

Supporting Information

Bismuth Single-Atom Alloying of Palladium Nanosheets Promotes Selective Electrochemical Valorization of Glycerol to C₃ Products

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Experimental methods

Chemicals

All chemicals were purchased and used without further purification. Palladium(II) acetylacetonate ($\text{Pd}(\text{acac})_2$, Pd 34.9%), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, $\geq 99.5\%$), bismuth chloride (BiCl_3 , AR) and *N,N*-dimethylformamide (DMF, $\geq 99.9\%$) were purchased from Shanghai Macklin Biochemical Co., Ltd. Cetyltrimethylammonium bromide (CTAB, $\geq 99\%$), polyvinylpyrrolidone (PVP, $M_w = 30000$), glycerol ($\text{C}_3\text{H}_8\text{O}_3$, $\geq 99.9\%$) and potassium hydroxide (KOH) were purchased from Sigma-Aldrich Shanghai Trading Co., Ltd. Ketjenblack electroconductive carbon black (KB, Carbon ECP 200L) was purchased from Lion Specialty Chemicals Co., Ltd. Commercial Pd/C (20 wt% palladium on Vulcan XC72) was purchased from Premetek Co. Perfluorinated resin solution (Nafion 1100EW, 5 wt.% in lower aliphatic alcohols and water, contains 15-20% water) was purchased from Sigma-Aldrich. Deionized water was prepared with a Milli-Q purification system and used throughout all the experiments.

Material synthesis

Preparation of Pd NS

Pd NS was prepared using a solvothermal method. In brief, 10 mg of $\text{Pd}(\text{acac})_2$, 34 mg of PVP and 37 mg of CTAB were dissolved in a mixture of 10 mL of DMF and 2 mL of distilled water. The resultant homogeneous solution was transferred to a glass pressure vessel and charged with CO to 1 bar. The solution was then heated at 100 °C for 3 h in an oil bath. At the end of the reaction, the solid product was collected, washed with a mixture of ethanol and acetone for at least three times, and finally vacuum dried to yield Pd NS.

Preparation of Bi_1Pd NS

To prepare Bi₁Pd NS, 3 mg of Pd NS was dispersed in 10 mL of ethylene glycol within a flask, and then heated to 80 °C in an oil bath. After the addition of 5 mg of BiCl₃, the solution was further magnetically stirred for 30 min. The solid product was collected by centrifugation, washed with a mixture of ethanol and acetone for at least three times, and finally vacuum dried to yield Bi₁Pd NS.

Structural characterizations

XRD was performed on a PANalytical X-ray diffractometer with monochromatic Cu K α radiation. TEM images and EDS mapping were carried on an FEI Talos transmission electron microscope equipped with a Super-X EDS detector and operated at an accelerating voltage of 200 kV. Atomic-resolution HAADF-STEM images were taken using a Thermo Fisher Themis Z microscope equipped with two aberration correctors at an operation voltage of 300 kV. XPS results were obtained on an Ultra DLD X-ray photoelectron spectrometer. Bi *L*₃-edge and Pd *K*-edge XANES and EXAFS spectra were collected at the beamline 13SSW of Shanghai Synchrotron Radiation Facility. Pd *K*-edge XANES spectra were collected from ~200 eV below to ~800 eV above the Pd *K*-edge in the transmission mode. Bi *L*₃-edge XANES and EXAFS spectra were collected from ~200 eV below to ~800 eV above the Bi *L*₃-edge in the fluorescence mode.

Electrochemical measurements

H-cell measurements: For the preparation of the working electrodes, 1 mg of Bi₁Pd NS, 0.5 mg of Ketjenblack carbon, and 7.5 μ L of 5 wt% Nafion solution were dispersed in 250 μ L of ethanol and 60 μ L of deionized water. The mixture was sonicated for 30 min to form a uniform catalyst ink. The ink was then dropcast onto a 1 \times 1 cm² carbon fiber paper (AvCarb P75T) and dried on a hot plate to achieve a catalyst loading of 1 mg cm⁻². The working electrodes of Pd NS and commercial 20 wt% Pd/C (Premetek Co.) were prepared similarly at

the same precious metal loading. H-cell measurements were conducted in a three-electrode configuration with the catalyst-loaded working electrode and a saturated calomel reference electrode (SCE) in the anodic compartment, and a Pt foil counter electrode in the cathodic compartment. The two compartments were separated by an anion exchange membrane (Fumasep FAA-3-PK-130). The anolyte was 30 mL of 1 M KOH + 0.5 M glycerol, and the catholyte was 30 mL of 1 M KOH. All the potential readings were measured against SCE and converted to RHE with 90% iR compensation. Polarization curves were recorded at a scan rate of 10 mV s⁻¹. Chronoamperometric experiments were conducted at selected working potentials ranging from 0.6 V to 0.79 V.

