Supporting Information

Hematite photoanode with gradient structure shows an unprecedentedly low onset potential for photoelectrochemical water oxidation

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Experimental details:

Materials

Iron foil with a purity of 99.995% was purchased from Alfa Aesar company and ultrasonic cleaned with ethanol and deionized water for 5 min in sequence prior to use. Other chemicals were analytical grade and were used as purchased without further purification. Solutions were prepared using high purity water (Millipore Milli-Q purification system, resistivity > 18 MΩ cm).

Preparation of hematite photoanodes

The hematite was prepared by heat treatment of iron foil (10 mm * 6 mm * 0.5 mm) in hydrogen-oxygen flame at ca. 1700 K for 1 s (HT-1S), 5 s (HT-5S), 10 s (HT-10S) and 15 s (HT-15S) respectively. The temperature of the flame was controlled by the ratio of hydrogen and oxygen and tested by a thermoelectric couple. Then the film cooled down to room temperature in air naturally.

Loading of cobalt-phosphate (Co-Pi) cocatalyst

Hematite electrodes were loaded with Co-Pi cocatalyst via electrodeposition method carried out in 0.5 M sodium phosphate buffer solution (pH 7) containing 0.5 mM Co^{2+}. The electrodeposition of Co-Pi was carried out in a standard three-electrode cell at 1.0 V with hematite as working electrode, Ag/AgCl as reference electrode, and Pt as counter electrode. The time chosen for the deposition of Co-Pi on hematite was 10 s.

Characterizations of the electrodes

The prepared photoanodes were characterized by X-ray powder diffraction (XRD) on an X'pert Powder diffractometer using Cu Kα radiation with an operating voltage of 40 kV and an operating current of 40 mA. A scan rate of 12 °/min was applied to record the patterns in the range of 20~70 °. X-ray photoelectron spectroscopy (XPS) was performed using a monochromatized Al Kα source (hν = 1486.6 eV), operated at 225 W, on a Kratos Axis Ultra DLD system at a takeoff angle of 0 ° relative to the surface normal and a pass energy for narrow scan spectra of 20 eV, corresponding to an instrument resolution of approximately 600 meV. Survey spectra were collected with a pass energy of 80 eV. Spectral positions were corrected by shifting the primary C 1s core level position to 285 eV. The morphologies and energy dispersive spectrometer (EDS) analysis of the photoanodes was examined by a Quanta 200 FEG scanning electron microscope (SEM) equipped with an energy dispersive spectrometer at an accelerating voltage of 20 kV. Raman spectra and mapping analysis were measured on Renishaw Company spectrograph with spectral resolution of 2 cm^{-1}. The laser line at 532 nm of a solid laser was used as an exciting source. The power of laser line, measured at the samples, was about 0.3 mW. The step for the Raman mapping analysis is 1 μm. The spectra of all samples were recorded at room temperature.

Electrochemical measurements

The photoelectrochemical performances of hematite photoanodes were measured in a three-electrode setup with Pt counter electrode and SCE reference electrode in 1 M NaOH (pH 13.6) electrolyte unless other statement. Before measurement, the areas of electrodes were fixed by insulating cement. Linear sweep voltammetry (LSV) with a scanning rate of 20 mV s^{-1} was performed using an Ivium electrochemical station and a Newport Oriel sol3A light source at 100 mW cm^{-2} illumination. The Mott-Schottky (MS) plots and electrochemical impedance spectroscopy (EIS) were measured on the same electrochemical station in the same three-electrode setup. The potentials are vs. the reversible hydrogen electrode (RHE) and were calculated from the Nernst equation, $E_{RHE} = E_{SCE} + 0.059 * pH + 0.245$.

Quantitative analysis of O_2 evolution

O_2 evolution was measured in an “H type” reactor using a CHI760d electrochemical station in 1.0 M NaOH electrolyte with an argon flow rate of 2.0 ml min^{-1} under 300 W high-intensity Xe lamp irradiation (400 mW cm^{-2}, PLS-SXE300C，Perfectlight company). The use of this light source instead of AM 1.5 G light source will increase the amount of O_2 evolved during the measurement and facilitate the quantitative analysis of the O_2 product. The amount of O_2 generated during i-t test was analysed by an Agilent 7890a GC station. LSV analysis before and after amperometric i-t test was performed with a scanning rate of 20 mV s^{-1} under the same conditions.

