



Full Length Article

Copper-promoted nitrogen-doped carbon derived from zeolitic imidazole frameworks for oxygen reduction reaction

Yunchao Xie^a, Chi Zhang^a, Xiaoqing He^b, Jheng-Wun Su^a, Thomas Parker^c, Tommi White^{b,d}, Mark Griep^c, Jian Lin^{a,*}^a Department of Mechanical & Aerospace Engineering, University of Missouri, Columbia, MO 65211, United States^b Electron Microscopy Core Facility, University of Missouri, Columbia, MO 65211, United States^c U.S. Army Research Laboratory, Weapons and Materials Research Laboratory, ATTN: RDRL-WM, Aberdeen Proving Ground, MD 21005-5069, United States^d Department of Biochemistry, University of Missouri, Columbia, MO 65211, United States

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ABSTRACT

Rational design of oxygen reduction reaction (ORR) electrocatalysts based on earth-abundant elements is critical important towards sustainable energy applications. Among various reported ORR electrocatalysts, transition metal-nitrogen doped carbon (TM-N/C) materials such as Fe-N_x/C and Co-N_x/C exhibit excellent catalytic activity. Nevertheless, comprehensive understanding of these TM-N/C electrocatalytic systems is still lacking, which demands extension of investigation to other TM-N/C systems (Cu, and Mn, etc.). Herein, we developed a Cu promoted nitrogen-doped carbon (Cu-N/C) *via* high temperature pyrolysis of Cu-adsorbed zeolite imidazole frameworks (Cu@ZIF-8). The Cu-N/C electrocatalyst exhibited satisfactory ORR activity with half-wave potential of 0.813 V in 0.1 M KOH electrolyte. Moreover, it also showed excellent methanol tolerance and long-term stability. The enhanced ORR electrocatalytic performance is attributed to the strong synergetic effect between Cu(II)-N ligands and Cu⁰ NPs, sufficient active sites, and fast mass transfer.

1. Introduction

The electrochemical oxygen reduction reaction (ORR) is pivotal for various electrochemical storage and conversion devices including fuel cells and metal-air batteries [1]. Though they are widely explored as superior electrocatalysts for ORR, the precious-metal-group (PMG) materials suffer from low earth abundance, high cost, and low chemical stability [2–4]. Therefore, it is highly desired to develop high-efficiency ORR electrocatalysts based on earth-abundant elements [5,6]. Recently, transitional-metal-containing nitrogen-doped carbon (TM-N/C) materials derived from zeolitic imidazolate frameworks (ZIFs) possesses large specific surface area, tunable pore structures, and abundant N species [7–10]. Rationally tailoring the coordination configuration between transition metals and nitrogen atoms can be optimized to efficiently absorb and activate oxygen molecules, which makes Fe(Co)-N_x sites superior electrocatalysts for ORR [11–15]. However, it is necessary to investigate other TM-N/C (such as Cu and Mn) in order to understand ORR mechanism in wider and deeper views.

Theoretical calculation has predicted that Cu has higher activity than other transition metals (Fe, Co and Ni, etc.) [16]. Moreover, as the material with the second highest electrical conductivity, Cu only shows

6% lower than Ag, which exhibits the potential to promote charge transfer between active sites and reactants [17,18]. Early studies of using Cu-based materials for catalyzing the ORR mainly focus on copper macrocycles with the coordinately unsaturated Cu(I)-N centers [19]. The major drawbacks of these copper macrocycles are their limited chemical and thermal stabilities, poor electrical conductivities, and low O₂ reduction activities. Recently, researchers develop an alternative route that direct pyrolysis of copper salts or nanostructures, carbon and nitrogen precursors to fabricate Cu-N/C nanostructures in an inert gas atmosphere, resulting in hybrid nanocatalysts that show enhanced stability, conductivity, and activity [17,18,20,21]. For instance, Cu@NC was synthesized by annealing the mixture of copper nitrate, sucrose, and ammonia sulfate, and it exhibited superior ORR activities with a half-wave potential ($E_{1/2}$) of 0.83 V in 0.1 M KOH electrolyte [20]. Yu et al. synthesized Cu-N-C *via* carbonizing Cu-containing in ZIF-8 and demonstrated it showed $E_{1/2}$ of -0.156 V (*vs.* SCE) and four electron transfer pathway. The resulting Cu-N-C catalyst shows excellent ORR performance [17]. Kuang and his colleagues fabricated CuCo@NC *via* a facile Cu-confined thermal conversion strategy and obtained $E_{1/2}$ of 0.884 V (*vs.* RHE) [18]. Despite these research progresses, it is worthy of extending the scope of Cu-N/C to well understand the

* Corresponding author.

