Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Metal-organic framework-derived $CoSe_2$/(NiCo)Se_2 box-in-box hollow nanocubes with enhanced electrochemical properties for sodium-ion storage and hydrogen evolution

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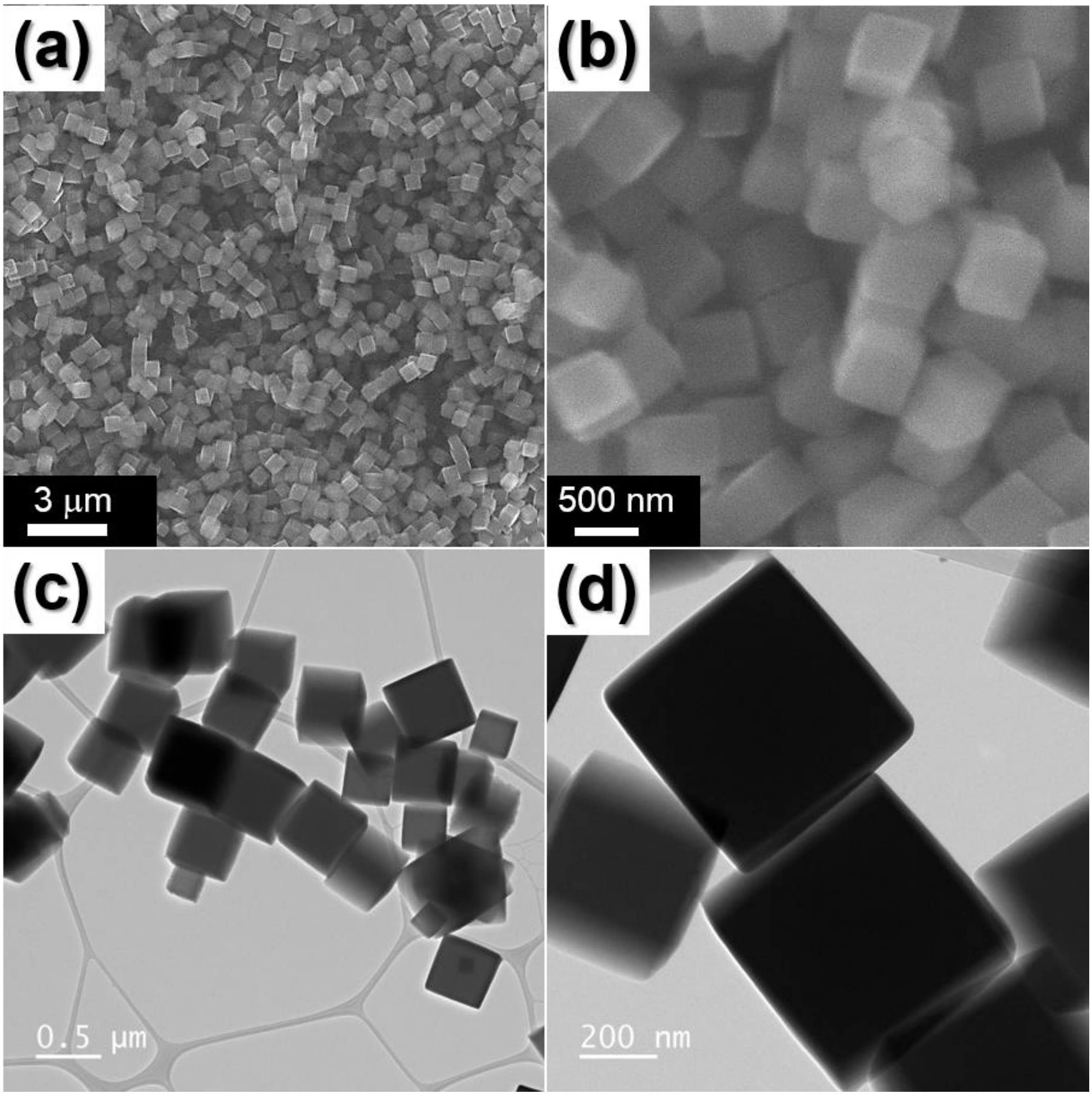


Fig. S1 Morphologies of the bare ZIF-67 nanocubes: (a) and (b) SEM and (c) and (d) TEM images.

