Supporting Information

A Mechanistic Study into the Catalytic Effect of Ni(OH)$_2$ on Hematite for Photoelectrochemical Water Oxidation

Gongming Wang,$^a$ Yichuan Ling,$^a$ Xihong Lu,$^{a,b}$ Teng Zhai,$^b$ Hanyu Wang,$^a$ Fang Qian,$^c$

Yexiang Tong,$^b$ and Yat Li,*$^a$

$^a$ Department of Chemistry and Biochemistry, University of California, Santa Cruz, California 95064 United States

$^b$ KLGHEI of Environment and Energy Chemistry, MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, SunYat-Sen University, Guangzhou 510275, People’s Republic of China

$^c$ Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, California 94550, USA

*Corresponding Author. E-mail: vli@chemistry.ucsc.edu
Experimental section

**Synthesis of hematite (α-Fe₂O₃) nanowire arrays:**

Akaganéite (β-FeOOH) nanowire arrays were grown on a fluorine-doped tin oxide (FTO, TEC 8) glass substrate using a hydrothermal method reported elsewhere. A Teflon-lined stainless steel autoclave was filled with 20 mL 0.15M FeCl₃ and 1M NaNO₃ aqueous solution at pH 1.5 (adjusted by HCl). A cleaned FTO substrate was placed into the autoclave with the conductive side facing down. The sealed autoclave was heated at 95 °C for 5h in an electric oven and allowed it to cool down in air. A uniform yellow layer of β-FeOOH nanowire arrays was coated on the FTO glass. The nanowire-coated FTO glass was washed with ethanol and water, and then air dry. α-Fe₂O₃ nanowire arrays were obtained by thermal decomposition β-FeOOH nanowire. The β-FeOOH nanowires were annealed in a home-built CVD system. The tube furnace was first vacuumed to a pressure of 15 Torr, and then filled with ultrahigh purity N₂. The sample was annealed at 550 °C for 2h at 740 Torr pressure with a N₂ gas flow of 50 sccm.

**Deposition of Ni(OH)₂ catalyst:**

Ni(OH)₂ was deposited onto hematite nanowire arrays by successive dip coating method. The hematite nanowire electrode was first dipped into 0.1 M Ni(NO₃)₂ solution for 10 seconds, and blow-dried with compressed air. Then the electrode was dipped into 1.0 M KOH solution for 10 seconds, and blow-dried with compressed air. This two-step dip-coating process was repeated for 3 times. For the sample with small loading of Ni catalyst, we used 5 mM Ni(NO₃)₂ solution and repeated the deposition cycles for 2 times only.
**Material characterization:**

Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) spectra were collected on a field emission SEM (Hitachi S-4800II). X-ray diffraction (XRD) spectra of hematite and blank FTO glass were collected on a Rigaku Americas Miniflex Plus powder diffractometer with the angle from 20 to 70 degree. X-ray photoelectron spectroscopy (XPS, ESCALab 250, Thermo VG) with 200W Al Kα radiation in twin anode. The binding energy was calibrated using the C 1s at 284.6 eV as a reference. Electrochemical and photoelectrochemical measurements were carried out using an electrochemical workstation CHI 660D coupled with a 150W xenon lamp (Newport 6255) and an AM 1.5 global filter (Newport 81094). The electrolyte was 1.0 M KOH aqueous solution. Ag/AgCl (1 M KCl) and Pt wire were used as reference and counter electrode in the three-electrode system.
Figure S1. (a) SEM image of hematite nanowire arrays grown on a FTO glass substrate. (b) XRD spectra collected for hematite nanowires coated FTO substrate and a blank FTO substrate. The dashed lines highlight the (110) and (300) diffraction peaks of hematite. (c) EDS spectrum collected for the Ni(OH)$_2$ decorated hematite film.
Figure S2. Photocurrent densities vs. time ($j$-$t$) curves of the Ni-Fe$_2$O$_3$ electrode collected in 1.0 M KOH solution at different potentials. The dark currents observed in (c) and (d) are due to the electrochemical oxidation of Ni(OH)$_2$ ($\text{Ni}^{2+}/\text{Ni}^{3+}$), which occurs at around 0.35V vs. Ag/AgCl.

Figure S3. Current density retention measured for pristine $\alpha$-Fe$_2$O$_3$ and Ni-Fe$_2$O$_3$ at the scan...
rate of 50 mV/s.

**Figure S4.** Cyclic voltammograms of α-Fe$_2$O$_3$ and Ni-Fe$_2$O$_3$ in the absence of glucose in 1.0 M KOH solution at the scan rate of 50 mV/s.
Figure S5. Linear sweep voltammograms of (a) Ni-Fe$_2$O$_3$ and (b) α-Fe$_2$O$_3$ collected in 1.0 M KOH solution at a scan rate of 10, 20, and 50 mV/s under light illumination (AM 1.5G 100 mW/cm$^2$). The dashed lines are the dark scans collected at 50 mV/s.
Figure S6. Digital pictures collected for Ni-Fe$_2$O$_3$ electrode before and after irradiated with white light (AM 1.5G, 100 mW/cm$^2$) at 0.3V vs. Ag/AgCl for 200 seconds.

Figure S7. Linear sweep voltamogramms of Fe$_2$O$_3$ and Ni-Fe$_2$O$_3$ collected in 1.0 M KOH solution at a scan rate of 50 mV/s, in the presence and absence of glucose. Solid and dashed lines are $j$-$V$ curves collected, light illumination (AM 1.5G, 100 mW/cm$^2$) and in the dark.
Figure S8. (a-d) Photocurrent densities vs. time curves collected for Ni-Fe$_2$O$_3$ in 1.0 M KOH solution in the presence of 0.1 M glucose at different potentials.

Figure S9. Overlay of the normalized Ni 2p XPS spectra collected for Ni-Fe$_2$O$_3$ before (black curve) and after (red curves) light illumination in the presence of glucose at 0.3 V vs. Ag/AgCl for 200 seconds.
Figure S10. (a) SEM image of Ni-Fe$_2$O$_3$ electrode with small loading of Ni(OH)$_2$ catalyst. (b) Corresponding EDS spectrum collected for the Ni-Fe$_2$O$_3$ electrode.
Figure S11. Current densities vs. time curves of s-Ni-Fe$_2$O$_3$ measured in 1.0 M KOH solution (without glucose) at different potentials.
References