For product quantification, the anolyte after chronoamperometric experiments was properly diluted, and analyzed by a high performance liquid chromatograph (HPLC, Thermo Scientific, UltiMate 3000) equipped with a HyperREZ XP (H⁺) column, a refractive index detector and an ultraviolet detector (DAD-3000, $\lambda = 210$ nm). The FEs for different products were calculated as follows:

$$FE (\%) = \frac{N \times n_i \times F}{Q} \times 100\% \quad (1)$$

where N is the number of electron transfer during the formation of the target product (DHA, TA, GLA, LA, OA, GA or FA), n_i is the amount of product detected by HPLC based on its calibration curve, $F = 96485$ C mol⁻¹ is the Faraday constant, and Q is the total amount of charge passed during chronoamperometric tests.

Flow cell measurements: For the flow cell measurements, a 0.5×2 cm² carbon fiber paper (AvCarb P75T) was loaded with Bi₁Pd NS at 1 mg cm⁻² as the working electrode. SCE and an IrO_x loaded Ti mesh were used as the reference electrode and counter electrode, respectively. The flow cell was custom-made, and its anodic chamber was separated from the cathodic chamber by an anion exchange membrane (Fumasep FAA-3-PK-130). During the

measurements, the cathodic chamber was circulated with 4 M KOH, and the anodic chamber was circulated with 4 M KOH + 2 M glycerol (unless otherwise specified) at a flow rate of 12.5 mL min⁻¹ (unless otherwise specified) using peristaltic pumps. All the potential readings were measured against SCE and converted to RHE with 90% *iR* compensation. Polarization curves were collected at a scan rate of 10 mV s⁻¹. Chronoamperometric measurements were conducted at the selected working potential ranging from 0.6 V to 0.77 V. Liquid products in the anolyte were quantified by HPLC analysis. The short-term stability of Bi₁Pd NS, Pd NS and Pd/C were evaluated at 0.71 V for 10 h by continuously circulating 400 mL of anolyte. The long-term stability of Bi₁Pd NS was evaluated at 0.71 V by circulating 400 mL of anolyte for 5 h and then refreshing the electrolyte periodically.

GOR-CO₂RR coupling

GOR-CO₂RR coupling was conducted in a two-electrode flow cell. The Bi₁Pd anode was prepared in the same way as above. The Cu cathode was prepared by sputtering a 150 nm thick Cu film on a 0.5×2 cm² polytetrafluoroethylene (PTFE) membrane (450 nm pore size, from Membrane Solutions LLC (Nantong)) using a magnetron sputtering system (Quorum Q150T). The catholyte was 4 M KOH, and the anolyte was 4 M KOH + 2 M glycerol circulated at a flow rate of 12.5 mL min⁻¹ using peristaltic pumps. CO₂ was continuously fed to the cathode gas chamber at a flow rate of 20 sccm controlled by a digital mass flow controller. Polarization curves were collected at a scan rate of 10 mV s⁻¹. Chronopotentiometric measurements were conducted at the current density of 100 mA cm⁻², 150 mA cm⁻² and 200 mA cm⁻². The full-cell voltages reported were recorded without *iR* correction. The oxidation products from GOR were analyzed in the same way as above. The gaseous reduction products from CO₂RR were analyzed using an online gas chromatograph (GC2060, Wuhao Information Technology Shanghai Co., Ltd) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The liquid products from

CO₂RR were analyzed by a nuclear magnetic resonance spectrometer (400 MHz Bruker Avance NMR) with water peak suppression. The FEs of reduction products from CO₂RR were calculated as follows:

$$FE_{gas} (\%) = \frac{Q_{gas}}{Q_{total}} \times 100\% = \frac{\left(\frac{v}{60 \text{ s/min}}\right) \times \left(\frac{y}{24000 \text{ cm}^3/\text{mol}}\right) \times N \times F}{i} \times 100\% \quad (2)$$

$$FE_{liquid} (\%) = \frac{Q_{liquid}}{Q_{total}} \times 100\% = \frac{N \times n_{liquid} \times F}{Q} \times 100\% \quad (3)$$

where v is the gas flow rate at the cathode outlet, y is the measured product concentration in the 1 mL sample loop based on the standard calibration curve, N is the number of electron transfer during the formation of the target product (C₂H₄, C₂H₅OH, CH₃COOH and n-C₃H₇OH), j is the total current, n_{liquid} is the amount of liquid products. The OER-CO₂RR coupling was conducted under the same conditions except for replacing an IrO_x loaded Ti mesh as the anode and 4 M KOH as the anolyte.

