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Modular Multi-Interface Nanocrystals for Enhanced Ethanol Oxidation Electrocatalysis

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SUMMARY

Electrochemical processes that utilize biomass-derived ethanol as a source of electrons and protons offer a sustainable energy strategy, yet their practical implementation is limited by sluggish ethanol oxidation reaction (EOR) kinetics and catalyst poisoning. Here we report a modular multi-interface nanocrystal catalyst comprising core/shell Co_2P/Pd and Pd-Au heterostructured interfaces that exhibit complementary functions for the enhanced EOR catalysis. The Co_2P/Pd interface boosts Pd atom utilization and lowers the kinetic barriers for ethanol-to-acetate conversion, while the Pd-Au interface effectively alleviates CO poisoning caused by C-C bond cleavage of ethanol. In-depth analyses using in-situ attenuated total reflectance–surface enhanced infrared absorption spectroscopy, differential electrochemical mass spectrometry, and density functional theory calculations elucidates the mechanistic roles of these interfaces. The optimized $Co_2P/Pd\text{-}Au_{0.08}$ nanorods achieve an excellent mass activity, underscoring the potential of modular, multi-interface nanocrystals for advancing EOR catalysis and offering a generalizable strategy for broader catalytic innovations.

INTRODUCTION

Anion-exchange membrane fuel cells powered by biomass-derived alcohols like ethanol, which offer high volumetric energy density, represent a promising approach to renewable electricity generation.[1–3] However, the primary challenge lies in the sluggish ethanol oxidation reaction (EOR) kinetics at the anode. This limitation arises from complex multi-step cleavage of C-H and C-C bonds, as well as the formation of poisoning intermediates during the EOR process.[4–8] Such a challenge is also present when employing EOR in other electrochemical devices, such as the anode in CO_2 and CO reduction.[9–11]

Under alkaline conditions, Pd has demonstrated superior EOR activity compared to other precious metals.[12,13] As shown in **Scheme 1**, two primary EOR pathways on Pd surfaces have been identified: Pathway 1 (also referred to as the C_2 pathway, steps 1-8) produces acetate through stepwise oxidation, while Pathway 2 (the C_1 pathway, steps 1-5, followed by 6′-8′ and 9) involves C-C cleavage, generating CO and subsequently CO_2 (CO_3^{2-} in base).[4,12,14–17] In situ spectroscopy confirms acetate as the dominant product in alkaline solutions, though small amounts of CO are unavoidably formed, causing catalyst poisoning and diminished Pd activity.[12] Therefore, improving the kinetics for C_2 pathway and simultaneously alleviating CO poisoning are the keys to optimizing Pd-based catalysts for EOR. Enormous efforts have been devoted to alloy Pd with other transition metals (e. g., Bi, Co, Ni, Ru, Au, or Ag) to promote EOR due to the increased OH surface coverage for the facilitated oxidation of reaction intermediates (like acetyl oxidation to acetate) or the easier CO oxidation.[17–25] However, Pd utilization remains inefficient as many Pd atoms are buried within nanocrystals, reducing active site availability and mass activity, thereby compromising the cost-effectiveness of the catalyst.

Herein, we report the development of an emerging class of nanocrystals, wherein multiple heterostructured interfaces, including core/shell Co_2P/Pd interface and Pd-Au hetero-interface, are modularly integrated to substantially enhance the electrocatalytic performance towards EOR. By forming core/shell Co_2P/Pd nanocrystal, Pd surface utilization and cost-effectiveness are improved, as Pd atoms are primarily positioned in a thin shell. More importantly, a comprehensive investigation combining in-situ attenuated total reflectance (ATR) – surface enhanced infrared absorption spectroscopy (SEIRAS), differential electrochemical mass spectrometry (DEMS), and density functional theory (DFT) calculation reveals complementary functions of Co_2P/Pd and Pd-Au interfaces. The former lowers the kinetic barriers for acetate formation (C_2 pathway), while the latter facilitates CO elimination (C_1 pathway). The integration of two functional modules within a single nanostructure, specifically the Co_2P/Pd-$Au_{0.08}$ nanorods (Au:Pd atomic ratio is 0.08:1), leads to mass activity of 10,188 mA mg_{Pd+Au}^{-1} for the EOR, representing one of the most efficient catalysts reported for this reaction.

RESULTS

The Co_2P/Pd–Au multi-interface nanorods were synthesized using a modular seed-mediated growth strategy, as illustrated in **Figure 1A**. This synthetic approach was previously demonstrated with Co_2P/Pt nanorods, representing the first example of core/shell nanocrystals composed of a non-precious metal phosphide core and an ultrathin precious metal shell.[26] Such a configuration significantly improves Pt utilization and its oxygen reduction reaction performance. In this work, we extend the method to Co_2P/Pd nanorods by depositing Pd onto preformed Co_2P seeds.

The initial Co_2P nanorod seeds were produced through the thermal decomposition of cobalt acetate ($Co(Ac)_2 \cdot 4H_2O$) in a mixture of trioctylphosphine oxide (TOPO), benzyl ether (BE), tributylphosphine (TBP), and oleic acid (OAc). Our previous studies have shown that these nanorods preferentially elongate along the [010] direction, exposing the (001) and (100) facets on their lateral surfaces. The resulting nanorods exhibit well-defined morphologies, measuring approximately 20–30 nm in length and 2.1 ± 0.4 nm in width, as shown in the transmission electron microscopy (TEM) image (**Figure S1)**.

The formation of Co_2P/Pd core/shell nanorods was achieved by reducing palladium acetylacetonate ($Pd(acac)_2$) over Co_2P seeds. The product is illustrated in representative TEM (**Figure S2**) and scanning transmission electron microscopy (STEM) (**Figure 1B)** images. The core/shell architecture is clearly visualized in high-angle angular dark-field (HAADF) STEM imaging (**Figure 1C**), where the higher Z-contrast of Pd relative to Co and P reveals an ultrathin Pd shell approximately 0.5-1 nm thick, corresponding to two to three atomic layers of Pd. STEM electron energy loss spectroscopy (EELS) 2D elemental mapping further confirms the core/shell structure (**Figure 1D**), showing that Co atoms are localized within the core region, which is uniformly encapsulated by a Pd shell.

