Electronic Supplementary Material

$CoSe_x$ Nanocrystalline-Dotted CoCo Layered Double Hydroxide Nanosheets: A Synergetic Engineering for Enhanced Electrocatalytic Water Oxidation

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Experimental section

According to the previous reports[S1], NaHSe solution was prepared on the basis of the following reaction:

$$4NaBH_4 + 2Se + 7H_2O = 2NaHSe + Na_2B_4O_7 + 14H_2\uparrow$$

Briefly, selenium powder (0.25 mmol) and $NaBH_4$ (5 mmol) was mixed in deionized water (5 mL) using ultrasonication for a while.

Results and discussion

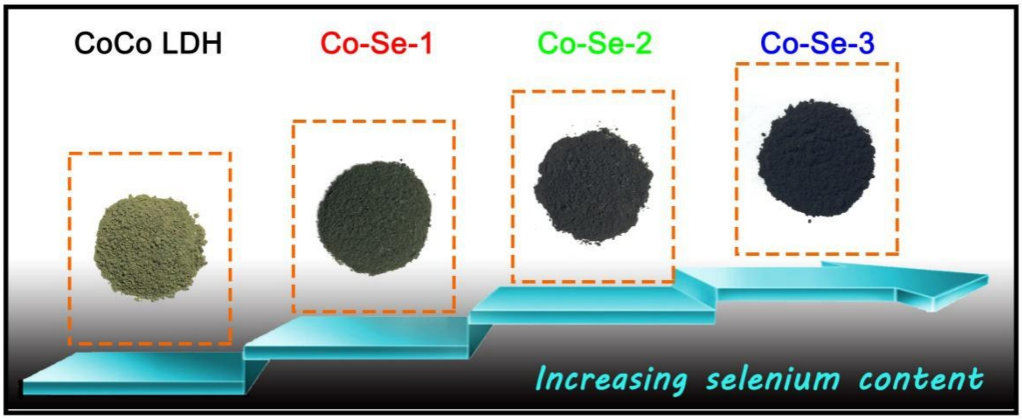

Fig. S1 The photos of the obtained CoCo LDH and various Co-Se NSs.

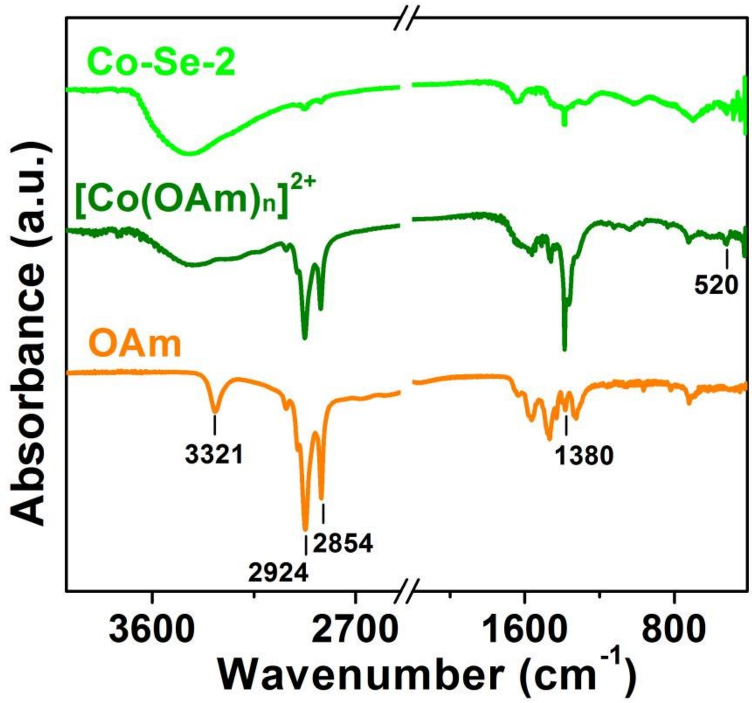

Fig. S2 FT-IR spectra of OAm, $[Co(OAm)_n]^{2+}$ complex, and Co-Se-2 NS.

