Development of Robust Electrocatalysts Comprising Single-atom Sites with Designed Coordination Environments

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ABSTRACT

Single-atom catalysts (SACs), which are composed of singly isolated metal sites and heterogeneous supports, have recently attracted intensive attention as a novel category of electrocatalysts. SACs can not only ultimately reduce the loading amount of noble metals but also exhibit unique reaction activity and selectivity for many reactions. However, the design flexibility of conventional supports of SACs, including nanocarbons and metal oxides, is poor. Therefore, designing coordination environments of metal centers in SACs, which are one of the most significant parameters governing their electrocatalytic properties, has been challenging. This review outlines the synthesis of two kinds of SACs with defined coordination structures and their unique electrocatalytic activities. First, graphenes doped with metals (Fe, Cu, and Ni) and nitrogen atoms, which were prepared by a short-duration heat treatment, function as efficient electrocatalysts for oxygen reduction reactions and CO₂ reduction reactions. Second, metal-doped covalent organic frameworks, which are a class of porous conjugated polymers, exhibit unique electrocatalytic selectivity compared with bulk metals.

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Keywords : Single-atom Electrocatalyst, Covalent Organic Frameworks, Metal-nitrogen-doped Graphenes

1. Introduction

Electrochemical devices for applications related to solving energy and environmental issues, such as electrochemical energy storage,^{1,2} artificial photosynthesis,^{3,4} and pollutant degradation,^{5,6} are becoming increasingly vital because they can operate under mild conditions without toxic reactants. Electrocatalysts are one of the most important components governing the activity and selectivity of such electrochemical devices. Existing electrocatalysts are classified

into two broad categories: molecular-based catalysts (e.g., organo-metallics and organic molecules) and inorganic bulk materials (e.g., metal and metal oxide nanoparticles and nanocarbons). The most important advantage of molecular-based catalysts is their high design flexibility, which enables the efficient modulation of the geometrical and electronic structures of metal centers. However, the fragility of these materials remains a substantial problem. By contrast, although inorganic bulk materials exhibit high durability, their design flexibility is relatively poor. Thus, imparting electrocatalysts with both design flexibility and robustness is an essential and challenging task.

Single-atom catalysts (SACs) might simultaneously satisfy the two aforementioned requirements. SACs are composed of singly isolated metal sites and heterogeneous and robust conductive supports.^{7–12} Thus, SACs should be as relatively stable as inorganic catalysts. In addition, when highly designable materials are used as supports for SACs, the coordination environments of the metal centers become highly flexible, similar to homogeneous organo-metallic catalysts, which likely leads to unique catalytic activity and selectivity. However, the coordination structure of single-metal sites on conventional supports, such as nanocarbons and metal oxides, is limited because of the low design flexibility of the supports. Given this background information, we have developed two novel approaches to attaining designable coordination structures of

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Figure 1. Schematic of the metal center with heat-treatment duration used to synthesize *M*-N-Gr. Reproduced with permission from Ref. 22. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA.

single-atom sites in electrocatalysts: (i) a short-duration heat treatment of graphene oxides in the presence of metal complexes and (ii) the use of covalent organic frameworks (COFs) as supports. The present paper details our recent studies on SAC electrocatalysts with unique catalytic properties.

2. Metal–nitrogen-doped Graphenes

2.1 Oxygen reduction reactions catalyzed by Fe–N- or Cu–N-doped graphenes

Functioning as the cathode reaction in various types of fuel cells, the oxygen reduction reaction (ORR) is a critical process. Pt is used as a practical ORR electrocatalyst; however, because Pt is rare and therefore expensive, interest in a non-noble-metal replacement for Pt is increasing. One promising class of candidates for such catalysts is carbon-based materials synthesized by the pyrolysis of organic substances containing nitrogen.^{13–20} In this method, metals such as Co and Fe are needed during the pyrolysis. The aggregated metal nanoparticles catalyze graphitization. The resultant carbon materials containing metals and nitrogen exhibit ORR activity. The overpotential for these catalysts is 100–300 mV greater than that for the standard Pt/C catalysts. In general, the graphitization process requires a high-temperature heat treatment longer than 1 h. However, this long-period heat treatment leads to the desorption of the dopants and to the formation of metal aggregates such as metal nanoparticles or metal carbides; both of which decrease the ORR electrocatalytic activity.