Theoretical calculations

All the DFT calculations were performed using the Perdew-Burke-Ernzerhof functionals (PBE) (*Phys. Rev. B* **1992**, *45*, 13244; *Phys. Rev. Lett.* **1997**, *77*, 3865) of the generalized gradient approximation (GGA) implemented in the Vienna Ab-initio Simulation Package (VASP) code (*Phys. Rev. B* **1996**, *54*, 11169; *Comput. Mater. Sci.* **1996**, *6*, 15). The projector-augmented wave (PAW) method (*Phys. Rev. B* **1993**, *47*, 558; *Phys. Rev. B* **1994**, *50*, 17953) was applied to describe the electron-ion interactions. The D₃ Grimme's scheme (*J. Chem. Phys.* **2010**, *132*, 154104) was adopted to account for London dispersion interactions. The kinetic energy cutoff for the plane wave expansions was set to 400 eV. The Methfessel-Paxton (MP) method was applied, and the smearing width was chosen as 0.2 eV. A 5 × 5 supercell with five atomic layers was used to simulate the face-centered Pd(111) surface. The

two bottom layers were fixed at $a = 3.88 \text{ \AA}$. At the first layer of Pd(111), one Pd atom was replaced by a Bi atom to simulate the Bi₁Pd surface. Approximately 15 Å of vacuum space was used to avoid interactions with adjacent images. For sampling the reciprocal space, k-points of Γ -centered $2 \times 2 \times 1$ were used for slab calculations. To simulate gaseous molecules, electronic structure calculations were performed in a $15 \text{ \AA} \times 15 \text{ \AA} \times 15 \text{ \AA}$ vacuum box with a Gaussian smearing of 0.05 eV, and the Γ -point was adopted for sampling the Brillouin zone of the simulation cell. All structures were fully relaxed until all the forces were less than 0.03 eV Å⁻¹.

The adsorption energy for the molecules was calculated as follows:

$$E_{\text{ads}(i)} = E_{*i} - E^* - E_i \quad (4)$$

where i stands for glycerol, GLA, TA, or DHA, $E_{\text{ads}(i)}$ represents the adsorption energy of a specific molecule, E_{*i} represents the total energy of the slab with adsorbate, E^* represents the total energy of the slab, and E_i represents the total energy of the adsorbate in gas phase.

The charge density difference was determined using the following equation:

$$\Delta\rho = \rho_{*i} - \rho^* - \rho_i \quad (5)$$

where ρ_{*i} , ρ^* , and ρ_i are the charge density of the adsorption intermediate, the substrate, and the adsorbed molecule, respectively.

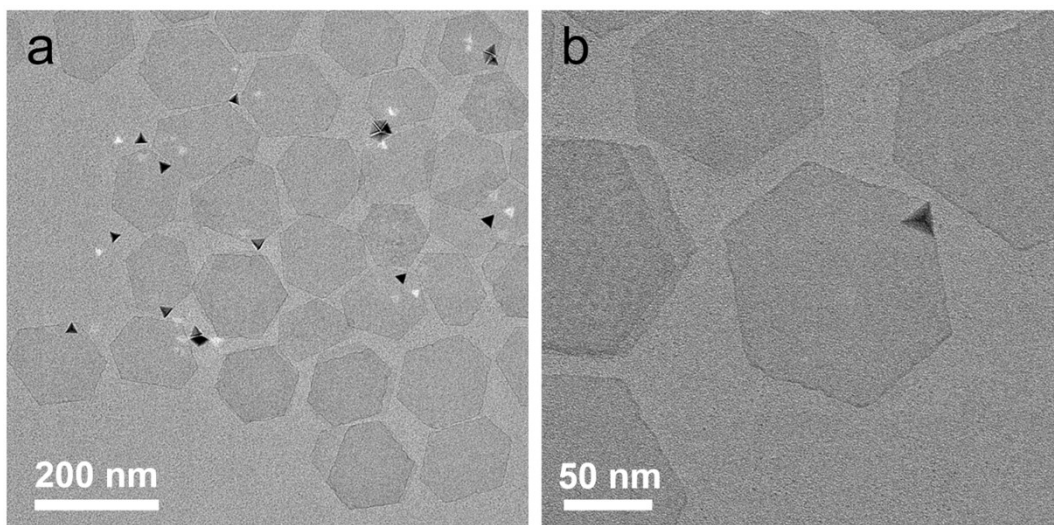


Fig. S1 TEM images of Pd NS.