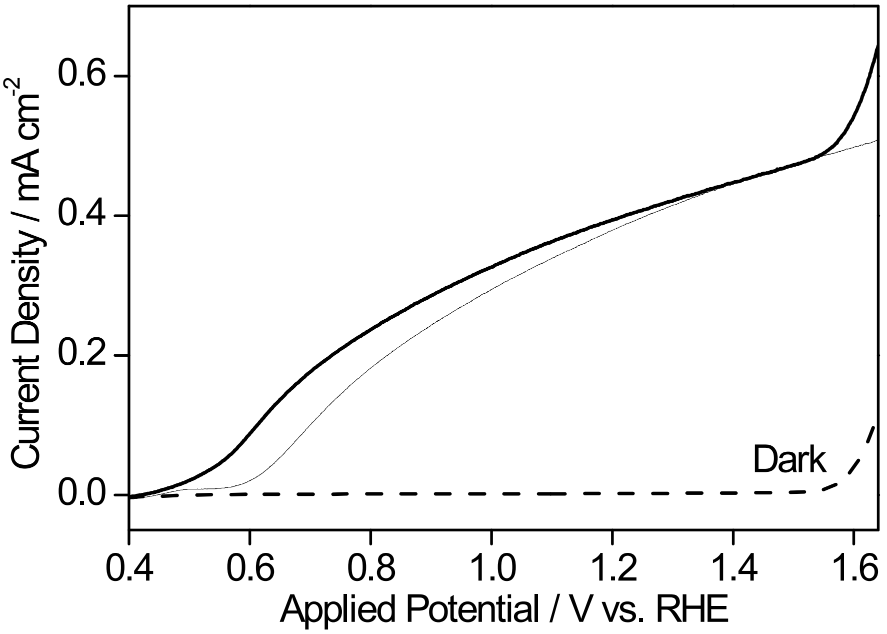


Fig. S1 LSV curve for Co-Pi/HT-10S electrode under light irradiation and in dark. Electrolyte: 1.0 M NaOH (pH 13.6) aqueous solution; Light source: AM 1.5 G 100 mW cm^{-2}; Scan rate: 20 mV s^{-1}. The solid and dash lines indicate the scans under light and dark conditions, respectively. The fine line shows the LSV curve of HT-10S.

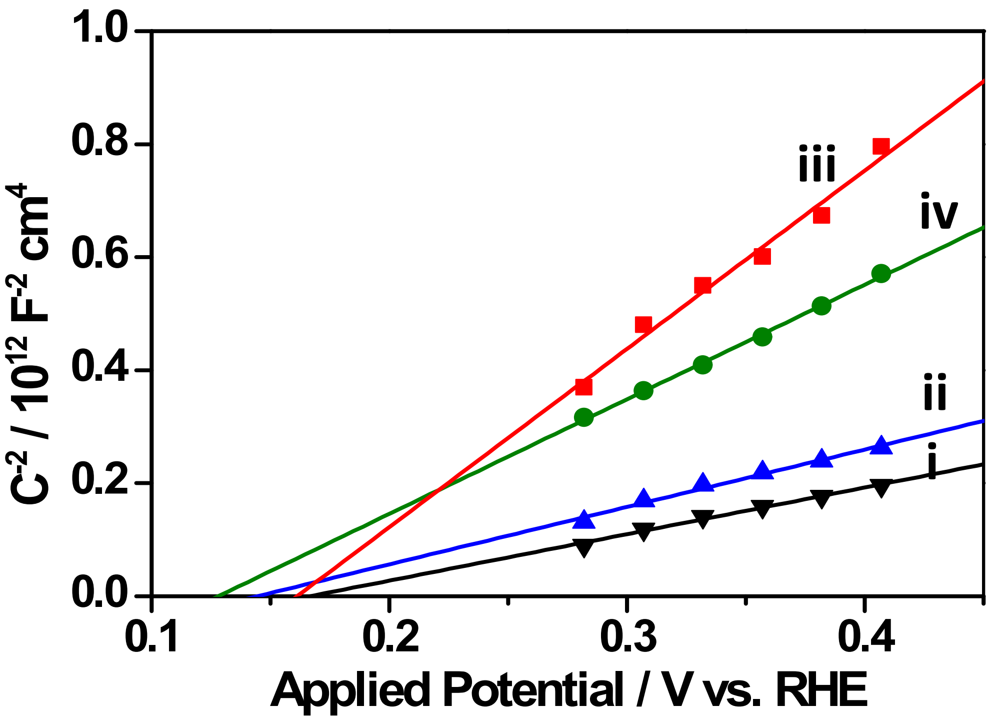


Fig. S2 Mott–Schottky plots for HT-1S (i), HT-5S (ii), HT-10S (iii) and HT-15S (iv) electrodes measured in 1 M NaOH (pH 13.6) electrolyte. Frequency: 1000 Hz; Amplitude: 25 mV.

