Electrocatalytic Oxygen Reduction over $Co@Co_3O_4$/N-doped Porous Carbon Synthesized by Pyrolysis of ZIF-8/67 on Cellulose Nanofibers

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Abstract: $Co@Co_3O_4$ nanoparticles highly dispersed on N-doped porous carbon (C-Co,N/TOCNF) were prepared by pyrolysis of the carboxylate-functionalized cellulose nanofibers (TOCNF) with bimetallic ZIFs *in situ* grown on the surface. The material was characterized thoroughly using various instruments and applied for the oxygen reduction reaction (ORR). The interconnected three-dimensional network in TOCNF prevented the aggregation of the catalytically active Co nanoparticles with promotion of electron transfer and mass diffusion, and C-Co,N/TOCNF demonstrated comparable catalytic performances in alkaline medium when compared with the commercial Pt/C with improved stability.

Keywords: Oxygen reduction reaction, ZIF-derived catalyst, Cellulose nanofibers

1. Introduction

Oxygen reduction reaction (ORR) is important for fuel cells.[1] Despite Pt-based catalysts being considered as the most effective for ORR, their high cost and CO deactivation with low stability limit their practical applications in fuel cell devices. Recently, there has been rapidly growing interest shown in utilizing metal–organic frameworks (MOFs) as a potential candidate for non-Pt based electrocatalysts for ORR.[2] Typically, MOFs can be directly converted into ORR-active materials after carbonization under an inert atmosphere with potentially abundant active sites simply from the choice of metal ions and organic linkers. However, ORR performances of the reported MOF-derived catalysts have been often inferior to the commercially available Pt-based catalysts because of the agglomeration of metal nanoparticles (NPs) occurred during pyrolysis, which reduce the number of active sites and therefore lower the catalytic activity.[3]

In this work, we report a facile synthesis of a well-dispersed $Co@Co_3O_4$,N co-doped porous carbon without agglomeration of Co NPs (C-Co,N/TOCNF) derived from bimetallic ZIFs (Zn-ZIF-8 and Co-ZIF-67) grown on the surface of cellulose and subsequent pyrolysis treatment. The physicochemical properties of the material were examed using diverse instruments, and it was applied as an ORR electrocatalyst.

2. Experimental

Figure 1 illustrates the synthesis steps of the C-Co,N/TOCNF. Firstly, cellulose nanofibers from extracted tunicate were functionalized with carboxylate groups by TEMPO-mediated oxidation (TOCNF). Secondly, ZIF precursors dissolved in methanol were added sequentially to the mixture containing TOCNF with stirring for 2 h to obtain a product (Zn,Co-ZIF/TOCNF). Finally, C-Co,N/TOCNF was prepared *via* pyrolysis of Zn,Co-ZIF/TOCNF in N_2 gas at 900 °C (5 °C/min) for 2 h. The material was characterized by XRD, SEM/TEM, N_2-adsorption desorption isotherm, FT-IR, Raman, and XPS. The electrocatalytic activities were measured using a potentiostat in 3-electrode system consisting of working-, Pt counter-, and reference electrodes. Electrolyte was firstly saturated with nitrogen and was subsequently saturated with oxygen for both cyclic voltammetry (CV) and linear sweep voltammetry (LSV). CV was conducted at a scan rate of 20 mV/sec in the range of 0.05 - 1.2 V (vs. RHE). Hydrodynamic LSV measurement was carried out from 0.2 to 1.0 V (vs. RHE) at a scan rate of 5mV/sec using a rotating disk electrode (RDE).

