

Electronic Supplementary Material

High-Performance Hierarchical Ultrathin Sheet-Based CoOOH Hollow Nanospheres with Rich Oxygen Vacancies for Oxygen Evolution Reaction

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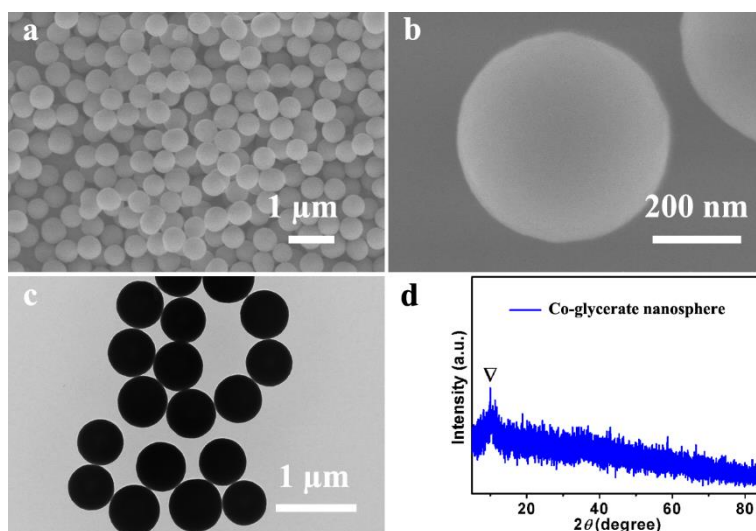


Fig. S1 (a, b) SEM images, (c) TEM image and (d) XRD pattern of the Co-glycerate nanospheres.

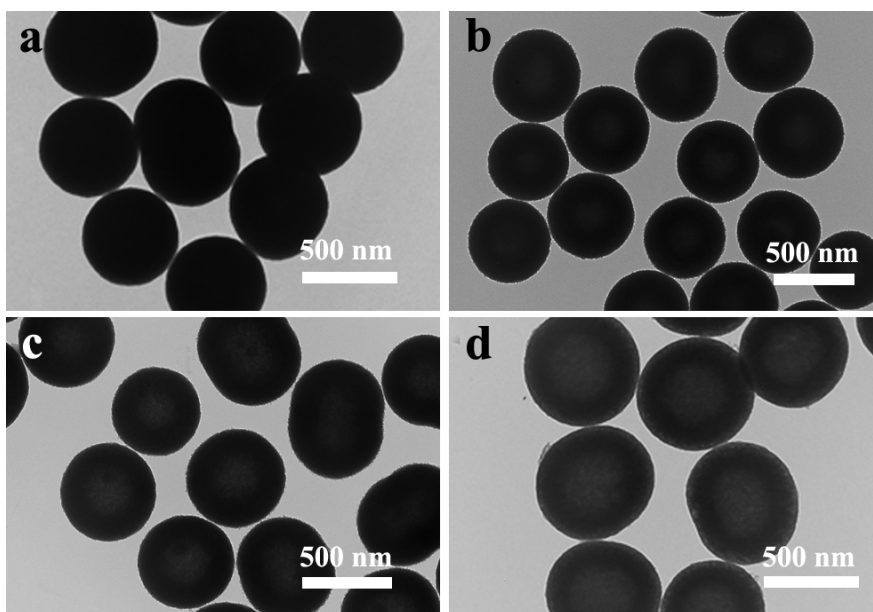


Fig. S2 TEM images of the intermediates collected at different reaction time during the transformation from the Co-glycerate solid nanospheres to the Pi-Co-glycerate hollow nanosphere: (a) 0 h, (b) 6 h, (c) 24 h, and (d) 72 h.

