Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

New findings and the current controversies for the water oxidation by a copper(II)-azo complex: homogeneous or heterogeneous?

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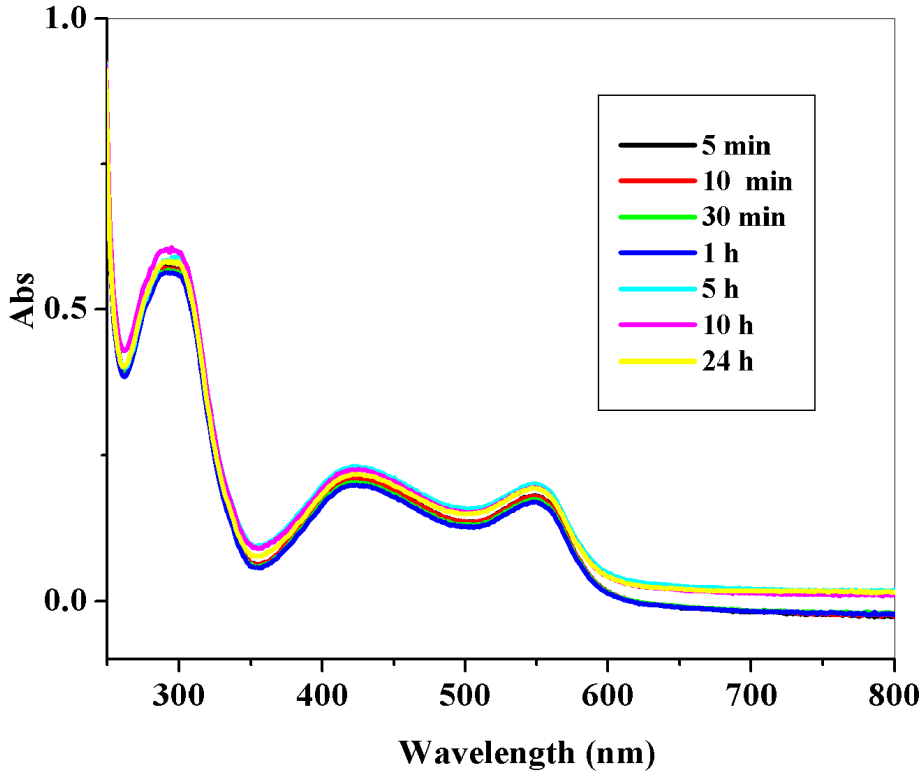
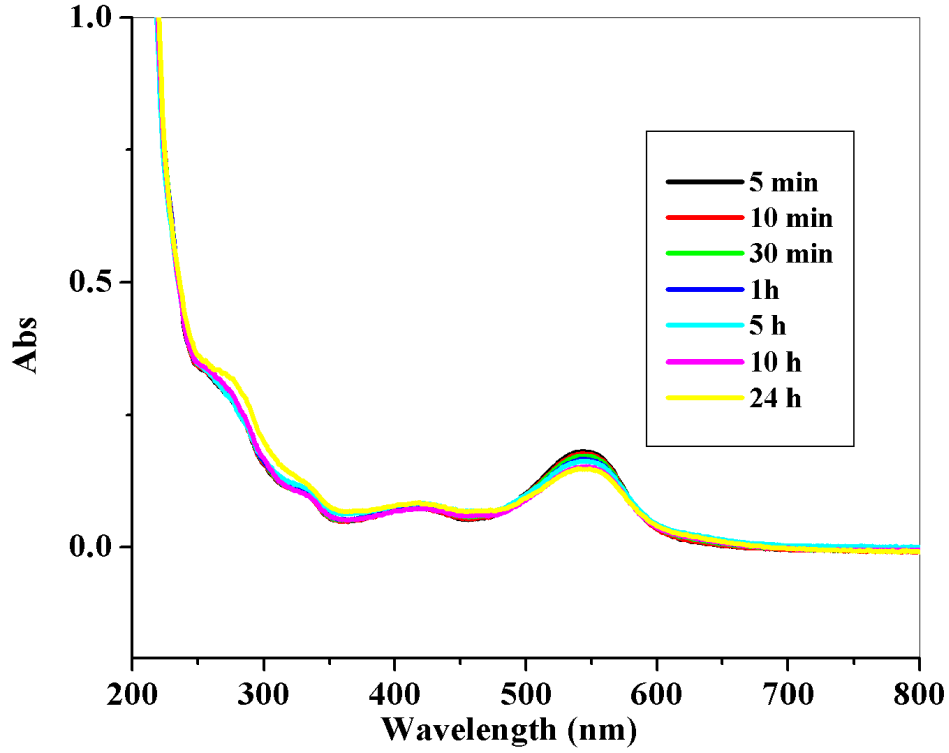

1.0
0.5
0.0
Abs
300
400
500
600
700
800
Wavelength (nm)
5 min
10 min
30 min
1 h
5 h
10 h
24 h

a



b

Fig. S1 UV-Vis for **1** (1.2 mM) at pH ~ 1.0 (using HNO_3) (a) and **1** (0.3 mM) at pH ~ 11.0 (using sodium phosphate as a buffer) (b) at different times. The results show that the main structure of complex is stable at least for a few hours in water.

