Short communication

Highly efficient supporting material derived from used cigarette filter for oxygen reduction reaction

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A B S T R A C T

Bimodal porous nitrogen (N) doped carbon supported Pt composite was prepared as a catalyst for oxygen reduction reaction (ORR). The N-doped carbon (NCF) support was obtained via one-pot pyrolysis of the used cigarette filters. Physical characterizations and electrochemical tests proved that the presence of N dopant on the surface of the NCF not only provided highly dispersive active sites for the growth of the Pt nanoparticles but also the active centers for ORR itself. It was demonstrated that these combinative effects contributed on higher ORR activity and durability than those for the commercial carbon (Vulcan XC) supported Pt composites.

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1. Introduction

Developing proper catalysts for the oxygen reduction reaction (ORR) is the current issue for the industrial development of fuel cells [1]. During the past years, Pt has been used as the commercial electrocatalyst for the ORR due to its high activity [2]. Owing to the high cost and limited storage of Pt, however, decreasing the amount of usage with enhancing the catalytic activity of Pt catalyst has been come into a compulsory aim [3].

One of the available strategies to meet the demand is the increase of the active surface area of Pt by adopting appropriate supporting material (e.g., carbon material), which enables the high dispersion of Pt nanoparticles [4,5]. It has been reported that the catalytic performances such as onset potential, current density, and durability are susceptible to the type of catalytic supporting material [6]. The requirements for carbon material as a support are high surface area, good conductivity, and proper pore structure, which provide the uniformly distributed anchoring sites for Pt catalysts and facilitate the smooth electrolyte flux for effective catalytic reaction without hampering electron transfer [7].

Nitrogen (N)-doped carbon with bimodal structure, which consists of micropores and mesopores, is a proper candidate material for supporting the Pt nanoparticles [8]. Typically, the bimodal pore system can induce the high surface area, which confers an increased distribution of C–N catalytic center and provide the easier accessibility to active sites for reactants [9]. More importantly, it has been reported that the presence of N dopants on the carbon surface not only can donate excess electrons for the fine nucleation of Pt nanoparticles but also limit the mobility of Pt nanoparticles by metal–N interaction, which prevent them from agglomeration [10]. Moreover, the substituted N atoms are known to have the catalytic activity toward ORR [11]. Thus, it could be another contribution factor for exhibiting high catalytic performance. These physicochemical properties are beneficial to design an effective Pt-based electrocatalyst possessing highly dispersive Pt nanoparticles by inducing N species on the entire surface of the carbon supporting material.

There have been several methods for the preparation of the N-doped carbon supporting material such as carbonization of organic material that readily containing N species, heat treatment of organics and/or carbon with N-containing gases, and utilizing N-containing chemicals with carbon sources together before the carbonization [12–15]. Among these, carbonization of organic material with ammonia (NH_3) gas enables N doping within the carbon matrix and simultaneously allows formation of porous structure on the whole surface by a pyrolysis, which can be a powerful approach for achieving the desirable physicochemical properties for the carbon based electrocatalyst toward the ORR at one-step procedure [16].

In this study, we report on a simple and environmentally benign route to the scalable production of well dispersed Pt on hierarchical N-doped porous carbon (Pt/NCF) via one-pot carbonization of used cigarette filters and direct reduction of Pt. This synthetic strategy possesses

the following desirable advantages: (1) recycling used cigarette filters as a carbon source for use in a Pt support, (2) developing the bimodal pore structure, which can provide large surface area and fast oxygen insertion and desertion and (3) simultaneous introduction of the N functional groups into this supporting material, which can play a key role in the formation of homogeneous nucleation sites for highly dispersed Pt nanoparticles and catalytic active sites toward the ORR. To the best of our knowledge, a study of the feasibility of preparing bimodal porous carbon material synthesized from used cigarette filters and its usage as a supporting material of Pt nanoparticles for ORR have not been reported yet.

2. Experimental

2.1. Preparation of catalysts

As a feasible approach, we chose the world-widely consumed cigarette brand (Marlboro Light Gold produced by Philip Morris Int.) and popular brands (The One Orange and Bohem Cigar Mojito produced by Korea Tobacco & Ginseng Corp.) in our country, Republic of Korea together, as a model case. These industrial cigarette filters are largely composed of cellulose acetate (>95%), which reveals that no significant differences toward the origin of carbon source between each brand is chemically negligible [17]. The used cigarette butts from these brands were collected and filters were separated. N-doped carbon (NCF) and carbon without N-doping (CF) were obtained from heat treatments of the separated filters at 900 °C for 2 h under the NH_3 and Ar, respectively. Identical mass of filters from each brand without any pretreatments (including washing) were used before the pyrolysis.

NCF-supported Pt catalysts were prepared by the conventional impregnation method. Proper amounts of chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) solution (50 mL g^{-1}) were added into the 0.05 g of NCF powder dispersed deionized water (200 mL). Sodium borohydride (0.1 M, 30 mL) was added to each solution and stirred it for 12 h in order to reduce the Pt ions to Pt nanoparticles. The dispersion was filtered and dried at 60 °C for 12 h. The Pt contents for Pt/NCF were examined to be 15.08 wt% and 20.46 wt%, which are denoted as Pt/NCF15 and Pt/NCF20, respectively. Pt/CF (21.99 wt%) and Pt/Vulcan XC (20.29 wt%) synthesized by using above method and commercial Pt/C (Alfa Aesar, 20 wt%) were compared as control samples, which are denoted herein as Pt/CF20, Pt/VC20, and Pt/C20, respectively.

