Oxygen evolution reaction electrocatalyzed on a Fenton-treated gold surface

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Supporting Information

Part (S.a): Materials and Methods

All chemicals, hydrogen peroxide (A.R), Mohr salt (A.R) (Ferrous ammonium sulphate hexahydrate), acetic acid (A.R), sodium acetate (A.R) and sodium hydroxide (A.R) were purchased from Merck. The electrochemical experiments were carried out using IVIUM Compactstat. A standard three-electrode cell consisting of 1.6 mm dia gold disk as working electrode, Hg/HgO (0.1 M NaOH) as reference electrode (avoiding chloride contamination), and 1 cm^2 Pt foil counter electrode was used. The potential values are referred to Reversible Hydrogen Electrode, RHE (by adding 165 mV + 780 mV in 0.1M NaOH (pH 13)). The value, 780 mV is calculated from pH 13*59.9 mV for OER. The other electrochemical experiments are performed with an Ag/AgCl reference electrode, which is also referred to RHE by adding 196 mV for pH = 0.1. All solutions were prepared using Millipore water (18.2 MΩ.cm) and the cell temperature was maintained at 27 $^{\circ}$C. The X-ray photoelectron spectra were collected by Multilab 2000 (Thermoscientific UK) and atomic force microscopy was performed on Agilent 5500 instrument in contact mode.

Part (S.b): Treatment with Fenton reagent

For the treatment of the mechanically-polished gold surface (mp-Au) with the hydroxyl radicals produced from the Fenton reagent, Scholz' procedure was followed [A.M.Nowicka, U.Hasse, M.Hermes, F.Scholz, Angew. Chem. Int. Ed., 2010, 49, 1061–1063]. The Fenton reagent was prepared by mixing 1mM of EDTA, 1mM of Mohr salt dissolved in 10 mM of acetate buffer (pH 4.3). An aliquot of 10 ml of the above solution was taken in a 15 ml amber vial and 10 mM of H_2O_2 added. Bubble formation was noticed immediately after the addition of H_2O_2. The bubble formation is indicative of hydroxyl radical production. The gold electrode was exposed to this Fenton Reagent for varying time durations.

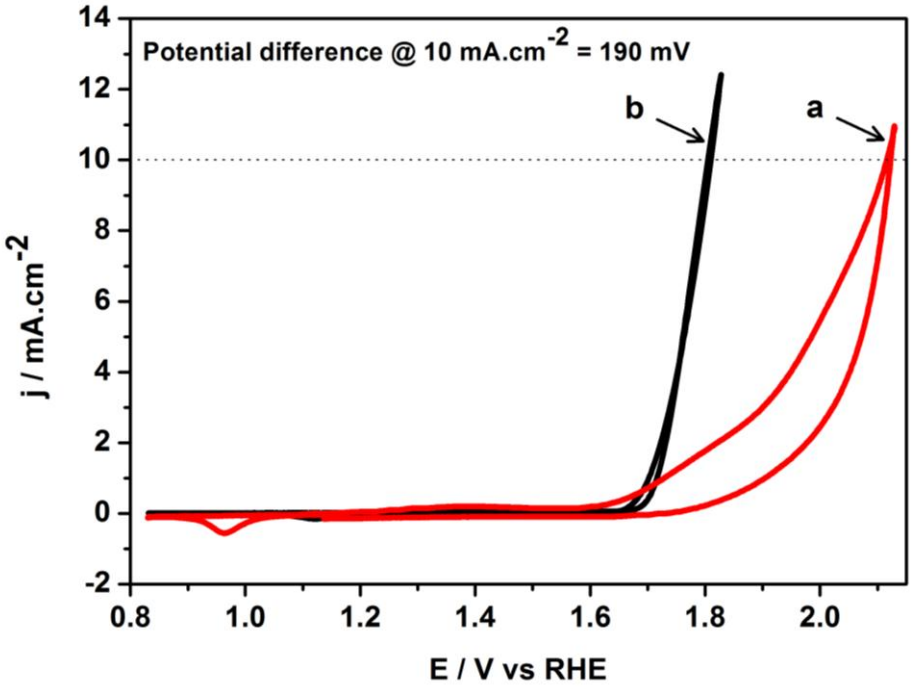
Part (S.c): AFM Analysis

Surface smoothening was confirmed by a non-electrochemical technique like atomic force microscopy (Fig.S2a), which yielded reduced values for the roughness factor after Fenton-treatment of the gold surface. The surface roughness profile decreases with increasing exposure to the Fenton reagent (line profile, Fig.S2b). Root mean square roughness profile (Rq) from the AFM analysis shows that mp-Au surface is associated with Rq of 24.5 nm, and the surfaces after Fenton-treatment for 10 minutes: 4.26 nm, 30 minutes: 1.83 nm, and 60 minutes: 1.48 nm respectively.

