

Supplementary Information

Sea Urchin-like Cobalt-Iron Phosphide Nanostructures as an Efficient Catalyst for the Oxygen Evolution Reaction

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Chemicals and Materials: Fe(acac)₃, Co(acac)₂ (acac =acetylacetonate), oleylamine (OAm, >70%), oleic acid (OAc), benzyl ether (BE, >98%), 1-octadecene (ODE, 90%) hexane, ethanol and Nafion (5%) were purchased from Sigma Aldrich. Sodium oleate (90%) was from Spectrum Chemicals. Trioctylphosphine (97%) was from Strem Chemicals and the commercial C-Ir catalyst (20% on Vulcan XC-72) was from Premetek.

Instrumentation: Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) samples were prepared by depositing a drop of diluted nanoparticle (NP) dispersion in hexane on formvar/carbon coated copper grids. Standard TEM images were obtained from a Philips CM20 operating at 200 kV. TEM with a field-emission electron source and Scanning TEM analyses were obtained on a Hitachi HD2700C (200 kV) with a probe aberration-correction at Brookhaven National Laboratory. HRTEM images were obtained from a JEOL 2010 with an S2 accelerating voltage of 200 kV. Metal components within NPs were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a JY2000 UltraTrace ICP Atomic Emission Spectrometer equipped with a JY AS 421

autosampler and 2400g/mm holographic grating, and the mass ratios were converted into atomic ratios. Electrochemical measurements were carried out on an Autolab potentiostat from Metrohm Instrument Company (Autolab 302). A three-electrode system consisting of a glassy carbon (GC) working electrode (5-mm in diameter), an Ag/AgCl reference electrode (in 4 M KCl) and a platinum wire counter electrode, was used.

Catalyst Preparation: The as-synthesized NPs were mixed with Ketjen-300 J carbon at a weight ratio of 1:1 in 20 mL mixture of hexane and sonicated for 1 h. The C-NPs were washed first with hexane and then with ethanol (twice for each step) and finally separated from the solvents by centrifugation. The C-NPs (both as-made C-NPs and commercial C-Ir) were suspended in a mixture of deionized water, isopropanol and Nafion (V/V/V=4/1/0.05) to form a catalyst ink (2 mg/ml). The glassy carbon (GC) rotating disk electrode (RDE) was polished by 0.1 μm and 0.05 μm alumina powder and rinsed with deionized water, followed by sonication in ethanol and deionized water. Unless specified, for each measurement, 20 μL of the catalyst ink was deposited on the GC working electrode and dried at ambient conditions.

Electrochemical Measurements: All potentials reported on this paper are referenced to the reversible hydrogen electrode (RHE) potential. The 0 V point vs RHE was calibrated by measuring HOR/HER currents on the Pt electrode, where the potential at zero current corresponds to 0 V. Cyclic voltammograms (CVs) were obtained by scanning between 0.1 V to 1.5 V at a scan rate of 50 mV/s in N_2 -saturated solution. OER polarization curves were obtained by linear sweep voltammetry scanning from 0.9 V to 2 V at a scan rate of 10 mV/s in N_2 -saturated 0.1 M KOH with RDE at 1600 rpm.

Table S1. OER activities of Co-, Fe-, CoFe-, and Ir-based oxide/phosphide catalysts.

