Electrocatalysis

International Edition: DOI: 10.1002/anie.201503637
German Edition: DOI: 10.1002/ange.201503637

Copper-Modified Covalent Triazine Frameworks as Non-Noble-Metal Electrocatalysts for Oxygen Reduction

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Abstract: *The electrochemical oxygen reduction reaction (ORR) is an important cathode reaction of various types of fuel cells. The development of electrocatalysts composed only of abundant elements is a key goal because currently only platinum is a suitable catalyst for ORR. Herein, we synthesized copper-modified covalent triazine frameworks (CTF) hybridized with carbon nanoparticles (Cu-CTF/CPs) as efficient electrocatalysts for the ORR in neutral solutions. The ORR onset potential of the synthesized Cu-CTF/CP was 810 mV versus the reversible hydrogen electrode (RHE; pH 7), the highest reported value at neutral pH for synthetic Cu-based electrocatalysts. Cu-CTF/CP also displayed higher stability than a Cu-based molecular complex at neutral pH during the ORR, a property that was likely as a result of the covalently cross-linked structure of CTF. This work may provide a new platform for the synthesis of durable non-noble-metal electrocatalysts for various target reactions.*

Molecular oxygen is an ideal electron acceptor because of its nontoxicity, high abundance, and redox potential. Thus, the reduction of oxygen has been utilized as a cathode reaction in various types of fuel cells. Although hydrogen–oxygen fuel cells generally operate under acid or alkaline conditions, oxygen reduction reactions (ORR) in neutral solutions have recently attracted increased attention for application in bioelectrochemical systems, such as enzymatic and microbial fuel cells.[1] At present, platinum (Pt) is still the most efficient ORR catalyst. However, as Pt is scarce and expensive, the use of non-noble-metal catalysts operating in neutral solutions is desirable for developing sustainable systems.[2]

In Cu-containing oxidases, such as laccase and amine oxidases, Cu serves as the active center for the ORR.[3–5] Notably, laccase supported on a conductive substrate catalyzes electrochemical ORRs in neutral solutions with almost no over-potential,[4] suggesting that Cu may potentially have higher catalytic activity than Pt. For Cu-based enzymes, modulation of the electronic state and molecular structures of the atomic Cu active sites through coordination with amino acid residues is believed to be essential for the superior ORR catalytic activity. For this reason, numerous researchers have attempted to develop ORR electrocatalysts using organometallic complexes to mimic the coordination structure of Cu-based enzymes.[6–9] However, because such molecular electrocatalysts generally exhibit poor robustness, they are not suitable for practical applications.

Covalent triazine frameworks (CTFs) are microporous conjugated polymers linked together with 1,3,5-triazine units.[10] The following properties make CTFs potentially suitable as novel platforms for the synthesis of electrocatalysts: 1) CTFs have abundant nitrogen atoms with lone pairs for metal coordination; 2) the electronic state of coordinated metals in CTFs can be modified by the choice of the building blocks with different geometries, sizes, and reactive groups; and 3) CTFs are mechanically robust because of the covalently bonded framework. Considering these properties, we recently synthesized a Pt-atom-modified CTF hybridized with conductive carbon nanoparticles (Pt-CTF/CPs) as an ORR electrocatalyst.[11] Although Pt-CTF/CP showed high methanol tolerance, a unique property that was attributed to the atomic dispersion of the Pt atoms, the ORR activity of Pt-CTF/CP was lower than that of bulk Pt catalysts. The decrease in the ORR activity of Pt-CTF/CP compared to bulk Pt catalysts was assumed to be as a result of the excessively strong interaction between the isolated Pt atoms in Pt-CTF/CP and the intermediate oxygen species.[12,13] To overcome this limiting factor, atomically dispersed Cu^{II} species are predicted to have a more optimal adsorption energy with oxygen species than Pt, as Cu−N organometallic complexes exhibited a higher ORR activity than bulk Cu metal.[6–9] Thus, CTFs modified with individual Cu atoms are expected to have high stability and activity for the ORR. In the present work, we synthesized a Cu-modified CTF hybridized with CPs and examined the electrocatalytic activity of this novel ORR catalytic material.