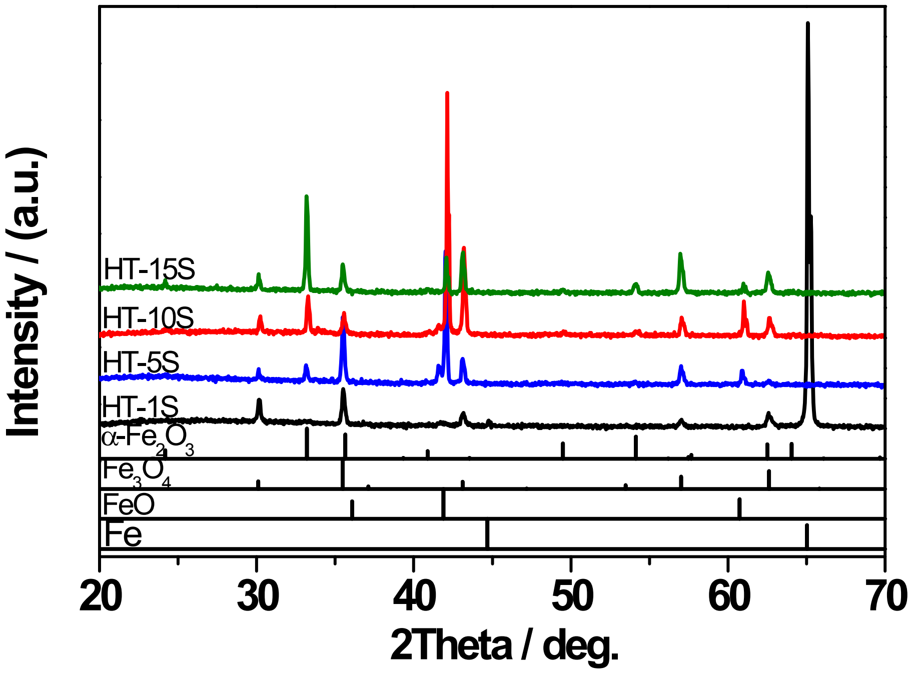


Fig. S3 XRD patterns of HT-1S, HT-5S, HT-10S and HT-15S electrode.

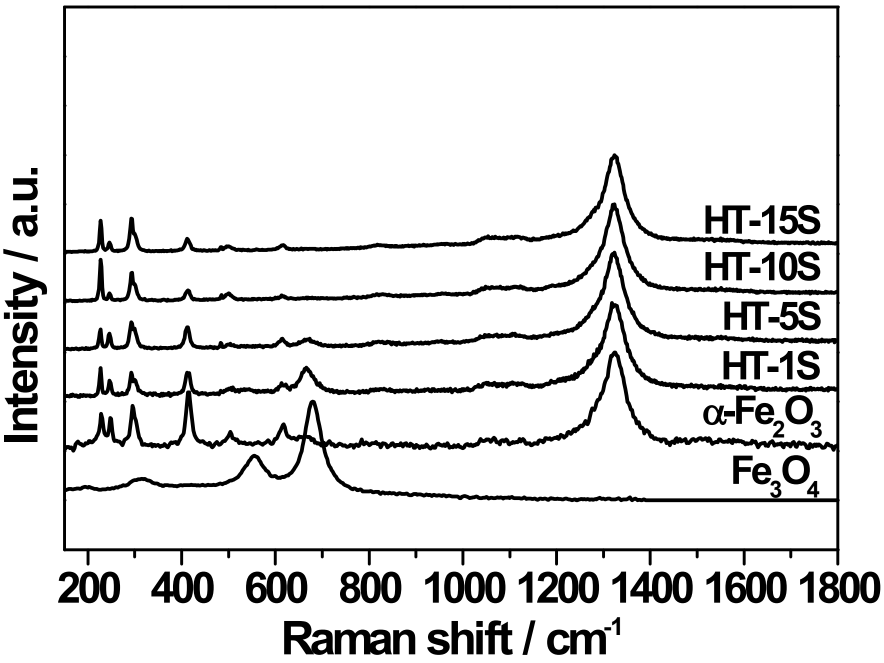


Fig. S4 Raman spectra of HT-1S, HT-5S, HT-10S and HT-15S electrodes.

