

Enhanced photocatalytic water oxidation efficiency with Ni(OH)₂ catalysts deposited on α -Fe₂O₃ via ALD

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Supporting Information

Electrode fabrication

Working electrodes were fabricated by atomic layer deposition (ALD) (Savannah 100 [Ga₂O₃, Fe₂O₃] and Savannah 200 [NiO], Cambridge Nanotech) onto fluorine-doped tin oxide (FTO) coated glass substrates (Hartford Glass, 12 Ω cm⁻²). Prior to deposition of Ga₂O₃, FTO glass was sonicated in detergent and DI water, rinsed, sonicated in clean DI water, and then finally rinsed and sonicated in isopropyl alcohol (IPA). Substrates were blown dry with N₂ directly before being placed in the ALD chamber. Approximately 2nm (18 ALD cycles) of Ga₂O₃ was deposited onto cleaned FTO substrates via ALD using tris(dimethylamido)gallium (III) (Ga₂(NMe₂)₆) (Strem Chemicals Inc.) as Ga precursor and H₂O as an oxidant following a modified version of a previously reported procedure.¹ The thickness of Ga₂O₃ was confirmed with ellipsometry on control Si wafers in the ALD chamber during deposition. The substrate was held at 200°C and the Ga precursor was heated to 150 °C, pulsed for 0.2 s, held under exposure mode for 8 s, followed by 12 s N₂ purge. Subsequently, a 0.015 s pulse of H₂O was introduced under the same exposure-purge time conditions to oxidize the Ga precursor. As deposited Ga₂O₃ on FTO substrate was subsequently coated with ~20 nm (300 ALD cycles) of Fe₂O₃ in the same chamber. Thickness of the hematite was confirmed using absorbance measurements and Beer-Lambert calculations. Briefly, the substrate remained at 200 °C ferrocene (sublimed from Sigma Aldrich)

held at 70°C was pulsed for 20s, purged with N₂ for 5s followed by a 0.015s pulse of H₂O, immediately followed by a 1s pulse of ozone (Yanco Industries ozone generator). The H₂O and O₃ pulse was repeated ten times for a single oxidation macrocycle in order to oxidize ferrocene.² Fe₂O₃ with the Ga₂O₃ underlayer will be referred to simply as Fe₂O₃. Following deposition, Fe₂O₃ was annealed to 500°C in an oxygen environment at a rate of 17°C per minute, sintered at 500°C for 30 minutes and allowed to cool slowly to 110°C over 2 hours. Subsequently, approximately 10 nm (100 ALD cycles) of NiO was deposited onto the annealed Fe₂O₃ by ALD (Savannah 200, Cambridge Nanotech) following a modified procedure.³ Nickel alkyl amidinate (Ni-amd) (AccudepTM Nickel Precursor, Dow) was used as the nickel precursor and H₂O as the oxidant. The substrate was heated to 150°C and the Ni-amd cylinder was heated to 130°C. The Ni(amd) was pulsed for 0.2s and held under exposure mode for 20 seconds, purged with N₂ for 30 s, followed by a water pulse of 0.015 s under exposure mode for 20 s. This cycle was repeated until the desired thickness was obtained. A Growth rate of 1.01 Å/cycle was determined by ellipsometry (Horiba Smart SE) measurements on Si wafers for varying cycles of NiO from 1-300. NiO-coated Fe₂O₃ was annealed to 300 °C in an oxygen environment at a rate of 5°C per minute and sintered for 1 hour. NiO coated electrodes were allowed to cool to 80°C over 4 hours and stored in an 80°C oven when not in use. Storing in an 80° oven was imperative to electrode performance as electrodes showed reduced performance when left out on the benchtop.

Photoelectrochemical measurements

Electrochemical measurements were performed in a custom glass 3-electrode cell with a quartz window to allow illumination from the solution side, SS, (striking the NiO-Fe₂O₃ first) with a Pt mesh counter electrode, homemade Ag/AgCl reference electrode (calibrated by referencing to a pristine commercial SCE reference electrode), and a Fe₂O₃ or NiO-coated Fe₂O₃ working

electrode clamped to the cell. All cells were measured in 1M KOH (pH 14 measured by Fischer Scientific Accumet pH meter) with 0.2M KCl as the supporting electrolyte. Additional control measurements without KCl added to the electrolyte were performed which resulted in no differences in behavior. Current-voltage curves were measured using Eco Chemie Mini Autolab interfaced with Nova 1.9 software at a scan rate of 20 mV/s. Cells were illuminated with a xenon arc lamp with a Horiba- Jobin monochromator and fitted with an A.M. 1.5 filter (Sciencetech Inc). All cells were measured under 1 sun (100W m^{-2}) illumination.