CTF/CP was synthesized by polymerizing 2,6-dicyanopyridine in molten $ZnCl_2$ containing CPs.[11] The synthesized CTF/CP was then functionalized with Cu atoms using an impregnation method in $CuCl_2$ solution (for details see the Experimental Section in the Supporting Information). As no large CTF particles were evident upon inspection of transmission electron microscopic (TEM) images of CTF/CP (Figure S1 in the Supporting Information), the CTFs appeared to be well mixed with CP. Figure 1 shows a high-magnification TEM image of Cu-CTF/CP and the corresponding elemental maps (C, N, and Cu) obtained by energy dispersive X-ray (EDX) analysis. High-resolution TEM

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201503637.

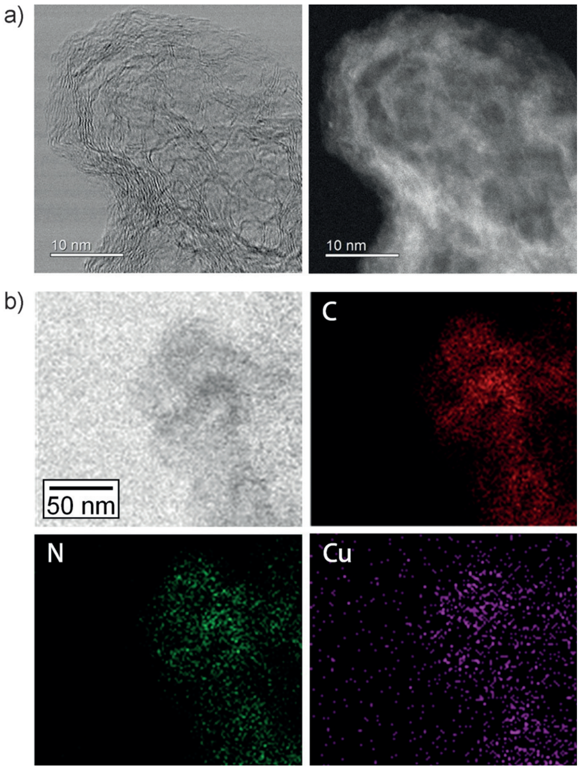

Figure 1. a) Representative high-resolution transmission electron microscopy (HR-TEM) images of Cu-CTF/CP (left) and the corresponding high-angle annular dark-field scanning image (right). b) HR-TEM image of Cu-CTF/CP and the corresponding EDX mappings for C, N, and Cu atoms. Scale bar in (a) = 10 nm. Scale bar for all images in (b) = 50 nm.

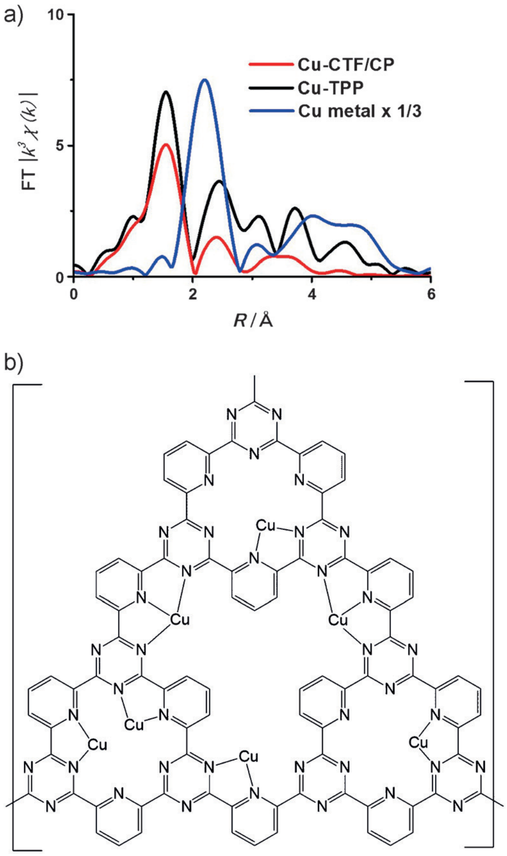

Figure 2. a) k^3-weighted Fourier transform of EXAFS spectra of the Cu K edge for Cu-CTF/CP (red), Cu-TPP (black), and Cu metal (blue). The peak intensity for Cu metal is shown at one-third of the measured values for comparison. b) Schematic representation of Cu-CTF/CP.

analysis (Figure 1 a) revealed that no metal nanoparticles (> 1 nm) were formed on Cu-CTF/CP. As shown in the EDX maps (Figure 1 b), Cu and N atoms were homogeneously distributed on the CPs. These results demonstrated that the CPs were almost fully covered with CTFs, and that Cu atoms were uniformly distributed throughout the CTF/CPs material.

