Electronic Supplementary Information

EXPERIMENTAL SECTION

Chemicals and Materials: Diethylenetriamine (DETA), potassium hydroxide (KOH), ethylene glycol (EG), Palladium acetylacetone ($Pd(acac)_2$), triphenylphosphine sulfide (TPS), ethanol (C_2H_5OH), isopropanol, acetone, and N, N-Dimethylformamide (DMF) were provided from Aladdin. Nafion (5 wt%) was supplied from Sigma-Aldrich. Commercial Pt/C (20 wt%), commercial Pd black (99.9%), and ruthenium oxide (RuO_2) were purchased from Alfa Aesar.

Characterization: The morphological and structural archtecture for the prepared samples were characterized by transmission electron microscopy (TEM, Hitachi HT 7700, 120 kV) assembled with an energy dispersive X-ray spectroscopy (EDX) system. Besides, high-resolution TEM (HRTEM), high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) with selected area electron diffraction (SAED) were displayed on FEI Tecnai G2 F30 at a voltage of 300 kV for further analysis. Atomic force microscopy (AFM) was conducted on Bruker Dimension ICON. The crystallinity, electronic state and surface information of samples were captured by X-ray diffractometer (XRD, Bruker D8 advance) and X-ray photoelectron spectroscopy (XPS, ULVAC PHI Quantera) instruments.

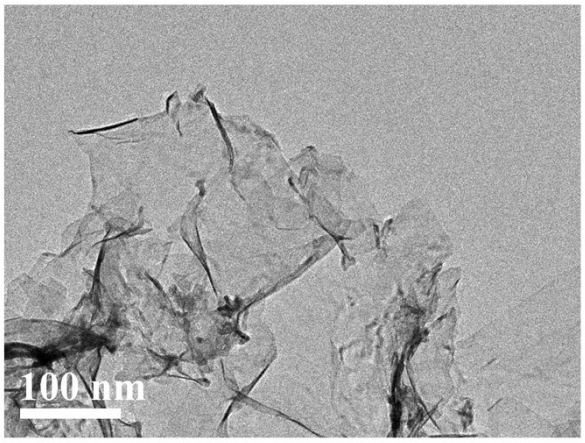

Fig. S1 TEM image of the Pd metallene.

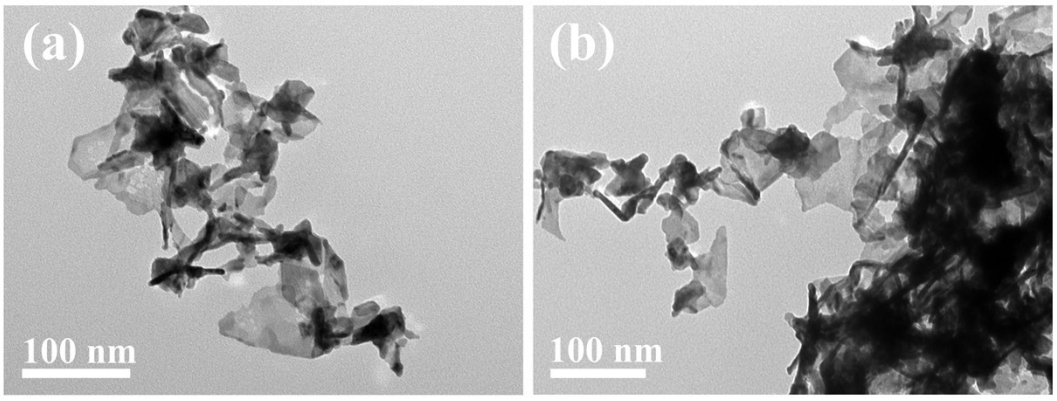

Fig. S2 TEM images of the prepared PdSP samples with different amounts of TPS under the typical synthesis conditions: (a) 5 mg and (b) 10 mg.

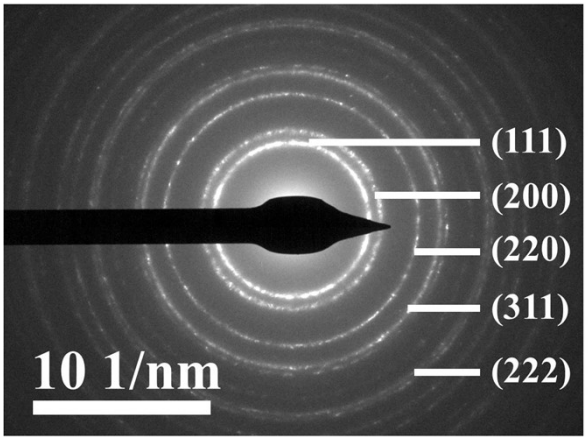

Fig. S3 SAED pattern of the PdSP metallene.

