Electronic Supplementary Information

for

A robust iron oxyhydroxide water oxidation catalyst operating under near neutral and alkaline conditions

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(i) Chemicals and Electrodes:

Ferrocene, decamethyl ferrocene, sodium perchlorate monohydrate, concentrated sulfuric acid, potassium chloride were obtained from Sigma Aldrich. Ferrocene carboxylic acid was purchased from Spectrochem, India. Sodium hydroxide, boric acid, potassium ferrocyanide and acetonitrile were obtained from Merck, India. ITO has been bought from Techinstro. Platinum (Pt) wire, Ag/AgNO$_3$ (10 mM AgNO$_3$) and Ag/AgCl (3M KCl) reference electrodes were purchased from CH Instruments Inc. TX, USA. For all of the experiments, deionized water was used. Millipore water was used to prepare the required solutions.

(ii) Electrochemistry:

All electrochemical experiments were carried using CH Instruments, Austin, TX potentiostat (Model CHI 760D). Conventional three electrodes electrochemical cell has been used where the reference electrodes were either an Ag/AgCl (3 M KCl) or an Ag/AgNO$_3$ (10 mM AgNO$_3$) non-aqueous electrode. Pt wire and indium tin oxide electrode (ITO) were used as counter and working electrodes respectively. All the experiments were performed at 25±2ºC in the presence of ambient oxygen. All the results were collected at an uncompensated cell resistance of 0.2 Ω using iR compensation tool of CH potentiostat. The potentials reported in this work were converted to the reversible hydrogen electrode (RHE) or normal hydrogen electrode (NHE). For RHE conversion[i] in different pH solution, following equation was used. E(RHE) = E(Ag/AgCl) +E^0(Ag/AgCl) + 0.059pH. In this equation, E(Ag/AgCl) is the observed potential while experiments were performed using Ag/AgCl (3 M KCl) reference electrode. E^0(Ag/AgCl) is the potential of Ag/AgCl (3 M KCl) versus normal hydrogen electrode (NHE), i.e., 0.197 V. The potential for Ag/AgNO$_3$ nonaqueous reference electrode was 0.54 V versus NHE. All experiments were repeated at least twice to check their reproducibility.

(iii) Cyclic voltammetry experiment for Fig. S1:

Cyclic voltammetry measurements of 5 mM conc. of ferrocene and its derivative were performed using glassy carbon, Pt wire and Ag/AgNO$_3$ as working, counter and reference electrodes respectively in acetonitrile solvent having 0.1 M NaClO$_4$ as supporting electrolyte at a scan rate of 100 mVs^{-1}.

(iv) Electrodeposition of iron oxyhydroxide in non aqueous medium:

The electrodeposition of iron oxyhydroxide was performed by constant potential electrolysis (CPE) at 0.697 and 0.897 V (*vs* NHE) for different time (1, 2, 4, 6, 8, 10 min) using a 5 mM solution of ferrocene and ferrocene carboxylic acid respectively in acetonitrile solvent containing 0.1 M NaClO$_4$ electrolyte. 0.27 cm^2 ITO, Pt wire and Ag/AgNO$_3$ electrodes were used as working, counter and reference electrodes respectively. ITO electrode has been washed and sonicated three times in soap water, water and acetone respectively before use. The experiments were carried out in an H shaped cell in which the two arms are separated by a frit. The ITO electrode, and reference electrode were placed in one arm and the counter electrode was placed in other arm of the cell. After the deposition, the films were washed with deionized water and

then transferred to fresh 1 M NaOH or 0.5 M borate buffer for further water oxidation studies. For borate buffer preparation, 0.5 M boric acid solution was prepared and 2 M sodium hydroxide solutions of different amounts were added to adjust the pH.

(v) Electrodeposition of iron based film in aqueous medium:

For deposition in aqueous medium a 0.27 cm^2 ITO, Ag/AgCl (3M KCl) and Pt wire were used as working, reference and counter electrode. 1 mM FeSO$_4$ in 1 M acetate buffer (pH=7) was used. The solution was vigorously bubbled with nitrogen gas for minimum 30 min to remove oxygen in the solution before adding FeSO$_4$. Constant potential electrolysis has been done at 1.547 V *vs*. NHE for 2 min.

(vi) Water oxidation studies
Linear sweep voltammetry (LSV) measurements for the electrodeposited films were performed at a scan rate of 5 mVs^{-1} using Pt wire and Ag/AgCl (3 M KCl) electrodes as counter and reference electrodes, respectively. For long term stability of the electrodeposited films, constant potential electrolysis (CPE) experiments were performed by holding potential of the electrode at the potentials mentioned in the main manuscript. For this experiment, a four mouth electrochemical cell was used with continuous stirring.

