

# Designing a Nanoscale Three-phase Electrochemical Pathway to Promote Pt-catalyzed Formaldehyde Oxidation

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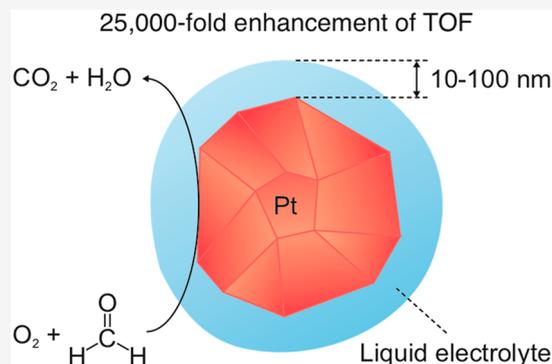
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Supporting Information

**ABSTRACT:** Gas-phase heterogeneous catalysis is a process spatially constrained on the two-dimensional surface of a solid catalyst. Here, we introduce a new toolkit to open up the third dimension. We discovered that the activity of a solid catalyst can be dramatically promoted by covering its surface with a nanoscale-thin layer of liquid electrolyte while maintaining efficient delivery of gas reactants, a strategy we call three-phase catalysis. Introducing the liquid electrolyte converts the original surface catalytic reaction into an electrochemical pathway with mass transfer facilitated by free ions in a three-dimensional space. We chose the oxidation of formaldehyde as a model reaction and observed a 25000-times enhancement in the turnover frequency of Pt in three-phase catalysis as compared to conventional heterogeneous catalysis. We envision three-phase catalysis as a new dimension for catalyst design and anticipate its applications in more chemical reactions from pollution control to the petrochemical industry.

**KEYWORDS:** formaldehyde, volatile organic compounds, three-phase catalysis, heterogeneous catalysis



Formaldehyde is a common indoor air pollutant primarily emitted from pressed wood products used in home construction and furnishings.<sup>1</sup> Catalytic degradation of formaldehyde at room temperature is a promising solution,<sup>2</sup> and Pt is thus far the best catalyst.<sup>3,4</sup> However, the catalytic activity of Pt still cannot justify its high cost. The catalytic mechanism<sup>5,6</sup> of Pt is summarized in Figure 1a. First, O<sub>2</sub> dissociatively adsorbs onto adjacent Pt atoms, yielding two O adatoms. Then, formaldehyde is oxidized by an O adatom to form adsorbed formate as an intermediate, followed by decomposition into adsorbed CO and adsorbed OH. Finally, adsorbed CO is oxidized to CO<sub>2</sub> by an O adatom, which is replenished by O<sub>2</sub> in the air or regenerated from adsorbed OH. There are two major problems hindering the kinetics of this heterogeneous catalytic process. (i) The reactive species need to be adsorbed adjacently; otherwise, the reaction is limited by surface diffusion<sup>7</sup> (e.g., the reaction between adsorbed CO and O adatom<sup>8</sup>). (ii) Most reactive species are adsorbed with particular configurations, leading to geometric restrictions for some surface reactions to happen<sup>9</sup> (e.g., O adatom is not able to attack the proton on bridge-adsorbed formate; thus, the reaction can only proceed through formate decomposition<sup>5</sup>).