We also measured the nitrogen adsorption–desorption isotherms of Cu-CTF/CP to evaluate its porosity and surface area (Figure S2). Cu-CTF/CP was found to have a hierarchical pore system composed of micro- and mesopores with pore diameters of 1–2 and 2.5–4 nm, respectively. This pore size distribution was essentially consistent with the reported values of CTFs that were prepared using monomers of 2,6-dicyanopyridine.[14] The BET surface area was estimated to be 491 $m^2 g^{-1}$.

We next performed a detailed characterization of the synthesized Cu-CTF/CP. The surface elemental concentrations of Cu-CTF/CP and CTF/CP, as determined by X-ray photoelectron spectroscopy (XPS), are summarized in Table S1. Cu and N atoms were clearly detected in Cu-CTF/CP, whereas no Cu species were found on CPs that were treated with $CuCl_2$ solution in a similar manner to Cu-CTF/CP. This result indicated that the Cu atoms were anchored on the CTF by coordination with N atoms.

The formation of Cu–N bonds in Cu-CTF/CP was directly confirmed using extended X-ray absorption fine structure (EXAFS) analysis. Fourier transformations of k^3-weighted EXAFS oscillations for Cu-CTF/CP are shown in Figure 2 a. A peak at 1.6 Å, corresponding to the Cu–N bond, was clearly detected. However, peaks corresponding to Cu–Cu (2.2 Å) and Cu–O–Cu bonds (2.7 Å) were not detected.[15] The coordination number of the Cu species could also be determined from the EXAFS spectra. The intensity of the Cu–N peak for Cu-CTF/CPs at 1.6 Å was approximately two thirds of that for Cu-5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (Cu-TPP), suggesting that the first coordination number for Cu-CTF/CP is smaller than four (Cu-TPP has a coordination number of 4). We also analyzed the Cu 2p XPS spectrum to obtain information on the electronic state of the Cu atoms in Cu-CTF/CP (Figure S3). The Cu $2p_{1/2}$ peak (955 eV) in the spectrum can be assigned to the Cu^{II} valence state, and almost no peaks corresponding to metallic Cu were detected.[16] The X-ray absorption near-edge structure (XANES) of Cu-K edge also indicated that the Cu^{II} valence state is dominant in Cu-CTF/CP (Figure S4). Taken together, the TEM, nitrogen isotherms, EXAFS, and XPS results indicate that the Cu atoms in Cu-CTF/CP were individually isolated from each other and have an unsaturated first coordination sphere containing N atoms in the pores of CTF, as shown in Figure 2 b.

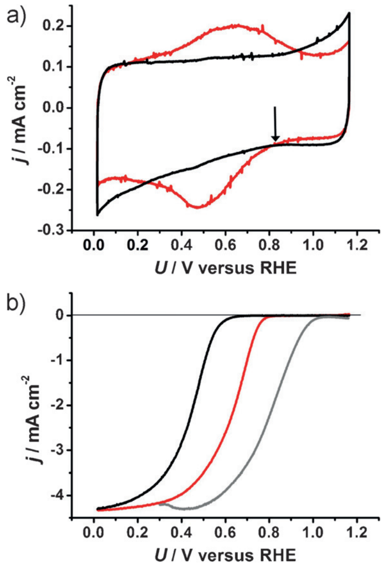

Figure 3. Current density (j) versus potential (U) curves under a) argon and b) oxygen for Cu-CTF/CP (red), CTF/CP (black), and 20 wt% Pt/C (gray) in phosphate buffer solution (pH 7). Scan rate = 10 mV s^{-1}. Rotational speed = 1500 rpm. The arrow indicates the potential at which the Cu^{II} species are reduced.