Part (S.d): Nickel deposition on Au surface

Nickel was deposited on a 1.6 dia gold disk electrode galvanostatically from a solution of 10 mM nickel(II)nitrate hexahydrate + 1 M sodium acetate with the passage of 1 µA current for 50 s deposition time (50 µC) and then the electrode was rinsed thoroughly in Millipore water.

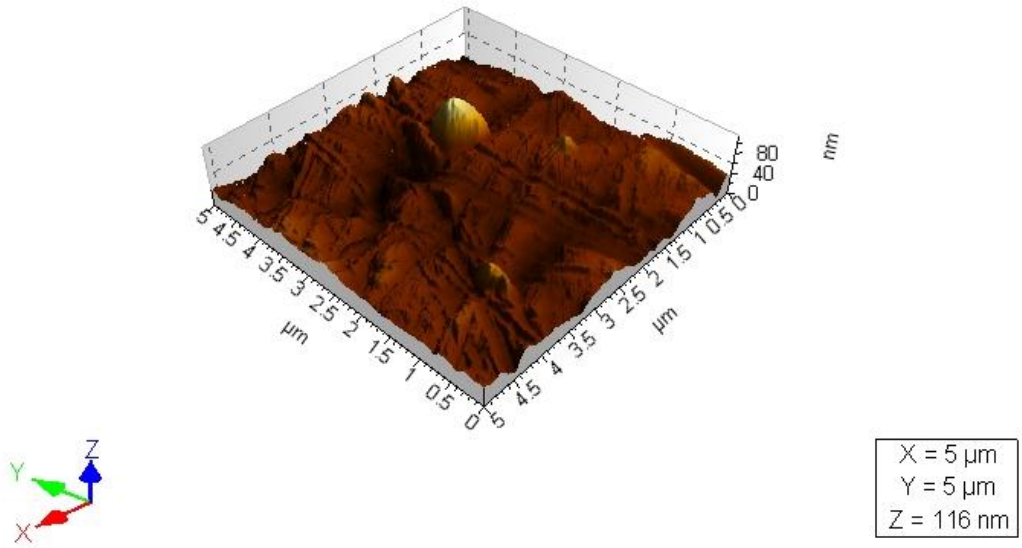
Figure S1



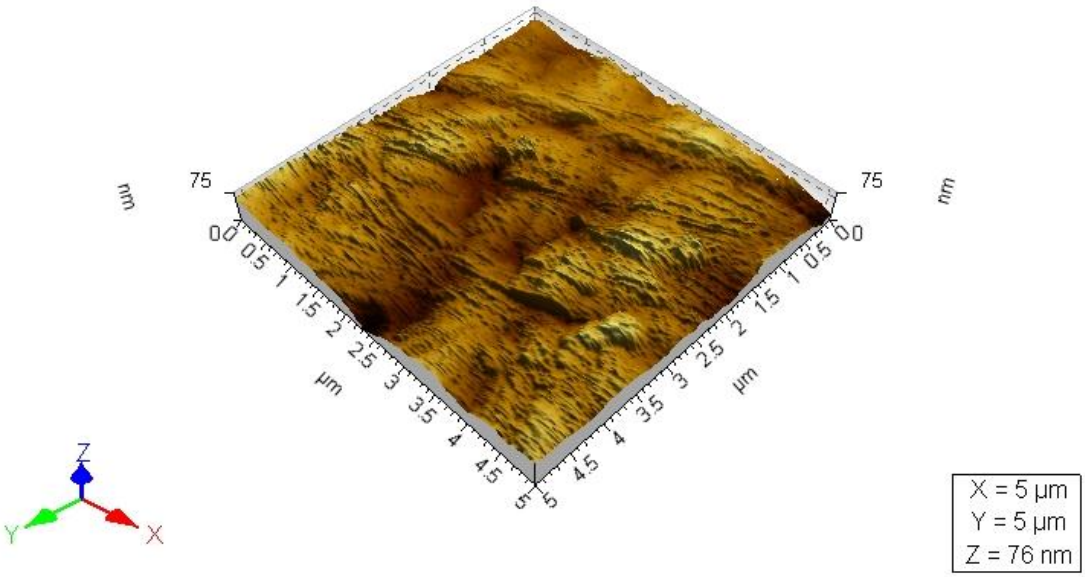
Cyclic voltammograms of mp-Au surface (a), ft-Au surface (b) measured at the scan rate of 10 mV s^{-1} in 0.1 M NaOH. The potential is compared at a fixed current density of 10 $mA.cm^{-2}$.