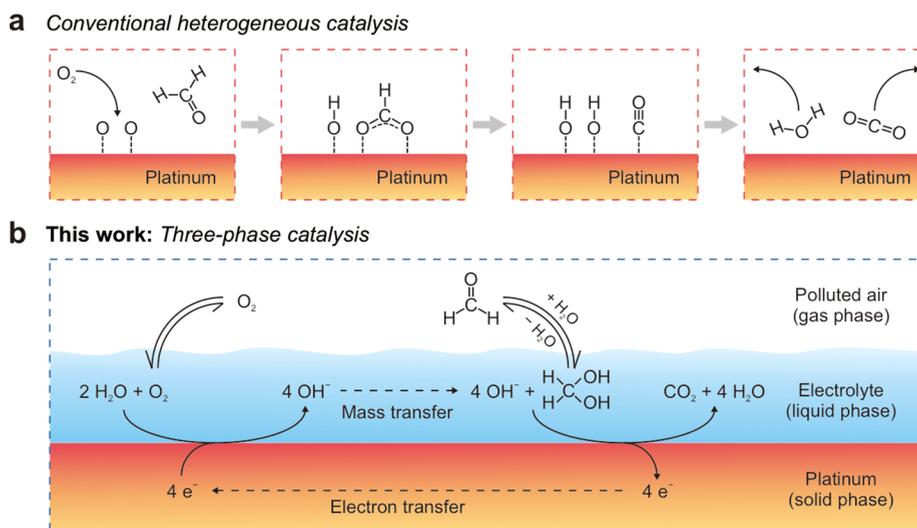
Here, we discover that the activity of Pt for catalyzing the oxidation of formaldehyde can be dramatically promoted by covering the Pt surface with a nanoscale-thin layer of aqueous electrolyte (Figure 1b). We term this strategy of using a solid-

liquid binary-phase complex to catalyze a gas-phase reaction as three-phase catalysis.

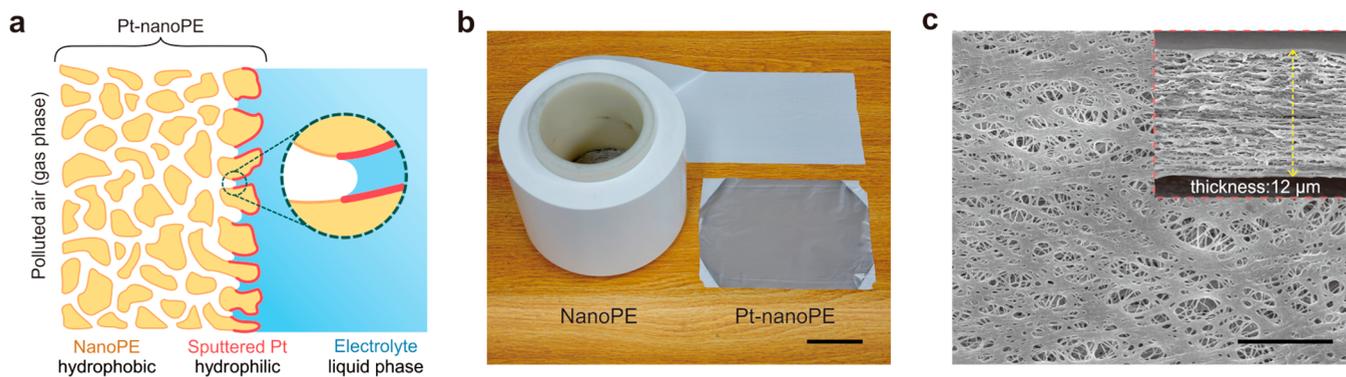
In nature, iron rusts much faster when in contact with salt water, where the salt water serves as an electrolyte that converts the original surface oxidation into an electrochemical process.<sup>10</sup> Likewise, in this contribution, introducing an electrolyte layer on Pt converts the original chemical reaction between O<sub>2</sub> and formaldehyde into two electrically shorted electrochemical reactions (Figure 1b). Such conversion solves the two aforementioned problems for conventional heterogeneous catalysis. (i) There is no more need for O<sub>2</sub> and formaldehyde to find each other on Pt since the two electrochemical reactions here are electrically connected and can thus be spatially apart. (ii) Surface reactions are no longer restricted by adsorption configurations. For example, when hydrated formaldehyde is electrochemically oxidized, H<sub>2</sub>O or OH<sup>-</sup> can attack its protons from any direction in three dimensions to form H<sub>3</sub>O<sup>+</sup> or H<sub>2</sub>O, respectively, depending on pH.<sup>11,12</sup> Similarly, O<sub>2</sub> can receive protons directly from the electrolyte when electrochemically reduced.<sup>13</sup>

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**Figure 1.** Reaction schemes for the oxidation of formaldehyde on Pt. (a) Conventional heterogeneous catalysis involves adsorption, diffusion, reaction, and desorption, constrained on a two-dimensional surface. (b) Three-phase catalysis speeds up the process by introducing a new liquid phase, with mass transfer and electron transfer facilitated by the electrolyte and Pt, respectively.



