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Surface-clean PdB/C as superior electrocatalysts toward ethanol oxidation in alkaline media

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ABSTRACT

Developing highly active, low-cost and organic surfactants-free Pd-based catalysts for ethanol oxidation reaction (EOR) is now critically important for direct ethanol fuel cells. Herein, surface-clean PdB/C catalysts are successfully prepared in an aqueous condition without adding any organic surfactants. TEM characterization shows that as-prepared PdB nanoparticles are evenly distributed on carbon support. Cyclic voltammograms of as-prepared PdB/C in 0.5 M NaOH + 1 M C₂H₅OH indicate that its onset oxidation potential of ethanol is ca. 80–120 mV more negative than that on commercial Pd/C. Meanwhile, the EOR mass activity of our home-made catalysts is up to 4018 mA·mg⁻¹ Pd. Moreover, the durability on PdB/C catalysts is at most 2 times higher than that on commercial Pd/C. Geometric and electronic effects are adopted to understand the above mentioned enhancement of activity and durability. This work may provide a facile, low-cost and green strategy on preparing electrocatalysts toward EOR in alkaline media.

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1. Introduction

Recently, ethanol oxidation reaction (EOR) has attracted much attention because direct ethanol fuel cells (DEFCs) are considered as a promising power source for automobile and portable applications [1,2]. Specially, Pd has a comparable activity with Pt for ethanol oxidation reaction (EOR) in alkaline media [2,3] which may make Pd as an alternative to Pt [4,5]. To approach this goal, considerable efforts have been devoted to prepare Pd-based catalysts, including but not limited to Pd nanocrystals [6,7], Pd-metal oxide composites and Pd-based alloy [8–16]. Unfortunately, in these literatures, the complexity of synthetic strategy and post-treatment may limit their wide applications. Moreover, organic surfactants such as polyvinyl pyrrolidone (PVP), cetyltrimethyl ammonium bromide (CTAB), and oleylamine were commonly used as surface capping agents to control particle size and specific surface structure [2,17,18]. Nevertheless, these surface covering surfactants may lead to activity loss for structure-sensitivity reactions [19–22], although several post-treatments (such as UV-Ozone [22], basic bath rinse [23] and CO replacement [6]) have been proposed to solve this issue; a great challenge remains since these cleaning treatment could disrupt underlying surface structures, resulting in dis-

torted electrochemical responses [22,24,25]. Along this line, highly active, low-cost and organic surfactants-free Pd-based catalysts for EOR should be developed.

As for surfactant-free Pd nanoparticles, Burton et al. [26] produced a suspension of Pd nanoparticles using a slow reduction of Pd(OAc)₂ in MeOH, but the anhydrous conditions was quite critical and the aggregation of Pd nanoparticles cannot be effectively avoided. Hyotanishi et al. [27] first reported ca. 1.5-nm Pd nanoclusters synthesized by a N,N-dimethylformamide (DMF) reduction method, and the as-prepared Pd nanoclusters showed high catalytic activity in cross-coupling reactions. After that, Li et al. [28] realized a shape-controlled synthesis of Pd nanosheets by simply mixing a dinuclear Pd^I carbonyl chloride complex with H₂O in DMF. Recently, Wang et al. [29] also employed the DMF as solvent to prepared Vulcan XC-72-supported ultrafine Pd catalysts to electrooxidize ethanol and formic acid. Nevertheless, their precursor Pd(acac)₂ is too expensive. More importantly, DMF containing a free electron pair may also be strongly adsorbed on Pd nanoparticles and interact with surface Pd atoms, tuning the electronic structure of Pd so that the reaction pathway may be modulated. Similar catalytic modulation was observed by Bi et al. when they produced H₂ from formic acid on Au-based catalysts by adding triethylamine [30] or dimethylethanolamine [31] into the reaction solution. Thus, DMF-contained materials seem to lead to uncertainty for the surface-sensitive catalysis. To avoid this, Chen et al. [32] prepared “very clean” ultrafine Pd nanoparticles on graphene oxide (GO) surfaces in aqueous condition simply by the redox