E-mail address: linjian@missouri.edu (J. Lin).

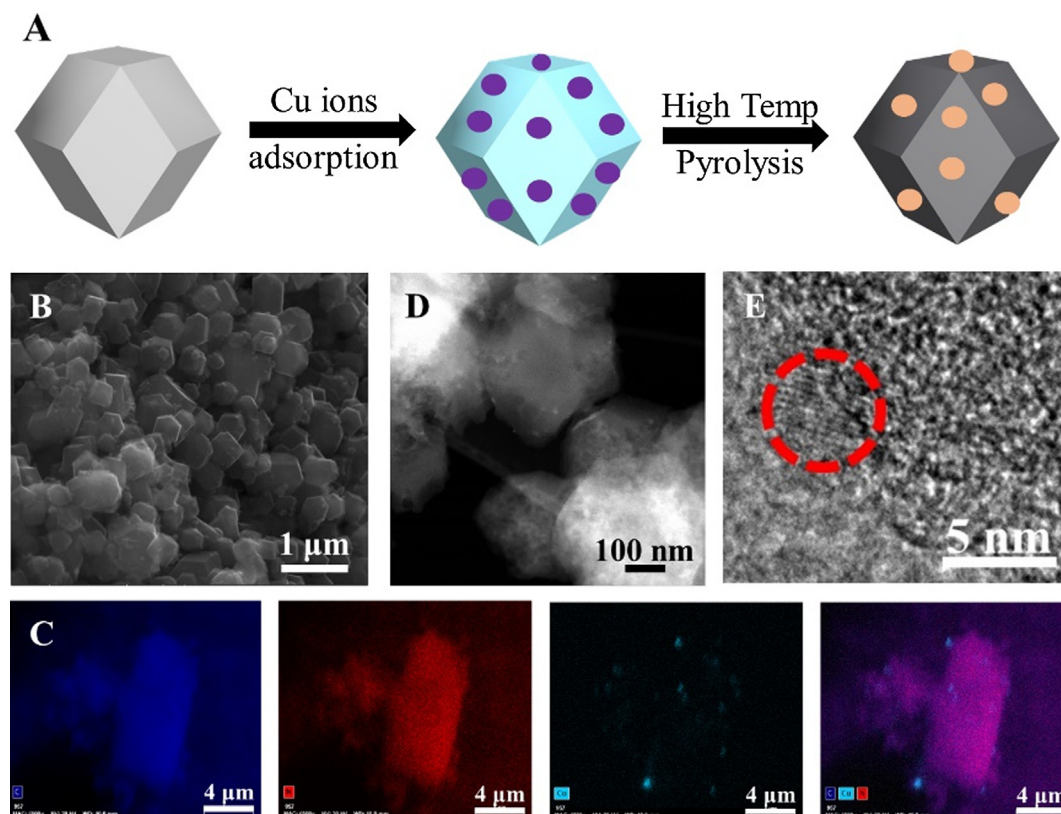


Fig. 1. (A) Schematic of fabrication procedure for Cu-N/C catalysts. (B) SEM, (C) elemental mapping image, and (D) STEM-HAADF and (E) HRTEM of Cu-N/C.

electrocatalytic mechanism.

Herein, we developed Cu promoted nitrogen-doped carbon (Cu-N/C) via high temperature pyrolysis of Cu@ZIF-8 under Ar/H₂ atmosphere. The Cu-N/C electrocatalyst exhibited satisfactory ORR activity with E_{1/2} of 0.813 V in 0.1 M KOH electrolyte, which are comparable to recently published work. Moreover, it also showed better methanol tolerance and long-term stability. This impressive ORR catalytic performance can be ascribed to the strong synergistic effect between Cu(II)-N ligands and Cu⁰ NPs, abundant active sites, and fast mass transfer.