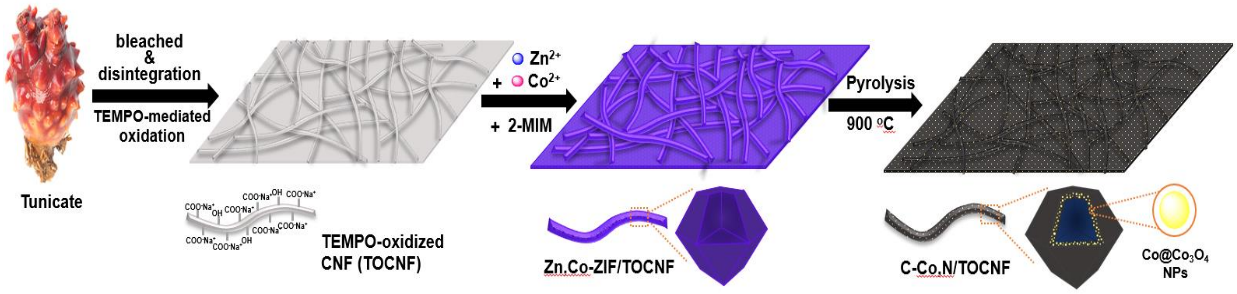

Figure 1. Schematic illustration of the synthesis steps of C-Co,N/TOCNF.

3. Results and discussion

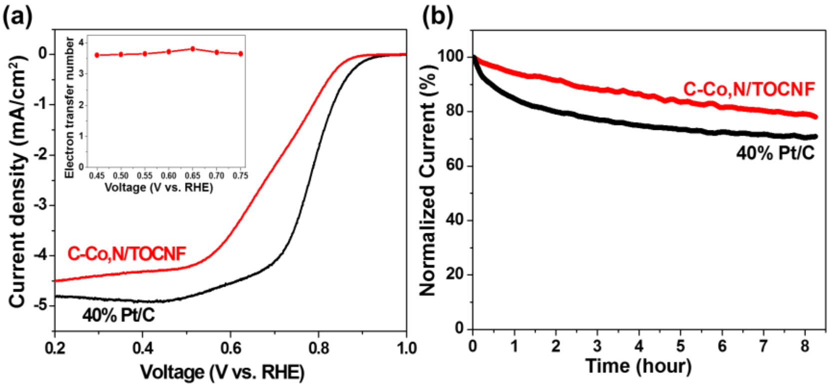

Figure 2. (a) RDE voltammograms (insert : the corresponding Koutecky-Levich plots (J-1 vs. ω-0.5) at different potential presented), and (b) chronoamperometry in O_2-saturated 0.1M KOH ambient of C-Co,N/TOCNF (red) and commercial 40% Pt/C (black) at 1600 rpm.

C-Co,N/TOCNF was made of Co@Co_3O_4 nanoparticles of 15-22 nm uniformly embedded in carbon nanofibers (both graphitic and disordered) of TOCNF with the BET surface area of ca. 1492 m^2/g and pores between 1.5 to 25 nm in diameter. XPS confirmed the presence of Co, C, N (3.14 %), and O. No Zn was detected due to its volatilization during the pyrolysis step. As shown in Fig. 2, the onset potential of C-Co,N/TOCNF (0.86 V) was close to that of the commercial 40 % Pt/C (0.90 V). However, a half-wave potential ($E^{1/2}$) and diffusion-limited current density (0.74V for $E^{1/2}$ and 4.51 mA/cm^2) were slightly lower than those of the commercial Pt/C (0.78 V for $E^{1/2}$ and 4.73 mA/cm^2). The electron transfer numbers (*n*) value of C-Co,N–/TOCNF was between 3.6 - 3.8 estimated on the basis of Koutecky-Levich equation, indicating an efficient 4 e^- dominated ORR process (inset in Fig. 2 (a)). C-Co,N/TOCNF exhibited a very slow attenuation after 8 h, at which time 83% of the relative current was still maintained, whereas Pt/C lost nearly 30% of its initial activity (Fig. 2 (b)). This result confirmed the high durability of C-Co,N/TOCNF, which may be ascribed to the high thermal and chemical stability of the material obtained by pyrolysis at high temperature (900 °C).

4. Conclusions

Co@Co_3O_4,N-doped porous carbon (C-Co,N/TOCNF) was obtained by pyrolysis of bimetallic ZIFs supported on cellulose fibers (TOCNF). The catalyst composed of highly dispersed Co@Co_3O_4 nanoparticles strongly bound to the surface of the interconnected 3D network of TOCNF showed excellent catalytic activity for oxygen reduction reaction comparable to the commercial Pt/C in alkaline medium with superior durability.

References

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