Supporting Information

Soft Chemical Fabrication of Iron-based Thin Film Electrocatalyst for Water Oxidation under Neutral pH and Structure-Activity Tuning by Cerium Incorporation

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Content	**Page**

FESEM images, EDXS maps

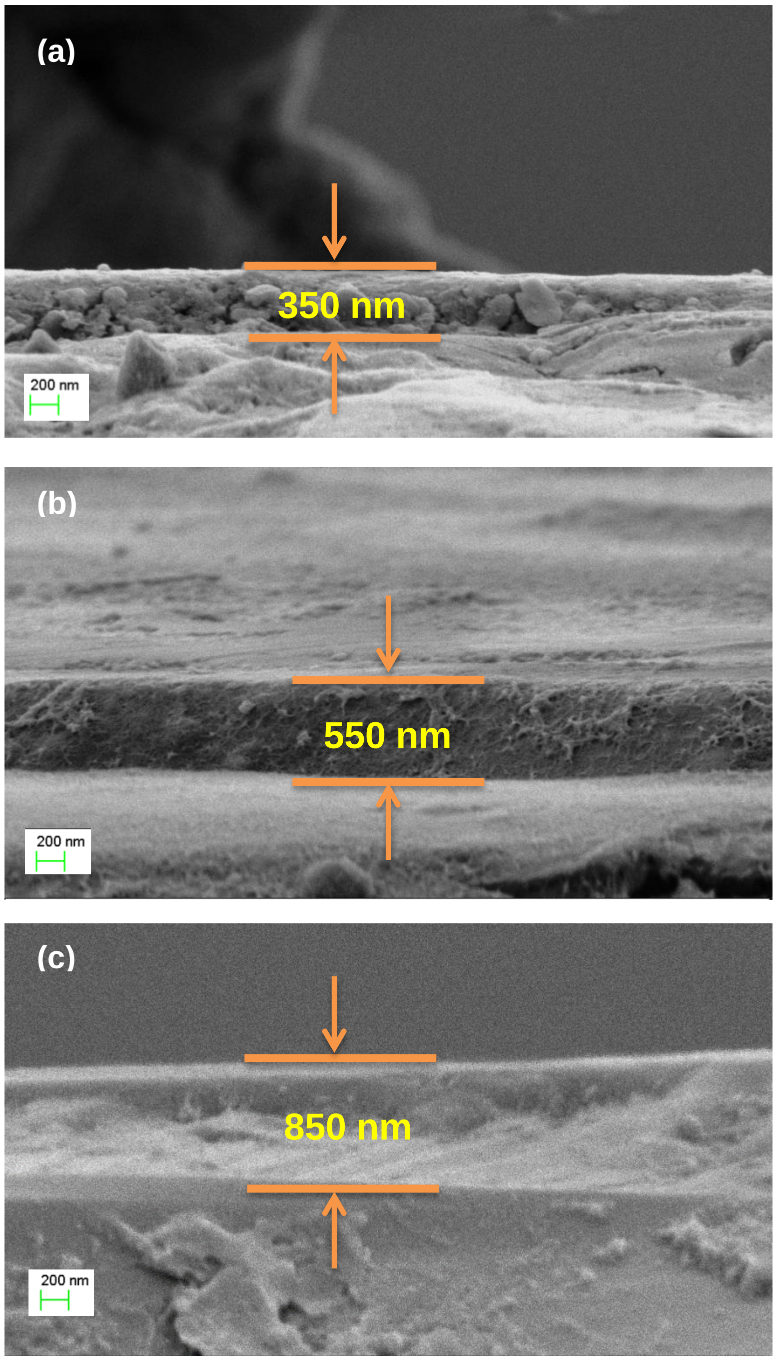


Figure S1. Thickness of the film from FESEM analysis; **(a)** FePH, **(b)** FeCePH2 and **(c)** FeCePH4; electrocatalyst films coated on closely placed substrate plates were sectioned by taking the substrates apart, and the cross-section imaged.