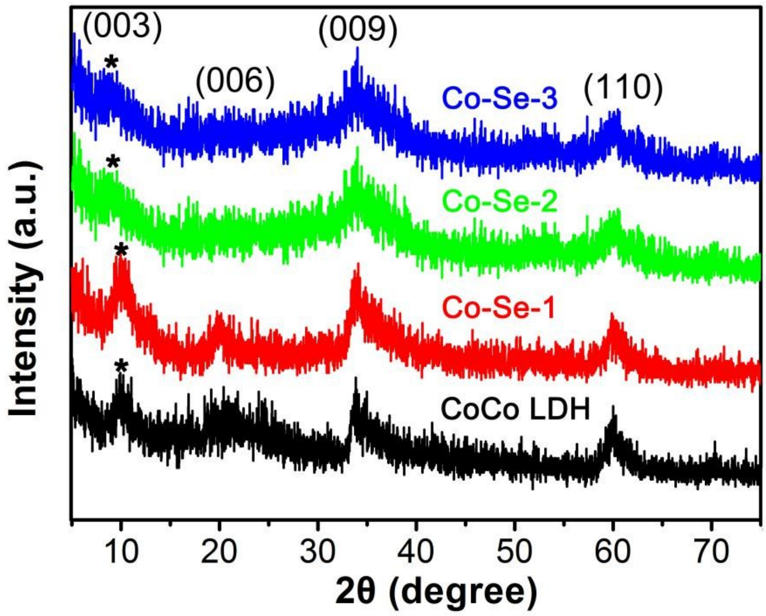

Fig. S3 X-ray diffraction data for CoCo LDH (black) and various Co-Se NSs: Co-Se-1 (red), Co-Se-2 (green) and Co-Se-3 (blue), respectively.

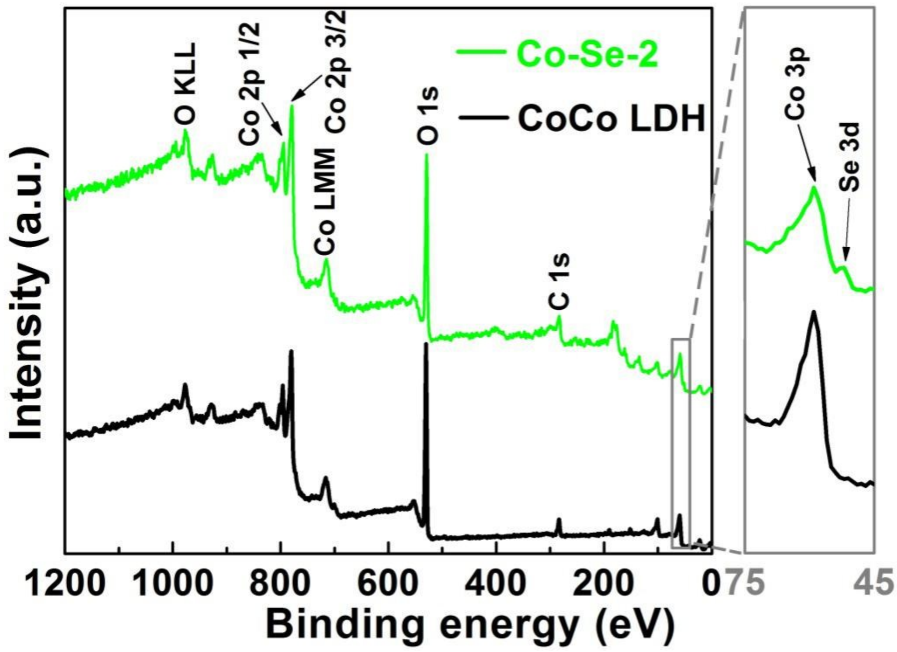

Fig. S4 XPS survey spectra of CoCo LDH and Co-Se-2 NS.

Table. S1 The content of Co^{2+}, Co^{3+}, and Co-Se in Co-Se NSs and CoCo LDH, respectively.

