Supporting information

Plasma modified C-doped Co_3O_4 nanosheets for oxygen evolution reaction designed by Butler-Volmer and first principle calculations

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Table S1 All of parameters and their elucidations involved in theoretical study

OER: $4OH^- \leftrightarrow 2H_2O + O_2 + 4e^-$			
parameters	meanings	values	units
j_a	current density of anodic (oxidation) direction	--	$A \cdot m^{-2}$
j_c	current density of cathodic (reduction) direction	--	$A \cdot m^{-2}$
η	overpotential	--	V
n	stoichiometric number of electrons involved in OER	4	--
F	Faraday constant	96,485	$Cmol^{-1}$
k_0	rate constant when the reaction arrive equilibrium	--	s^{-1}
$[R]$	concentration of reductant, $[OH^-]$	--	$mol \cdot L^{-1}$
$[O]$	concentration of oxidant, $[O_2]$	--	$mol \cdot L^{-1}$
α	transfer coefficient	0-1	--
R	ideal gas constant	8.31	$J \cdot mol^{-1}$
T	temperature	298	K
φ	electrode-electrolyte potential at random situation	--	V
φ_e	electrode-electrolyte potential at equilibrium situation	--	V
κ	transmission coefficient	1	--
k	Boltzmann constant	1.38×10^{-23}	$J \cdot K^{-1}$

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h	Planck constant	6.63×10^{-34}	J·s
$\overrightarrow{\Delta G}$	Gibbs activation free energy of anodic (oxidation) direction	DFT	kJ·mol^{-1}
$\overleftarrow{\Delta G}$	Gibbs activation free energy of cathodic (reduction) direction	--	kJ·mol^{-1}
E	applied voltage on metal current-collector	--	V
E'	actual voltage on the surface of catalyst	--	V
E_e	equilibrium voltage of OER reaction occurred on catalyst | electrolyte	--	V
φ_{sc}	potential drop at the interface between metal electrode and catalyst	--	V
σ	conductivity of catalyst	--	S·m^{-1}
l	thickness of catalyst	--	m
$\bar{\mu}$	electrochemical potentials	--	J·mol^{-1}
μ	chemical potentials	--	J·mol^{-1}
μ^0	chemical potential of the solute on standard situation	Ref []	J·mol^{-1}
a	activity of solute	$a = \frac{\gamma m}{m^0}$	mol·L^{-1}
m^0	concentration of solute on standard situation	Ref []	mol·L^{-1}
φ_M	absolute potential of catalyst material	--	V
φ_{sol}	absolute potential of solution	--	V
μ_e	electron affinity	--	J·mol^{-1}
E_{vacu}	vacuum level energy	assumed as zero	J·mol^{-1}
E_{LUMO}	energy of lowest unoccupied molecular Oorbital	DFT	J·mol^{-1}
E_{HOMO}	energy of highest occupied molecular orbital	DFT	J·mol^{-1}
E_g	band gap of catalyst,	$E_g = E_{LUMO} - E_{HOMO}$	J·mol^{-1}
E_{Fermi}	Fermi level of metal current collector	could be calculated by DFT but here keeps constant owing to the same substrate	J·mol^{-1}
W_F	surface work function of metal current collector,	$W_F = E_{vacu} - E_{Fermi}$	J·mol^{-1}
C_1	almost unchanged coefficient related to conductance of catalyst	$C_1 = \frac{0.01 k_B T x}{c_n(c_n - 1)e^2 \nu_e l} \exp(2\alpha x)$	--
c_n	ratio of the concentration of	2/3	--

	Co^{3+} over the total amount of Co ions in matrix		
ν_e	attempt electronic frequency	--	s^{-1}
α'	rate of wave function decay for Co ion	--	--
x	distance between two neighboring Co ions in the normal spinel structure corresponding to the hopping distance	--	m
E_a	activation barrier of the polaron	DFT	$J \cdot mol^{-1}$
C_2	almost unchanged coefficient related to solution properties	$C_2 = \frac{RT}{\alpha nF} ln0.01 - \frac{RT}{\alpha nF} ln\left(\frac{nFkT*10^{-14}}{h}\right) - \frac{1}{4F}\sum_i n_i\mu_i^0 - \frac{RT}{4F} ln\frac{a[O_2]}{\{a[OH^-]\}^4} + \frac{RT}{\alpha nF} pH$	--