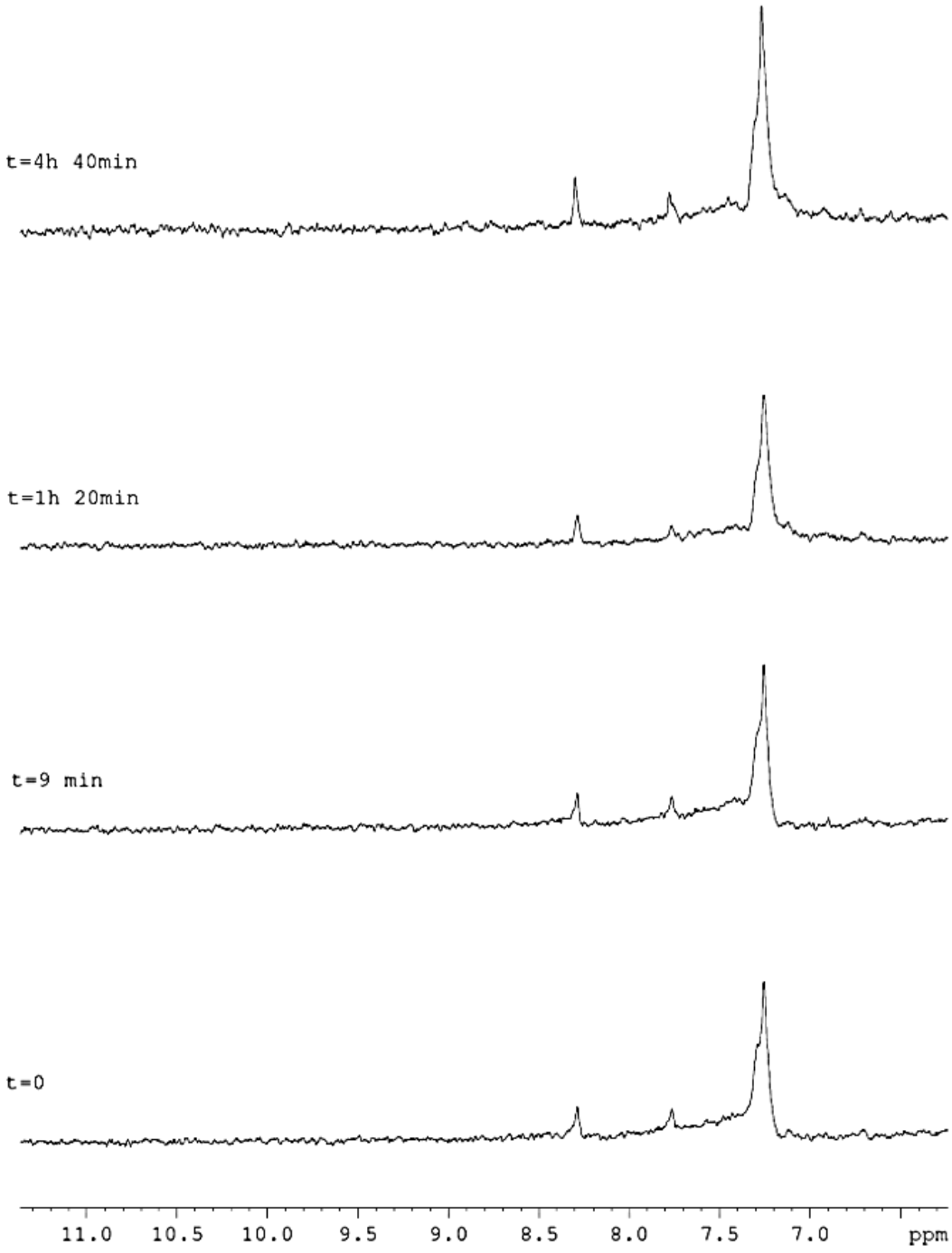
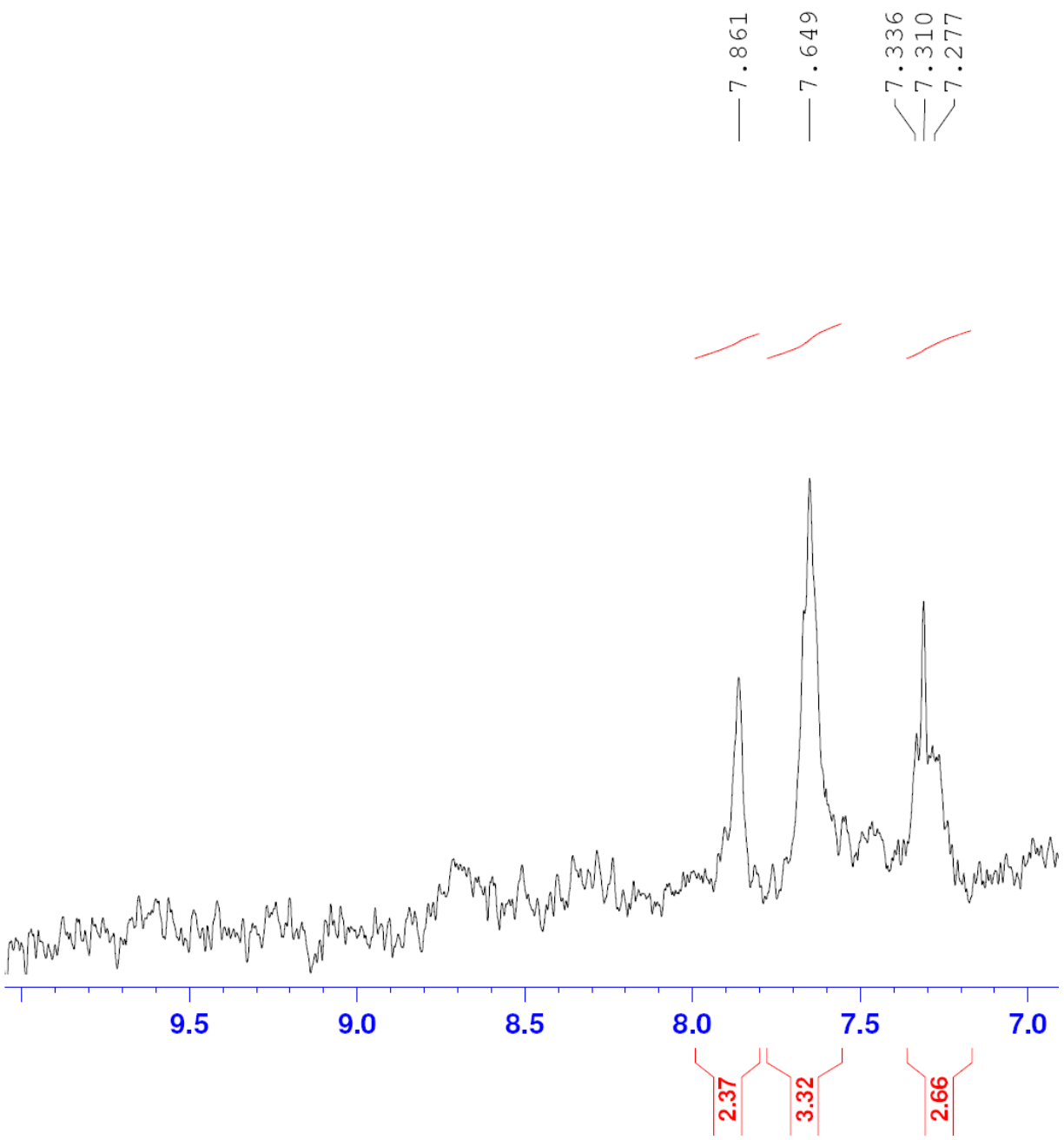
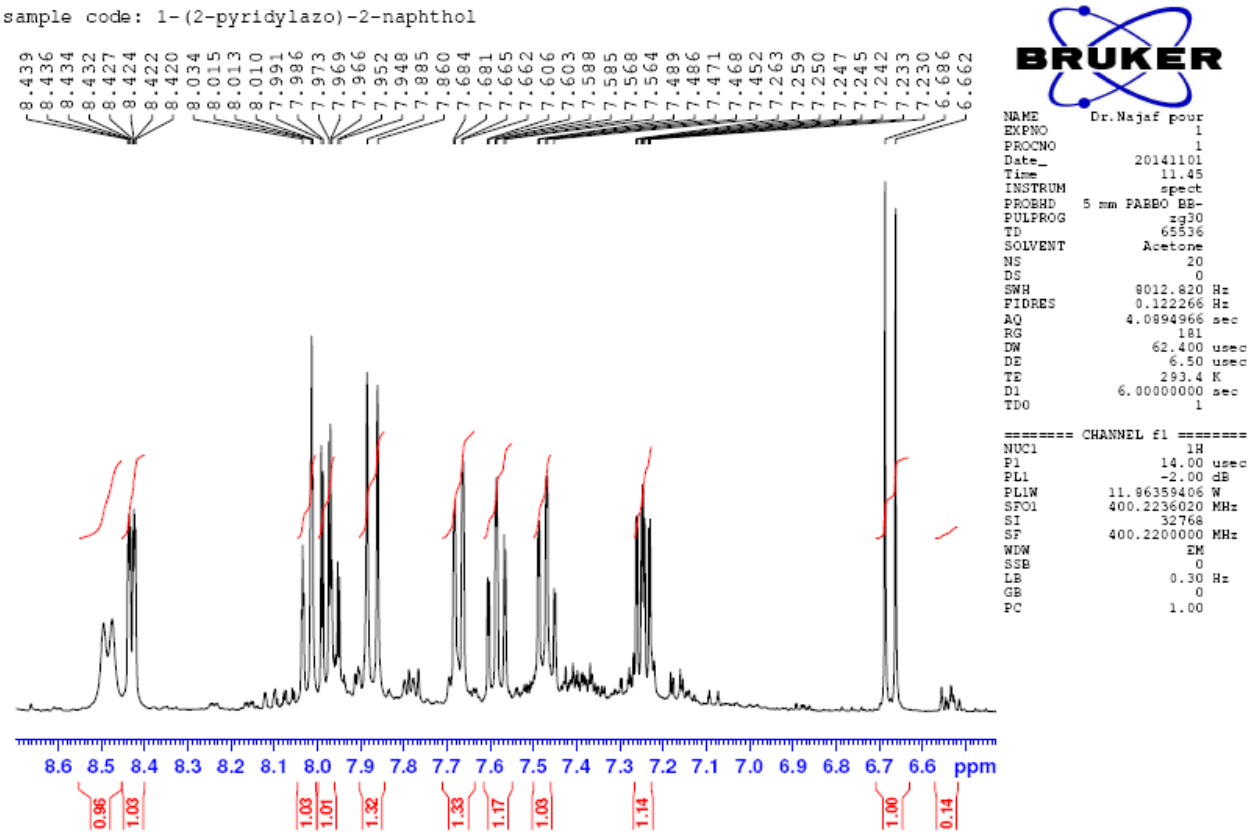


Fig. S2 ^{1}H NMR for **1** (0.5 mM in D_2O). The results show that the complex is stable at least for a few hours in water. The peaks are not sharp because the complex is paramagnetic.