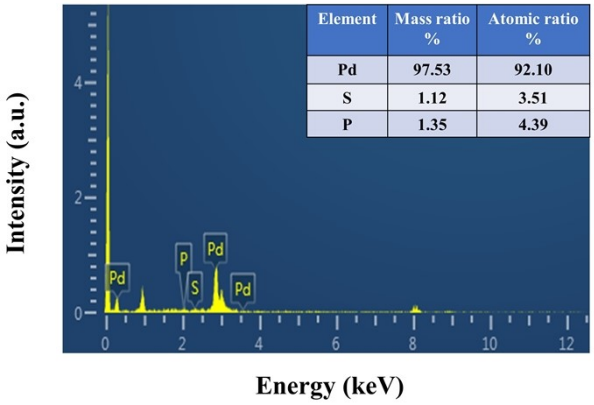

Fig. S4 EDX spectrum of the PdSP metallene.

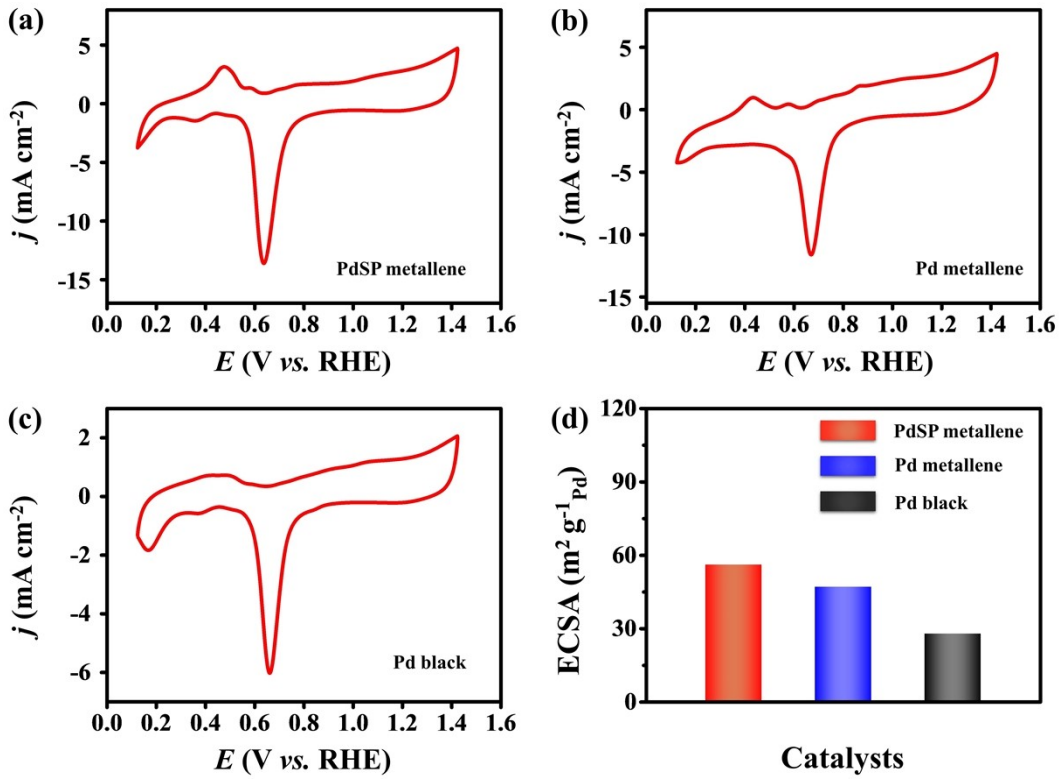

Fig. S5 CV curves for various catalysts recorded in 0.1 M KOH with a scan rate of 50 mV s^{-1}: (a) PdSP metallene, (b) Pd metallene, (c) Pd black, and (d) the corresponding ECSAs.

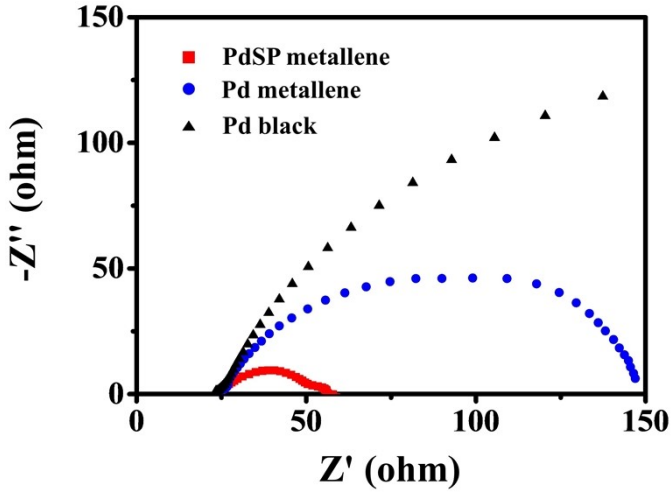

Fig. S6 EIS curves of various electrocatalysts in 1 M KOH under –0.47 V (vs. RHE) with a frequency range from 100 kHz to 0.1 Hz and an amplitude of 5 mV.