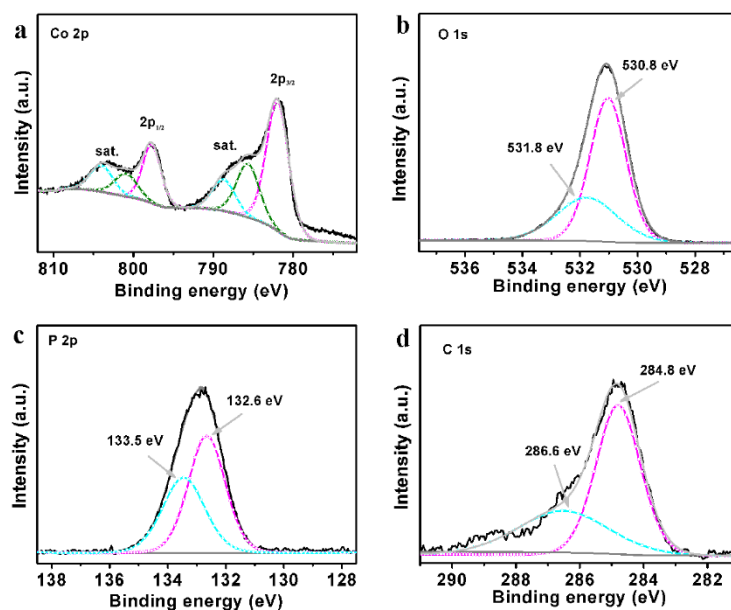


Fig. S3 Co 2p (a), O 1s (b), P 2p (c) and C 1s (d) XPS spectra of the Pi-Co-glycerate hollow nanospheres. The Co 2p spectra exhibits two main peaks at 797.8 and 781.9 eV, which are ascribed to Co 2p_{1/2} and Co 2p_{3/2}, respectively. The binding energy of two shakeup satellites (identified as “Sat.”) at 789 and 804 eV are corresponding to Co with oxidation states (Co²⁺).¹ The peak of O 1s can be deconvoluted into two peaks, with one peak at 530.8 eV for the O atom in H₂PO₂⁻ group² and the other peak at 531.8 eV for the O-H group³. The peak of P 2p can be deconvoluted into two peaks, with the peak at 132.6 eV for the P-H group⁴ and the peak at 133.5 eV for the P-O binding. The C1s peak can be deconvoluted into two peaks (284.8 and 286.6 eV), corresponding to carbon atom in C-C binding and C-O binding. These results confirms that the inorganic-organic hybrid Pi-Co-glycerate hollow nanospheres are successfully fabricated.

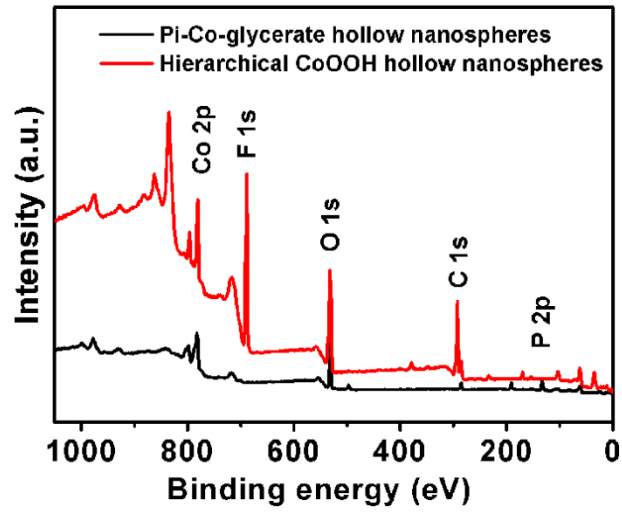


Fig. S4 XPS survey spectra of the Pi-Co-glycerate hollow nanospheres and the hierarchical CoOOH hollow nanospheres.