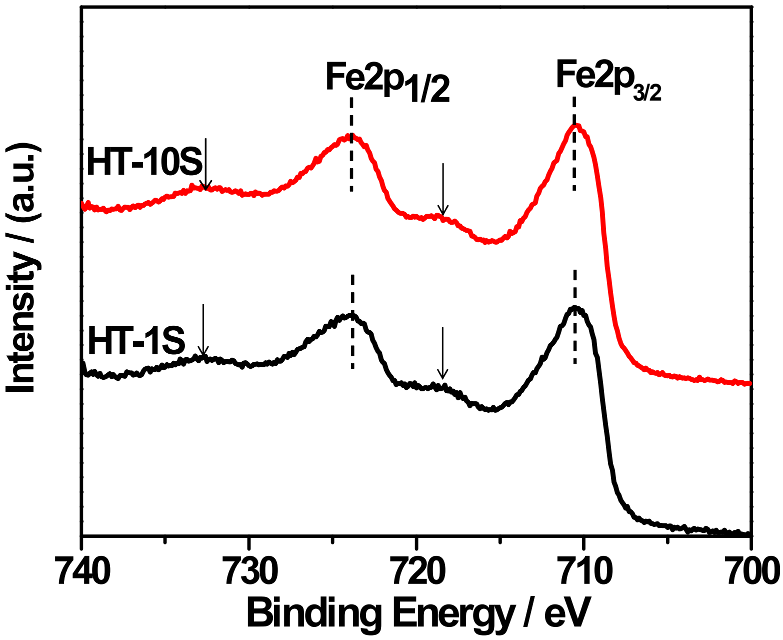


Fig. S5 XPS spectra of HT-1S and HT-10S (the binding energies are calibrated by the binding energy of C1s 285 eV). The binding energy of Fe2p3/2 and Fe2p1/2 are 710.6 eV and 723.9 eV respectively, which is a characteristic position for Fe^{3+}. Particularly, the satellite peaks (see arrows) at high binding energy give the existence of Fe^{3+} species on the surface.

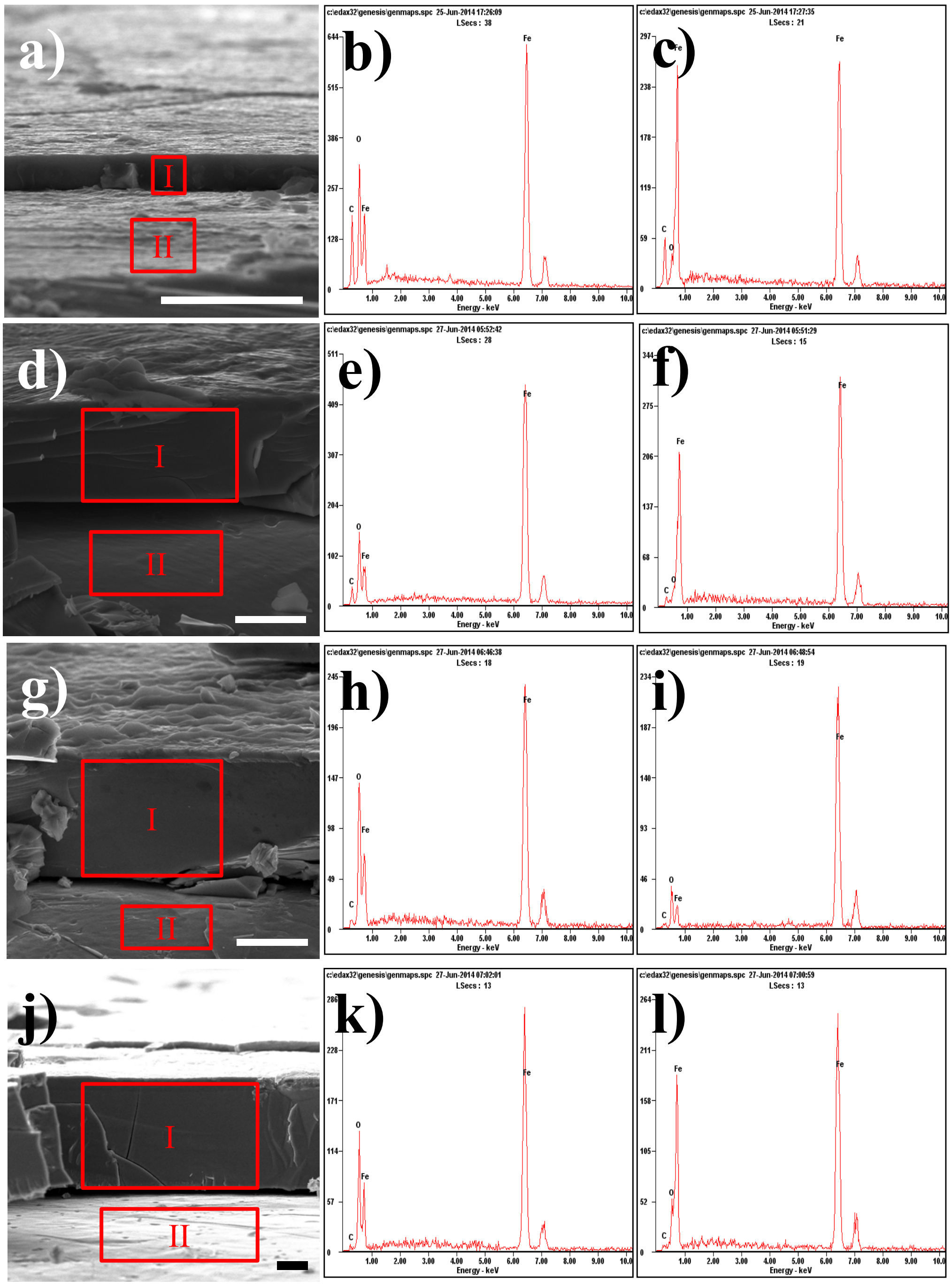


Fig. S6 a) cross sectional SEM images of HT-1S, b) EDS analysis in area I in a), c) EDS analysis in area II in a), d) SEM side images of HT-5S, e) EDS analysis in area I in d), f) EDS analysis in area II in d), g) SEM side images of HT-10S, h) EDS analysis in area I in g), i) EDS analysis in area II in g), j) SEM side images of HT-15S, k) EDS analysis in area I in j), l) EDS analysis in area II in j), (scale bar stands for 10 μm).