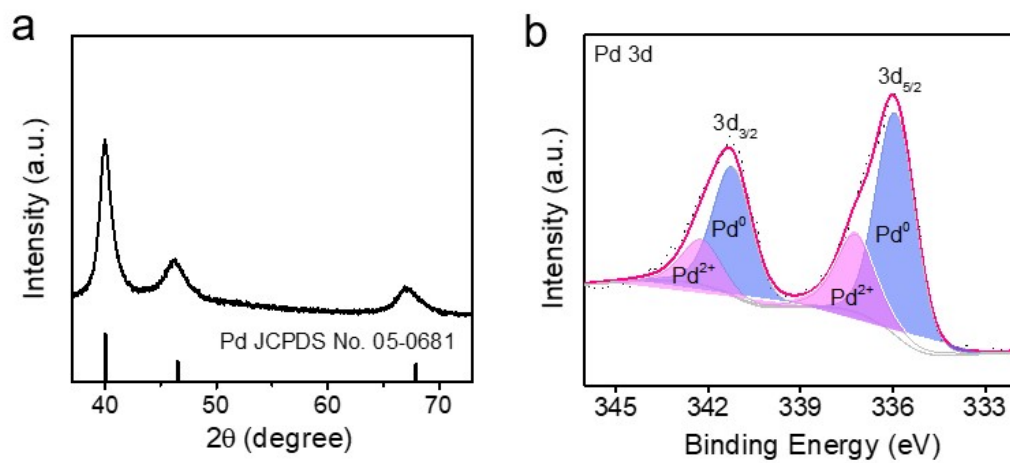


Fig. S2 (a) XRD pattern and (b) Pd 3d XPS spectrum of Pd NS.

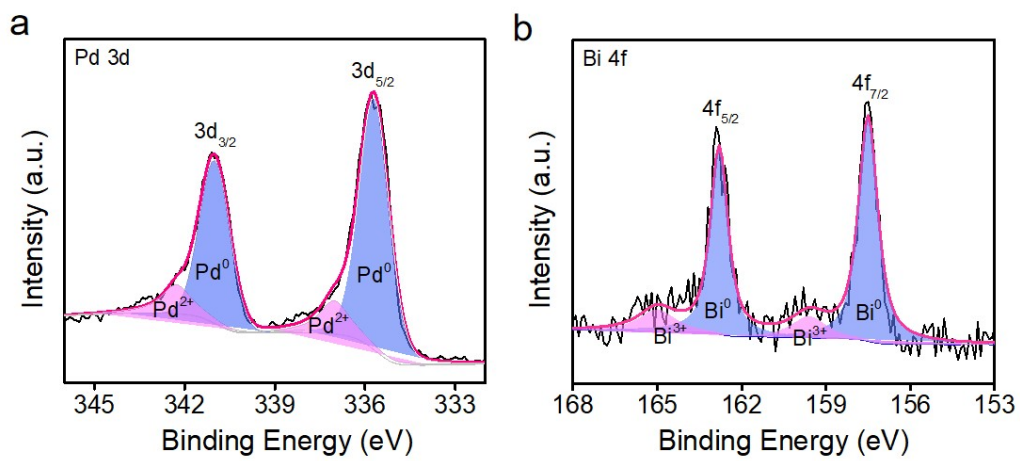


Fig. S3 (a) Pd 3d and (b) Bi 4f XPS spectra of Bi_1Pd NS.

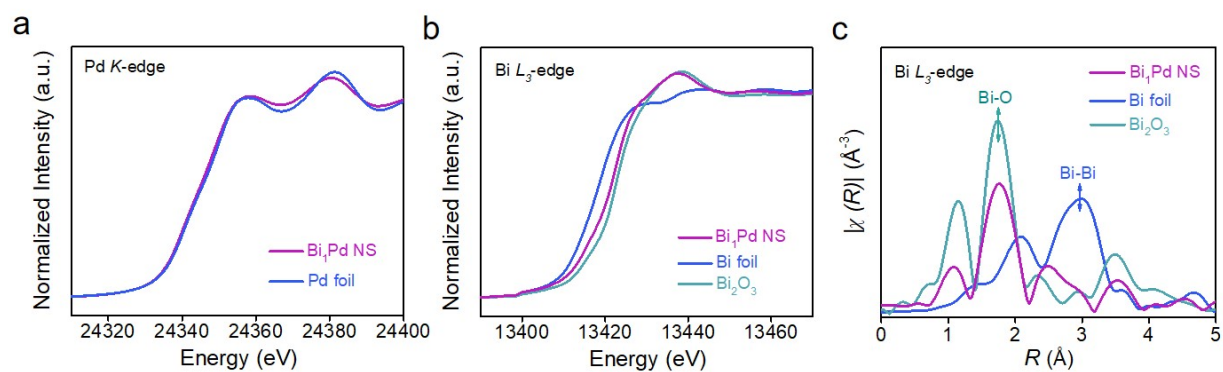


Fig. S4 (a) Pd *K*-edge XANES spectra of Bi₁Pd NS and Pd foil. (b) Bi *L*₃-edge XANES spectra and (c) corresponding Fourier transform EXAFS spectra of Bi₁Pd NS, Bi₂O₃ and Bi foil references.