Samples	**Co^{2+} (at%)**	**Co^{3+} (at%)**	**Co-Se (at%)**	**Co^{2+}/Co^{3+} (atomic ratio)**
CoCo LDH	34.07	16.27	0	2.09
Co-Se-1	27.20	14.00	5.70	1.94
Co-Se-2	30.16	16.01	6.86	1.88
Co-Se-3	25.55	15.84	10.22	1.61

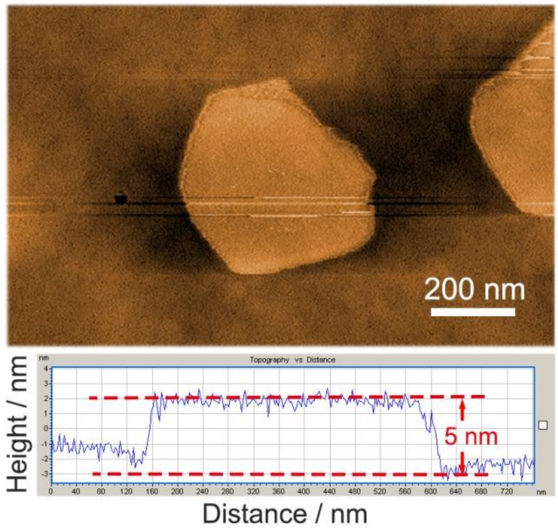

Fig. S5 AFM and line profile images of Co-Se-2 NS (contact mode).

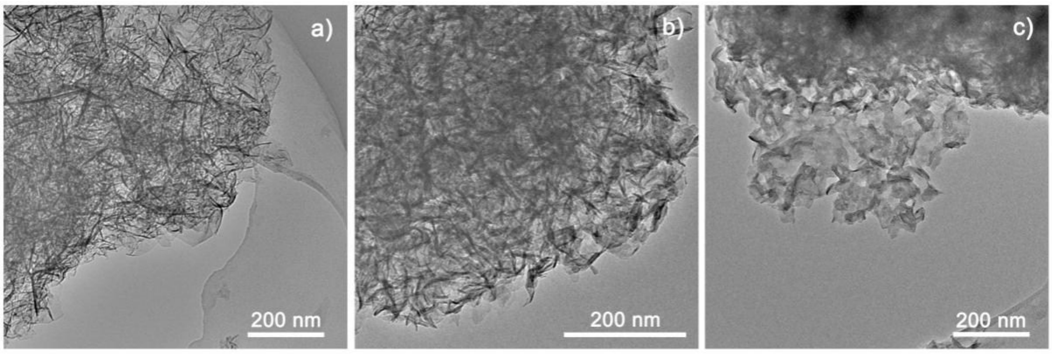

Fig. S6 The typical TEM images of CoCo LDH (a), Co-Se-1 NS (b), and Co-Se-3 NS (c).

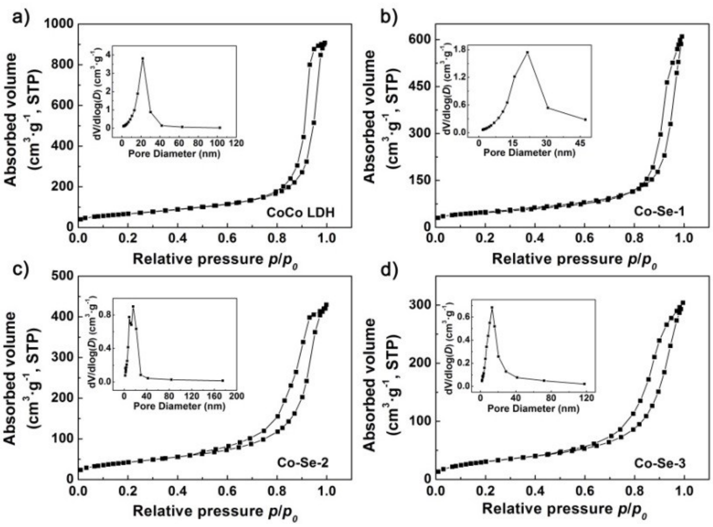

Fig. S7 N_2 adsorption-desorption isotherms of CoCo LDH and various Co-Se NSs.

Table. S2 Comparison of BET surface area and desorption average pore diameter of CoCo LDH and various Co-Se NSs.