**Figure 2.** Materials design for three-phase catalysis. (a) Schematic of a Pt–nanoPE membrane separating air from the electrolyte, with the triple-phase contact lines pinned at the hydrophilic–hydrophobic boundaries (i.e., the Pt–PE boundaries). (b) Photo of a roll of commercial nanoPE membrane and a piece of Pt–nanoPE membrane. The gray color indicates Pt coating via magnetron sputtering. Scale bar, 5 cm. (c) SEM image of the Pt–nanoPE membrane with a pore size ranging from 50 to 1000 nm. Scale bar, 2  $\mu\text{m}$ . Inset, cross-sectional SEM image measuring the thickness of the Pt–nanoPE membrane.

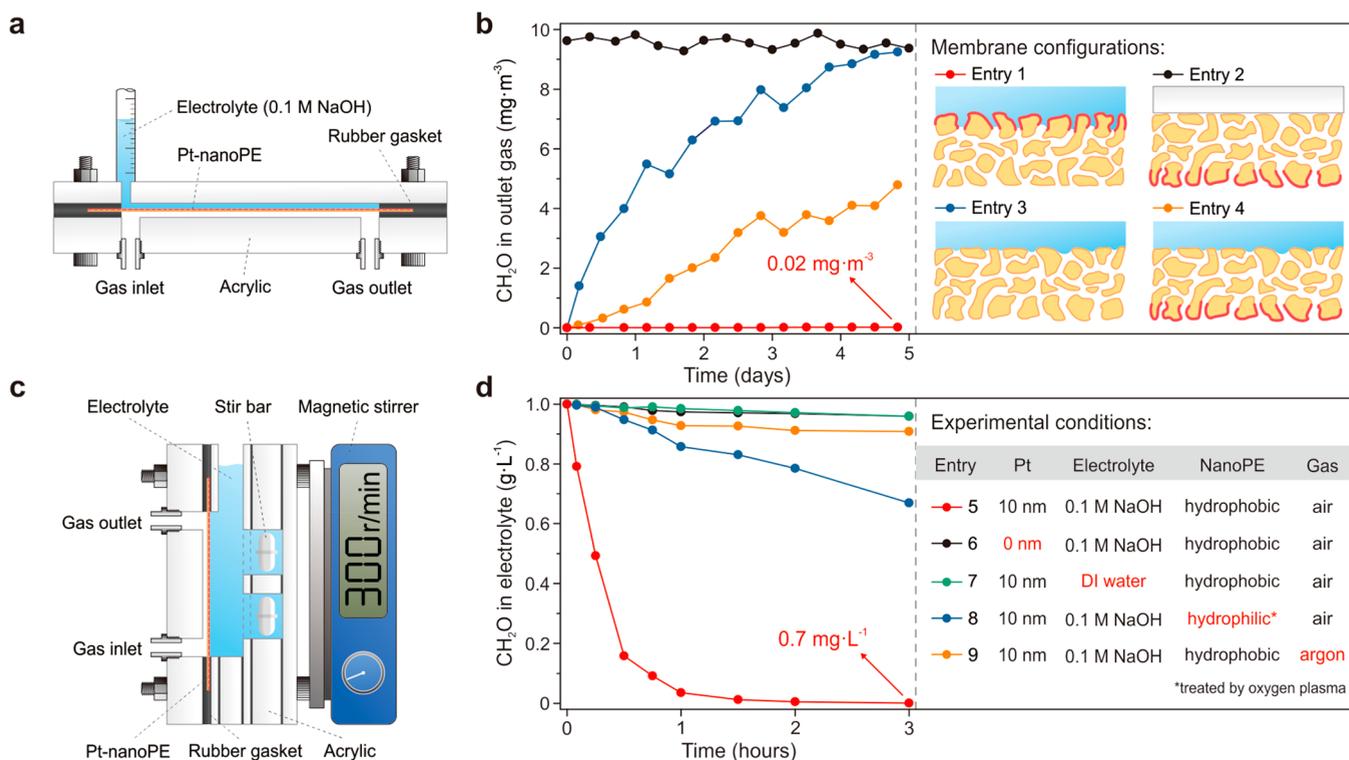
Although the presence of salt water accelerates the corrosion of iron, a piece of iron fully immersed in salt water rusts much slower than a half-immersed one,<sup>14</sup> which is due to the low solubility of  $\text{O}_2$  (8 ppm). Likewise, introducing an electrolyte layer into heterogeneous catalysis might also be counterproductive because it builds a physical barrier between the gas-phase reactants and the solid-phase catalyst.  $\text{O}_2$  and formaldehyde need to be dissolved first and then reach the Pt surface by diffusion, which is driven by the concentration gradient. Therefore, the thickness of the electrolyte layer must be minimized; otherwise, reactants with less solubility would be readily depleted, resulting in hindered reaction kinetics.<sup>15</sup>