To incorporate Au into the Co_2P/Pd nanorods, hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$) was reduced directly onto their surfaces, producing Co_2P/Pd–Au_x nanorods (where x represents atomic ratio of Au relative to Pd). Characterization by TEM (**Figure S3**) and HAADF-STEM (**Figure 1E**) revealed that Au preferentially forms dendritic structures at the nanorod tips and some parts of side surfaces rather than uniformly coating the Pd shell (**Figure 1F**). This arrangement minimizes the chance to block the underlying Pd active sites. By varying the Au precursor concentration, the Pd:Au ratio can be tuned from 1:0.04 to 1:0.22 (**Figure S3**). HAADF-STEM and STEM-EELS 2D mapping (**Figure 1G and S4**) further confirm that Au dendrites predominantly anchor at the ends of the Co_2P/Pd nanorods. Synchrotron radiation X-ray diffraction (SR-XRD) (λ = 0.6197 Å) patterns (**Figure S5**) of carbon-supported Co_2P/Pd–$Au_{0.08}$ samples (**Figure S6**) also confirm the presence of both Pd and Au phases. The characteristic fcc Pd (311) and Au (222) diffraction peaks appear at 29.51° and 31.04°, respectively, while the peaks at 20.85° and 25.64° are indexed to the orthorhombic Co_2P (002) and (130) planes, respectively (**Figure S5**).

To further elucidate the chemical states of Pd and Au on the Co_2P/Pd–Au nanorods, X-ray photoelectron spectroscopy (XPS) was conducted on both carbon-supported Co_2P/Pd and Co_2P/Pd–Au catalysts. The XPS survey scan (**Figure S7A**) confirms the presence of Co, P, Pd, and Au, along with some surface-adsorbed oxygen. High-resolution Pd 3d spectra of Co_2P/Pd and Co_2P/Pd–Au (**Figure S7B**) display a pair of doublet peaks at 335.8 eV and 341.0 eV, corresponding to Pd $3d_{5/2}$ and $3d_{3/2}$, respectively, confirming that Pd is present in the metallic state in both catalysts. Notably, after Au incorporation, the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peaks in Co_2P/Pd–Au shift to higher binding energies (336.0 eV and 341.3 eV), indicating a decrease in Pd's surface electron density. This reduction in electron density is believed to down-shift Pd d-band center and weaken the adsorption of CO poisoning intermediates during electrocatalysis, thereby enhancing the EOR activity.[27–31]

The electrocatalytic activities of Co_2P/Pd and Co_2P/Pd-Au_x for the EOR were investigated in 1.0 M KOH containing 1.0 M ethanol and compared with commercial Pd/C and PdAu nanoparticles (synthesized and supported on carbon, as shown in **Figure S8**). As shown in **Figure 2A**, Co_2P/Pd enhances Pd mass activity, achieving a peak mass current density of 2823 mA mg_{Pd}^{-1}, which is more than twice that of Pd/C (1320 mA mg_{Pd}^{-1}). Notably, the EOR activity is further improved with the introduction of surface Au decoration. Co_2P/Pd-$Au_{0.04}$ exhibits nearly double the mass current density compared to undecorated Co_2P/Pd. The activity is maximized at an Au decoration level of 8% (Co_2P/Pd-$Au_{0.08}$), where the mass current density reaches an impressive 10,188 mA mg_{Pd+Au}^{-1}. This represents a five-fold enhancement over PdAu nanoparticles with the same Pd:Au ratio (2217 mA mg_{Pd+Au}^{-1}, **Figure 2B**), demonstrating the unique effectiveness of the multi-interfacial architecture in promoting EOR activity. This activity represents one of the highest for the EOR, as summarized in **Table S1**.[25,32–49]

However, higher Au ratios reduce performance, as Au itself is inactive for the EOR under these conditions. Excessive Au blocks Pd active sites, as confirmed by the decreased Pd electrochemical surface area (ECSA) shown in **Figure S9** and **Table S2**. Consequently, the mass current density decreases to 6887 mA

mg_{Pd+Au}^{-1} for Co_2P/Pd-$Au_{0.22}$. This trend is corroborated by slow linear scan results (**Figure S10A**), which also identify Co_2P/Pd-$Au_{0.08}$ as the optimal catalyst composition.

Beyond enhanced activity, Au decoration significantly improves the catalyst's stability (**Figure S10B**). At a fixed potential of 0.62 V for chronoamperometry (CA) measurement, the current densities of both Pd and Co_2P/Pd rapidly decay to near zero. In contrast, Co_2P/Pd-$Au_{0.08}$ maintains a mass current density of 890 mA mg_{Pd+Au}^{-1} after one hour of CA operation. Impressively, the Co_2P/Pd-Au catalysts demonstrate excellent electrochemical reactivation capabilities (**Figure 2C**). Following each one-hour stability test, Co_2P/Pd-$Au_{0.08}$ could be reactivated via potential cycling in a refreshed 1.0 M KOH + 1.0 M ethanol, regaining its original EOR activity for at least 10 consecutive cycles. Moreover, TEM imaging (**Figure S11**) confirms that the catalyst maintains its morphology, while ICP analysis indicates negligible changes in composition.

A comprehensive DFT study was conducted to deepen our understanding of the structural and catalytic properties observed in experiments. We utilized slab models of Co_2P(001)/Pd(111) interfaces to represent the Co_2P/Pd core/shell nanorods, as depicted in **Figure S12**. The mechanism of EOR remains a topic of debate due to its intricate nature; however, it is generally accepted that this process follows a dual-pathway mechanism, known as C1 and C2 pathways (**Scheme 1**). The C1 pathway features the cleavage of the C−C bond and results in the generation of C1 fragments, such as CH_x and CO species. These C1 species are known to form strong bonds with the catalyst surface, leading to the blockage of active sites and thus are considered as contributors to the poisoning of the catalyst. Conversely, the C2 pathway represents the partial oxidation of ethanol, characterized as the reactive-intermediate pathway. Due to the significantly higher energy barrier for C-C bond cleavage associated with the C1 pathway, it has been observed that the C2 pathway predominates EOR on Pd under alkaline conditions.

In the C2 pathway, the C−C bond is preserved, facilitating the oxidation of ethanol to acetaldehyde and subsequently to acetate in alkaline environments. The adsorbed acetyl (CH_3CO) moiety emerges as a pivotal intermediate that distinguishes between these pathways. With the slab models, our investigations extend to both pathways of EOR across Pd and Co_2P/Pd surfaces, examining the thermodynamics of both the reactive and poisoning processes. **Figure 3** and **Figure 4** show the free energy diagram for the proposed reaction pathway for ethanol electro-oxidation to acetate and CO_2. The geometric structures of the most important intermediates and transition states involved in the EOR on Pd site are shown in **Figure S13-S16**.