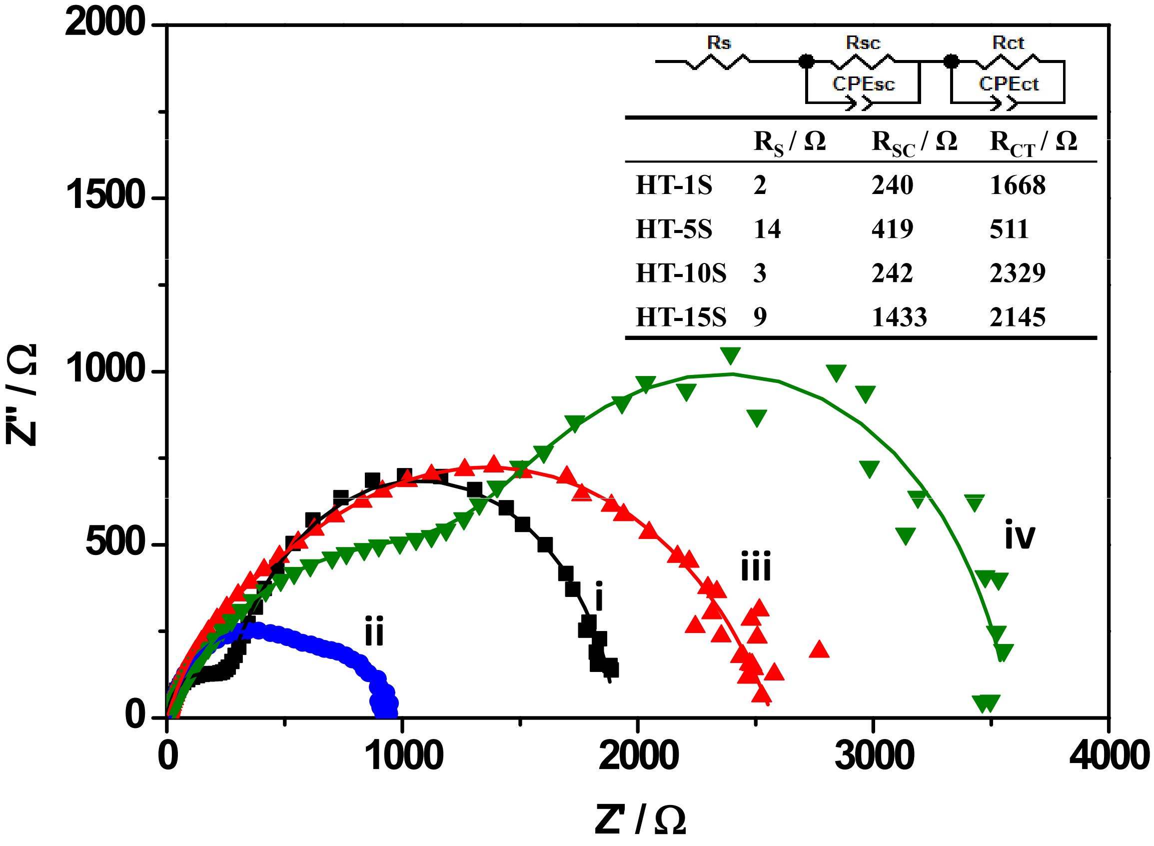
Table S1 The thickness of mixed iron oxides layers of electrodes prepared at different conditions.

Sample	**Thickness of mixed iron oxides / μm**
HT-1S	3
HT-5S	15
HT-10S	20
HT-15S	40

Fig. S7 Schematic illustration of the gradient structure of the as-prepared hematite electrodes.

Table S2 The thickness of Fe_2O_3, Fe_3O_4 and FeO layers of HT-15S electrode

Iron oxides	**Raman / µm**	**SEM / µm**
Fe_2O_3	2-3	2
Fe_3O_4	2-3	3
FeO	--	35



	R_S / Ω	R_{SC} / Ω	R_{CT} / Ω
HT-1S	**2**	**240**	**1668**
HT-5S	**14**	**419**	**511**
HT-10S	**3**	**242**	**2329**
HT-15S	**9**	**1433**	**2145**

Fig. S8 Nyquist plots for impedance spectroscopy data measured at pH 13.6 at 1.23 V vs. RHE of HT-1S (i), HT-5S (ii), HT-10S (iii) and HT-15S (iv) electrodes under AM 1.5 G illumination. A simple model with two interfaces is used to simulate the IS of hematite.