Table S2 Gibbs free energy, absorption energy, zero point energy and entropy for various kinds of Co_3O_4

			TS	ZPE	ΔE_{ads}	ΔG_{ads}
Co_3O_4		*O	0	0.07	2.46	2.13
		*OH	0	0.33	0.57	0.84
		*OOH	0	0.43	3.39	3.69
B-Co_3O_4	octahedral	*O	0	0.07	2.31	1.93
		*OH	0	0.38	0.84	1.16
		*OOH	0	0.45	3.43	3.75
	tetrahedral	*O	0	0.07	2.53	2.18
		*OH	0	0.35	0.62	0.91
		*OOH	0	0.45	3.40	3.72
	lattice	*O	0	0.07	2.47	2.14
		*OH	0	0.34	0.88	1.16
		*OOH	0	0.43	3.39	3.68
C-Co_3O_4	octahedral	*O	0	0.08	2.70	2.36
		*OH	0	0.35	0.74	1.03
		*OOH	0	0.45	3.21	3.52
	tetrahedral	*O	0	0.07	2.70	2.38
		*OH	0	0.32	0.76	1.02
		*OOH	0	0.45	2.94	3.26
	lattice	*O	0	0.07	2.68	2.35
		*OH	0	0.33	0.53	0.80
		*OOH	0	0.43	3.18	3.48
N-Co_3O_4	octahedral	*O	0	0.07	2.73	2.40
		*OH	0	0.33	0.68	0.95
		*OOH	0	0.42	3.68	3.97
	tetrahedral	*O	0	0.06	2.46	2.13

		*OH	0	0.32	0.84	1.10
		*OOH	0	0.45	2.93	3.26
	lattice	*O	0	0.08	2.39	2.05
		*OH	0	0.35	0.58	0.87
		*OOH	0	0.43	3.21	3.50
P-Co_3O_4	octahedral	*O	0	0.07	2.93	2.60
		*OH	0	0.33	0.51	0.78
		*OOH	0	0.45	2.98	3.30
	tetrahedral	*O	0	0.08	2.11	1.80
		*OH	0	0.32	0.34	0.60
		*OOH	0	0.43	3.02	3.31
	lattice	*O	0	0.08	2.52	2.19
		*OH	0	0.34	0.52	0.80
		*OOH	0	0.43	3.47	3.76
V_O	lattice	*O	0	0.07	2.32	2.00
		*OH	0	0.32	0.43	0.69
		*OOH	0	0.41	3.07	3.35
		H_2O	0.58	0.57	--	--
		H_2	0.41	0.27	--	--

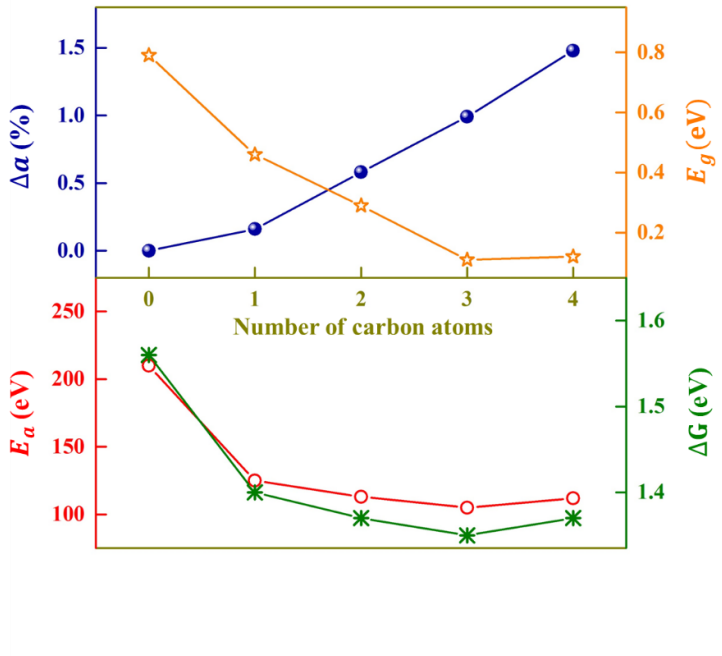

Fig. S1 The effect of multiple carbon atoms in the unit Co_3O_4 cell.