(vi) Oxygen detection experiments:

A Clark type electrode was used for recording the change in dissolved oxygen concentration during a single turn over reaction. The oxygen sensor was calibrated before each experiment following a two point calibration 0% (zero solution) and 100% (air). For evaluation of O$_2$ formation, 1 M NaOH solution was taken in a sealed four mouth cell containing the Clark type electrode. The solution was thoroughly purged with N$_2$ such that the O$_2$ concentration was close to zero and recorded by the Clark electrode. The change in dissolved O$_2$ concentration during CPE was monitored after that.

(vii) Determination of electrochemically active surface area:

In order to measure the electrochemically active surface area of the electrode CVs at different scan rate have been taken in a solution of 0.1 mM K$_4$Fe(CN)$_6$ in 0.1 M KCl. The current vs scan rate relationship for the electrochemical reaction of K$_4$Fe(CN)$_6$ which diffuses to the electrode surface is described according tp the Randles-Sevcik equation:
$I_p = 2.69 \times 10^5 A D^{1/2} n^{3/2} v^{1/2} C$
Where I_p, A, D, n, v, C are peak current, electrochemically active surface area (cm^2), diffusion coefficient (cm^{2}s^{-1}), no of electrons transferred (n = 1 for [Fe(CN)$_6$]$^{3-/4-}$), scan rate (Vs^{-1}), and concentration of ferrocyanide (molL^{-1}) respectively. Diffusion coefficient of ferrocyanide is 6.20x10^{-6} cm^{2}s^{-1}.

(viii) Characterization:

X-ray photoelectron spectroscopy (XPS):

XPS has been done with an ESCA Lab spectrometer having Al kα X-ray source (hν = 1486.6 eV) operating at 150 W using a Physical Electronics 04-548 dual Mg/Al anode and in a UHV system with a base pressure of $\leq 5 \times 10^{-9}$ Torr. Both the incident and take off angles were 55° with respect to the surface normal. The analysis depth was around 10 to 15 Å. The spectra were energy-analyzed with an Omicron Nanotechnology EA 125 Hemispherical Energy Analyzer in pulse-count mode with pass energies of 50 eV for broad scan data and 25 eV for specific, narrow-range core-level transitions. The XPS data were curve-resolved using XPSPEAK 4.123 after correction of a Shirley background. The curve resolved spectra were fit with the minimum number of peaks needed to reproduce the spectral features using Gaussian−Lorentzian product function.

Raman spectrometry:

Raman scattering spectra were measured using the high resolution Micro Raman spectrometer (HORIBA Scientific Lab Ram) equipped with a He-Ne laser (632.8 nm) with a spot size of 10 μm. The laser power was 3 mW.

Scanning electron microscopy (SEM):

Morphological investigations were performed on a high resolution scanning electron microscope (HRSEM, Carl Zeiss Ultra Plus). Energy dispersive X-ray spectroscopy (EDS) was performed using a spectrometer (Oxford Instruments X-Max^N) attached to a SEM.

X-ray Diffraction (XRD):

The powder X-ray diffraction pattern (PXRD) were recorded by using a Bruker AXS with D8 advance with Cu Ka radiation (1.54 Å) with a step size of 0.02 in a 2θ range of 5–80^0.

Inductively coupled plasma mass spectrometry (ICPMS):

