $t_{sp} = 20$ s sample suggests the presence of a different surface material than that observed
287 for either bare TiO_2 or for the thicker Ni-coated TiO_2 surfaces. This behavior is consistent with
288 expectations for a $\text{NiO}_x/\text{TiO}_2$ surface that does not contain underlying metallic Ni. The increasing
289 trend in deformation from $t_{sp} = 20$ s to $t_{sp} = 300$ s suggests that only after a 20 s deposition of Ni
290 did a substantial metallic phase exist at the $\text{TiO}_2/\text{NiO}_x$ interface. This conclusion is also supported
291 by XPS data of the Ni 2p core level (Fig. 7).

292

293 **Energy relations by AP-XPS measurements**

294 The XPS technique integrates the signal over the spot examined in the experiment. Fig. 8
295 shows a schematic of the energy-band relations and the resulting description of the structures
296 considered herein. In the physical representation, the kinetic energies plus the work function, E_K ,
297 of the photoelectrons are referred to the Fermi level E_F of the working electrode, which coincides
298 with that of the analyzer, to deduce E_B . In the electrochemical frame of reference, kinetic
299 energies are referred to the reference electrode potential to define E_B' . To be consistent, changes
300 in E_B' were measured with respect to the potential at which the flat-band condition was observed
301 for the bare TiO_2 electrode. This approach allows evaluation of the shift in the band edges with
302 respect to the solution potential as the applied potential is varied. If the shift in E_B' with potential
303 is greater than zero (see equation 1), band-edge movement occurs. Provided that the sampling
304 depth of the technique is smaller than the width of the space-charge region, the shift of E_B , Δ , and
305 of E_B' , Δ' , with potential should approximately be related by equation (2):

$$306 \quad \Delta' = \Delta + 1 \text{ eV V}^{-1} \quad (2).$$

307 Hence, the semiconductor core levels in an ideal semiconductor/liquid junction will have
308 corrected peak shifts Δ' , relative to the reference electrode, of $\Delta' = 0.0 \text{ eV V}^{-1}$; the electrolyte will

309 also exhibit no shift; while the metal core levels in a pure metal/electrolyte junction will shift
310 with the full applied potential *relative to the reference electrode*, i.e. $\Delta' = 1.0 \text{ eV V}^{-1}$.

311 Analysis of the electrochemical data alone does not directly allow assessment of whether
312 a rectifying or an ohmic contact was formed, because the high resistivity ($t_{\text{sp}} = 20 \text{ s}$) could also be
313 observed for an isolated system that contains a buried Schottky barrier. The AP-XPS data,
314 however, enables this evaluation of the electrical properties of the materials in the device and at
315 the interfaces of interest.

316 As shown in Fig. 6b, the average solution-corrected binding energies of the Ti $2p_{3/2}$ core
317 level for the TiO_2/Ni (20 s) interface shifted by 1.0 eV V^{-1} ; those for TiO_2/Ni (60 s) shifted by
318 0.9 eV V^{-1} ; and those for TiO_2/Ni (300 s) shifted by 1.0 eV V^{-1} , all showing metal-like behavior.
319 For comparison, the band edges for bare TiO_2 were observed to shift only in the potential range
320 in which defect states occurred, and were otherwise stationary (at potentials more positive than
321 the conduction-band edge))⁷, suggesting that the bare TiO_2 acts like a semiconductor outside of
322 the potential range where the defect states induce Fermi level pinning. Hence, the TiO_2/Ni (20 s),
323 TiO_2/Ni (60 s) and the TiO_2/Ni (300 s) electrodes all exhibited only small amounts of
324 rectification in the underlying TiO_2 layer. The improvements in observed conductivity (Fig. 2) of
325 the TiO_2/Ni electrodes in the order $t_{\text{sp}} = 0 \text{ s} < 20 \text{ s} < 60 \text{ s} < 300 \text{ s}$ therefore likely result from more
326 than simply the removal of rectification in the underlying TiO_2 . Furthermore, as shown in Fig. 7,
327 the amount of interfacial metallic Ni increased significantly, with almost no Ni(0) present for $t_{\text{sp}} =$
328 20 s and half of the layer consisting of Ni(0) for $t_{\text{sp}} = 300 \text{ s}$ ²⁴. Hence, the data are consistent with
329 the presence of Ni, as opposed to NiO_x , at the TiO_2/Ni interface playing a dominant role in
330 determining the charge conduction through the device.

