# Supporting Information

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

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# Experimental section

***Synthesis of hematite ($\alpha$-$Fe_2O_3$) 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 [1]. A Teflon-lined stainless steel autoclave was filled with 20 mL 0.15M $FeCl_3$ and 1M $NaNO_3$ 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 $^oC$ 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. $\alpha$-$Fe_2O_3$ 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 $N_2$ [1]. The sample was annealed at 550 $^oC$ for 2h at 740 Torr pressure with a $N_2$ 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 [2]. The hematite nanowire electrode was first dipped into 0.1 M $Ni(NO_3)_2$ 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 $Ni(NO_3)_2$ 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.

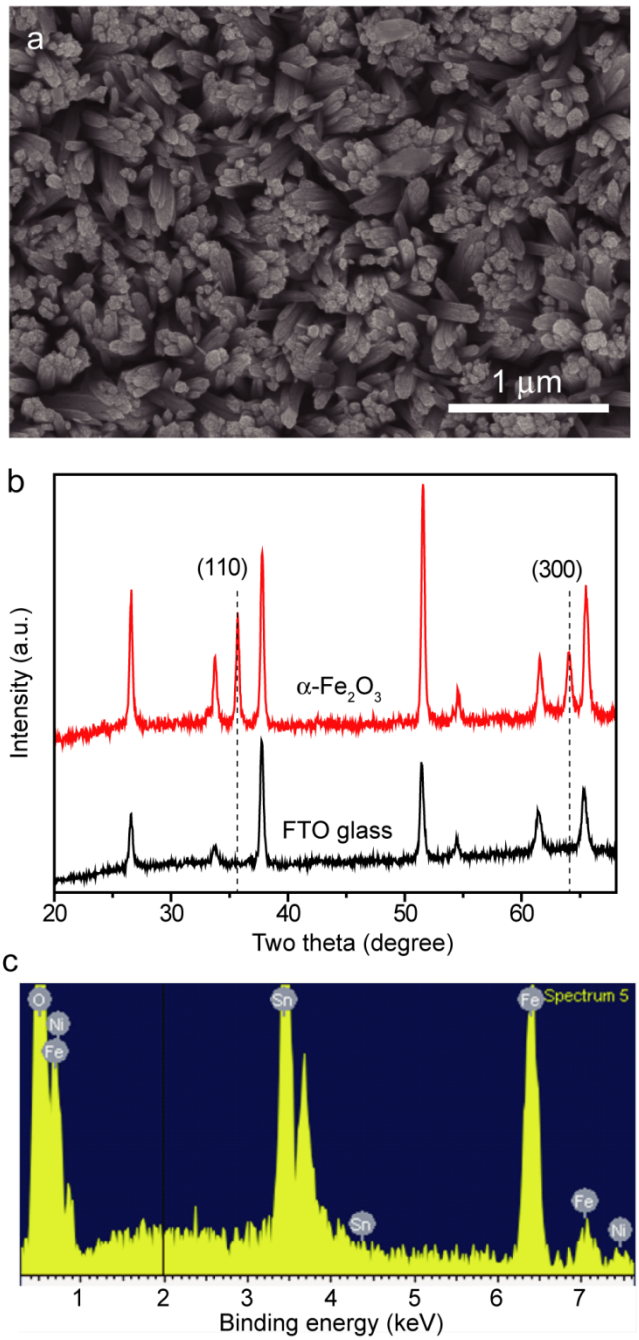


**Figure S1.** (a) SEM image of hematite nanowire arrays grown on a FTO glass substrate. (b) XRD spectra collected for hematite nanowires coated FTO substrate and a blank FTO substrate. The dashed lines highlight the (110) and (300) diffraction peaks of hematite. (c) EDS spectrum collected for the $Ni(OH)_2$ decorated hematite film.