ICPMS experiments were performed on a Thermo IRIS Intrepid spectrum apparatus. Sample was prepared by washing the films first with de-ionized water. Then all the films were washed with 5 ml concentrated acid for the quantitative analysis of Fe using the ICPMS instrument.
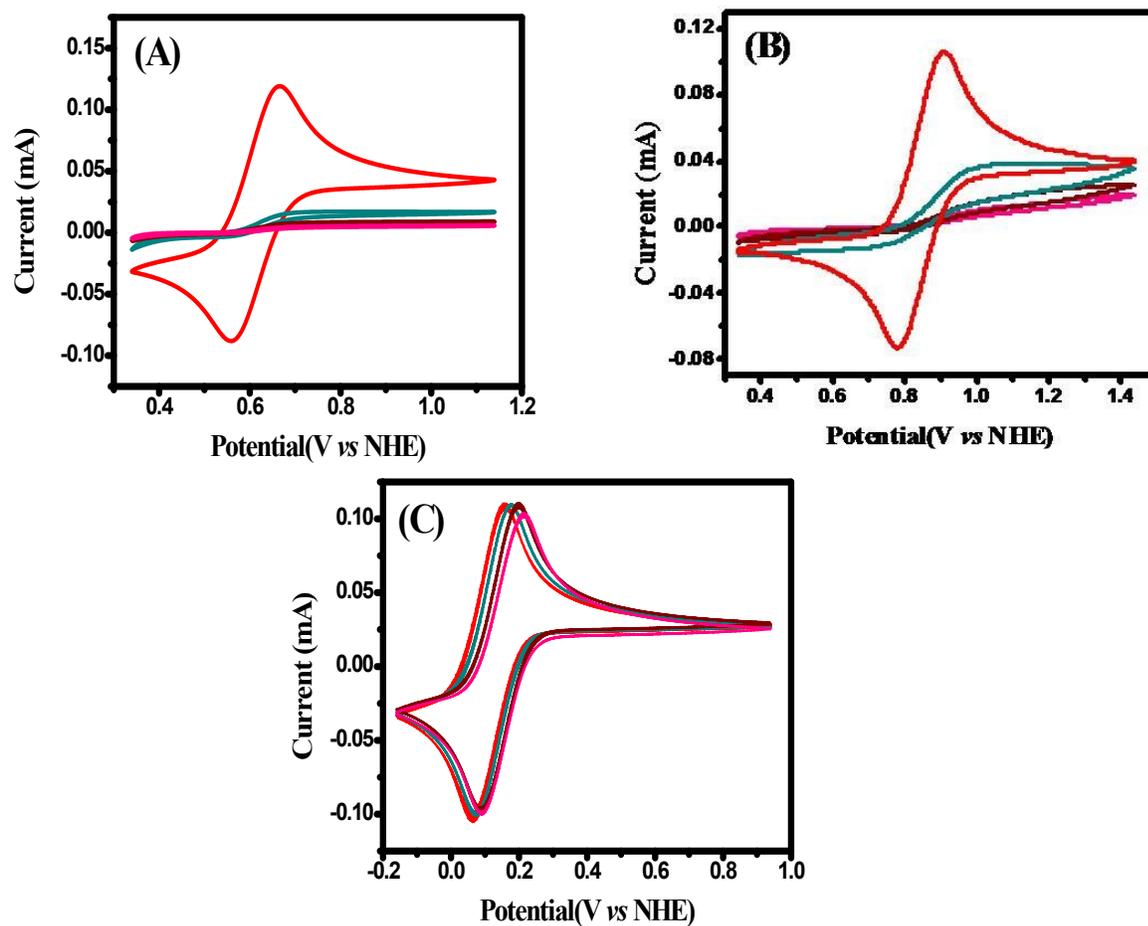
Fig. S1: 2nd (Red), 50th (Dark Cyan), 100th (Wine), 150th (Pink) scans of consecutive 100 CV scans recorded for 5 mM solution of (A) ferrocene, (B) ferrocene carboxylic acid, (C) decamethyl