a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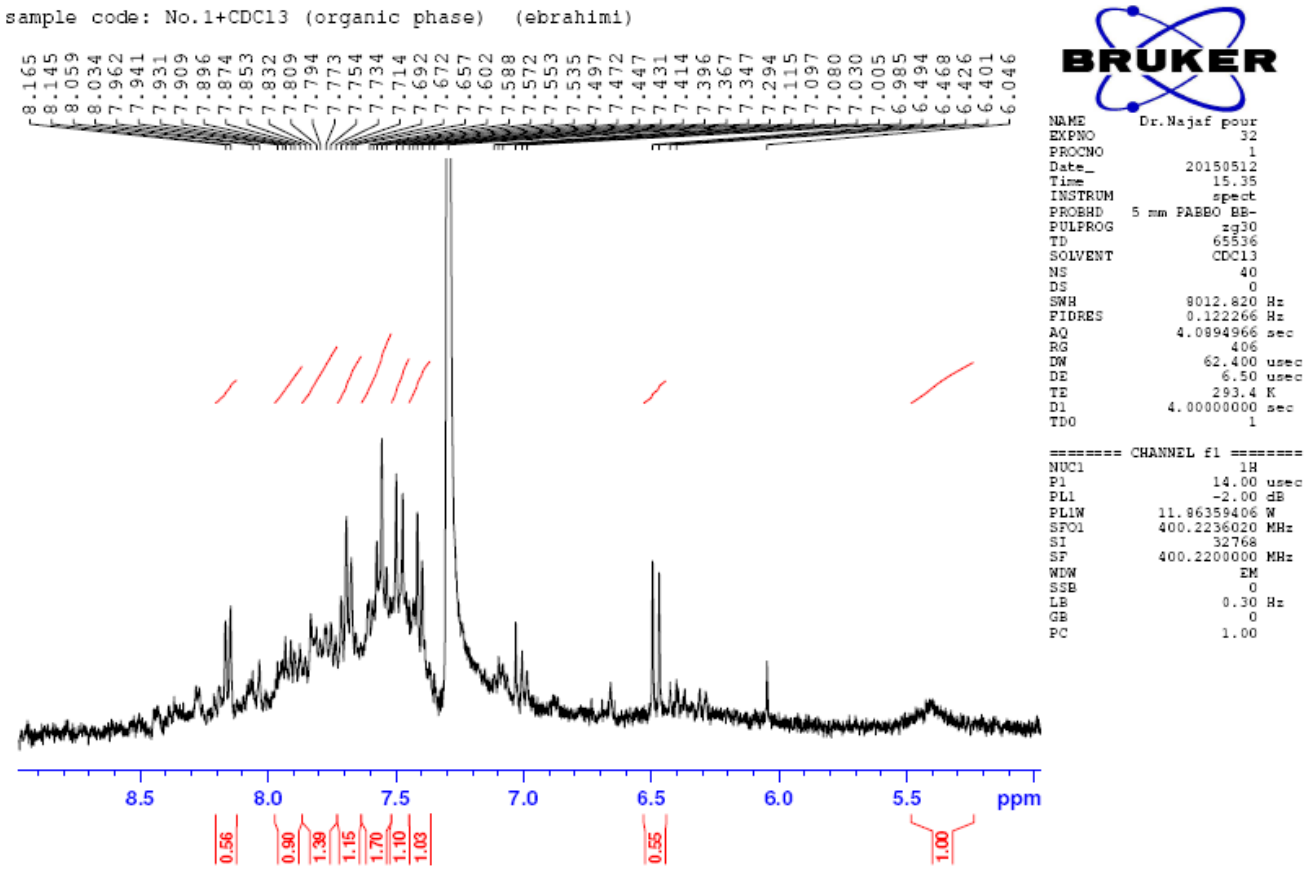
8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 ppm
0.96 1.03 1.03 1.01 1.32 1.33 1.17 1.03 1.14 1.00 0.14
BRUKER
NAME Dr.Najaf pour
EXPNO 1
PROCNO 1
Date_ 20141101
Time 11.45
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 20
DS 0
SWH 9012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 181
DW 62.400 usec
DE 6.50 usec
TE 293.4 K
D1 6.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PL1W 11.86358406 W
SFO1 400.2236020 MHz
SI 32768
SF 400.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

b



c

Fig. S3 ^{1}H NMR for **1** (0.5 mM in D_2O) at pH~ 1 in HNO_3 after one hour. The results show that **1** is stable at least for one hour in this condition. The peaks are not sharp because the complex is paramagnetic (a). ^{1}H NMR for ligand (b) and the extracted ligand by $CHCl_3$ after treatment with Ce(IV) (0.33 mM, 0.5 mL in D_2O) (c).

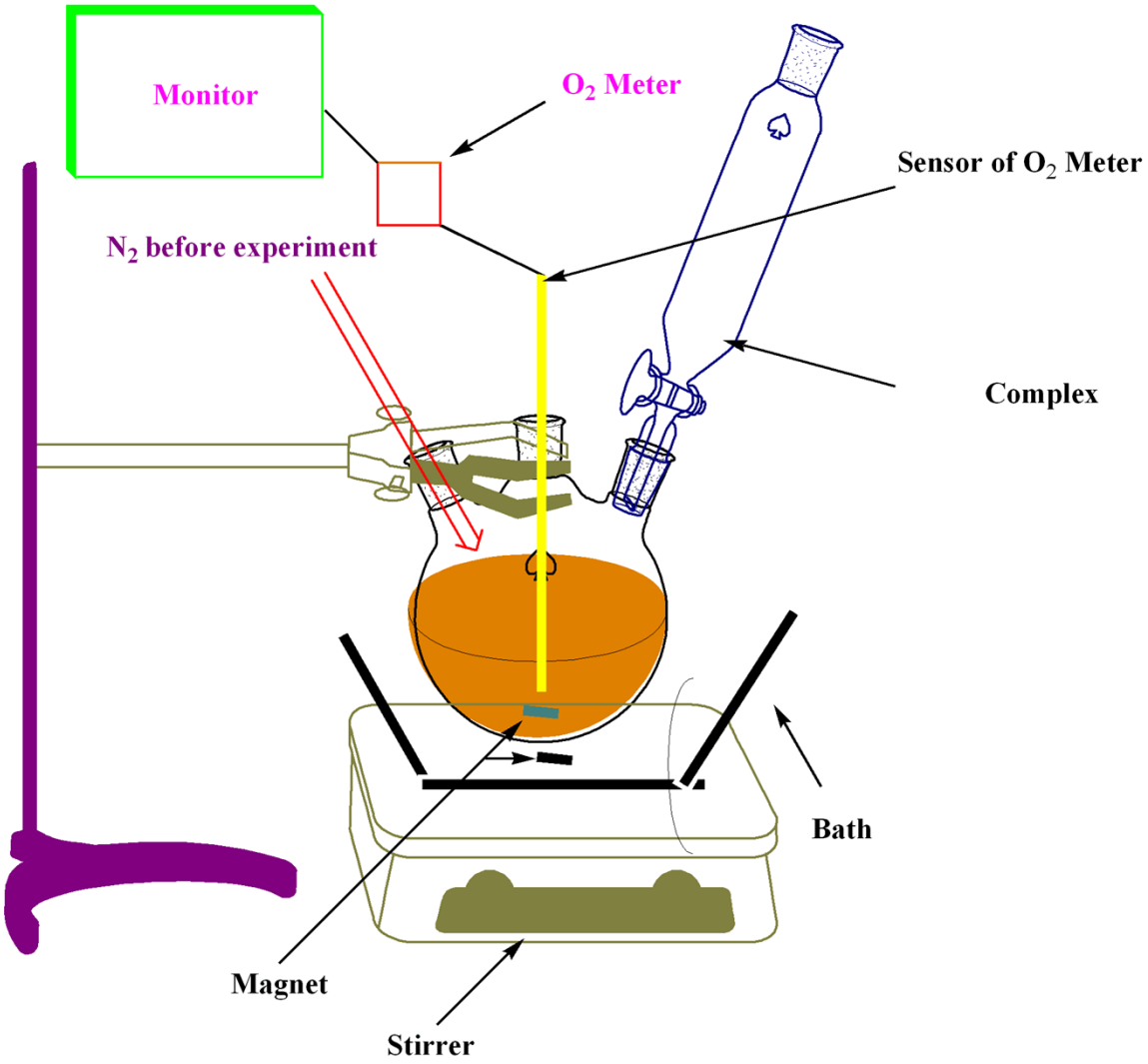
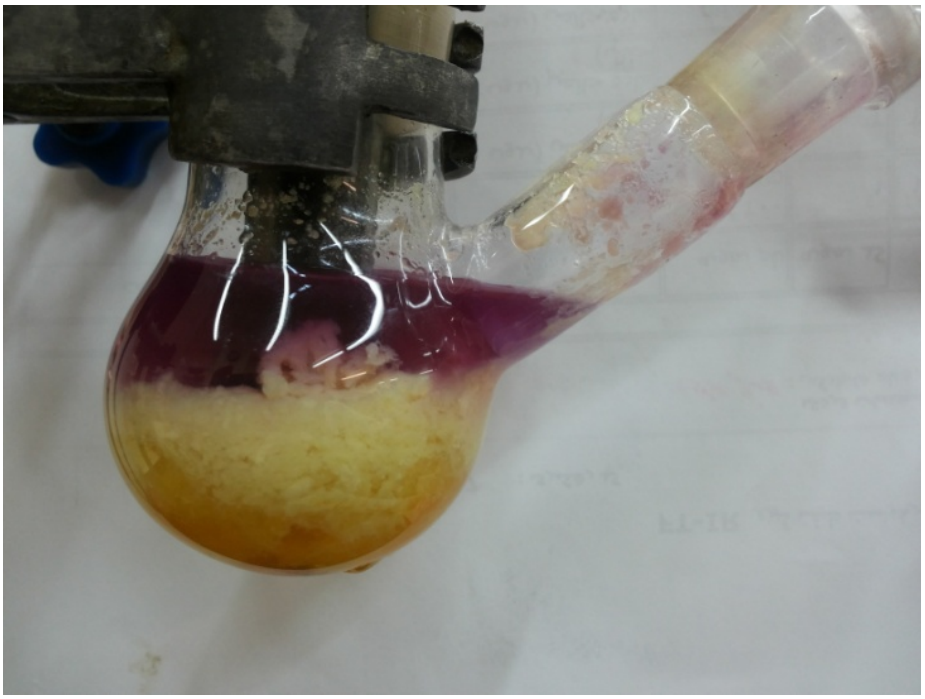
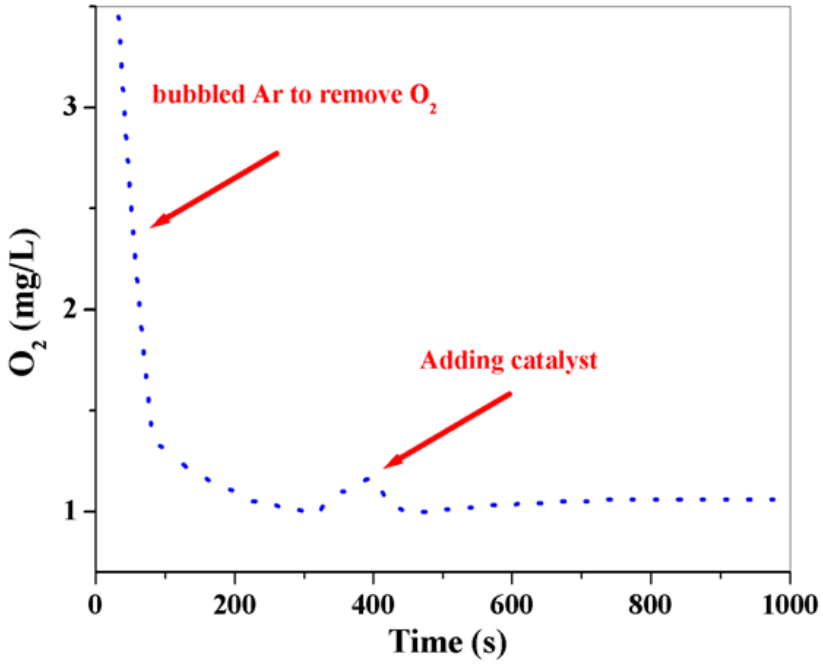


