

Topological Metal and Noncentrosymmetric Superconductor α -BiPd as an Efficient Candidate for Hydrogen Evolution Reaction

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Experimental

1. Chemicals and materials

Palladium powder (-22 mesh, 99.995 %), bismuth powder (99.9 %) and 20wt.% Pt/C were purchased from Alfa Aesar. N, N-dimethylformamide (DMF) (AR), Isopropanol (AR), N-butanol (AR) and toluene (AR) were purchased from Guangzhou Chemical Reagent Factory. Nafion binder (5 wt.% in ethanol) was purchased from Sigma-Aldrich. All the chemicals were used without any treatment. Carbon fiber paper (TPG-H-090, thickness of 0.28 mm, resistivity of 5 mΩ cm, porosity of 78 %) was purchased from Toray, Japan. Silicon wafer with 300 nm SiO₂ and copper grid with 200 mesh size were purchased from Beijing Emcn Technology Co., Ltd.

2. Synthesis of catalysts

The preparation of bulk α -BiPd was achieved via solid-state synthesis. Briefly, stoichiometric bismuth and palladium powder were sealed inside evacuated quartz tube and heated to 900 °C in 1 °C/min then kept at 900 °C for 1 day. Thereafter it was cooled down to 600 °C in 3 days and finally quenched into ice water. The as-prepared bulk α -BiPd was then ground to powder and exfoliated into nanosheets by isopropanol with the aid of sonication for 2 h. Subsequently, the catalytic α -BiPd nanosheets were loaded onto the carbon fiber paper with Nafion binder and dried naturally. As the catalyst carrier, carbon fiber paper (1.5 cm * 0.5 cm) was previously washed by dipping in the concentrated sulfuric acid for 1 hour.^[1] Finally, electrochemical performance of the α -BiPd-contained carbon fiber paper was measured at 0.5 M H₂SO₄. To comparison, bulk α -BiPd was dispersed in ethanol for 30 min and under the same electrochemical measurement.

3. Materials characterization

Powder X-ray diffraction (XRD) was performed on a Rigaku D-MAX 2200 VPC with monochromated Cu K α radiation (40 kV, 40 mA). X-ray photoelectron spectroscopy (XPS) spectra were carried out by using a Thermo Scientific ESCALab250 instrument with an Al K α X-ray source. The morphology was observed with scan electronic microscope (SEM, Zeiss Merlin) operated at 5 kV. Transmission electronic microscope (TEM), energy-dispersive X-ray spectroscopy (EDS) and selected area electron diffraction (SAED) were performed using a FEI Tecnai G2 F20 operated on 200 kV. Atomic force microscope (AFM) was conducted on Bruker Multimode 8 using a silicon

AFM probe with resonant frequency of 300 kHz and force constant with 40 N m⁻¹ provided by Budget Sensor, which could be applied in tapping mode and intermittent contact.

4. Electrochemical measurement

The electrochemical experiments for hydrogen evolution reaction (HER) were carried out with a Multi Autolab M204 (Metrohm, Switzerland) at room temperature using a three-electrode configuration with the catalysts-contained carbon fiber paper, Pt sheet and saturated Ag/AgCl electrode as working electrode, counter electrode and reference electrode, respectively. The as-prepared samples were directly used as working electrodes without any treatment. The carbon fiber paper supported catalysts were cut into the size of 1.5 × 0.5 cm² and the active area is 0.25 cm². Linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), chronoamperometry (CA) and other electrochemical measurements were obtained in an argon-saturated electrolyte of 0.5 M H₂SO₄ at a scan rate of 0.02 V s⁻¹ without IR-correction. The potentials in this work were converted to a reversible hydrogen electrode (RHE) scale according to the Nernst equation,^[2] $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0596 \text{ pH} + 0.1976$.