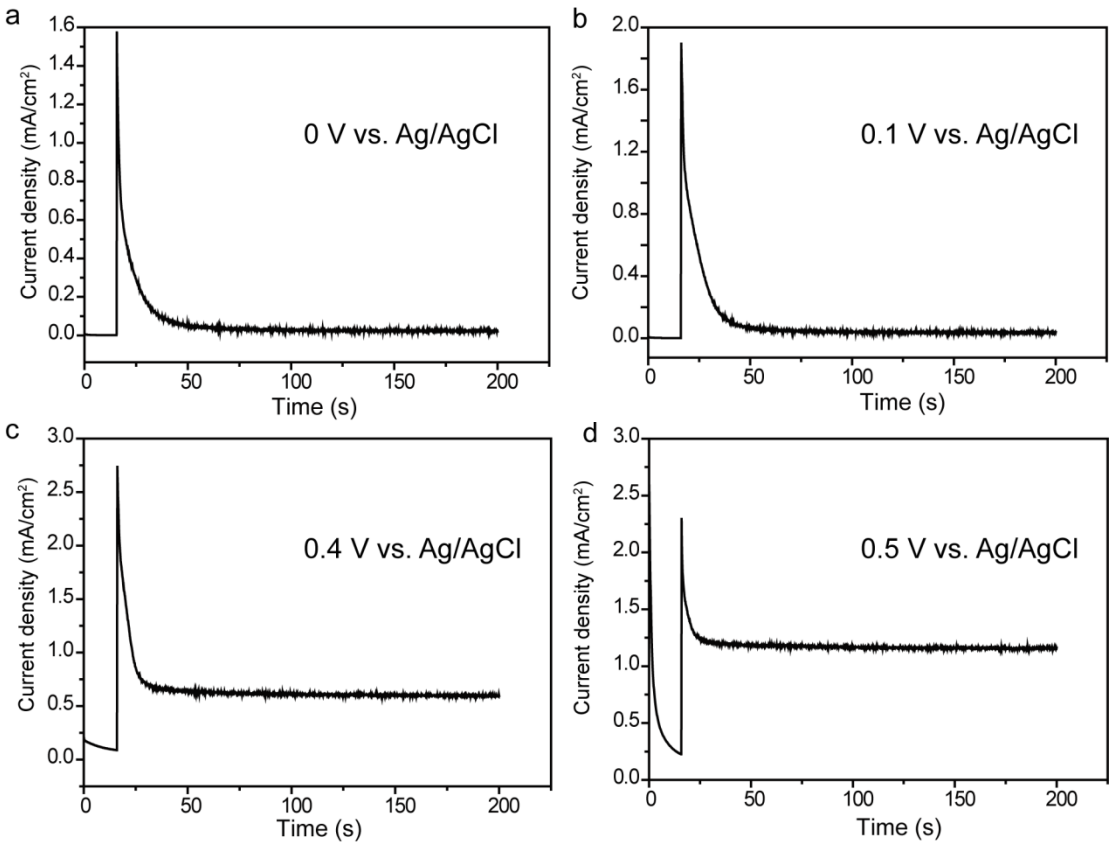


**Figure S2.** Photocurrent densities vs. time (*j*-*t*) curves of the Ni-$Fe_2O_3$ electrode collected in 1.0 M KOH solution at different potentials. The dark currents observed in (c) and (d) are due to the electrochemical oxidation of $Ni(OH)_2$ ($Ni^{2+}/Ni^{3+}$), which occurs at around 0.35V vs. Ag/AgCl.

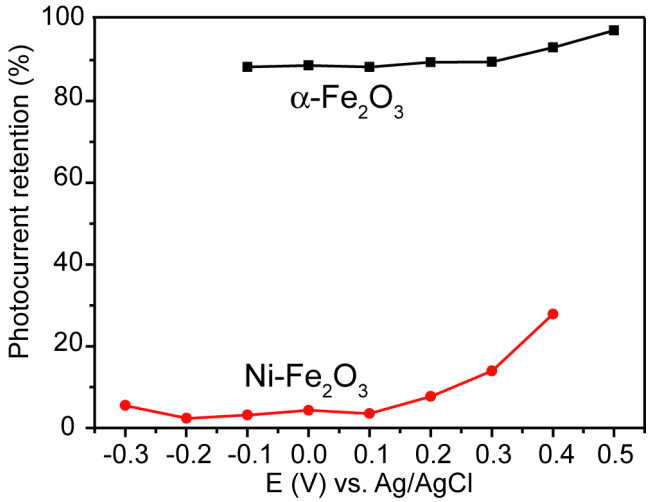


**Figure S3.** Current density retention measured for pristine α-$Fe_2O_3$ and Ni-$Fe_2O_3$ at the scan

rate of 50 mV/s.