Catalyst	V (vs. RHE) at 10 mA/cm ²	Electrolyte	Reference
Co _x O _y /NC	1.66 V	0.1 M KOH	<i>Angew. Chem. Int. Ed.</i> 2014 , <i>53</i> , 8508
Mesoporous Co ₃ O ₄ -35	1.76 V	0.1M KOH	<i>Nano Res</i> 2013 , <i>6</i> , 47-54
Co ₃ O ₄ shell/Au core NPs	1.62 V	0.1 M KOH	<i>Adv. Mater.</i> 2014 , <i>26</i> , 3950-3955
Co ₃ O ₄ NPs / Ni foam	1.56 V (5.9 nm NPs)	1 M KOH	<i>J Phys Chem C</i> 2009 , <i>113</i> ,15068-15072 Notice concentration of electrolyte
	1.59 V (21 nm NPs)	1 M KOH	
	1.61 V (46 nm NPs)	1 M KOH	
Co ₃ O ₄ / N-graphene	1.63 V	0.1 M KOH	<i>Nat. Mat.</i> 2011 , <i>10</i> , 780-786 Notice concentration of electrolyte
Co ₃ O ₄ /N-graphene + Ni foam	1.54 V	1 M OH	
FeO(OH)/PtO substrate	1.76 V (5 mA/cm ²)	0.1 M KOH	<i>Nat. Mat.</i> 2012 , <i>11</i> , 550–557 Note: At 10 mA cm ² the V will be even higher.
CoO(OH)/PtO substrate	1.68 V (5 mA/cm ²)	0.1 M KOH	
Co ₃ O ₄ –CoFe ₂ O ₄ mesoporous composite	1.73 V	0.1 M KOH	<i>Chem Mater</i> 2013 , <i>25</i> , 4926-4935.
Crystalline CoFe ₂ O ₄	1.79 V	0.1 M KOH	<i>J Am Chem Soc</i> 2014 , <i>136</i> , 17530-6.
Amorphous CoFe ₂ O ₄	1.72 V	0.1 M KOH	
CoFe ₂ O ₄ /graphene	1.65 V	0.1 M KOH	<i>J. Power Sources</i> , 2014 , <i>250</i> , 196
CoFeO _x (Electrodeposited)	1.60 V	1 M NaOH	<i>J. Am. Chem. Soc.</i> , 2013 , <i>135</i> , 16977 Notice concentration of electrolyte
CoFe ₂ O ₄ / (Triton X-100/Ni support)	1.58 V	1 M KOH	<i>Int. J. Hyd. Energy</i> , 1999 , <i>24</i> , 433 Notice concentration of electrolyte
Co/Fe oxide 64	1.73 V	0.1 M KOH	<i>Chem. Mater.</i> , 2014 , <i>26</i> , 3162–3168 Note: Fe-doped Co ₃ O ₄ (hard templating). Number corresponds to ratios.
Co/Fe oxide 32	1.73 V	0.1 M KOH	
Co/Fe oxide 16	1.74 V	0.1 M KOH	
Co/Fe oxide 7	1.76 V	0.1 M KOH	
Co/Fe oxide 3	1.83 V	0.1 M KOH	
Co/Fe oxide 1	1.90 V	0.1 M KOH	
IrO ₂ NPs	>1.70 V	0.1 M KOH	<i>J. Phys. Chem. Lett.</i> 2012 , <i>3</i> , 399
IrO ₂ /C	1.60 V	0.1 M KOH	<i>Nat Commun.</i> 2013 , <i>4</i> , 1-7
IrO ₂ thin film	1.63 V ~18 mA/cm ²	0.1 M KOH	<i>Science</i> 2011 , <i>334</i> , 1383-1385
CoP nanorods/C	1.55 V	1 M KOH	<i>ACS Catal.</i> 2015 , <i>5</i> , 6874-6878
Commercial C-Ir (Premetek)	1.62 V	0.1 M KOH	This work
CoO/C nanocubes	1.74 V	0.1 M KOH	This work
Fe ₃ O ₄ /C nanocubes	1.91 V	0.1 M KOH	This work
Co _{1.32} Fe _{1.68} O ₄ /C nanocubes	1.70 V	0.1 M KOH	This work
Co ₂ P/C NPs	1.66 V	0.1 M KOH	This work
Fe ₂ P/C nanowires	1.79 V	0.1 M KOH	This work
(Co _{0.54} Fe _{0.46}) ₂ P/C	1.51 V	1 M KOH	<i>Angew. Chem. Int. Ed.</i> 2015 , <i>127</i> , 9778
	1.60 V	0.1 M KOH	This work

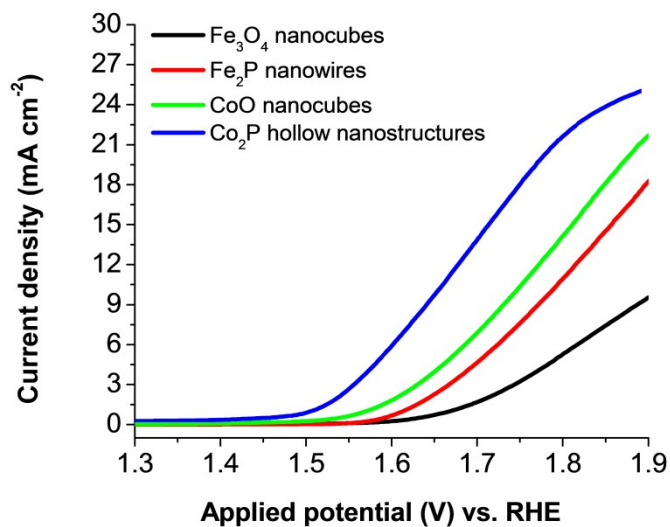


Figure S1. OER polarization curves of C-Co- and C-Fe-based NPs at 1600 rpm in N₂-saturated 0.1 M KOH at a scan rate of 10 mV/s.

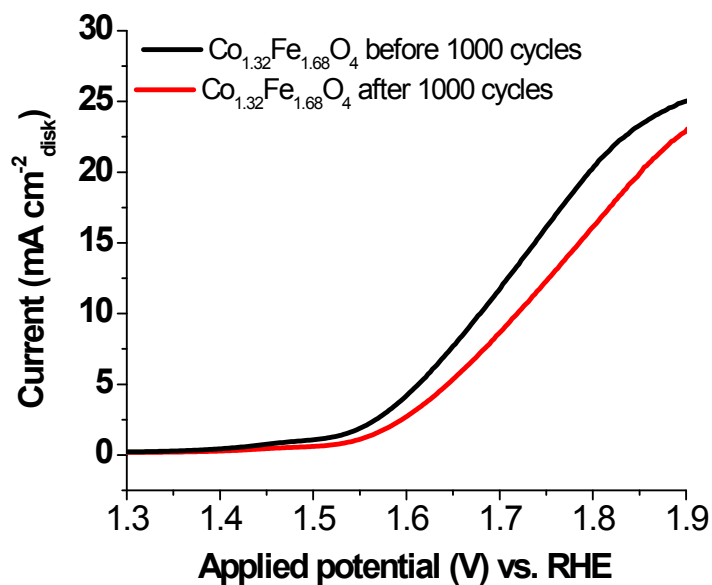


Figure S2. OER polarization curves for the C- Co_{1.32}Fe_{1.68}O₄ nanocubes before and after 1000 potential cycles (between 1.4 and 1.8 V) in 0.1 M KOH.