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

Supporting Information

Hollow Bimetallic Cobalt-based Selenide Polyhedrons Derived from Metal–organic Framework: An Efficient Bifunctional Electrocatalyst for Overall Water Splitting

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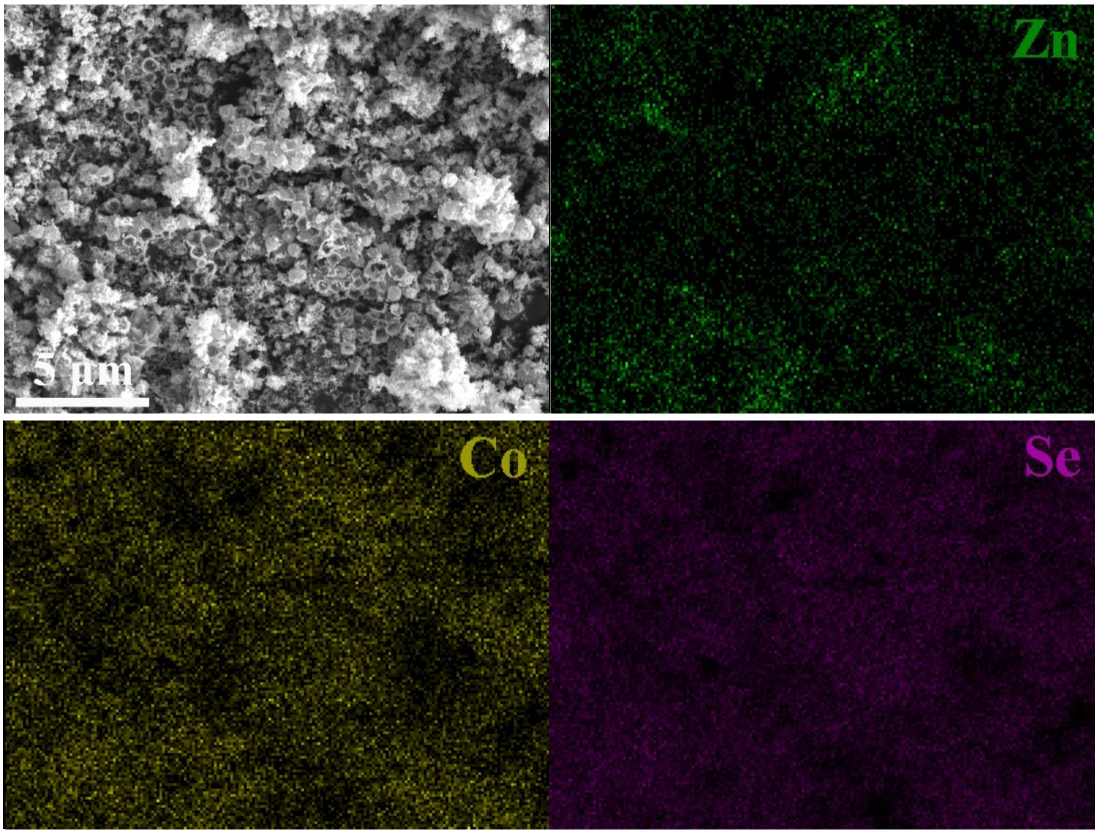
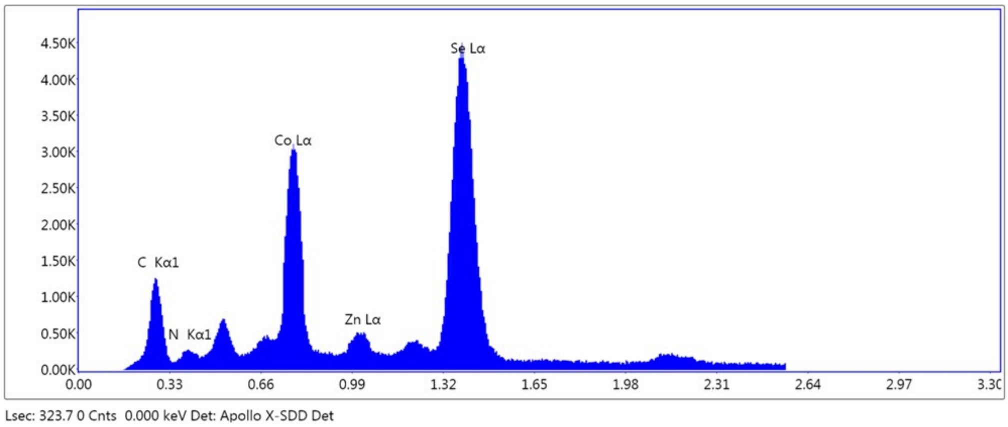
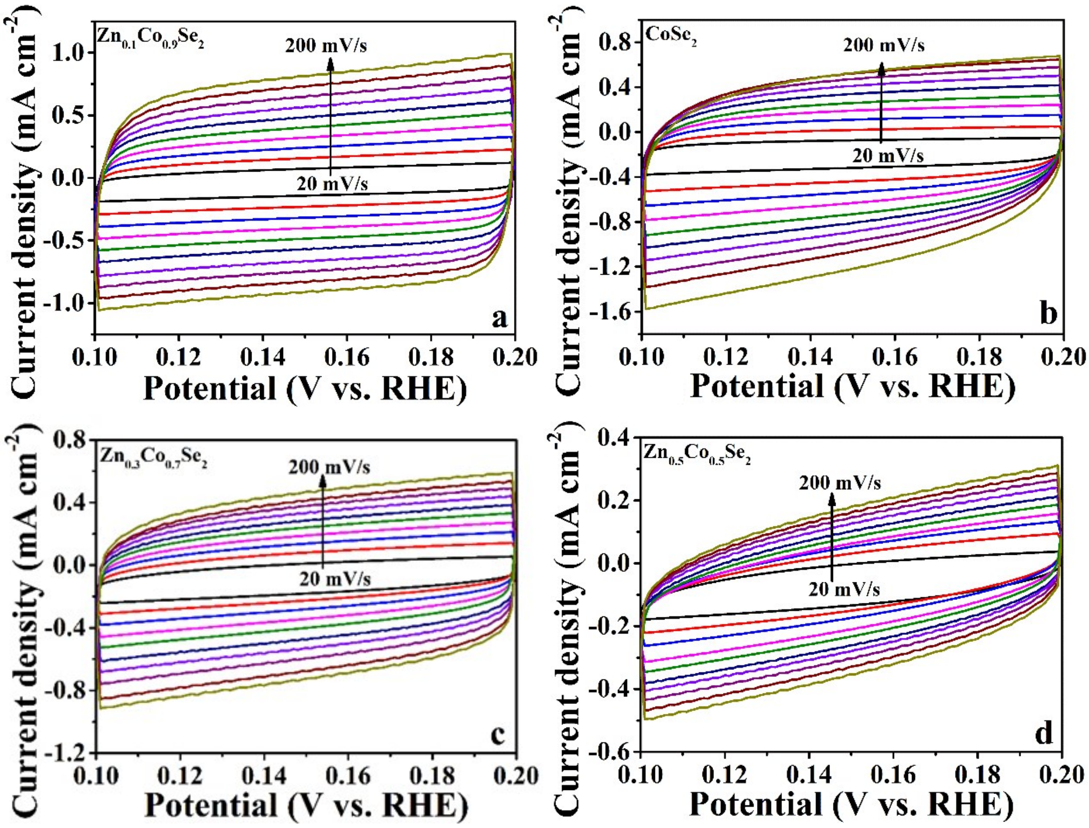