Depletion of gas reactants in liquid electrolyte is also a commonly encountered problem in many gas-involving electrochemical systems, such as fuel cells,<sup>16</sup>  $\text{CO}_2$  reduction,<sup>17,18</sup>  $\text{H}_2\text{O}_2$  electrosynthesis,<sup>19</sup> etc. Gas diffusion electrodes (GDE) have been developed to overcome this problem by constructing triple-phase contact lines close to the catalysts and thus minimizing the diffusion distances from the gas phase to the catalysts.<sup>20–22</sup> Here, we apply the knowledge obtained through the development of GDE to gas-phase heterogeneous

catalysis beyond electrochemical systems. It is worth noting that in our system of formaldehyde oxidation, we do not extract or apply electricity through an external circuit, and the shorting circuit illustrated in Figure 1b is localized on each catalyst particle.

We designed our catalyst by utilizing the self-assembly behavior of an aqueous electrolyte on a nanoporous amphiphilic membrane (Figure 2a). Specifically, we deposited  $20 \mu\text{g cm}^{-2}$  of Pt ( $\sim 10 \text{ nm}$  thick) on one side of a nanoporous polyethylene (nanoPE) membrane through magnetron sputtering (Figure 2b). Because Pt is hydrophilic and PE is hydrophobic (Supporting Figure 1a–d), when the Pt-deposited side gets in contact with an aqueous electrolyte, the electrolyte will spontaneously wet the hydrophilic surfaces (i.e., the surfaces coated with Pt) through capillary action and finally stop at the hydrophilic–hydrophobic boundaries (i.e., the Pt–PE boundaries), while the hydrophobic and interconnected pores of nanoPE remain dry, enabling efficient gas delivery.

Such design offers three major advantages. (i) The amphiphilic nanopores (Figure 2c) of the Pt–nanoPE



**Figure 3.** Benchmarking of three-phase catalysis against conventional heterogeneous catalysis. (a) Schematic of a fixed-bed type reactor. (b) Concentrations of formaldehyde in outlet gas plotted against the duration of experiments. Reactor, fixed-bed type reactor with a membrane area of  $6 \text{ cm}^2$ . Inlet gas, air containing  $10 \text{ mg m}^{-3}$  formaldehyde. Gas flow rate,  $40 \text{ mL min}^{-1}$ . Electrolyte,  $0.1 \text{ M NaOH}$  aqueous solution. (c) Schematic of a stirred-tank type reactor. (d) Concentrations of formaldehyde in electrolyte plotted against the duration of experiments. Reactor, stirred-tank type reactor with a membrane area of  $3 \text{ cm}^2$ . Gas flow rate,  $20 \text{ mL min}^{-1}$ . Formaldehyde ( $1 \text{ g}\cdot\text{L}^{-1}$ ) was predissolved in the liquid chamber. All the experiments were conducted at  $25 \text{ }^\circ\text{C}$  in a constant-temperature room.