Fig. S4 The reactor setup for oxygen evolution experiments.



a



b

Fig. S5 The reaction of Ce(IV) (0.3 M) with **1** (0.1 mM) at pH=11 (using sodium phosphate as a buffer). The precipitation of cerium is observed in this condition (a) without any oxygen evolution (b).

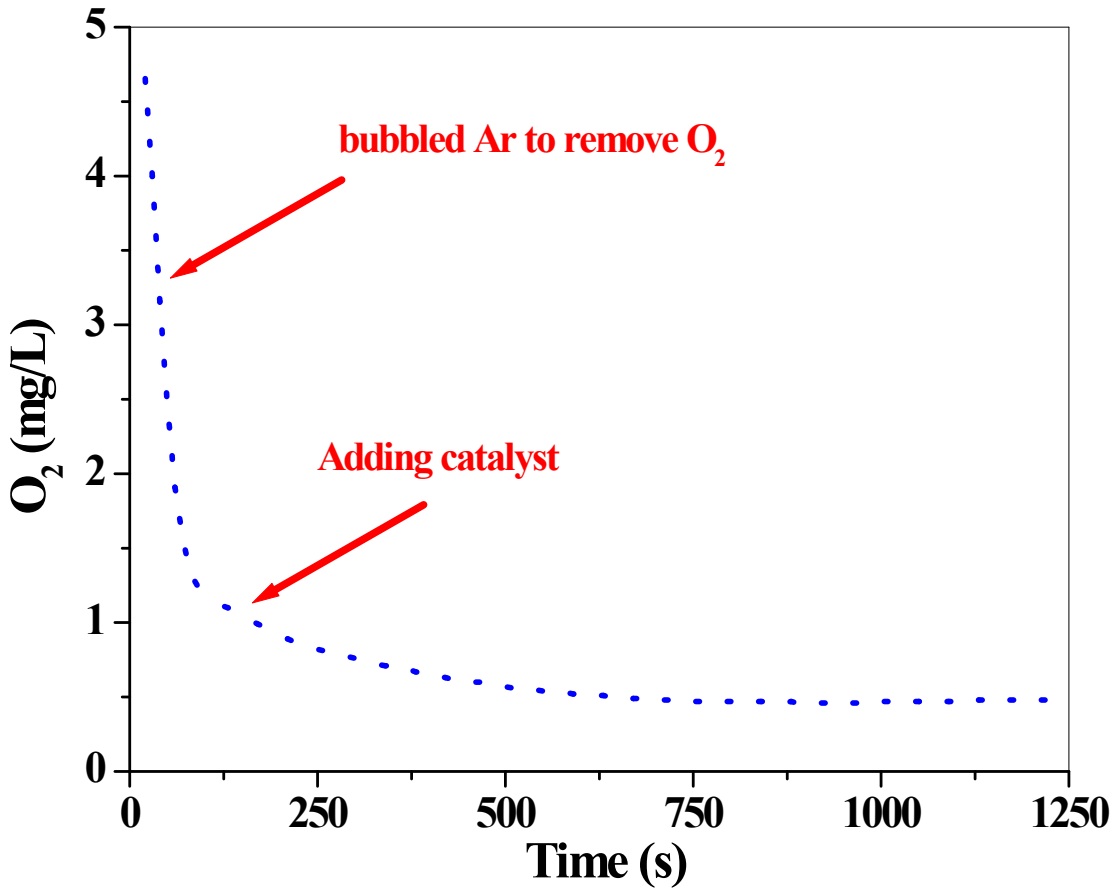


Fig. S6 The oxygen evolution by the reaction of Ce(IV) (0.11 M) at pH=1 in the presence of **1** (0.5 mM).

