Supporting Information

The Role of the Metal Element in Layered Metal Phosphorus Triselenides Upon Their Electrochemical Sensing and Energy Applications

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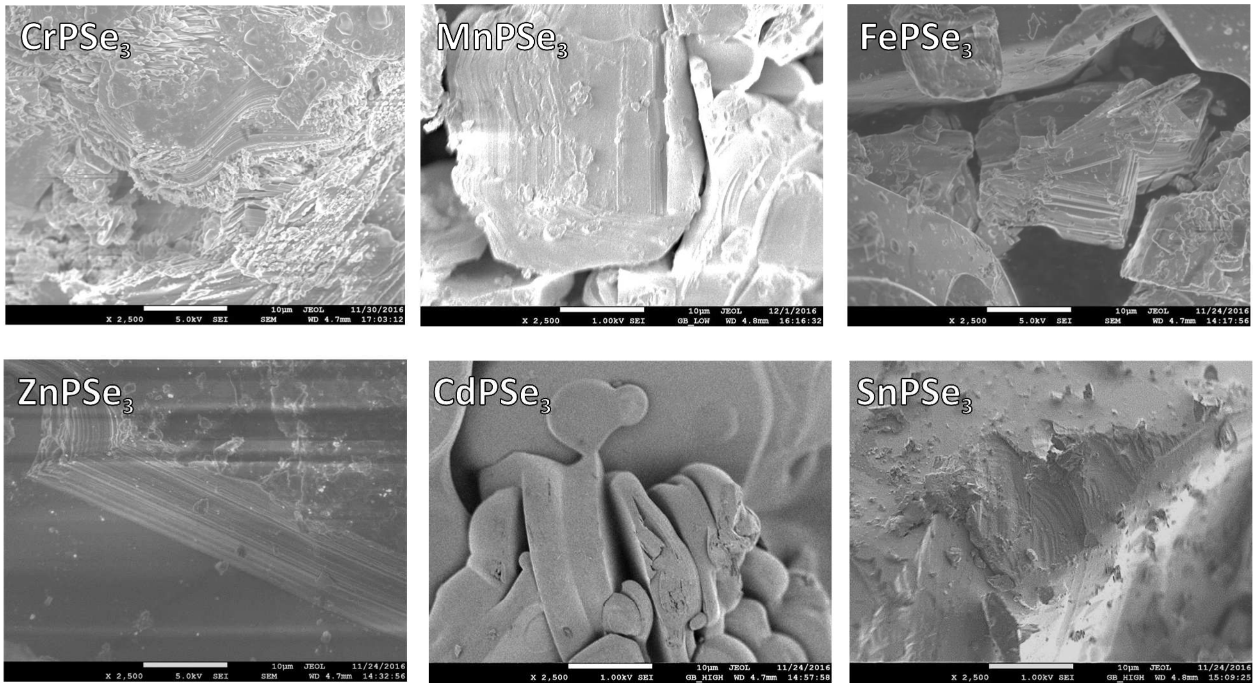

Figure S1. SEM images of the different metal selenophosphite. From left to right, top row: $CrPSe_3$, $MnPSe_3$, and $FePSe_3$; bottom row: $ZnPSe_3$ $CdPSe_3$ and $SnPSe_3$. Bars in the image represent 10 μm.

