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Dry-grinding Synthesized Multi-walled Carbon Nanotubes Supported PdO Catalyst for Ethanol Oxidation Reaction

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ABSTRACT

For the first time, it was found that dry-grinding the mixture containing technical grade PdO and multi-walled carbon nanotubes (MWCNTs) can generate a catalyst with ultrahigh electrocatalytic activity for ethanol oxidation reaction (EOR). The as-prepared catalysts were denoted as PdO/MWCNTs. For a comparison, the graphene and graphite supported PdO samples were also prepared using the same process, leading to the formation of PdO/graphene and PdO/graphite catalysts respectively. The structural details, the morphologies as well as the particle sizes of the prepared catalysts are mainly characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Although no novel diffraction peaks were observed in the XRD patterns of the resulting samples, the morphologies of the samples after the dry-grinding process have changed greatly as compared to the starting materials of PdO. The results also indicate that the PdO/MWCNTs catalysts show the smallest particle sizes among all the prepared catalysts. The catalytic activities of the prepared PdO/MWCNTs catalysts towards EOR are examined by electrochemical measurements, and the results obtained from cyclic voltammery (CV) test demonstrated that the PdO/MWCNTs catalyst delivers a forward peak current density for EOR of 5029 mA mg^{-1} at a scan rate of 50 mV s^{-1}, which is about 2.1 times higher than the reported value (2361 mA mg^{-1}) obtained on the (Pd/C) catalyst. After detailed analysis, it is thought that the easier hydrogen evolution process on the PdO/MWCNTs catalyst is regarded as the main reason for its excellent electrochemical performance as compared to other catalysts, i.e., PdO/graphene and PdO/graphite. Most interestingly, the as-prepared catalyst has electrocatalytic activity for both methanol oxidation reaction and formic acid oxidation, which were also explored approximately in this preliminary work.

1. Introduction

The development of novel methods to fabricate highly efficient electrocatalysts for ethanol oxidation reaction (EOR) has attracted considerable attention mainly due to the unique properties of ethanol such as low toxicity, high energy density, biocompatibility and abundant availability [1]. Recently, the electrocatalytic activity of Pd towards EOR in alkaline media is reported to be higher and more stable than that of Pt [2]. Therefore, many approaches have been developed to fabricate Pd or Pd based alloy or composite nanocatalysts. For instance, Zhou et al. [3] described a chemical approach for preparing Pd nanoparticles that were immobilized on the manganese dioxide modified reduced graphene oxide, where $(NH_4)_2PdCl_6$ and $NaBH_4$ were employed as the starting materials. Prof. Wang's [4] group found that carbon supported Pd nanoparticles could be simply synthesized through an ultrasound assisted way. In their work, H_2PdCl_4 and ethylene were, respectively, employed as the precursor of Pd and reducing reagent. Aggarwal's group [5] have reported the synthesis of palladium nanoparticles on a platinum (Pt) electrode which was accomplished by using an electrodeposition method of a potentiostatic pulse, where the plating solution was 0.1 M H_2SO_4

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containing 1 mM K_2PdCl_4. Although a large number of methods have been developed to prepare Pd nanoparticle catalysts, the works concerning the preparation of Pd-based composite nanoparticle catalysts by a very simple process of dry-grinding have not been reported yet.

Additionally, many kinds of Pd salts have been used as the precursors to prepare the Pd based nanocatalysts. For instance, Lan's group [6] prepared Pt-Pd nanowire arrays and Pt-Pd nanotube arrays by using one-step electrodeposition, in which $(NH_4)_2PdCl_4$ was employed as the precursor of palladium. Wang and his coworkers [7] reported a simple and facile method for the preparation of reduced graphene oxide nanosheets (RGOs) supported Au-Pd bimetallic alloyed nanoparticles. In the work, $PdCl_2$ was utilized as the starting material for producing Pd nanoparticles. Zhou et al. [8] investigated the formic acid electrooxidation on a Pd decorated Fe/C nanocatalyst, in which K_2PdCl_4 and $NaBH_4$ were applied as the precursor of Pd and reducing agent, respectively. To the best of our knowledge, however, the work, that used technical grade PdO as the precursor to prepare the Pd-based composite nanoparticle catalyst *via* a very simple dry grinding method, has not been published yet.