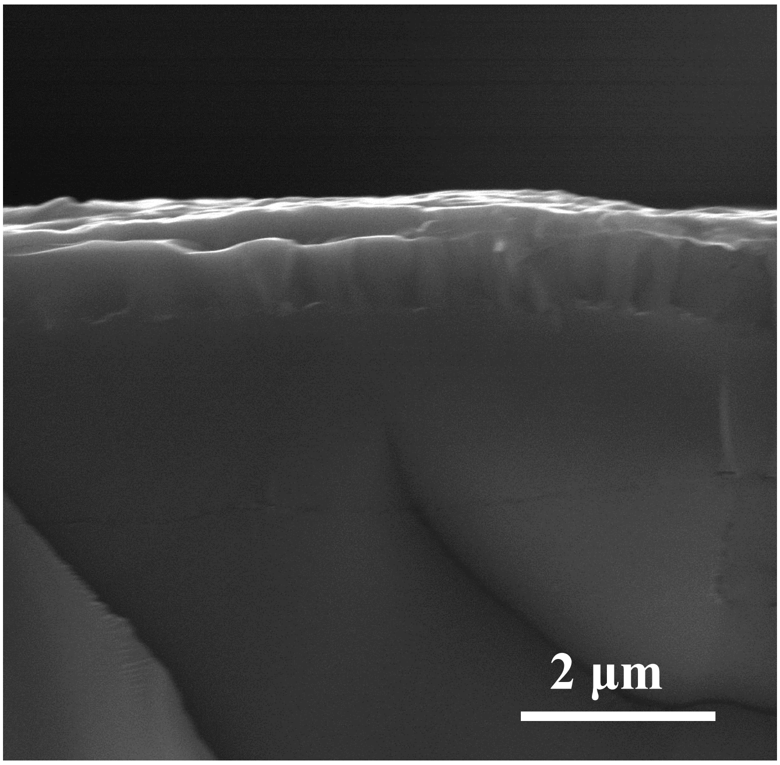


Fig. S9 cross sectional SEM image of HT-10S.

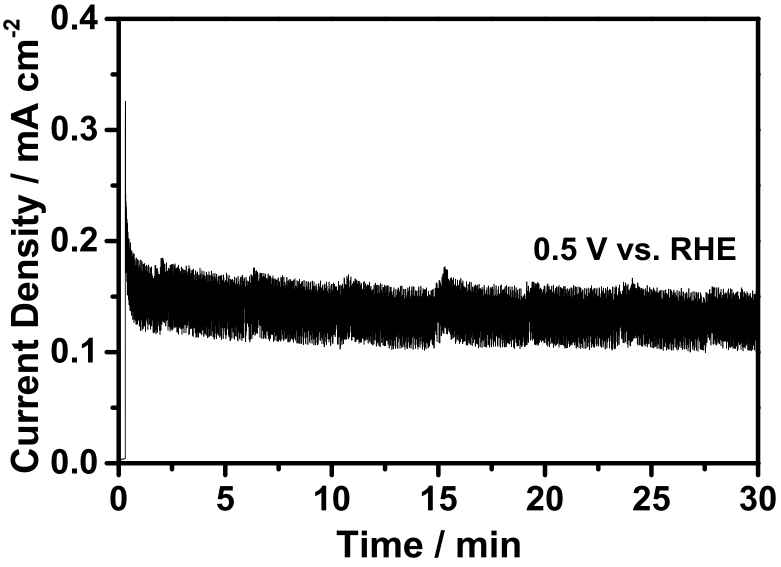


Fig. S10 Amperometric i-t curve for HT-10S electrode in 1 M NaOH (pH 13.6) at 0.5 V vs. RHE. Light source: 300 W Xe lamp. The use of the high intensity Xe lamp instead of low intensity AM 1.5 G light source during the measurement will facilitate the analysis of the experimental results.