331 The importance of the Ni contact, as opposed to NiO_x , to the TiO_2 , is evident based on the
332 combination of the electrochemistry (Fig. 2), the solution corrected Ti 2p and Ni 2p core level

333 shifts from AP-XPS data (Fig. 6), and the catalyst compositions (chemical states) from the
334 Ni 2p_{3/2} core level AP-XPS (Fig. 7). The bare TiO₂ sample is both nonconductive and observed to
335 be generally rectifying (Fig. 2 and 6), whereas the TiO₂ samples with substantial amounts of
336 metallic Ni ($t_{sp} \geq 60$ s) are ohmic at the semiconductor/liquid junction (i.e band-edge shifts of
337 $\Delta' \sim 1.0$ eV V⁻¹), and are electrically conductive, as evidenced by the $J-U$ behavior. The sample
338 with the NiO_x layer ($t_{sp} = 20$ s) is, therefore, unique, in that it displays similar AP-XPS data in
339 that the band edges of the TiO₂ appear to be similarly disconnected from the solution, such that
340 they shift with respect to the solution potential, as is the case for the samples that have substantial
341 metallic Ni. However, the TiO₂ in the NiO_x-containing samples is nonconductive, as observed in
342 electrochemical analysis (Fig. 2). The junction between NiO_x and TiO₂ appears electronically
343 distinct from that between Ni and TiO₂ in that charge conduction is not present for the NiO_x/TiO₂
344 structure even though rectification at the TiO₂/liquid junction has largely been removed²⁴. If a
345 purely conduction-band transport mechanism operates in the TiO₂, such that Ni metal is not
346 required to contact the TiO₂, the loss of rectification for the $t_{sp} = 20$ s sample should have allowed
347 for conduction to be observed for the device in contact with the Fe(CN)₆^{3-/4-} redox solution.
348 Therefore, the lack of conduction in the samples for $t_{sp} = 20$ s is consistent with the presence of
349 NiO_x, as opposed to Ni, heavily influencing the electrical behavior of the TiO₂, leading to an
350 increase in resistivity and a consequent loss in film conductivity. The E_B for the Ti 2p_{3/2} core
351 level in the TiO₂/Ni samples with thick Ni was observed to be equal to that observed for the bare
352 TiO₂ films at a potential at the midpoint of the mid-gap states (459.0 eV to 459.1 eV), suggesting
353 an interplay between the mid-gap “defect” states and the Ni overlayer. These results are
354 summarized in Fig. 9 by the schematic energy diagrams of the solid/liquid interface. Fig. 9a-c
355 shows the situation for negative potentials U with respect to the flat-band condition, and Fig. 9d-f
356 depicts the situation for positive potentials U with respect to flat-band of the TiO₂/electrolyte

357 (Fig. 9a and 9d), TiO₂/NiO_x/electrolyte (Fig. 9b and 9e) and TiO₂/Ni/NiO_x/electrolyte (Fig. 9c
358 and 9f) systems. In the presence of NiO_x and Ni, Fermi level pinning at the mid-gap states occurs.
359 In the absence of Ni or NiO_x, TiO₂ develops a space-charge region with fixed band-edge
360 positions outside of regions involving Fermi-level pinning or accumulation ⁷.