In the present study, we developed a method for the instantaneous synthesis of graphene doped with N and Fe (Fe–N–Gr) by using graphene oxides (GOs) as a precursor.^{21,22} Although the existing pyrolysis method requires an extended heat treatment to form *sp*² carbon structures, as previously mentioned, the use of GOs as the precursor enables the heat-treatment time to be drastically shortened. In the proposed method, GOs prepared by the modified Hummers method are quickly placed under an Ar atmosphere at 900 °C, along with N and Fe sources; the sample is then maintained at 900 °C under Ar for just 45 s (Fig. 1).

The ORR activity of the resultant Fe–N–Gr in 0.5 M H₂SO₄ solution is shown in Fig. 2a. The onset potential of our Fe–N–Gr catalyst for the ORR was approximately 0.85 V vs. a reversible hydrogen electrode (RHE).^{21,22} Notably, the ORR activity is much lower for Fe- and N-graphenes than for Fe–N–Gr. Thus, codoping of

Fe and N is necessary to achieve enhanced catalytic activity. We have confirmed that, when the heat-treatment period is extended, the Fe–N coordination bond is broken and the electron numbers for the ORR decrease (Fig. 2b).

The aforementioned method was also applied to the synthesis of Cu–N–Gr as an ORR catalyst using 3,5-diamino-1,2,4-triazole (Cu-DAT) as the precursor.²³ The resultant Cu-based catalysts exhibited high activity toward the ORR, with an onset potential of 790 mV in a neutral solution (Fig. 2c). Importantly, the catalyst exhibited greater stability than Cu-DAT without heat treatment because of the anchoring of active Cu-sites into the graphene substrate via the Cu–N coordination bonds (Figs. 2c and 2d).

2.2 CO₂ reduction to CO by Ni–N-doped graphene

Numerous studies on developing organometallic-based carbon dioxide (CO₂) reduction electrocatalysts have been reported. Nickel-1,4,8,11-tetraazacyclotetradecane (Ni-cyclam) and its derivatives have been reported to efficiently reduce CO₂ to carbon monoxide (CO) with almost no hydrogen evolution, which is a reaction that competes with the CO₂ reduction reaction (CRR).^{24,25} Given that carbon-based catalysts containing nitrogen and metal atoms catalysts are more stable than the corresponding organometallics, we expected the Ni–N coordination sites in an *sp*² carbon matrix to exhibit both efficient CO₂ reduction activity and high robustness. Although Varela et al. have reported that single Fe–N- or Mn–N-doped carbon-based materials catalyze the reduction of CO₂ to CO,^{26,27} our work was the first report of Ni–N-doped carbon materials. This scarcity of information related to Ni–N-doped carbon materials is likely attributable to Ni–N bonds being more fragile under high-temperature heat treatment conditions than Fe–N and Co–N bonds.^{28,29} We therefore used the short heat treatment to synthesize Ni/N–Gr as a CRR electrocatalyst (Fig. 3a).³⁰

Figures 3b through 3g show current density (*j*) vs. potential (*U*) curves and faradaic efficiencies (FEs) of CO production for Ni/N–Gr, a Ni metal electrode, and N–Gr. The increases in the onset potential and cathodic current by the addition of CO₂ were observed for Ni/N–Gr, whereas the current clearly decreased in the presence of CO₂ for a Ni-metal electrode and N–Gr. In addition, with Ni/N–Gr, the FE of CO is greater than 90 % in the potential range from –0.7 to –0.9 V vs. RHE. We note here that the only other main product is H₂ over the entire examined potential region.³⁰ At more negative potentials, the hydrogen evolution reaction (HER) gradual-

Figure 2. (a) j vs. U curves for Fe–N–Gr, Fe–Gr, and N–Gr. Reproduced with permission from Ref. 21. 2012 The Royal Society of Chemistry. (b) Electron numbers for the Fe–N–Gr after heat treatments for 45 s, 5 min, and 20 min. Reproduced with permission from Ref. 22. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA. (c, d) j vs. U curves for Cu-DAT/graphene (c) with and (d) without the short-duration heat treatment before (black) and after ((c) red, (d) blue) 1000 CV cycles. Electrolytes: (a, b) 0.5 M H₂SO₄ (pH 0.33) and (c, d) 0.1 M phosphate buffer solution (pH 7.0); rotation rate: 1500 rpm; scan rate: 10 mV s⁻¹. Reproduced with permission from Elsevier from Ref. 23.

ly became dominant. By contrast, the FEs(CO) of N–Gr and the Ni-metal electrode were negligible in all of the examined potential regions, indicating that both Ni and N are necessary for high CRR catalytic activity. Importantly, we also confirmed that Ni/N–Gr exhibited excellent stability over a prolonged electrolysis time.