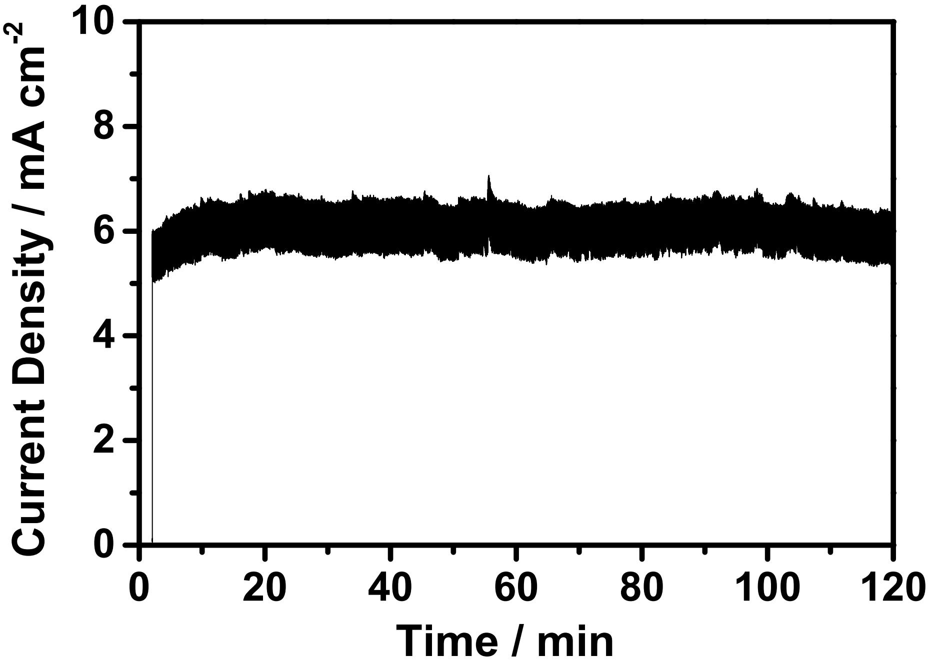


Fig. S11 Amperometric i-t curve for HT-10S electrode in 1 M NaOH (pH 13.6) at 1.23 V vs. RHE. Light source: 300 W Xe lamp.

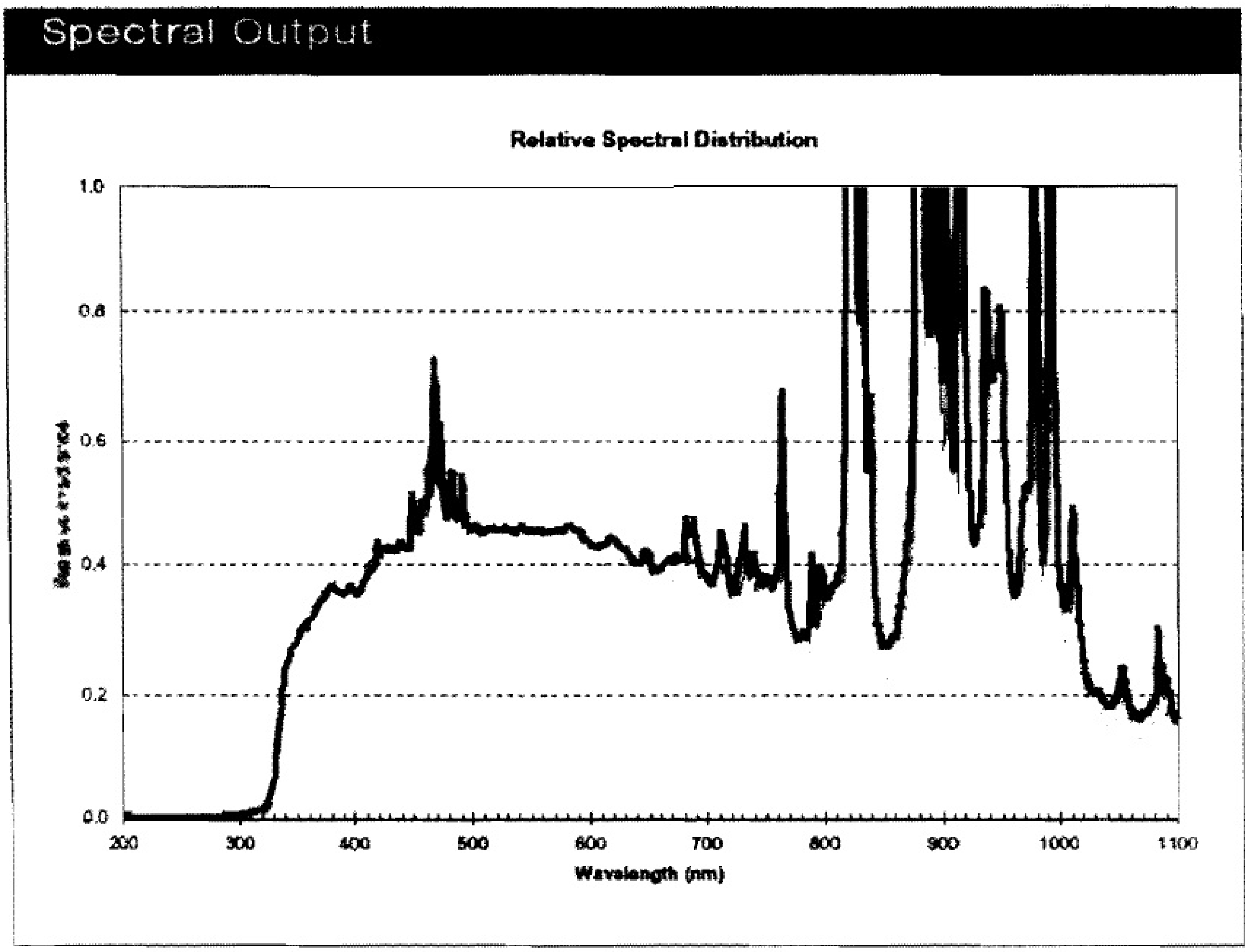


Fig. S12 the relative spectral distribution of the 300 W Xe lamp.