Fig. S1 SEM image corresponding EDX mapping of $Zn_{0.1}Co_{0.9}Se_2$



Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A
C-K	15.65	48.39	43.2	10.94	0.08	1.47	0.86	0.36
N-K	3.61	9.57	8.6	13.11	0.02	1.43	0.87	0.44
Co-L	23.89	15.06	72.7	5.02	0.22	0.96	1.02	0.97
Zn-L	2.47	1.40	7.4	10.61	0.02	0.94	1.03	0.91
Se-L	54.39	25.59	164.2	5.70	0.45	0.86	1.05	0.95

Fig. S2 SEM image corresponding EDS spot and the eZAF Smart Quant Results of $Zn_{0.1}Co_{0.9}Se_2$.



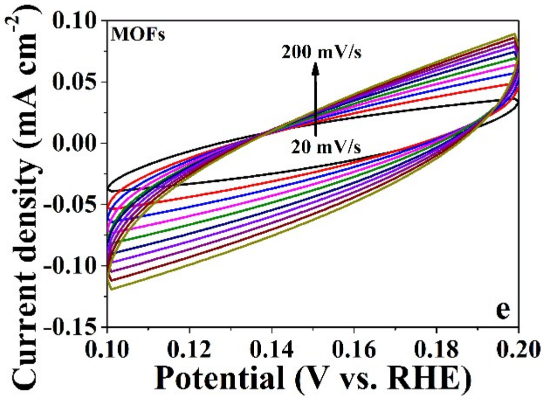


Fig. S3 Voltammograms of the (a) $Zn_{0.1}Co_{0.9}Se_2$ (b) $CoSe_2$ (c) $Zn_{0.3}Co_{0.7}Se_2$ (d) $Zn_{0.5}Co_{0.5}Se_2$ (e) MOFs at various scan rate (20-200 mV s^{-1}) in 0.5 M H_2SO_4 solution.

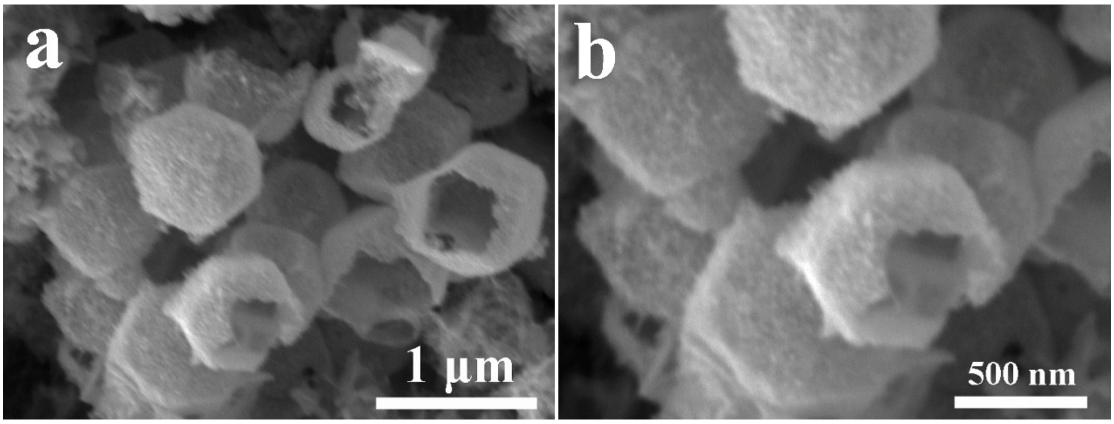
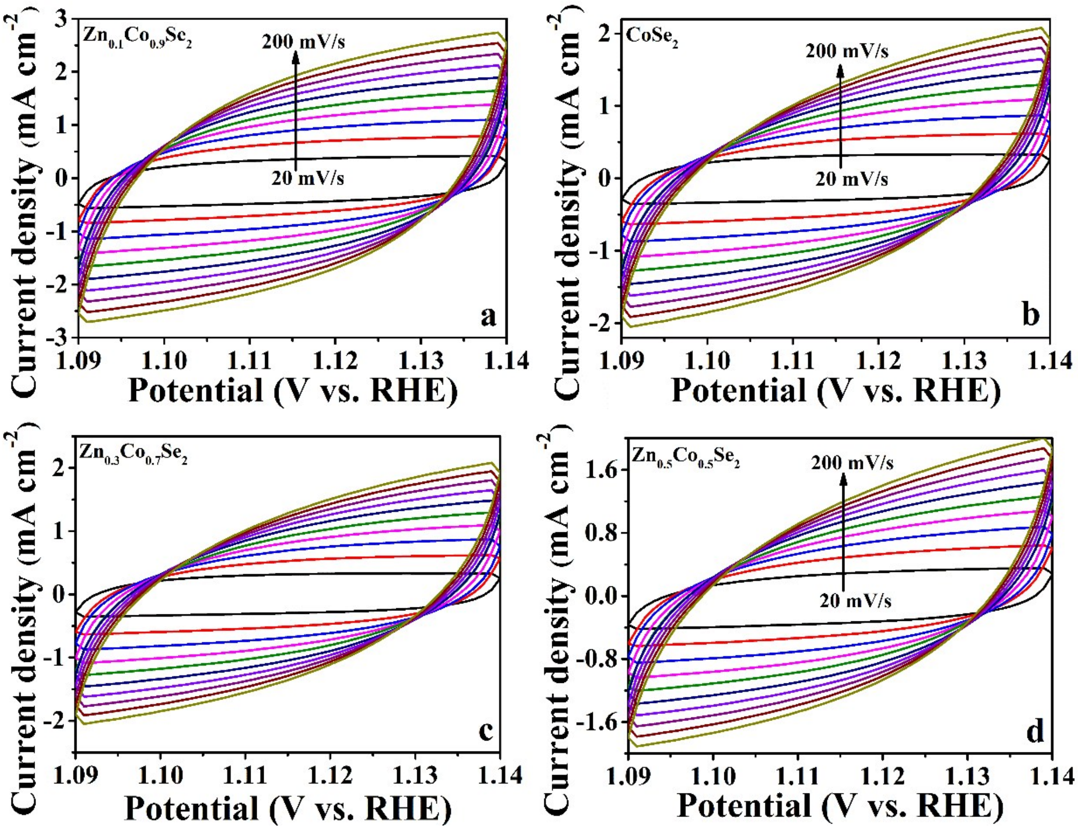