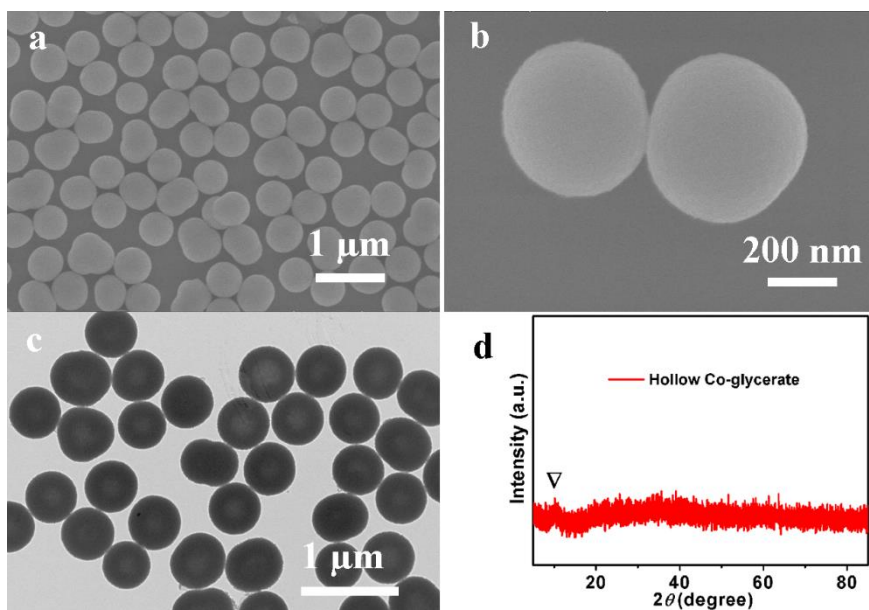


Fig. S5 SEM images (a and b), TEM image (c) and XRD pattern (d) of the Co-glycerate hollow nanospheres obtained by using similar synthesis approach of the Pi-Co-glycerate except for NaH_2PO_2 . The SEM images reveal that the obtained samples are nanospheres (Figure S5a-b), but the TEM image show that they are hollow (Figure S5c). The diffraction peak at 11° suggests the hollow nanospheres are Co-glycerate (Figure S5d).⁵ These results confirm that the hollow in the center of Co-glycerate is formed via high temperature-mediated component dissolution.