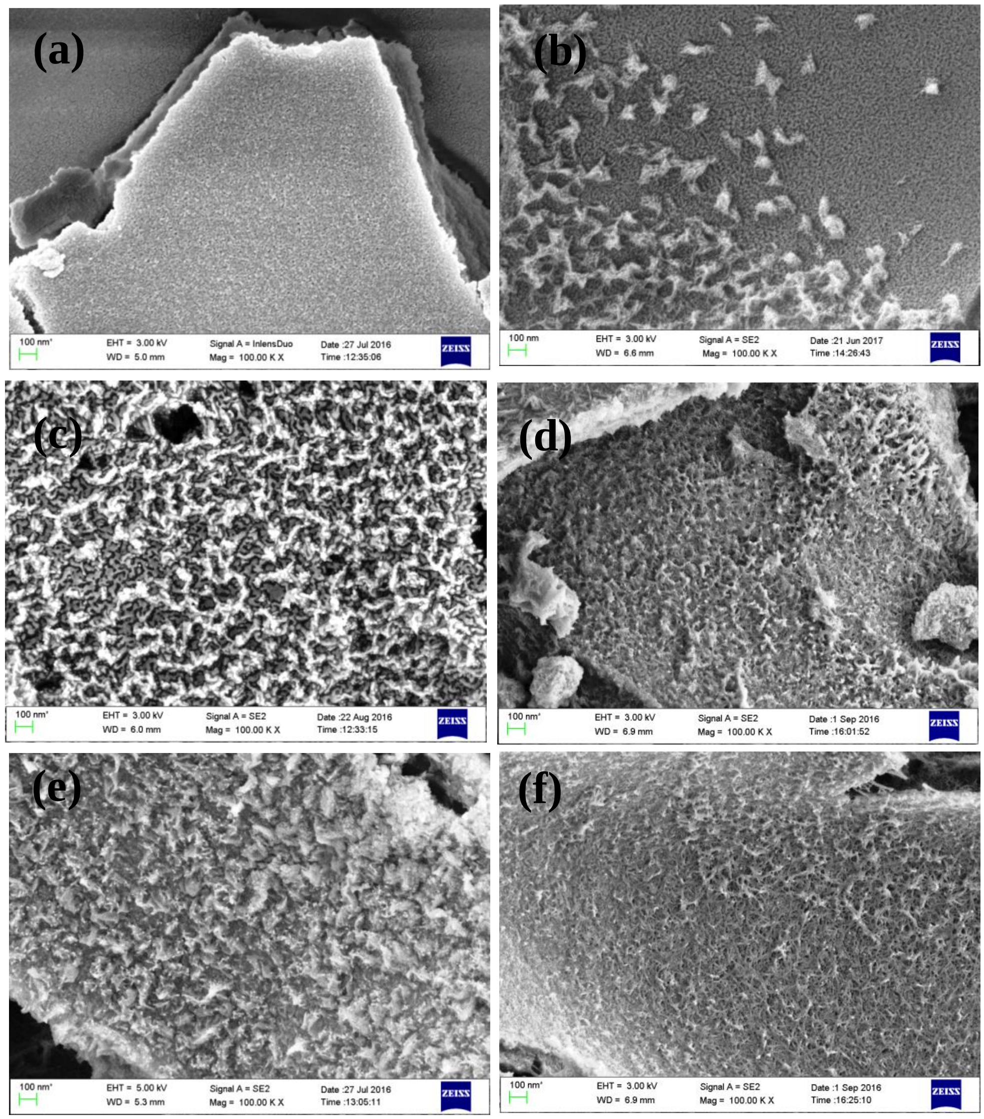


Figure S2. FESEM images of FePH films formed with different amount of cerium acetate **(a)** FePH, **(b)** FeCePH1, **(c)** FeCePH2, **(d)** FeCePH3,**(e)** FeCePH4 and **(f)** FeCePH5. Scale bar= 100 nm.