To examine the electrocatalytic ORR activity of Cu-CTF/CP, current density (j) versus potential (U) curves for Cu-CTF/CP and CTF/CP were measured (Figure 3). Although no redox peaks for CTF/CP (black curve) were detected in Ar-saturated phosphate buffer solution, a single pair of redox peaks with a mid-point potential of 0.57 V versus the reversible hydrogen electrode (RHE), which were ascribed to the Cu$^{I/II}$ redox couple, was detected for Cu-CTF/CP (red curve; Figure 3 a, see also Figure S5). When the electrolyte was saturated with dissolved oxygen, a catalytic ORR current (Figure 3 b) and the corresponding ring current assignable to hydrogen peroxide (H_2O_2) oxidation (Figure S6a) were detected. As shown in Figure 3 b, the ORR onset potential for Cu-CTF/CP was 0.81 V (versus RHE), a value that is 0.13 V higher than that for CTF/CP, indicating that the Cu in Cu-CTF/CP enhanced the ORR catalytic activity. To our knowledge, the ORR onset potential (0.81 V) determined for Cu-CTF/CP is higher than that reported to date for other Cu-based electrocatalysts,[6–9] although the ORR activity is still lower than that of Pt/C (U_{onset} for Pt/C was 1.04 V versus RHE). The electron number for the ORR estimated from the yield of H_2O_2 was in the range of 3.75–3.95 in all examined potential regions (Figure S6b). It was also confirmed that Cu-CTF/CP showed efficient ORR activity with an onset-potential of 0.91 V versus RHE in alkaline solution (see Figure S7).[6,9]

We next discuss the properties of the active species for the ORR based on the electrochemical characterizations. It is important to note that the ORR onset potential (0.81 V; Figure 3 b) at pH 7 was similar to the potential at which Cu^{II} is converted into Cu^{I} (as indicated by the arrow in Figure 3 a). Therefore, we compared the Cu$^{I/II}$ redox potentials with the ORR onset potential at various pH values, as shown in Figure S8. The ORR onset potential increased linearly by 23.5 mV/pH unit, a finding that is in good agreement with the change of the Cu$^{I/II}$ redox potential (23.4 mV/pH). These results indicate that the ORR was mediated by the Cu^{I} species in Cu-CTF/CP. Consistent with this finding, several studies have reported that Cu^{I} species readily react with dioxygen to form copper–dioxygen adducts (that is, $Cu^{I} + O_2 \rightarrow CuO_2$).[5,8b,17]

Let us consider why the Cu-CTF/CP exhibited higher ORR electrocatalytic activity than the other reported Cu-based catalysts. First, as described above, Cu^{I} species are essential for the ORR. In Cu-CTF/CP, the potential of Cu$^{I/II}$ (0.57 V versus RHE) is one of the highest reported values among Cu–N-based complexes in neutral solutions.[7–9] Metal cations within the polypeptide structure of enzymes have higher redox potential than those in aqueous solutions because a cation with a lower valence state is relatively more stable than that with a higher valence state in low dielectric conditions, such as organic frameworks.[3,18] Therefore, we speculate that the low dielectric environment in the pores of CTF stabilizes Cu^{I} species, resulting in a positive shift of the Cu$^{I/II}$ potential and an increase in the ORR onset potential.

Another possible explanation for the higher ORR activity of Cu-CTF/CP is that the coordinatively unsaturated nature of the Cu centers allows them to strongly interact with molecular oxygen, thereby facilitating the breaking of O–O bonds.[9,19] In general, the interaction of d^{10} Cu-based complexes with oxygen molecules is weaker than that of the other 3d metal-based complexes, as oxygen-binding energy depends largely on vacancies in the d orbitals of the metal center. Consistent with this property, Cu–N4 macrocycles (Cu porphyrins or Cu phthalocyanines) show little ORR activity, whereas Fe–N4 and Co–N4 macrocycles function as efficient electrocatalysts.[9,13,20] However, because the coordinatively unsaturated Cu atoms of Cu-CTF/CP were relatively stable, as demonstrated by the EXAFS spectra (Figure 2 a), they are expected to have more accessible d orbitals and less steric hindrance than those in coordinatively saturated Cu-based complexes, such as Cu–N4 macrocycles.[12,13,21] To confirm this assumption, we calculated the adsorption energies of the oxygen atom (ΔE_{O}) as an indicator of binding strength with oxygen species (such as dioxygen molecules) using the density functional theory (DFT) method.[22] The ΔE_{O} of Cu-CTF was only 0.2 eV smaller than the ΔE_{O} of Pt metal, whereas the ΔE_{O} of Cu–N4 macrocycles was 1.7 eV lower than that of Pt metal (for details of the DFT calculations, see the Supporting Information). The DFT results suggest that the chemical interaction between oxygen molecules and the Cu atoms supported by CTF is sufficiently strong to enhance the ORR activity. Further studies aimed at determining the detailed molecular structure and ORR mechanism of Cu-CTF/CP are currently in progress in our laboratory.