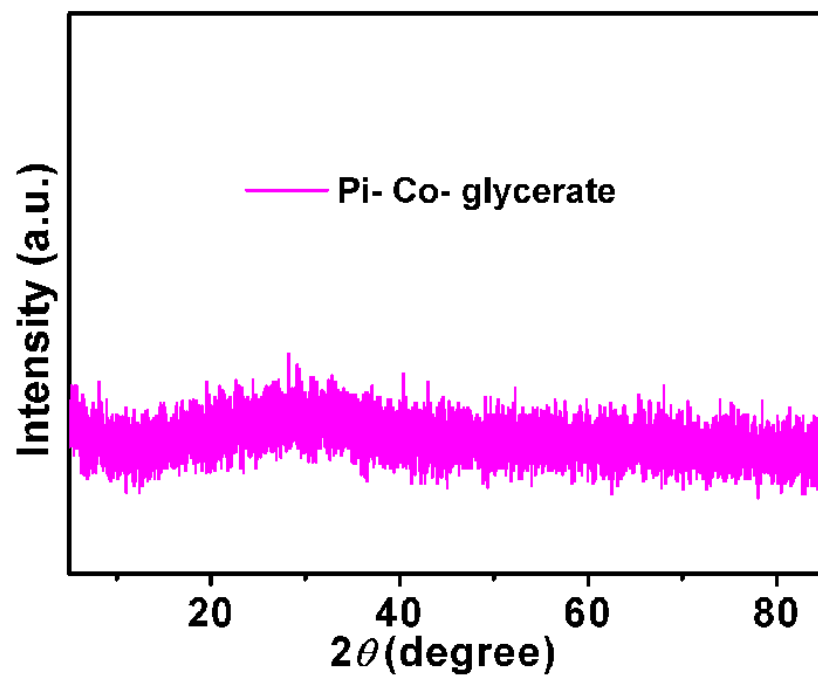


Fig. S6 XRD pattern of the Pi-Co-glycerate hollow nanospheres

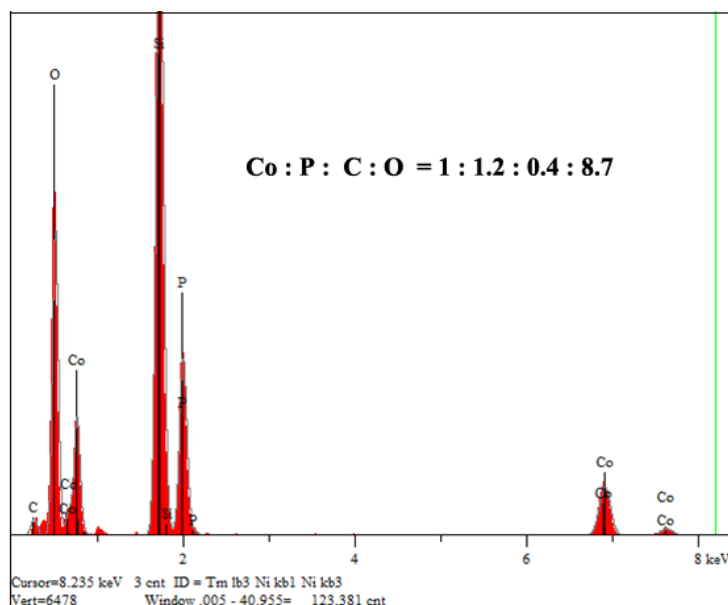


Fig. S7 EDS image of the Pi-Co-glycerate hollow nanospheres. There are four elements (i.e., C, O, P, and Co) in the Pi-Co-glycerate hollow nanospheres. The molar rate of Co, P, C and O is 1 : 1.2 : 0.4 : 8.7. The molecular formula of the Pi-Co-glycerate hollow nanosphere is $\text{Co}_3(\text{H}_2\text{PO}_2)_{3.6}(\text{C}_3\text{H}_6\text{O}_3)_{0.4}$ based on EDS analysis and charge balance. The C/H/N elemental analysis (Table S1) confirms the chemical composition of the Pi-Co-glycerate hollow nanosphere. The 3.22 wt % carbon and 2.15 wt % hydrogen in the Pi-Co-glycerate hollow nanosphere are consistent with the calculated results (C 4.73 wt % and H 2.11 wt %)

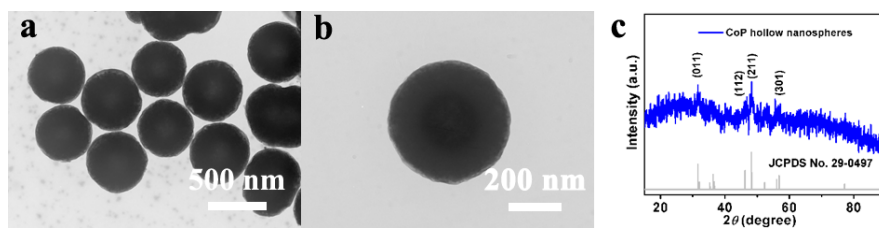


Fig. S8 TEM images (a and b) and XRD pattern (c) of the CoP hollow nanospheres synthesized using Co-glycerate solid nanospheres as the template and annealed at 400 °C for 1 h with a heating rate of 1 °C min⁻¹ in Ar atmosphere in a tube furnace device. After phosphorization in a tube furnace device, the CoP hollow nanospheres with thick shell are obtained (Fig. S8a, b), which are different from the Pi-Co-glycerate produced in a teflon autoclave. The diffraction peaks are consistent with the orthorhombic CoP (JCPDS No.29-0497), the weak peak indicates the low crystalline (Fig. S8c).