Meanwhile, PdO has been widely utilized as a catalyst in the research field of catalysis. For example, Weaver's group [9] investigated the molecular adsorption and dissociation of n-butane on a PdO(101) thin film using temperature-programmed reaction spectroscopy (TPRS) experiments and density functional theory (DFT) calculations, and found that the formation of relatively strongly-bound complexes on PdO(101) serves to electronically activate C-H bonds in addition to prolonging the surface lifetimes of these reactive precursors. Ferri [10] studied the influence of the synthesis method on the structure of Pd-substituted perovskite catalysts for methane oxidation, and reported that the exposure of PdO on the perovskite oxide surface is crucial for the catalytic activity. Neurock and his co-worker [11] studied the diverse pathways by which C-H bonds in CH_4 react on bare Pd clusters, Pd cluster surfaces saturated with chemisorbed oxygen (O*), and PdO clusters by using mechanistic assessments and density functional theory. Above review strongly indicated the molecule of PdO has an evident catalysis towards some peculiar organic reactions. Or in other words, there must be some interactions between PdO and some organic molecules, which may be beneficial to the catalysis of the PdO-contained catalysts.

Very recently, it is found that PdO played a key role in improving the electrocatalysis of the Pd-based catalysts. For example, Xing's research group [12] prepared a novel Pd-based catalyst by annealing commercial Pd/C catalyst under the O_2 atmosphere, and found that as-prepared catalysts exhibited excellent catalytic activity and stability for formic acid electrooxidation (FAEO), and it was thought that the formed Pd oxides/hydrous oxides (POHOs) could provide the required oxygen species for intermediate CO oxidation during the oxidation process of formic acid. Pan and his coworkers [13] studied electrocatalytic performance of Pt nanoparticles electrodeposited on the PdO thin film in methanol oxidation reaction (MOR) in acidic media, and found that the resulting Pt/PdO electrode had a high electrocatalytic activity toward MOR, and deemed that the synergism of the bifunctional mechanism and the electronic effect should be responsible for the excellent electrochemical performance of the prepared Pt/PdO catalyst. As far as we are aware, except above two reports, the detailed works on the electrocatalysis of PdO towards EOR are less.

In the present work, ultrahigh electrocatalytic activity toward EOR of the MWCNTs supported PdO nanoparticle catalysts prepared by a very simple dry-grinding method is reported. The crystalline structure, chemical composition, and morphology of the prepared PdO/MWCNTs catalyst were mainly characterized by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM). The graphene and graphite supported PdO nanoparticle catalysts were also prepared using the same method for comparison.

2. Experimental

2.1. Reagents and materials

MWCNTs (purity>95%) of 10–20 nm diameter were purchased from Shenzhen nanotech port Co., Ltd. (China). All electrodes were supplied by Tianjin Aida Co., Ltd (China). All chemicals were used as received without further purification. Doubly distilled water was used to prepare aqueous solutions.

2.2. Preparation of carbon supported PdO

The synthesis of carbon supported PdO catalyst was achieved by a very facile dry-grinding method. Briefly, 4.1 mg PdO (technical grade, PdO > 50 wt.%) was mixed with 15 mg carbon materials (MWCNTs, graphene, or graphite). Then the mixture was ground in a mortar for 20 min, as a result, the carbon supported PdO catalysts were produced. The obtained samples supported on MWCNTs, graphene and graphite were denoted as PdO/MWCNTs, PdO/graphene and PdO/graphite, respectively. The preparation processes of KCl/MWCNTs, KCl/graphene and KCl/graphite catalysts were identical to above process except for using KCl (2.5 mg) instead of PdO.

2.3. Preparation of PdO/MWCNTs modified electrode

5 mg of PdO/MWCNTs catalysts was dispersed with the aid of ultrasonic agitation in 1 mL of 0.1 wt.% Nafion ethanol solution, and the resulting suspension solution was ultrasonicated for 30 min. The glassy carbon (GC) electrode with a geometric area of 0.07 cm^2 was polished with 0.05 μm alumina slurry and washed with distilled water. The GC electrode was coated by casting 10 μL ink of the catalyst and slowly dried in air to give PdO/MWCNTs modified electrodes, thus, the loading amount of PdO particles on a GC electrode was about 1.533 mg cm^{-2}. The PdO/graphene and PdO/graphite electrodes were also fabricated based on the same procedure.

2.4. Characterization

X-ray diffraction (XRD, Bruker D8 ADVANCE X-ray diffractometer equipped with a Cu Kα source ($\lambda = 0.154$ nm) at 40 kV and 30 mA), transmission electron microscopy (TEM, HITACHI, TEM H-7650), Energy-dispersive X-ray spectroscopy (EDX, PV-9900, USA) and X-ray photoelectron spectroscopy (XPS, Kratos Analytical spectrometer, Al Kα radiation) were employed to characterize the crystal structure, morphology and chemical composition of the prepared catalysts.

All electrochemical measurements including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA) were performed in a traditional three electrode cell. A Pt wire and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. The electrochemical experiments were carried out in an N_2-saturated solution of 1.0 M KOH containing 1.0 M C_2H_5OH.

3. Results and Discussion

3.1. Characterization

Typically, XRD patterns of pure MWCNTs, raw material of PdO and the prepared PdO/MWCNTs are presented in Fig. 1A-(a, b&c),