Sample name	BET Surface area ($m^2 \cdot g^{-1}$)	Pore diameter (nm)
CoCo LDH	239.4700	13.2728
Co-Se-1	173.7823	14.1968
Co-Se-2	152.5266	9.3263
Co-Se-3	112.7479	8.9415

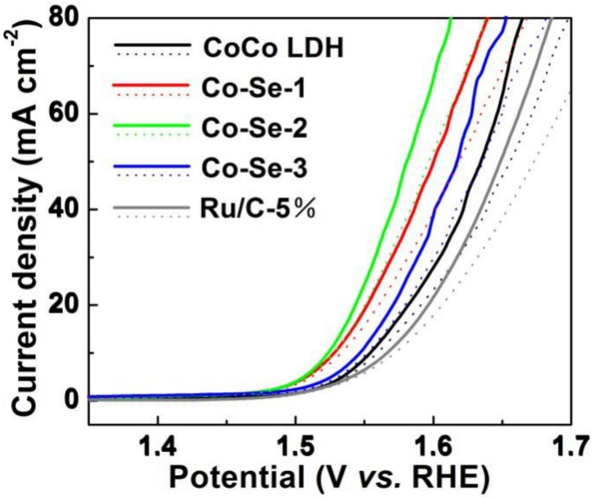

Fig. S8 *iR*-compensated LSV (solid line) and LSV (dotted line) curves for Co-Se NSs, CoCo LDH and Ru/C-5% towards OER in 1 M KOH solution.

Table. S3 Comparison of OER performance of Co-Se-2 NS with recently reported Co-based electrocatalysts in alkaline electrolyte.

Catalysts	Substrate	η@10 mA·cm^{-2} (mV)	Tafel slope (mV/dec)	Electrolyte	Reference
Co-Se-2	**GCE**	**290**	**70**	**1.0 M KOH**	**This work**
CoSe amorphous films	Ti mesh	292	69	1.0 M KOH	*Chem. Commun. 2015, 51, 16683.*
Ni_3Se_4 Nanoassemblies	Ni foam	243	30	1.0 M KOH	*Appl. Mater. Interfaces. 2017, 9, 8714*
CoFe hydroxide spiral nanosheets	GCE	380	44.9	1.0 M KOH	*Chem. Sci. 2015, 6, 3572.*
1.0%Ag-$CoSe_2$ lamellar nanobelts	GCE	320	56	0.1M KOH	*Angew. Chem. Int. Ed. 2017, 56, 328.*
Au_{25}/$CoSe_2$ nanosheets	GCE	410	---	0.1 M KOH	*J. Am. Chem. Soc. 2017, 139, 1077.*
Single-unit-cell thick $CoSe_2$ sheets	GCE	~ 350	64	1.0 M KOH	*Angew. Chem. Int. Ed. 2015, 54, 12004.*
$Co_{0.85}Se$ nanotube arrays	CFC	324	85	1.0 M KOH	*Adv. Mater. 2016, 28, 77.*
CoCo single-layer LDH nanosheets	GCE	353	45	1.0 M KOH	*Nat. Commun. 2014, 5, 4477.*
Amorphous Co phyllosilicate	GCE	367	60	1.0 M KOH	*Adv. Mater. 2017, 29, 1606893.*
Coral-like CoSe	GCE	295	40	1.0 M KOH	*Electrochimica Acta. 2016, 194, 59*