Conditioning Dark J-V Curves

Dark J - V curves were measured for bare (gray) and initial (red), 1 hour (yellow), 2 hours (green) and 3 hours of conditioning (blue) for NiO-coated Fe_2O_3 are shown in Figure S1.

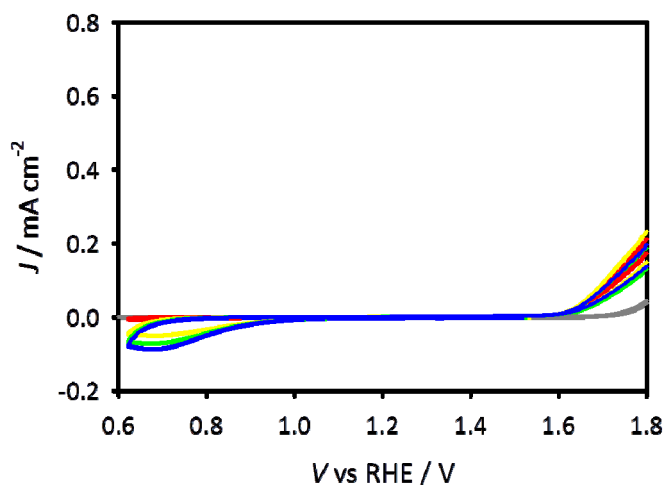


Figure S1. Plots of dark J - V curves for bare (gray) and initial (red), 1 hour (yellow), 2 hours (green) and 3 hours of conditioning (blue) for NiO-coated Fe_2O_3 .

Absorbance Measurements

Transmittance and reflectance values were measured using a labsphere RSA-PE-20 integrating sphere housed in a Lambda 35 UV-Vis Spectrometer. Absorbance was calculated using equation

1. The addition of Ni(OH)_2 to Fe_2O_3 slightly decreases the absorptance measured for wavelengths between 375 and 550 nm.

$$\%Absorptance = 100 - \%R - \%T \quad (1)$$

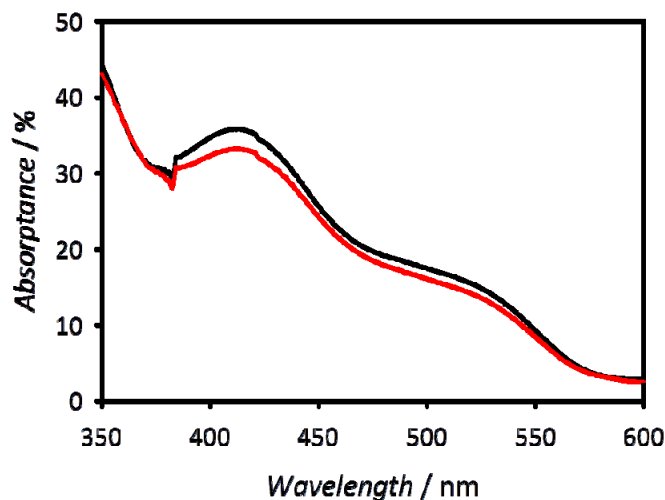


Figure S2. Calculated absorptance from transmittance and reflectance measurements for bare Fe_2O_3 (black) and Ni(OH)_2 -coated Fe_2O_3 (red) electrodes.

XPS

XPS measurements were taken at the Composite Materials and Structures Center in the College of Engineering at Michigan State University for as deposited, annealed, and conditioned NiO-coated Fe_2O_3 films. Approximately 50 nm of NiO was deposited onto Fe_2O_3 to ensure signal was not complicated by the underlying FTO substrate. Electrodes were stored overnight in a drying oven at 80° C and were then analyzed using a Perkin Elmer Phi 5600 ESCA system with a magnesium $\text{K}\alpha$ X-ray source at a takeoff angle of 45°. Survey scans for the region of 1100-0 eV binding energy, and subsequent scans for C 1s, O 1s, , and NiO 2p regions were scanned for all samples. Peak shifts as a result of apparent charging were corrected with the C 1s peak, which was set to 284.8 eV. After the spectra were corrected for charging, Shirley background