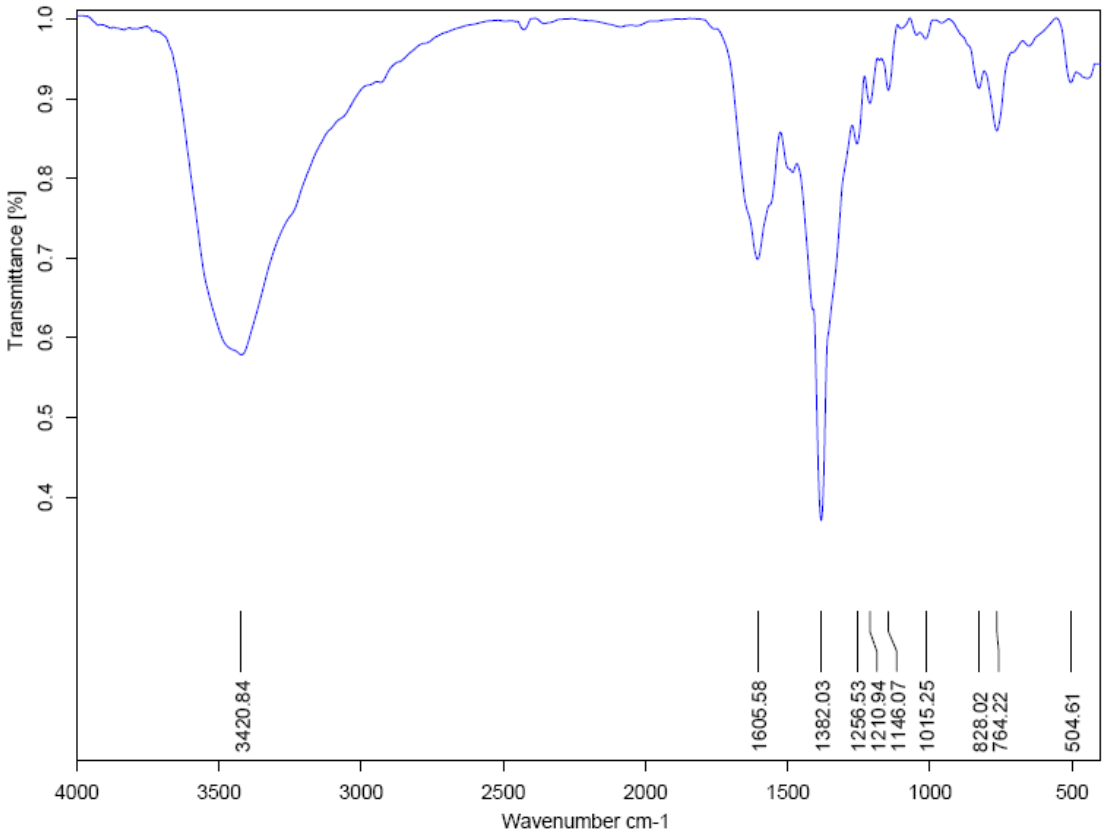


Fig. S7 FTIR spectrum of **1**.

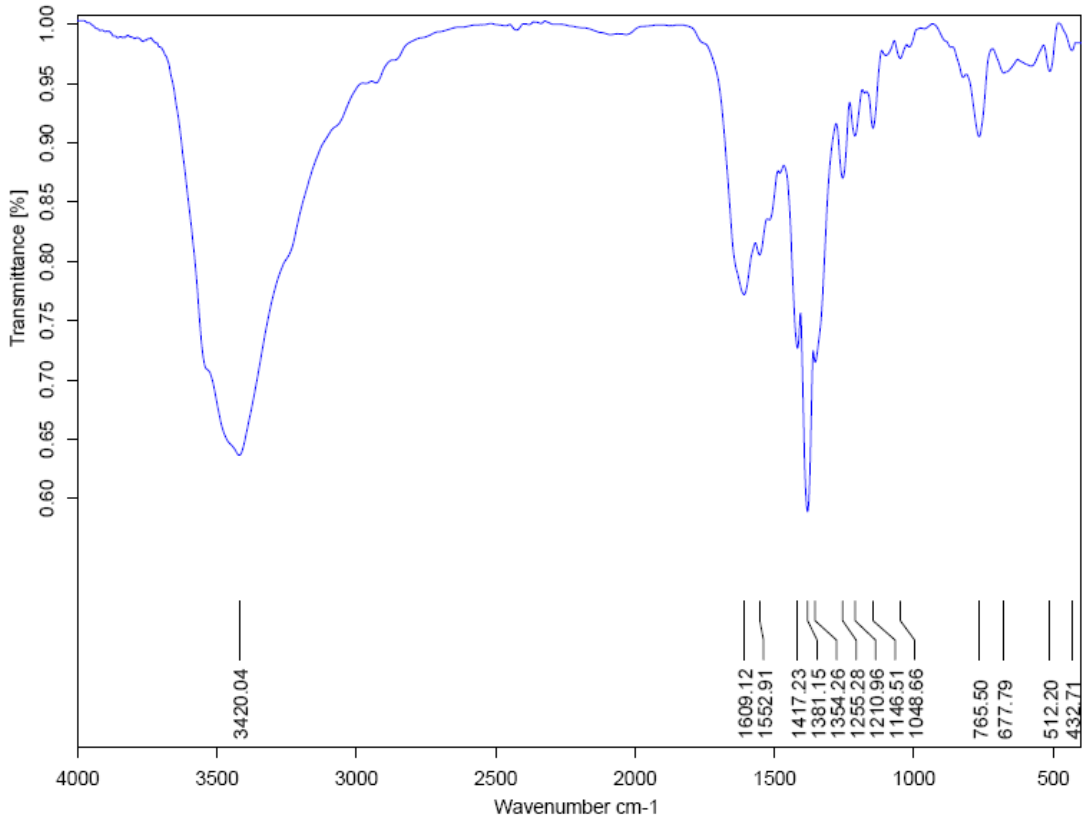


Fig. S8 FTIR spectrum of **1** (20 mg**)** after treatment by Ce(IV) (0.11 M) for 10 minutes.

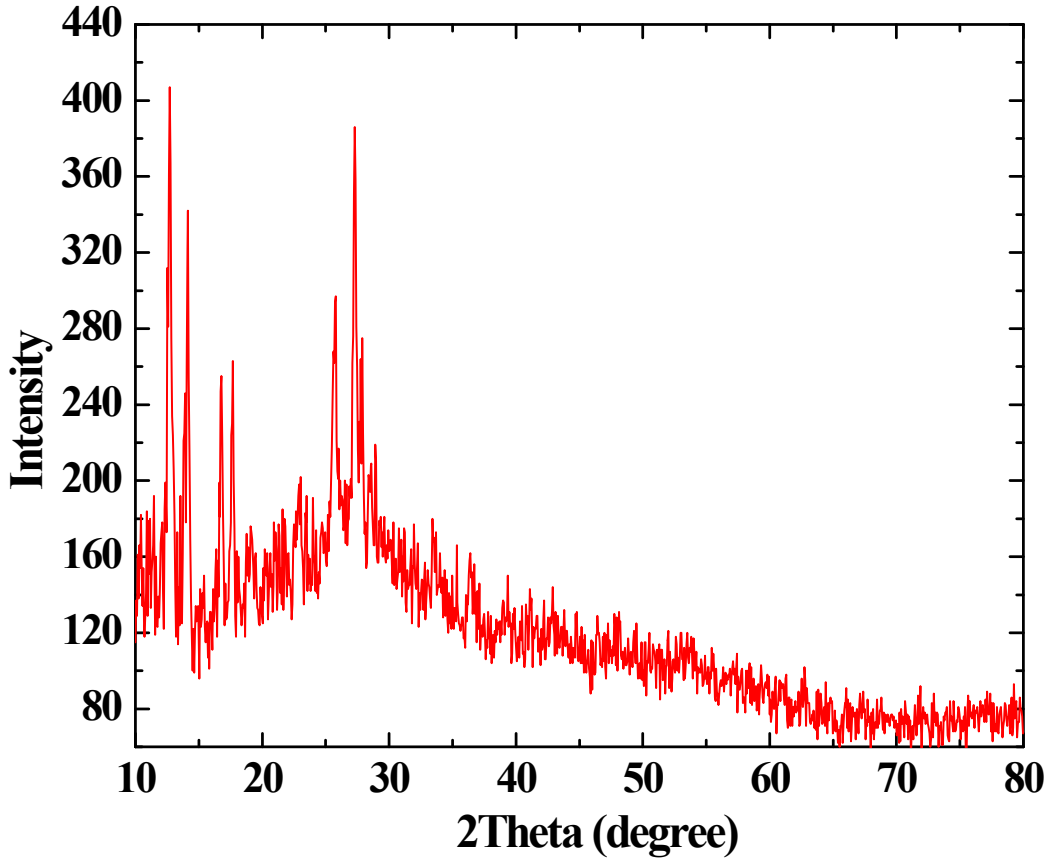


Fig. S9 XRD patterns for **1** (20 mg) after treatment by Ce(IV) (0.11 M) for 10 minutes.