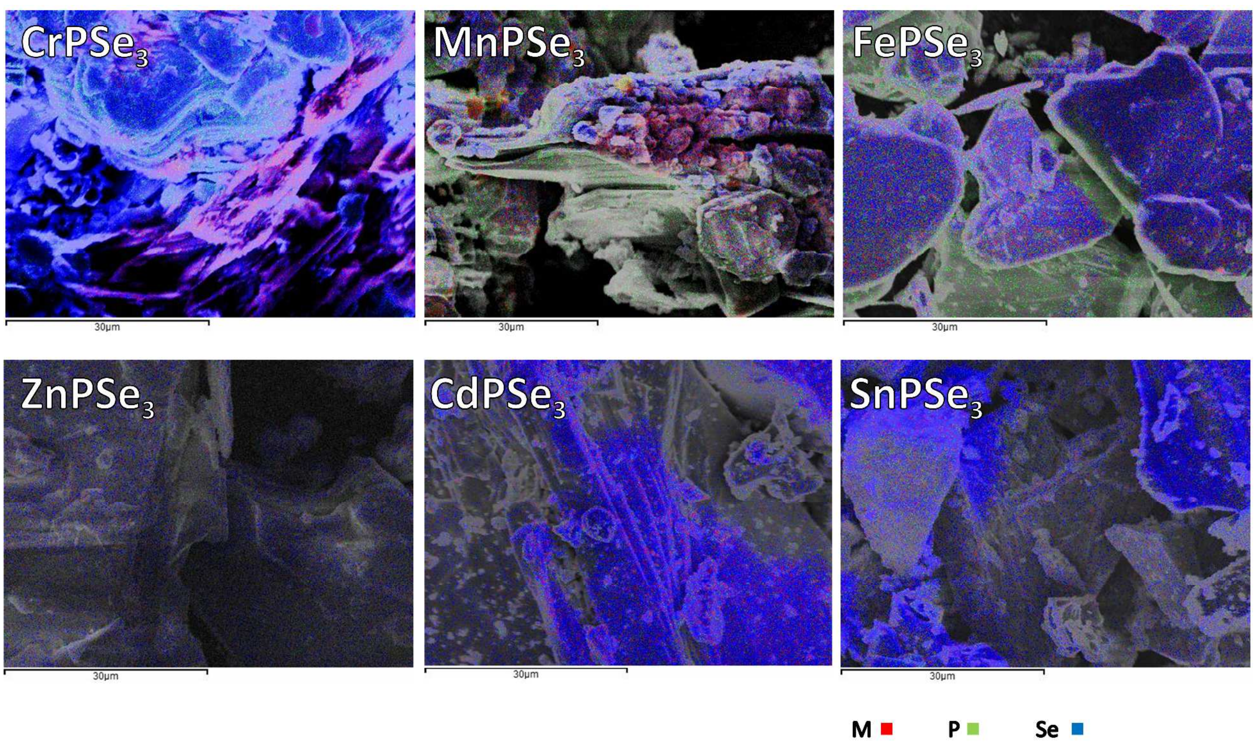

Figure S2. EDS elementary mapping of the $MPSe_3$ layered materials.

Table S1. Selenium/metal and phosphorus/metal ratio from the elemental composition obtained from the energy-dispersive X-ray spectroscopy (EDS).

	M at.%	P at.%	Se at.%	O at.%	C at.%	Se/M	P/M
$CrPSe_3$	7.1	8.5	19.5	34.7	30.3	2.7	1.2
$MnPSe_3$	7.7	6.0	19.2	18.4	49.8	2.5	0.8
$FePSe_3$	9.5	8.8	24.7	7.8	49.1	2.6	0.9
$ZnPSe_3$	11.3	10.7	29.5	6.2	42.4	2.6	1.0
$CdPSe_3$	11.7	9.6	29.4	4.6	44.7	2.5	0.8
$SnPSe_3$	13.2	10.0	33.6	5.5	38.0	2.6	0.8