Figure S2a

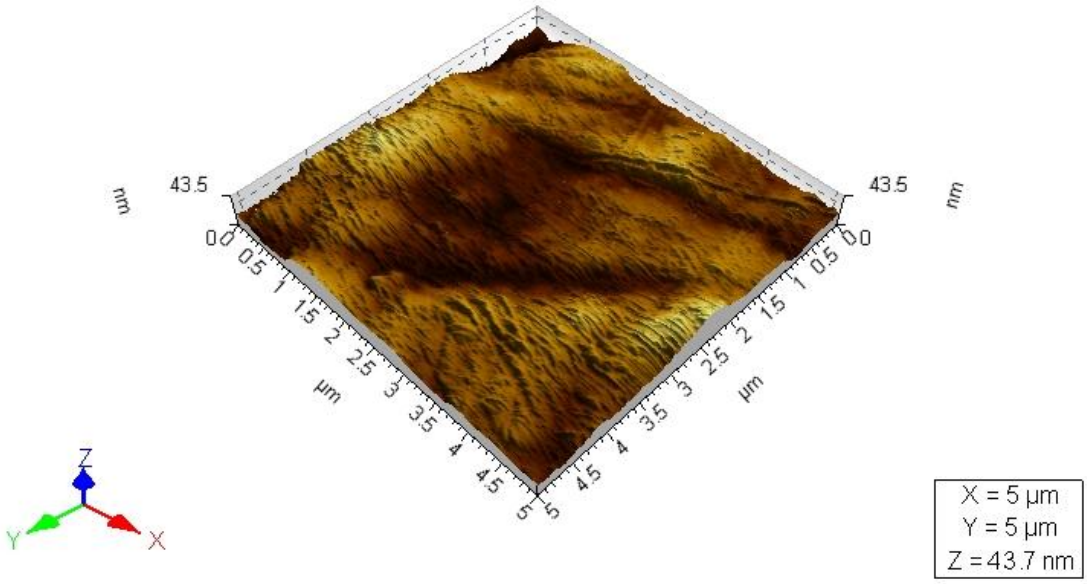
(A)



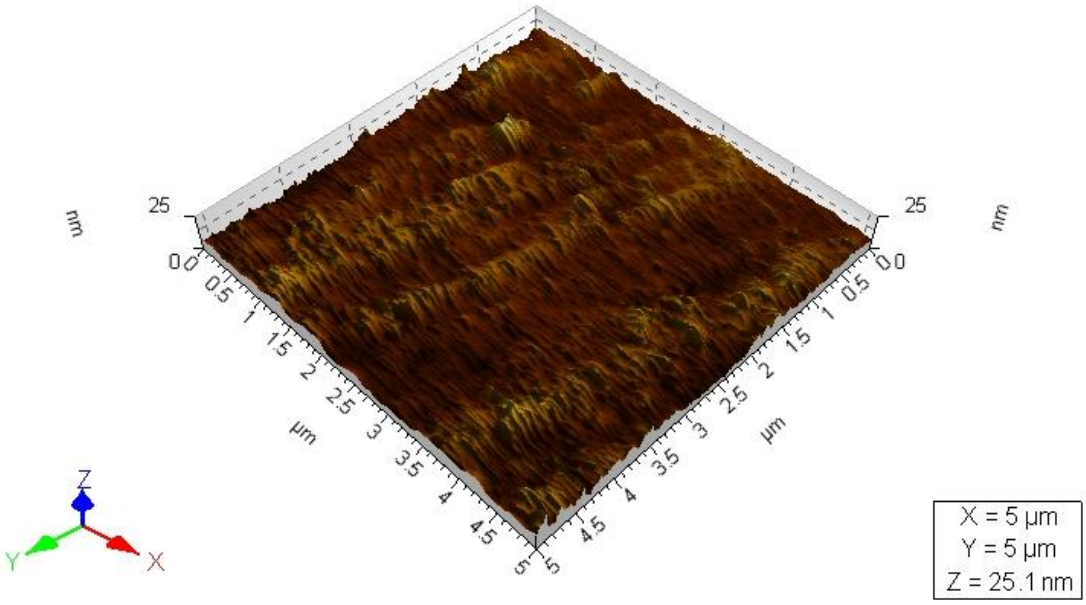
(B)



(C)



(D)



3D AFM image of (A) mp-Au; ft-Au, after Fenton-treatment for (B) 10; (C) 30; (D) 60 minutes

Figure S2b

(A)