361

362 **Conclusions**

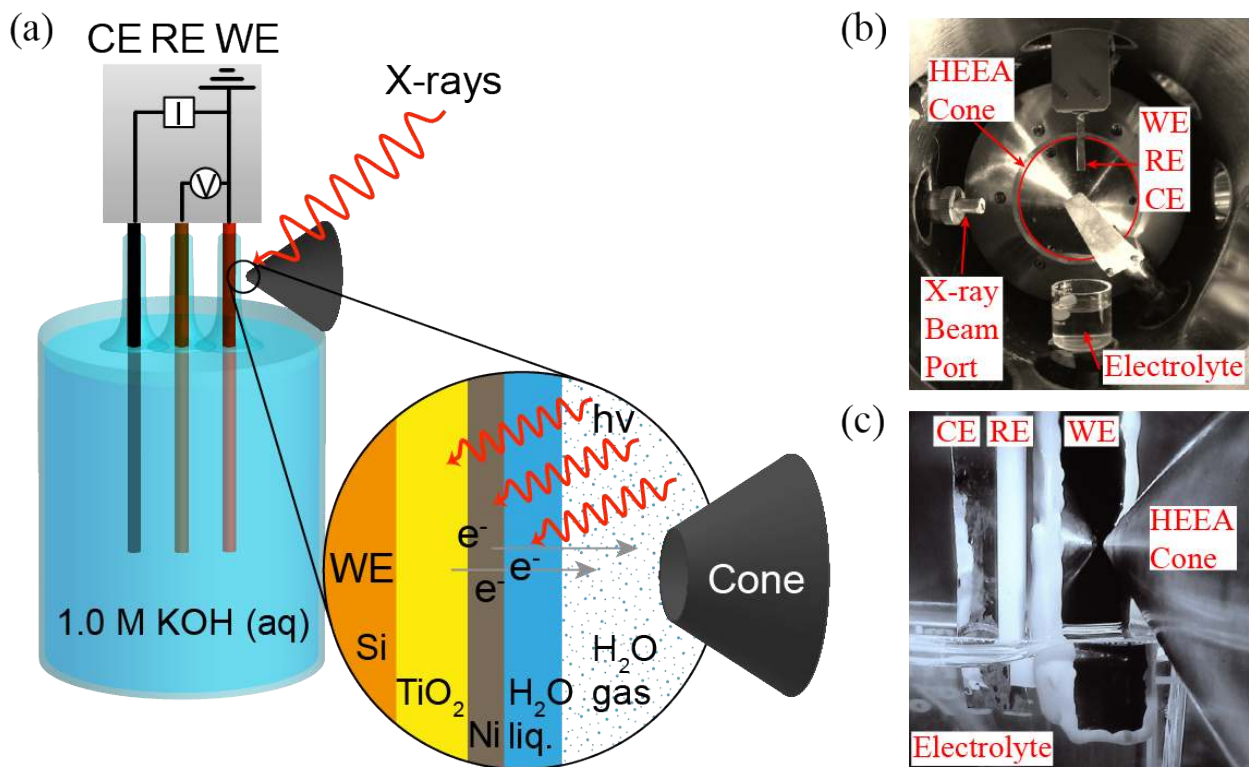
363 The results presented herein demonstrate that *operando* AP-XPS can be used to observe
364 and quantify the degree to which catalysts influence the band energetics of underlying protection
365 layers and the ECDL. In addition to providing information regarding the band energetics, layer
366 composition and chemical state, AP-XPS also provides direct evidence regarding the nature of
367 the rectification and contact at the interface. For various thicknesses of deposited Ni or NiO_x, the
368 rectification in the underlying TiO₂ is mostly removed; however, the increase in conductivity for
369 deposited Ni only occurs when the Ni phase contains a substantial amount of metallic Ni and not
370 merely an oxide phase. As a result, the data indicate that the band lineups between the
371 semiconductor and the metal or metal oxide overlayer, as well as electronic effects that result
372 from this equilibration, are the crucial factors that induce conduction in the TiO₂ films under
373 evaluation. Sufficiently dense metallization allows for stable conduction through such films.

374

375 **Acknowledgments**

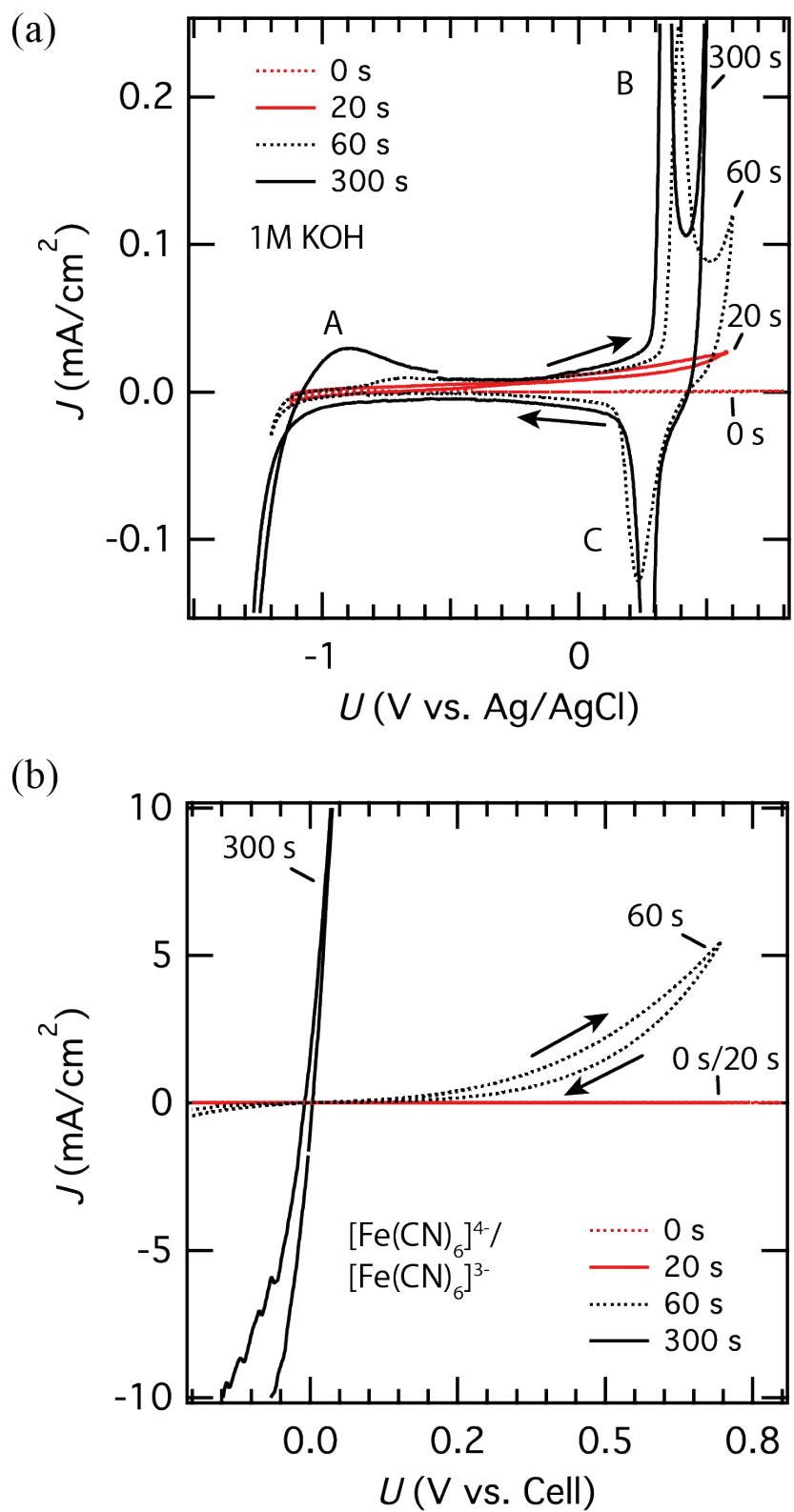
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380 05CH11231. We thank Dr. Philip Ross for contributions to the conceptual development of the
381 AP-XPS end station and experimental design.



