



Synthesis of hollow carbon nanostructures as a non-precious catalyst for oxygen reduction reaction



Seul Lee, Da-Hee Kwak, Sang-Beom Han, Eui-Tak Hwang, Min-Cheol Kim, Jin-Yeon Lee, Young-Woo Lee, Kyung-Won Park*

Department of Chemical Engineering, Soongsil University, Seoul 156743, Republic of Korea

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ABSTRACT

Carbon-based nanostructures as a non-precious catalyst for oxygen reduction reaction (ORR) exhibit excellent electrocatalytic activities due to high specific surface areas and favorable active sites supported by the doped transition metals and nitrogen species. We synthesize the metal-nitrogen doped carbon nanostructures (MPC-C, M = Fe, Co) by using a template method in the presence of metal phthalocyanine including FePc, CoPc, and FeCoPc as metal and nitrogen as well as carbon sources. The as-prepared carbon nanostructures show a high specific surface area, porous structure, and metal-nitrogen dopants, as observed by field-emission scanning electron microscopy (FE-SEM), field-emission transmission electron microscopy (FE-TEM), X-ray photo-electron spectroscopy (XPS), and nitrogen sorption measurement. Especially, among the doped carbon nanostructures, FeCoPc-C exhibits superior ORR electrocatalytic properties in an alkaline medium: an electron transfer number close to 4, high half-wave potential, improved electrochemical stability, and methanol tolerance.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been well-known as a promising electrochemical power source that can efficiently convert chemical energy into electrical energy [1–5]. In the PEMFCs, since the oxygen reduction reaction (ORR) on the cathode is much more sluggish than the anodic activation and oxidation of hydrogen, large amounts of platinum (Pt) as a noble metal catalyst need to be provided on the cathode to accelerate the ORR [6–11]. Accordingly, Pt-based nanostructure materials have been the most widely used as an electrocatalyst for the ORR. However, it has been reported that Pt-based cathode catalysts present critical issues: slow kinetics for oxygen reduction in a wide range of pH, deteriorated stability, high cost, and poisoning effect by carbon monoxide. Many efforts have been made to overcome these problems by developing low-Pt or Pt-free cathode catalysts for PEMFCs [12–14].

In order to develop non-precious metal (NPM) and metal-free electrocatalysts as an alternative to Pt-based catalysts, non-precious catalysts synthesized using metal porphyrin systems for the ORR in an alkaline medium have been strongly suggested [15–21]. Recently, carbon nanomaterials (carbon nanotubes,

graphene, graphitic arrays, and porous carbons), doped by heteroatoms such as N, B, S, P, Fe, and Co, were reported to exhibit an improved electrocatalytic performance for the ORR [22–29]. The doping of certain transition metals (e.g., Fe, Co) into nitrogen-doped carbon frameworks can result in a nonprecious metal catalyst system with an improved ORR activity in alkaline media as follows [30]: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ ($E^\circ = 0.401$ V vs. NHE). Two crucial factors affecting the activity of NPM catalysts are: (i) content of dopants and the interactions between different dopants, which play a key role as active sites; and (ii) porous structure with high specific surface area, which determines the accessible active sites and the transport properties of ORR-relevant species [31,32].

Metal phthalocyanine as a precursor for the synthesis of heteroatom-doped carbon for ORR was reported in 1964 by R. Jastnski [20]. The phthalocyanines, which are planar with the metal symmetrically surrounded by four nitrogen atoms, possess chemical stability and insolubility in water and alkali solutions. Iron and cobalt phthalocyanines can be more easily synthesized or purchased more cheaply compared with other specially designed metal porphyrins or phthalocyanines [33]. Previous approaches to NPM-based M/N/C (M = Fe or Co) catalysts focused on the use of two or three separate sources for metal, nitrogen, and carbon. Moreover, to obtain high ORR activity of the NPM catalysts, employing multiple pyrolysis steps or toxic ammonia gas should be needed. In contrast, we prepared M-N-C catalysts from a single

* Corresponding author. Tel.: +82 2 820 0613; fax: +82 2 812 5378.
E-mail address: kwpark@ssu.ac.kr (K.-W. Park).

metalloporphyrin precursor in a single pyrolysis step under inert atmosphere without using ammonia gas [11,34,35]. Herein, we reported the metal-nitrogen doped carbon nanostructures for ORR using a template method under a nitrogen atmosphere with spherical silica beads in the presence of metal phthalocyanine (Pc) as a dopant of nitrogen and metal as well as a carbon source. The structure of the as-prepared samples was characterized using FE-SEM and FE-TEM. The chemical state/elemental composition and surface area/porous structure of the as-prepared carbon nanostructures were characterized using XPS and nitrogen sorption measurement, respectively. The electrochemical properties and ORR electrocatalytic performance of the as-prepared catalysts were measured using voltammetry in an electrochemical cell.

2. Experimental

2.1. Synthesis of the metal-nitrogen doped carbon nanostructures

As illustrated in Fig. 1, for synthesis of the Fe and Co-nitrogen doped carbon nanostructures (denoted as FeCoPc-C), 0.25 g cobalt (II) Pc (CoPc, Aldrich) and 0.25 g iron(II) Pc (Aldrich) as metal, nitrogen, and carbon sources were homogeneously mixed with 0.5 g silica beads (500 nm, Alfa Aesar) as a template in 50 mL dimethylformamide (DMF, Aldrich) as a solvent. Similarly, for the Fe or Co-nitrogen doped carbon nanostructures (denoted as FePc-C or CoPc-C, respectively), 0.5 g iron(II) Pc or 0.5 g cobalt(II) Pc were mixed with 0.5 g silica beads in 50 mL DMF, respectively. For the homogeneous mixtures, the solutions were continuously stirred and were then transferred to a glass dish. The transferred samples were evaporated at 80 °C to completely remove the solvent. After drying, the products were pyrolyzed at 900 °C under nitrogen atmosphere and then washed in 10 vol% hydrofluoric acid solution for 1 h to completely remove the silica beads as the template. The obtained powders were precipitated and washed with water and ethanol several times to remove acid solution and impurities. The resulting samples were dried in an oven at 60 °C for 24 h. Also, to confirm the metal doping effect, the Pc-C nanostructure was prepared by using the same procedure with pure Pc not containing metal. 또한.

