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Enhanced photocatalytic water oxidation efficiency with Ni(OH)$_2$ catalysts deposited on $\alpha$-Fe$_2$O$_3$ via ALD

Kelley M. H. Young and Thomas W. Hamann*
reproducibility across all sets. See supporting information for detailed electrode preparation and experimental procedures.

Current density vs. applied voltage (J-V) measurements of bare and NiO-coated Fe$_2$O$_3$ electrodes were performed in the dark and under illumination. Figure 1 shows a typical J-V curve under 1 sun illumination (black curve) of bare Fe$_2$O$_3$ electrodes with a photocurrent onset of ~1.1 V vs RHE. Plots of dark currents are provided in supporting information (Fig S1). Electrodes with freshly annealed NiO-coated films, shown by the red curve in Figure 1, exhibit a small cathodic shift in the photocurrent onset and a small decrease in saturated photocurrent as compared to bare Fe$_2$O$_3$. Results of UV-vis measurements (Fig S2) show a negligible change in absorption due to the addition of NiO; thus differences in light absorption cannot account for the change in J-V behaviour.

Figure 1. Plots of J-V curves for bare Fe$_2$O$_3$ (black) and NiO-coated Fe$_2$O$_3$ electrodes for as-deposited (red), and following 1 hour (yellow), 2 hours (green), and 3 hours (blue) of conditioning at 1.42 V vs RHE under 1 sun illumination.

The Boettcher group recently reported a conditioning procedure in which an anodic current density of 10 mA cm$^{-2}$ was applied for 6 hours to NiOx electrocatalysts prepared by spin-coating. Their Initial cyclic voltammetry (CV) scans showed a slight redox wave, but subsequent CV scans taken at 1 hour intervals indicated an increase in the redox wave attributed to the NiOOH/Ni(OH)$_2$ redox couple; a concomitant cathodic shift in the oxygen evolution reaction (OER) was observed. It was determined that NiOx underwent a structural change following electrochemical conditioning in which NiOx transforms from a rock salt to a layered, ion-permeable hydroxide/oxyhydroxide structure. The resulting NiOOH structure in these studies was determined to be the active catalyst for the OER. We therefore adapted a similar conditioning procedure in which NiO-coated Fe$_2$O$_3$ electrodes were held at a constant voltage of 1.42 V vs RHE under illumination for 1 hour increments. After one hour of conditioning there was an additional 100 mV cathodic shift (Figure 1, yellow) in the photocurrent onset potential as compared to the initial scan (red). In addition, a redox wave developed, which can be attributed to the Ni$^{3+}$/Ni$^{2+}$ redox reaction. Successive hours of conditioning were performed to monitor the electrode evolution, indicated by the arrows in Figure 1. In addition to the magnitude of the onset shift, the redox wave continued to increase with conditioning. This result correlates the increased magnitude of the Ni$^{3+}$/Ni$^{2+}$ redox wave with an apparent cathodic shift in the photocurrent onset. This correlation of improved photocurrent onset is likely due to the increased number of available Ni$^{2+}$ sites as the film becomes more ion-permeable during conditioning, as shown in previous studies and discussed below. This procedure was repeated for three hours at which point no change in the redox wave or J-V was observed. All electrodes used for photoelectrochemical measurements were therefore conditioned by this method for 3 hours.

X-ray photoelectron spectroscopy (XPS) measurements were performed on NiO-coated Fe$_2$O$_3$ before and after photoelectrochemical measurements to determine the nature of any structural change during the conditioning process (Fig S3). The Ni 2p$_{3/2}$ peak was fitted using relative peak positions for both Ni$^{3+}$ and Ni$^{2+}$ oxides, which did not allow unambiguous identification of the oxidation state. The spectra are nominally identical for all samples, however, and are consistent with either NiO or Ni(OH)$_2$. Fits of the O 1s peaks are more informative and indicate that as-deposited and annealed films are comprised of NiO, which is consistent with previous reports of the ALD of NiO under similar conditions. The O 1s peaks changed upon conditioning; OH$^-$ is the primary component for the O 1s peaks in the conditioned films, although some O$^2-$ is still evident. The conditioned films are therefore composed primarily of Ni(OH)$_2$ with a small fraction of NiO and/or NiOOH. Thus, we attribute the conditioning process to the structural change from cubic NiO to the layered Ni(OH)$_2$, a well known ion-permeable water oxidation catalyst. The redox wave that develops in the J-V curves shown in figure 1 is therefore attributed to the NiOOH/Ni(OH)$_2$ redox couple.