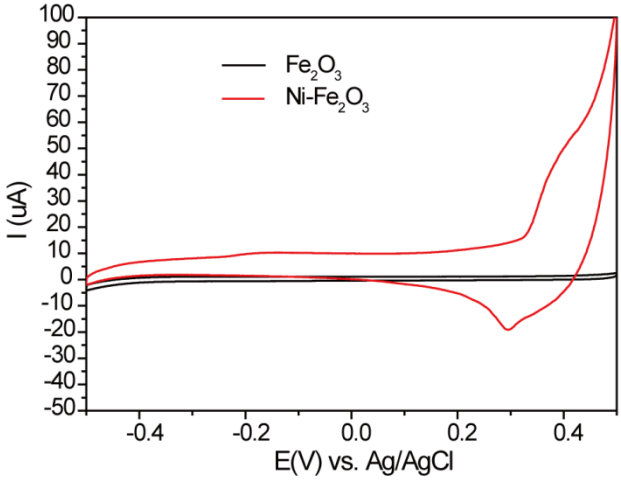


**Figure S4.** Cyclic voltammograms of α-$Fe_2O_3$ and Ni-$Fe_2O_3$ in the absence of glucose in 1.0 M KOH solution at the scan rate of 50 mV/s.

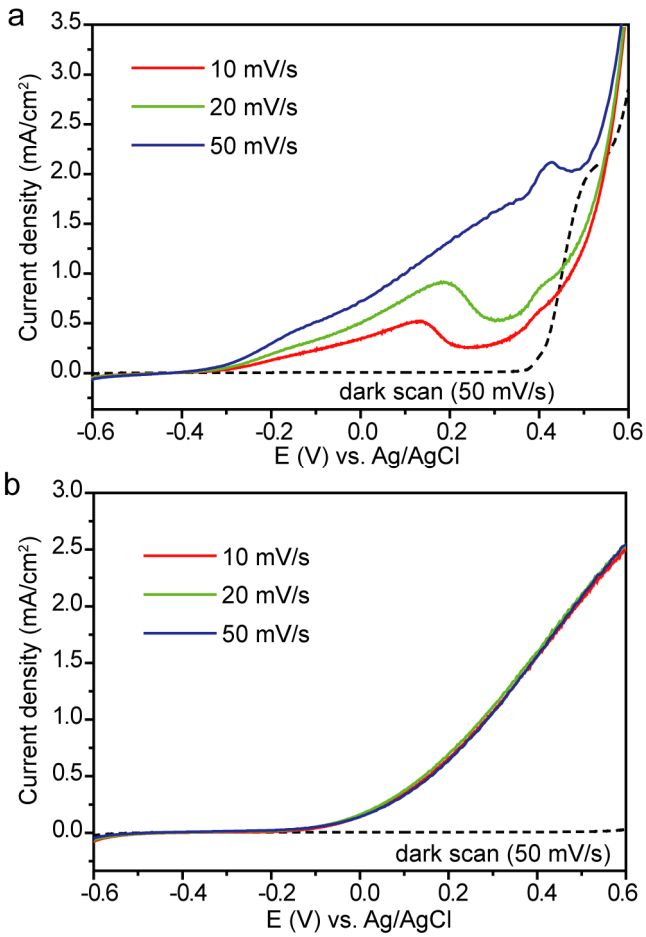


**Figure S5.** Linear sweep voltammograms of (a) Ni-$Fe_2O_3$ and (b) α-$Fe_2O_3$ collected in 1.0 M KOH solution at a scan rate of 10, 20, and 50 mV/s under light illumination (AM 1.5G 100 $mW/cm^2$). The dashed lines are the dark scans collected at 50 mV/s.