Fig. S4 the SEM of $Zn_{0.1}Co_{0.9}Se_2$ after 5000 cycles in 0.5M H_2SO_4 solution.



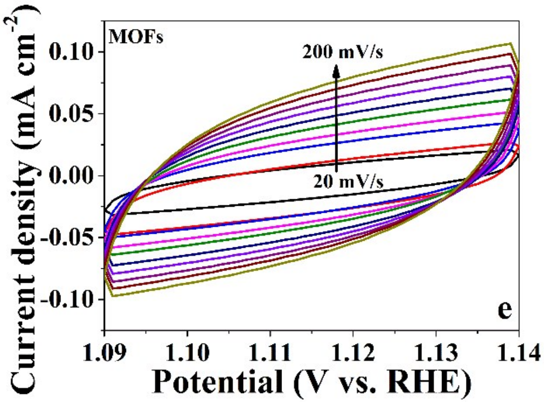


Fig. S5 Voltammograms of the (a) $Zn_{0.1}Co_{0.9}Se_2$ (b) $CoSe_2$ (c) $Zn_{0.3}Co_{0.7}Se_2$ (d) $Zn_{0.5}Co_{0.5}Se_2$ (e) MOFs at various scan rate (20-200 mV s^{-1}) in 1.0 M KOH solution.

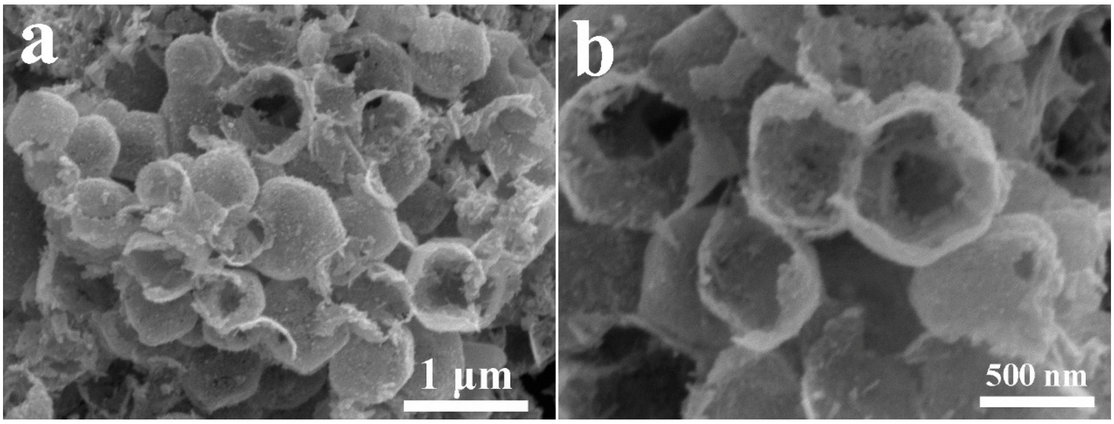


Fig. S6 the SEM of $Zn_{0.1}Co_{0.9}Se_2$ after 5000 cycles in1.0 M KOH solution.