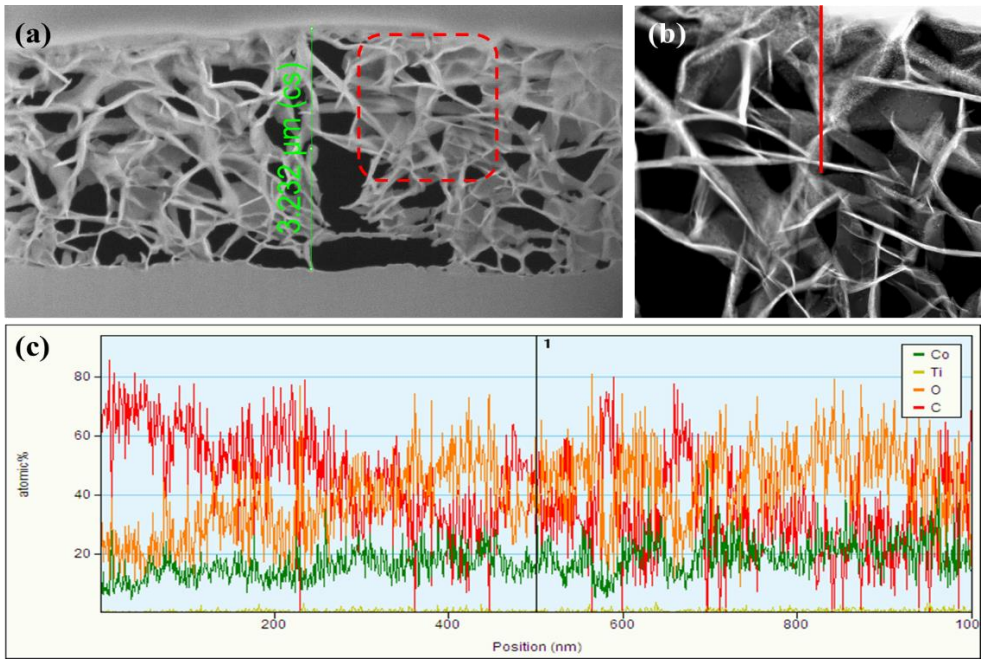

Fig. S2 SEM and EDS results for the section of C-doped Co_3O_4 under 300 W treatment

