



# Facile synthesis of a ternary Pd-P-B nanoalloy: Enhanced catalytic performance towards ethylene glycol electrooxidation



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## ABSTRACT

In this study, a carbon-supported Pd-P-B ternary catalyst (Pd-P-B/C) for ethylene glycol electrooxidation is prepared via a simple aqueous solution phase synthesis. Physical characterization reveals that phosphorus (P) and boron (B) atoms could modify the crystal structure of palladium (Pd) and lead to strong electronic interaction among P, B and Pd. Electrochemical results indicate that the Pd-P-B/C catalyst presents larger electrochemically active surface area, higher electrocatalytic activity and better stability compared to Pd/C and Pd-P/C. This may strongly depend on unique electronic and synergistic effects involved in this ternary nanoalloy. All results demonstrate that incorporating nonmetal P and B holds great promise to improve the performance of Pd in direct alcohol fuel cells.

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## 1. Introduction

Palladium (Pd) and Pd-based electrocatalysts have continued to be a subject of intense research interest for application in direct alkaline alcohol fuel cells [1–3]. This owes to their lower cost and better performance compared to platinum (Pt)-based catalysts [4,5]. However, the activity and stability of Pd catalysts need to be further improved. Alloying Pd with less expensive elements is an effective strategy for improving the electrocatalytic activity and CO tolerance, mainly due to the synergistic effects and rich diversity among different Pd components [6]. A series of Pd-based alloy catalysts, such as PdCo [7], PdSn [3], PdAg [8] and Pd<sub>2</sub>NiAg [9], have been reported to exhibit higher catalytic activity and stability for alcohol electrooxidation than commercial Pd. Among them, most of the promoter components are metal element, only few reports are related to the composite catalysts of Pd and nonmetal element [10,11].

Nevertheless, nonmetal could promote the electrocatalytic activity of the primary metal by modifying its electronic structure and geometric property [11,12]. Phosphorus (P), an inexpensive nonmetal element in the same group as nitrogen, bears abundant valence electrons, which could affect the electronic states of metal

elements to generate a significant effect on catalytic performance [13]. Back in 2006, Zhang et al. reported a Pd-P/C catalyst towards formic acid electrooxidation for the first time. The results proved that the electrocatalytic activity and stability of the Pd-P/C catalyst are much higher than that of Pd/C [14]. Since then, more studies have been focused on incorporating P into Pd or Pt based alloys [15–17]. Specially, in 2014, Chang et al. demonstrated that Ni<sub>2</sub>P can act as a stable cocatalyst in the Pd-Ni<sub>2</sub>P/C, and it showed remarkable catalytic performance for Pd-catalyzed formic acid oxidation [18]. These researches are very significant towards developing Pd-P system catalysts for fuel cells.

Meanwhile, boron (B) is also a nonmetal element widely used for modifying the physicochemical properties of metal elements [19,20]. In addition, B atom is much smaller than Pd atom, which may incorporate into Pd-Pd lattice spaces rather than substitute Pd atoms [21]. Simultaneously, different from P, B usually serves as an electron donor, leading to further shrink the size of B atoms, favoring their doping in the interstice of the Pd lattice [22]. As B donates electrons to Pd, P accepts electrons from Pd, it is expected that electronic interaction is existed between Pd, P and B. Therefore, incorporating nonmetal B into Pd-P system is supposed to exhibit more flexibility in tuning the geometric and electronic properties of Pd surfaces, which would make a positive impact on catalytic performance of Pd-P system catalysts. Nevertheless, there are still no reports about doping binary nonmetal elements into Pd-based electrocatalysts.

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In this study, to improve the performance of Pd-P system catalysts, P and B were co-doped. Herein, a carbon-supported Pd-P-B ternary catalyst (Pd-P-B/C) was prepared, and its electrocatalytic performance towards ethylene glycol oxidation reaction (EGOR) was investigated. Compared to Pd/C and Pd-P/C catalysts, the Pd-P-B/C catalyst shows higher catalytic activity and better stability due to the unique electronic and synergistic effects.

## 2. Experimental

### 2.1. Preparation of catalysts

The ternary catalyst Pd-P-B/C was prepared via an aqueous solution phase synthesis, similar to literature reported [12]. Specifically,  $C_6H_5Na_3O_7 \cdot 2H_2O$  (138.2 mg) and  $PdCl_2$  (41.7 mg) were mixed into 30 mL ultrapure water and stirred for 0.5 h. After the pH was adjusted to 8 using NaOH (5%), carbon black (Vulcan XC-72R, 100.0 mg) was added, then, stirring and sonicating for 0.5 h, respectively. Afterwards, 10 mL  $NaH_2PO_2$  (contains 103.4 mg) and 10 mL  $KBH_4$  (contains 63.4 mg) solution were slowly dropped into the slurry under vigorous stirring, respectively. After being continuously stirred at 80 °C for 4 h, the suspension was filtered, washed with ultrapure water and dried for 6 h at 50 °C. Finally, the Pd-P-B/C (14.36 wt.% Pd loading) catalyst was obtained. Pd-P/C (15.49 wt.% Pd loading) catalyst was also prepared in the same procedure except that  $KBH_4$  was absent.

Pd/C catalyst was prepared by a traditional polyol method. Firstly, 41.7 mg  $PdCl_2$  was dispersed into 30 mL ethylene glycol (EG) by ultrasonication. Then,  $C_6H_5Na_3O_7 \cdot 2H_2O$  (138.2 mg) was mixed and stirred for 1 h. After the pH was adjusted to 8 using 5% KOH/EG, the carbon black (100.0 mg) was added, stirring and sonicating for 0.5 h, respectively. Subsequently, the suspension was reacted for 4 h at 180 °C in  $N_2$  atmosphere, then centrifuged, washed with ultrapure water and dried at 50 °C for 6 h. Finally, the Pd/C (20 wt.% Pd loading) catalyst was obtained.