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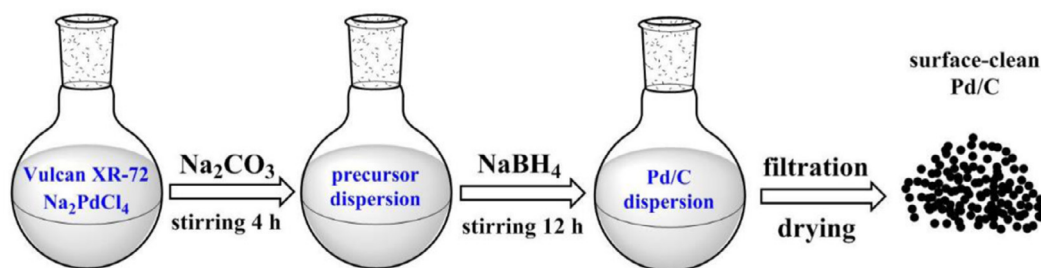


Fig. 1. Schematic illustration of the synthesized process of surface-clean Pd/C catalysts (no organic surfactants is added).

49 reaction between PdCl_4^{2-} and GO. The as-made catalyst expressed
 50 high electrocatalytic ability in formic acid and ethanol oxidation
 51 relative to a commercial Pd/C catalyst. Nevertheless, the durabil-
 52 ity should be improved owing to the aggregation of ultrafine Pd
 53 nanoparticles during the catalytic reactions.

54 In this work, considering above-mentioned issues, we adopted
 55 a facile, green and organic surfactant free routine to prepare
 56 surface-clean, high-dispersion Pd nanoparticles loaded on Vulcan
 57 XC-72. The structural and compositional properties, as well as the
 58 catalytic activity and stability of surface-clean Pd/C, were charac-
 59 terized and compared with a commercial Pd/C (Johnson Matthey)
 60 catalyst. The enhanced activity and durability for ethanol electro-
 61 oxidation in alkaline media was also briefly discussed.

62 2. Experimental

63 2.1. Catalysts' preparation and characterization

64 As shown in Fig. 1, surface-clean Pd/C catalysts were synthe-
 65 sized according to a modified protocol initially adopted by Zhang
 66 et al. [33] targeting for H_2 production from formic acid. In de-
 67 tail, 43 mg of Vulcan XC-72 and 2.23 mL of 45 mM Na_2PdCl_4 were
 68 added into 40 mL of Milli-Q water (18.2 $\text{M}\Omega\text{-cm}$), the mixture was
 69 kept under vigorous stirring for ca. 4 h. Then, the solution alkalin-
 70 ity was adjusted to designated pH value by 0.1 M Na_2CO_3 solution.
 71 Successively, 10 mL 3 mg/mL $\text{NaBH}_4 + 0.05$ M Na_2CO_3 mixture was
 72 added dropwise to the suspension with a vigorous stirring by a
 73 peristaltic pump at 0.5 mL/min. After 12-hour stirring, the suspen-
 74 sion was filtered and washed with copious amounts of Milli-Q wa-
 75 ter and then dried in vacuum at 323 K overnight. For comparison,
 76 the reaction pH was also adjusted to 7.5 and 8.5. The obtained cat-
 77 alysts are denoted as PdB/C-pH x hereafter, where x is the pH value
 78 of reaction solution.

79 As-prepared Pd/C catalysts were detected by a SPECTRO ARCOS
 80 inductively coupled plasma-atomic emission spectroscopy (ICP-
 81 AES) to analyze the metal loading. The morphology and size dis-
 82 tributions of Pd nanoparticles were characterized by a Tecnai G2
 83 F20 transmission electron microscopy (TEM). Electronic and lattice
 84 structure was analyzed by a Thermo Fisher K-Alpha X-ray photo-
 85 electron spectroscopy (XPS) and a D8 QUEST X-ray diffractometer
 86 with $\text{Cu } K_{\alpha}$ radiation (0.15418 nm), respectively.