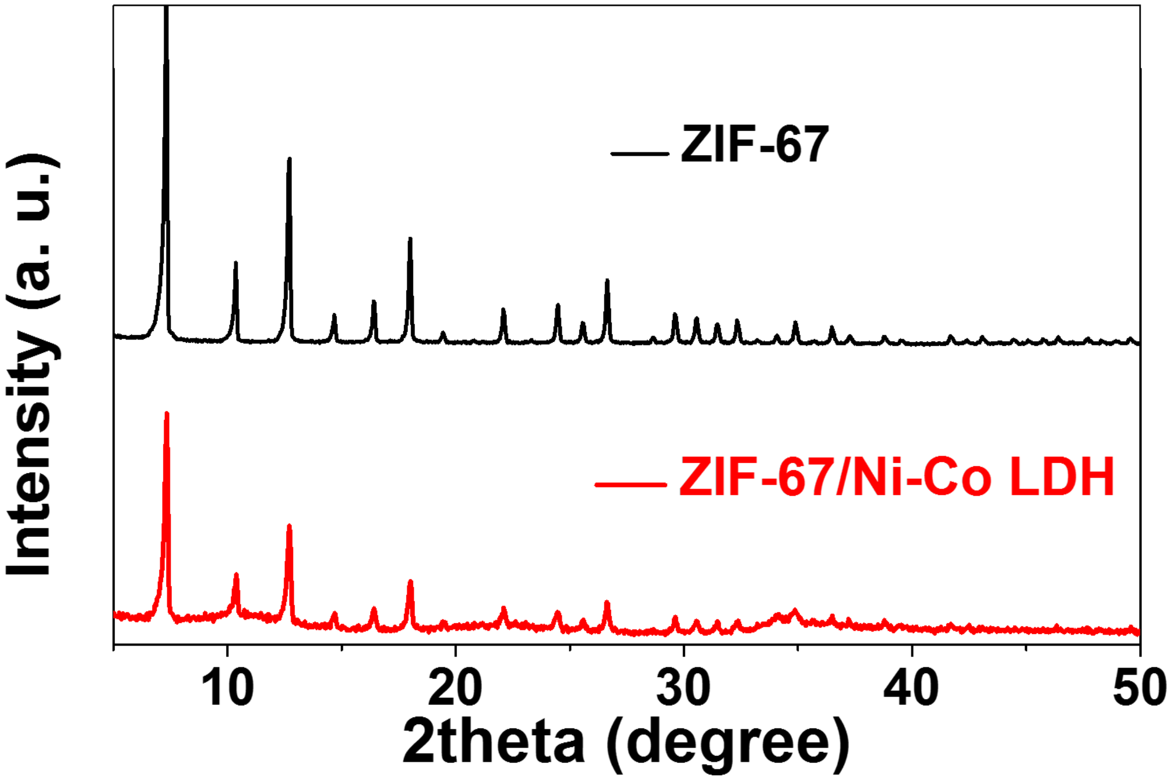


Fig. S2 XRD patterns of the ZIF-67 and ZIF-67/Ni-Co LDH nanocubes.

