Supporting Information

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

Zhenghao Mao⁹, Lin Jia⁹, Xinnan Mao⁹, Xue Ding⁹, Binbin Pan⁹, Tianran Yan⁹, Jie Xu⁴, Liang Zhang⁹, Lu Wang*⁹, Na Han*⁹, and Yanguang Li*⁹

⁹ Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, Suzhou, 215123 China.

* Jiangsu Key Laboratory for Advanced Negative Carbon Technologies, Soochow University, Suzhou 215123, China

* Macao Institute of Materials Science and Engineering (MIMSE), MUST–SUDA Joint Research Center for Advanced Functional Materials, Macau University of Science and Technology, Taipa 999078, Macau SAR, China

* College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, China

† These authors contributed equally.

Correspondence to: yanguang@suda.edu.cn; hanna@suda.edu.cn; lwang22@suda.edu.cn
Experimental methods

Chemicals

All chemicals were purchased and used without further purification. Palladium(II) acetylacetonate (Pd(acac)$_2$, Pd 34.9%), ethylene glycol (C$_2$H$_6$O$_2$, ≥99.5%), bismuth chloride (BiCl$_3$, AR) and N,N-dimethylformamide (DMF, ≥99.9%) were purchased from Shanghai Macklin Biochemical Co., Ltd. Cetyltrimethylammonium bromide (CTAB, ≥99%), polyvinylpyrrolidone (PVP, M$_w$ = 30000), glycerol (C$_3$H$_8$O$_3$, ≥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 Pd(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$_x$Pd NS
To prepare Bi$_1$Pd 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 BiCl$_3$, 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 Bi$_1$Pd NS.

**Structural characterizations**

XRD was performed on a PANalytical X-ray diffractometer with monochromatic Cu Kα 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 Bi$_1$Pd NS, 0.5 mg of Ketjenblack carbon, and 7.5 µL of 5 wt% Nafion solution were dispersed in 250 µL of ethanol and 60 µL of deionized water. The mixture was sonicated for 30 min to form a uniform catalyst ink. The ink was then dropcast onto a 1×1 cm$^2$ 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:

\[
FE (\%) = \frac{N \times n_i \times F}{Q} \times 100\% 
\]

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 cm\(^2\) carbon fiber paper (AvCarb P75T) was loaded with Bi\(_1\)Pd 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 Bi\(_{1}\)Pd 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 Bi\(_{1}\)Pd NS was evaluated at 0.71 V by circulating 400 mL of anolyte for 5 h and then refreshing the electrolyte periodically.

**GOR-CO\(_2\)RR coupling**

GOR-CO\(_2\)RR coupling was conducted in a two-electrode flow cell. The Bi\(_{1}\)Pd 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 cm\(^2\) 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. CO\(_2\) 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 CO\(_2\)RR 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:

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

\[
FE_{\text{liquid}}(\%) = \frac{Q_{\text{liquid}}}{Q_{\text{total}}} \times 100% = \frac{N \times n_{\text{liquid}} \times F}{Q} \times 100% \tag{3}
\]

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, \(n_{\text{liquid}}\) is the amount of liquid products. The OER-CO₂RR coupling was conducted under the same conditions except for replacing an IrOₓ 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.
two bottom layers were fixed at \( a = 3.88 \, \text{Å} \). At the first layer of Pd(111), one Pd atom was replaced by a Bi atom to simulate the Bi\(_1\)Pd surface. Approximately 15 Å of vacuum space was used to avoid interactions with adjacent images. For sampling the reciprocal space, \( \Gamma \)-centered \( 2 \times 2 \times 1 \) were used for slab calculations. To simulate gaseous molecules, electronic structure calculations were performed in a 15 Å × 15 Å × 15 Å vacuum box with a Gaussian smearing of 0.05 eV, and the \( \Gamma \)-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:

\[
E_{\text{ads}}(i) = E_{*i} - E_{*} - E_{i}
\]

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:

\[
\Delta \rho = \rho_{*i} - \rho_{*} - \rho_{i}
\]

where \( \rho_{*i} \), \( \rho_{*} \), and \( \rho_{i} \) 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$_4$Pd NS.
Fig. S4 (a) Pt K-edge XANES spectra of Bi$_1$Pd NS and Pd foil. (b) Bi $L_3$-edge XANES spectra and (c) corresponding Fourier transform EXAFS spectra of Bi$_1$Pd NS, Bi$_2$O$_3$ and Bi foil references.
**Fig. S5** Cyclic voltammogram curves of Pd NS and Bi\_2Pd 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 Bi$_2$Pd 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 $C_3$ FEs on Bi$_2$Pd NS in the flow cell at different anolyte 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 Bi$_2$Pd 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 Bi$_2$Pd NS.
Fig. S11 Possible reaction pathways for GOR on Bi$_x$Pd NS.
Fig. S12 Polarization curves of GOR-CO$_2$RR couple and OER-CO$_2$RR couple in the two-electrode configuration.