ferrocene in 0.1 M $NaClO_4$ electrolyte recorded at scan rate of 0.1 V/s.
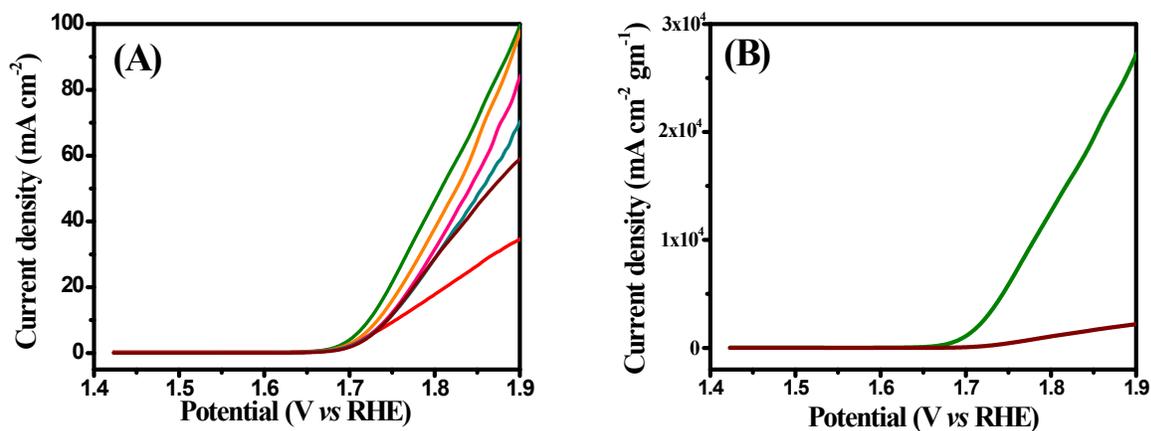
Fig. S2: (A) Linear sweep voltammograms of A-Fe film in 1(M) NaOH for 2 (green), 4 (orange), 6 (pink), 8 (cyan), 10 (wine), and 1 min (red) deposition. (B) Current densities normalized to the mass of iron deposited on the electrodes of A-Fe film in 1(M) NaOH for 2 min (green) and 10 min (wine) deposition.
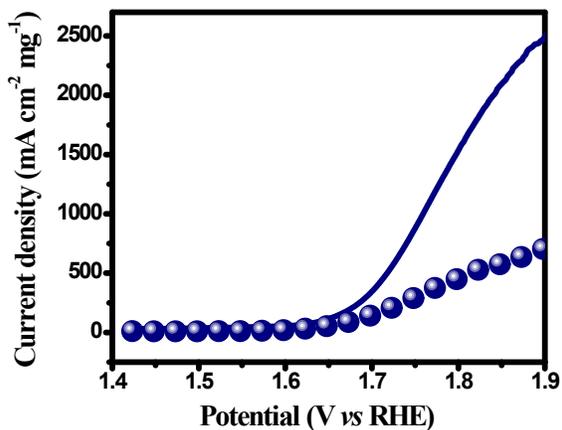