In the proposed reaction pathway, the coupling of adsorbed hydroxyl (OH) and acetyl (CH_3CO) intermediates facilitates the formation of acetate, constituting the rate-limiting step (RDS) in C2 pathway. This crucial step is significantly influenced by the destabilization of both the initial and final states during the carbon-oxygen (C-O) coupling reaction to yield acetate on the Co_2P/Pd surface. This destabilization effectively lowers the energy barrier, enhancing the coupling of chemisorbed CH_3CO and OH (**Figure 3**). Our investigation into the transition states (TS) for the RDS, utilizing the nudged elastic band (NEB) and dimer methods, reveals that the incorporation of Co_2P substrate markedly reduces the activation energy required for the C-O coupling step by approximately 0.4 eV when compared to Pd.[50,51] These findings underscore the potential of Co_2P/Pd core/shell nanorods as significantly improved catalysts for the EOR. Concurrently, it was observed that the interface between Co_2P/Pd also slightly lowers the energy barrier for C-C bond cleavage in the conversion process from $*CH_3CO$ to *CO. Computational analyses reveal activation barriers of 0.91 eV for Pd and 0.86 eV for Co_2P/Pd. Despite the likely minor presence of these CO species during the reaction, they pose a substantial risk of poisoning the Pd catalyst.

In modeling Au dendrites on Co_2P/Pd nanorods, we approximate the dendritic structures with three-atom Au clusters to simplify the computational complexity while capturing the essential surface interactions and catalytic activity. This approach allows for a tractable yet effective representation of the Au-decorated interface, focusing on the key atomic interactions that drive the material's properties. The calculated adsorption energies of adsorbed CO and OH on different sites on the surfaces are summarized in **Table S3**. Notably, Au decoration significantly weakens the interaction of CO with the surface across all the sites. The Pd-C bond length in the case of Pd-Au is slightly elongated (1.93 Å) compared to the Pd (1.85 Å). These results confirm the observation of an alleviation in the CO poisoning of Pd in the presence of a small amount of gold. This also favors the rapid oxidation of CO to CO_2. The electro-oxidation of CO goes through a mechanism that assumes a Langmuir-Hinshelwood (LH) type reaction between the adsorbed CO and OH; where the coupling of CO and OH on the surface follows by the formation of an adsorbed (COOH*) that subsequently deprotonates to the CO_2. **Table S3** summarizes the binding properties of adsorbed CO and OH on Pd sites on the three slabs. The energy profile of the reaction path for the oxidation of CO to CO_2 on Pd, Co_2P/Pd and PdAu surfaces is shown in **Figure 4**. The NEB calculated activation energy for the CO+OH reaction step on the PdAu surface (1.18 eV) is significantly lower than the Pd surface (1.53 eV) which translates to an easier oxidation of CO to CO_2 on this surface. Even though we did not carry out similar calculations for the reaction on the surfaces with Au decoration on Co_2P/Pd, we anticipate that this trend due to the presence of Au on the surface still holds because the binding of CO, OH, and COOH on the surfaces with the Co_2P core is weaker and raises the overall energy profile. This illustrates that the activation energy for CO oxidation would be comparable to, or potentially lower than, that on Pd and PdAu.

The theoretical strain effect of –5.1%, indicative of a compressive nature, arising from the lattice mismatch between the Pd shell and the Co_2P (001) core introduces alterations to the electronic structure of the Pd shell, which in turn influence the adsorption properties. These changes in the EOR catalytic activity of Pd surfaces and the adsorption energy of intermediate species can be described in terms of the d-band center theory. The d-band center theory of Hammer and Nørskov states that the closer the d-band center is to the Fermi level, the stronger the interaction with the adsorbate is.[31,52,53] The atomic projected density of states of all the considered slabs in this work is shown in **Figure S17** and the d-band center and d-band width were calculated as the first and second moment of the projected d-band DOS on the surface atoms referenced to the Fermi level, tabulated in **Table S4**. Both d-band center and CO-binding strength decrease in the following order: Pd> Co_2P/Pd > PdAu > Co_2P/Pd-Au. Au decoration and Co_2P (001) core combination shifts the d-band center to lower energies and thus further weakens the interaction of the adsorbates to the surface. As shown in **Figure S17**, our DFT analysis reveals a downward shift of the Pd d-band center upon Au decoration and Co_2P support, which directly tracks with the shifts observed in the XPS spectra (**Figure S7**). This electronic modulation weakens the Pd-CO interaction, as reflected in the reduced CO adsorption energy, and thereby facilitates CO desorption. Calculation details are listed in **Table S5-7**.

To evidence the formation of CO species during EOR that poison the Pd surface, probe the EOR mechanism, and demonstrate the Au decoration enhancing the CO removal, we employed the in-situ attenuated total reflectance (ATR) – surface enhanced infrared absorption spectroscopy (SEIRAS) analyses (**Figure 5A-C**). We found that ethanol dissociated upon its exposure to the pure Pd film at the open circuit potential (OCP, 0.8 V), resulting in CO_{ad} peak that heavily poisons Pd surface at 1840 cm^{-1} (**Figure S18A**).[54] In addition to the dominant C-O stretching band of adsorbed *CO, several other minor peaks are observed in the spectra. However, these features remain constant under various potentials and do not exhibit a Stark shift (i.e., a potential-dependent frequency shift), which is a hallmark of an adsorbed reaction intermediate.[55] Their potential-independent behavior suggests that they likely originate from solution-phase species, bulk reaction products, or vibrational modes of the electrode material itself, rather than from surface-adsorbed intermediates pertinent to the reaction pathway. Consequently, the following discussion will focus primarily on the behavior of the adsorbed *CO intermediate.

The evolution of CO_{ad} peak was further investigated by cycling the Pd film from the stable OCP to 1.6 V. It is found that the CO_{ad} peak is well-maintain in the course of positive polarization until 1.4 V, where the intensity of CO_{ad} started to decrease and fully disappeared at potentials ≥ 1.5 V, indicating the CO_{ad} is fully oxidized to CO_2 above this potential. In the reverse scan, the CO_{ad} peak is regenerated at potentials ≤ 0.9 V, further confirmed the CO poisoning on Pd surface at low potential regions. On Pd-Au thin film interface, a similar ethanol dissociation and CO poisoning is observed at OCP (0.6 V vs. RHE, **Figure S18B**). The elevation of CO poisoning using the Pd-Au interface is obvious under the electrode polarization, where the reduction of CO_{ad} peak starts at 0.9 V and fully disappeared at ≥ 1.0 V in the positive scan. The reduced overpotential for CO oxidation suggests a diminished CO poisoning effect on Pd-Au compared to Pd film. Compared with Pd and Pd-Au interfaces, the Co_2P/Pd-Au interfaces keep intact in the whole course of ATR-SEIRAS analysis, with no ethanol dissociation or CO_{ad} peak being observed both under OCP and cyclic voltammetry (**Figure S18C and 5C**), indicating the combination of Co_2P/Pd and Pd-Au will significantly inhibit CO poisoning on Pd surface, despite the non-quantitative nature of SEIRAS. The enhanced CO removal/oxidation over Co_2P/Pd-$Au_{0.08}$ interfaces is also evidenced under CO stripping and CO oxidations (**Figure S19**), which shows a lower onset potential and higher CO oxidation current being achieved on the Co_2P/Pd-Au nanorods, compared with Co_2P/Pd nanorods and Au nanoparticle catalysts.