membrane reshape the gas–liquid interface into countless nanosized menisci (the inset of Figure 2a). The aforementioned  $\text{O}_2$ -depletion problem is alleviated because the distance from the gas–liquid menisci to Pt (equivalent to the thickness of the electrolyte layer in Figure 1b) is at the nanoscale. (ii) Such a special liquid morphology can be steadily maintained despite its fluidic nature. This is because the triple-phase contact lines are pinned at the Pt–PE boundaries within a huge pressure-difference range ( $-166 \text{ kPa} < P_{\text{gas}} - P_{\text{liquid}} < 288 \text{ kPa}$ ) due to Laplace pressure (Supporting Information Part 2). Such pinning effect provides great ease and flexibility for reactor design in practical applications. (iii) Water can be continuously supplied to the gas–liquid menisci to compensate for evaporation since a plentiful amount of aqueous electrolyte is stored as a water reservoir with direct connection to the gas–liquid menisci without blocking the gas diffusion pathway.

We benchmarked three-phase catalysis against conventional heterogeneous catalysis by using a fixed-bed type reactor (Figure 3a and Supporting Figure 3a). The reactor is composed of two chambers. A  $6 \text{ cm}^2$ -large membrane separates the upper chamber, which contains  $0.6 \text{ mL}$  of  $0.1 \text{ M NaOH}$  aqueous solution, from the lower chamber, where  $10 \text{ mg m}^{-3}$  formaldehyde-contaminated air passes through at a flow rate of  $40 \text{ mL min}^{-1}$ . The thicknesses of both chambers are  $1 \text{ mm}$ . Further,  $0.3 \text{ mL}$  of  $0.1 \text{ M NaOH}$  is stored in the graduated cylinder with connection to the liquid chamber in order to compensate for evaporation during the tests. We conducted a series of experiments with four different membrane configurations and measured the outlet formaldehyde concentration over 5 days (Figure 3b).

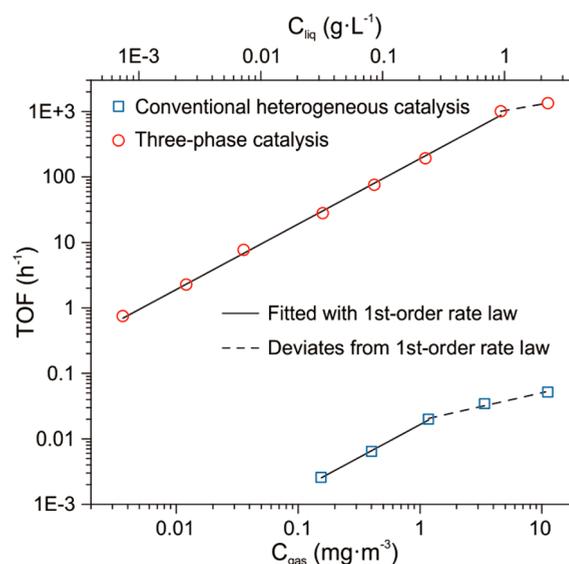
For three-phase catalysis (entry 1 in Figure 3b), a Pt–nanoPE membrane was used with the Pt-coated side facing toward the liquid chamber. The result shows that a 99.8% removal efficiency was kept after 5 days on stream, with an outlet formaldehyde concentration of  $0.02 \text{ mg}\cdot\text{m}^{-3}$ , which is well below the WHO indoor air quality guideline<sup>1</sup> ( $0.1 \text{ mg m}^{-3}$ ). For conventional heterogeneous catalysis (entry 2), the Pt–nanoPE membrane in entry 1 was flipped over with the Pt-coated side exposed toward the gas chamber and the PE side sealed by an acrylic sheet (Supporting Figure 3b). The result shows that less than 10% removal efficiency was achieved, which is much less than that of three-phase catalysis. In order to confirm that the extraordinary performance of three-phase catalysis was not merely due to dissolution, we repeated entry 1 with a nanoPE membrane without Pt coating (entry 3). Not surprisingly, dissolved formaldehyde accumulated in the liquid chamber rather than being oxidized, and finally, the dissolution reached equilibrium. In the last experiment of this series, we repeated entry 2 without sealing the PE side (entry 4), which can be regarded as a simple combination of heterogeneous catalysis and dissolution. The poor performance of entry 4 compared to the performance of entry 1 corroborates that the synergistic effect between Pt and electrolyte arises from the thoughtfully designed assembly as shown in Figure 2a, where nanoPE plays an essential role. The results of entries 1–4 successfully demonstrate the supremacy of three-phase catalysis over conventional heterogeneous catalysis.