ISO 4287			
Amplitude parameters - Roughness profile			
Rp	50.3	nm	*Rp: Maximum Peak Height of the roughness profile.*
Rv	37.1	nm	*Rv: Maximum Valley Depth of the roughness profile.*
Rz	87.4	nm	*Rz: Maximum Height of roughness profile.*
Rc	87.4	nm	*Rc: Mean height of the roughness profile elements.*
Rt	87.4	nm	*Rt: Total Height of roughness profile.*
Ra	19.7	nm	*Ra: Arithmetic Mean Deviation of the roughness profile.*
Rq	24.5	nm	*Rq: Root-Mean-Square (RMS) Deviation of the roughness profile.*
Rsk	0.842		*Rsk: Skewness of the roughness profile.*
Rku	2.47		*Rku: Kurtosis of the roughness profile.*
Material Ratio parameters - Roughness profile			
Rmr	100	%	*Rmr: Relative Material Ratio of the roughness profile.*
Rdc	47.6	nm	*Rdc: roughness profile Section Height difference*

(B)

ISO 4287			
Amplitude parameters - Roughness profile			
Rp	8.70	nm	*Rp: Maximum Peak Height of the roughness profile.*
Rv	8.36	nm	*Rv: Maximum Valley Depth of the roughness profile.*
Rz	17.1	nm	*Rz: Maximum Height of roughness profile.*
Rc	*****	nm	*Rc: Mean height of the roughness profile elements.*
Rt	17.1	nm	*Rt: Total Height of roughness profile.*
Ra	3.70	nm	*Ra: Arithmetic Mean Deviation of the roughness profile.*
Rq	4.26	nm	*Rq: Root-Mean-Square (RMS) Deviation of the roughness profile.*
Rsk	0.263		*Rsk: Skewness of the roughness profile.*
Rku	2.01		*Rku: Kurtosis of the roughness profile.*
Material Ratio parameters - Roughness profile			
Rmr	100	%	*Rmr: Relative Material Ratio of the roughness profile.*
Rdc	8.41	nm	*Rdc: roughness profile Section Height difference*

(C)

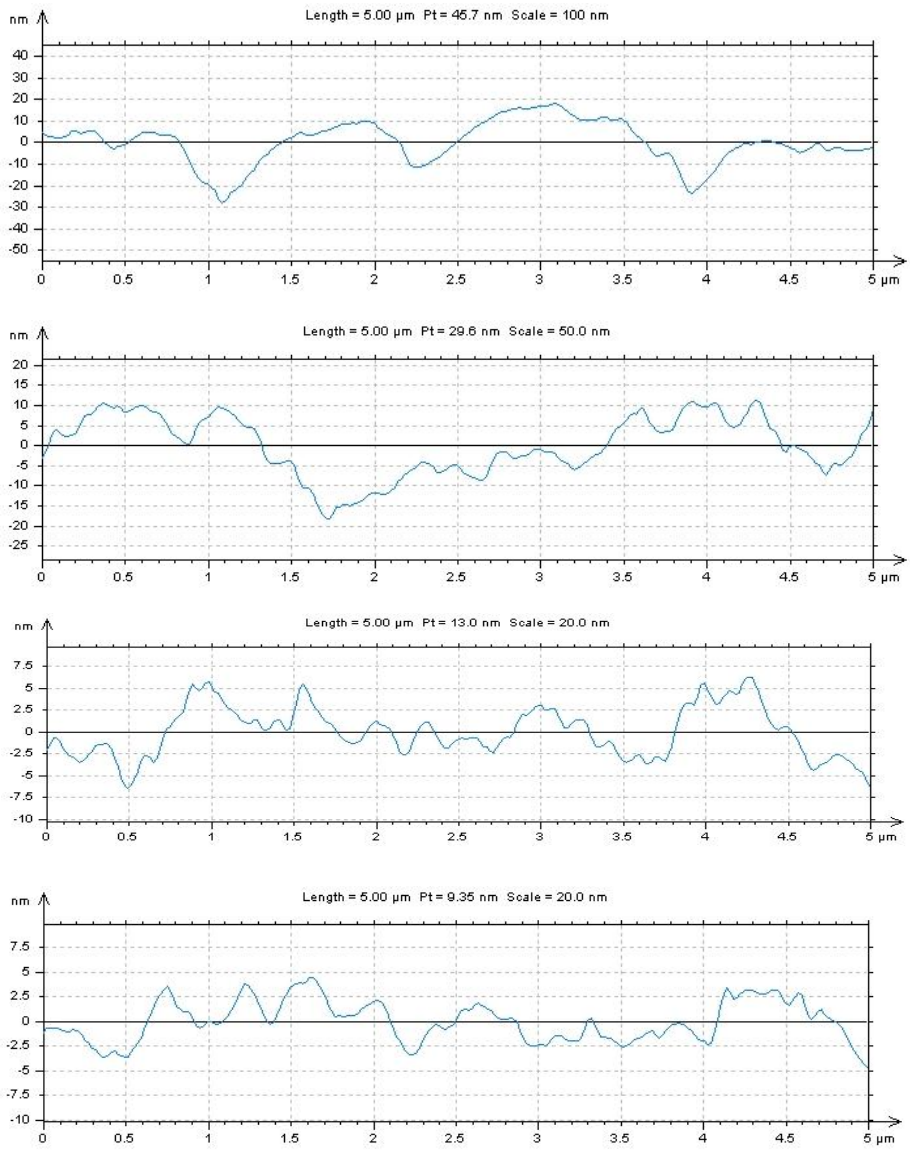
ISO 4287			
Amplitude parameters - Roughness profile			
Rp	4.64	nm	*Rp: Maximum Peak Height of the roughness profile.*
Rv	3.66	nm	*Rv: Maximum Valley Depth of the roughness profile.*
Rz	8.31	nm	*Rz: Maximum Height of roughness profile.*
Rc	3.73	nm	*Rc: Mean height of the roughness profile elements.*
Rt	8.31	nm	*Rt: Total Height of roughness profile.*
Ra	1.49	nm	*Ra: Arithmetic Mean Deviation of the roughness profile.*
Rq	1.83	nm	*Rq: Root-Mean-Square (RMS) Deviation of the roughness profile.*
Rsk	0.249		*Rsk: Skewness of the roughness profile.*
Rku	2.63		*Rku: Kurtosis of the roughness profile.*
Material Ratio parameters - Roughness profile			
Rmr	100	%	*Rmr: Relative Material Ratio of the roughness profile.*
Rdc	3.01	nm	*Rdc: roughness profile Section Height difference*