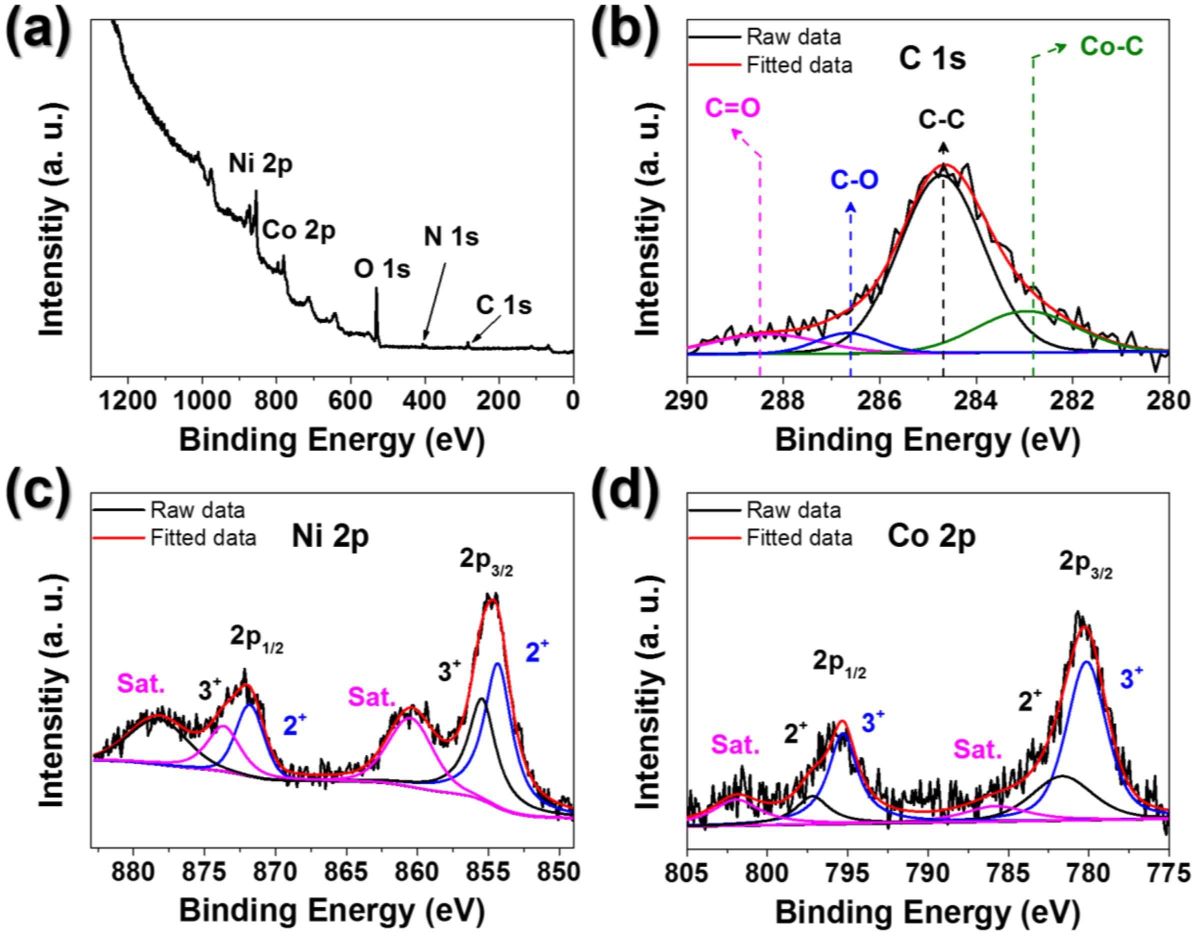


Fig. S3 XPS spectra of the ZIF-67/Ni-Co LDH yolk-shell nanocubes: (a) survey scan, (b) C 1s, (c) Ni 2p, and (d) Co 2p.

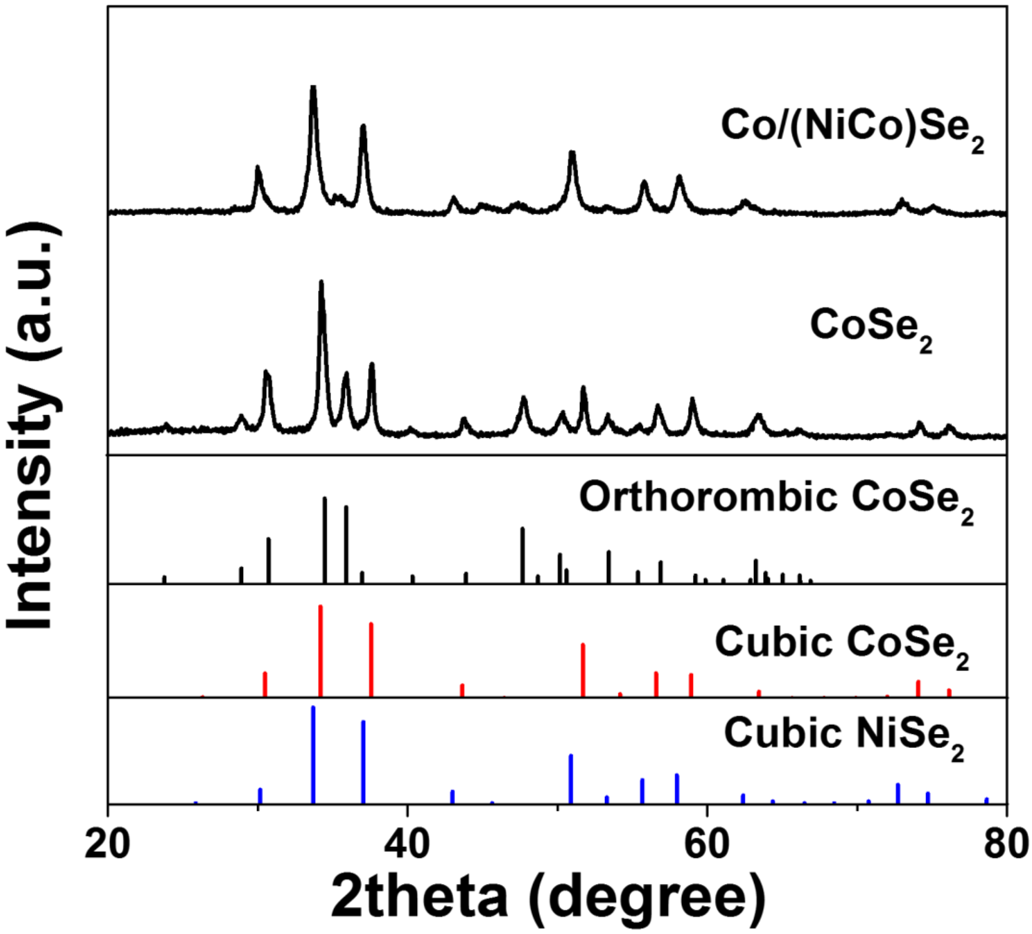


Fig. S4 XRD patterns of the Co/(NiCo)Se_2 and $CoSe_2$ nanocubes.