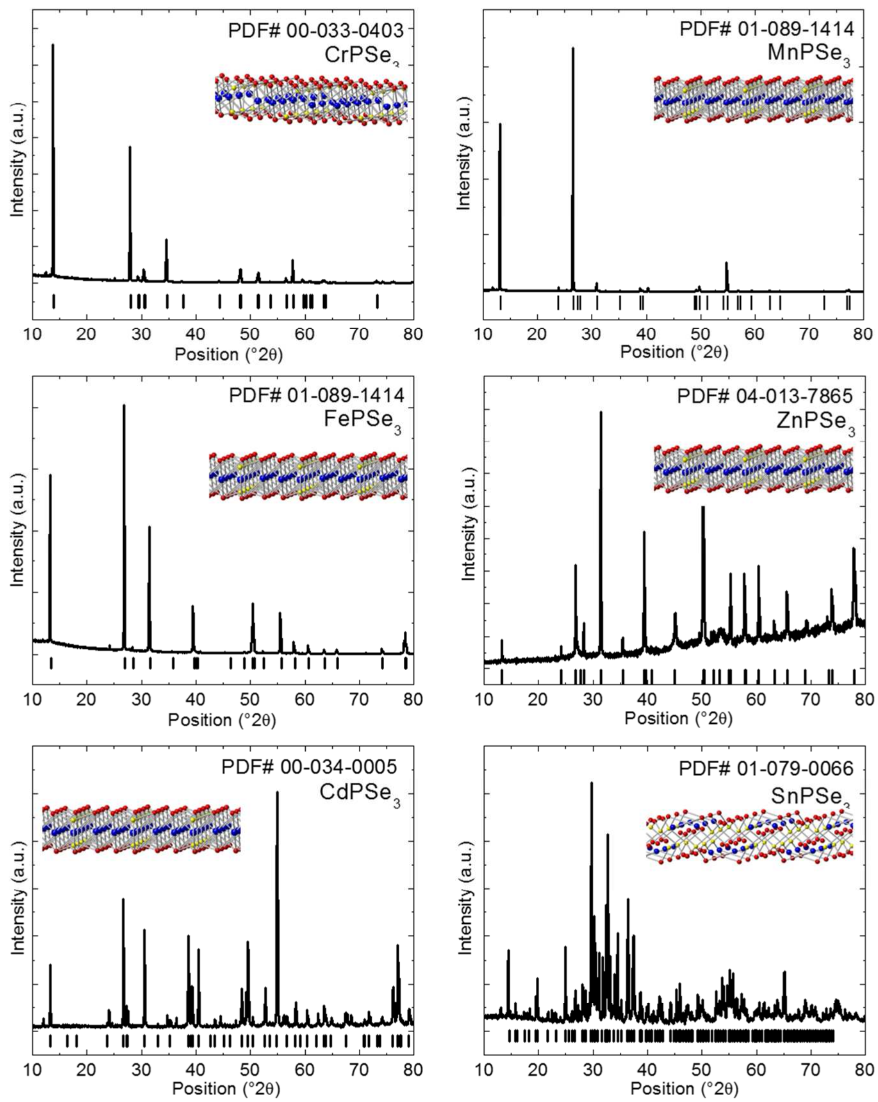

Figure S3. X-ray diffraction patterns with schematic crystal structure representations (insets) of metal selenophosphites ($MPSe_3$).

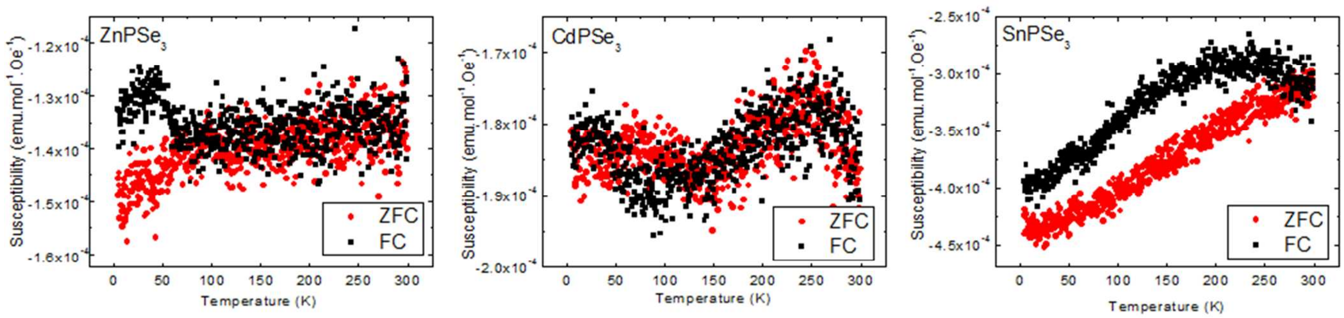

Figure S4. The magnetic susceptibility of diamagnetic $ZnPSe_3$, $CdPSe_3$ and $SnPSe_3$.