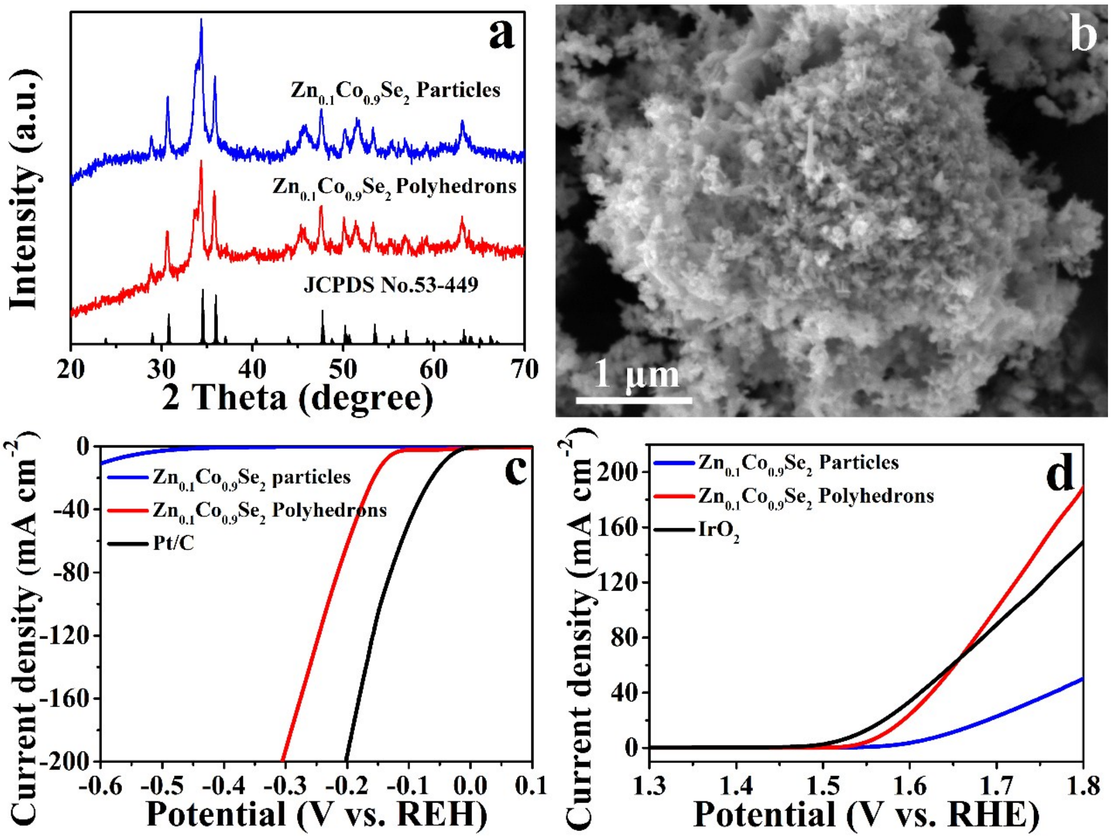


Fig. S7 the XRD patterns (a), SEM (b) and the polarization curves for HER in 0.5M H_2SO_4 solution (c) and OER in 1.0M KOH solution (d) of $Zn_{0.1}Co_{0.9}Se_2$ Particles.

Table S1. Element composition of various $M_xCo_{1-x}Se_2$ (a represent mass ratio of M/Co detected by ICP-AES and b represent the molar ratio after converting).

Samples	[Mass(M:Co)][a]	[Molar(M:Co)][b]
$Zn_{0.1}Co_{0.9}Se_2$	0.1163	0.1048
$Zn_{0.3}Co_{0.7}Se_2$	0.4588	0.4136
$Zn_{0.5}Co_{0.5}Se_2$	0.8967	0.8084
$Ni_{0.1}Co_{0.9}Se_2$	0.1128	0.1133
$Cu_{0.1}Co_{0.9}Se_2$	0.1183	0.1097

Table S2. XPS results of $Zn_{0.1}Co_{0.3}Se_2$ on the atomic percentages of C, N, O, Zn, Co and the Se distributions.

element	C	N	O	Zn	Co	Se
percentage	79.76	1.88	7.87	0.31	2.51	7.67

Table S3 The atomic percentage distributions of C, N, O, Zn, Co and Se in $Zn_{0.1}Co_{0.9}Se_2$ (C, N and O detected by Elemental Analyzer, Zn, Co and Se detected by ICP-AES)

element	C	N	O	Zn	Co	Se
atom percent	66.97	3.47	3.96	0.76	7.27	17.57

Table S4. Comparison of the HER activity of some reported transition metal selenide electrocatalysts in 0.5 M H_2SO_4.