To give solid evidence on the promoted CO removal over Co_2P/Pd-$Au_{0.08}$ interfaces, we further performed the DEMS study, which allows the direct detection of CO oxidation product, CO_2, from EOR in the alkaline electrolyte (0.1 M KOH, 0.1 M EtOH). As shown in **Figure 6A-C**, all three catalysts present a similar product generation profile, including CH_4 (m/z = 15) from the reduction of CH_x species by adsorbed hydrogen, CO_2 (m/z = 22 and 44) from the oxidation of poisoning CO species, CH_3CHO (m/z =15, 29 and 44) from the ethanol partial oxidation, and $CH_3CH_2OOCCH_3$ (m/z = 61) from the reaction of ethanol with partially oxidized product acetate. The product distribution is enabled after background correction and integration over the whole potential cycle. A current efficiency (i.e. Faradaic efficiency) for CO_2 formation of ca. 1.5 % is obtained on Co_2P/Pd-$Au_{0.08}$ during a potential cycle, a significant enhancement compared with that on Co_2P/Pd (0.9%) and commercial Pd (0.04%), indicating more CO species being oxidized to CO_2 on Co_2P/Pd-Au. The dominant product is acetate for all three catalysts.

Despite its superior stability compared to other catalysts in chronoamperometry measurements, Co_2P/Pd-$Au_{0.08}$ still experiences a gradual decline during continuous operation (**Figure 2C**). This degradation is likely caused by the widening of the diffusion layer and by poisoning effects from other species beyond CO, including CH_3 and CH_x species produced during C–C bond cleavage. To address the limitation from poisoning, modifying the Pd-Au interface with additional oxyphilic metals could provide the functionality needed for efficient CH_x oxidation, offering a promising strategy for further catalyst enhancement. In addition, the Co_2P/Pd module is expected to be tunable by incorporating other metal phosphide nanocrystal cores. Controlling the metal phosphide/metal interfaces may further open opportunities to either decrease the activation barrier for the C2 pathway or lower the C–C cleavage barrier to promote the C1 pathway. These concepts warrant detailed investigation in future.

Discussion

The modular design of multi-interface nanocrystals holds promise for the modulation and optimization of electrocatalysis. By integrating two functionally complementary interfaces, core/shell Co_2P/Pd to reduce the RDS barrier of EOR and enhance Pd utilization efficiency, and Pd-Au to effectively mitigate CO poisoning, Co_2P/Pd-Au_x nanorods demonstrate substantially improved EOR activity and durability. This design approach offers a versatile platform that can be further refined for even greater catalytic performance in EOR. A deeper understanding of the structure-property relationships in interfaces and other structural motifs will expand the potential of modular catalyst designs. Such advancements can unlock new opportunities across a wide array of electrocatalytic and thermocatalytic applications.

METHODS

Synthesis of Co_2P nanorods. Co_2P nanorods were synthesized following the procedure described in our previous publication.[56,57] Initially, 2 g of $Co(Ac)_2{\cdot}4H_2O$ and 3.2 g of TOPO were dissolved in 80 mL of BE and 8 mL of OAc at 140 °C under a nitrogen (N_2) atmosphere. Once the $Co(Ac)_2{\cdot}4H_2O$ was fully dissolved, the temperature was reduced to 90 °C, and the mixture was subjected to vacuum for 1 hour to eliminate impurities and moisture. The reaction vessel was then refilled with N_2 and heated to 220 °C at a rate of approximately 5 °C min^{-1}. Subsequently, 12 mL of TBP was added via syringe, and the reaction mixture was maintained at 260 °C for 2 hours. After cooling to room temperature, the product was carefully transferred into a N_2-filled glovebox using a Schlenk tube to prevent air exposure. For purification, the nanorods were collected by centrifugation at 8000 rpm for 8 minutes following the addition of dried isopropanol. The nanorods underwent 2–3 additional centrifugation cycles, involving dispersion in dried hexane and precipitation with dried isopropanol. The purified Co_2P nanorods were finally re-dispersed and stored in dried hexane within the N_2-filled glovebox.

Synthesis of Co_2P/Pd nanorods. Co_2P/Pd were synthesized by modifying a reported method for Co_2P/Pt.[26] 40 mg of $Pd(acac)_2$ was dissolved in 10 mL of octadecene (ODE), 2 mL of oleylamine (OAm), and 1 mL of OAc. This mixture was heated to 60 °C under vacuum for 1 hour to remove residual impurities and moisture and then purged with N_2. Next, 45 mg of Co_2P seeds dispersed in hexane was introduced via syringe, followed by evacuation for 5 minutes to remove the solvent. Under N_2, 0.025 mL of iron pentacarbonyl ($Fe(CO)_5$) was injected, and the solution was gradually heated to 160 °C at 2–3 °C min^{-1} and maintained at this temperature for 30 minutes. As reported in Co_2P/Pt, the addition of $Fe(CO)_5$ acts as a CO source during synthesis, promoting the formation of a uniform metal shell. Unlike the Co_2P/Pt, we reduced the reaction temperature from 180 °C to 160 °C, which rendered the Fe content in the resulting Co_2P/Pd product negligible. After cooling, the core/shell nanorods were precipitated by adding isopropanol at room temperature and collected by centrifugation (8000 rpm, 8 min). The nanorods were further purified by two additional cycles of dispersion in hexane and precipitation with isopropanol. Finally, the purified Co_2P/Pd nanorods were re-dispersed and stored in hexane under ambient conditions.

Synthesis of Co_2P/Pd-Au_x nanorods. To synthesize Co_2P/Pd-$Au_{0.08}$, 11 mg of $HAuCl_4 \cdot 3H_2O$ was dissolved in the mixture of 10 mL of ODE and 0.4 mL of OAm at 70 °C under N_2. 40 mg of Co_2P/Pd seeds dispersed in hexane were then added into the reactor using a syringe. The system was then briefly purged with N_2 to remove the hexane and held at that temperature for two hours to allow the growth of Au on Co_2P/Pd. The Co_2P/Pd-Au_x nanorods were separated, purified, and stored in hexane using the same procedure described above. The concentration of Au on the nanorods is tuned by adjusting the amounts of Au precursor and OAm as surfactant. Using 5.5 mg of $HAuCl_4 \cdot 3H_2O$ and 0.2 mL of OAm yielded Co_2P/Pd-$Au_{0.04}$, while 22 mg of $HAuCl_4 \bullet 3H_2O$ and 0.8 mL of OAm led to Co_2P/Pd-$Au_{0.22}$.

