Multifunctional Noble Metal Phosphide Electrocatalysts for the Organic Molecule Electro-Oxidation

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**ABSTRACT:**

Small organic molecule electro-oxidation (OMEO) is the important anodic reaction occurring in direct liquid fuel cells and requires efficient and durable electrocatalysts to promote the reactivity and operational stability. Noble metals (e.g. Pt, Pd) are currently the state-of-the-art catalysts for the OMEO; however, for practical applications their electrocatalytic performance needs to be improved. Herein, we report a simple and potentially cost-effective approach to the synthesis of noble metal phosphide (MxPy, M = Pd, Pt) catalysts, which is realized by phosphidating commercially available supported noble metal catalysts in red phosphorous vapor at different temperatures. We demonstrate that the derived PdP2-Pd/C heterostructured catalysts show the best electrocatalytic performance toward a number of OMEO model reactions including formic acid oxidation reaction (FAOR), methanol oxidation reaction (MOR), ethanol oxidation reaction (EOR), and ethylene glycol oxidation reaction (EGOR), in terms of not only apparent activity, but also of specific and mass activities, poisoning tolerance and catalytic stability, with respect to both the starting Pd/C and other prepared palladium phosphide control catalysts. Similar performance enhancement is also observed for the PtP2-Pt/C heterostructured catalysts for all model reactions. The enhancement may result from the synergy between noble metal phosphide and noble metal, where the formed phosphide facilitates the adsorption of hydroxyl species and promotes the oxidation of poisoning intermediates giving rise to improved activity, poisoning tolerance and stability. Our work demonstrates an easy way of boosting the electrocatalytic performance of commercial catalysts toward multiple OMEO reactions and shows substantial promise for their usage in direct liquid fuel cells.

**KEYWORDS:** *noble metal phosphide; organic molecule electro-oxidation; multifunctionality; facile catalyst synthesis; fuel cell catalyst*.

**INTRODUCTION**

The increasing global demand for sustainable energy and the aggravation of environmental problems have sparked extensive research interest in novel, efficient and fossil-fuel-free energy systems, such as fuel cells that can directly convert chemical energy into electricity. Fuel cells can be used as both primary and backup power in a number of applications including fuel cell vehicles and are expected to play a key role in the current transition to a sustainable economy.1-2 Among many types of fuel cells developed so far, the proton-exchange membrane fuel cell (PEMFC), which uses hydrogen as a fuel during its operation, is the most popular one.3 However, the storage and transport of hydrogen along with the safety issues have been serious concerns for large-scale commercialization. Compared to PEMFC, direct liquid fuel cells (DLFCs) such as direct alcohol fuel cell (DAFC)4-8 and direct formic acid fuel cell (DFAFC)9-10 using small molecules as a fuel (e.g. methanol,6 ethanol,7 ethylene glycol8 or formic acid9-10), offer a number of advantages including higher energy density, ease of storage and transport, and better safety.

Two half reactions usually occur in DLFCs, namely, the small organic molecule electro-oxidation (OMEO) at the anode, and the oxygen reduction at the cathode. To improve the cell efficiency and expedite the reaction kinetics, usage of electrocatalysts to promote the OMEO is in general indispensable. Platinum (Pt) and palladium (Pd) are by far the most commonly used anode electrocatalysts in DLFCs fed with low molecular weight alcohols.11-14 However, the high price and low earth abundance of noble metal Pt and Pd impose a grand challenge for market penetration of DLFCs.5, 11 In addition, the partially oxidized intermediates during the OMEO such as carbon monoxide (CO), even at ppm level, are known to be able to poison noble metal catalysts, causing gradual performance degradation and eventually a failure.15-16 Thus, considerable research effort has been dedicated to engineering the microstructure and composition of catalysts to improve the catalytic performance and lifetime toward the OMEO.5, 12, 17-19 For example, many researches were focused on improved dispersion of Pt or Pd nanoparticles on a better catalyst support20-21 and development of Pt- or Pd-based alloy catalysts such as noble metal alloys,22-24 noble metal – transition metal alloys,25,26 noble metal – oxide composites,27,28 and noble metal compounds (e.g. PtP, PdP2).29-32 Among them, the noble metal phosphides is characterized with improved mass activity,29-30 enhanced corrosion resistance and poisoning tolerance,31-33 which has drawn significant research interest. Despite some recent progress, most noble metal based OMEO catalysts only demonstrate good catalytic performance for one specific reaction, such as formic acid oxidation reaction (FAOR),25, 33 methanol oxidation reaction (MOR),20, 22, 23, 25, 28, 29, 31 ethanol oxidation reaction (EOR)21, 25-28, 32 and ethylene glycol oxidation reaction (EGOR),24, 25, 28, 30 and the potential for using one catalyst to promote multiple OMEO reactions, though desired, has been rarely explored by far.