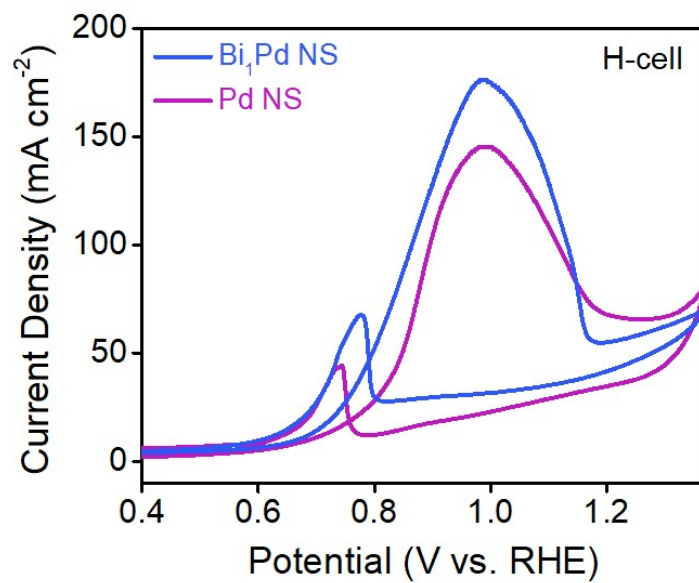


Fig. S5 Cyclic voltammogram curves of Pd NS and Bi₁Pd NS in an H cell with 1 M KOH containing 0.5 M glycerol at a scan rate of 10 mV s⁻¹.

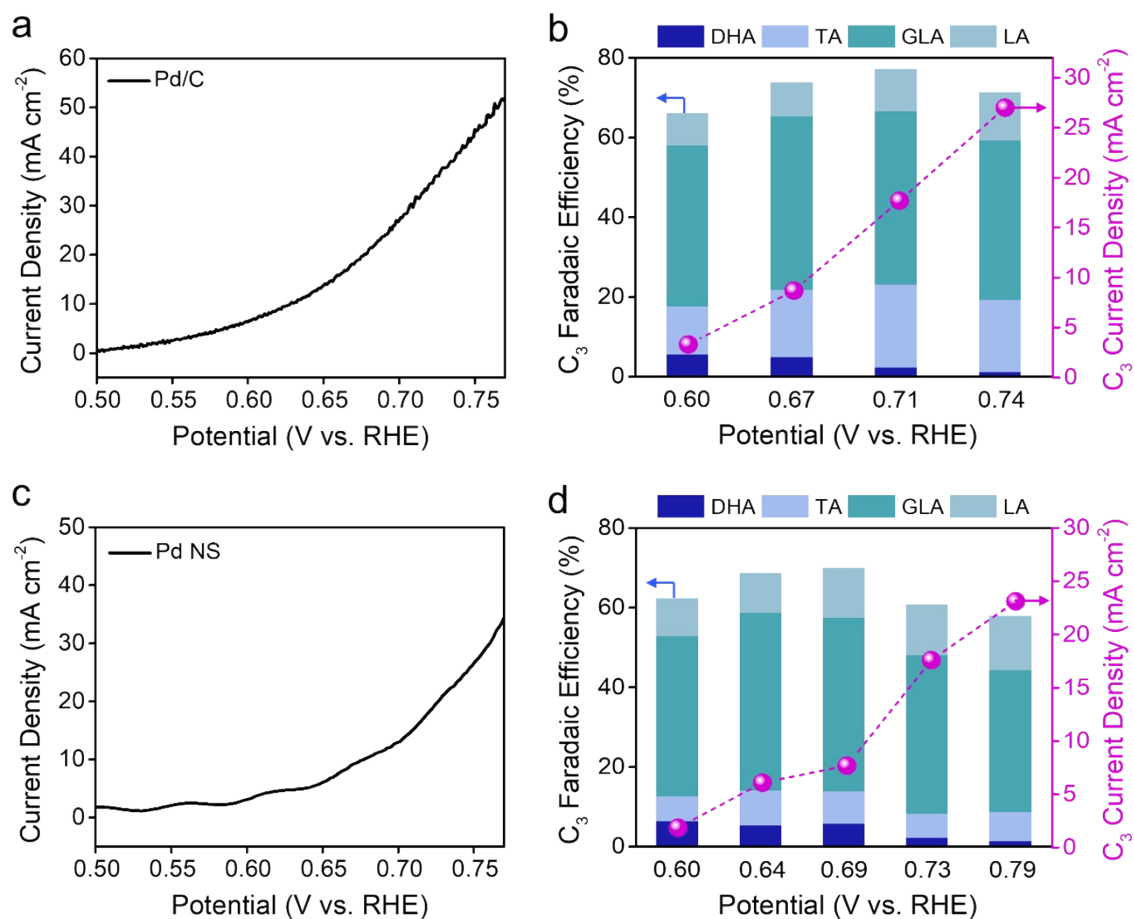


Fig. S6 (a) Polarization curve and (b) potential-dependent C₃ FEs and partial current densities of Pd/C in an H-cell with 1 M KOH + 0.5 M glycerol. (c) Polarization curve and d potential-dependent C₃ FEs and partial current densities of Pd NS in an H-cell with 1 M KOH + 0.5 M glycerol.

