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Full Length Article

Controlled decoration of Pd on $Ni(OH)_2$ nanoparticles by atomic layer deposition for high ethanol oxidation activity

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A new catalysts electrode was prepared by in situ controllable deposition of Pd shell layer on the gas diffusion layer (GDL) supported $Ni(OH)_2$ nanoparticles using atomic layer deposition (ALD) technology. High resolution transmission electron microscope confirmed that the $Ni(OH)_2$ core was coated by several atomic layers of Pd. The core-shell $Ni(OH)_2$@Pd catalysts with different thickness of Pd shell are easily prepared by controlling ALD cycle. Electrochemical tests showed that the 100-$Ni(OH)_2$@Pd/GDL catalyst prepared via 100 ALD cycles presented the highest catalytic activity for ethanol electro-oxidation reaction (EOR). The peaking current density of $Ni(OH)_2$@Pd/GDL was 1439 mA mg_{Pd}^{-1}, which was about 2.75 times as high as that of Pd/GDL (522 mA mg_{Pd}^{-1}). The shift in binding energy of the XPS peak of Pd in $Ni(OH)_2$@Pd catalyst confirmed the strong interaction between the Pd shell and the $Ni(OH)_2$ core. We suggested that the high catalytic activity of $Ni(OH)_2$@Pd/GDL catalyst layer may be due to following factors: high Pd dispersion arising from the core-shell structure, high Pd utilization because of the in situ deposition of Pd on catalyst layer and the interaction between the Pd shell and the $Ni(OH)_2$ core. Herein, the ALD technology exhibits a promising application prospect for preparing core-shell structure and precisely controlling shell thickness of nano-composite as an electro-catalyst toward EOR.

1. Introduction

With the energy demand and deterioration of the environment on our planet, developing energy conversion devices which are high efficient and environmentally friendly is urgent for the sustainable development of our society. Because of high energy conversion efficiency and power density, fuel cells are potential candidates to replace internal combustion engine [1]. Among various types of fuel cells, the direct ethanol fuel cells (DEFCs) is deemed to be promising energy converter because ethanol possess several inherent advantages, such as eco-friendly, low toxicity, low cost, higher energy density and easily produced [2,3]. However, it is very difficult that ethanol is completely oxidized at low temperature. Hence, it is necessary to synthesize highly effective catalysts toward electro-oxidation of ethanol (EOR). As well known, platinum (Pt) is one of the most commonly electro-catalysts. However, high cost and poor tolerance to carbonaceous species from ethanol oxidation of Pt will gravely obstruct the commercialized application of DEFCs.

Palladium (Pd) what is more abundant on the earth, cheaper and higher tolerant to carbonaceous species rooting in ethanol oxidation than Pt has received much interest. In addition, Pd also has high electro-active for EOR in alkaline solution [2,4,5]. Although Pd presents more merits than Pt for EOR, the single Pd nanoparticles (NPs) also exists some drawback, such as weak electro-active, low utilization, and poor stability. So it is very important to further promote the capacity factor and catalytic activity of Pd. The research discovered that formation of an alloy or special structure with cheaper metals can not only minimize the usage of Pd but also enhance electro-catalytic activities [3]. Furthermore, the formation of alloy can change the d-band center of Pd, thus facilitating the desorption of carbonaceous species and making more active sites available on the metal surface [6]. To achieve the target of ultralow Pd and high catalytic activity, a conventional strategy is to design core-shell nanostructures by coating Pd on the surface of cheaper metal [7,8]. Currently, the core-shell nanostructure is prepared mainly through multi-step wetting chemical reduction method and pulse electro-deposition, etc. Such as, Cui et al. [9] prepared Pd@Pt core-shell nanocrystals by multi-step wetting chemical reduction method. The nanocrystals enhanced electrocatalytic activity and long-term stability toward ORR at a sub–10 nm

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scale. Dang et al. [10,11] prepared Ir@Pt and Pd@Pt core-shell catalysts in membrane electrode assemblies using the facile pulse electro-deposition approach. Even if the Pt loading was ultralow (0.015 mg cm^{-2} at the anode), it still presented high power density of 0.6 W cm^{-2} toward the proton exchange membrane fuel cell. It is still a big challenge to accurately control the particle size or thickness of shell-layer.