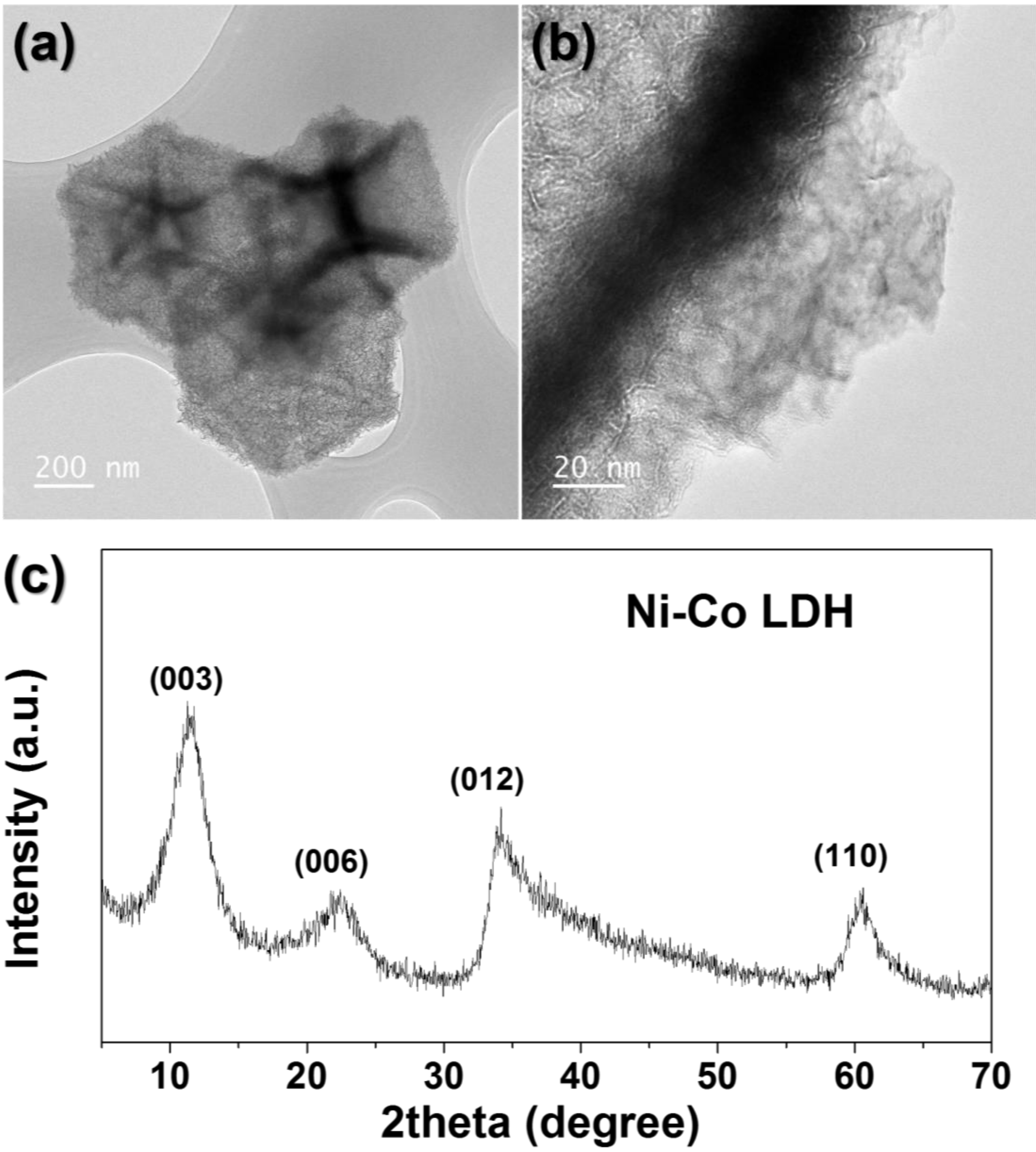


Fig. S5 (a) Low resolution, (b) high resolution TEM images and (c) XRD pattern of fully hollowed Ni-Co LDH nanocubes.