Synthesis of $PdAu_x$ Nanoparticles. Pd nanoparticle seeds were prepared following a modified literature procedure.[58] In brief, 100 mg of $Pd(acac)_2$ was dissolved in 12 mL of OAm and subjected to vacuum at 60 °C for 1 hour to remove air and low-boiling impurities, after which the system was purged with N_2. Separately, 200 mg of borane tert-butylamine (BTB) complex was dissolved in 3 mL of OAm and rapidly injected into the Pd precursor solution. The reaction mixture was maintained at 60 °C for 30 minutes. The resulting Pd nanoparticles were isolated, purified, and stored in hexane using the purification protocol described previously. For the synthesis of $PdAu_x$ nanoparticles, the same procedure used to prepare Co_2P/Pd–Au_x nanorods was followed, but with Pd serving as the seed material.

Catalysts Preparation. The as-synthesized nanorods or nanoparticles were first dispersed in hexane with Vulcan 72R carbon black and sonicated, followed by centrifugation at 8000 rpm for 5 minutes to ensure a uniform distribution of nanorods or nanoparticles on the carbon support. The resulting carbon-supported catalysts were then treated with acetic acid at 70 °C under N_2 for 12 hours to remove surfactants and residual Fe in the synthesis.[26] Afterward, the catalysts were rinsed three times with ethanol to eliminate any remaining acetic acid, and subsequently dried under vacuum.

Electrochemical Measurements. The electrochemical analyses were performed on a Biologics VMP3 potentiostat in a three-electrode system consisting of a glassy carbon working electrode (GCE), a Hg/HgO reference electrode (1.0 M KOH), and a platinum foil counter electrode. The Hg/HgO electrode was calibrated vs. reversible hydrogen electrode (RHE) prior to electrochemical measurement to allow all potentials to be reported vs. RHE in this work. To prepare the working electrode, catalyst ink was first prepared by dispersing a solution containing catalysts and Nafion (9:1) in isopropanol. The ink was then drop-casted onto a freshly polished GCE to achieve a catalyst loading of ~ 20 μg. Cyclic voltammograms of commercial Pd, Co_2P/Pd, and Co_2P/Pd-Au_x were recorded in N_2-saturated 1.0 M KOH from 0.03 – 1.45 V with a sweep rate of 50 mV s^{-1} to access the electrochemical surface area (ECSA) of Pd. The EOR activity was measured by cyclic voltammetry from 0.05 – 1.2 V in 1.0 M KOH + 1.0 M EtOH with a sweep rate of 50 mV s^{-1}. Stability of these catalysts for EOR was estimated by chronoamperometry at 0.62 V. The CO stripping experiments were conducted in 1.0 M KOH. High-purity gaseous CO was first bubbled into the electrolyte at an open circuit for 30 min to allow the CO adsorption. The electrolyte was then purged with N_2 for 20 min to eliminate the dissolved CO in the solution, and two complete cycles of CO-stripping were subsequently recorded from 0.05 – 0.9 V. The CO oxidation activity was evaluated via linear polarizations 1 mV s^{-1} from 0.05 – 0.9 V in CO-saturated 1.0 M KOH, using a rotating disk electrode (RDE) with a spin rate of 1600 rpm.

Further details regarding the methods can be found in the supplemental information.

RESOURCE AVAILABILITY

Lead contact

Requests for further information and resources should be directed to and will be fulfilled by the lead contact, Sen Zhang (sz3t@virginia.edu).

Materials availability

This study did not generate new unique reagents.

Data and code availability

All data of this study are available within the article and the supplemental information or from the corresponding authors on reasonable request.

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AUTHOR CONTRIBUTIONS

Z.Z., N.O., Y.Z., and X.C. contributed equally to this work and jointly developed the research concept under the supervision of H.D.A., B.X., H.X., and S.Z.. Z.Z. and Y.Z. synthesized the materials and performed structural and electrochemical measurements. N.O. carried out the DFT calculations. X.C. conducted the ATR-SEIRAS characterizations. H.W. performed the DEMS studies. G.J. and C.L. assisted with material fabrication and performed XPS analyses. S.W. conducted STEM imaging, and L.M. analyzed the catalysts using SR-XRD. Z.Z., N.O., and Y.Z. co-wrote the manuscript with input and revisions from all co-authors.

DECLARATION OF INTERESTS

The authors declare no competing interests.

SUPPLEMENTAL INFORMATION

Supplemental methods, Figures S1-S19, and Tables S1-7.

REFERENCES

1. Debe, M.K. (2012). Electrocatalyst approaches and challenges for automotive fuel cells. Nature *486*, 43–51. https://doi.org/10.1038/nature11115.

2. Antolini, E., and Gonzalez, E.R. (2010). Alkaline direct alcohol fuel cells. Journal of Power Sources *195*, 3431–3450. https://doi.org/10.1016/j.jpowsour.2009.11.145.

3. Chen, J., Zhang, Y., Ye, H., Xie, J.-Q., Li, Y., Yan, C., Sun, R., and Wong, C.-P. (2019). Metal–Organic Framework-Derived $Co_x Fe_{1-x} P$ Nanoparticles Encapsulated in N-Doped Carbon as Efficient Bifunctional Electrocatalysts for Overall Water Splitting. ACS Appl. Energy Mater. *2*, 2734–2742. https://doi.org/10.1021/acsaem.9b00065.

4. Fu, X., Wan, C., Huang, Y., and Duan, X. (2022). Noble Metal Based Electrocatalysts for Alcohol Oxidation Reactions in Alkaline Media. Adv Funct Materials *32*, 2106401. https://doi.org/10.1002/adfm.202106401.

5. Perez, J.M., Beden, B., Hahn, F., Aldaz, A., and Lamy, C. (1989). “In situ” infrared reflectance spectroscopic study of the early stages of ethanol adsorption at a platinum electrode in acid medium. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry *262*, 251–261. https://doi.org/10.1016/0022-0728(89)80026-9.

6. Leung, L.-W.H., Chang, S.-C., and Weaver, M.J. (1989). Real-time FTIR spectroscopy as an electrochemical mechanistic probe. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry *266*, 317–336. https://doi.org/10.1016/0022-0728(89)85078-8.

7. Wang, H.-F., and Liu, Z.-P. (2008). Comprehensive Mechanism and Structure-Sensitivity of Ethanol Oxidation on Platinum: New Transition-State Searching Method for Resolving the Complex Reaction Network. J. Am. Chem. Soc. *130*, 10996–11004. https://doi.org/10.1021/ja801648h.