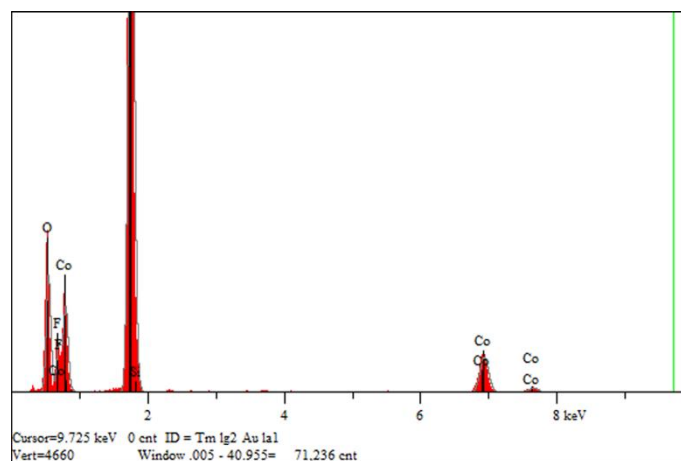


Fig. S9 EDS image of the hierarchical ultrathin sheet-based CoOOH hollow nanospheres. The molar rate of Co and O is 1 : 1.6.

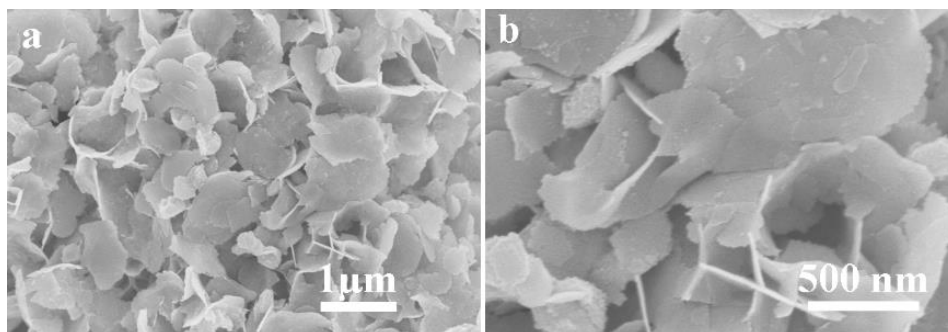


Fig. S10 SEM images of sample obtained using the template Pi-Co-glycerate hollow nanospheres without Nafion membrane.

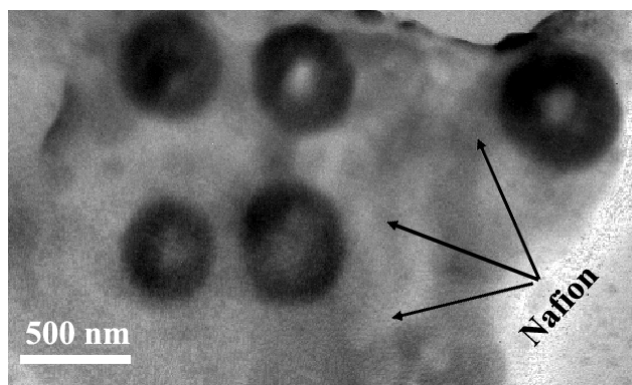


Fig. S11 TEM images of the products obtained using the Co-glycerate hollow nanospheres as the templates, with other conditions remaining no change.