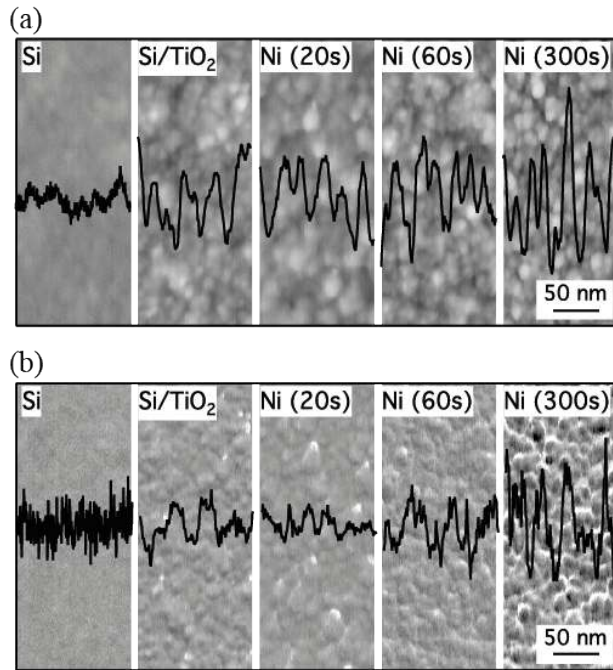
382

383 **Figure 1:** (a) Scheme of the *operando* XPS-PEC setup. The working electrode and the
 384 hemispherical electron energy analyzer (HEEA) were grounded to each other. The potential of
 385 the working electrode was changed with respect to the reference electrode. The PEC-beaker
 386 containing the electrolyte could be moved in the z direction whereas the three-electrode mount
 387 could be moved in the x-, y-, and z-directions. (b) View into the high-pressure analysis chamber.
 388 The X-ray beam enters through the window on the left, the three-electrode setup is on the top, the
 389 electrolyte beaker on the bottom, and the electron analyzer cone is in the center. (c) Three-
 390 electrode setup pulled up and in measurement position (compare to (a)).