### 2.2. Characterization

X-ray diffraction (XRD) patterns were recorded on a diffractometer (Rigaku D/Max-2400, Japan), using  $Cu K\alpha$  radiation operated at 40 kV and 150 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed on a monochromatic Al  $K\alpha$  X-ray source ( $h\nu = 29.35$  eV, Thi-5702, America). Transmission electron microscopy (TEM) measurements were collected on an electron microscope (FEI TECNAI  $G^2$  TF20, America) using Cu grids as substrate. Samples for TEM were prepared by dispersing the catalysts in ethanol, sonicating for 30 min to ensure adequate dispersion. It was then mounted onto copper grids and left to dry in air. Energy dispersive X-ray spectroscopy (EDX) and elemental mapping were observed by scanning electron microscopy (SEM, Carl Zeiss Ultra Plus, Germany).

All electrochemical measurements were tested on a CHI 760E electrochemistry workstation with a conventional three-electrode system (working electrode: glassy carbon electrode with a diameter of 5 mm, reference electrode: an Ag/AgCl electrode, and counter electrode: Pt sheet with a size of  $10 \times 10 \times 0.3$  mm). The working electrode was prepared as follows: 5.0 mg catalyst was dispersed ultrasonically in 1 mL Nafion/ethanol (0.25% Nafion). Then, 8  $\mu$ L catalyst ink was transferred onto the surface of glassy carbon electrode and allowed to dry at room temperature. Before each measurement, the solution was purged with Ar gas for 20 min to ensure gas saturated. All potentials mentioned in this work were measured against Ag/AgCl, and normalized with respect to RHE in the results. All currents were normalized to Pd mass on the electrodes.

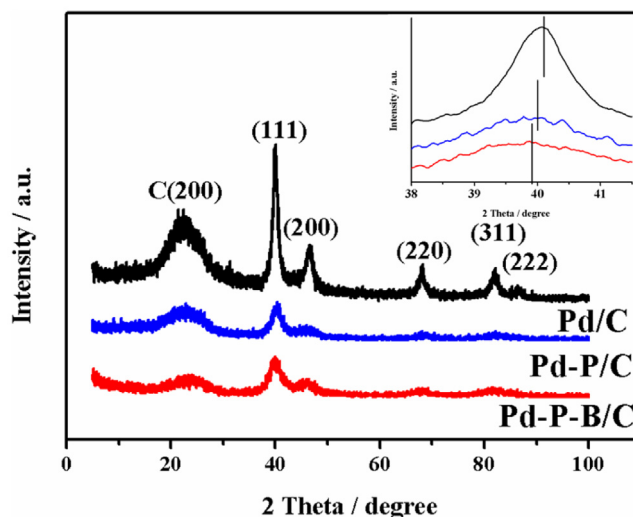


Fig. 1. XRD patterns of Pd/C, Pd-P/C and Pd-P-B/C catalysts. Inserted: enlarged Pd (111) peaks of the corresponding catalysts.

Table 1

Physical characteristic of Pd/C, Pd-P/C and Pd-P-B/C catalysts.

Physical Characteristic	Pd/C	Pd-P/C	Pd-P-B/C
Pd (111) at $2\theta$ (°)	39.98	39.88	39.79
Crystallite size (nm)	8.2	3.4	2.9
$d_{(111)}$ (Å)	2.253	2.259	2.264
Lattice parameter (Å)	3.903	3.912	3.921
Particle size by TEM (nm)	8.7	–	3.5
Pd content by EDX (wt.%)	20.62	15.61	14.38

## 3. Results and discussion

### 3.1. Physical characterization

XRD is applied to examine the alloying effect of P and B on the Pd lattice [23]. The first peaks at 24.8° for all catalysts and support are associated with the graphite (200) plane of carbon support shown in Figs. 1 and S1. For Pd/C catalyst, the typical diffraction peaks at 40.0°, 46.4°, 68.2°, 81.8° and 86.4° correspond to the (111), (200), (220), (311) and (222) planes of Pd face-centered cubic (fcc) crystalline structure, respectively. Compared to Pd/C, the (111) planes become broader in Pd-P/C and Pd-P-B/C, which suggests that the obtained catalysts develop a more amorphous structure after doping P or B [11]. Meanwhile, the inserted figure shows the enlarged Pd (111) peak of the catalysts. Apparently, the (111) peak position of Pd-P/C and Pd-P-B/C shifts to a slightly lower  $2\theta$  degree in comparison with Pd/C, which is mainly due to the incorporation of P and B atoms into the Pd fcc crystal lattice at the atomic level, leading to the formation of Pd-P-B alloys [24]. In addition, the generation of cell-strains typical of nanoparticles would also lead to this phenomenon [25,26]. Moreover, the crystallite sizes and lattice parameters of the as-prepared catalysts are calculated from Pd (111) peak using Scherrer formula and Bragg equation [27,28] (listed in Table 1). It can be clearly seen that the average crystallite sizes are 8.2 nm, 3.4 nm and 2.9 nm for Pd/C, Pd-P/C and Pd-P-B/C, respectively. In addition, the lattice parameters of Pd (fcc) crystal decrease in the order: Pd-P-B/C > Pd-P/C > Pd/C, which indicates that the Pd lattice structure expands after doping P and B atoms [12].

The surface morphology and structural feature of the prepared Pd/C and Pd-P-B/C catalysts are examined by TEM. Fig. 2a and b show successful dispersion of Pd and Pd-P-B nanoparticles onto the surface of carbon support (the black is nanoparticles and the gray area is carbon support). It can be seen that the Pd nanoparticles dis-

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