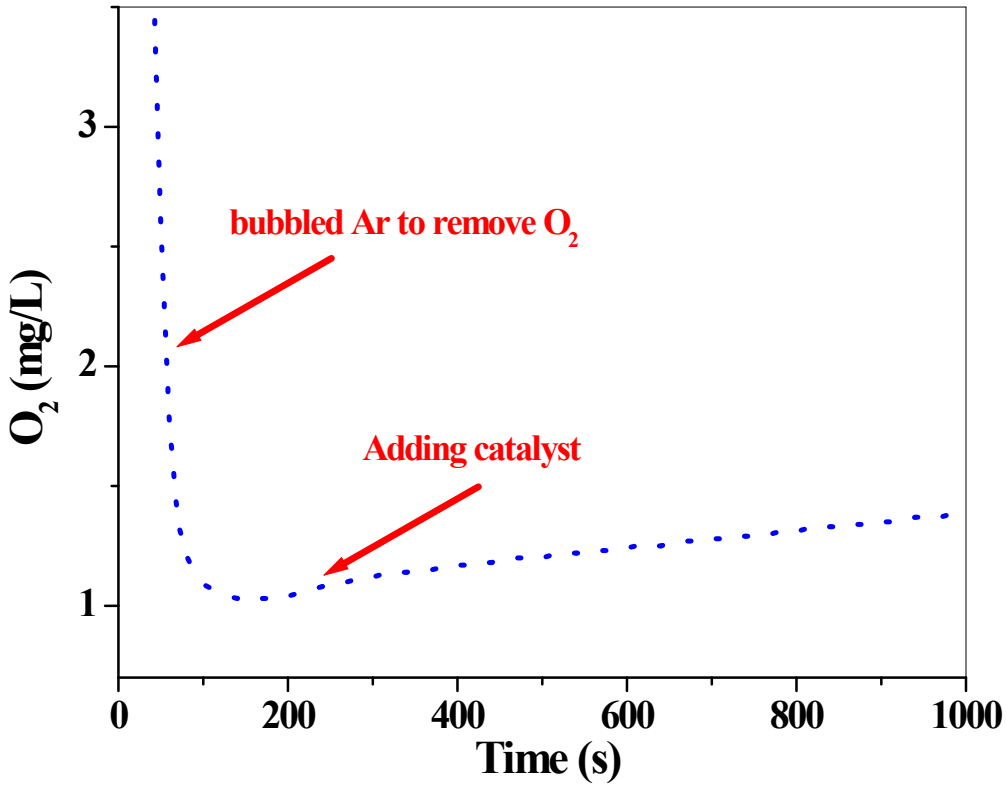
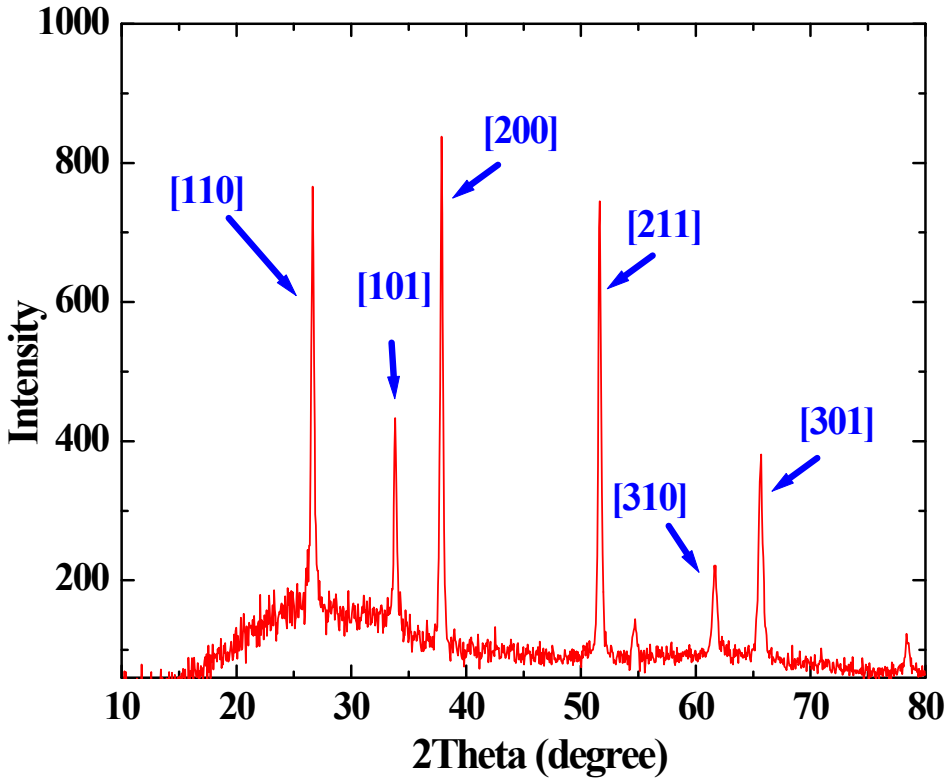
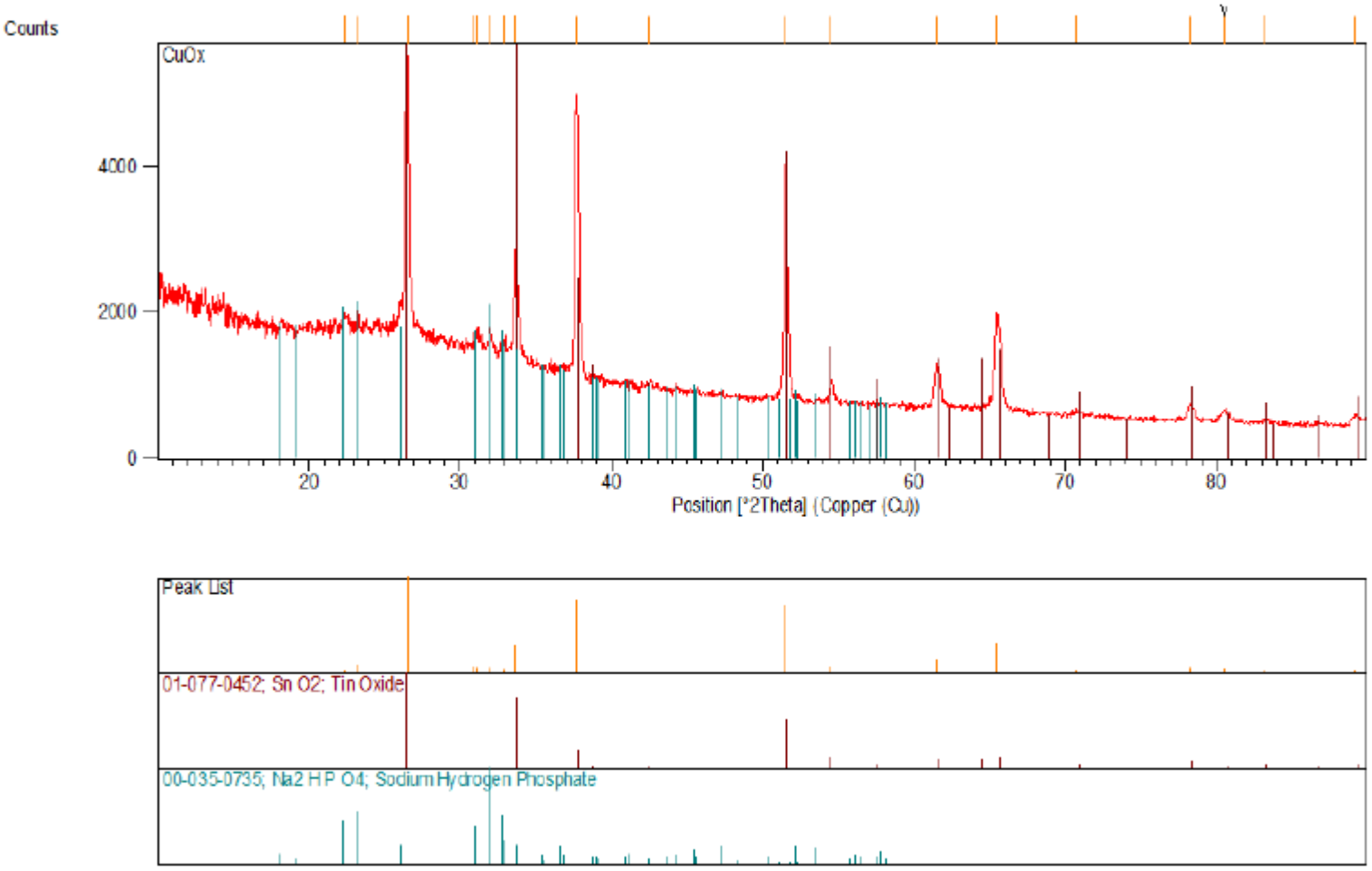


Fig. S10 The oxygen evolution experiment by the reaction of Ce(IV) (0.11 M) at pH=1 in the presence of CuO (50 mg, average particle size < 50 nm, specific surface area 80 m^2/g).