Herein, we report facile synthesis of palladium phosphide electrocatalysts with different microstructures and compositions (i.e. PdP2/C, PdP2-Pd/C and Pd5P2-Pd/C) by one-step phosphidation of commercially available Pd/C catalysts at different temperatures. Compared to the commercial Pd/C catalysts, the best-performing PdP2-Pd/C catalysts show markedly enhanced electrocatalytic performance toward all OMEO reactions including the FAOR, MOR, EOR and EGOR, in terms of not only the apparent activity, but also poisoning tolerance, mass activity, specific activity, and catalytic stability. Furthermore, we demonstrate that one-step phosphidation of commercial Pt/C catalysts enables the formation of platinum phosphide catalysts (i.e. PtP2/C and PtP2-Pt/C), which enhance the electrocatalytic performance for the OMEO as well.

**EXPERIMENTAL SECTION**

**Materials Synthesis.** The PdP2/C, PdP2-Pd/C and Pd5P2-Pd/C catalysts were prepared by directly phosphorizing commercial Pd/C powders (20 wt% Pd, FuelCellStore, product code: 3151611) at 430, 500 and 700 oC, respectively, using red P as the source of phosphorus.32 Similarly, PtP2/C and PtP2-Pt/C catalysts were synthesized by phosphorizing commercial Pt/C powders (30 wt% Pt, FuelCellStore, product code: 591378) at 500 and 700 oC, respectively, in the red P vapor. Firstly, 20 mg commercial Pd/C or Pt/C was placed in a ceramic boat, while 200 mg of red P was loaded 2 cm away from the catalysts at the upstream side. Then, the boat was transferred into a tube furnace, with high-purity N2 (99.999 %) purged at a flow rate of 800 SCCM for 1 h before heating. The furnace was subsequently ramped to a given temperature at a rate of 10 oC min-1, held at this temperature for 2 h, and then cooled down naturally to room temperature. A constant N2 flow was maintained throughout the whole process.

**Materials characterization.** X-ray diffractometry (XRD) experiments were conducted on an X’Pert PRO diffractometer (PANalytical) set at 45 kV and 40 mA, using Cu *K*α radiation (λ = 1.541874 Å) and a PIXcel detector. Data were collected with the Bragg–Brentano configuration in the 2θ range of 20 – 100o at a scan speed of 0.011o s-1. X-ray photoelectron spectroscopy (XPS) characterization was carried out on an ESCALAB 250 instrument with Al *K*α X-rays (1486.6 eV). Scanning electron microscopy (SEM) examination was performed on a FEI Quanta 650 FEG microscope equipped with INCA 350 spectrometer (Oxford Instruments) for energy-dispersive X-ray spectroscopy (EDX) analysis. Transmission electron microscopy (TEM) and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) investigations were conducted on a probe-corrected transmission electron microscope FEI ChemiSTEM 80-200 operated at 200 kV.

**Electrochemical measurements.** All the electrochemical tests were performed in a three-electrode system at room temperature using a Biologic VMP-3 potentiostat/galvanostat. A glass carbon (GC) was utilized as the working electrode, while a saturated calomel electrode (SCE) and a graphite rod were used as reference and the counter electrodes, respectively. Prior to each measurement, the SCE reference electrode was calibrated in Ar/H2-saturated 0.5 M H2SO4 solution using a clean Pt wire as the working electrode. A 5 mg of catalysts and 50 μL of Nafion® solution (Sigma, 5 wt%) were dispersed into 950 μL of ethanol. Subsequently, 20 μL of ink was loaded onto the polished glassy carbon (GC) electrode with an exposed area of 0.78 cm2, resulting in a loading density is 0.128 mg cm-2.