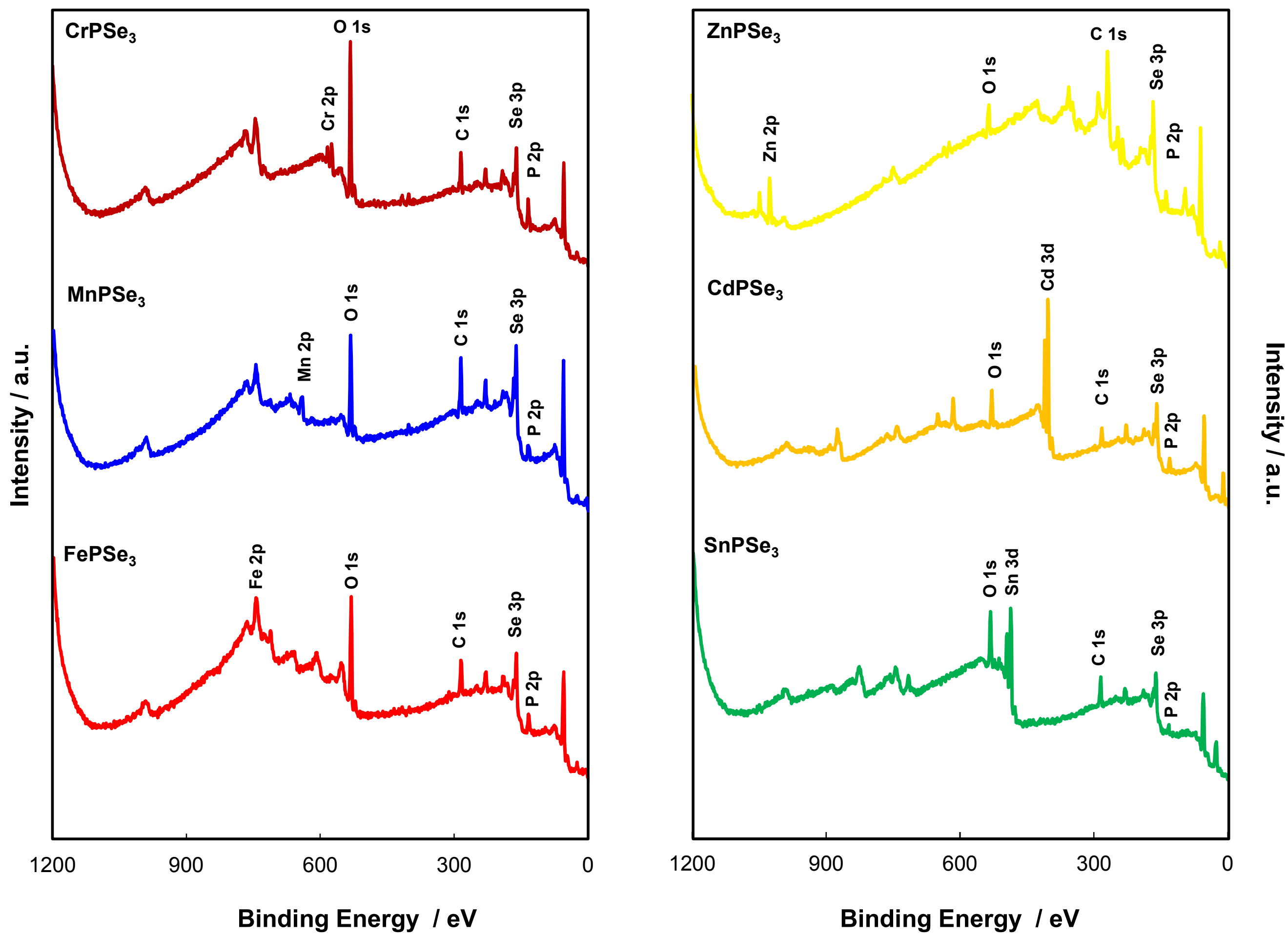

Figure S5. Wide-scan X-ray photoelectron spectra of layered $MPSe_3$ crystals.