3. Covalent Organic Frameworks as Supports for Single-metal Sites

COFs, which are constructed with organic building blocks linked by strong covalent bonds, are promising candidates for catalysts or catalytic supports because of their unique porous structure, robustness, and flexibility of design.^{31–34} Importantly, COFs have abundant heteroatoms such as N, O, and S in their pores; thus, they can strongly immobilize various single-metal atoms by forming coordination bonds with these heteroatoms. On the basis of these properties, COFs are considered as ideal supports for SACs. However, the inherent electronic conductivity of COF-based materials is low; thus, COF-based materials exhibit low electrocatalytic activity. Our group has overcome this problem by polymerizing COFs onto conductive carbon nanoparticles (CPs) to form hybrid materials.³⁵ The resultant COFs hybridized with CPs can support a wide variety of single-metal atoms via coordination bonds. Interestingly, these metal-doped COFs (*M*-COFs) exhibit electrocatalytic functions that depend on the metal species (Fig. 4). In this section, we describe our recent work related to SAC-doped COFs.

3.1 Oxygen-tolerant hydrogen oxidation reaction by single-Pt-doped CTFs

Pt is the only practical catalyst for numerous important reactions, including the hydrogen–oxygen fuel cell reaction and the water–gas

shift reaction, which are necessary for various environmentally friendly and energy conserving applications. However, because Pt is scarce and expensive, our group has focused on using Pt-SACs to reduce the use of Pt. Moreover, Pt-SACs are expected to exhibit unique reaction selectivity that cannot be achieved with bulk metals or metal nanoclusters. However, Pt-SACs are easily aggregated under electrochemical conditions because of their high surface energy.⁷ We therefore focused on triazine-linked COFs (i.e., covalent triazine frameworks (CTFs)) as a support for Pt-SACs because the CTFs have abundant N atoms in their pores to immobilize single Pt atoms. Pt-modified CTFs (Pt-CTFs) were synthesized by the polymerization of 2,6-dicyanopyridine in the presence of carbon nanoparticles and the impregnation of Pt into K₂[PtCl₄] solution was carried out.^{35,36} Figures 5a and 5b show the Pt L₃-edge extended X-ray absorption fine structure (EXAFS) spectrum and a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of 0.29 wt% Pt-CTF. The peak corresponding to Pt–Pt bonds at 2.6 Å is not observed in the EXAFS spectra of the Pt-CTF. In the HAADF-STEM image, bright spots corresponding to Pt atoms are uniformly dispersed throughout Pt-CTF, whereas almost no Pt nanoparticles are observed. These results indicated that Pt atoms in the Pt-CTF are singly isolated.

We applied Pt-CTF to the hydrogen oxidation reaction, which is a key half-reaction in polymer electrolyte fuel cells (PEFCs). The j vs. U curves obtained with the Pt-CTF in an acidic electrolyte with and without dissolved hydrogen using rotating-disk electrodes (Fig. 6a) clearly indicate that Pt-CTF efficiently catalyzed the hydrogen oxidation reaction (HOR).³⁶ The EXAFS spectra and HAADF-STEM image showed that almost all of the Pt atoms in the Pt-CTF were still singly isolated even after the HOR electrolysis, indicating that single Pt atoms served as the catalytic center for the HOR.

Figure 3. (a) Schematic of CO₂ reduction to CO by Ni/N-Gr. Cyclic voltammograms of (b) Ni/N-Gr, (c) Ni foil, and (d) N-Gr in CO₂-saturated 0.1 M KHCO₃ and Ar-saturated 0.1 M KH₂PO₄/K₂HPO₄ (pH = 6.8) at 10 mV s⁻¹, and FEs for the reduction products generated by (e) Ni/N-Gr, (f) Ni foil, and (g) N-Gr. Reproduced with permission from Ref. 30. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.

These results are the first demonstration of the application of Pt-SACs to HOR electrocatalysis.