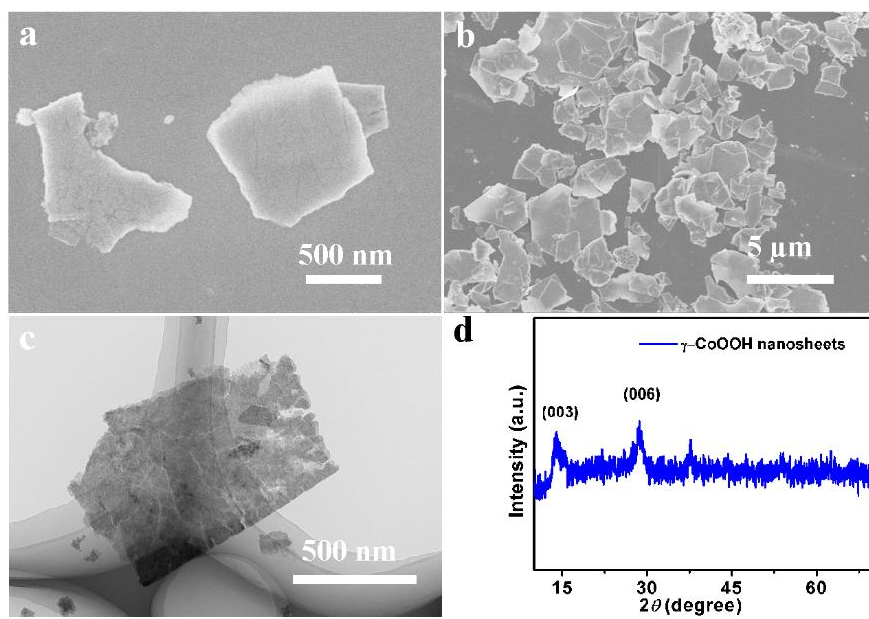


Fig. S12 SEM (a, b), TEM images (c) and XRD pattern (d) of the γ -CoOOH nanosheets.

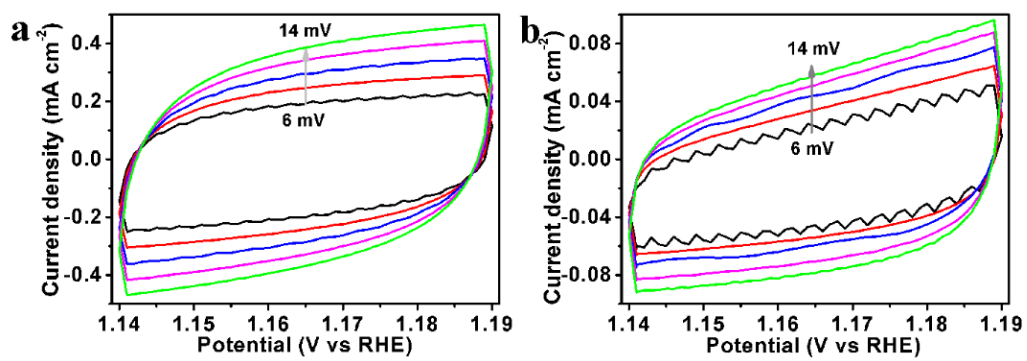


Fig. S13 CV curves of the hierarchical CoOOH hollow nanospheres (a) and the γ -CoOOH nanosheets (b) at different scan rates.

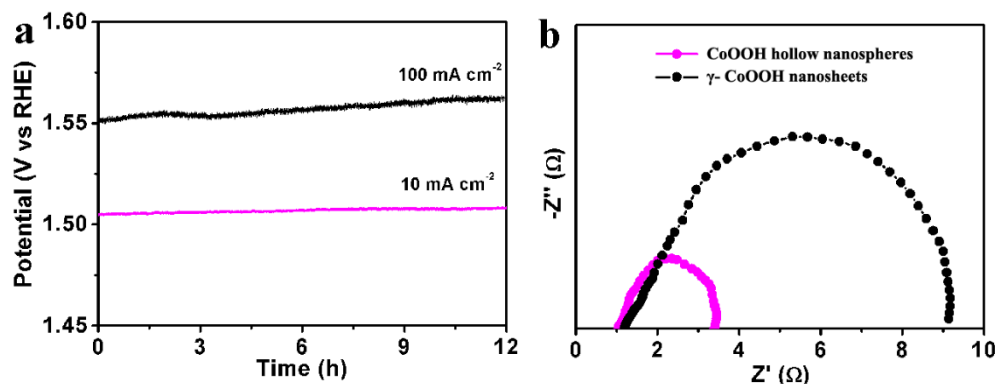


Fig. S14 (a) OER chronopotentiometric measurements of the hierarchical CoOOH hollow nanospheres at the current density of 10 mA cm⁻² (magenta) and 100 mA cm⁻² (black) for 12 h. (b) Nyquist plots of the hierarchical CoOOH hollow nanospheres (magenta) and the γ -CoOOH nanosheets (black) at 0.6 V vs Hg/HgO.