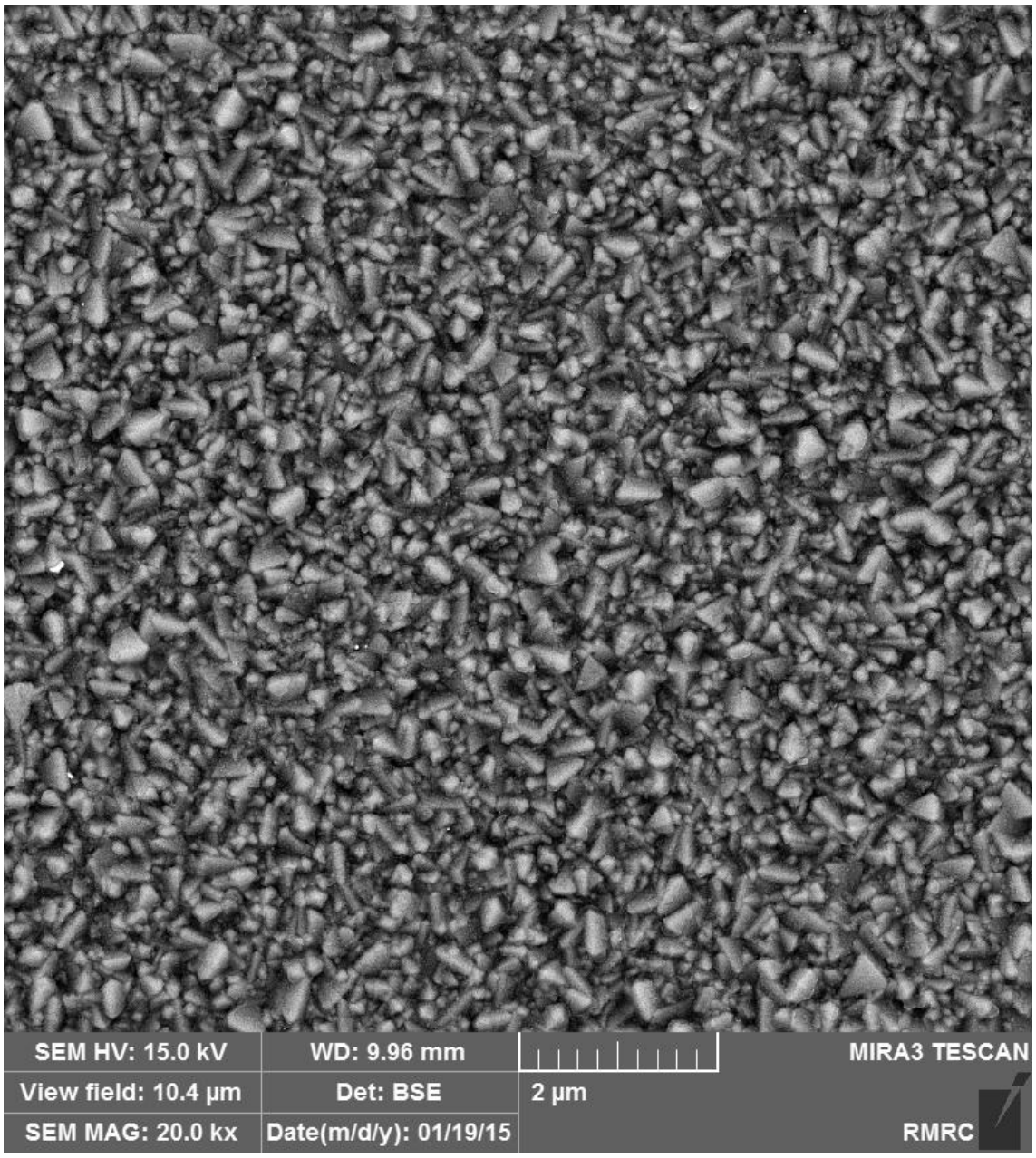

1000
800
600
400
200
Intensity
[110]
[101]
[200]
[211]
[310]
[301]
10
20
30
40
50
60
70
80
2Theta (degree)

a



b

Fig. S11 XRD patterns for appeared film on the FTO electrode in 1 h in the bulk electrolysis of **1** at 1.2 V. Only peaks for FTO are observed and the formed film is amorphous (a). XRD patterns for appeared film on the FTO electrode in 6 h in the bulk electrolysis of **1** at 1.2 V after washing with water to remove **1** (b). Only peaks for FTO and Na_2HPO_4 are observed.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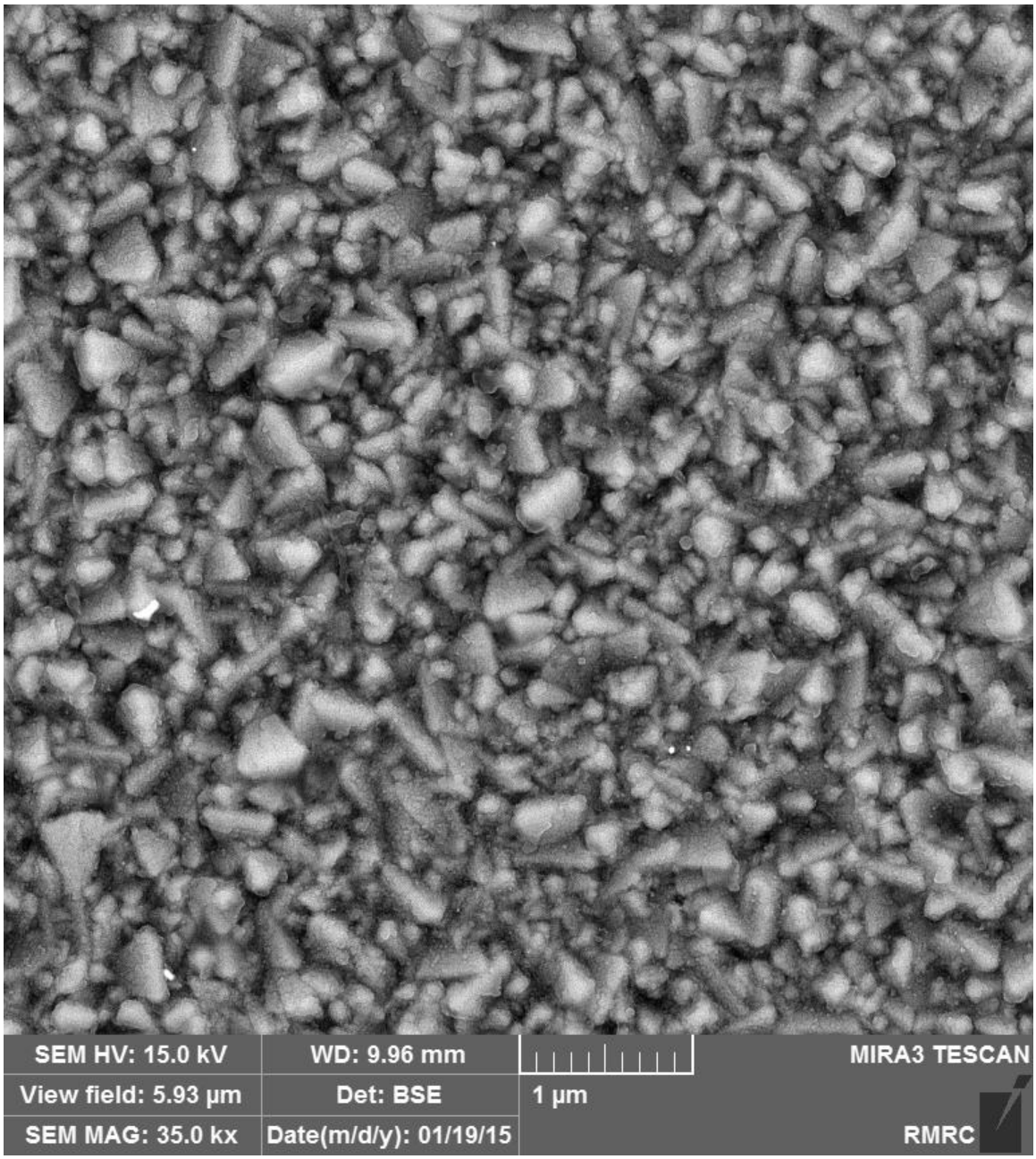
WD: 9.96 mm
MIRA3 TESCAN
View field: 10.4 µm
Det: BSE
2 µm
SEM MAG: 20.0 kx
Date(m/d/y): 01/19/15
RMRC