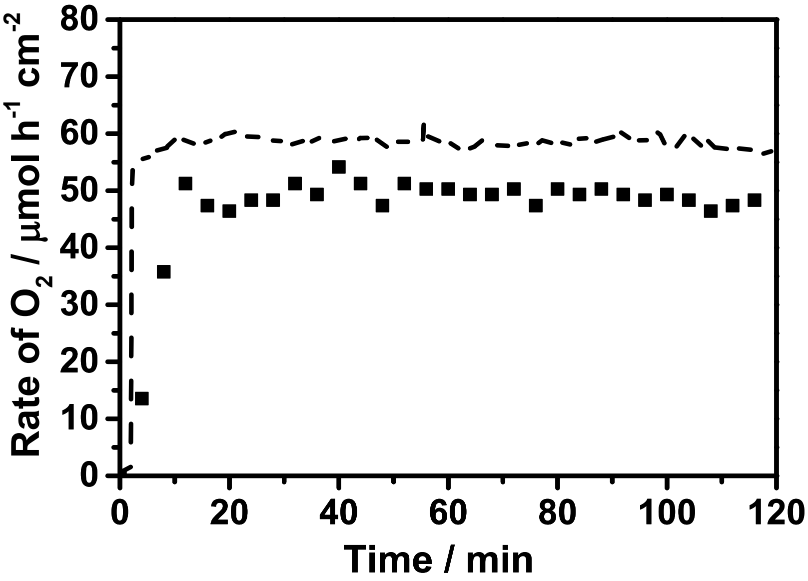


Fig. S13 The rate of O_2 evolution for HT-10S electrode in 1 M NaOH (pH 13.6) at 1.23 V vs. RHE. Light source: 300 W Xe lamp. Dash line corresponds with a Faraday efficiency of 100%.

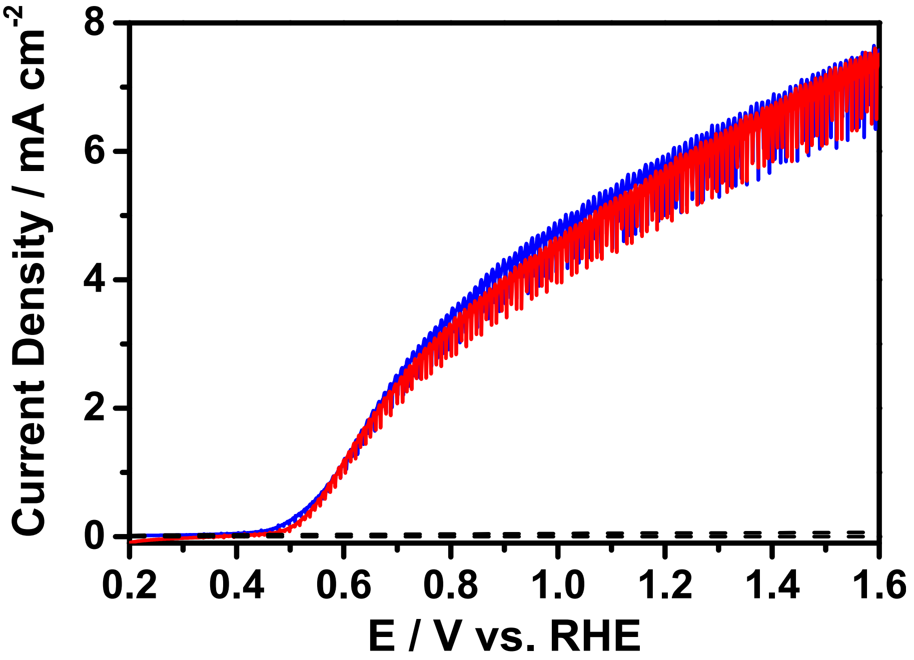


Fig. S14 LSV curves for HT-10S electrode in 1 M NaOH (pH 13.6) before (blue) and after (red) i-t test. Light source: 300 W Xe lamp. The onset potential obtained with high-intensity Xe lamp was found to be 0.05 V more negative than that obtain using low-intensity AM 1.5 G light source. These results demonstrated the high stability of the present hematite photoelectrode.