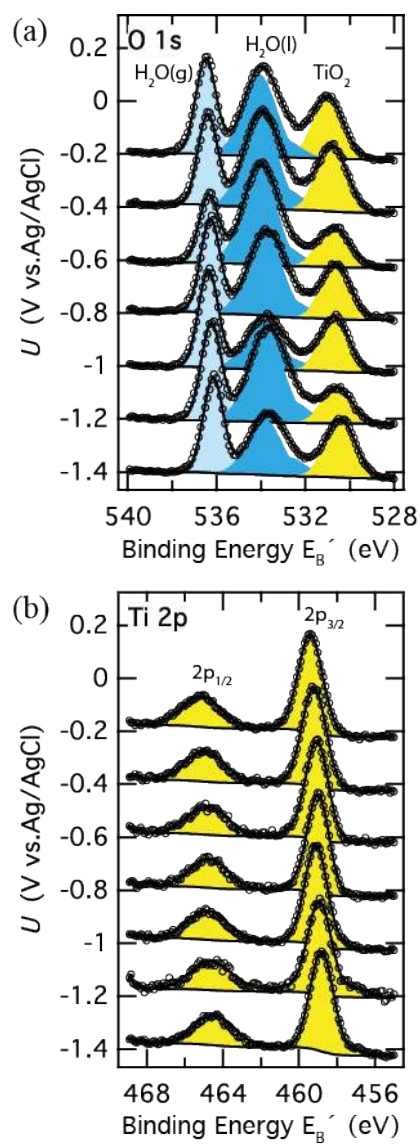
391
 392 **Figure 2:** (a) $J-U$ data collected for bare TiO₂, TiO₂/Ni (20 s), TiO₂/Ni (60 s), and
 393 TiO₂/Ni (300 s) electrodes, respectively, in 1.0 M KOH(aq). Three peaks are observed: for

394 $t_{sp} = 60$ s, an anodic peak A at -0.7 V, an anodic peak B at $+0.39$ V, and a cathodic peak at
395 $+0.23$ V vs. Ag/AgCl. For $t_{sp} = 300$ s, these peaks shifted to -0.85 V, $+0.34$ V and $+0.28$ V vs.
396 Ag/AgCl. (b) $J-U$ data measured in $50/350$ mM $\text{Fe}(\text{CN})_6^{3-/4-}(\text{aq})$ solution. Arrows show the scan
397 direction.

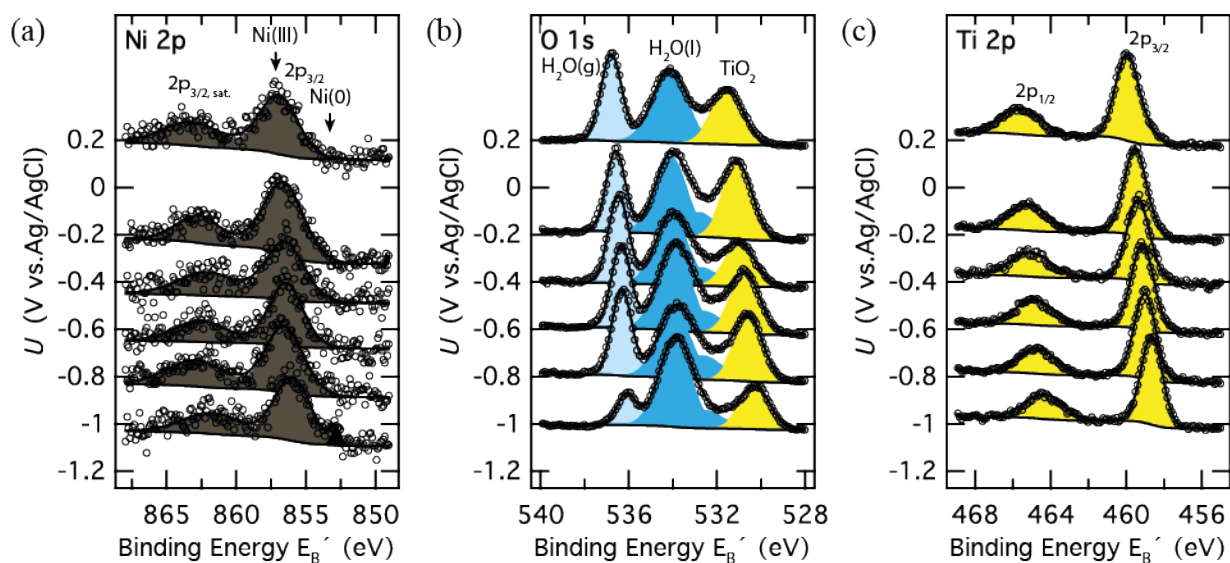


398

399 **Figure 3:** AFM microtopographs of bare silicon, ~ 70 nm thick TiO₂ on silicon, Si/TiO₂/Ni
 400 (20 s), Si/TiO₂/Ni (60 s), and Si/TiO₂/Ni (300 s). (a) depicts the height information and (b) the
 401 surface deformation by the AFM tip. The sub-micrographs in (a) and (b) have the same height
 402 scaling. In each graph the insets show line scans from the middle of the microtopographs.



403
 404 **Figure 4:** O 1s (a) and Ti 2p (b) X-ray photoemission spectra of the bare TiO₂ electrode in 1.0 M
 405 KOH(aq) for $U = -1.4$ V to -0.2 V vs. Ag/AgCl. The binding energies are referenced to the
 406 solution potential as explained in the text and corrected by the applied potential with respect to
 407 flat-band conditions at $U_{fb} = -0.9$ V vs. Ag/AgCl⁷.