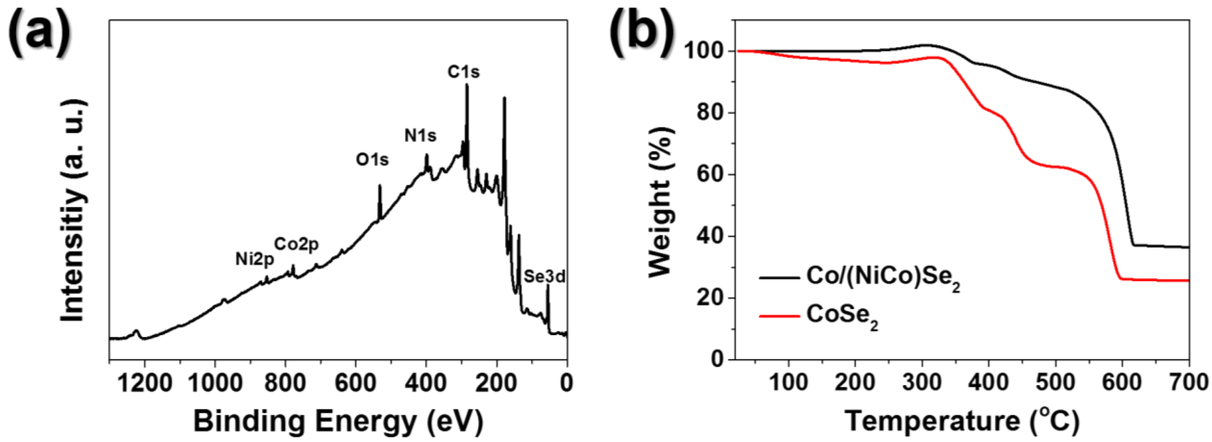


Fig. S6 (a) XPS survey scan of Co/(NiCo)Se_2 nanocubes and (b) TGA curves of the Co/(NiCo)Se_2 and $CoSe_2$ nanocubes.

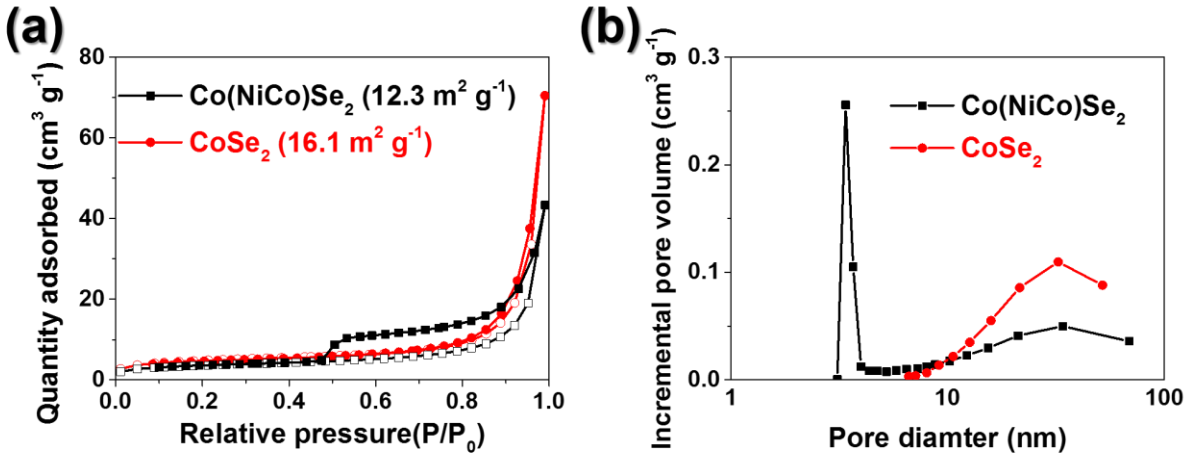


Fig. S7 (a) N_2 adsorption and desorption isotherms and (b) BJH pore size distributions of the nanocubes.

