Facile Aqueous Phase Synthesis of Pd$_3$Cu-B/C Nanocatalyst for Glucose Electrooxidation

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Abstract. A novel Pd$_3$Cu-B/C nanocatalyst was facilely synthesized through an aqueous phase process. And it was developed for use in the glucose electrooxidation reaction in fuel cells. Cyclic voltammetry shown that the electrochemical surface area of Pd$_3$Cu-B/C is 2.25 times that of Pd/C. Glucose electrooxidation curves revealed that peak current on the Pd$_3$Cu-B/C is actually 1.73 times of the Pd/C. This high performance of Pd$_3$Cu-B/C could be ascribed to the synergistic effect between Pd, Cu and B.

Keywords: Pd-based catalysts; B-doped; Glucose electrooxidation; Fuel cells.

1. Introduction
Glucose is inexpensive, abundantly available and can be easily extracted in biomass [1, 2]. Based on these merits, electrochemical oxidation of glucose has been extensively investigated with regard to its promising application in direct fuel cells and sensors [3-5]. In alkaline media, Pd/C catalyst has been paid much attention because of its effective electroactivity towards anode oxidation [6]. However, in addition to its high cost and rare reserves, monometallic Pd/C catalyst also suffers from insufficient activity and stability in practical fuel cells [7].

It is reported that alloying Pd with other transition metal elements exhibit better electrocatalytic activity than pure Pd, because of the synergetic contributions of each component [8]. Meanwhile, nonmetals also can enhance the performance of Pd by adjusting its morphology and electronic properties [9, 10]. However, there are still no works to realize the high electrochemical performance of glucose electrooxidation by simultaneously incorporating transition metal and nonmetal.

Therefore, in this work, we have initially made such an effort to obtain a desired Pd$_3$Cu-B/C nanocatalyst toward electrochemical oxidation of glucose in alkaline condition. The as-prepared Pd$_3$Cu-B/C catalyst exhibits high catalytic activity and stability for glucose electrooxidation. All results prove a great potential of Pd$_3$Cu-B/C for future application in glucose fuel cells.

2. Experimental Section
2.1. Preparation of Pd$_3$Cu-B/C and Pd/C Catalyst
The Pd$_3$Cu-B/C was prepared by aqueous solution-phase method [11]. The dimethylamine borane was used as a reducing agent. At first, 69.0 mg NH$_4$Cl, 137.9 mg HBO$_3$, 16.3 mg CuSO$_4$ and 34.8 mg PdCl$_2$ were dissolved in 20 mL of ultrapure water by sonicating. Then, the pH was adjusted to 8 by adding NH$_3$·H$_2$O. After that, 100.0 mg carbon black (Vulcan XC-72R) was added with stirring and ultrasonic dispersion for half an hour. Next, 10 mL of 0.1 M dimethylamine borane solution was added dropwise into the above slurry. The reduction was reacted for 2 h in an ice-water bath under N$_2$. 
After that, the suspension was further stirred at 30 °C for another 2 h. Then, the suspension was centrifuged and washed. Finally, the sample was dried at 50 °C for 6 h. The sample was thermally treated at 240 °C in N₂ atmosphere for 2 h. The catalyst obtained here was noted as Pd₃Cu-B/C.

For Pd/C catalyst, the rest procedures were the same as those for Pd₃Cu-B/C catalyst, besides the 10 mL of 0.1 M NaBH₄ aqueous solution as the reducing agent instead of dimethylamine borane.

3. Results and Discussion

The crystal structure of Pd₃Cu-B/C and Pd/C catalysts was determined by XRD, as shown in Fig. 1. The broad peaks at approximately 24.8° belong to graphite (200) planes of carbon support. Other diffraction peaks at 40.21°, 46.48°, 68.07°, 82.00° and 86.62° can be indexed to the facecentered cubic of Pd lattice about the (111), (200), (220), (311) and (222) reflection facets [1, 12-14].

![Figure 1. XRD patterns of Pd3Cu-B/C and Pd/C.](image)

The electrochemical behaviors of Pd₃Cu-B/C and Pd/C in 0.1M KOH solution were shown in Fig. 2. Pd₃Cu-B/C shows the higher peak current of PdO reduction about -0.5 V than that of Pd/C [15]. Additionally, the corresponding electrochemically active surface area (EASA) of the electrocatalysts was calculated from integration of the charge density (Q) during the reduction of PdO monolayer in the cathode scan [16]. According to Eq. (1):

\[
\text{EASA} = \frac{Q}{SI}
\]

\(Q\) is the columbic charge for the reduction of Pd oxide in mC; \(S\) is a proportionality constant used to relate charge with area; \(l\) is the catalyst loading in mg. Herein, the EASA of Pd₃Cu-B/C is calculated to be 259.1 cm² g⁻¹ Pd, which is much larger than that of Pd/C catalyst (115.2 cm² g⁻¹ Pd). The large EASA of Pd₃Cu-B/C which may be mainly attributed to the addition of Cu and B content, providing to more active sites.
Electrocatalytic activities of Pd$_3$Cu-B/C and Pd/C catalysts for glucose oxidation were studied in 0.1M KOH + 0.5 M glucose solution at a scan rate of 50 mV s$^{-1}$. As shown in Fig. 3, the maximum peak current is shown in the forward scan, which may due to the electrooxidation of glucose. Remarkably, the peak current of Pd$_3$Cu-B/C (0.105 A mg$^{-1}$Pd) is actually 1.73 times of the Pd/C (0.06 A mg$^{-1}$Pd). This high performance of Pd$_3$Cu-B/C could be ascribed to the synergistic effect between Pd, Cu$^+$ and B.

I-t experiments were performed in 0.1 M KOH + 0.5 M glucose to explore the stability of the two catalysts. In Fig. 4, during the whole 3600 s test, the Pd$_3$Cu-B/C shows a sustaining and much higher current than that of Pd/C, demonstrating significantly enhanced electrocatalytic stability of Pd$_3$Cu-B/C.
4. Conclusions
In conclusion, a novel Pd/Cu-B/C nanocatalyst was designed and synthesized through an aqueous phase process. The Pd<sub>3</sub>Cu-B/C exhibited significantly improved catalytic activity and stability, in comparison with Pd/C catalyst. These results suggest that the enhancement of electrocatalytic performance can be ascribed to the synergistic effect between Pd, Cu and B. This work provides an effective strategy to improve the electrocatalytic performance of Pd-based catalyst. And it is pregnant for future development of Pd<sub>3</sub>Cu-B/C catalyst in the application of direct glucose fuel cells.

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6. References
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