2.2. Structural analysis

FE-SEM images of the as-prepared samples were obtained using a Carl Zeiss SIGMA microscope operating at 5 kV. FE-TEM and EDX analysis were carried out using a Philips Tecnai F20 system operating at 200 kV. The TEM samples were prepared by placing a drop of the powder suspension in ethanol on carbon-coated copper grid substrates. Structural analysis of the samples was carried out using the X-ray diffraction (XRD) method with a Bruker, D2 Phase System with a Cu K α radiation source of $\lambda = 0.15406$ nm and a Ni filter. The tube current and voltage were 10 mA and 30 kV, respectively. Raman spectra were measured using a High Resolution Micro Raman spectrometer (Horiba Jobin Yvon, LabRAM HR

UV/Vis/NIR PL). XPS analysis was performed with the Al K α X-ray source of 1486.8 eV at the chamber vacuum pressure of less than 7.8×10^{-9} Torr and beam power of 200 W (Thermo Scientific, K-Alpha). The high resolution spectra were collected with the pass energy of 50 eV and a step size of 0.1 eV. Nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020. Before the adsorption measurements, all samples were outgassed at 473 K for 360 min in the port of the adsorption analyzer. The starting relative pressure was 0.995 P/P $_0$ and the ending relative pressure was 0.01 P/P $_0$.

2.3. Electrochemical analysis

The ORR performance and electrochemical properties of the as-prepared samples were measured in a three-electrode cell with Pt wire and Hg/HgO as the counter and reference electrodes, respectively, at 25 °C using a potentiostat (PGSTAT302N, AUTOLAB). All electrode potentials were converted into a reversible hydrogen electrode (RHE). The sample suspension was prepared by ultrasonically dispersing the powder in an appropriate amount of Millipore water and isopropanol. The suspension was dropped at 1 μ L increments onto a carbon rotating disk electrode with an area of 0.0706 cm 2 . After drying in an oven at 50 °C, the total loading of each sample was 400 μ g cm $^{-2}$. In order to compare the electrochemical properties and the ORR activity of the samples, cyclic voltammograms (CVs) and linear sweep voltammograms (LSVs) were obtained in a 0.1 M NaOH. The transferred electron numbers (n) of the samples in the ORR were determined using Koutecky-Levich plots. The ORR stability test was carried out by scanning between -0.4 and +0.1 V (vs. Hg/HgO) for 2000 cycles at a scan rate of 50 mV s $^{-1}$ in O $_2$ -saturated 0.1 M NaOH at 25 °C. Oxygen reduction current-potential curves before and after the stability test for the as-prepared samples were obtained by linear sweep voltammetry (LSV) with a rotation disk speed of 1600 rpm. The methanol-tolerant ORR activity of the samples was evaluated in O $_2$ -saturated 0.1 M NaOH + 0.5 M CH $_3$ OH. To determine the role of metal elements as the ORR active sites in the catalysts, the ORR polarization curves for the samples were obtained in O $_2$ -saturated 0.1 M NaOH with CN $^-$.

3. Results and discussion

Fig. 2(a–c) show FE-SEM images of FePc-C, CoPc-C, and FeCoPc-C, respectively, synthesized using a template method with metal Pc as metal, nitrogen, and carbon sources. The as-prepared samples displayed porous spherical shapes with \sim 500 nm in diameter, implying a homogeneous carbon coating by metal-Pc sources on the SiO $_2$ templates (\sim 500 nm in diameter) during the pyrolysis under a nitrogen atmosphere. Fig. 2(d–f) show FE-TEM images of FePc-C, CoPc-C, and FeCoPc-C, respectively. The as-prepared carbon nanostructures exhibited porous spherical shapes with \sim 500 nm in diameter with a wall of 6.78–7.6 nm thickness, implying a complete transfer of the SiO $_2$ beads as a template into

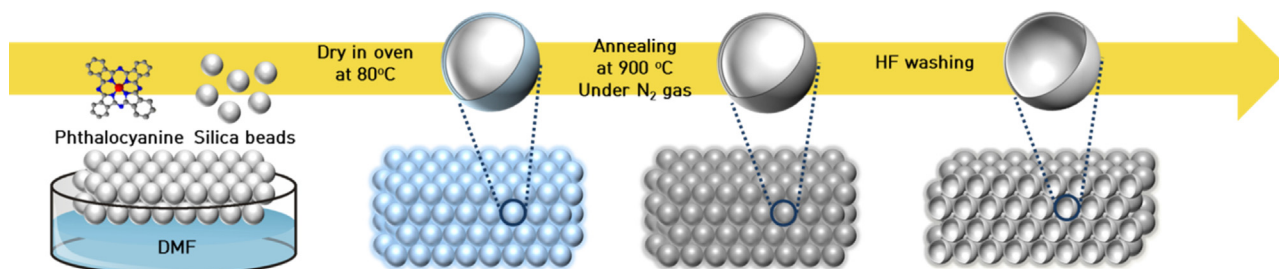


Fig. 1. Schematic illustration of synthesis of metal-nitrogen doped carbon nanostructures prepared using a one-pot template method.

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