(D)

ISO 4287			
Amplitude parameters - Roughness profile			
Rp	3.27	nm	*Rp: Maximum Peak Height of the roughness profile.*
Rv	3.55	nm	*Rv: Maximum Valley Depth of the roughness profile.*
Rz	6.82	nm	*Rz: Maximum Height of roughness profile.*
Rc	4.59	nm	*Rc: Mean height of the roughness profile elements.*
Rt	6.82	nm	*Rt: Total Height of roughness profile.*
Ra	1.22	nm	*Ra: Arithmetic Mean Deviation of the roughness profile.*
Rq	1.48	nm	*Rq: Root-Mean-Square (RMS) Deviation of the roughness profile.*
Rsk	0.047		*Rsk: Skewness of the roughness profile.*
Rku	2.64		*Rku: Kurtosis of the roughness profile.*
Material Ratio parameters - Roughness profile			
Rmr	100	%	*Rmr: Relative Material Ratio of the roughness profile.*
Rdc	2.73	nm	*Rdc: roughness profile Section Height difference*

AFM parameters of (A) mp-Au; ft-Au, after Fenton-treatment for (B) 10; (C) 30; (D) 60 minutes

Figure S2c



(A), 50 nm depth to height

(B), 25 nm depth to height

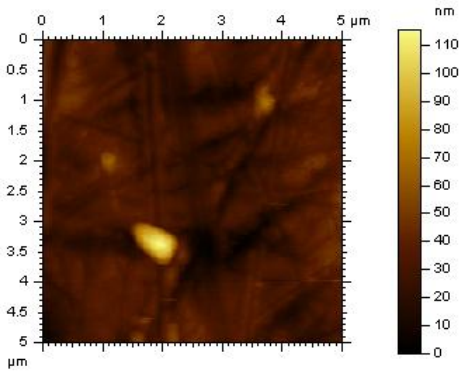
(C), 12 nm depth to height

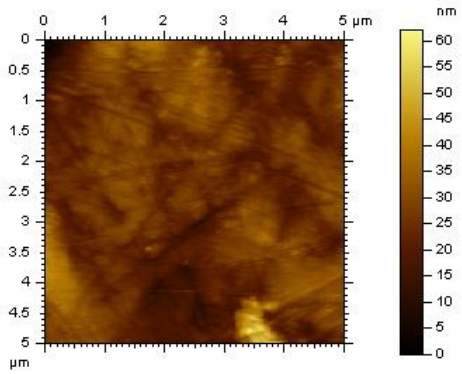
(D), 8 nm depth to height

2D AFM line profile of (A) mp-Au; ft-Au, after Fenton-treatment for (B) 10; (C) 30; (D) 60 minutes