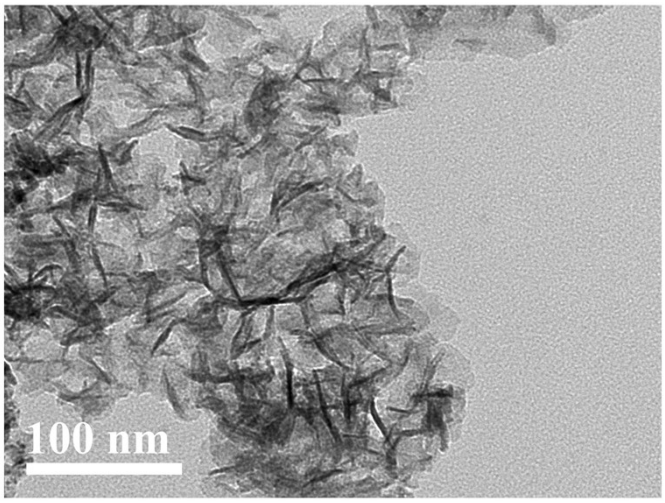

Fig. S7 TEM image of the PdSP metallene after HER stability testing.

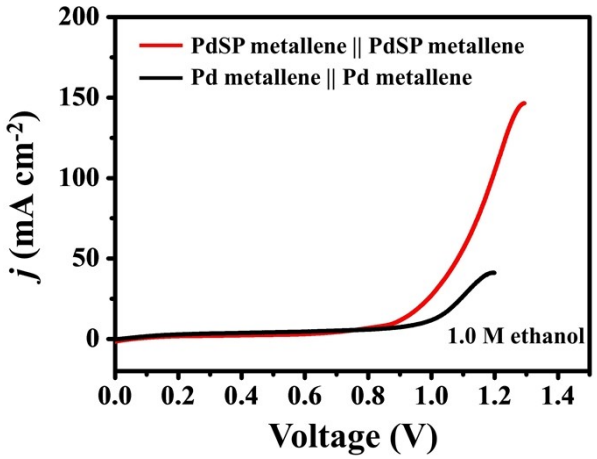

Fig. S8 LSV curves of different electrocatalysts in 1.0 M KOH electrolyte containing 1.0 M ethanol in a two-electrode system.

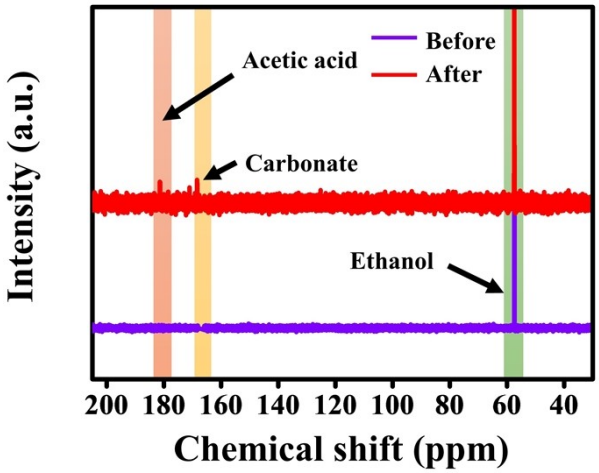

Fig. S9 ^{13}C NMR spectra of electrolyte before and after 10 h anodic ethanol oxidation on PdSP metallene electrode.

Table S1. The comparison of cell voltage at 10 mA cm^{-2} for various small molecule oxidation assisted-water electrolysis systems.

Anode electrocatalyst	Cathode electrocatalyst	Anode substrate molecule	Electrolytes	Cell voltage @ 10 mA cm^{-2} (V)	Ref.
PdSP metallene	**PdSP metallene**	**ethanol**	**1 M KOH + 1 M C_2H_5OH**	**0.88**	**This work**
Pt-NP/NiO-NS	Pt-NP/NiO-NS	methanol	1 M KOH + 1 M CH_3OH	1.39	[1]
NiIr-MOF/NF	NiIr-MOF/NF	methanol	1 M KOH + 4 M CH_3OH	1.39	[2]
Ni-Fe-P/NF	Ni-Fe-P/NF	ethanol	1 M KOH + 1 M C_2H_5OH	1.53	[3]
PdCu nanosheets	PdCu nanosheets	ethanol	1 M KOH+1 M C_2H_5OH	0.7	[4]
Rh/RhOOH metallene	Rh/RhOOH metallene	ethylene glycol (EG)	1 M KOH + 6 M EG in sea water solution	0.678	[5]
Co-Ni alloy	Co-Ni alloy	glucose	1 M KOH + 0.1 M glucose	1.39	[6]
Pd_2Ga/C	Pd_2Ga/C	ethanol	0.5 M KOH + 0.5 M C_2H_5OH	0.62	[7]
$Co(OH)_2$@HOS/CP	$Co(OH)_2$@HOS/CP	methanol	1 M KOH + 3 M CH_3OH	1.49	[8]

References

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