Supporting Information

A significant cathodic shift in onset potential of photoelectrochemical water splitting for hematite nanostructures grown from Fe–Si alloys

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Experimental Details: Iron metal and iron-silicon alloys (0, 0.5, 1, and 5 at.% - Fe, Fe0.5Si, Fe1Si, and Fe5Si) were prepared by vacuum arc melting (GKSS-Research Center, Geesthacht, Germany) using iron flakes (ChemPur, Feinchemikalien und Forschungsbedarf GmbH, 99.9%) and silicon flakes (ChemPur. Feinchemikalien und Forschungsbedarf GmbH, 99.9995%). The metal sheets were cut from the ingot into 1 × 2 cm, approximately 2 mm thick pieces, and ground with 800, 1200, 2400, and 4000 grinding papers, and finally degreased by sonicating in ethanol for several minutes, followed by rinsing with distilled water and drying in a nitrogen stream. The samples were thermally annealed in a furnace (Heraeus, TYP R0K 6.5/60) in air at 500 °C for 0.5 h (or 400 °C for 1 h). For this, the samples were placed in a ceramic boat and inserted in the furnace at room temperature. The temperature was ramped up with a heating rate of 20 °C min⁻¹, kept at the desired temperature for 0.5 h, and finally the samples were removed from the furnace. Moist air was flown into the furnace during the
annealing. The moist air was obtained by bubbling air through a one foot column of low conductivity water keeping the pressure of 1.6 \text{ to } 1.8 \text{ (bar)}. The annealed samples were subsequently annealed in a furnace (Heraeus, ZEW 1450-4, Germany) at 600 °C for 1 h in argon atmosphere. For the argon atmosphere, the furnace was purged with argon (99.999%, Linde Gas, Germany) at least for 20 min in a flux of 50 ml min\(^{-1}\) before the annealing treatment.

The photoelectrochemical experiments were carried out under simulated AM 1.5 (100 mW cm\(^{-2}\)) illumination provided by a solar simulator (300 W Xe with optical filter, Solarlight; RT) in 1 M KOH solution. A three-electrode configuration was used in the measurement, with the \(\alpha\)-Fe\(_2\)O\(_3\) electrode serving as the working electrode (photoanode), an Ag/AgCl (3 M KCl) as the reference electrode, and a platinum foil as the counter electrode. Photocurrent vs. voltage (\(I - V\)) characteristics were recorded by scanning the potential from 0.5 V to 1.0 V (vs. Ag/AgCl) with a scan rate of 2 mV s\(^{-1}\) using a Jaissle IMP 88 PC potentiostat. The measured potentials vs. Ag/AgCl (3 M KCl) were converted to the reversible hydrogen electrode (RHE) scale using the relationship \(E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} + E_{0Ag/AgCl}^0\), where \(E_{Ag/AgCl}\) is the experimentally measured potential and \(E_{0Ag/AgCl}^0 = 0.209 \text{ V}\) at 25 °C for an Ag/AgCl electrode in 3 M KCl. Photocurrent spectra were acquired at applied potentials of 0 V\(_{Ag/AgCl}\), 0.23 V\(_{Ag/AgCl}\), and 0.5 V\(_{Ag/AgCl}\) in 1 M KOH recorded with 10 nm steps in the range of 300–700 nm using an Oriel 6365 150 W Xe-lamp equipped with a Oriel Cornerstone 7400 1/8 m monochromator.