Fig. S3: Current densities normalized to the mass of iron deposited on the electrodes of C-Fe film in 1(M) NaOH for 2 (line) and 10 min (sphere) deposition.
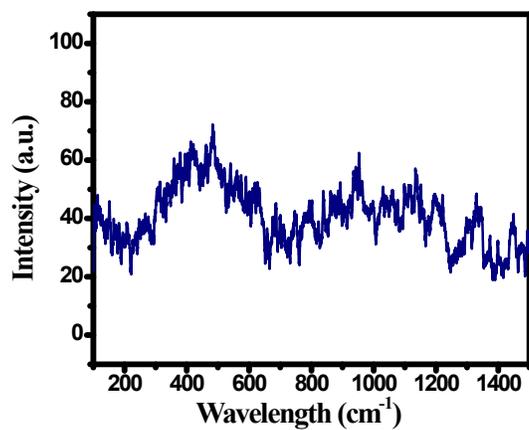
Fig. S4: Raman spectra of C-Fe film.
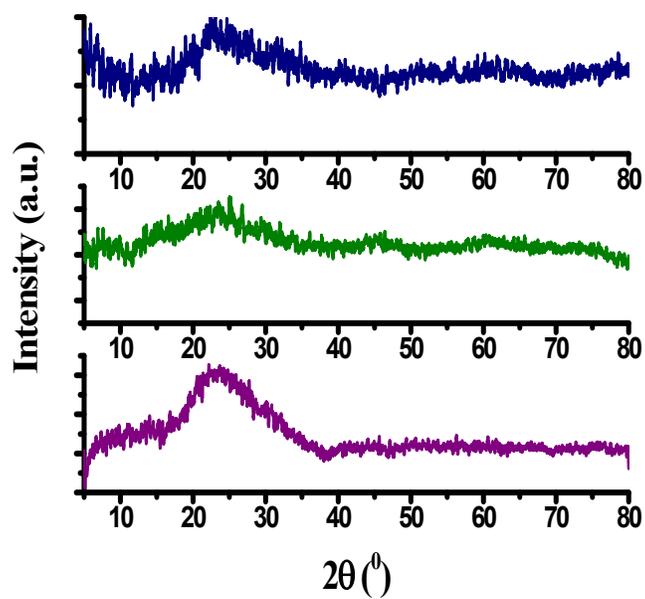
Fig. S5: XRD patterns for ITO substrate (purple), A-Fe film (green) and C-Fe film (blue).
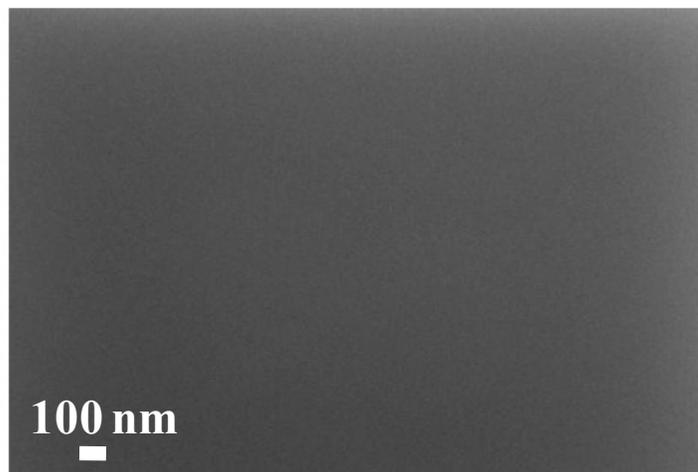
Fig. S6: SEM image of blank ITO conducting glass.
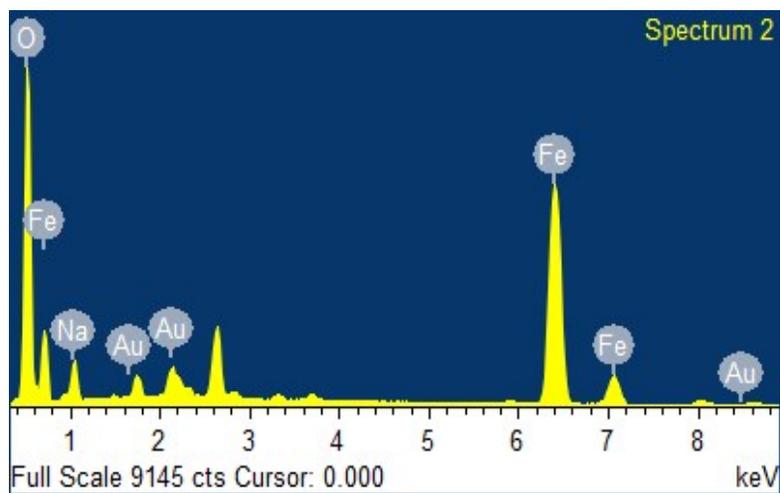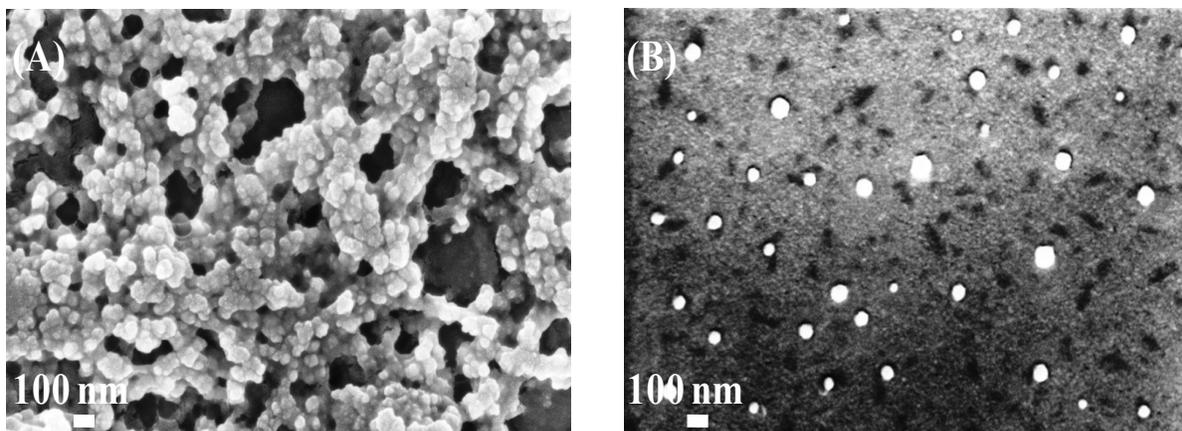