The electrocatalytic OMEO were tested using cyclic voltammetry (CV) at a scan rate of 20 mV s-1. The chronoamperometry (CA) measurements were conducted at 0.2 and 0.6 V *vs.* SCE in 1.0 M HClO4 + 0.5 M HCOOH and 0.1 M HClO4 + 0.5 M CH3OH, respectively, in order to evaluate the catalytic stability of the FAOR and MOR in acidic electrolyte (denoted as FAOR-H and MOR-H, respectively). Meanwhile, the catalytic durability of MOR, EOR, and EGOR in alkaline electrolyte (denoted as MOR-OH, EOR-OH and EGOR-OH, respectively) were tested at −0.3 V *vs.* SCE using CA in 1.0 M KOH + 0.5 M CH3OH, 1.0 M KOH + 0.5 M CH3CH2OH and 1.0 M KOH + 0.5 M EG, respectively.

The electrochemical surface areas (ECSAs) of Pd-based electrocatalysts were calculated based on the integrated charges in the reduction region of PdO in N2-purged 0.1 M HClO4, 1.0 M HClO4 or 1.0 M KOH solution using the following equation, in which the value of the charge density of the reduction of a PdO monolayer on the catalyst surface is assumed to be C0 = 405 µC cm-2 according to previous report:32

ECSA = Q / mmetalC0 (1)

The ECSA of Pt-based electrocatalysts was computed using the same formula by integrating the charge associated with H desorption in N2-purged 0.1 M HClO4, 1.0 M HClO4 or 1.0 M KOH solution in the range of the hydrogen adsorption–desorption (QH) regions, in which the value of the charge density related to a monolayer of hydrogen adsorbed on platinum is assigned to be C0 = 210 µC cm-2.35, 36

In equation (1), Q represents the integral charge in the reduction region of PdO or the charge associated with H desorption of Pt, and mmetal stands for the mass of Pd or Pt loaded on the electrode surface.

**RESULTS AND DISCUSSION**

According to the P-Pd37 and P-Pt38 phase diagrams, Pd and Pt are easy to react with P forming phosphide even in the presence of a small amount of phosphorus (e.g. 20 – 30 at%) at comparatively low temperatures.37 Moreover, the stoichiometry of the formed phosphide is dependent on the ratio of metal and P fed for the reaction. Our XRD examination revealed that by changing the phosphidation temperature, palladium phosphide with different phase structures can be obtained. For example, for the sample phosphorized at 430 °C (i.e. PdP2/C), diffraction peaks exclusively from the PdP2 phase (ICDD No. 04-007-1929) were observed and those from metallic Pd disappeared (**Figure 1a**), indicating that Pd was completely converted into PdP2. As the temperature was increased to 500 °C, diffractions from both PdP2 and metallic Pd (as evidenced by the broadened bump centered at 40.1°) were visible, with PdP2 as the dominant phase (denoted as PdP2-Pd/C). The co-existence of PdP2 and Pd suggests that Pd is partially phosphorized into PdP2, which was corroborated by our HAADF-STEM imaging and XPS study, as will be discussed below. Further increasing the phosphidation temperature to 700 °C resulted in the formation of mixed phases of Pd5P2 (ICDD No. 00-019-0887) and Pd (denoted as Pd5P2-Pd/C), characterized by a broad diffraction peak in the range of 35.3 – 46.1°. We believe that the temperature-dependent phase composition evolution results from the amount of P vapor available to react with Pd nanoparticles. At high temperatures, phosphorus has a high vapor pressure and the generated P vapor would be rapidly carried away by the N2 gas flow, such that Pd cannot be completely phosphorized and the formed phosphide is Pd-rich. While at comparatively low temperatures, the generated P vapor would have a longer dwelling time due to the low vapor pressure, and therefore more P is available to react with Pd forming a P-rich PdP2 phase and enabling complete conversion of Pd into phosphide. This is consistent with the phase distribution in the P-Pd phase diagram.37



**Figure 1.** (a) XRD patterns of commercial Pd/C, the obtained PdP2/C, PdP2-Pd/C and Pd5P2-Pd/C catalysts. HAADF-STEM images of (b) commercial Pd/C, (c) PdP2/C, (d) PdP2-Pd/C and (e) Pd5P2-Pd/C. Insets of (b-e): histograms showing the nanoparticle size distribution.