Electrochemical active surface area (ECSA) of samples were measured by using a simple cyclic voltammetry (CV) method.^[3] In this work the potential is typically range from - 0.12 V ~ - 0.02 V (vs. RHE). CV measurements were conducted in quiescent solution by sweeping the potential across the non-Faradaic region from the more positive to more negative potential and back at 4 different scan rates: 0.05, 0.2, 0.4, and 0.8 V s⁻¹. The working electrode was held at each potential vertex for 10 s before beginning the next sweep.

Computation details

We performed first-principles calculations using Vienna ab-initio simulation package (VASP)^[4,5]. Perdew-Burke-Ernzerhof (PBE) functional^[6] was used throughout our calculations. A 2×2×1 supercell of BiPd was used with 8 Bi atoms and 8 Pd atoms. We used a 15 Å vacuum spacing, 500 eV energy cutoff, and 4×3×1 k-point mesh, The spin-orbit coupling was included in the self-consistent cycles. The energy convergence criterion was set to be 10⁻⁵ eV and the force is below 0.05 eV/Å.

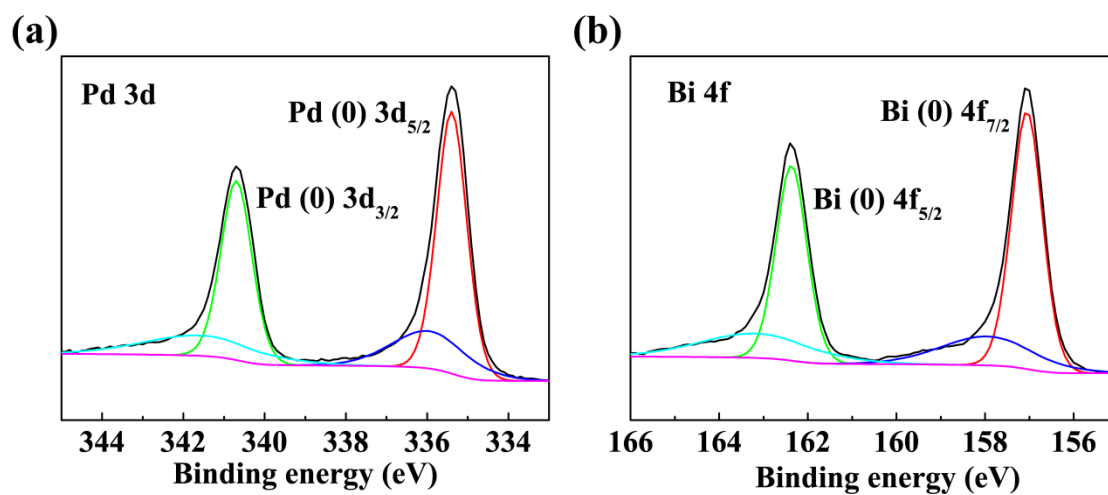


Figure S1. XPS spectra of (a) Pd 3d and (b) Bi 4f of α -BiPd.

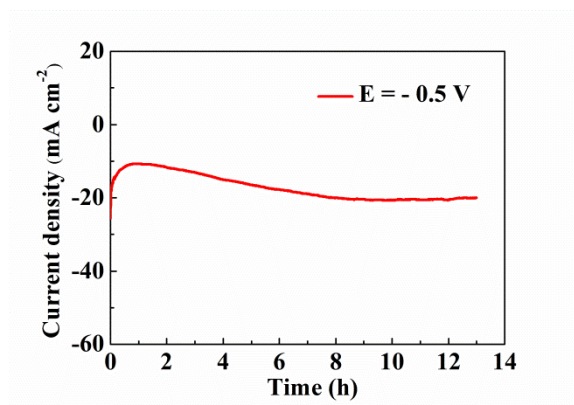


Figure S2. Time-dependent current density under an applied potential of -0.5 V in 0.5 M H_2SO_4 .

