Supporting Information for

Metal Diselenide Nanoparticles as Highly Active and Stable Electrocatalyst for Hydrogen Evolution Reaction

Jia Liang,^{a,b} Yingchao Yang,^a Jing Zhang,^a Jingjie Wu,^a Pei Dong,^a Jiangtan Yuan,^a Gengmin Zhang,^b and Jun Lou.^{a,*}

^aDepartment of Materials Science and NanoEngineering, Rice University, 6100 Main Street, Houston,

Texas 77005, United States

^bKey Laboratory for the Physics and Chemistry of Nanodevices and Department of Electronics, Peking

University, Beijing 100871, China

*Corresponding Author: jlou@rice.edu (J. Lou)

Experimental Section

Preparation of NiSe₂, CoSe₂ and PdSe₂ powders

NiSe₂ powder was prepared by a facile and low-cost hydrothermal method. Typically, after stirring 30 min, a 30 mL mixture aqueous solution, containing 0.1 mol NaOH, 1 mmol NiCl₂·6H₂O, 2 mmol Se powder and 1.6 mmol Ethylene Diamine Tetraacetic Acid (EDTA) was transferred into a 50 mL Teflonlined autoclave. Then, the sealed autoclave was put in an electric oven at 200 °C for 10 hr. After the reaction finished, the autoclave was taken out of the oven and rapidly cooled under tap water flushing for 10 min. The precipitates were then washed with deionized water several times and collected by centrifugation. Finally, the NiSe₂ powder was achieved by drying at 50 °C overnight. Other metal chalcogenides powders, such as CoSe₂ and PdSe₂, can also be prepared with the same synthetic strategy, by using their own precursors of CoSO₄·7H₂O or PdCl₂.

Preparation of working electrodes

Before the electrochemical measurement, the working electrodes of glassy carbon containing NiSe₂, CoSe₂ and PdSe₂ should be prepared first. In short, 3 mg as-synthesized NiSe₂ (or CoSe₂, PdSe₂) powder was dispersed in 80 μ L of 5:3 v/v water/isopropanol with 7 μ L Nafion solution. This dispersive process was lasted at least 15 hr by sonication to generate a homogeneous ink. Then, 2 μ L of the ink was transferred onto a glassy carbon electrode (loading ~ 1 mg/cm²). Finally, the as-prepared catalyst film was dried at room temperature. As a control experiment, a Pt/C working electrode was fabricated.

Electrochemical measurements

Electrochemical measurements were performed at room temperature using a standard three-electrode electrochemical cell setup with 0.5 M H₂SO₄ solution. The glassy carbon containing catalyst film was used as the working electrode. A Pt foil and the Ag/AgCl were used as counter and reference electrodes, respectively. The reference electrode was calibrated with respect to reversible hydrogen electrode (RHE), yielding the relation E(RHE) = E(Ag/AgCl) + 0.247. The polarization curves were obtained by sweeping the potential from -0.156 to -0.756 V vs. Ag/AgCl with a scan rate of 5 mV/s. AC impedance measurements were carried out with the frequency range from 1 Hz to 100 KHz. To get Tafel plots, the polarization curves were replotted as overpotential vs. log current density. The stability test was investigated by the continuous cyclic voltammograms with scan rate of 100 mV/s for 1000 times. After cycling, the polarization curves were measured again with a scan rate of 5 mV/s. Based on impedance spectroscopy, all data in this report have been corrected.

Characterization

The morphology and microstructure of these samples were examined by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The crystallinities of these samples were investigated using X-ray diffraction (XRD). These samples were also characterized by X-ray photoelectron spectroscopy (XPS). The C 1s line, which is generally believed to have arisen from the adventitious carbon due to the exposure to the atmosphere, was also found in the spectra of all the samples and used as the standard for calibration during data processing.



Fig. S1 SEM (a) and TEM (b) images of CoSe₂ nanoparticles; SEM (c) and TEM (d) images of PdSe₂ nanoparticles.



Fig. S2 Energy Dispersive X-ray spectra (EDX) of NiSe₂ nanoparticles



Fig. S4 XPS (a) and EDX (b) spectra of PdSe₂.



Fig. S5 Nyquist plots from electrochemical impedance spectra of the NiSe₂, CoSe₂, and PdSe₂ catalysts.



Fig. S6 Polarization curves for five individual electrodes comprised of NiSe₂ (a), CoSe₂ (b) and PdSe₂ (c) catalysts in 0.5 M H₂SO₄.



Fig. S7 Electrochemical cyclic voltammogram (CV) of NiSe₂ (a), CoSe₂ (b) and PdSe₂ (c) catalysts are taken in a selected potential range without faradaic current at different potential scanning rates. The scan rates are 20, 40, 60, 80, 100, 120, 140, 160, and 180 mV/s.



Fig. S8 Cathodic current density as a function of the reaction time at the fixed overpotential of -170 mV (after *iR* correction).



Fig. S9 Polarization curves of CoSe₂ (a) and PdSe₂ (b) catalysts before and after 500 or 1000 cycles for stability tests.

Table S1 Electrochemical parameters of the electrodes comprised of NiSe ₂ , CoSe ₂ , and	$PdSe_2$ in 0.5 M
$H_2SO_4.$	

Samples	Numbe	Overpotential (mV) @ 10	Tafel slope	Exchange current density (10 ⁻³
	r	mA/cm ²	(mV/dec)	mA/cm ²)
NiSe ₂	1 st	170	31.1	0.04
	2^{nd}	180	30.8	0.02
	3 rd	175	36.0	0.1
	4 th	186	30.6	0.08
	5 th	187	35.7	0.06
CoSe ₂	1 st	196	39.6	0.09
	2^{nd}	189	41.0	0.20
	3 rd	198	38.1	0.07
	4 th	199	39.0	0.02
	5 th	192	35.5	0.04
PdSe ₂	1 st	255	61.2	0.66
	2^{nd}	259	62.4	0.70
	3 rd	255	64.6	1.08
	4 th	258	61.9	0.67
	5 th	265	63.9	0.71

Table S2 Summary of electrochemical parameters of some catalysts in previous works and our work.

Samples	Loading	Overpotential	Tafel slope	Exchange	Electrolyte	Reference
	(mg/cm^2)	(mV)/Current	(mV/dec)	current		
		Density		density (10-		
		(mA/cm^2)		3 mA/cm ²)		
NiSe ₂	1	170/10	31.1	0.04	0.5 M H ₂ SO ₄	This work
$CoSe_2$	1	196/10	39.6	0.09	$0.5 \text{ M H}_2\text{SO}_4$	This work
PdSe ₂	1	255/10	61.2	0.66	$0.5 \text{ M H}_2\text{SO}_4$	This work
NiSe ₂	2.2	147/10	50.1	N/A	$0.5 \text{ M H}_2\text{SO}_4$	1

H ₂ -NiCat	N/A	220/2	226	N/A	0.1 M NiBi	2	
Ni-Mo	3	80/20	N/A	N/A	0.5 M H ₂ SO ₄	3	
NiMoN _x	0.25	~225/5	35.9	0.24	0.1 M HClO ₄	4	
MoS_2	?	~170/0.36	55~60	0.13~0.31	0.5 M H ₂ SO ₄	5	
MoSe ₂	N/A	250/10	59.8	0.38	0.5 M H ₂ SO ₄	6	
Li-MoS ₂	3.4-3.9	118/10	62	0.167	0.5 M H ₂ SO ₄	7	
1T MoS ₂	N/A	~200/10	40	N/A	0.5 M H ₂ SO ₄	8	

Supplementary References

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