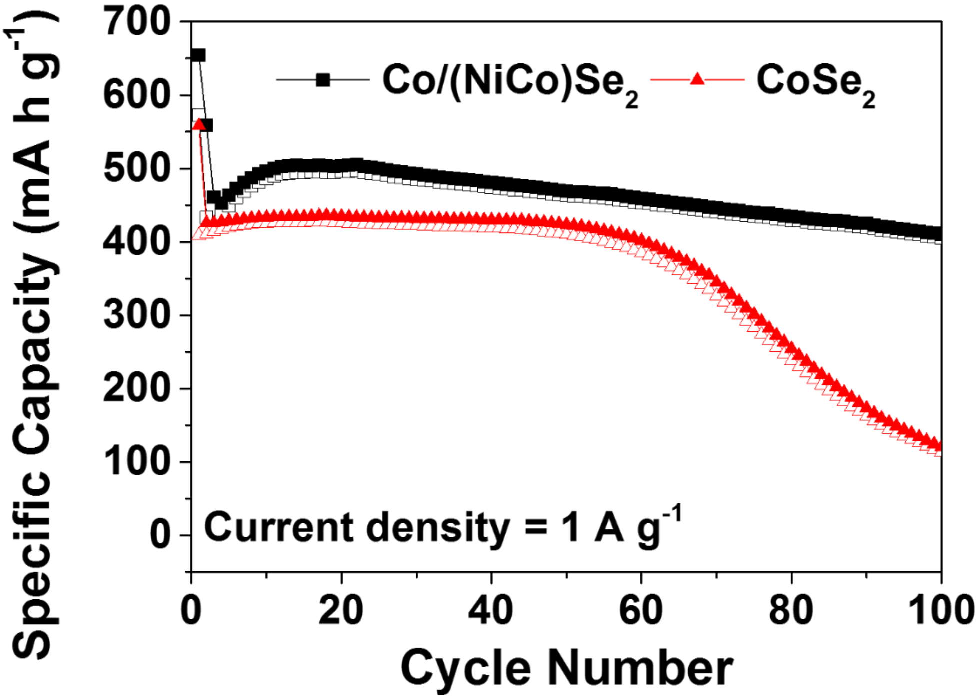
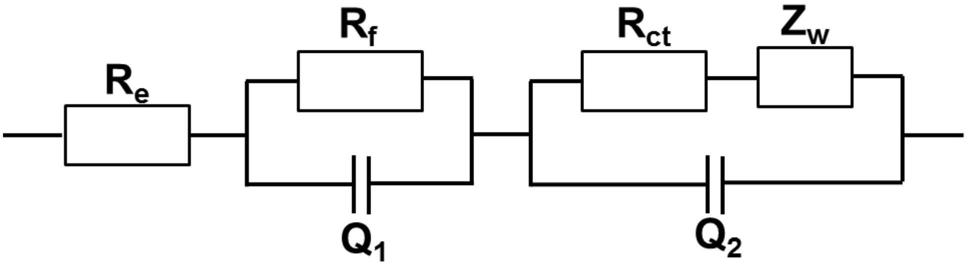


Fig. S8 Cycling performances of the Co/(NiCo)Se_2 and $CoSe_2$ nanocubes at a current density of 1 A g^{-1}.



R_e: the electrolyte resistance, corresponding to the intercept of high frequency semicircle at Z_{re} axis

R_f: the SEI layer resistance corresponding to the high-frequency semicircle

Q_1: the dielectric relaxation capacitance corresponding to the high-frequency semicircle

R_{ct}: the denote the charger transfer resistance related to the middle-frequency semicircle

Q_2: the associated double-layer capacitance related to the middle-frequency semicircle

Z_w: the Na-ion diffusion resistance

Fig. S9 Randle-type equivalent circuit model used for AC impedance fitting.