The photocurrent onset for bare Fe$_2$O$_3$ is approximately 1.1 V vs RHE with a photocurrent density of ~0.18 mA cm$^{-2}$ at 1.23 V vs RHE. The addition of a conditioned Ni(OH)$_2$ film on Fe$_2$O$_3$ produces a cathodic shift of the photocurrent onset potential, although the precise magnitude cannot be accurately determined since the large NiOOH/Ni(OH)$_2$ capacitive redox wave obscures the Faradic current voltage behaviour. In order to separate the capacitive and Faradaic currents and indentify the true onset potential, anodic current transients were measured. Figure 2a shows the current response to turning on the light at a constant potential of 1.17 V vs RHE. For the bare hematite electrode, there is a short spike of photocurrent which is attributed to trapping of photogenerated holes in surfaces states, which quickly decays to a very low steady state current density. The Ni(OH)$_2$-coated Fe$_2$O$_3$ electrodes also exhibited an initial spike, however in this case it was followed by a relatively slow (4 second) multi-exponential decay to a steady-state Faradaic current. The photocurrent measured over the last 170 seconds was averaged to determine the steady state Faradaic photocurrent. Analogous measurements were performed at varying applied potentials and are shown as open symbols superimposed on the J-V scans in Figure 2b. From this, it can be seen that the photocurrent onset for Ni(OH)$_2$-coated Fe$_2$O$_3$ is indicated by the forward sweep of the J-V at approximately 800 mV vs RHE, which represents an approximately 300 mV cathodic shift for the photocurrent onset as compared to bare Fe$_2$O$_3$. We note that similar catalyst charging behaviour was observed for Co-Pi on hematite, however the resulting cathodic shift of the J-V curve was lower with a photocurrent onset of ~1 V vs RHE. We further note that a previous report Ni(OH)$_2$-coated Fe$_2$O$_3$ indicated instability of the catalyst, with photocurrents dropping to very low values over 30 seconds. For these measurements, once a plateau current was reached, the performance did not diminish rapidly; there is however, a slight decrease in photocurrent density over time, which is due to bubbles forming on the photoanode active area. When electrodes are cleared of bubbles and measured again, the original photocurrent is observed, indicating no degradation of electrode performance. We tentatively assign the greatly improved stability demonstrated here, compared to previous reports, to the Ni(OH)$_2$ deposition method,
however more work is required to confirm this. The steady state photocurrent is approximately 0.4 mA cm$^{-2}$ at 1.23 V vs RHE, which is more than double that of the bare electrode.

Cathodic current transients were also measured in response to turning off the light at several applied potentials. Figure 2c shows cathodic transient currents measured at potentials negative of the photocurrent onset, 1.05 V and 0.80 V vs RHE for bare (black trace) and Ni(OH)$_3$-coated Fe$_2$O$_3$ (red trace), respectively. For the bare Fe$_2$O$_3$ electrode, the transient spike is attributed to the de-trapping of holes, or the reduction of surface states.$^{15}$ The cathodic transient for Ni(OH)$_3$-coated Fe$_2$O$_3$, however, is attributed to the reduction of Ni$^{3+}$ back to Ni$^{2+}$. This cathodic transient has an initial spike slightly larger than untreated Fe$_2$O$_3$ and takes a much longer time to decay back to essentially zero current density, indicating a greater amount of charge passed. This difference can be quantified by integrating the current transients. This integration produced a charge passed of approximately 1.6 x 10$^{14}$ electrons per cm$^2$ for bare Fe$_2$O$_3$ electrodes and 1.6 x 10$^{16}$ electrons per cm$^2$ passed for Ni(OH)$_3$-coated Fe$_2$O$_3$ electrodes. Assuming just the 0001 crystal face is exposed, the total density of iron atoms at the surface is 3.9 x 10$^{14}$ cm$^{-2}$, thus 1.6 x 10$^{14}$ cm$^2$ is consistent with a surface species. One hundred times more charge is stored in the 10 nm Ni(OH)$_3$ film; this indicates that the Ni(OH)$_3$-coated Fe$_2$O$_3$ must become ion-permeable to allow charge compensating ions to intercalate to the active Ni$^{3+/2+}$ sites, consistent with the large redox wave in the J–V curves.

Conclusions

We have shown that using by using ALD we were able to deposit thin films of NiO onto Fe$_2$O$_3$ photoelectrodes. XPS measurements indicated that freshly annealed NiO resulted in a slight improvement in the water oxidation J–V response in comparison to bare Fe$_2$O$_3$ electrodes. Photoelectrochemical conditioning of the NiO films produced a structural change to a layered Ni(OH)$_2$, as determined by XPS measurements. The structural change was monitored through the growth of a large NiOOH/Ni(OH)$_2$ redox wave in conjunction with further improvement in the water oxidation onset potential. The correlation of the increased stored charge (magnitude of redox wave in the J–V curve) upon conditioning with an the improvement of the J–V curve indicates that the primary attribute of the Ni(OH)$_2$ film is the ability to separate charge. This charge separation allows holes stored by Ni(OH)$_2$, as NiOOH, to oxidize water competitively with recombination with conduction band electrons. This behaviour is consistent with previous results of Co–Pi on Fe$_2$O$_3$ and Ni(OH)$_2$ on TiO$_2$ electrodes.$^{19,20,27}$ These results provide important insight into the design of water oxidation catalysts in contact with semiconductor electrodes. The most important parameter appears to be ion-permeability which allows charge separation, rather than intrinsically faster water oxidation kinetics of an electrocatalyst. Finally, the results reported herein are in contrast to previous reports of Ni(OH)$_2$ on Fe$_2$O$_3$, however the cause of this discrepancy is still not clear. Further investigations are ongoing in our lab in order to better understand the mechanistic details of these exciting results.

Figure 2. Bare Fe$_2$O$_3$ (black) and Ni(OH)$_3$-coated Fe$_2$O$_3$ (red) a) anodic (light on) current transient measurements at 1.17 V vs RHE, b) J–V plots under illumination and in the dark with superimposed steady-state Faradaic photocurrent measurements (open symbols), and c) cathodic (light off) current transient measurements for bare Fe$_2$O$_3$ (black) and Ni(OH)$_3$-coated Fe$_2$O$_3$ (red) at 1.05 and 0.800 V vs RHE, respectively.

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Notes and references

Department of Chemistry, Michigan State University
578 South Shaw Lane
East Lansing, MI 48824 United States
E-Mail: hamann@chemistry.msu.edu

Electronic Supplementary Information (ESI) available: Detailed experimental procedures, plots of dark J–V curves and
absorptance measurements, and XPS results and analysis. See DOI: 10.1039/c000000x/