Fig. S7: EDS spectrum of A-Fe film.

Fig. S8: SEM images of A-Fe film (A) and C-Fe film (B) for 10 min deposition.
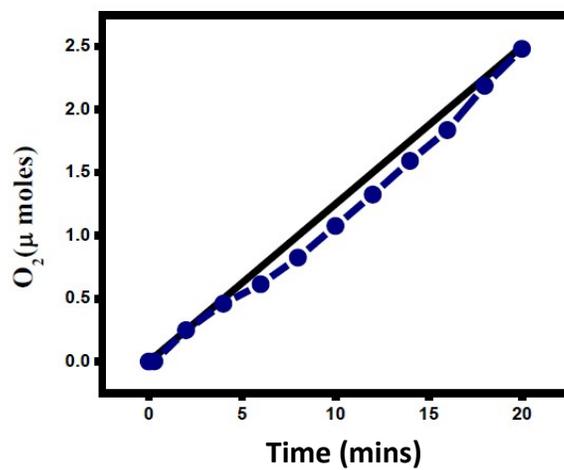

Fig. S9: Experimental (Blue) and theoretical (Black) O_2 evolution data for A-Fe film in 1 M NaOH. Theoretical value was calculated from the current measured during CPE.
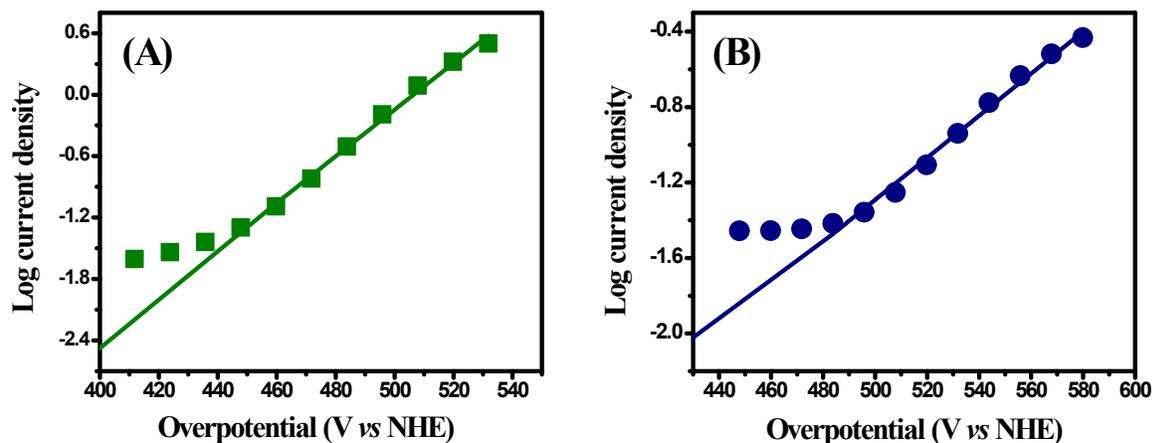
Fig. S10: Tafel plots for the (A) A-Fe and (B) C-Fe films calculated from LSV data measured in 0.5M Borate buffer.
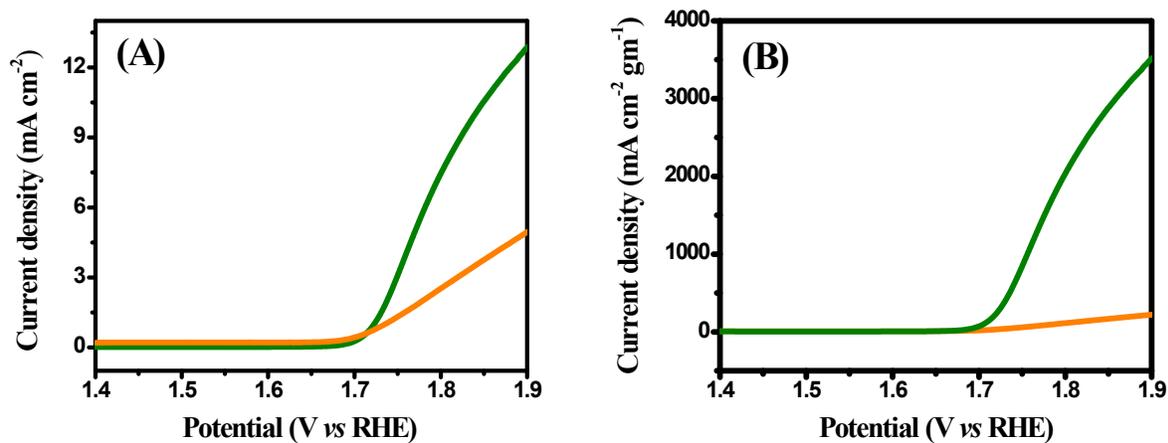

Fig. S11: (A) Linear sweep voltammograms in 0.5 M borate buffer (pH=9.2) of A-Fe film (green), film deposited from $FeSO_4$ salt (Orange). (B) Current densities normalized to the mass of iron deposited on the electrodes of A-Fe (green) and film deposited using $FeSO_4$ salt (Orange).