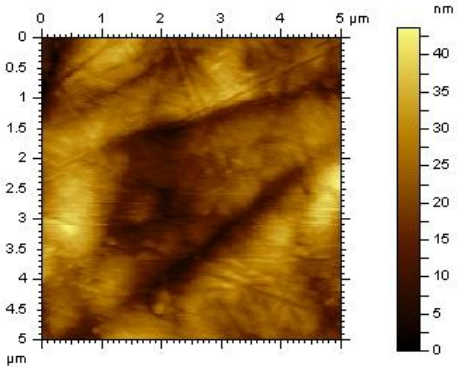
Figure S2d

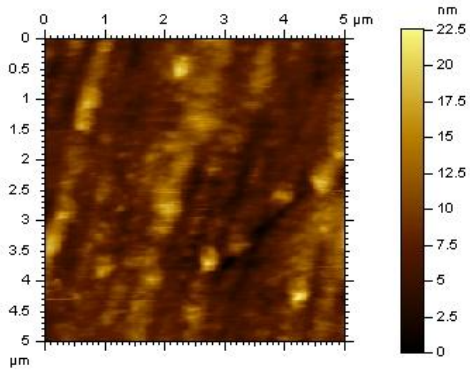
(A) (B)





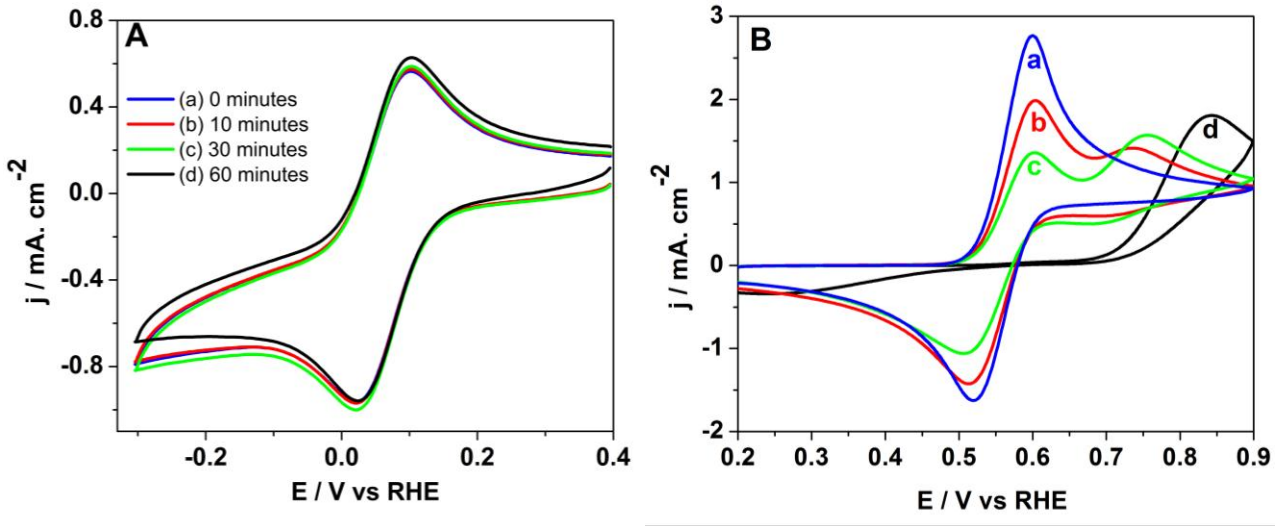
(C) (D)





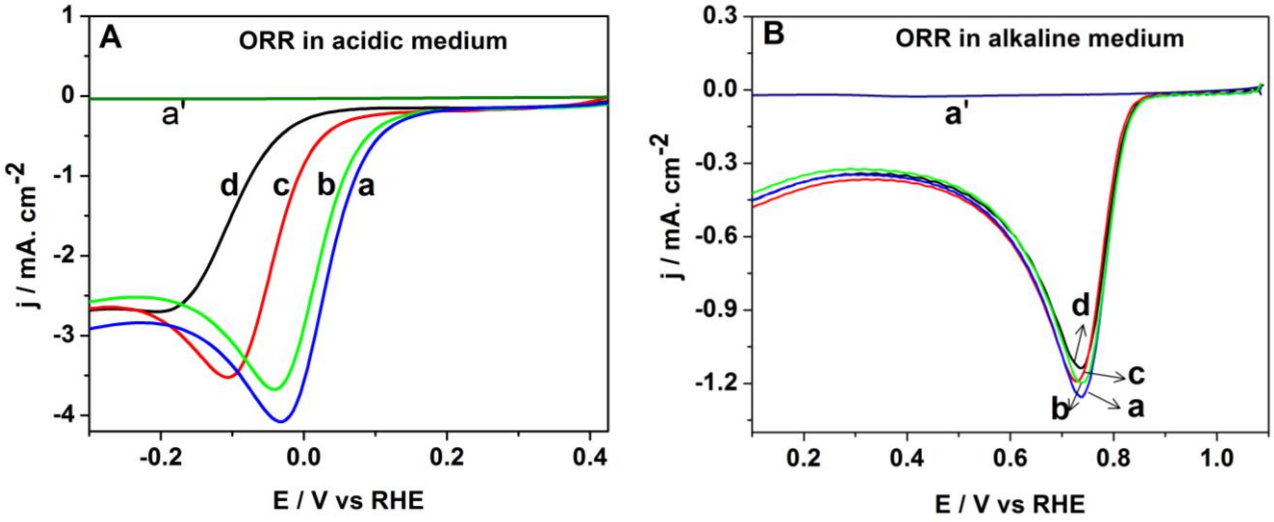
2D AFM image of (A) mp-Au; ft-Au, after Fenton-treatment for (B) 10; (C) 30; (D) 60 minutes