The complexity stemming from the coupling of the dissolution kinetics and the degradation kinetics in the fixed-bed type reactor hinders their quantitative analysis. Therefore,

we designed a stirred-tank type reactor (Figure 3c and Supporting Figure 3c), the major differences of which from the fixed-bed type reactor are as follows. (i) The volume of the liquid chamber is expanded by 10-fold, providing enough solution for sampling. (ii) Two magnetic stirrers are added, enabling a homogeneous concentration for quantification. We first used the reactor to quantitatively measure the thermodynamics and kinetics of the dissolution of formaldehyde in 0.1 M NaOH, the experimental details and results of which are provided in Supporting Information Part 4. We then used the reactor to study the effects of Pt, electrolyte, gas composition, etc., on the degradation kinetics of formaldehyde (Figure 3d). In a typical experiment, formaldehyde was predissolved in the liquid chamber with an initial concentration of  $1 \text{ g L}^{-1}$ , and uncontaminated air passed through the gas chamber to deliver  $\text{O}_2$ . The concentration of formaldehyde in the liquid chamber was measured over 3 h.

Entry 5 in Figure 3d is a positive control that represents three-phase catalysis. As expected, the concentration of formaldehyde rapidly decreased, and merely  $0.7 \text{ mg L}^{-1}$  (i.e., 99.93% removal efficiency) formaldehyde remained in the electrolyte after 3 h. In entry 6, we used a nanoPE membrane without Pt coating and observed negligible loss of formaldehyde due to vaporization, indicating the critical catalytic role of Pt. In entry 7, we used deionized (DI) water in place of 0.1 M NaOH and found minimal degradation, suggesting that the electrolyte is crucial for the fast degradation. In entry 8, the nanoPE membrane was treated by  $\text{O}_2$  plasma and thus became hydrophilic. As a result, electrolyte flooded all the pores in nanoPE, and the diffusion distance for  $\text{O}_2$  in the gas phase to reach Pt increased from nanoscale to  $12 \mu\text{m}$  (i.e., the thickness of the nanoPE membrane as shown by the inset of Figure 2c). The insufficient supply of  $\text{O}_2$  slowed the degradation, justifying the necessity of having the hydrophobic nanoPE to pin the triple-phase contact lines near Pt. In entry 9, argon instead of air passed through the gas chamber. The initial  $\sim 10\%$  degradation of formaldehyde was attributed to the dissolved  $\text{O}_2$ , and no more degradation was observed after the dissolved  $\text{O}_2$  was consumed, confirming that the degradation of formaldehyde was due to oxidation by  $\text{O}_2$ . The performance gap between entries 6–9 and entry 5 clearly shows that Pt, electrolyte, hydrophobic nanoPE, and  $\text{O}_2$  are indispensable elements for three-phase catalysis.

To quantitatively compare three-phase catalysis with conventional heterogeneous catalysis, we measured the turnover frequency (TOF) in both cases at different formaldehyde concentrations (Figure 4), the experimental details of which are provided in Supporting Information Part 5. Impressively, three-phase catalysis promotes the TOF of Pt by  $\sim 25000$  times as compared to conventional heterogeneous catalysis. Such enhancement is not due to changes in the intrinsic properties of Pt since the Pt in both cases was deposited in the same manner. Indeed, such enhancement presents itself because of the introduction of the electrolyte, which completely changes the catalytic pathway as explicated in previous texts. Another remarkable feature of three-phase catalysis is the excellent fitting of the degradation-kinetics data with first-order rate law until a TOF of  $1000 \text{ h}^{-1}$ , indicating that  $\text{O}_2$  delivery is not rate limiting, which justifies the design of the amphiphilic nanostructure of Pt–nanoPE. On the contrary, the degradation kinetics for conventional heterogeneous catalysis deviates from first-order rate law at a TOF of merely  $0.02 \text{ h}^{-1}$ .