408

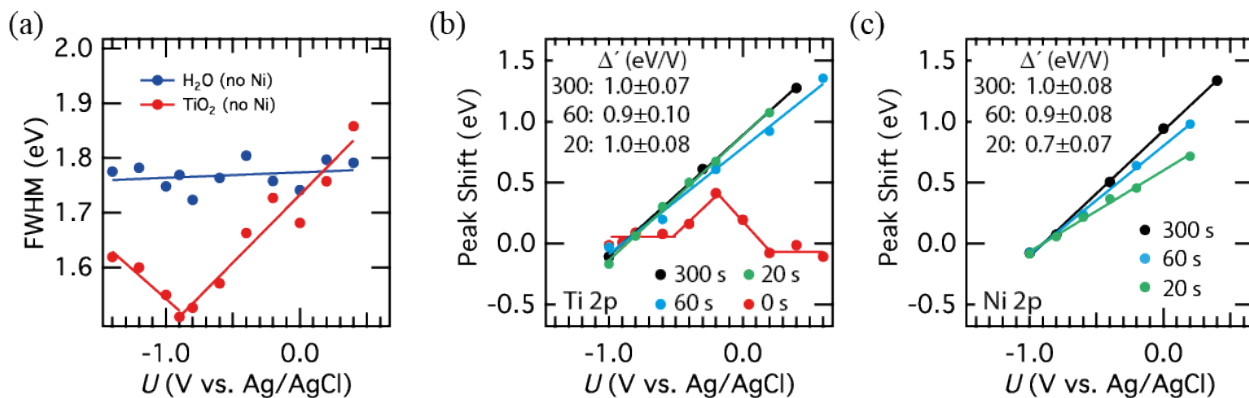
409 **Figure 5:** Ni 2p (a), O 1s (b), and Ti 2p (c) X-ray photoemission spectra of a TiO₂/Ni (20 s)

410 electrode in 1.0 M KOH(aq) for $U = -1.0$ V to $+0.2$ V vs. Ag/AgCl. The binding energies are

411 referenced to the solution potential as explained in the text and corrected by the applied potential

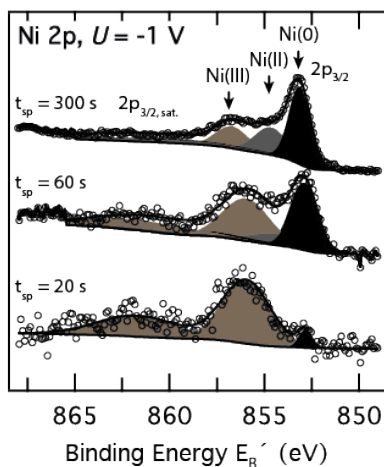
412 with respect to flat-band conditions at $U_{fb} = -0.9$ V vs. Ag/AgCl⁷ (see Equation 1 and 2). The

413 positions of metallic (Ni(0)) and fully oxidized Ni (Ni(III)) are indicated in (a) by arrows.



414
 415 **Figure 6:** (a) Full width at half maximum (FWHM) peak data for the water O 1s and TiO₂ O 1s
 416 core levels for a bare TiO₂ electrode. (b) The core level peak shifts with respect to the binding
 417 energy at flat-band, which indicate the band-edge shift of the semiconductor with respect to the
 418 electrolyte, of the Ti 2p_{3/2} core level for TiO₂/electrolyte, TiO₂/Ni (20 s)/electrolyte,
 419 TiO₂/Ni (60 s)/electrolyte, and TiO₂/Ni (300 s)/electrolyte geometries. (c) Similar to (b) but
 420 plotting only the Ni 2p_{3/2} core level peak shift for the $t_{sp} = 20$ s, 60 s, and 300 s electrodes. The
 421 binding energies are referenced to the solution potential as explained in the text, and are corrected
 422 by the applied potential with respect to flat-band conditions at $U_{fb} = -0.9$ V vs. Ag/AgCl ⁷ (see
 423 Equation 1 and 2).