$CoSe_2$ Nanocrystals	GCE	430	50	1.0 M KOH	*Appl. Mater. Interfaces. 2016, 8, 5327*
ZIF-$Co_{0.85}Se$	GCE	360	62	1.0 M KOH	*Appl. Mater. Interfaces. 2016, 8, 20534*
MOF derived $CoSe_2$ nanoparticles	CFP	297	41	1.0 M KOH	*Nano Res. 2016, 9, 2234*
$(Ni, Co)_{0.85}Se$@NiCo-LDH	CFP	216	77	1.0 M KOH	*Adv. Mater. 2016, 28, 77*
Janus Co/CoP nanoparticles	GCE	340	79.5	1.0 M KOH	*Adv. Energy Mater. 2017, DOI: 10.1002/aenm.201602355.*
NiCo LDH nanosheets	CFP	367	40	1.0 M KOH	*Nano Lett. 2015, 15, 1421.*
CoS doped $Co(OH)_2$@$aMoS_{2+x}$/NF networked nanoplates	Ni foam	380	68	1.0 M KOH	*Adv. Funct. Mater. 2016, 26, 7386.*
Co_3O_4/rGO	GP	346	47	1.0 M KOH	*Nano Energy 2017, 33, 445.*
RGO@$CoNiO_x$	GCE	280	42	1.0 M KOH	*Adv. Funct. Mater. 2017, 27, 1606325.*
$NiCo_2O_4$ hollow nanowall arrays	CC	340	72	1.0 M KOH	*Adv. Energy Mater. 2017, DOI: 10.1002/aenm.201602391*
Co_3O_4 hollow microtube arrays	GCE	310	84	1.0 M KOH	*Angew. Chem. Int. Ed. 2017, 56, 1324.*
FeCo oxide nanosheets	GCE	308	36.8	0.1 M KOH	*Adv. Mater. 2017, 29, 1606793.*
NiCoP/C nanoboxes	GCE	330	96	1.0 M KOH	*Angew. Chem. Int. Ed. 2017, 56, 3897.*
CoNi(20:1) phosphide nanosheets	GCE	273	45	1.0 M KOH	*Energy Environ. Sci. 2017, 10, 893.*
Amorphous CoFe hydroxide nanosheet	Graphite	280	28	1.0 M KOH	*Adv. Funct. Mater. 2017, 27, 1603904.*
Amorphous Co_2B	GCE	380	45	1.0 M KOH	*Adv. Energy Mater. 2016, 6, 1502313.*
CoO_x nanoparticles/B,N-decorated graphene	GCE	295	57	0.1M KOH	*Angew. Chem. Int. Ed. 2017, 10.1002/anie.201702430*
Co_3O_4 nanocrystals	CFP	320	101	1.0 M KOH	*Chem. Commun. 2015, 51, 8066.*
CP/Carbon tube/Co-S sheet arrays	CP	306	72	1.0 M KOH	*ACS Nano 2016, 10, 2342.*
$CoNi(OH)_x$ nanotubes	Cu foil	280	77	1.0 M KOH	*Adv. Energy Mater. 2015, 6, 1501661.*

$Co_{1-x}S$/rGO	GCE	310	79	1.0 M KOH	*Nano Research 2017, 10, 1819.*

Abbreviations: GCE = Glassy carbon electrode; LDH = Layered double hydroxide; CFP = Carbon fiber paper; CFC = Carbon fiber cloth; MOF = Metal organic framework; ZIF = Zeolitic Imidazolate Framework; CC = Carbon cloth; CP = Carbon paper; NF = Nickel foam.

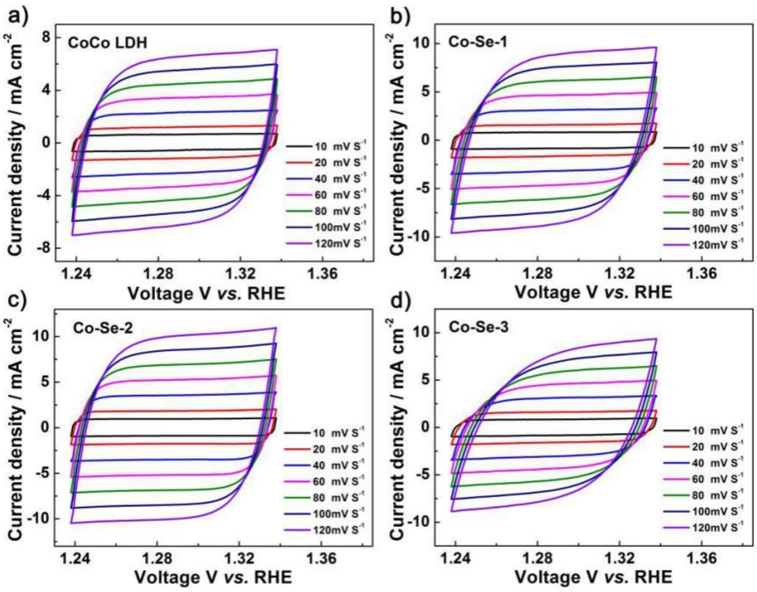

Fig. S9 (a-c) CVs for CoCo LDH and Co-Se NSs at various scan rate (10, 20, 40, 60 80, 100, and 120 mV·s^{-1}).