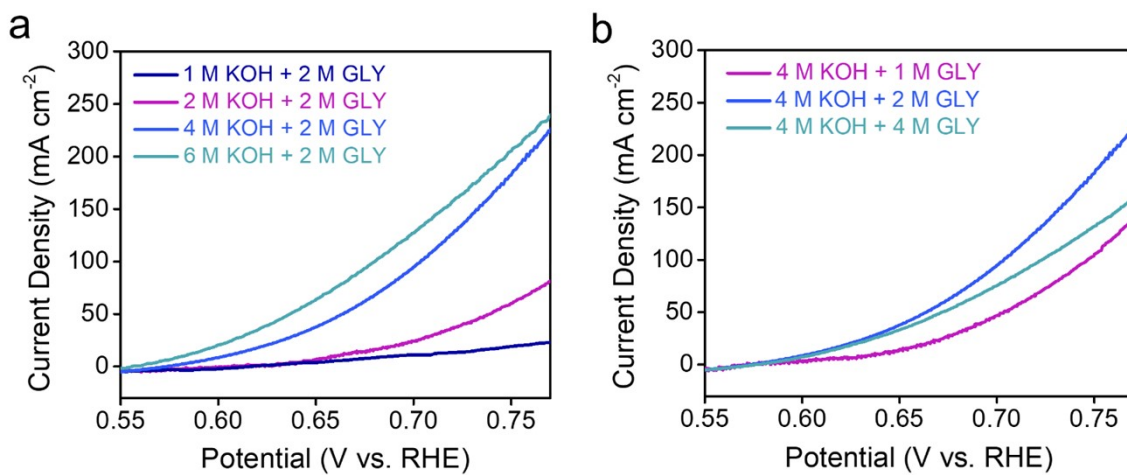


Fig. S7 Polarization curves of Bi₁Pd NS in a flow cell with (a) different concentrations of KOH solution containing 2 M glycerol and (b) 4 M KOH solution containing different concentrations of glycerol.

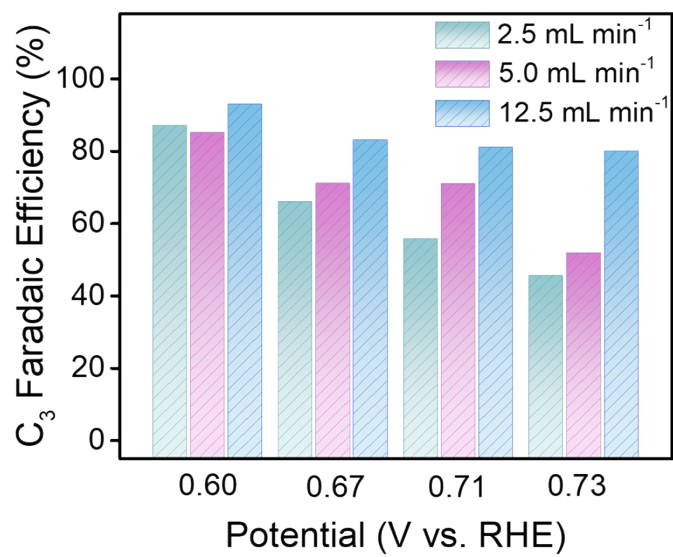


Fig. S8 Potential-dependent C₃ FEs on Bi₁Pd NS in the flow cell at different analyte flow rates of 2.5 mL min⁻¹, 5 mL min⁻¹ and 12.5 mL min⁻¹.