Figure S3



(A) Cyclic voltammetric response of 10 mM of $Ru(NH_3)_6^{2+/3+}$ redox on (a) mp-Au, (b, c & d) ft-Au surfaces (Fenton treatment time in minutes: (b) 10; (c) 30; (d) 60) measured at a scan rate of 50 mV s^{-1} in 0.1 M sodium perchlorate + 0.1 M perchloric acid. (B) Cyclic voltammetric response of 10 mM hydroquinone redox on (a) mp-Au surface, (b, c & d) ft-Au surfaces (Fenton treatment time in minutes: (b) 10; (c) 30; (d) 60) measured at a scan rate of scan rate of 50 mV s^{-1} in 0.1 M sodium perchlorate + 0.1 M perchloric acid.

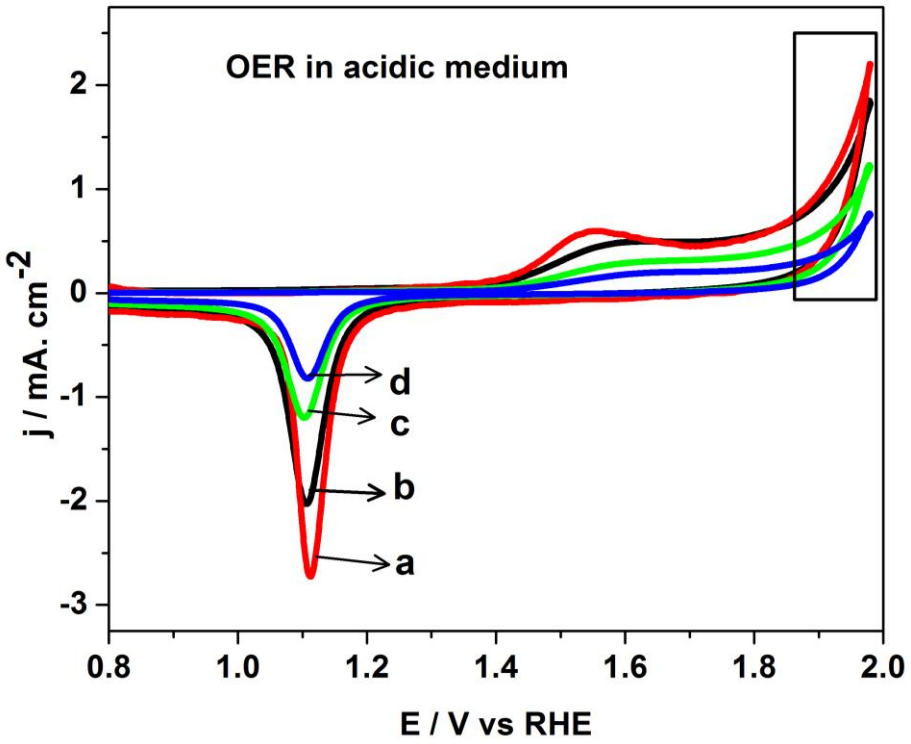
Figure S4



(A) Linear sweep voltammograms of oxygen reduction reaction in oxygen-saturated 0.5 M H_2SO_4 on (a) mp-Au surface; (b, c & d) ft-Au surfaces (Fenton treatment time in minutes: 10 (b); 30 (c); 60 (d)); and oxygen-free solution (deaerated by argon gas) (a'). (B) Linear sweep voltammogram of oxygen reduction reaction in oxygen-saturated 0.1 M NaOH on (a) mp-Au surface; (b, c & d) ft-Au surfaces (Fenton treatment time in minutes: 10 (b); 30 (c); 60 (d)); and oxygen-free solution (deaerated by argon gas) (a'). Scan rate = 50 mV s^{-1}.

In figure S4, the voltammograms are shown for ORR in both acid and alkaline solutions on Fenton treated gold surfaces (differing in exposure time) in oxygen-saturated solutions. In acid solutions, the behavior is that shown by Scholz et al [A.M.Nowicka, U.Hasse, G.Sievers, M.Donten, Z.Stojek, S. Fletcher, F. Scholz, *Angew. Chem. Int. Ed.*, 2010, 49, 3006] whereas in alkaline solutions, the peak potential for ORR remains unchanged showing that ORR kinetics are unaffected in the alkaline solutions.