Recently, atomic layer deposition (ALD) presents great potential for controlling the thickness of metal oxide thin film, as well the size of metal NPs [12,13]. ALD is a variation on chemical vapor deposition technique relied on a sequence of self-limiting reactions and it is known for its atomic level thickness control [2,7,13,14]. Very recently, we reported that Pd NPs were uniformly dispersed on the three-dimensional GNF support by ALD technology, and the as-prepared catalysts showed well catalytic activity for ethanol electro-oxidation in alkaline media [2]. Lu and co-workers prepared lots of remarkable nanometer or several-atoms material by ALD, such as Pd-TiO_2 [15], single-atom Pd_1/Graphene [16], Au@Pd core–shell bimetallic catalyst [7] and Pd@Pt core-shell nanostructures [17]. However, it is also limited that the Pd-based core-shell catalysts are prepared by ALD. To the best of our knowledge, there are only several catalysts that are employed TiO_2 and Au particles as core materials for Pd ALD deposition [7,15]. As we all know, the core materials are also very important for constructing core-shell structure catalysts, because the core materials will affect the deposition of shell materials. Inspired by this, we try to develop new Pd-based core-shell catalyst with controlling shell layer by ALD.

The key is how to choose the new core material. Fortunately, Gong et al. [18] have reported that Pd can be well deposited on activated carbon of containing hydroxyl (-OH) surface functional group by ALD method. Therefore, we imagine that metal hydroxides may be a good candidate for preparing Pd-based core-shell catalyst. Recently, metal hydroxides of proliferative defects were decorated by noble metal to serve as electro-catalysts in alkaline medium, indicating excellent catalytic activity and stability to hydrogen evolution and methanol oxidation [19,20]. Among them, nickel hydroxide ($Ni(OH)_2$) presents better electrochemical activity to water dissociation in alkaline electrolytes [20]. The result is mainly that the $Ni(OH)_2$ can promote dissociation of water and production of hydrogen intermediates, which subsequently adsorb on the nearby noble metal surfaces and recombine into molecular hydrogen [20,21]. In addition, Subbaraman et al. [22] discovered that the catalysts Pt-$Ni(OH)_2$ can promote CO oxidation via the Langmuir-Hinshelwood pathway, leading to a significant reduction of reaction onset over potential. Based on these merits, Huang et al. [23] reported Pt-$Ni(OH)_2$-Graphene ternary hybrids to increase activity and durability for methanol oxidation. They also discovered that the catalyst was very sable toward methanol oxidation with negligible activity loss after 500000 s.

Inspired by the above analysis, For the first time, we design a strategy in which Pd nanometer-shell is grown on $Ni(OH)_2$ core by ALD technology, forming the novel core-shell structure. Besides, we also try to accurately control the thickness of Pd shell and investigate the catalytic activity of as-prepared catalysts for ethanol electro-oxidation.

2. Experimental section

2.1. Fabrication of gas diffusion layer

Gas diffusion layer (GDL) was prepared according to the following procedure. Carbon paper (CP) substrate (TGPH, Toray Composites Inc., Japan) was cut into area of 3.5 × 3.5 cm^2 and carefully washed by ethanol and deionized water, finally dried in a vacuum. Similar to that previously reported [24], a microporous layer (MPL) was prepared to form proper ratio. Vulcan XC-72R carbon black (CB, Boston, USA), 15 wt% polytetrafluoroethylene (PTFE), a percentage of the water and isopropanol were mixed by 30 min ultrasonic agitation. Homogeneously mixed ink was then sprayed onto one side of the CP and followed by drying at 50 °C. Finally, the CB-coated CP were heated to 340 °C for 1.5 h. The weight loading of CB powders onto the CP was set at approximately 1 mg cm^{-2}.