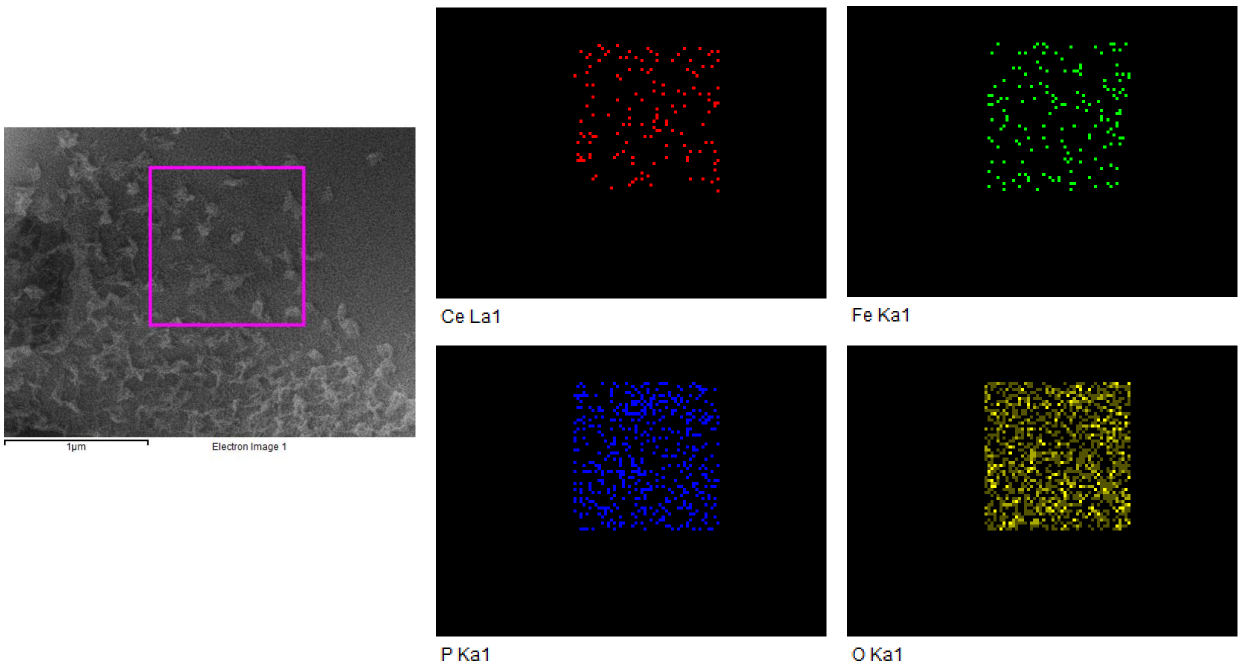


Figure S3. FESEM images of FeCePH1 with EDXS area color mapping.

Electrochemical data

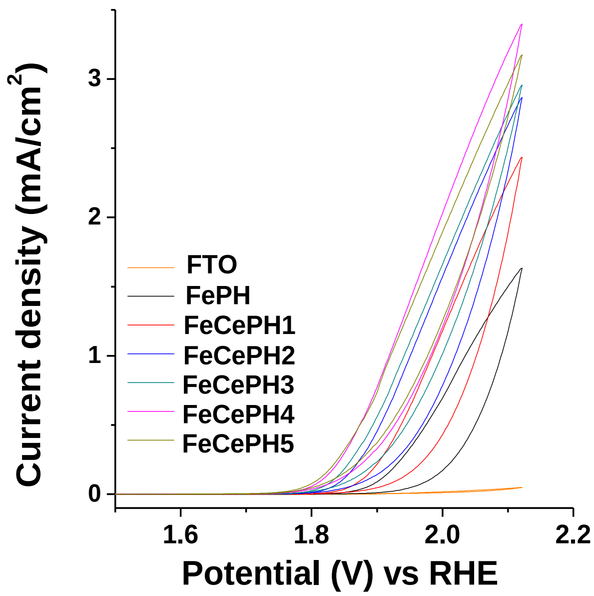


Figure S4. CVs for electrochemical OER using FePH and FeCePHX film catalysts at scan rate = 5 mV/s