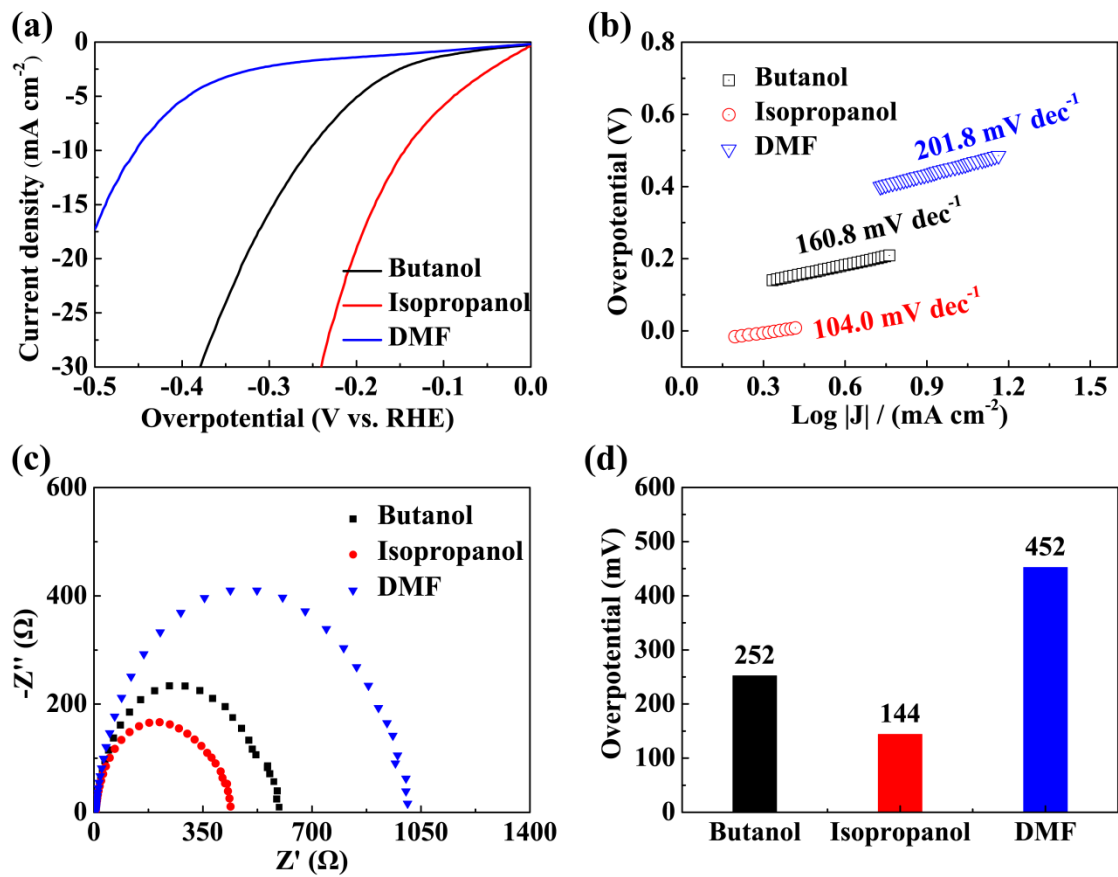


Figure S3. Solvent effect on catalytic activity of α -BiPd nanosheets in 0.5 M H_2SO_4 (sonication time = 120 min, concentration = 10 mg mL^{-1}). (a) Linear sweep voltammetry curves at a scan rate of 0.02 V s^{-1} , (b) Tafel plots for the catalysts derived from (a), (c) electrochemical impedance spectroscopy and (d) column chart of overpotentials at -10 mA cm^{-2} .