In order to prepared the support of $Ni(OH)_2$, mixed acid treating CB (MATCB) that exists the number of oxygen-containing functional groups onto the surface was applied. Similared to our previous work [25], CB power was pretreated in a 8 M nitric acid and sulfuric acid mixture at 40 °C for 1 h under an ultrasonic condition. After washing and drying, the specified amounts of MATCB, 1 mL isopropanol, 1 mL deionized water, and 100 μL of a 5 wt% Nafion was mixed by ultrasonic agitation. Afterwards, homogeneously mixed ink was sprayed onto one side of the MPL and followed by drying at 50 °C, forming GDL electrode.

2.2. Synthesis of $Ni(OH)_2$ NPs on the GDL electrode

$Ni(OH)_2$ NPs were synthesized onto GDL support by applying the hydrothermal method, and this method was performed by following the synthesis method disclosed in ref [26]. by a little modification. In brief, 148 mg of $Ni(NO_3)_2{\cdot}6H_2O$, 60.5 mg of $CO(NH_2)_2$, and 170 mg of SDS was dissolved in 20 mL deionized water. After the solution was dispersed by ultrasonic agitation for 10 min at room temperature, the hybrid solution and GDL electrode were transferred into a Teflon-lined stainless-steel autoclave of 100 mL capacity. After heating at 180 °C for 6 h, the tank was cooled down to room temperature naturally. Finally, the GDL was carefully washed, and dried under vacuum at 80 °C for 8 h. And it was denoted as $Ni(OH)_2$/GDL. The inductively coupled plasma-atomic emission spectrometry (ICP, iCAP 7000, Thermo Scientific, USA) analysis suggest that the content of $Ni(OH)_2$ is about 25.5 ± 0.7 μg cm^{-2} in $Ni(OH)_2$/GDL samples.

2.3. Preparation of $Ni(OH)_2$@Pd by atomic layer deposition

Similared to our previous work [2], the Pd were grown on the $Ni(OH)_2$/GDL support by using ALD technology. Pd(II) hexafluoroacetylacetonate ($Pd(hfac)_2$, Sigma-Aldrich, >97 wt%) and formalin (Changzhen Huabo Instruments Ltd, China) as precursors. The $Pd(hfac)_2$ precursor contained in a stainless steel bubbler was heated to 50 °C to produce a practical vapor pressure. The reactor pressure was about 700–800 hPa. The one ALD cycle included in exposure to $Pd(hfac)_2$ (5 s), after N_2 purge (5 s), then exposure to formalin (10 s), finally N_2 purge (6 s). The Pd were deposited with the support temperature at 200 °C on $Ni(OH)_2$/GDL by 50, 100, 150 and 200 cycle, respectively. Meanwhile, Pd/GDL was prepared by 200 Pd ALD cycle as comparison. And they were denoted as 50-$Ni(OH)_2$@Pd/GDL, 100-$Ni(OH)_2$@Pd/GDL, 150-$Ni(OH)_2$@Pd/GDL, 200-$Ni(OH)_2$@Pd/GDL and Pd/GDL, respectively. The whole synthesis process was illustrated in Fig. 1.

2.4. Characterization of as-prepared catalysts

The crystalline structure and chemical composition of as-prepared catalysts was characterized by X-ray diffraction (XRD, X'Pert PRO, PAnalytical, Netherlands) with Cu-Ka radiation. Field-emission scanning electron microscope (SEM, S-4800) and transmission electron microscope (TEM, FEI Tecnai G2 F20, USA) were utilized to examine the dispersion and particle size distribution of as-prepared catalysts. As well, high resolution transmission electron microscope (HRTEM, FEI Tecnai G2 F20, USA) was applied to certain binding patterns of $Ni(OH)_2$ with Pd. X-ray photoelectron spectroscopy (XPS, Escalab 250 Xi, Thermo Scientific,