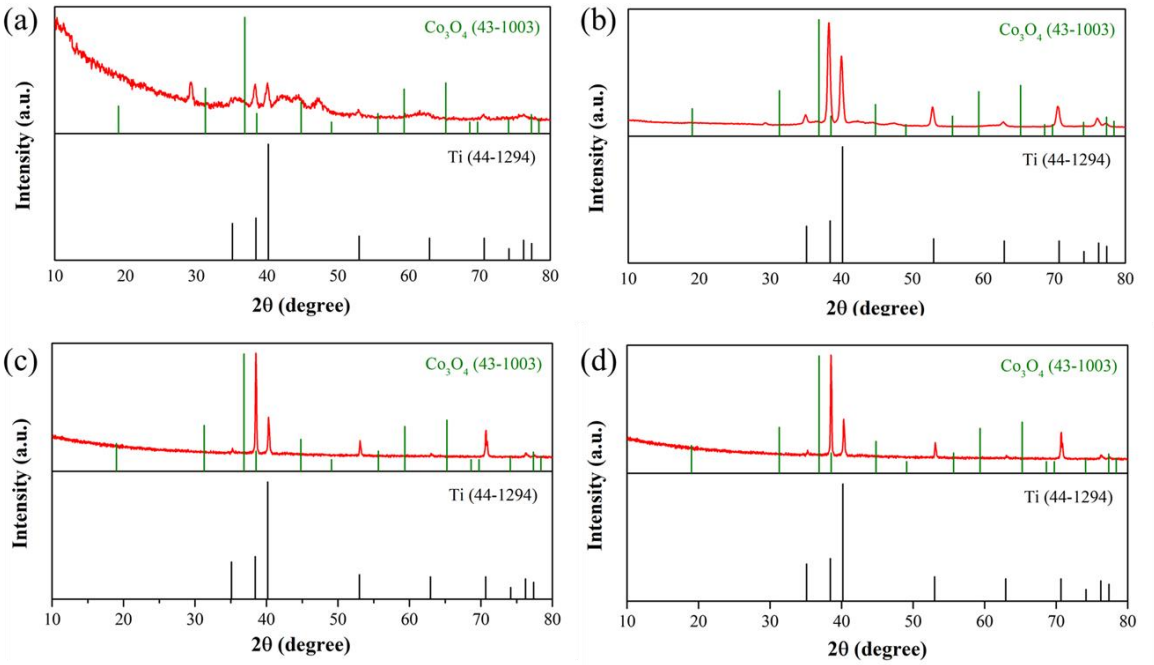

Fig. S3 GIXRD patterns of C-doped Co_3O_4 sample under 300 W with (a) 1°; (b) 5°; (c) 10° input angle and (d) XRD pattern.

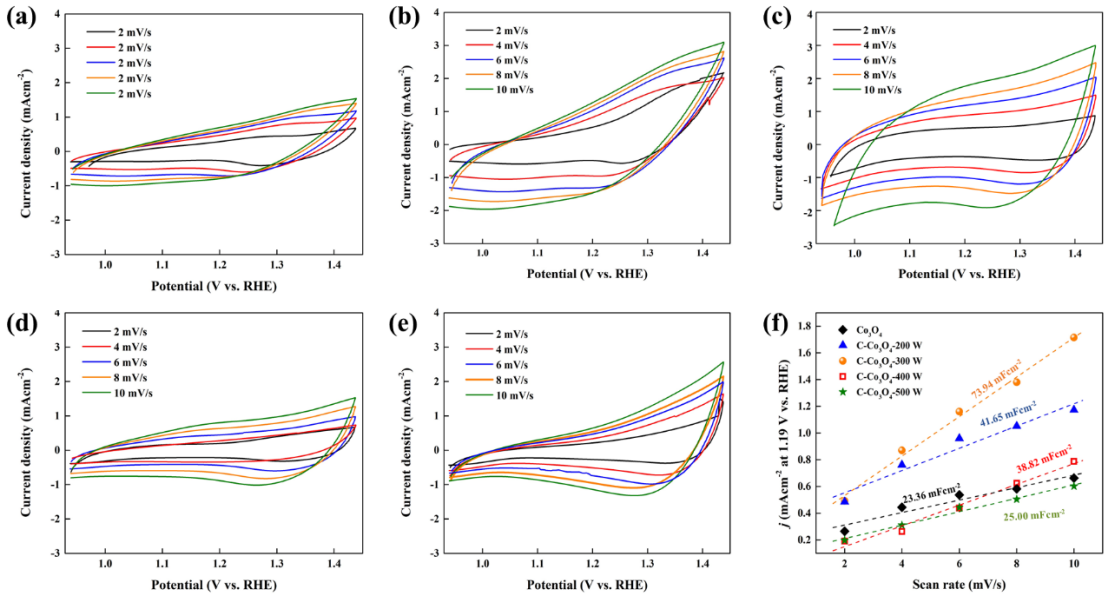

Fig. S4 CV plots for (a) pristine Co_3O_4; (b) treated under 200 W; (c) 300 W; (d) 400 W; (e) 500 W; (f) ECSA determined by the capacitive currents at 1.19 V vs. RHE

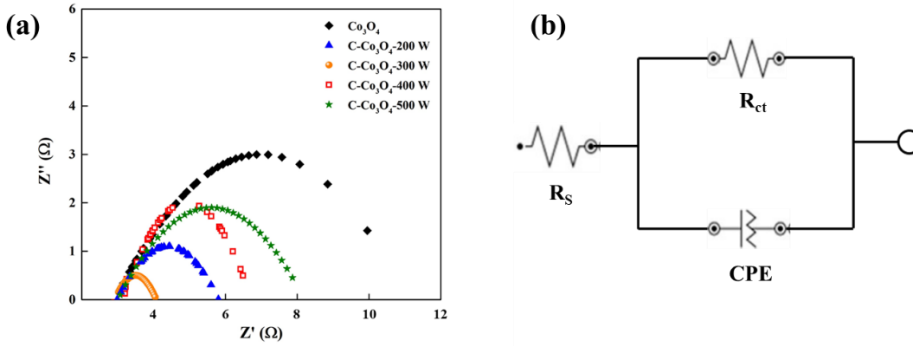

Fig. S5 (a) EIS plots for various kinds of Co_3O_4; (b) equivalent circuit diagram for fitting EIS.