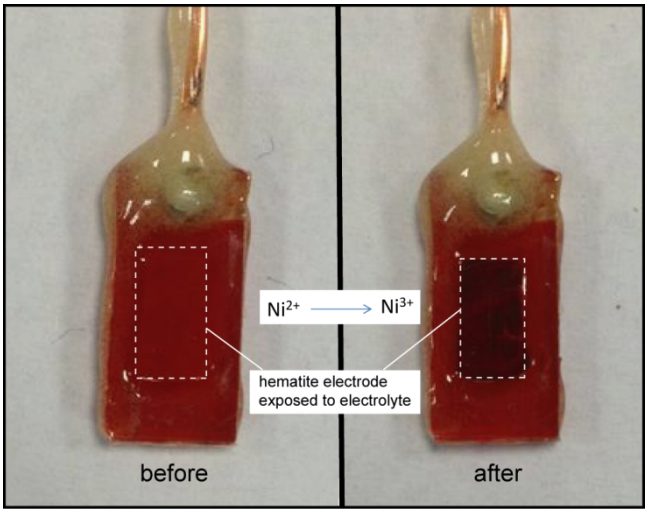


**Figure S6.** Digital pictures collected for Ni-$Fe_2O_3$ electrode before and after irradiated with white light (AM 1.5G, 100 mW/cm$^2$) at 0.3V vs. Ag/AgCl for 200 seconds.

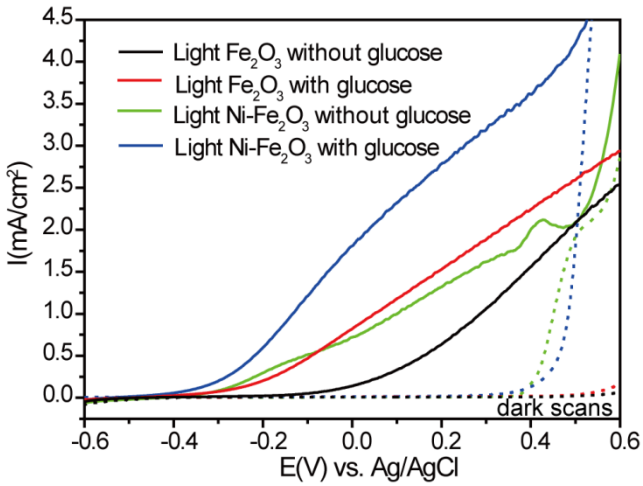


**Figure S7.** Linear sweep voltamogramms of $Fe_2O_3$ and Ni-$Fe_2O_3$ collected in 1.0 M KOH solution at a scan rate of 50 mV/s, in the presence and absence of glucose. Solid and dashed lines are *j-V* curves collected, light illumination (AM 1.5G, 100 mW/cm$^2$) and in the dark.