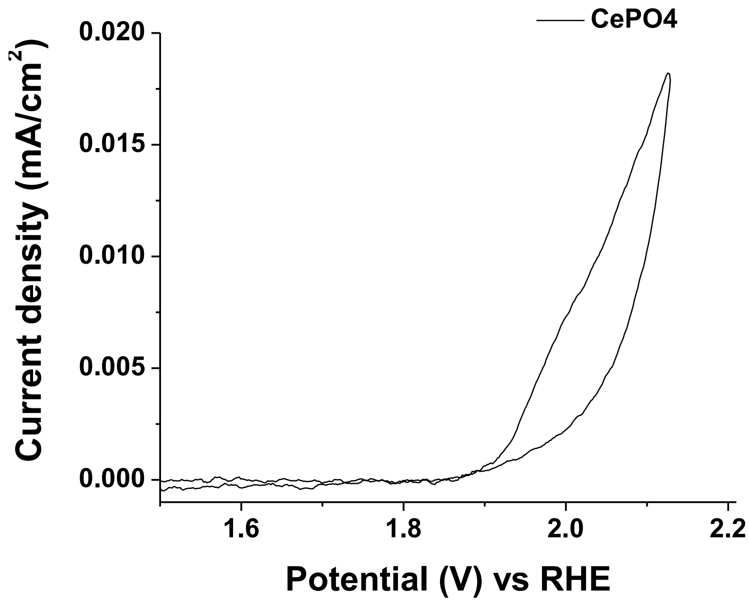


Figure S5. Cyclic voltammetry for OER using $CePO_4$ thin film.

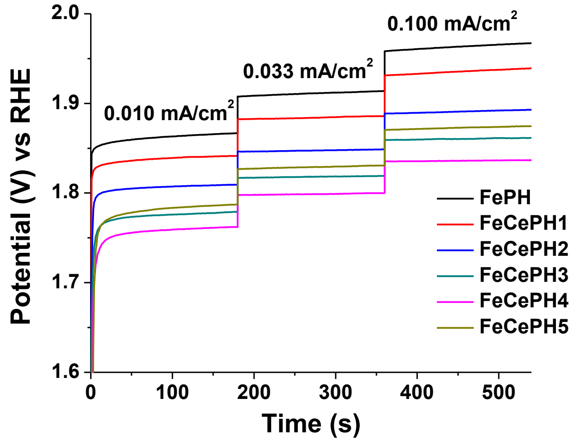


Figure S6. Plots of potential versus time for electrolysis carried out at 0.01, 0.033 and 0.1 mA/cm^2 current densities for 3 min each, using the different thin film catalysts.

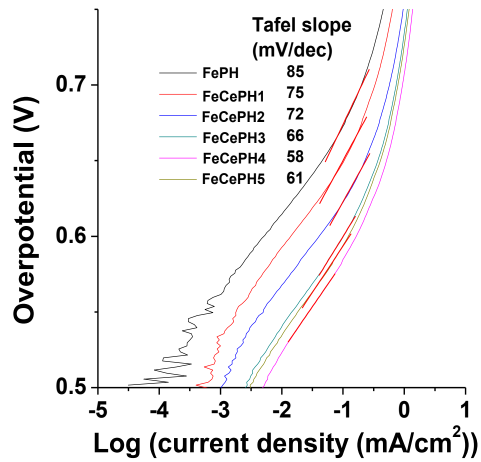


Figure S7. Tafel plots derived from the anodic current density of CV.

XPS data from literature

Table S1. XPS peak positions for Fe^{3+}, Fe^{4+}, Ce^{3+} and Ce^{4+} reported in earlier studies.

Elements	**Peak position (eV)**	**References**
Fe^{3+}	711.9 711	Cao et al., *Phys. Chem. Chem. Phys.* **2015**, *17*, 13112
	725.5	Huang et al., *RSC Adv.* **2015**, *5*, 102610
Fe^{4+}	712.5 725.6	Xin et al., *Chin. Phys. B* **2015**, *24*, 017503
Ce^{3+}	881.2 886.5 901.2 904.5	Daniels et al., *J. Power. Sources* **2015**, *279*, 94
	884.9 903.3	Zhou et al., *J. Phys. Chem. C* **2010**, *114*, 11853
Ce^{4+}	884 903	Wu et al., *J. Mater. Chem. A* **2015**, *3*, 13563
	882.1 907. 0	Zhou et al., *J. Phys. Chem. C* **2010**, *114*, 11853