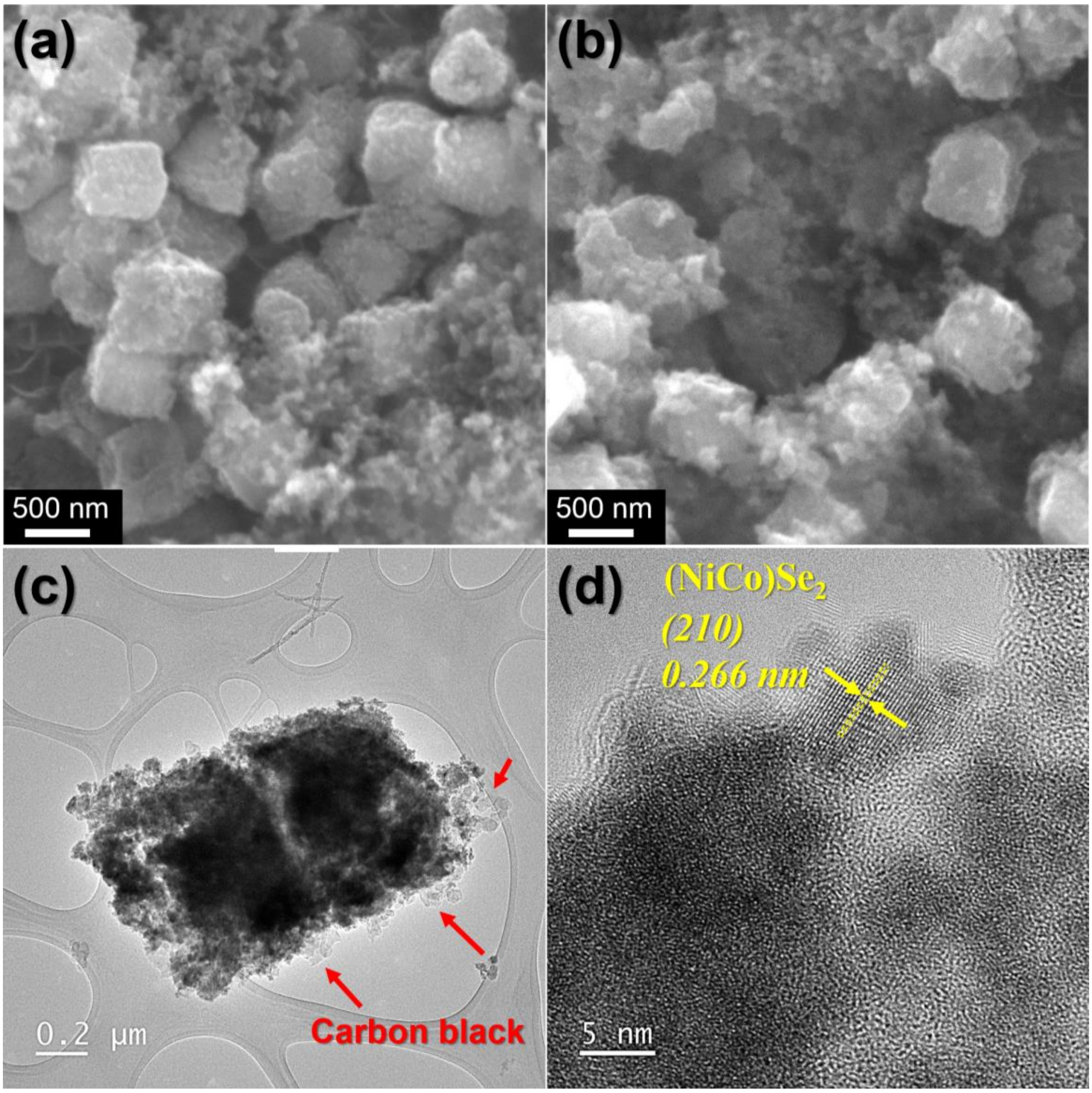


Fig. S10 (a, b) SEM and (c, d) TEM images of the Co/(NiCo)Se_2 nanocubes obtained after 80 cycles.