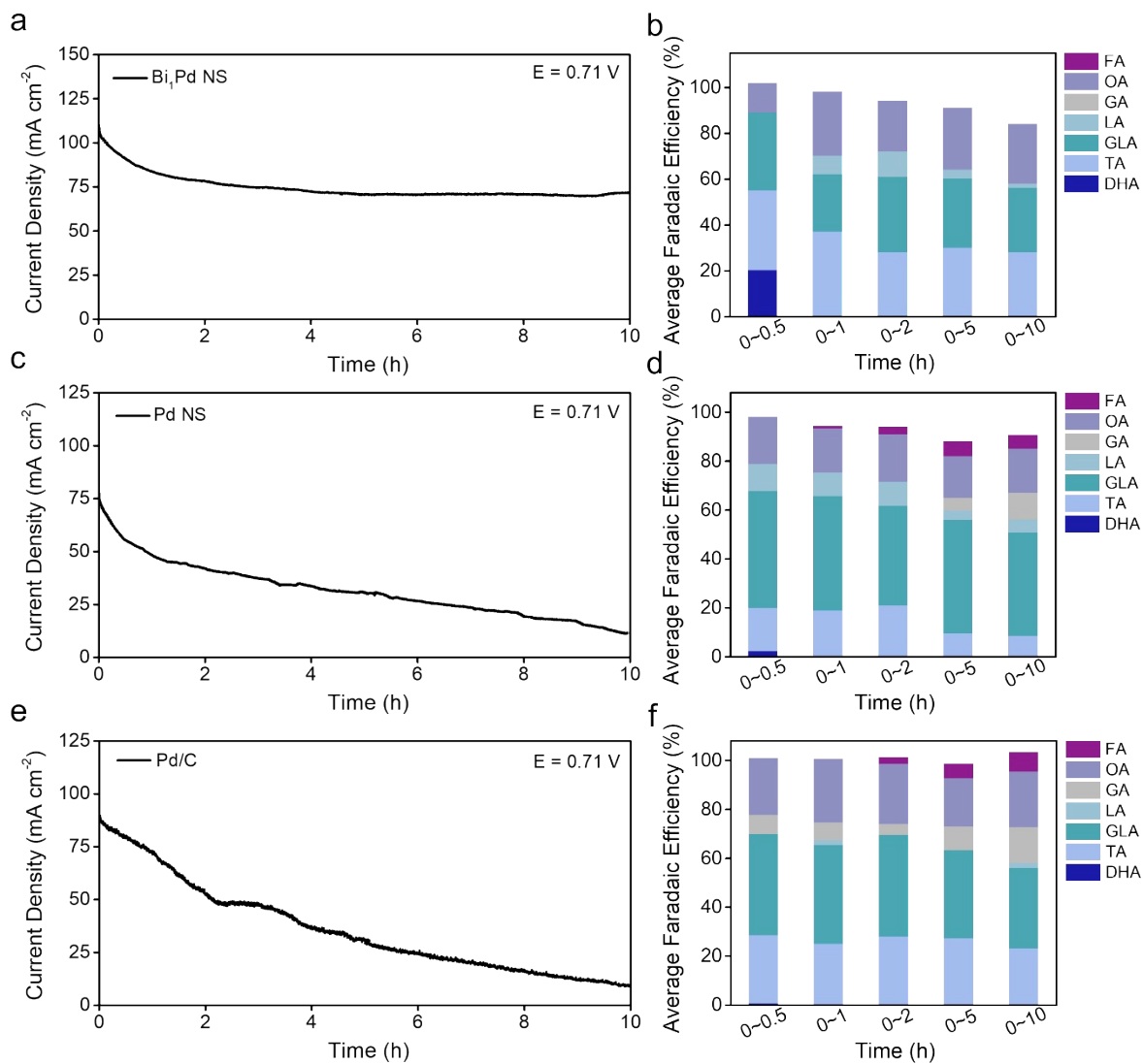


Fig. S9 (a) Chronoamperometry curve and (b) average FE of Bi₁Pd NS at 0.71 V in a flow cell with 4 M KOH + 2 M glycerol. (c) Chronoamperometry curve and (d) average FE of Pd NS at 0.71 V in a flow cell with 4 M KOH + 2 M glycerol. (e) Chronoamperometry curve and (f) average FE of Pd/C at 0.71 V in a flow cell with 4 M KOH + 2 M glycerol.

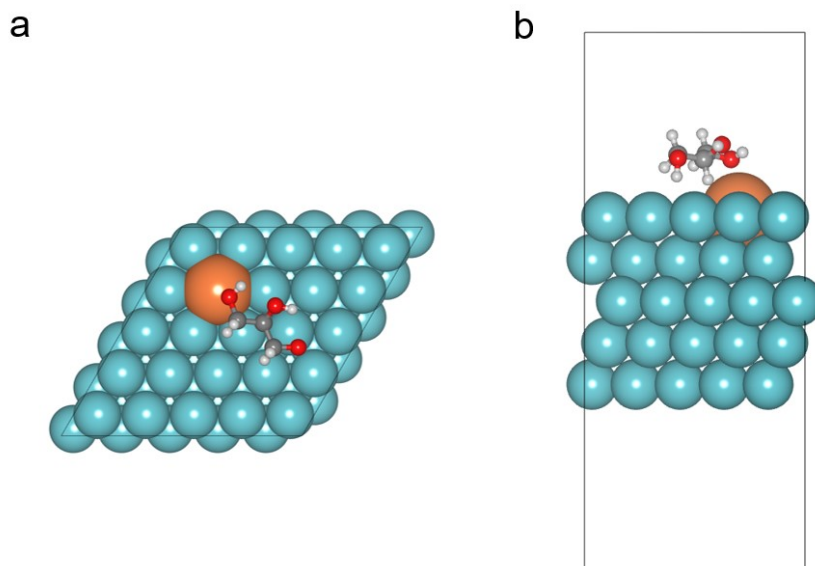


Fig. S10 (a) Top view and (b) side view of the adsorbed glycerol on Bi₁Pd NS.