87 2.3. Electrochemical measurements

88 The electrochemical measurement was taken on a CHI 660E
 89 electrochemistry workstation with a three-electrode system. A Pt
 90 sheet and a saturated calomel electrode (SCE) (or Hg/HgSO_4) were
 91 employed as the counter and reference electrodes, respectively.
 92 The working electrode (WE) was prepared by pipetted a certain
 93 amount of catalyst ink that contains 2.0 mg Pd/C, 1.0 mL $\text{C}_2\text{H}_5\text{OH}$
 94 and 120 μL Nafion (5 wt%, Aldrich) onto a freshly polished glassy
 95 carbon (GC) electrode. Note that, a 28 $\mu\text{g cm}^{-2}$ of Pd loading on
 96 the WE was kept. As for the CO stripping voltammograms, firstly

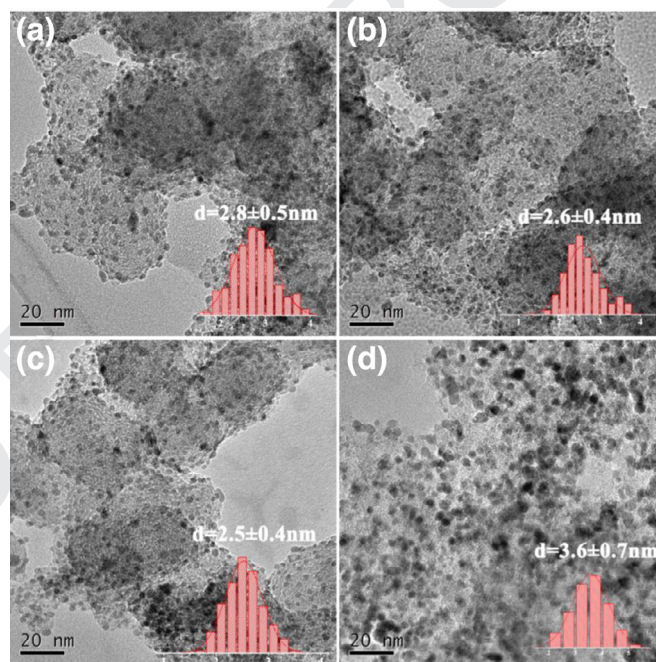


Fig. 2. TEM images and corresponding histograms of Pd particle-size distributions of the as-prepared PdB/C-pH 9.5 catalyst (a), PdB/C-pH 8.5 catalyst (b), PdB/C-pH 7.5 catalyst (c) and commercial Pd/C (JM) (d).

CO (> 99.99% purity) was bubbled and adsorbed onto WE that
 is immersed in 0.5 M NaOH for 20 min, and then dissolved CO
 was removed by high purity N_2 flow for at least 1 h. The WE po-
 tential was controlled at -0.9 V (SCE) throughout the whole pre-
 treatment process. At last, CO stripping voltammograms were col-
 lected at a scan rate of 10 mV s^{-1} . All electrolytes were performed
 deaeration by bubbling high-purity N_2 before use, and all electro-
 chemical measurements are proceeded at room temperature.

105 3. Results and discussion

106 Particle sizes and distributions of supported nanoparticles are
 107 critical parameters influencing the catalytic activity of the materi-
 108 als [34,35]. As a result, the morphologies and particle-size distri-
 109 butions for commercial Pd/C (JM) and as-prepared PdB/C catalysts
 110 were characterized by TEM. As shown in Fig. 2, Pd nanoparticles
 111 are uniformly distributed on the carbon support, and nearly no ag-
 112 glomeration is observed. The histograms of particle size and distri-
 113 bution are obtained based on the measurements of 400 nanopar-
 114 ticles in a randomly selected area of the TEM images. Specifically,
 115 the average size of as-prepared catalysts is ca. 2.5 ± 0.4 nm (PdB/C-
 116 pH 7.5), 2.6 ± 0.4 nm (PdB/C-pH 8.5) and 2.8 ± 0.5 nm (PdB/C-
 117 pH 9.5), respectively. This indicates that the particle size can be finely
 118 regulated by changing the reaction solution pH value.

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