8. Camara, G.A., and Iwasita, T. (2005). Parallel pathways of ethanol oxidation: The effect of ethanol concentration. Journal of Electroanalytical Chemistry *578*, 315–321. https://doi.org/10.1016/j.jelechem.2005.01.013.

9. Bevilacqua, M., Filippi, J., Lavacchi, A., Marchionni, A., Miller, H.A., Oberhauser, W., Vesselli, E., and Vizza, F. (2014). Energy Savings in the Conversion of CO_2 to Fuels using an Electrolytic Device. Energy Tech *2*, 522–525. https://doi.org/10.1002/ente.201402014.

10. Verma, S., Lu, S., and Kenis, P.J.A. (2019). Co-electrolysis of CO_2 and glycerol as a pathway to carbon chemicals with improved technoeconomics due to low electricity consumption. Nat Energy *4*, 466–474. https://doi.org/10.1038/s41560-019-0374-6.

11. Overa, S., Crandall, B.S., Shrimant, B., Tian, D., Ko, B.H., Shin, H., Bae, C., and Jiao, F. (2022). Enhancing acetate selectivity by coupling anodic oxidation to carbon monoxide electroreduction. Nat Catal *5*, 738–745. https://doi.org/10.1038/s41929-022-00828-w.

12. Yang, Y.-Y., Ren, J., Li, Q.-X., Zhou, Z.-Y., Sun, S.-G., and Cai, W.-B. (2014). Electrocatalysis of Ethanol on a Pd Electrode in Alkaline Media: An *in Situ* Attenuated Total Reflection Surface-Enhanced Infrared Absorption Spectroscopy Study. ACS Catal. *4*, 798–803. https://doi.org/10.1021/cs401198t.

13. Bianchini, C., and Shen, P.K. (2009). Palladium-Based Electrocatalysts for Alcohol Oxidation in Half Cells and in Direct Alcohol Fuel Cells. Chem. Rev. *109*, 4183–4206. https://doi.org/10.1021/cr9000995.

14. Hren, M., Božič, M., Fakin, D., Kleinschek, K.S., and Gorgieva, S. (2021). Alkaline membrane fuel cells: anion exchange membranes and fuels. Sustainable Energy Fuels *5*, 604–637. https://doi.org/10.1039/D0SE01373K.

15. Zhou, Z.-Y., Wang, Q., Lin, J.-L., Tian, N., and Sun, S.-G. (2010). In situ FTIR spectroscopic studies of electrooxidation of ethanol on Pd electrode in alkaline media. Electrochimica Acta *55*, 7995–7999. https://doi.org/10.1016/j.electacta.2010.02.071.

16. Fang, X., Wang, L., Shen, P.K., Cui, G., and Bianchini, C. (2010). An in situ Fourier transform infrared spectroelectrochemical study on ethanol electrooxidation on Pd in alkaline solution. Journal of Power Sources *195*, 1375–1378. https://doi.org/10.1016/j.jpowsour.2009.09.025.

17. Wang, A., He, X., Lu, X., Xu, H., Tong, Y., and Li, G. (2015). Palladium–Cobalt Nanotube Arrays Supported on Carbon Fiber Cloth as High-Performance Flexible Electrocatalysts for Ethanol Oxidation. Angew Chem Int Ed *54*, 3669–3673. https://doi.org/10.1002/anie.201410792.

18. Chen, Y., Fan, Z., Luo, Z., Liu, X., Lai, Z., Li, B., Zong, Y., Gu, L., and Zhang, H. (2017). High-Yield Synthesis of Crystal-Phase-Heterostructured 4H/fcc Au@Pd Core–Shell Nanorods for Electrocatalytic Ethanol Oxidation. Advanced Materials *29*, 1701331. https://doi.org/10.1002/adma.201701331.

19. Ahmed, M.S., and Jeon, S. (2014). Highly Active Graphene-Supported $Ni_{x}Pd_{100-x}$ Binary Alloyed Catalysts for Electro-Oxidation of Ethanol in an Alkaline Media. ACS Catal. *4*, 1830–1837. https://doi.org/10.1021/cs500103a.

20. Jiang, K., Wang, P., Guo, S., Zhang, X., Shen, X., Lu, G., Su, D., and Huang, X. (2016). Ordered PdCu-Based Nanoparticles as Bifunctional Oxygen-Reduction and Ethanol-Oxidation Electrocatalysts. Angew Chem Int Ed *55*, 9030–9035. https://doi.org/10.1002/anie.201603022.

21. Ludwe L. Sikeyi, Thabo Matthews, Abolanle S. Adekunle, and Nobanathi W. Maxakato (2020). Electro-oxidation of Ethanol and Methanol on Pd/C, Pd/CNFs and Pd- Ru/CNFs Nanocatalysts in Alkaline Direct Alcohol Fuel Cell. Electroanalysis *32*, 2681–2692. https://doi.org/10.1002/elan.202060260.

22. Du, W., Yang, G., Wong, E., Deskins, N.A., Frenkel, A.I., Su, D., and Teng, X. (2014). Platinum-Tin Oxide Core–Shell Catalysts for Efficient Electro-Oxidation of Ethanol. J. Am. Chem. Soc. *136*, 10862–10865. https://doi.org/10.1021/ja505456w.

23. Shaofang Fu, Yuehe Lin, Chengzhou Zhu, and Dan Du Facile One-Step Synthesis of Three-Dimensional Pd−Ag Bimetallic Alloy Networks and Their Electrocatalytic Activity toward Ethanol Oxidation. ACS Applied Materials & Interfaces *7*, 13842–13848.

24. Zhou, M., Liu, J., Ling, C., Ge, Y., Chen, B., Tan, C., Fan, Z., Huang, J., Chen, J., Liu, Z., et al. (2022). Synthesis of Pd_3Sn and PdCuSn Nanorods with $L1_2$ Phase for Highly Efficient Electrocatalytic Ethanol Oxidation. Advanced Materials *34*, 2106115. https://doi.org/10.1002/adma.202106115.

25. Yuan, X., Zhang, Y., Cao, M., Zhou, T., Jiang, X., Chen, J., Lyu, F., Xu, Y., Luo, J., Zhang, Q., et al. (2019). $Bi(OH)_3$ /PdBi Composite Nanochains as Highly Active and Durable Electrocatalysts for Ethanol Oxidation. Nano Lett. *19*, 4752–4759. https://doi.org/10.1021/acs.nanolett.9b01843.

26. Liu, C., Ma, Z., Cui, M., Zhang, Z., Zhang, X., Su, D., Murray, C.B., Wang, J.X., and Zhang, S. (2018). Favorable Core/Shell Interface within Co_2P/Pt Nanorods for Oxygen Reduction Electrocatalysis. Nano Lett. *18*, 7870–7875. https://doi.org/10.1021/acs.nanolett.8b03666.