a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1 µm
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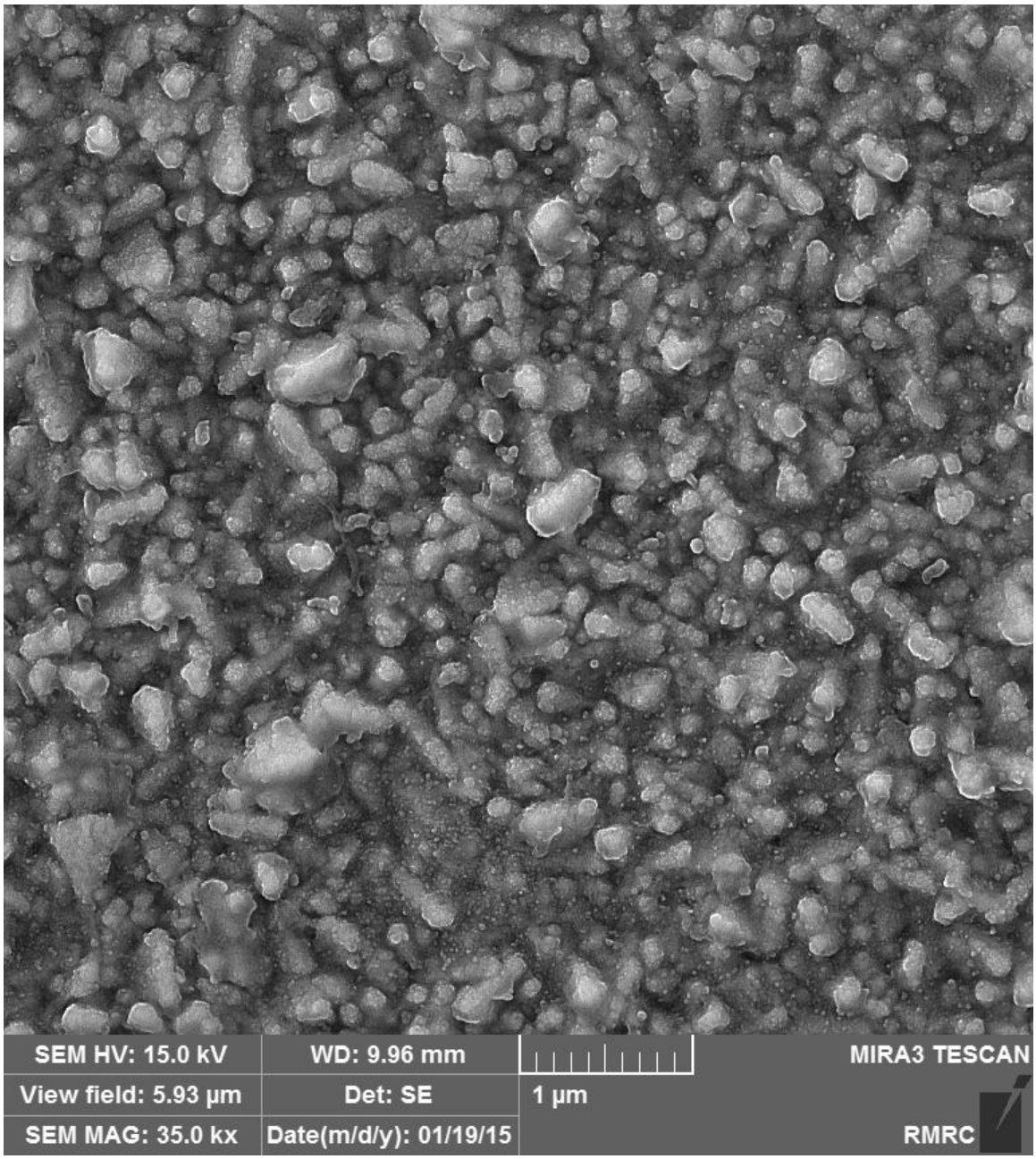
RMRC

b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WD: 9.96 mm
MIRA3 TESCAN
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1 µm
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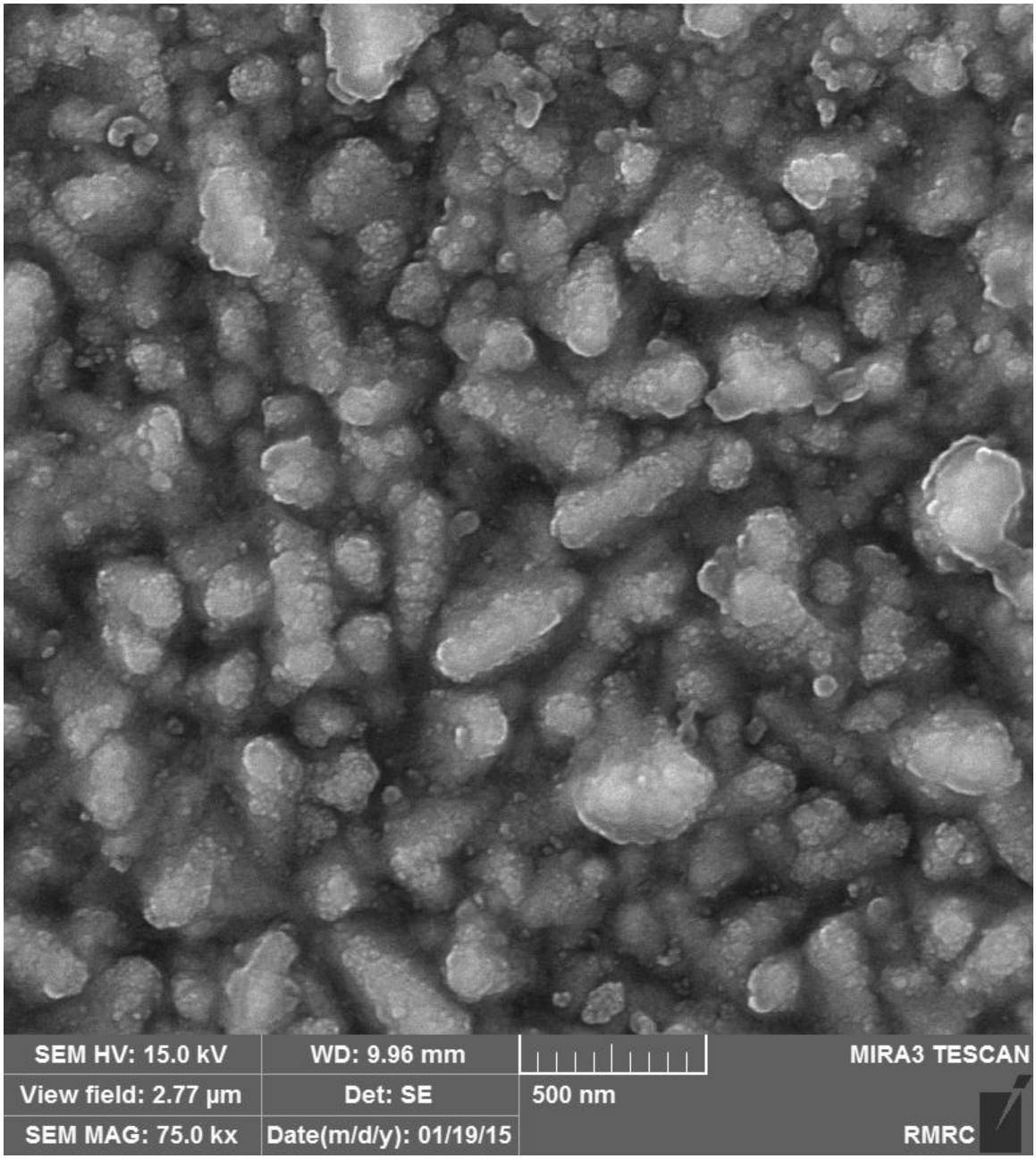
Date(m/d/y): 01/19/15
RMRC

c



d

Fig. S12 SEM for appeared film on the FTO electrode in 1 h in the bulk electrolysis of **1** at 1.2 V (a-d). Cyclic voltammetry studies were carried out with a conventional three-electrode setup, in which a FTO, an Ag|AgCl|KCl_{sat} and a platinum rod served as the working, reference and auxiliary electrodes, respectively. The phosphate buffer solution (0.1 M, pH = 11) has been deoxygenated with pure N_2 in order to the removal of dissolved oxygen from the sample solution.