X-ray photoelectron spectra

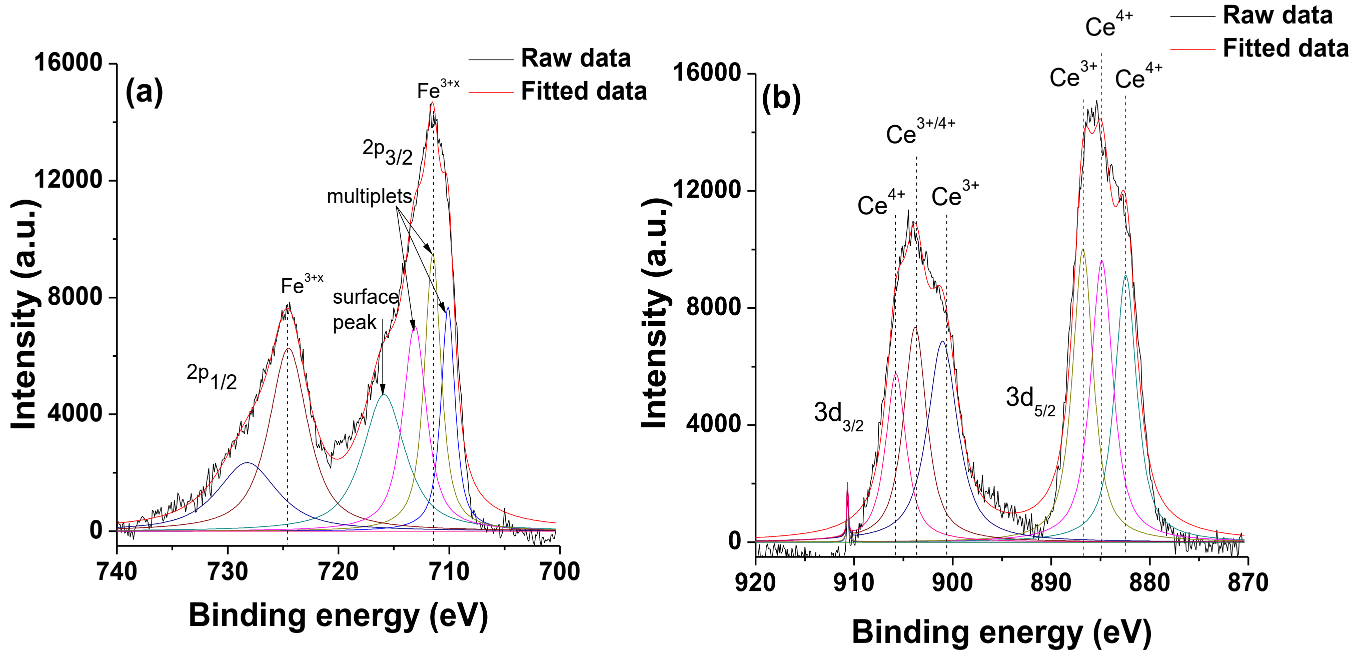
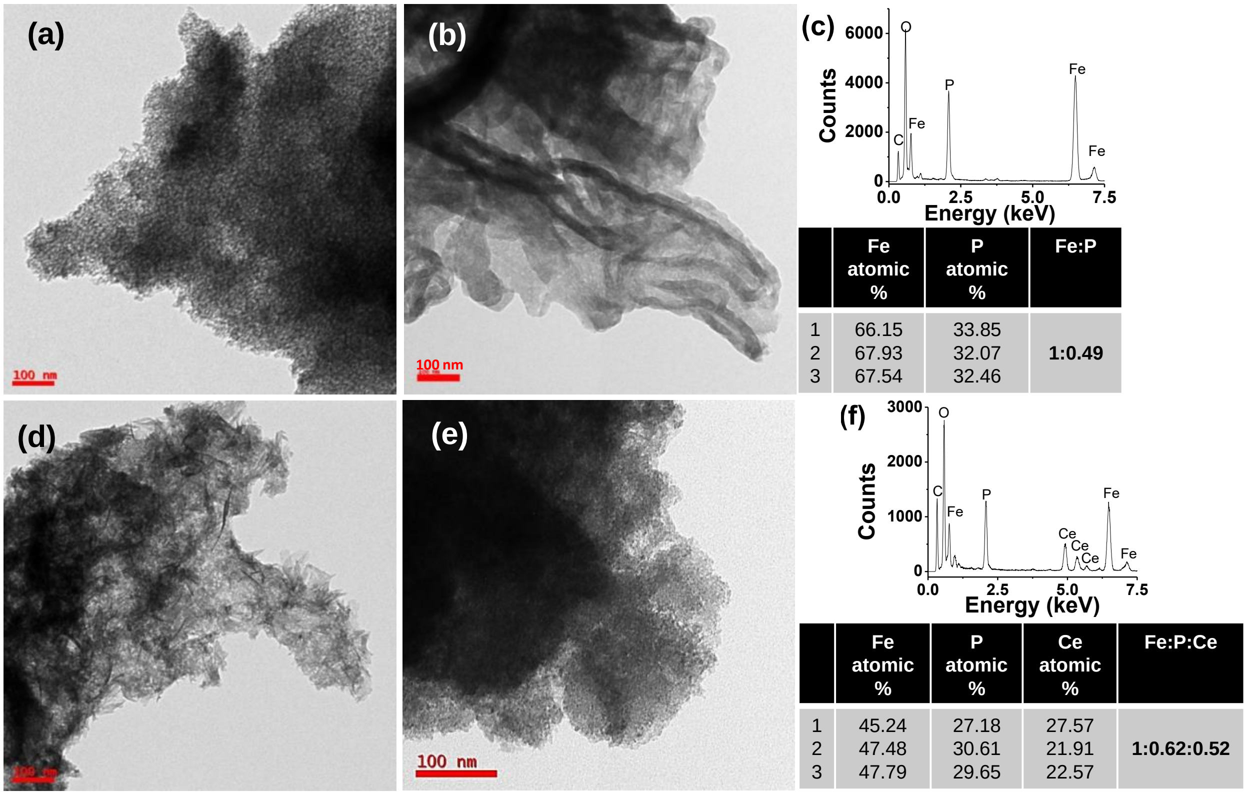