A field-emission scanning electrode microscope (Hitachi FE-SEM S4800, Japan) was used for the morphological characterization of the electrodes. X-ray diffraction (X'pert Philips MPD with a Panalytical X'celerator detector, Germany) was carried out using graphite monochromized Cu K\(\alpha\) radiation (Wavelength 1.54056 Å). Chemical characterization was carried out by X-ray photoelectron spectroscopy (PHI 5600, spectrometer, USA) using AlK\(\alpha\) monochromatized radiation. In order to investigate the depth distribution of the elements, time
of flight secondary ion mass spectrometry (ToF-SIMS) negative and positive depth profiles were recorded on an Ion-ToF ToF.SIMS V instrument in dual beam mode. A pulsed 25 keV Bi\(^+\) liquid-metal ion beam bunched down to \(< 0.8\) ns was used for spectra generation and a 2 keV Cs\(^+\) ion beam for sputter-removal of the samples. Spectra for depth profiles were recorded on a 150 × 150 \(\mu\text{m}^2\) area in the center of a 300 × 300 \(\mu\text{m}^2\) sputter crater. Signals were identified according to their isotopic pattern as well as exact mass, and Poisson correction was employed. Auger Electron Spectroscopy (AES) was performed in a PHI Model 670 SAM instrument. The primary electron beam voltage and the current were 10 kV and 10 nA, respectively. Glow discharge optical emission spectroscopy (GDOES) was conducted at a radio frequency of 13.56 MHz and a power of 50 W. High-purity argon (99.9999 \%) was used as a discharge gas at a pressure of 700 Pa. The samples for transmission electron microscopy (TEM) were carefully thinned down to a thickness of about 10 \(\mu\text{m}\). Afterwards a polishing step using Argon ions was employed until the region of the oxide layer was electron transparent. For the TEM measurements, a Philipps CM30 microscopy operating at an acceleration voltage of 300 kV was used.
Figure S1. Schematic diagram for oxide films resulting from Fe and FeSi alloy by thermal oxidation.
Figure S2. SEM top views and cross-sections of oxide films resulting from FeSi alloys ((a) 0, (b) 0.5, (c) 1, and (d) 5 at.% Si) annealed at 500 °C for 0.5 h in air.
Figure S3. (a-d) SEM top views and cross sections of oxide films resulting from the annealed Fe (≈500 nm thickness oxide layer) in (a,b) air and (c,d) in air + Ar; (e) current-potential characteristics with chopped light of α-Fe₂O₃ layers from the corresponding pure Fe. Condition: 1 M KOH solution (pH 13.6), 2 mV s⁻¹ scan rate. Photocurrents are excited with AM 1.5, 100 mW cm⁻² simulated sunlight.

The same thickness of oxide layer (≈500 nm) from pure Fe was examined in the experiment. It shows the lower photoresponse in air and air + Ar conditions compared to Fe₅Si alloy.
**Figure S4.** SEM cross-section of oxide film resulting from Fe5Si alloy annealed at 500 °C for 0.5 h in air + 600 °C for 1 h in Ar.
Figure S5. Current-potential characteristics with chopped light of (a) $\alpha$-Fe$_2$O$_3$ nanoflakes and nanorods from pure Fe and (b) $\alpha$-Fe$_2$O$_3$ nanorods from FeSi alloys. (nanoflakes: annealing at 500 °C for 0.5 h in air; nanorods: annealing at 500 °C for 0.5 h in air + 600 °C for 1 h in Ar) Condition: 1 M KOH solution (pH 13.6), 2 mV s$^{-1}$ scan rate. Photocurrents are excited with AM 1.5, 100 mW cm$^{-2}$ simulated sunlight.
Figure S6. (a) XRD patterns of oxide films from FeSi alloys annealed at 500 °C for 0.5 h in air and (b) high magnifications between 2θ=32 ° and 37 °.
**Figure S7.** TEM images of the annealed (a) Fe and (b) Fe5Si alloy.

The larger grains obtained for the 5 at.% Si sample in comparison to Fe are clearly observed.
Figure S8. Photocurrent at 360 nm at 1.0 $V_{\text{RHE}}$ (1.23 $V_{\text{RHE}}$) and 1.5 $V_{\text{RHE}}$ in 1 M KOH for (a,b) Fe and (c,d) Fe5Si alloy annealed at 500 °C for 0.5 h in air and 500 °C for 0.5 h in air + 600 °C for 1 h in Ar.
**Figure S9.** Semi-quantitative evaluation of Si concentration for the annealed Fe5Si alloy from ToF-SIMS (using an reference oxide layer (dashed) with 0.2 at.% Si as a reference).
Figure S10. SEM top views and cross-sections of oxide films resulting from (a,c) Fe and (b,d) Fe5Si alloy annealed at 400 °C for 1 h in air and 400 °C for 1 h in air + 600 °C for 1 h in Ar.

This two stage growth in air (400 °C) followed by conversion treatment to nanorods in Ar (600 °C) was formed most suitable to create a certain density of whisker growth in air while the use of Ar in the second step was formed beneficial to avoid collapse of the structures at the higher temperatures.
Figure S11. XPS depth profiles of Fe and Fe5Si alloy after polishing treatment.
Figure S12. GDOES elemental depth profiles of oxide layer from pure Fe annealed at 500 °C for 0.5 h in air + 600 °C for 1 h in Ar.