2. Results and discussion

Cu-N/C electrocatalysts were synthesized via the high-temperature pyrolysis of Cu@ZIF-8 precursors at 1000 °C under Ar/H₂ atmosphere, as shown in Fig. 1A. Briefly, Cu(NO₃)₂ ethanol solution was slowly injected into the ZIF-8/*n*-hexane dispersion and stirred for 3 h at room temperature. Afterward, the collected powder was pyrolyzed at 1000 °C in an Ar/H₂ atmosphere and Cu-N/C electrocatalysts were obtained directly without any purification procedure. The color of samples in each preparation steps was shown in Fig. S1. During the high-temperature pyrolysis, the organic linkers transform into a nitrogen-doped carbon skeleton and free N sites are formed due to the evaporation of Zn [12,22]. Meanwhile, the adsorbed Cu ions are stabilized by the N coordination and then reduced by the surrounding carbon.

To perform these material characterizations, scanning electron microscopy (SEM) were conducted to reveal the morphology and shapes of the as-prepared Cu-N/C. In Fig. 1B and Fig. S2, both Cu-N/C and N/C retained their initial dodecahedral morphology after high temperature pyrolysis. Elemental mapping images illustrate that carbon, nitrogen, and copper are uniformly distributed in Cu-N/C (Fig. 1C). Scan transmission electron microscopy-high angle annular dark field (STEM-HAADF) image of Cu-N/C displays that Cu NPs with sizes of ~5 nm are supported on N/C (Fig. 1D). More importantly, Cu-N/C exhibits porous structures which enables more exposed active sites and fast mass

transfer. High-resolution TEM (HRTEM) image of one of the bright particles in STEM-HAADF image shows a *d* spacing of 0.21 nm, which is attributed to the (1 1 1) plane of Cu NPs (Fig. 1E).

The structural features of Cu-N/C and N/C (Fig. 2A) were investigated further using X-ray diffraction (XRD). Both Cu-N/C and N/C exhibit broad diffraction peaks at ~23.4° and 43.5°, which are assigned to amorphous and graphitic carbon, respectively [17]. For Cu-N/C, the other two sharp peaks centered at ~43.2° and 50.4° correspond to the (1 1 1) and (2 0 0) of metallic copper, indicating existence of zero valent copper (Cu⁰) [23]. Raman spectra of Cu-N/C and N/C show two main characteristic peaks at 1350 and 1596 cm⁻¹, corresponding to the D and G band, respectively (Fig. 2B). Generally, the relative intensity ratio (I_D/I_G) of D and G bands provides a meaningful index in evaluating the crystallinity degree of graphitic materials [17]. The lower I_D/I_G of Cu-N/C (1.06) compared to that of N/C (1.10) suggest they have high degree of defects.

The elemental compositions and chemical states of Cu-N/C and N/C electrocatalysts were further investigated by X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum (Fig. 2C) shows that Cu-N/C consists of C, Cu, N, and O elements, while N/C only has C, N and O elements. Fig. 2D–F show high-resolution of N 1s and Cu 2p spectra. High-resolution N 1s spectra of N/C (Fig. 2D) can be convoluted into four peaks at 398.2 eV, 400.2 eV, 401.0 eV and 403.3 eV, ascribed to pyridinic-N, pyrrolic-N, graphitic-N, and oxidized-N, respectively [17,24,25]. In the high-resolution Cu 2p spectra of Cu-N/C (Fig. 2E), the main peak at binding energy of 933.0 eV is ascribed to the Cu⁰ [26]. The shoulder peak at 934.6 eV and satellite peak at ~945.0 eV (inset of Fig. 2E) can be assigned to the Cu(II) and it is proposed to coordinate with N atoms to form Cu(II)-N bonds [27]. The content of Cu in Cu-N/C was determined to be 0.69 wt% (Table S1). High-resolution N 1s spectra of Cu-N/C also shows similar configuration to N/C, however its total N content was determined to be 1.37 wt% (Table S1), which is lower than N/C (4.35 wt%) [13]. In detail, both the total N and pyridinic-N in Cu-N/C (1.21 and 0.18 at %) are lower than those of N/C (3.80 and 1.08 at

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