The obtained palladium phosphide catalysts were characterized by SEM, and their morphology was found to be very similar to that of the commercial Pd/C starting materials (**Figure S1**). Furthermore, the dispersion of palladium phosphide nanoparticles on carbon support was investigated by HAADF-STEM imaging. The average catalyst particle size of Pd/C is ca. 3.5 nm (**Figure 1b**), and the size was increased upon the phosphidation, being 4.5 nm for PdP2/C (**Figure 1c**), 5.0 nm for PdP2-Pd/C (**Figure 1d**) and 8.0 nm for Pd5P2-Pd/C (**Figure 1e**).

The atomic structure of the palladium phosphide nanoparticles and the Pd/C control sample was further investigated by STEM in the HAADF mode. Lattice fringes with an inter-planar spacing of 0.224 nm can be resolved for commercial Pd/C (**Figure 2a**), corresponding to the lattice distance of Pd (111) crystal planes. For PdP2/C, the inter-planar spacings of 0.206 and 0.288 nm correspond to the lattice distances of PdP2 (220) and (200) crystal planes (**Figure 2b**), respectively. Moreover, the measured angle between these two planes (44.5°) is in good agreement with that calculated based on the monoclinic PdP2 structure, corroborating the formation of PdP2 phase. EDX mapping confirmed that both Pd and P are uniformly distributed over a single nanoparticle (**Figure S2a**), and no obvious segregation was observed. For the PdP2-Pd/C obtained upon phosphidation at 500 °C, the lattice fringes from both PdP2 and metallic Pd can be resolved (**Figure 2c**). EDX mapping revealed that the intensity of P is attenuated and the distribution of P does not completely overlap with that of Pd (**Figure S2b**), suggesting the partial phosphidation. Similar heterostructure and elemental distribution were also observed in Pd5P2-Pd/C (**Figures 2d** and **S2c**), but the intensity of P signal in this sample was even lower.



**Figure 2.** HAADF-STEM images of (a) commercial Pd/C, (b) PdP2/C, (c) PdP2-Pd/C and (d) Pd5P2-Pd/C catalysts.

The surface composition and electronic structure of PdP2/C, PdP2-Pd/C and Pd5P2-Pd/C were further studied by XPS and compared to those of commercial Pd/C control catalysts. The XPS survey spectra confirm the presence of corresponding elements in each catalyst (**Figure S3**). **Figure 3** shows Pd 3d XPS spectra of all samples where two components assigned to Pd 3d5/2 and Pd 3d3/2 can be resolved. For commercial Pd/C, four binding energy (BE) peaks can be deconvoluted (**Figure 3a**): the ones appearing at 335.6 and 340.8 eV can be assigned to Pd0 and those at 336.9 and 342.3 eV to the Pd−O bonding, which arises from surface oxidation of Pd/C. Upon phosphidation at 430 °C, the BE peaks from both Pd0 and Pd−O disappeared, and new peaks at 337.5 and 342.8 eV, characteristic of Pd2+ in palladium phosphide,39 appeared (**Figure 3b**), indicating complete phosphidation of Pd.32 For PdP2-Pd/C, in addition to the Pd−P characteristic peaks, the BE peaks that can be assigned to Pd0 were also observed (**Figure 3c**), implying the partial phosphidation at 500 oC. Furthermore, for Pd5P2-Pd/C obtained at 700 oC, we found the components from both Pd0 and Pd−P (**Figure 3d**). However, the binding energy peaks from Pd−P show lower intensity compared to those from Pd0 and a red shift with respect to the peaks of PdP2 (**Figure 3d**), which suggest that the degree of phosphating in this sample is low and the oxidation state of Pd should be below 2+. This agrees well with the identification of the Pd5P2-Pd structure, as revealed by our XRD and TEM results discussed above.



**Figure 3.** High resolution Pd 3d XPS spectra of (a) commercial Pd/C, (b) PdP2/C, (c) PdP2-Pd/C and (d) Pd5P2-Pd/C catalysts.

In addition, in the P 2p spectra of all palladium phosphide catalysts (**Figure S4**), there are two BE peaks located at 129.7 and 130.6 eV, which can be assigned to the 2p3/2 and 2p1/2 core levels of P atoms, characteristic of metal phosphides.40 Another peak appearing at 133.4 eV is assigned to the oxidized phosphorus species resulting from the oxidation upon contact with air.34, 41 It is interesting to note that the intensity ratio of Pd−P characteristic peaks over phosphate characteristic peaks decreases in the following order: PdP2/C > PdP2-Pd/C > Pd5P2-Pd/C, implying that the phosphidation degree decreases as the phosphidation temperature increases, which agrees with the XRD and TEM data as well as the XPS Pd 3d spectra.