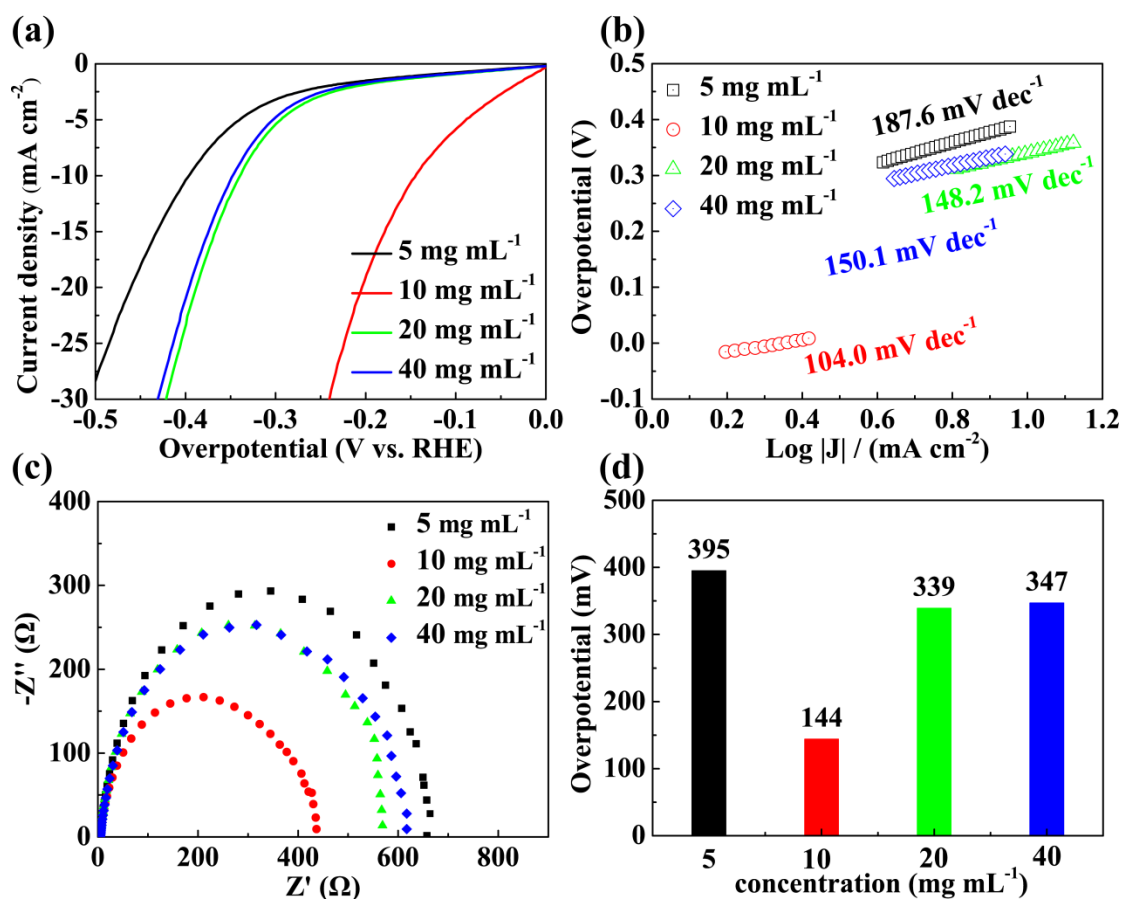


Figure S4. Concentration effect on catalytic activity of α -BiPd nanosheets in 0.5 M H_2SO_4 (sonication time = 120 min, isopropanol solvent). (a) Linear sweep voltammetry curves at a scan rate of 0.02 V s^{-1} , (b) Tafel plots for the catalysts derived from (a), (c) electrochemical impedance spectroscopy and (d) column chart of overpotentials at -10 mA cm^{-2} .