subtraction was performed. In Figure S3a XPS spectra are shown for as deposited (black), annealed (green), and conditioned (red) NiO-coated Fe_2O_3) for the Ni 2p region. Peak fitting for Ni $2p_{3/2}$ envelope was ambiguous but could be fit well with Ni^{2+} or Ni^{3+} oxides.^{4,5} The O 1s region, shown in Figure S3b gave the most information as to the composition of the films. Peak fittings for the O 1s region are shown for annealed and conditioned NiOx-coated Fe_2O_3 in Figure S3c and S3d, respectively. Fits for as-deposited NiO-coated Fe_2O_3 mimicked those of the annealed films. For as deposited and annealed films, the major contribution for the O 1s peak is for O^{2-} at 529.7 eV with a significant contribution from the oxygen deficiency peak at 531.2 eV.⁵ This is most consistent with NiO as the initial film material, as has been shown previously for similar ALD films.³ Upon conditioning, there is a clear change in the ratio of the two O 1s peaks. From peak fitting of the O 1s region, shown in Figure S3d, the peak attributed to O^{2-} , here at 529.4 eV, decreases while the two peaks at 531.2 and 531.8 eV, increase in intensity. $\text{Ni}(\text{OH})_2$ has a single O 1s peak at approximately 531.1 eV and NiOOH has peaks at approximately 529.5 and 531.1 eV for O^{2-} and OH^- , respectively.⁵ The dominance of the peaks at 531.2 and 531.8 indicate a major contribution of $\text{Ni}(\text{OH})_2$. Therefore, we conclude that upon conditioning, $\text{Ni}(\text{OH})_2$ is the primary composition of the film, with a minor component of NiO and/or NiOOH .

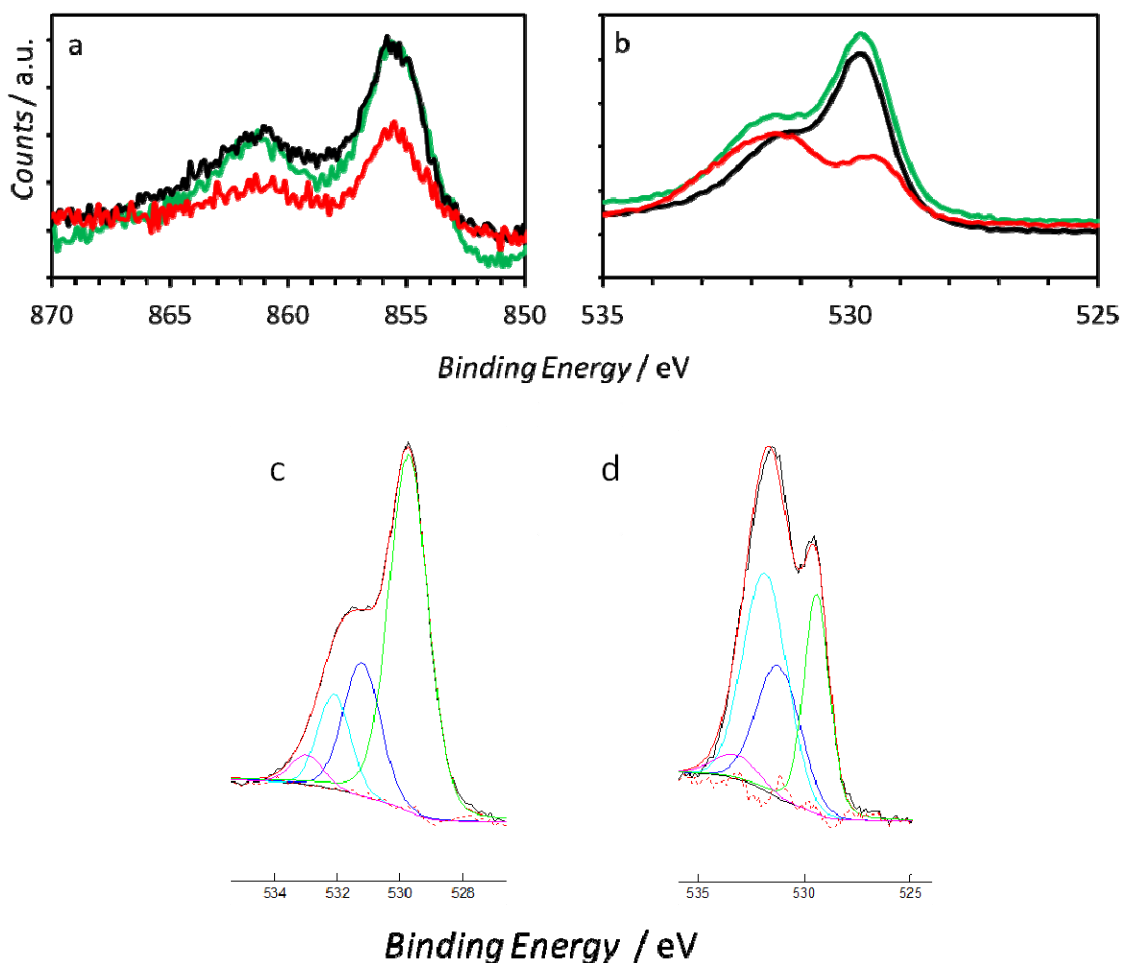


Figure S3. XPS spectra of as deposited (black), annealed (green) and conditioned (red) NiO-coated Fe_2O_3 showing a) the Ni 2p region and b) the O 1s region. Curve fits for c) annealed and d) conditioned NiOx-coated Fe_2O_3 are shown for the O1 s region.

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