The OMEO electrocatalytic activities of commercial Pd/C, PdP2/C, PdP2-Pd/C and Pd5P2-Pd/C were investigated toward several model reactions including FAOR-H, MOR-H, MOR-OH, EOR-OH and EGOR-OH. **Figure 4a** displays the CV curves of the catalysts for FAOR-H in 0.5 M HCOOH + 1.0 M HClO4. The apparent activities of PdP2-Pd/C is 5.56 mA cmgeo-2 at 0.24 V *vs* SCE, markedly outperforming Pd5P2-Pd/C (4.35 mA cmgeo-2), PdP2/C (3.06 mA cmgeo-2) and commercial Pd/C (1.94 mA cmgeo-2) at the same potential. For MOR-H, the PdP2-Pd/C catalyst delivers an apparent current density of 2.28 mA cmgeo-2 at 0.6 V *vs* SCE (**Figure** **4b**), 1.4, 2.2, 1.9 times that of the Pd5P2-Pd/C, PdP2/C and commercial Pd/C, respectively. For OMEO taking place in alkaline solution, PdP2-Pd/C can deliver geometric current densities of 31.7, 62.1, 68.8 mA cmgeo-2 at −0.25 V *vs* SCE, for the MOR-OH, EOR-OH and EGOR-OH, respectively, substantially higher than those of Pd5P2-Pd/C (26.2, 61.9 and 55.3 mA cmgeo-2), PdP2/C (9.6, 41.6 and 49.7 mA cmgeo-2) and commercial Pd/C reference catalysts (15.9, 50.7 and 43.8 mA cmgeo-2) tested under the same conditions.



**Figure 4.** Electrocatalytic performance of commercial Pd/C, PdP2/C, PdP2-Pd/C and Pd5P2-Pd/C catalysts. (a) FAOR-H recorded in 0.5 M HCOOH + 1.0 M HClO4. (b) MOR-H recorded in 0.5 M CH3OH + 0.1 M HClO4. (c) MOR-OH recorded in 1.0 M CH3OH + 1.0 M KOH. (d) EOR-OH recorded in 1.0 M CH3CH2OH + 1.0 M KOH. (e) EGOR-OH recorded in 1.0 M EG + 1.0 M KOH. All CV curves were recorded at 20 mV s-1.

To assess the intrinsic catalytic performance, the ECSA-normalized specific activities of PdP2-Pd/C and other control catalysts, which reflect the reactivity of each active site, were calculated and compared. The ECSAs were calculated by CV measurements in the acidic/alkaline electrolyte used for each model reaction (see Experimental section and **Figure S5**). PdP2-Pd/C exhibits highest ECSA with respect to that of other control catalysts in all three electrolytes used (i.e., 1.0 M HClO4, 0.1 M HClO4 and 1.0 M KOH), suggesting that the introduction of P is conducive to the exposure of more catalytically active sites. Nevertheless, after normalization PdP2-Pd/C still shows highest specific activity, followed by Pd5P2-Pd/C, PdP2/C and commercial Pd/C for all the reactions (**Figure S6**), indicating that PdP2-Pd/C is intrinsically more active than all other control catalysts.

The mass activities of all catalysts, which is an important consideration from cost perspective for practical applications, were also calculated and compared in **Figure** **S7**. All palladium phosphide catalysts show enhanced mass activities higher than that of the starting Pd/C catalysts, following the order of PdP2-Pd/C > Pd5P2-Pd/C > PdP2/C > Pd/C. This illustrates that the introduction of phosphorus into Pd markedly improves the degree of utilization of noble metal Pd.