Fig. S12: (A) Linear sweep voltammograms in 1(M) NaOH of A-Fe film (green), film deposited from $FeSO_4$ salt (Orange). (B) Current densities normalized to the mass of iron deposited on the electrodes of A-Fe (green) and film deposited using $FeSO_4$ salt (Orange).
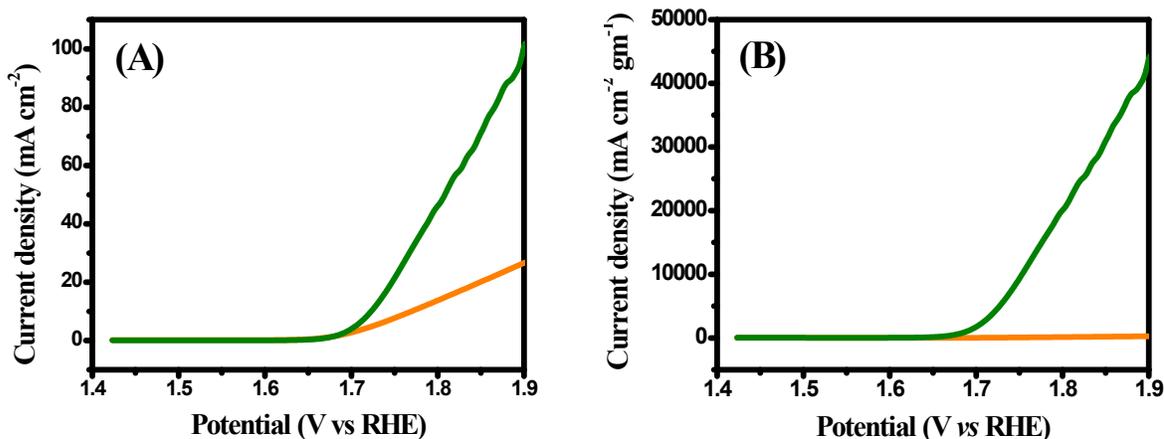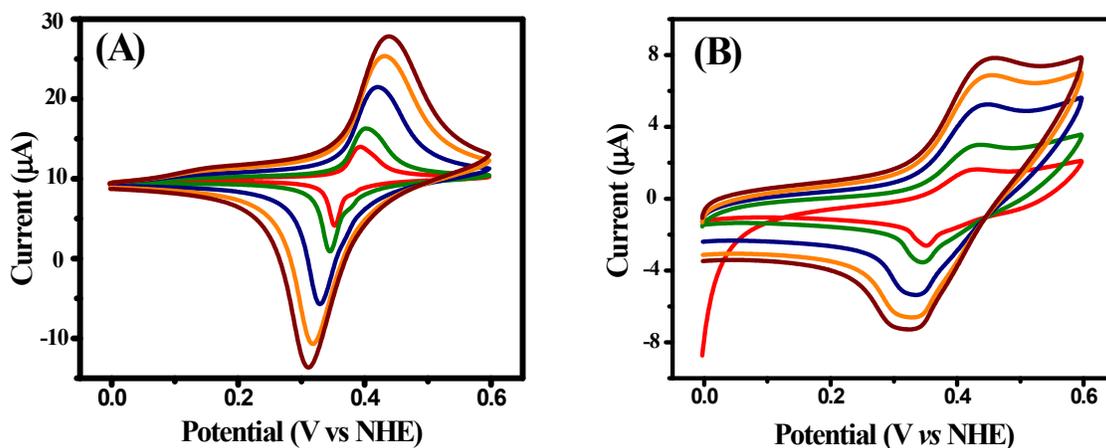

Fig. S13: Cyclic voltammograms at different scan rates (10, 20, 50, 100 mVs^{-1}) in 0.1 mM $K_4[Fe(CN)_6]$ solution having 0.1 M KCl as electrolyte for (A) A-Fe film, (B) C-Fe film.
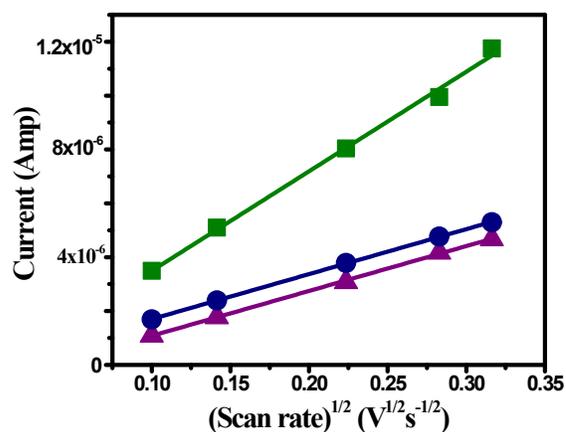
Fig. S14: Current vs. square root of the scan rate plot obtained for A-Fe film (green square), C-Fe film (blue circles) film blank ITO (purple triangle) in 0.1 mM $K_4[Fe(CN)_6]$ solution having 0.1 M KCl as electrolyte.
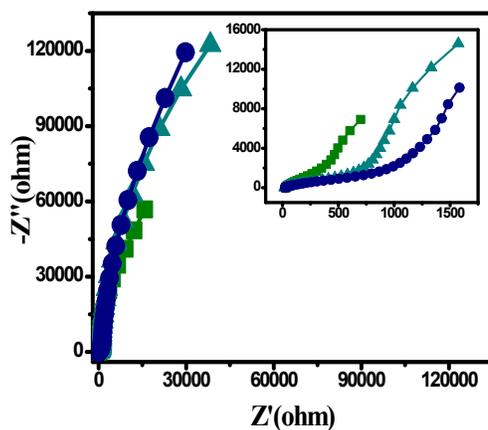