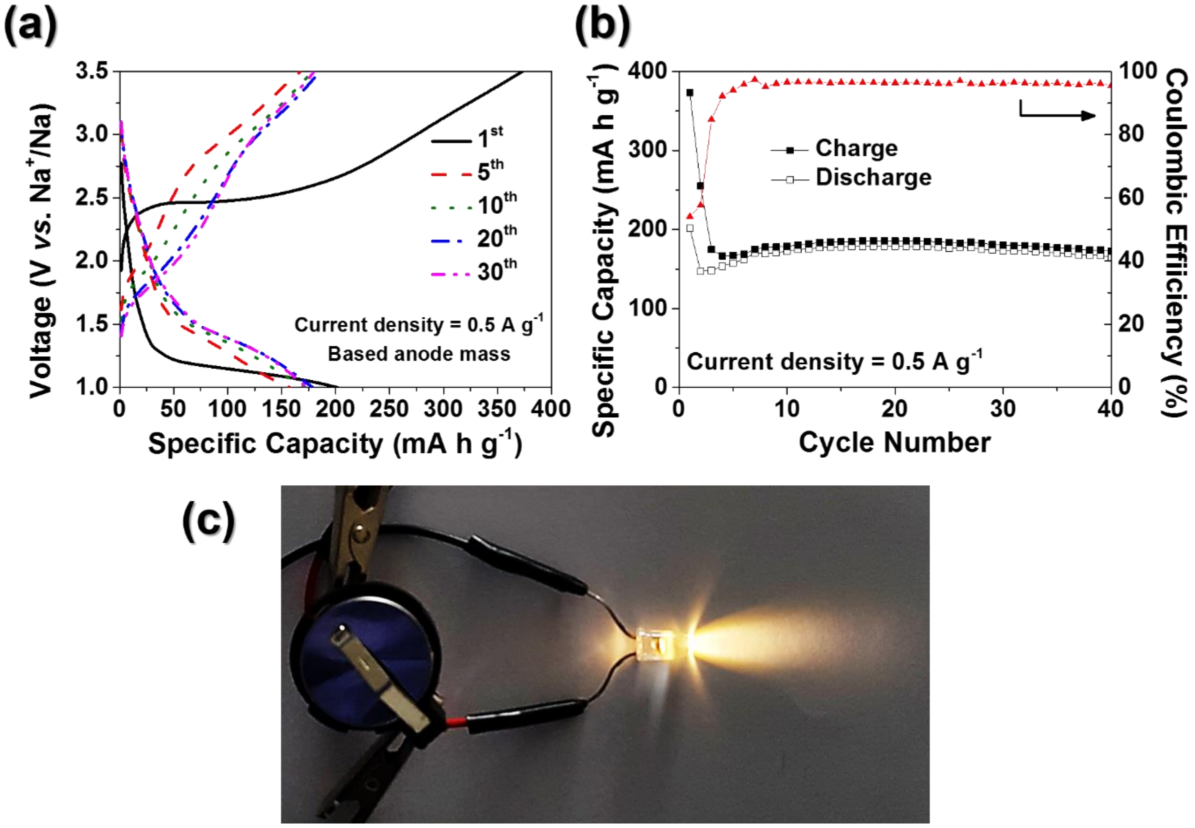


Fig. S11 Electrochemical properties of a Na-ion full cell of anode (Co(NiCo)Se_2)/cathode ($Na_3V_2(PO_4)_3$/carbon): (a) charge-discharge curves, (b) cycling performance at a current density of 0.5 A g^{-1} based on the anode mass, and (c) digital photograph of an LED diode powered by the fabricated Na-ion full cell.

Table S1. Electrochemical properties of various nanostructured $CoSe_x$ and $NiSe_x$ materials applied as sodium-ion batteries reported in the previous literatures.

Materials	Voltage range (V)	Current rate	Initial discharge/charge capacities [mA h g^{-1}]	Discharge capacity [mA h g^{-1}] and (cycle number)	Rate capacity [mA h g^{-1}]	Ref
Co/(NiCo)Se_2 nanocubes	**0.001-3**	**200 mA g^{-1}**	**661/526**	**497 (80)**	**470 (5.0 A g^{-1})**	**Our work**
Hollow $CoSe_2$ microspheres	0.001-3	500 mA g^{-1}	595/498	467 (40)	446 (0.9 A g^{-1})	[1]
$CoSe_x$-rGO composites	0.001-3	300 mA g^{-1}	656/459	420 (50)	357 (1.0 A g^{-1})	[2]
CoSe@porous carbon polyhedra	0.005-3	100 mA g^{-1}	504/340.2	341 (100)	208 (4.0 A g^{-1})	[3]
Co_9Se_8/rGO	0.01-3	50 mA g^{-1}	670/440	406 (100)	295 (5.0 A g^{-1})	[4]
N-doped yolk-shell CoSe/C	0.01-3	500 mA g^{-1}	850/x	531.6 (50)	457 (6.4 A g^{-1})	[5]
$NiSe_2$-rGO-C nanofibers	0.001-3	200 mA g^{-1}	755/575	468 (100)	243 (3.0 A g^{-1})	[6]
$NiSe_2$ nanoplates	0.005-3	100 mA g^{-1}	1008/517	400 (80)	249 (5.0 A g^{-1})	[7]
Core-shell NiSe/C	0.01-3	100 mA g^{-1}	480/355	280 (100)	186 (0.5 A g^{-1})	[8]

Table S2. Electrocatalytic activity for HER of various nanostructured $CoSe_x$ and $NiSe_x$ materials.

Materials	Electrolyte	Tafel slope [mV dec^{-1}]	Overpotential at current density = 10 mA cm^{-2} [mV]	Ref
Co/(NiCo)Se_2 nanocubes	**0.5M H_2SO_4**	**39.8**	**190**	**Our work**
$CoSe_2$ & $NiSe_2$ nanocrystals	0.5M H_2SO_4	$CoSe_2$ (40) $NiSe_2$ (44)	$CoSe_2$ (160) $NiSe_2$ (190)	[9]
$CoSe_2$ thin film	0.5M H_2SO_4	55	327	[10]
$CoSe_2$ nanoparticles coated on carbon black	0.5M H_2SO_4	42	200	[11]
$CoSe_2$@defective CNT	0.5M H_2SO_4	82	132	[12]
$NiCoSe_2$ nanowire on carbon cloth	0.5M H_2SO_4	40.1	131	[13]
Sea urchin-like NiSe	0.5M H_2SO_4	64	~280	[14]
Nanocrystalline $Ni_{0.85}Se$	0.5M H_2SO_4	49.3	~240	[15]
$CoMoS_3$ prisms	0.5M H_2SO_4	56.9	~170	[16]

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