According to the above discussion, the PdP2-Pd/C, obtained by phosphidation of Pd/C at 500 °C, exhibits the best electrocatalytic performance in terms of apparent, mass and specific activities. We believe that the ensemble effect might be essential for PdP2-Pd/C to achieve enhanced catalytic performance. It is known that the \*CO is an intermediate that is generally produced during the oxidation of formic acid and C1/C2 alcohols,11-12 which would cause serious degradation in the activity and lifetime of electrocatalysts. For our PdP2-Pd/C catalysts, we hypothesize that the presence of phosphorus may facilitate the adsorption of hydroxyl species at low potentials,33 as described in the following equations:

PdP2 + OH− → PdP2−OH + e− in alkaline solution (2)

PdP2 + H2O → PdP2−OH + H+ + e− in acidic solution (3)

The absorbed hydroxyl species would then oxidize the poisoning \*CO intermediate absorbed on active Pd sites as described in equations 4 – 5, in a way similar to the bifunctional mechanism reported for Pt-Ru catalysts toward the MOR.5, 15

2PdP2−OH + Pd−COad → 2PdP2 + Pd\* + CO2 ↑ + H2O + 2e− (4)

PdP2−OH + Pd−COad → PdP2 + Pd\* + CO2 ↑ + H+ + e−  (5)

In this case, the poisoning tolerance would also be enhanced, and this was indeed observed for PdP2-Pd/C toward all reactions under investigation with respect to the Pd/C catalysts (**Table S1**).



**Figure 5.** Stability of commercial Pd/C, PdP2/C, PdP2-Pd/C and Pd5P2-Pd/C catalysts. Chronoamperometric curves measured in (a) 0.5 M HCOOH + 1.0 M HClO4 solution at 0.2 V *vs* SCE. (b) 0.5 M CH3OH + 0.1 M HClO4 solution at 0.6 V *vs* SCE. (c) 1.0 M CH3OH + 1.0 M KOH, (d) 1.0 M CH3CH2OH + 1.0 M KOH, (e) 1.0 M EG + 1.0 M KOH solution at −0.3 V *vs* SCE.

Stability is a critically important indicator of electrocatalysts for practical applications in DLFCs. We have examined the catalytic stability of all catalysts for each model reaction using CA. As shown in **Figure 5**, PdP2-Pd/C turns out to be the best-performing electrocatalyst, although all of the catalysts show a decreased activity over time, which were commonly observed in nearly all previously reported Pd-based electrocatalysts.5, 12, 17, 32-33 The enhanced stability of PdP2-Pd/C catalysts could result from improved poisoning tolerance. Besides, metal phosphides might activate water and be prone to adsorbing −OHads species, which may oxidize the poisoning intermediates around the active sites, thereby prolonging the life of the catalysts.33 The enhanced activity and stability will be beneficial for future practical applications in DLFCs.

In addition to palladium phosphide, we demonstrated that the simple one-step phosphidation treatment can also be extended to synthesize supported platinum phosphide catalysts (e.g. PtP2/C and PtP2-Pt/C) using commercially available Pt/C as the starting materials. The XRD and XPS results confirmed the formation of PtP2/C and PtP2-Pt/C at different phosphidation temperatures, as illustrated in **Figures S8–9**. Furthermore, we proved that upon phosphidation treatment, the electrocatalytic performance of obtained PtP2-Pt/C catalysts showed obvious enhancement in terms of not only the apparent activity, but also specific and mass activities as well as poisoning tolerance (**Table S1**), for almost all model reactions (**Figures S10-12**), similar to the results we obtained for palladium phosphide catalysts, which highlights that phosphidation is an effective and generic strategy for improving the catalytic OMEO performance of commercial noble metal catalysts.

**CONCLUSION**

In summary, we demonstrate that a simple phosphidation treatment at different temperatures may convert commercial noble metal nanoparticles into metal phosphide or phosphide-metal heterostructures. Typically, the PdP2-Pd/C catalysts obtained by phosphidating commercial Pd/C at 500 °C show markedly improved electrocatalytic performance toward a number of small organic molecule electro-oxidation reactions, in terms of not only apparent catalytic activity, but also of specific and mass activities, poisoning tolerance and catalytic stability, showing preferable multifunctionalities. The enhanced performance likely results from the synergy between PdP2 and Pd, in which PdP2 facilitates the adsorption of hydroxyl species, promoting the oxidation of the poisonous \*CO intermediates leading to improved activity and durability. We also demonstrate applicability of the one-step phosphidation to synthesizing multifunctional platinum phosphide catalysts. Our study provides a new, simple and potentially cost-effective approach to improving electrocatalytic performance of commercial catalysts for use in direct liquid fuel cells.

**ASSOCIATED CONTENT**

**Supporting Information**. The Supporting Information is available free of charge at <https://pubs.acs.org/doi/>.

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**Notes**

The authors declare no competing financial interest.

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