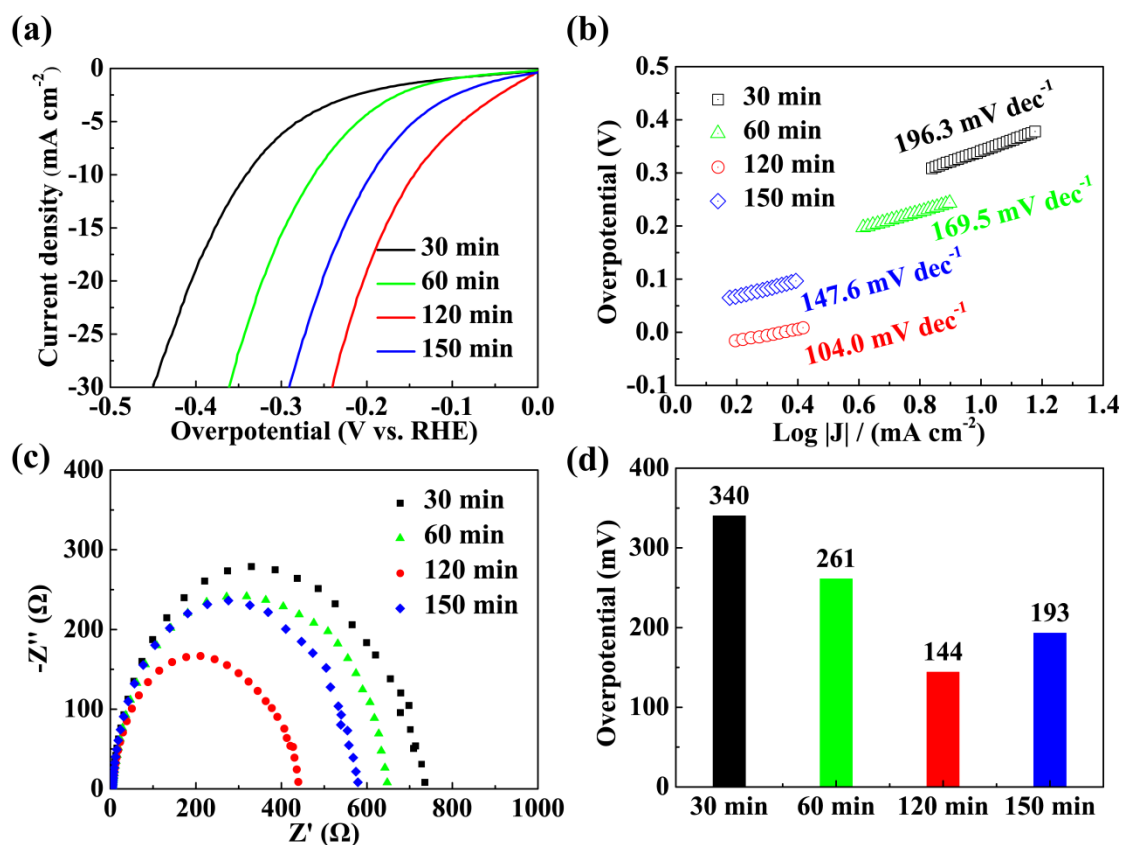


Figure S5. Sonication time effect on catalytic activity of α -BiPd nanosheets in 0.5 M H_2SO_4 (concentration = 10 mg mL^{-1} , isopropanol solvent). (a) Linear sweep voltammetry curves at a scan rate of 0.02 V s^{-1} , (b) Tafel plots for the catalysts derived from (a), (c) electrochemical impedance spectroscopy and (d) column chart of overpotentials at -10 mA cm^{-2} .