Table S2. Summary of the binding energies of the different XPS regions for the $MPSe_3$ layered materials.

	Peaks position in M (eV)	Peaks position in P (eV)	Peaks position in Se (eV)
$CrPSe_3$	Cr $2p_{3/2}$ ~ 573.4	P $2p_{3/2}$ ~ 130.1	Se $3d_{5/2}$ ~ 52.8
	Cr $2p_{1/2}$ ~ 582.8	P $2p_{1/2}$ ~ 131.9	Se $3d_{3/2}$ ~ 54.5
		P_4O_{10} ~ 134.1	
$MnPSe_3$	Mn $2p_{3/2}$ ~ 639.3	P $2p_{3/2}$ ~ 130.7	Se $3d_{5/2}$ ~ 53.8
	Mn $2p_{3/2}$ ~ 642.5 (MnO_2)	P $2p_{1/2}$ ~ 131.6	Se $3d_{3/2}$ ~ 54.9
		P_4O_{10} ~ 133.6	
$FePSe_3$	Fe $2p_{3/2}$ ~ 713.2	P $2p_{3/2}$ ~ 130.7	Se $3d_{5/2}$ ~ 54.4
	Fe $2p_{1/2}$ ~ 726.8	P $2p_{1/2}$ ~ 133.35	Se $3d_{3/2}$ ~ 56.1
		P_4O_{10} ~ 136.6	
$ZnPSe_3$	Zn $2p_{3/2}$ ~ 1020.9	P $2p_{3/2}$ ~ 130.2	Se $3d_{5/2}$ ~ 55.4
	Zn $2p_{1/2}$ ~ 1043.7	P $2p_{1/2}$ ~ 132.3	Se $3d_{3/2}$ ~ 53.5
$CdPSe_3$	Cd $3d_{5/2}$ ~ 404.8	P $2p_{3/2}$ ~ 131.0	Se $3d_{5/2}$ ~ 51.2
	Cd $3d_{3/2}$ ~ 411.7	P $2p_{1/2}$ ~ 132.0	Se $3d_{3/2}$ ~ 54.9
		P_4O_{10} ~ 133.6	
$SnPSe_3$	Sn $3d_{5/2}$ ~ 484.6	P $2p_{3/2}$ ~ 130.6	Se $3d_{5/2}$ ~ 55.3
	Sn $3d_{5/2}$ ~ 486.4 (SnO_2)	P $2p_{1/2}$ ~ 133.3	Se $3d_{3/2}$ ~ 53.8
	Sn $3d_{3/2}$ ~ 493.1	P_4O_{10} ~ 136.8	
	Sn $3d_{3/2}$ ~ 494.9 (SnO_2)		

Table S3. Oxidation and reduction peaks from inherent electrochemistry study when scanned anodically of metal selenophosphites.

