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Certain nitrogen functionalities on carbon nanofiber support for improving platinum performance

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ABSTRACT

Nitrogen (N) modification of carbon nanomaterial, which plays a critical role in improving platinum (Pt) performance, has shown fascinating applications. N-doped carbon nanofiber (CNF)-supported platinum catalysts were produced by an approach combined of plasma-enhanced chemical vapor deposition and *in situ* plasma activation. This approach can successfully introduce nitrogen functionalities into a carbon network, and at the same time, preserve the highly graphitic structure of the carbon support. XPS results indicate that NH_3 plasma modification mainly creates pyridinic nitrogen functionalities, while N_2 plasma modification mainly increases the percentage of pyrrolic nitrogen in the carbon network, which suggests a modification of certain nitrogen functionalities on the carbon support. By correlating TEM and XPS data with electrochemical measurements, we conclude that the N-modified CNF exhibits a significant improvement in Pt electrochemical activity and stability than pristine CNF support and Pt/CNF–NH_3 electrode with smallest Pt particle size, highest percentage of pyridinic nitrogen, exhibits the highest Pt utilization, electrochemical activity, and poisoning-resistance ability. Our study gives both insights on the influence of N modification of the carbon support in platinum catalytic effectiveness and a route for formation of certain nitrogen functionalities on the carbon support. This will be important for the further development of Pt catalysts.

1. Introduction

Polymer electrolyte fuel cell (PEFC) is expected to be an alternative power-generation for stationary, automobile, and portable power applications due to its high energy density, low operation temperature, renewable fuels (such as hydrogen, alcohol), and low air pollution [1,2]. Although the PEFC technique has been undergoing tremendous developments recently, some disadvantages for its commercialization still exist. One of the most significant barriers for PEFCs is the low activity and stability of platinum (Pt)-based catalysts [3]. The catalytic activity and stability of Pt-based catalysts depend on many factors, among which the carbon supports may play a crucial role. Generally speaking, carbon support materials should possess high surface area, excellent electrical conductivity, and good electrochemical stability under fuel cell operating conditions [4,5]. In the past decade, carbon nanomaterials, including one-dimensional carbon nanotubes, carbon nanofibers, and two-dimensional graphene, have attracted a wide range of interest due to their outstanding structure, excellent properties, and wide potential applications [6–10]. Most notably, carbon nanomaterials act as support for catalyst nanoparticles in various kinds of electrochemical applications [11–13]. However, the inert surface of the carbon nanomaterials requires a suitable chemical modification to achieve a favorable interaction with metal nanoparticle catalysts [1,14,15]. Functionalization of carbon nanomaterials with nitrogen has gained particular momentum and has been demonstrated to create beneficial support–catalyst interactions which substantially improve catalyst dispersion, activity, and stability [16–18].

Great efforts have been devoted to the synthesis and development of nitrogen (N)-modified carbon nanomaterials with high performance. Chemical vapor deposition (CVD), thermal treatment, and plasma treatment are the most widely used methods to prepare nitrogen-modified carbon nanomaterials. Dai and Tu synthesized N-doped graphene by CVD using NH_3 as the N precursor and demonstrated that N-doped graphene showed much better electrocatalytic activity, stability, and tolerance to poison effects than the commercial E-TEK catalysts for oxygen reduction [19,20]. Chen and coworkers prepared N-doped nanotubes by microwave-plasma

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-enhanced CVD using N-containing plasma as the precursor [18,21]. Stevenson and coworkers used pyridine precursor to prepare N-modified carbon nanofiber and nanotube electrodes and found that the exposed edge plane defects and N-doping of carbon support were important factors for affecting adsorption of reactive intermediates [22,23]. The N-modification is more likely to occur at the exposed edge and defects of carbon nanomaterials in the thermal treatment method. Sun and Wu modified graphene oxide in NH_3 by heat treatment and studied the influence of annealing temperature on the doping level [24,25]. Due to the insufficient defects in the carbon nanomaterials and instability of C–N bonds in high temperature, the N content of N-doped carbon nanomaterials synthesized by the thermal treatment method is relatively low [26]. Plasma treatment is an effective way in synthesis of N-modified carbon nanomaterials at low temperature [27]. The N content can be controlled by a series of parameters including the plasma input power, exposure time, N-containing type, and so on. Chiu and coworkers reported a plasma treatment method for N-doped graphene preparation [28]. Their findings suggest that the N-containing radicals in NH_3 plasma can readily form covalent bonds with the carbon lattice and keep stable. Li, Kang and Ramaprabhu modified graphene by N_2 plasma treatment [16,29,30]. N_2 plasma treatment can create pyrrolic nitrogen defects, which act as good anchoring sites for platinum nanoparticles [16]. It is well known that N-modified carbon-supported Pt-based catalysts exhibit improved electrochemical activity and durability toward both methanol oxidation reaction (MOR) and oxygen reduction reaction (ORR). Although there are some insights into how N modification enhances catalysts activity, durability, and dispersion, more careful studies are still necessary to fully understand the affecting factors of certain nitrogen functionalities in catalytic effectiveness [31]. Moreover, controlling synthesis of certain nitrogen functionalities in carbon nanomaterials is still a challenge [26].