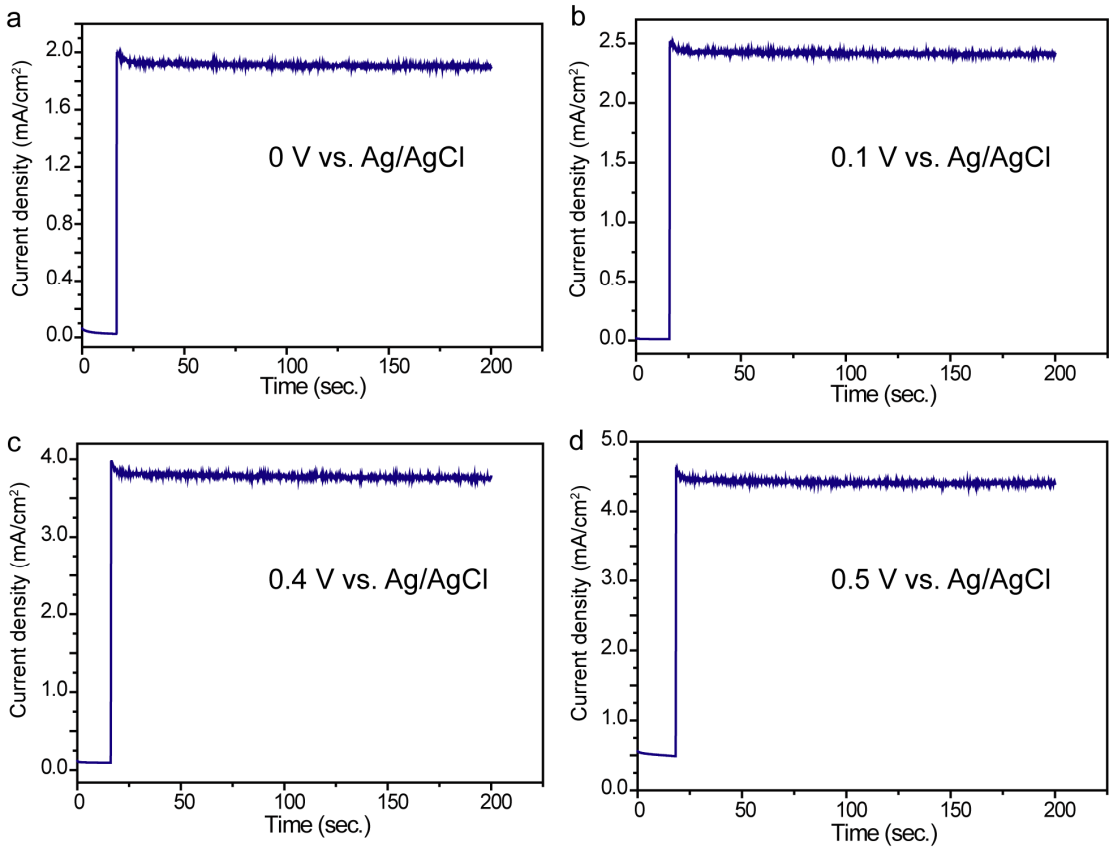


**Figure S8.** (a-d) Photocurrent densities vs. time curves collected for Ni-$Fe_2O_3$ in 1.0 M KOH solution in the presence of 0.1 M glucose at different potentials.

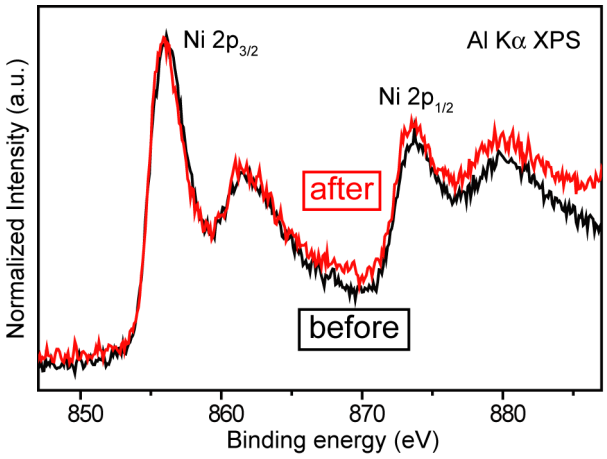


**Figure S9.** Overlay of the normalized Ni 2p XPS spectra collected for Ni-$Fe_2O_3$ before (black curve) and after (red curves) light illumination in the presence of glucose at 0.3 V vs. Ag/AgCl for 200 seconds.