	Anodic peaks										**Cathodic peaks**									
	Scan 1		Scan 2		Scan 3		Scan 4		Scan 5		Scan 1		Scan 2		Scan 3		Scan 4		Scan 5	
	E *(V)*	*I* *(A)*	*E* *(V)*	*I* *(A)*	*E* *(V)*	*I* *(A)*	*E* *(V)*	*I* *(A)*	*E* *(V)*	*I* *(A)*	*E* *(V)*	*I* *(A)*	*E* *(V)*	*I* *(A)*	*E* *(V)*	*I* *(A)*	*E* *(V)*	*I* *(A)*	*E* *(V)*	*I* *(A)*
$CrPSe_3$	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
$MnPSe_3$	0.815	4.0E-05	0.818	2.0E-05	0.818	1.8E-05	0.818	1.6E-05	0.818	1.5E-05	-1.362	-5.3E-05	-1.345	-1.3E-05	-1.345	-5.8E-06	-1.345	-5.1E-06	-1.345	-5.6E-06
	1.011	3.2E-06	—	—	—	—	—	—	—	—	—	—	-1.685	-2.0E-05	-1.685	-2.0E-05	-1.685	-2.0E-05	-1.685	-2.0E-05
	1.333	6.4E-04	1.433	7.0E-05	1.433	4.0E-05	1.433	3.6E-05	1.433	3.3E-05	—	—	—	—	—	—	—	—	—	—
$FePSe_3$	0.769	1.9E-04	—	—	—	—	—	—	—	—										
	-0.549	3.3E-04	-0.557	1.9E-04	-0.557	1.7E-04	-0.557	1.5E-04	-0.540	1.4E-04	-1.104	-2.0E-04	—	—	—	—	—	—	—	—
	-0.222	1.3E-04	—	—	—	—	—	—	—	—										
$ZnPSe_3$	1.221	2.7E-05	—	—	—	—	—	—	—	—	-0.952	-1.4E-05	—	—	—	—	—	—	—	—
	1.450	3.1E-05	1.502	1.5E-05	1.502	1.2E-05	1.502	9.9E-06	1.502	7.9E-06	-1.404	-1.9E-05	—	—	—	—	—	—	—	—
	-0.674	5.7E-06	-0.685	4.0E-06	-0.696	2.4E-06	-0.699	2.2E-06	-0.703	2.0E-06	-1.514	-2.2E-05	—	—	—	—	—	—	—	—
	-0.696	2.4E-06	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
$CdPSe_3$	1.228	4.6E-05	1.184	1.1E-06	—	—	—	—	—	—	-0.963	-3.4E-05	-0.963	-1.4E-06	—	—	—	—	—	—
	-0.674	8.2E-06	-0.671	5.0E-06	-0.684	3.0E-06	-0.691	2.7E-06	-0.691	1.1E-06	-1.379	-6.5E-06	-1.475	-4.6E-06	—	—	—	—	—	—
$SnPSe_3$	1.211	1.5E-05	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1.682	2.7E-05	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

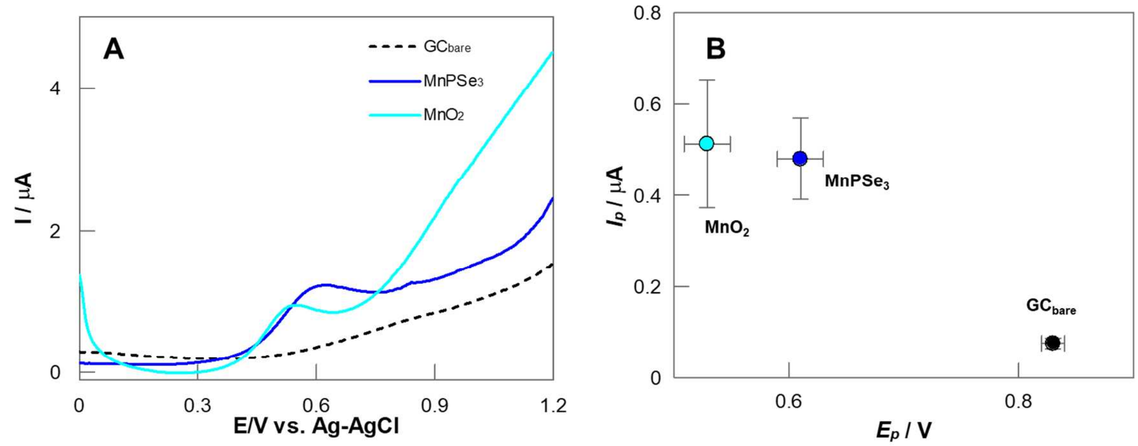

Figure S6. DPVs of bare GC and GC modified with different $MnPSe_3$ and MnO_2 in 1.0 mM Cysteine, 0.1 M PBS pH 7.2 (A). Average E_p and I_p for the oxidation process of Cys at GC and the modified electrodes. Error bars correspond to standard deviations based on triplicate measurements. Scan rate: 5 mV/s.