The goal of this work is to prepare N-doped carbon nanomaterial-supported platinum electrodes with certain nitrogen functionalities and gain a better understanding of the affecting parameters in the platinum nanoparticle growth and the electrochemical activity, poisoning-resistance ability of the integrated electrode. Since the formation of the C–N bond occurs mostly at the edges and defects of the graphite sheets, vertically aligned carbon nanofiber (VACNF), which exposes large amounts of edge-plane graphite, is optimal for this study [32]. Furthermore, the direct electrical contact between every carbon nanofiber and substrate can minimize the undesired impact on electrochemical testing results [33]. Plasma treatment presents an efficient approach for simple, tunable, and fast modification of N-doped carbon nanomaterials [30]. To avoid oxygen coordinated with the carbon support and reduce the impact of oxidized species in the carbon matrix on the platinum particle formation and electrocatalytic activity, an approach combined of plasma-enhanced chemical vapor deposition (PECVD) and *in situ* plasma activation was developed to synthesize N-modified VACNFs.

2. Experimental

2.1. Materials

Carbon paper was obtained from Hesen Electric Co. Ltd. (Shanghai, China). Platinum (99.9%) and iron (99.9%) targets were purchased from Tianyi Real Materials Co. Ltd. (Huizhou, China). High purity N_2 (99.999%), NH_3 (99.999%), H_2 (99.999%), Ar (99.999%), CO (99.999%), and CH_4 (99.999%) were received from Shangyuan Gas Co. Ltd. (Nanjing, China). Methanol (MeOH, AR grade), sulfuric acid (H_2SO_4, 98 wt%) and hydrochloric acid (HCl, 37 wt%) were purchased from Shanghai Chemical Reagent Store (China). Deionized water was used in the experiments. All reagents were used as received without further purification.

2.2. Activation of vertically aligned carbon nanofibers

The VACNFs were directly grown on carbon paper by inductively coupled plasma-enhanced chemical vapor deposition (ICP-PECVD) using CH_4 and H_2 as the working gas, as described in our previous study [34]. Carbon papers with iron catalyst particles were used as the substrate. The experimental details of the ICP-PECVD system are listed: 400 °C for the substrate temperature, −50 V for the substrate bias voltage, hydrogen and methane in the partial pressure ratio of 4:1, 20 Pa for the reactor total pressure, 40 min for the reaction time and at least 60 min for cooling down in argon atmosphere.

To activate the carbon nanofibers, the VACNFs were *in situ* treated by plasma in the ICP-PECVD reactor chamber [35]. Since the working gas for plasma treatment was different, there were three types of VACNF samples which could be labeled as CNF (not treated by plasma), CNF–N_2 (treated by N_2 plasma), and CNF–NH_3 (treated by NH_3 plasma). In this process, all the experimental parameters were fixed: 150 W for the plasma discharge power, 20 Pa for the working gas pressure, and 10 min for the activating time. Since all the VACNF samples were treated *in situ* and not transferred from one container to another, the influence from air or other chemicals could be minor and ignored.

2.3. Preparation of Pt/CNF electrodes

Pt nanoparticles about a loading of $0.025\,\mathrm{mg\,cm^{-2}}$ were deposited on the surface of CNF, CNF–N_2, and CNF–NH_3 samples by a radio-frequency magnetron sputtering system (RF-MS) [36]. The experimental details of RF-MS systems can be found in our previous study [12]. All the CNF samples were treated under the same conditions: Ar as the working gas, 5.0 Pa for the reactor total pressure, and 100 W for the input power.

2.4. Material characterization

The morphology of the CNF and Pt/CNF samples were characterized by scanning electron microscopy (SEM) (Sirion 200, FEI, USA) at the operation voltage of 5.0 kV. The morphology of the Pt/CNF, Pt/CNF–N_2, and Pt/CNF–NH_3 electrodes were also examined by using transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) (JEOL 2010) at the operation voltage of 200 kV. To identify the crystalline structure of CNFs and Pt nanoparticles, Pt/CNF, Pt/CNF–N_2, and Pt/CNF–NH_3 electrodes were examined by X-Ray diffraction (XRD) (X'Pert Pro. Philips, Holland) using CuK_α ($\lambda K\alpha 1 = 1.5418$ Å) as the radiation source. The X-ray photoelectron spectroscopy (XPS) analysis was carried out with a Thermo ESCALAB 250 spectroscopy (Thermo Electron Corporation) at a power of 150 W using monochromatic Al Kα radiation at 1486.6 eV. The information on spectrometer details and measurement conditions can be found in our previous literature [37]. For XPS measurements, the Pt/CNF catalysts were very carefully moved from the carbon paper by a blade. XPS for all the samples were recorded at pass energies of 70 eV for survey spectra and 20 eV for core level spectra. The spectra were calibrated with respect to the C 1s peak at 284.6 eV. Raman analysis was performed with a JY Raman microspectrometer (LABRAM-HR) at room temperature using the argon laser of 514.5 nm as the exciting radiation. By equipping with an optical microscope, the Raman microspectrometer can precisely position a 2 μm diameter sampling cross section. The Raman spectra were recorded with a resolution of $0.6\,\mathrm{cm^{-1}}$. The loading of platinum in the Pt/CNF electrodes were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Atomscan Advantage, Thermo