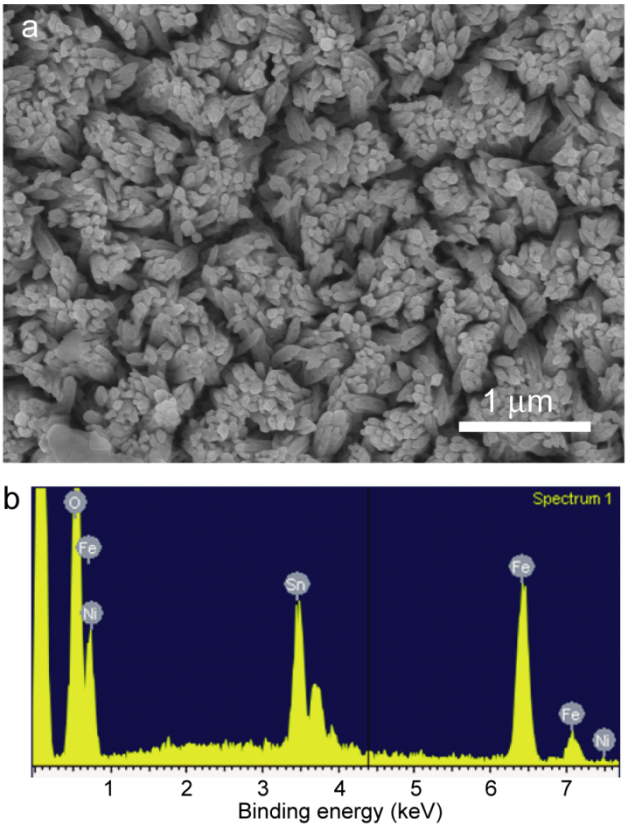


**Figure S10.** (a) SEM image of Ni-$Fe_2O_3$ electrode with small loading of $Ni(OH)_2$ catalyst. (b) Corresponding EDS spectrum collected for the Ni-$Fe_2O_3$electrode.

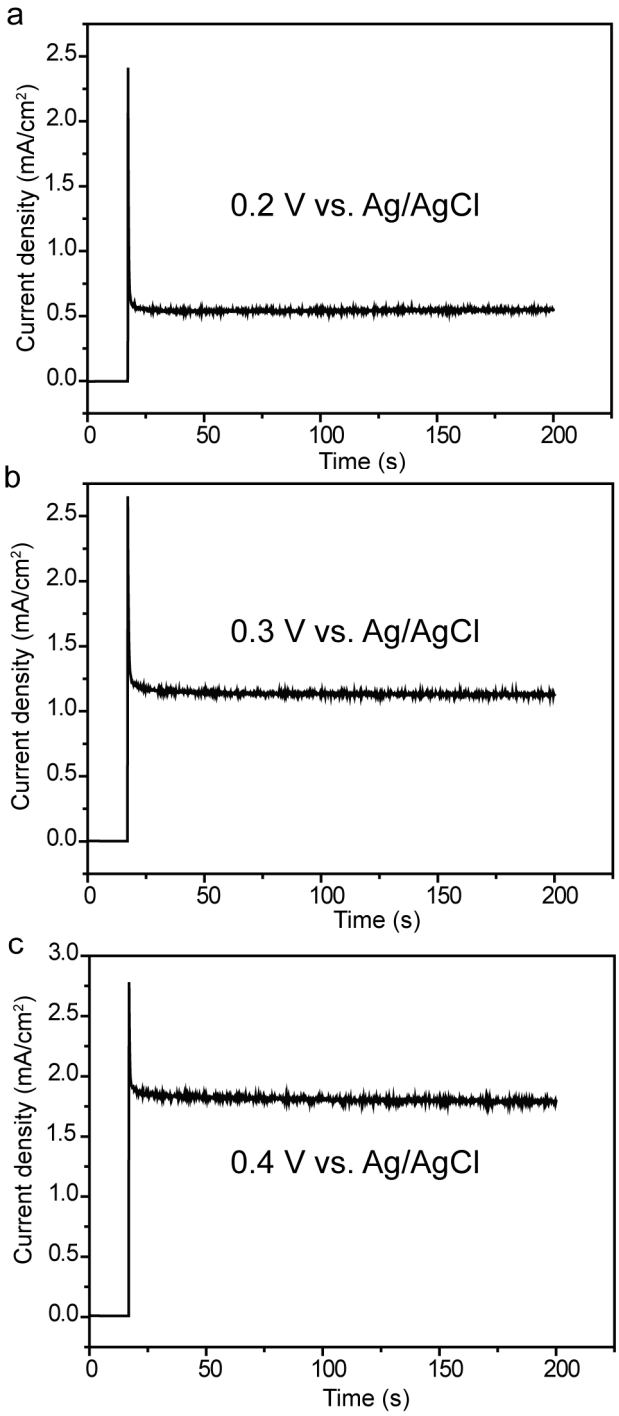


**Figure S11.** Current densities vs. time curves of s-Ni-$Fe_2O_3$ measured in 1.0 M KOH solution (without glucose) at different potentials.

## References

1. Y. C. Ling, G. M. Wang, J. Reddy, C. C. Wang, J. Z. Zhang and Y. Li, *Angew. Chem. Int. Ed.*, 2012, **51**, 4074-4079.
2. G. M. Wang, Y. C. Ling, X. H. Lu, H. Y. Wang, F. Qian, Y. X. Tong and Y. Li, *Energy Environ. Sci.*, 2012, **5**, 8215-8219.