Finally, the stability of Cu-CTF/CP during the ORR was evaluated under continuous cycles of cyclic voltammetry (CV). For comparison, a Cu-based organometallic complex, Cu-3,5-diamino-1,2,4-triazole (Cu-Hdatrz),[6] which shows a similar ORR onset potential to Cu-CTF/CP, was also tested. As shown in Figure 4 b, the current density for Cu-Hdatrz in the kinetic region (0.6 V versus RHE) decreased by

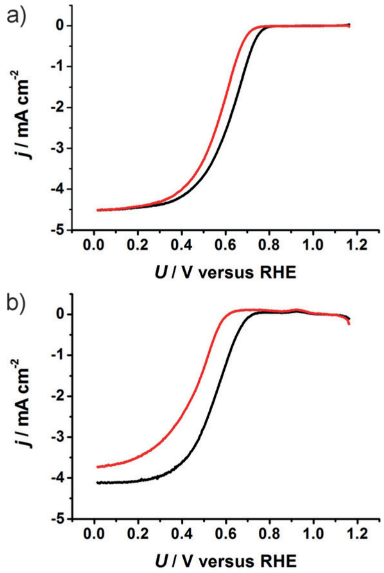

Figure 4. *j* versus *U* curves for a) Cu-CTF/CP and b) Cu-Hdatrz before (black trace) and after (red trace) 1000 CV cycles in phosphate buffer solution (pH 7) saturated with dissolved oxygen.

94% after 1000 CV cycles. In contrast, the current density of Cu-CTF/CP decreased by only 32% after the CV cycling, clearly indicating that Cu-CTF/CP had superior stability to Cu-Hdatrz. The high stability of Cu-CTF/CP can be attributed to its insolubility and resistance to oxidative decomposition. Notably, the CTF framework is completely insoluble in common solvents, including water, because of its highly cross-linked structure,[23] whereas small organic complexes have limited solubility in these solvents. Therefore, the desorption of the CTF layers from CPs (that is, from the electrode) was relatively suppressed. Furthermore, thermogravimetric analyses in air showed that Cu-CTF/CP and Cu-Hdatrz began to decompose at 478°C and 420°C (20% weight loss), respectively, indicating that CTF-based materials have higher resistance to oxidative decomposition than Cu-Hdatrz (Figure S9). Although the stability of Cu-CTF/CP is still lower than that of Pt/C (Figure S10), we anticipate that higher stability can be achieved by fine-tuning the frameworks.

In conclusion, we successfully functionalized the porous structure of CTF/CP with Cu atoms and demonstrated that the synthesized material functions as an efficient ORR electrocatalyst in neutral solution. The onset potential of Cu-CTF/CP for the ORR was the highest value among synthetic Cu-based ORR catalysts reported to date. Additionally, Cu-CTF/CP exhibited higher stability compared to other Cu-based organometallic catalysts as a result of the rigid cross-linked network of covalent bonds in CTFs. Notably, this is the first report of a CTF modified with a non-noble metal functioning as an electrocatalyst. Our findings suggest that large increases in ORR activity for Cu-based CTF materials are achievable through careful choice of the underlying framework and that these materials have the potential to serve as efficient cathodic catalysts in fuel cells. Additionally, because of their high catalytic activities and durability, non-noble-metal-modified CTF-based electrocatalysts may also be applicable for various useful reactions, such as carbon dioxide reduction and nitrate reduction.

Acknowledgements

This research was supported by the PRESTO Program of the Japan Science and Technology Agency (JST). Synchrotron radiation experiments were performed using the BL01B1 Beamline of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; Proposal Numbers 2013A1598, 2014B1252, and 2015A1302). We thank Dr T. Ina for providing technical support with the XAFS measurements at SPring-8.

Keywords: copper · electrocatalysis · fuel cells · nanostructures · oxygen reduction

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 11068–11072
Angew. Chem. **2015**, *127*, 11220–11224

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Received: April 21, 2015
Revised: June 22, 2015