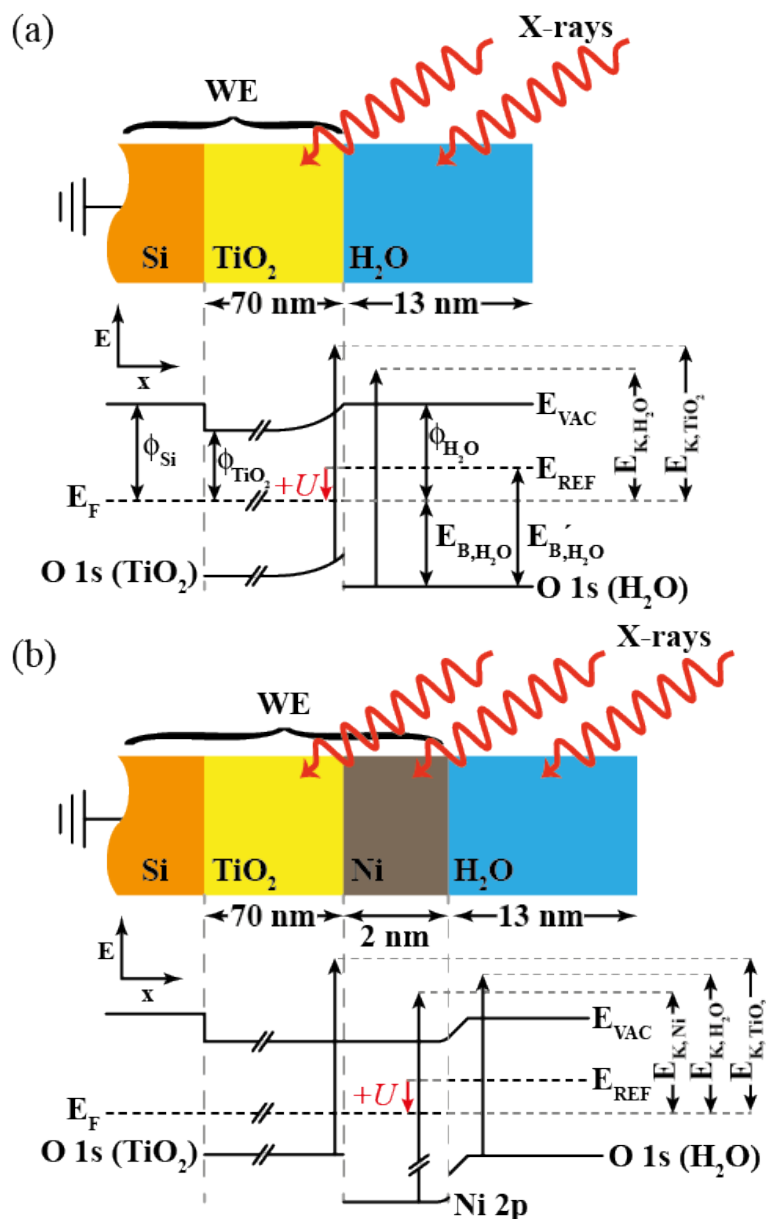
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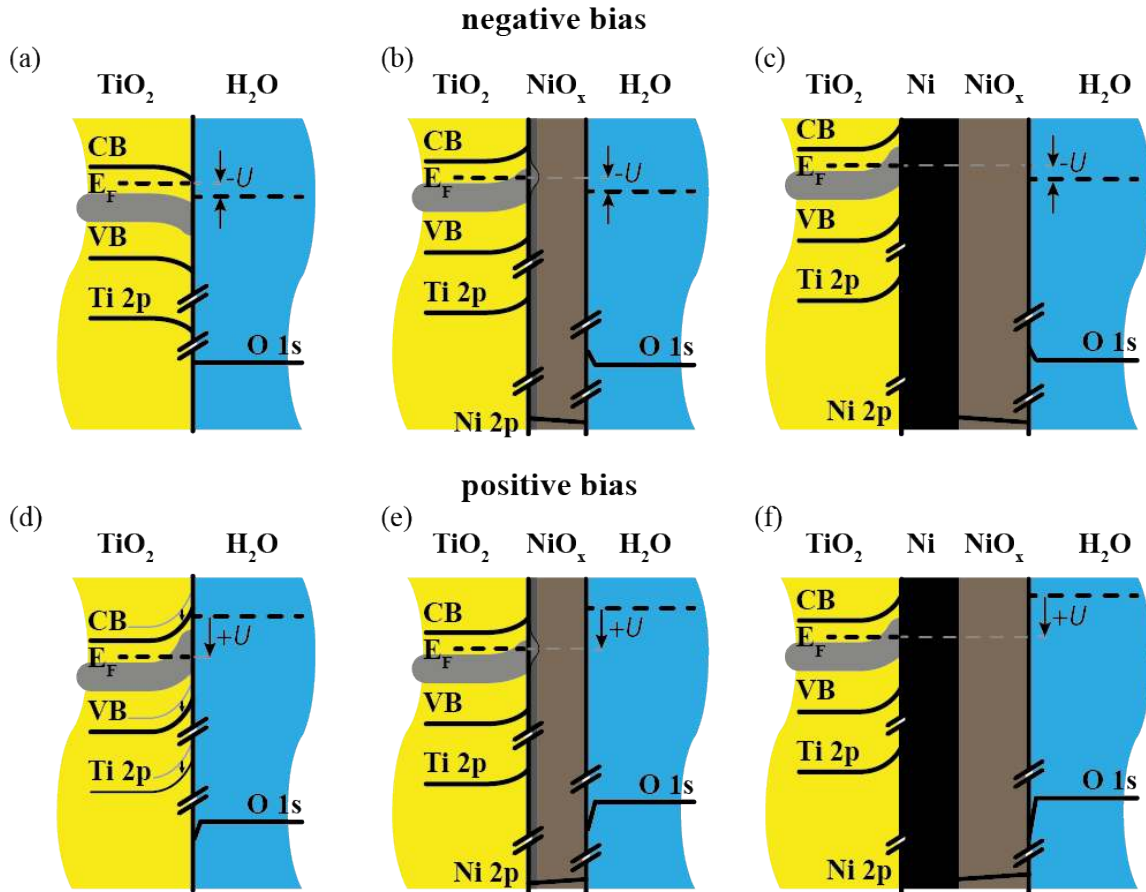
426 **Figure 7:** Ni $2p_{3/2}$ X-ray photoemission spectra for $t_{sp} = 20$ s, 60 s, and 300 s for $U = -1$ V vs.
 427 Ag/AgCl. The binding energies are referenced to the solution potential as explained in the text
 428 and corrected by the applied potential with respect to flat-band conditions at $U_{fb} = -0.9$ V vs.
 429 Ag/AgCl ⁷ (see Equation 1 and 2). The positions of metallic (Ni(0)), Ni(II), and fully oxidized Ni
 430 (Ni(III)) are indicated by arrows.