Catalysts	Mass Loading (mg cm^{-2})	η^{10} (mV vs. RHE)	Tafel slope (mV dec^{-1})	Reference
$Zn_{0.1}Co_{0.9}Se_2$	0.285	140	49.9	*This work*
$CoSe_2$@DC	0.357	132	82.0	*Nano Energy 28 (2016) 143–150*
CoSe2 NiSe2	1.0	160 190	40 44	*ACS Appl. Mater. Interfaces. 2016, 8, 5327-5334*
$Fe_{0.7}Co_{0.3}Se_2$/RGO-12	1.1	166	36	*ACS Appl. Mater. Interfaces 2016, **8**, 18036-18042*
$CoSe_2$ NPs @ carbon fiber	3.0	137	42.1	*J. Am. Chem. Soc., 2014,136, 4897*
$CoSe_2$ films@ Ti foil	2.8	135	62.0	*J. Mater. Chem. A, 2014, 2, 13835*
$CoSe_2$ necklace-like NWs@CFP	2.8	165	34.0	*J. Mater. Chem. A, 2015, 3, 9415*
Polymorphic $CoSe_2$		150	31.2	*ACS Appl. Mater. Interfaces 2015, 7, 1772*
Phase Pure $CoSe_2$		272	61.0	*ACS Energy Lett. 2016, 1, 607−61*
$CoSe_2$ NWs	1.3	130	32	*ACS Appl. Mater. Interfaces 2015,7,3877-3881*
$CoSe_2$ $NiSe_2$ $CoSe_2$/C NPs	0.150	170 180 70	42.4 56.9 40.2	*Energy Environ. Sci. 2013, 6,3553-3558*
$MoS_2/CoSe_2$ $CoSe_2$ NSs	1.0	70 120	36.0 48.0	*Nat. Commun. 2015, 6, 5982-5989*
$NiSe_2$ NWs $CoSe_2$ NWs	1.0	170 196	31.1 39.6	*Nanoscale 2015, 17, 14813-14816*
$NiSe_2$ NSs on Graphite disk		173	31	*ACS Catal. 2015, 5, 6355-6361*

Table S5. Comparison of the OER activity of some reported transition metal selenide electrocatalysts in 1.0 M KOH.

Catalysts	Mass Loading (mg cm^{-2})	η^{10} (mV vs. RHE)	Tafel slope (mV dec^{-1})	Reference
$Zn_{0.1}Co_{0.9}Se_2$	0.285	340	43.2	*This work*
Zn-doped $CoSe_2$/CFC		356	88	*ACS Appl. Mater. Interfaces, 2016, 8, 26902-26907*
$CoSe_2$/CF	2.9	297	41	*Nano Research, 2016, 9, 2234-2243*
Co_7Se_8		260	32.6	*ACS Appl. Mater. Interfaces, 2016, 8, 17292-17302*
EG/CoSe-NiFe-LDH	4.0	250	57	*Energy Environ. Sci. 2016, 9, 478−483*
coral-like $CoSe_2$		290	40	*ACS Catal. 2015, 5, 3625−3637.*
$CoSe_2$/Ti mesh		292	69	*Chem. Commun. 2015, 51, 16683−16686*
Ni_3Se_2		290	82	*Catal. Sci. Technol. 2015, 5, 4954−4958*
Ni_3Se_2/CF		300	80	*ACS Appl. Mater. Interfaces 2016, 8, 4718−4723*
NiSe NWs	2.8	400	64	*Angew. Chem. Int. Ed. 2015, 54, 9351-9355*
2D $FeSe_2$	0.01	330	48.1	*Nano Energy 31 (2017) 90–95*
$CoSe_2$ $NiSe_2$	1.0	430 250	50 38	*ACS Appl. Mater. Interfaces. 2016, 8, 5327-5334*
$NiSe_2$	1.4	323	83.6	*ACS Appl. Mater. Interfaces 2016, 8, 19386–19392*