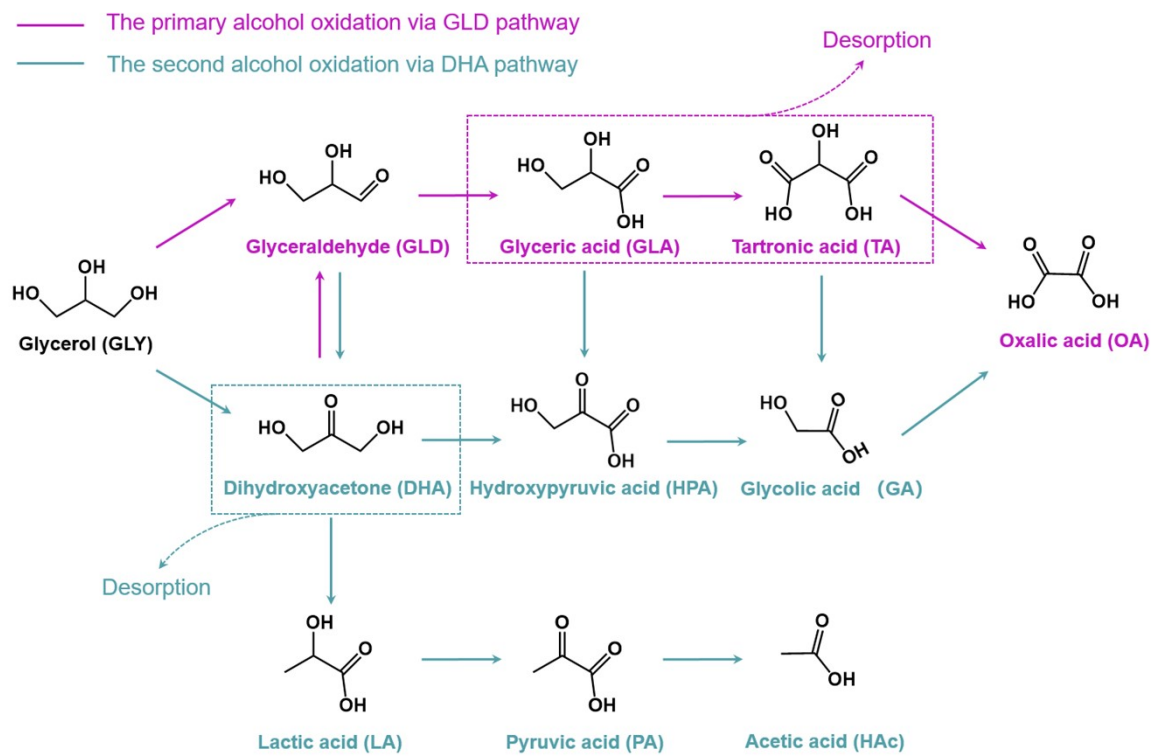


Fig. S11 Possible reaction pathways for GOR on Bi₁Pd NS.

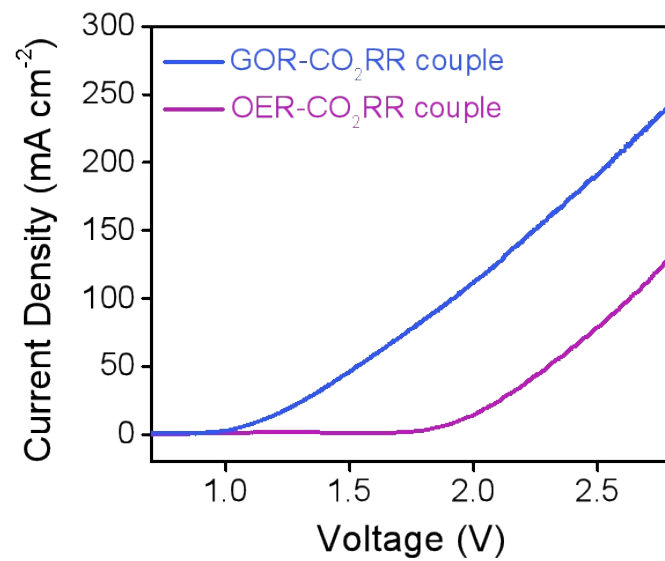


Fig. S12 Polarization curves of GOR-CO₂RR couple and OER-CO₂RR couple in the two-electrode configuration.