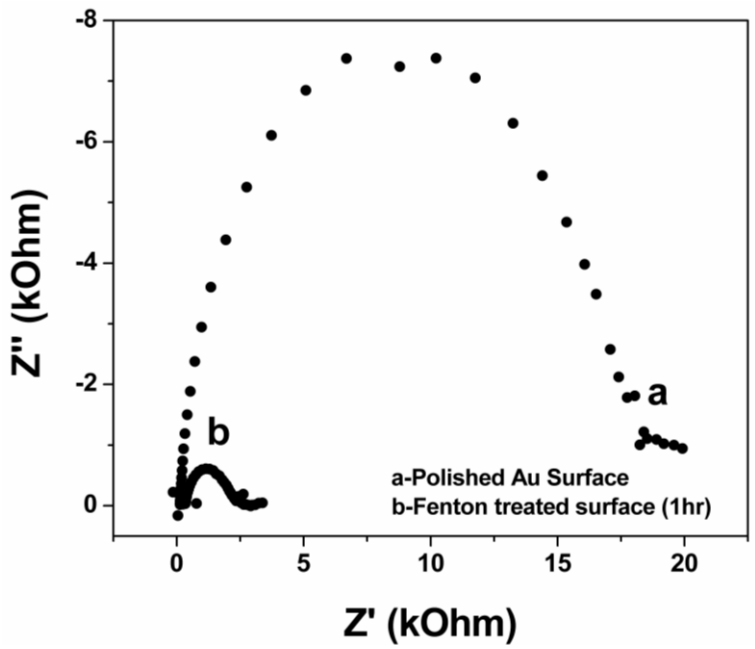
Figure S5



Cyclic voltammograms of (a) mp-Au surface; (b, c & d) ft-Au surfaces (Fenton treatment time in minutes: (b) 10; (c) 30; (d) 60) in 0.5 M H_2SO_4 at a scan rate of 10 mV s^{-1}. [The rectangular box shows decreasing OER current as Fenton treatment time increases].

OER is slower in the acidic medium due to limited surface oxidation (Fig.S5). With the increasing time of exposure to Fenton reagent, OER current falls. These observations are also supported by the studies of Bell et al. [B. S. Yeo, S. L. Klau, P. N. Ross, R. A. Mathies, A. T. Bell, *ChemPhysChem.,* 2010, 11, 1854-1857].

Figure S6



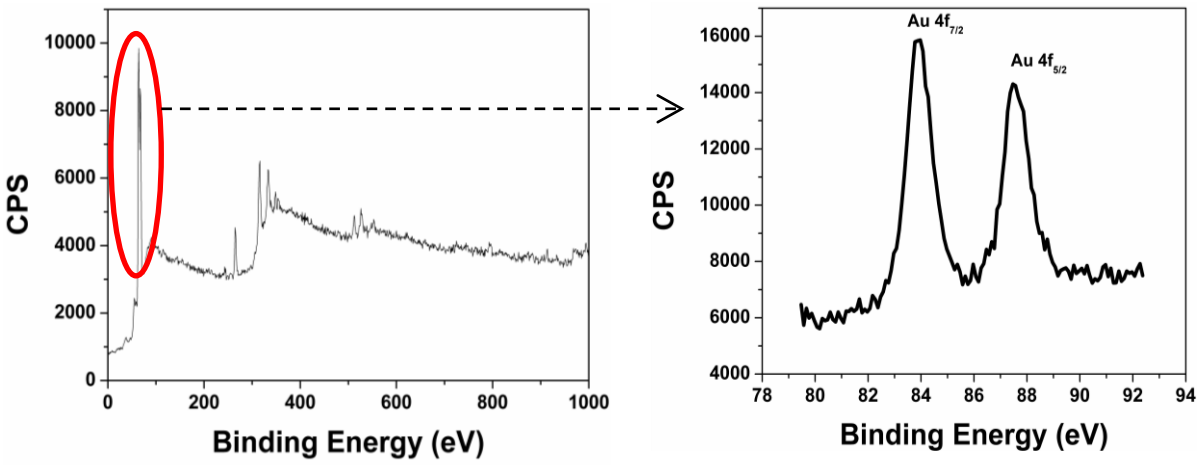
Nyquist plot for OER reaction on (a) mp-, (b) ft-Au surfaces in 0.1 M NaOH (bias potential = 1.62V vs. RHE).

Table S1

S.No	Gold Surface	R_{Ct} (kΩ)	C_{dl} (µF)	Time constant (ms)
1.	Polished	17.85	5.86	100
2.	Fenton-treated	2.65	2.96	7.8

Impedance parameters for mechanically polished and Fenton polished gold surfaces

Figure S7



X-ray photoelectron spectrum of Fenton-treated gold surface (ft-Au)