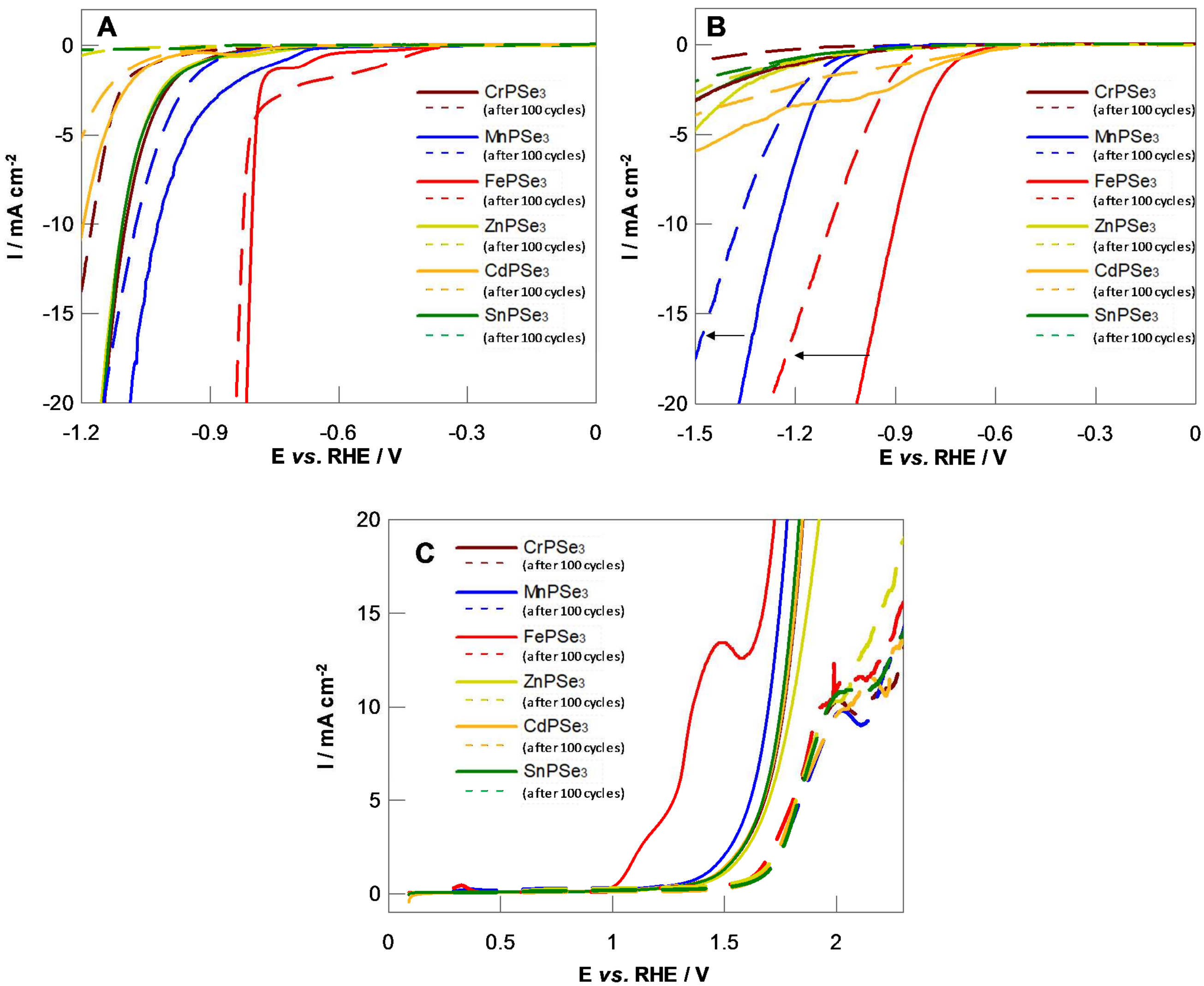

Figure S7. Stability test for the $MPSe_3$ as catalysts of HER and OER. LSV curves for HER before and after 100 CV cycles in 0.5M H_2SO_4 (A) and 1.0 M KOH (B). CV scan rate at 100 mV/s, 100 cycles, -0.5 V < E < 0.0 V vs. RHE. LSV curves for OERR before and after 100 CV cycles in 1.0 M KOH (c). CV scan rate at 100 mV/s, 100 cycles, 0.0 < E < 0.5 V vs. RHE.