**Figure 4.** Quantitative comparison of the degradation kinetics. Turnover frequency (TOF, moles of formaldehyde converted per mole of Pt per hour) is calculated based on the total metal content. Upper and lower axes represent the concentrations of formaldehyde in 0.1 M NaOH and air, respectively, which are aligned with each other according to Henry's law (i.e., any two concentrations on the two axes vertically aligned are in thermodynamic equilibrium).

In conclusion, we report the discovery of a new toolkit for promoting heterogeneous catalysis, namely, constructing a nanoscale-thin layer of liquid electrolyte on the surface of a conventional solid catalyst. As demonstrated in our experiments, three-phase catalysis provides a  $\sim 25000$ -fold boost in the activity of Pt for catalyzing the oxidation of formaldehyde. Such impressive enhancement indicates a high potential for commercialization, especially considering that Pt is only  $\sim 15000$  times more expensive than aluminum, the most abundant metal on Earth. A quantitative comparison of our result with previous studies (Supporting Information Part 6) shows that our catalyst, Pt promoted by three-phase catalysis, is the most economical one, even among many nonprecious-metal-based catalysts. The areal mass loading of Pt on the Pt–nanoPE membrane is merely  $20 \mu\text{g cm}^{-2}$ , that is,  $\sim \$5 \text{ m}^{-2}$ . On top of that, nanoPE is widely used in lithium-ion batteries as a separator to prevent electrical shorting and can be mass-produced at an extremely low cost,<sup>23</sup> that is,  $\sim \$1 \text{ m}^{-2}$ . Moreover, high-throughput manufacturing of the Pt–nanoPE membrane is readily achievable since magnetron sputtering is a very mature technology in semiconductor industry and can be carried out in a roll-to-roll manner. Finally, we provide an analytical model in Supporting Information Part 7 as a guideline for future reactor engineering.

In a broader context, we propose that three-phase catalysis is potentially applicable for a variety of heterogeneous catalytic reactions, such as ammonia oxidation,<sup>24</sup> methane functionalization,<sup>25</sup> water–gas shift reaction,<sup>26</sup> and hydrogenation of organic compounds.<sup>27</sup> The most vital feature of three-phase catalysis is the decoupling of electron transfer and mass transfer, which is enabled by adding a nanoscale-thin layer of electrolyte that converts the original chemical catalytic process into two electrochemical catalytic processes. Therefore, the tremendous amount of published research documenting the electrochemical behavior of diverse small molecules<sup>12,13,28–32</sup>

provides a promising foundation for exploring the versatility of three-phase catalysis.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.0c03560>.

(1) Experimental methods; (2) pinning of the triple-phase contact lines; (3) supporting schemes for apparatus setup; (4) dissolution of formaldehyde in 0.1 M NaOH; (5) details on the measurements of TOF; (6) comparison with literature data; (7) analytical model for reactor engineering; and (8) more supporting data (PDF)

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### Author Contributions

<sup>V</sup>J.X. and X.X. contributed equally to this work. J.X. and Y.C. conceived the initial idea. J.X. designed the catalyst and the reactors. X.X. designed the method to quantify the concentration of formaldehyde. J.X. and X.X. conducted the experiments. Z.Z. performed the SEM characterizations. Y.W. and W.H. helped with the magnetron sputtering. J.L. and Y.Z. helped with the device fabrication. J.X., X.X., W.M., and Y.C. wrote the manuscript with input from all coauthors.

### Notes

The authors declare no competing financial interest.

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