Figure S8. XPS spectra of **(a)** Fe ($2p_{1/2}$, $2p_{3/2}$) and **(b)** Ce ($3d_{3/2}$, $3d_{5/2}$) of FeCePH4 film after electrolysis at 1.9 V *vs* RHE for 3 h.

TEM images, EDX analysis



	Fe atomic %	P atomic %	Fe:P
1	66.15	33.85	1:0.49
2	67.93	32.07	
3	67.54	32.46	

	Fe atomic %	P atomic %	Ce atomic %	Fe:P:Ce
1	45.24	27.18	27.57	1:0.62:0.52
2	47.48	30.61	21.91	
3	47.79	29.65	22.57	

Figure S9. TEM image **(a)** before and **(b)** after catalysis, and **(c)** EDX spectrum and analysis after catalysis, of FePH film; **(d, e, f)** are corresponding figures for FeCePH4.

The EDX analysis of the samples after the catalysis shows that the Fe/P/Ce composition remains nearly unchanged from those given in Table 1 of the main text for the fresh samples.

Comparison of electrocatalsysts for OER under near neutral conditions

Table S2. Overpotential and TOF data from recent studies on transition metal based OER electrocatalysts operating under near neutral conditions, compared to FeCePH4.

Catalyst film	**pH**	**η (mV) (j = 1 mA/cm^2)**	**TOF (h^{-1}) [applied overpotential, mV]**	**References**
FeCePH4	6.4	689/707 (scan rate: 5 and 1 mV/s)	33 [689]	Present work
$Mn_3(PO_4)_2$	7.0	680 (j = 0.32 mA/cm^2)	4.4 [680]	Nam et al., *J. Am. Chem. Soc*. **2014**, *136*, 7435
$LiMnP_2O_7$	7.0	680 (j = 0.5 mA/cm^2)	4.2 [680]	Nam et al., *J. Am. Chem. Soc*. **2014**, *136*, 4201
Fe-based oxide	7.0	480	756 [530]	Cao et al., *Angew. Chem. Int. Ed*. **2015**, *54*, 4870
a-MnO_2-Py	7.5	660	11.3 [910]	Nakamura et al., *Nature Commun*. **2014**, *5*, 4256
Mn-based oxide	7.0	590	36 [530]	Dau et al., *Energy Environ. Sci*. **2012**, *5*, 7081
Brucite like Co-Ni-OH	7.0	760	-	Li et al., *Phys. Chem. Chem. Phys*. **2013**, *15*, 7363
Fe-based oxide	7.0	630 (j = 7 mA/cm^2)	1528 [630]	Cao et al., *ACS Appl. Mater. Interfaces* **2015**, *7*, 21852
$Ca_2Mn_3O_8$	7.0	833	-	Fiechter et al., *Nano Energy* **2012**, *1*, 282
micron sized Mn_5O_8	7.8	700	-	Nam et al., *ACS Catal*. **2015**, *5*, 4624
Amorphous Co oxide	7	410	-	Nocera et al., *Science* **2008**, *321*, 1072