Fig. S15: The Nyquist plot obtained for 2 min deposited A-Fe film (green square), 10 min deposited A-Fe film (cyan triangle), 2 min deposited C-Fe film (blue circle). Inset shows magnified view in the high frequency region.
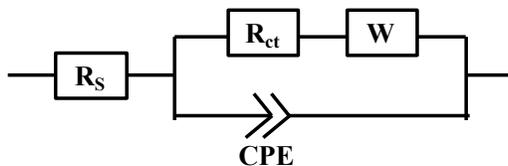

Fig. S16: EC model used for the fitting of the EIS data.

Table S1: Comparison of catalytic activities and conditions for different water oxidation catalysts at near neutral condition.

Catalyst	Catalyst loading (nmol cm^{-2})	Overpotential @1 mAcm^{-2}	TOF (h^{-1} at η= 600 mV)	pH	Reference
Fe based film (A-Fe)	153	490	612	9.2	This work
Ni-based film	100	540	36	9.2	*Proc. Natl. Acad. Sci.*, 2010, **107,** 10337-10341
O$_2$-NiO$_x$-MWCNT	-	330 at 0.5 mA cm^{-2}	-	9.2	*ACS Appl. Mater. Interfaces,* 2014, **6,** 15395-15402.
NiO$_x$-en	270	510	54 (ca. 610 mV)	9.2	*Energy Environ. Sci.*, 2013, **6,** 579-586.
NiO$_x$-NH$_3$	290	560	-	9.2	*Energy Environ. Sci.*, 2013, **6,** 579-586.
NiO$_x$-aqua	280	570	39.6 (ca. 610 mV)	9.2	*Energy Environ. Sci.*, 2013, **6,** 579-586.
Ni based oxide film	-	618 at 0.6 mA cm^{-2}	-	9.2	*J. Phys. Chem. C*, 2014, **118,** 4578-4584.
Cu-B$_i$	-	801 at 10 mA cm^{-2}	-	9	*ACS Catal.,* 2014, **5,** 627-630.

Co-W	-	420	36 (ca.640 mV)	8	*Chem. Asian j,* 2015, **10,** 2228-2233.
IrO$_x$,nH$_2$O	-	200 at 1.5 mA cm^{-2}	-	9	*Small,* 2011, **7,** 2087-2093.
IrO$_x$.nH$_2$O	-	220 at 0.5 mA cm^{-2}	-	9	*J.Phys.Chem.Lett.,* 2011, **2,** 402-406.

Table S2: Formal potentials ($E^{0\prime}$) for ferrocene derivatives in acetonitrile/ 0.1 M NaClO$_4$

Molecule	$E^{0\prime}$ (V vs NHE)
Ferrocene	0.64
Ferrocene carboxylic acid	0.89
Decamethyl ferrocene	0.14

Formal potentials ($E^{0\prime}$) were determined by using following equation where E_{pa} and E_{pc} are the peak potentials for anodic and cathodic peaks respectively.

$$E^{0\prime} = \frac{E_{pa} + E_{pc}}{2}$$

Table S3: Overpotential (η) and Tafel slope for A-Fe and C-Fe films in 0.5 M borate buffer (pH=9.2).

Film	Overpotential (mV) @ 10 mA cm^{-2}	Overpotential (mV) @ 1 mA cm^{-2}	Tafel slope (mV/decade)
A-Fe	600	490	45
C-Fe	Not achievable in potential range used	766	90

: For C-Fe film in borate buffer (pH 9.2), intensity of current was very low, so the current density was not able to reach 10 mAcm^{-2} even at high positive potential.

Table S4: Fitted result obtained for each element of the equivalent circuit.

Parameter	A-Fe film 2 min	A-Fe film 10 min	C-Fe film 2 min
R_S (Ω)	27.92	24.49	19.28
R_{ct} (Ω)	2.53	6.046	51.17
W (mho)	0.099792	0.03283	0.026083
CPE (mho)	1.9638×10^{-5}	2.1938×10^{-6}	6.6832×10^{-6}