Table. S4 Parameters obtained by fitting the impedance spectra of CoCo LDH, Co-Se-1, Co-Se-2 and Co-Se-3 NSs using the equivalent circuit in Fig. 4(d)

Sample name	R_{ct} (Ω)	R_s (Ω)
CoCo LDH	5.810	578.4
Co-Se-1	4.867	338.3
Co-Se-2	4.305	72.66
Co-Se-3	5.000	267.1

TOF measurements

The active surface redox sites of Co-Se NS and CoCo LDH were determined by integrating the anodic oxidation peak of Co^{II} to Co^{III} without the capacitive current[S2]. To fully oxidize the surface area, 30 scans of CV from 0.86 to 1.46 V (*vs.* RHE) with a scan rate of 20 mVs^{-1} in 1.0 M NaOH were carried out, until a steady CV curve obtained (Fig. S11). For the one electron reaction of Co^{II}/Co^{III}, the number of active atoms is equal to the integrated charge of the peak Q_S divided by the charge of an electron Q_e (1.6×10^{-19} C), $N_S = Q_S / Q_e$.

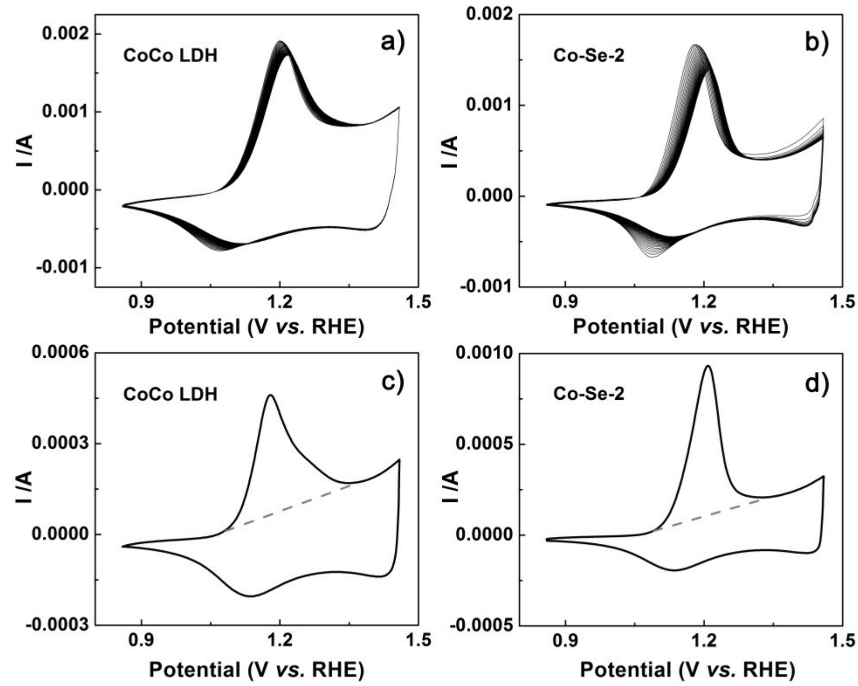

Fig. S10 Electrochemical CVs on CoCo LDH and Co-Se-2 NS for determining redox surface sites of Co^{II}/Co^{III}.

Notes and references

[S1] C. Xia, Q. Jiang, C. Zhao, M. N. Hedhili and H. N. Alshareef, *Adv. Mater.*, 2016, 28, 77-85.

[S2] X. M. Zhou, X. T. Shen, Z. M. Xia, Z. Y. Zhang, J. Li, Y. Y. Ma and Y. Q. Qu, *ACS Appl. Mater. Interfaces*, 2015, 7, 20322-20331.