27. Tanuja, Tomar, S., Singha, T., and Satpati, B. (2025). Tuning the d-Band Center via Strain and Ligand Effects in Core–Shell Pentatwinned Au@Pd Nanoparticles for Enhanced Ethanol Oxidation Reaction. Adv Funct Materials, e14936. https://doi.org/10.1002/adfm.202514936.

28. Yan, Z., Hitt, J.L., Zeng, Z., Hickner, M.A., and Mallouk, T.E. (2021). Improving the efficiency of CO_2 electrolysis by using a bipolar membrane with a weak-acid cation exchange layer. Nat. Chem. *13*, 33–40. https://doi.org/10.1038/s41557-020-00602-0.

29. Wang, H., Zhang, S., Cai, W., Xu, B.Z., Cai, Z., Wu, Y., Luo, X., Wei, X., Liu, Z., Gu, W., et al. (2020). Largely boosted methanol electrooxidation using ionic liquid/PdCu aerogels via interface engineering. Mater. Horiz. *7*, 2407–2413. https://doi.org/10.1039/D0MH00646G.

30. Nørskov, J.K., Abild-Pedersen, F., Studt, F., and Bligaard, T. (2011). Density functional theory in surface chemistry and catalysis. Proc. Natl. Acad. Sci. U.S.A. *108*, 937–943. https://doi.org/10.1073/pnas.1006652108.

31. Hammer, B., and Nørskov, J.K. (2000). Theoretical surface science and catalysis—calculations and concepts. In Advances in Catalysis (Elsevier), pp. 71–129. https://doi.org/10.1016/S0360-0564(02)45013-4.

32. Qiu, Y., Zhang, J., Jin, J., Sun, J., Tang, H., Chen, Q., Zhang, Z., Sun, W., Meng, G., Xu, Q., et al. (2021). Construction of Pd-Zn dual sites to enhance the performance for ethanol electro-oxidation reaction. Nat Commun *12*, 5273. https://doi.org/10.1038/s41467-021-25600-9.

33. Yang, H., Xie, J., Liu, Y., and Dong, Q. (2022). Rational design of PdBi nanochains with grain boundaries for enhanced ethanol oxidation reaction. International Journal of Hydrogen Energy *47*, 14859–14868. https://doi.org/10.1016/j.ijhydene.2022.02.235.

34. Lao, X., Li, Z., Yang, L., Zhang, B., Ye, W., Fu, A., and Guo, P. (2023). Monodispersed ultrathin twisty PdBi alloys nanowires assemblies with tensile strain enhance C_{2+} alcohols electrooxidation. Journal of Energy Chemistry *79*, 279–290. https://doi.org/10.1016/j.jechem.2022.12.056.

35. Lao, X., Yang, M., Sheng, X., Sun, J., Wang, Y., Zheng, D., Pang, M., Fu, A., Li, H., and Guo, P. (2022). Monodisperse PdBi Nanoparticles with a Face-Centered Cubic Structure for Highly Efficient Ethanol Oxidation. ACS Appl. Energy Mater. *5*, 1282–1290. https://doi.org/10.1021/acsaem.1c03703.

36. Su, D., Lam, Z., Wang, Y., Han, F., Zhang, M., Liu, B., and Chen, H. (2023). Ultralong durability of ethanol oxidation reaction via morphological design. Joule *7*, 2568–2582. https://doi.org/10.1016/j.joule.2023.09.008.

37. Ye, Y., Zhang, Y., Yan, X., Ning, G., and Hu, S. (2025). Pb–Pd alloy catalysts with intercalated Pb atoms: optimized electronic and lattice structures for enhanced electrochemical ethanol oxidation. Dalton Trans. *54*, 7071–7079. https://doi.org/10.1039/D5DT00117J.

38. Yang, X., Li, X., Jiang, Z., Wang, H., Guo, Q., Jin, C., Liu, Y., and Xie, H. (2025). Sub-2 nm Amorphous PdSn/C Nanocatalyst for Enhanced Ethanol Oxidation. ACS Electrochem. *1*, 115–122. https://doi.org/10.1021/acselectrochem.4c00091.

39. Zikhali, M., Matthews, T., Selepe, C.T., Mbokazi, S.P., and Maxakato, N.W. (2024). Studies on the Catalytic Properties of Palladium–Niobium Electrocatalysts Supported on Carbon Nano-onions toward Isopropanol and Ethanol Electro-oxidation in an Alkaline Medium. Chem. Mater. *36*, 6637–6650. https://doi.org/10.1021/acs.chemmater.4c01366.

40. Chen, C., Lao, X., Zhao, Y., Niu, M., and Guo, P. (2024). Lattice-Expanded PdAg Spatial Nanodendrites as Catalysts for the Ethanol Oxidation Reaction. ACS Appl. Nano Mater. *7*, 13426–13433. https://doi.org/10.1021/acsanm.4c01900.

41. Yun, Q., Lu, Q., Li, C., Chen, B., Zhang, Q., He, Q., Hu, Z., Zhang, Z., Ge, Y., Yang, N., et al. (2019). Synthesis of PdM (M = Zn, Cd, ZnCd) Nanosheets with an Unconventional Face-Centered Tetragonal Phase as Highly Efficient Electrocatalysts for Ethanol Oxidation. ACS Nano *13*, 14329–14336. https://doi.org/10.1021/acsnano.9b07775.

42. Wang, H., Guo, Y., Mao, Q., Yu, H., Deng, K., Wang, Z., Li, X., Xu, Y., and Wang, L. (2023). Sulfur and phosphorus co-doping optimized electronic structure and modulated intermediate affinity on PdSP metallene for ethanol-assisted energy-saving H_2 production. Nanoscale *15*, 7765–7771. https://doi.org/10.1039/D3NR01112G.

43. Liu, M., Xie, M., Jiang, Y., Liu, Z., Lu, Y., Zhang, S., Zhang, Z., Wang, X., Liu, K., Zhang, Q., et al. (2021). Core–shell nanoparticles with tensile strain enable highly efficient electrochemical ethanol oxidation. J. Mater. Chem. A *9*, 15373–15380. https://doi.org/10.1039/D1TA03365D.

44. Ye, S.-H., Feng, J.-X., and Li, G.-R. (2016). Pd Nanoparticle/CoP Nanosheet Hybrids: Highly Electroactive and Durable Catalysts for Ethanol Electrooxidation. ACS Catal. *6*, 7962–7969. https://doi.org/10.1021/acscatal.6b02263.

45. Yang, J., Xie, Y., Wang, R., Jiang, B., Tian, C., Mu, G., Yin, J., Wang, B., and Fu, H. (2013). Synergistic Effect of Tungsten Carbide and Palladium on Graphene for Promoted Ethanol Electrooxidation. ACS Appl. Mater. Interfaces *5*, 6571–6579. https://doi.org/10.1021/am401216s.