431



432
 433 **Figure 8:** Scheme of the energy-band relations of *operando* photoelectron spectroscopy for (a)
 434 the Si/TiO₂/electrolyte geometry and (b) the Si/TiO₂/Ni/electrolyte geometry. The working
 435 electrode and analyzer are grounded. A potential is applied to the working electrode in the
 436 electrolyte with respect to the reference electrode in a three-electrode configuration. The work
 437 function of the material Φ is the difference between the Fermi energy, E_F , and the vacuum energy
 438 E_{VAC} . The kinetic energies, $E_K = E_{K,VAC} + \Phi$, of the photoelectrons are measured with respect to
 439 the Fermi energy of the analyzer. The binding energy, E_B , is calculated based the photon energy

440 with $E_B = h\nu - E_K = h\nu - E_{K,VAC} - \Phi$ whereas the binding energy with respect to the reference
441 electrode is $E_B' = E_B + qU_{eff}$ (Equation 1) as illustrated for the binding energy of the water O 1s
442 core level in (a).



443
 444 **Figure 9:** Band diagrams that summarize the experimental findings described herein. (a-c) for
 445 negative potential U with respect to flat-band and (d-f) for negative potential U with respect to
 446 flat-band. The thick grey line marks the position of the mid-gap state band in TiO_2 . For (b, c and
 447 e, f), Fermi level pinning at the mid-gap states occurs. (a, d) In the absence of Ni or NiO_x , TiO_2
 448 develops a space-charge region with fixed band-edge positions outside of regions involving
 449 Fermi-level pinning or accumulation ⁷. For increasingly positive potentials, the Fermi level
 450 crosses the mid-gap states and band edge shifting in TiO_2 is observed (indicated by the arrows).
 451 The potential drop (the amount necessary to charge/discharge the surface states) occurs now in
 452 the electrochemical double layer. (b, e) The Fermi energy at the $\text{TiO}_2/\text{NiO}_x$ interface is pinned
 453 near the mid-gap states due to NiO_x interface states ²⁴. With Fermi level pinning, the band edges
 454 shift with the applied potential. (c, f) With a sufficiently dense and thick Ni film at the interface

455 to TiO₂, the TiO₂ band edges are effectively disconnected from the solution, and the presence of
456 metallic Ni allows for charge conduction.

457 **Table 1:** Surface roughness parameters obtained by AFM for the height distribution and the
 458 surface deformation. While the surface roughness and deformation parameters stay nearly
 459 constant up to 60 s (with a minimum for 20 s) the change (increase by up to 160 %) of the surface
 460 properties is more drastic after Ni deposition with a 300 s sputter time.

Ni \ Roughness	Height		Deformation	
	RMS (nm)	Ra (nm)	RMS (nm)	Ra (nm)
0 sec	0.71	0.55	0.17	0.12
20 sec	0.68	0.53	0.14	0.10
60 sec	0.69	0.55	0.17	0.13
300 sec	0.91	0.72	0.44	0.33

461

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