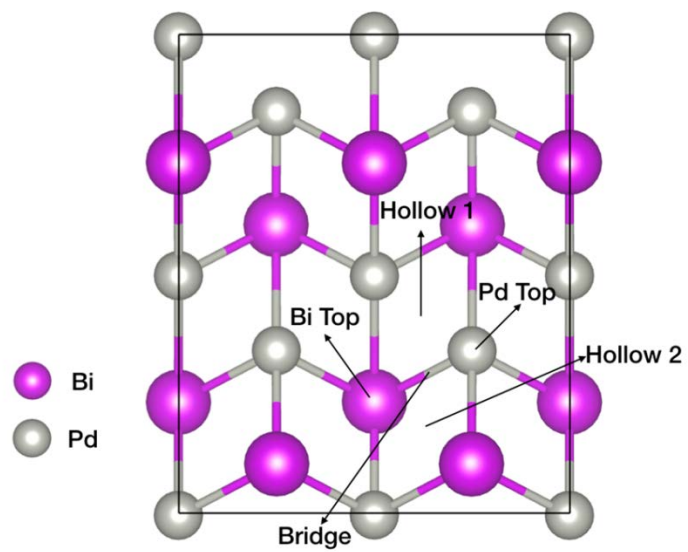


Figure S6. The $2 \times 2 \times 1$ supercell of the two-dimensional BiPd. The considered adsorption sites: Bi top, Pd top, bridge, and two different hollow sites (hollow1 and hollow2), are indicated in the figure.

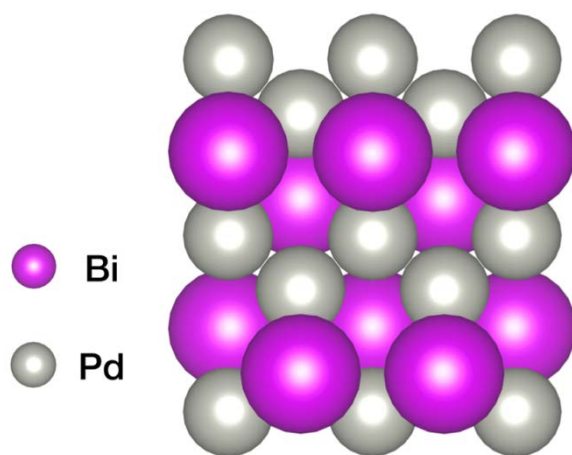


Figure S7. The top view of a $2 \times 2 \times 1$ supercell of the two-dimensional BiPd.

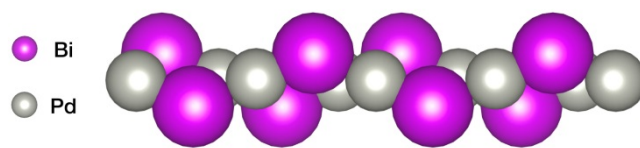


Figure S8. The side view of a $2 \times 2 \times 1$ supercell of the two-dimensional BiPd.

Table 1. HER performance among different superconductors

Superconductor	$\eta_{-10 \text{ mA cm}^{-2}}$ (mV)	Tafel slope (mV dec ⁻¹)	Refs.
1T-TaS ₂	545	158	<i>Solid State Commun.</i> , 19 82, 44, 1455. <i>J. Phys. Chem. C</i> , 2018, 122, 2382.
TaSe ₂	1000	180	<i>J. Phys. F: Met. Phys.</i> 1975, 5, 1713. <i>J. Mater. Chem. A</i> , 2016, 4, 14241.
TaTe ₂	1100	220	https://arxiv.org/ftp/arxiv/papers/1704/1704.08106.pdf <i>J. Mater. Chem. A</i> , 2016, 4, 14241.
NbS ₂	900	190	<i>Phys. Rev. Lett.</i> , 2008, 101, 166407. <i>J. Mater. Chem. A</i> , 2016, 4, 14241.
NbSe ₂	850	130	<i>J. Phys. Chem. Sol.</i> , 1965, 26, 1111. <i>J. Mater. Chem. A</i> , 2016, 4, 14241.
NbTe ₂	900	160	<i>J. Phys. Chem. Sol.</i> , 1993, 54, 895. <i>J. Mater. Chem. A</i> , 2016, 4, 14241.
PdTe ₂	740	92	<i>Phys. Rev. B</i> , 2017, 96, 075101. <i>ACS Appl. Mater. Interfaces</i> , 2017, 9, 25587.
1T'-MoTe ₂	356	127	<i>Nat. Commun.</i> , 2016, 7, 11038. <i>2D Mater.</i> , 2017, 4, 025061.
α -BiPd	144	104	This work

References

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