46. Zhao, X., Zhang, J., Wang, L., Liu, Z., and Chen, W. (2014). Pd_xCu_{100-x} networks: an active and durable electrocatalyst for ethanol oxidation in alkaline medium. J. Mater. Chem. A *2*, 20933–20938. https://doi.org/10.1039/C4TA04899G.

47. Chen, J., Tan, X., He, W., Guo, Y., Xiao, Y., Cui, H., and Wang, C. (2024). PdSnW Ternary Alloy Nanoparticle with Excellent CO Anti-Poisoning Activity for Boosting Alkaline Ethanol Oxidation Reaction. ChemCatChem *16*, e202400109. https://doi.org/10.1002/cctc.202400109.

48. Wang, H., Zheng, H., Ling, L., Fang, Q., Jiao, L., Zheng, L., Qin, Y., Luo, Z., Gu, W., Song, W., et al. (2022). Pd Metallene Aerogels with Single-Atom W Doping for Selective Ethanol Oxidation. ACS Nano *16*, 21266–21274. https://doi.org/10.1021/acsnano.2c09270.

49. Pang, M., Yang, M., Yan, J., Zhang, B., Zang, L., Fu, A., and Guo, P. (2022). Assembly of Alloyed PdCu Nanosheets and Their Electrocatalytic Oxidation of Ethanol. Langmuir *38*, 4287–4294. https://doi.org/10.1021/acs.langmuir.1c03466.

50. Henkelman, G., and Jónsson, H. (2000). Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. The Journal of Chemical Physics *113*, 9978–9985. https://doi.org/10.1063/1.1323224.

51. Henkelman, G., and Jónsson, H. (1999). A dimer method for finding saddle points on high dimensional potential surfaces using only first derivatives. The Journal of Chemical Physics *111*, 7010–7022. https://doi.org/10.1063/1.480097.

52. Greeley, J., Jaramillo, T.F., Bonde, J., Chorkendorff, I., and Nørskov, J.K. (2006). Computational high-throughput screening of electrocatalytic materials for hydrogen evolution. Nature Mater *5*, 909–913. https://doi.org/10.1038/nmat1752.

53. Hammer, B., Hansen, L.B., and Nørskov, J.K. (1999). Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. Phys. Rev. B *59*, 7413–7421. https://doi.org/10.1103/PhysRevB.59.7413.

54. Chang, X., Vijay, S., Zhao, Y., Oliveira, N.J., Chan, K., and Xu, B. (2022). Understanding the complementarities of surface-enhanced infrared and Raman spectroscopies in CO adsorption and electrochemical reduction. Nat Commun *13*, 2656. https://doi.org/10.1038/s41467-022-30262-2.

55. Chattopadhyay, A., and Boxer, S.G. (1995). Vibrational Stark Effect Spectroscopy. J. Am. Chem. Soc. *117*, 1449–1450. https://doi.org/10.1021/ja00109a038.

56. Zhang, Y., Li, N., Zhang, Z., Li, S., Cui, M., Ma, L., Zhou, H., Su, D., and Zhang, S. (2020). Programmable Synthesis of Multimetallic Phosphide Nanorods Mediated by Core/Shell Structure Formation and Conversion. J. Am. Chem. Soc. *142*, 8490–8497. https://doi.org/10.1021/jacs.0c02584.

57. Doan-Nguyen, V.V.T., Zhang, S., Trigg, E.B., Agarwal, R., Li, J., Su, D., Winey, K.I., and Murray, C.B. (2015). Synthesis and X-ray Characterization of Cobalt Phosphide (Co $_2$ P) Nanorods for the Oxygen Reduction Reaction. ACS Nano *9*, 8108–8115. https://doi.org/10.1021/acsnano.5b02191.

58. Metin, Ö., Kayhan, E., Özkar, S., and Schneider, J.J. (2012). Palladium nanoparticles supported on chemically derived graphene: An efficient and reusable catalyst for the dehydrogenation of ammonia borane. International Journal of Hydrogen Energy *37*, 8161–8169. https://doi.org/10.1016/j.ijhydene.2012.02.128.

Figure and Scheme Titles and Legends:

Scheme 1. Two reaction pathways for the EOR under alkaline conditions.

Figure 1. Synthesis and structural characterization of Co_2P/Pd and Co_2P/Pd-Au nanorods. (A) Schematic illustration of the modular seed-mediated growth for the preparation of Co_2P/Pd-Au nanorods. **(B)** STEM, **(C)** HR-STEM, and **(D)** STEM-EELS mapping images of Co_2P/Pd nanorods. **(E)** STEM, **(F)** HR-STEM, and **(G)** STEM-EELS mapping images of Co_2P/Pd-Au nanorods.

Figure 2. EOR performance of various catalysts. (A) EOR cyclic voltammetry (CV) curves of Co_2P/Pd, Co_2P/Pd-$Au_{0.08}$, Pd, and $PdAu_{0.08}$. **(B)** Mass activity of Pd, $PdAu_{0.08}$, Co_2P/Pd, and Co_2P/Pd-Au_x. **(C)** Recyclability of Co_2P/Pd-$Au_{0.08}$.

Figure 3. Lowest-energy pathway for the EOR to acetic acid (reactive pathway). Calculated at 0.6 V on Pd(111) (blue) and Co_2P(001)/Pd(111) (orange).

Figure 4. Lowest-energy pathway for the electrochemical oxidation of CO. Calculated at 0.6 V on Pd(111) (blue), PdAu (green) and Co_2P(001)/ Pd(111) (orange).

Figure 5. In situ ATR-SEIRAS analysis. EOR on (**A**) Pd film, (**B**) Pd-Au film, and (**C**) Co_2P/Pd on Au film.

Figure 6. DEMS analysis. EOR on **(A)** commercial Pd, **(B)** Co_2P/Pd, and **(C)** $Co_2P/Pd\text{-}Au_{0.08}$ nanorods. The red lines indicate the first positive-going scan. (a) is the cyclic voltammogram; (b) is the correspondent MS signal of H_2 at m/z =2, (c) is the MS signal of CH_4 and CH_3CHO at m/z=15 after correction of ethanol contribution. (d) is the MS signal of CO_2 at m/z = 22, (e) is the MS signal of CH_3CHO at m/z = 29 after correction of ethanol contribution, (f) is the MS signal of CO_2 and CH_3CHO at m/z = 44 after correction of ethanol contribution, (g) is the MS signal of ethyl acetate at m/z = 61. Only the signal at *m/z* = 15 exhibited a noticeable difference between the first and second positive-going scans. The calculation of current efficiency is based on the second positive-going scan.