Table S3 Fitting results of R_{ct} from EIS and TOF for various kinds of Co_3O_4

	R_{ct} (Ω)	TOF (s^{-1})
Co_3O_4	7.12	3.32×10^{-3}
C-Co_3O_4-200 W	3.72	5.20×10^{-3}
C-Co_3O_4-300 W	1.47	8.86×10^{-3}
C-Co_3O_4-400 W	3.50	5.13×10^{-3}
C-Co_3O_4-500 W	5.19	4.67×10^{-3}

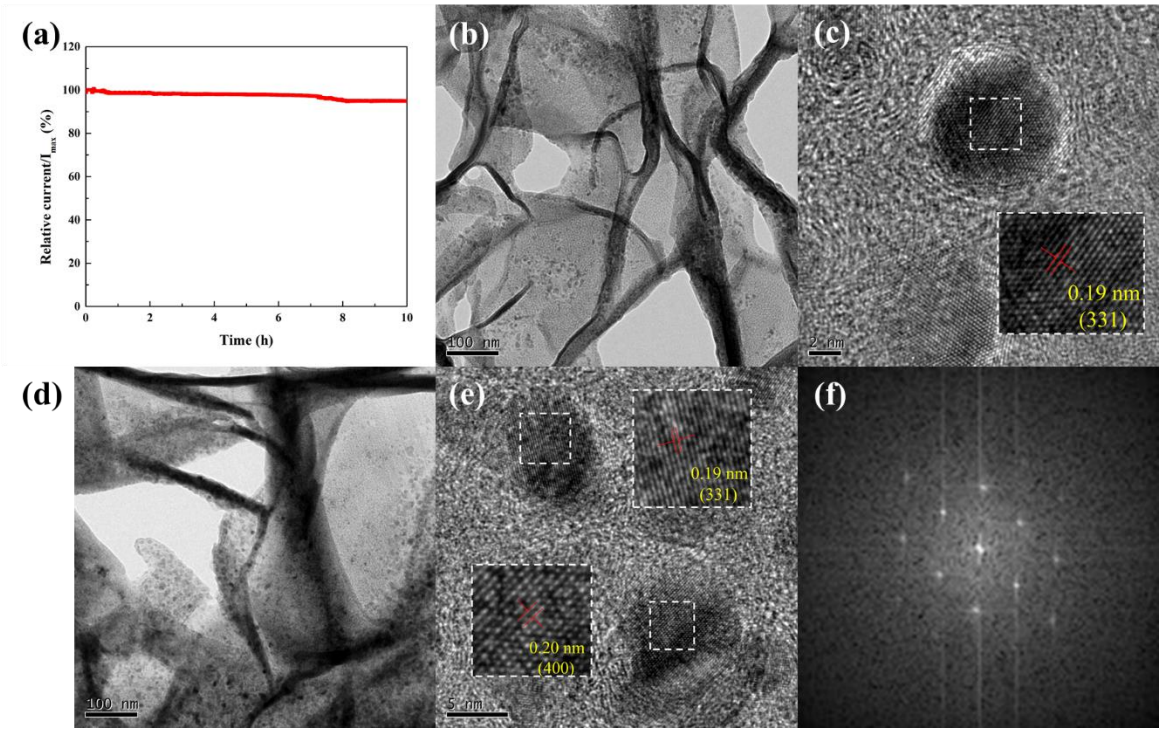

Fig. S6 (a) Chronoamperometry curve of C-Co_3O_4 sample treated at 300 W; (b) (d) FESEM, (c) (d) HRTEM and (f) Live Fast Fourier Transform (FFT) images of C-Co_3O_4 after stability tests.