2.2. Physicochemical characterization

The morphology of the sample was characterized by JEM-3010 high-resolution transmission electron microscopy (HR-TEM). An AXIS-HIS X-ray photoelectron spectroscopy (XPS) was used to investigate the elemental species. The amount of N in the Pt/NCF20 was determined by using a CHNS 932 analyzer. N_2 sorption isotherms were measured with a Micromeritics ASAP 2010 instrument. Atomic-distribution mapping was obtained by using HAADF-STEM (JEM-2100F, 200 kV). Pt contents were examined by JP/ICPS-7500 inductively coupled plasma with atomic emission spectrometry (ICP-AES).

2.3. Electrochemical measurements

All electrochemical experiments were performed with an Iviumstat workstation in a three-electrode cell. Rotating disk electrode (RDE) was used for the measurement. A catalyst loaded glassy carbon electrode (GCE, 5 mm dia.), an Ag/AgCl electrode (KCl saturated) and a platinum electrode served as working, reference and counter electrodes, respectively.

Catalyst inks were prepared by the following order. As-prepared catalysts (10 mg) were mixed with 20 μL deionized water for stable mixing with the binder in the next step. 57 μL of 5% Nafion and 800 μL of isopropyl alcohol were then inserted under vigorous stirring and sonication for both the 30 min. 7.0 μL of each ink was dropped onto the GCE and dried at room temperature. The linear sweep voltammetry (LSV) was performed between 0.4 and 1.2 V (vs. RHE) with a scan rate of 5 mV s^{-1} in O_2 saturated 0.1 M KOH aqueous solution at various rotating speeds from 400 to 2000 rpm. The stability test was performed at 0.5 V (vs. RHE) for 6000 s.
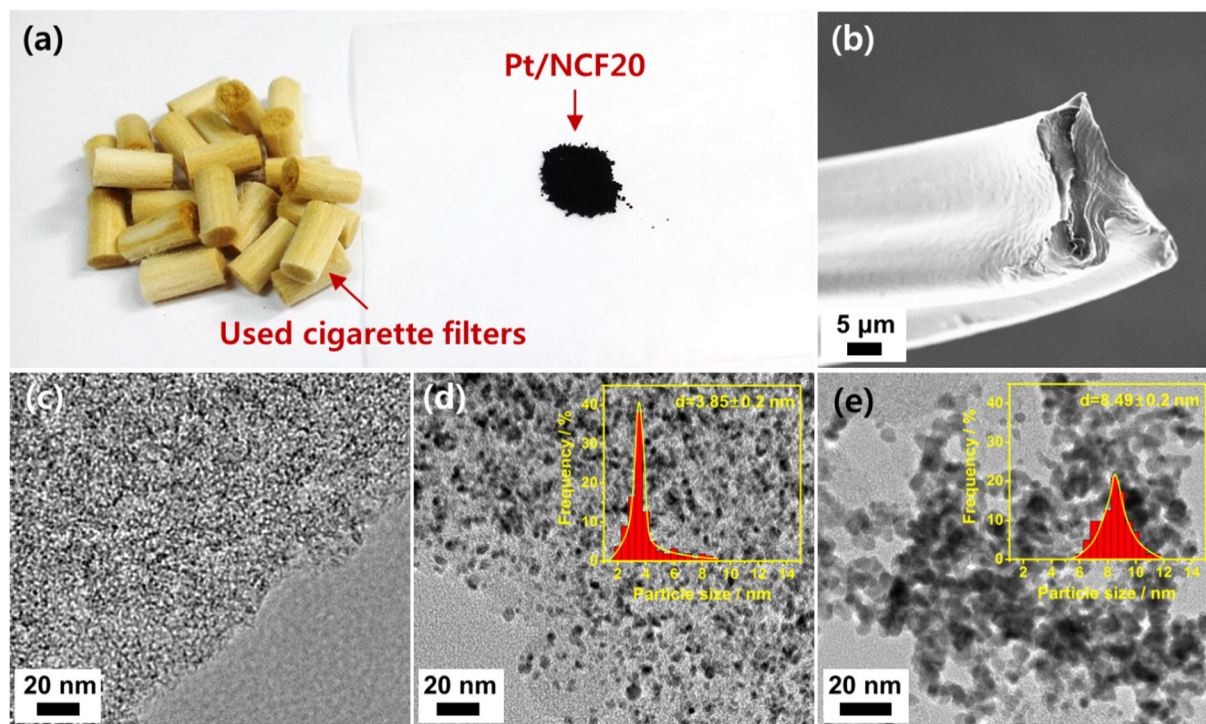

Fig. 1. (a) Photograph of the used cigarette filters and Pt/NCF20 powder. (b) SEM image of the fiber of cigarette filter. HR-TEM images of the (c) NCF, (d) Pt/NCF20 and (e) Pt/VC20. Insets for (d) and (e) are the size distribution of Pt nanoparticles.