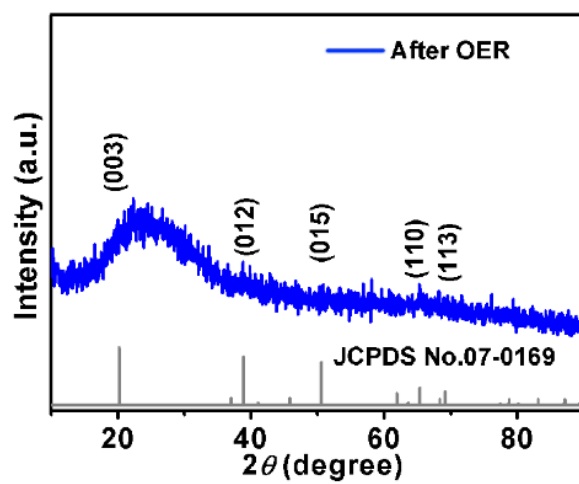


Fig. S15 XRD pattern of the hierarchical CoOOH hollow nanospheres after OER test.

Table S1. C/H/N elemental analysis of the Co-glycerate solid nanosphere, the Co-glycerate hollow nanosphere, and the Pi-Co-glycerate hollow nanosphere.

	Co-glycerate solid nanosphere	Co-glycerate hollow nanosphere	Pi-Co-glycerate hollow nanosphere
C wt%	26.04	15.97	4.73
H wt%	3.96	3.19	2.11

Table S2. Comparison of the electrochemical OER properties of the hierarchical CoOOH hollow nanospheres with those of the reported Co-based nanostructures.

electrode materials	$\eta@10 \text{ mAcm}^{-2}$	$\eta@200 \text{ mAcm}^{-2}$	Tafel Slope	electrolyte	substrate	Ref.
	(mV)	(mV)	(mV dec ⁻¹)	KOH		
CoOOH porous nanosheet arrays	330	> 370	56.4	1.0 M	carbon fiber	6
Ir-Co(OH) ₂ nanosheet	373	> 570	70.2	1.0 M	glassy carbon	7
Co ₃ O ₄ -C porous nanowire arrays	290	> 570	70	0.1 M	Cu foil	8
Co(OH) ₂ -TCNQ nanowire arrays		~ 370	101	1.0 M	copper foam	1
3D Co(OH)F microspheres	313	> 370	52.8	1.0 M	glassy carbon	9
FeCoP ultrathin nanosheet arrays		~ 370	63	1.0 M	nickel foam	10
Co-MOF ultrathin nanosheets	370	> 370	103	1.0 M	nickel foam	11
CoSe ₂ hollow microsphere	330	> 470	79	1.0 M	glassy carbon	12
Ni _{0.6} Co _{1.4} P nanocages	300	> 570	80	1.0 M	glassy carbon	13
NiCo ₂ O ₄ necklace-like	280	> 370	63	1.0 M	nickel foam	14
Co ₃ O ₄ porous nanotubes	285	> 470	80	1.0 M	nickel foam	15
Co ₃ O ₄ /Co-Fe oxide DSNBs	297	> 370	61	1.0 M	glassy carbon	16
activated Mn-Co oxyphosphide	320	> 370	52	1.0 M	glassy carbon	17
this work	275	340	49	1.0 M	nickel foam	

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