We subsequently loaded our Pt-CTF onto a PEFC device as the anode catalyst. A membrane electrode assembly (MEA) with 2.8 wt% Pt-CTF (0.020 mg_{Pt} cm⁻²) or 20 wt% Pt/C (0.10 mg_{Pt} cm⁻²) as the anode and 47 wt% Pt/C as the cathode catalyst was fabricated.³⁶ The obtained j - U curves (solid lines) and j -power density curves are shown in Fig. 6b. Notably, although the amount of Pt in the Pt-CTF anode was five times lower than that in the Pt/C anode, the power output with the Pt-CTF anode was almost equal to that with the Pt/C anode because the number of electrochemically active Pt atoms on the Pt-CTF was much larger than that on the Pt/C since the Pt was in single-atom form.

The Pt-SAC also exhibited an oxygen tolerance during the HOR. Figure 6c shows the change in the HOR current at 0.6 V vs. RHE

for Pt-CTF and conventional Pt/C catalysts. These two catalysts showed comparable HOR currents under pure H₂ gas. However, for the Pt/C catalysts, the polarity of the current shifted from anodic to cathodic upon the O₂ addition because the large cathodic ORR current overlapped with the HOR; by contrast, Pt-CTF showed little change in the HOR current upon the introduction of O₂.³⁶ These results clearly show that Pt-CTF exhibited high oxygen tolerance.

The ORR pathway through the end-on adsorption of O₂ molecules on a Pt atom is known to require a higher activation energy than the pathway involving bridge-type adsorption.³⁷ Because only the reactions via the end-on pathway can proceed on single Pt atoms, Pt-CTF reasonably exhibited lower ORR activity than Pt/C. Air contaminates fuel chambers, and the ORR proceeds on conventional Pt/C catalysts during PEFC startup,³⁸ leading to degradation of the carbon particles onto the oxygen chamber (i.e., at

Figure 4. Various electrocatalytic functions of metal-doped CTF/carbon nanoparticle hybrids. (In the left image, brown and white balls are C and N atoms of CTF framework, respectively. A pale honeycomb structure represents the sp^2 structure of carbon nanoparticles.)

Figure 5. (a) Fourier transformations of k^3 -weighted Pt L_3 -edge EXAFS oscillations and (b) a HAADF-STEM image of 0.29 wt% Pt-COF. Reproduced with permission from Ref. 36. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.

the cathode). Thus, the O_2 tolerance is a quite important for the anode of a PEFC.

In addition to an O_2 -tolerant HOR, the Pt-CTFs also show various unique electrocatalytic selectivities.^{35,39–44} For example, although the ORR activity of Pt-CTF is not as promising as its HOR activity, it exhibits excellent methanol tolerance during the ORR, which is an attractive property for anode catalysts used in direct

methanol fuel cells.³⁵ Pt-CTF was also inactive toward the nitrate reduction reaction, which is facilitated by bulk Pt metal. The unique selectivity of Pt-CTF, which was attributed to the atomic dispersion of Pt atoms, enables the use of low-purity substrates for electrolysis.

3.2 Oxygen reduction reaction by Cu-doped CTFs

In Cu-containing enzymes, such as bilirubin oxidase and laccase, Cu serves as the active center for the ORR. In particular, multicopper oxidases are known to catalyze the electrochemical ORR in neutral solutions with almost no overpotential, indicating that Cu could potentially exhibit catalytic activity superior to that of Pt.^{45,46} However, artificial Cu macrocyclic compounds (Cu-N4) such as Cu-porphyrin and Cu-phthalocyanine exhibit almost no ORR activity. Thorseth et al. reported that the binding strength between Cu sites in Cu-N4 and O_2 molecules is too weak to activate O–O bonds, resulting in poor ORR activity.⁴⁷ One of the critical factors affecting the binding strength between metal centers and intermediates or substrates is the coordination structure, especially the coordination number (CN). Our group and others have demonstrated using first-principles calculations that the metal centers with a lower CN generally adsorb various reaction intermediates more strongly than those with a higher CN.^{48–50} Therefore, low-CN Cu sites might be active toward the ORR. Although coordinatively unsaturated metal sites are generally unstable, the rigid porous framework of CTF is expected to stabilize open-coordination single-metal sites. Therefore, we prepared a Cu-doped CTF (Fig. 7a) and investigated its electrocatalytic ORR activity.^{51,52}

Figure 7b shows the EXAFS spectra of Cu-CTF (0.6 at% Cu). A peak at 0.16 nm corresponding to the Cu–N bond was observed, whereas peaks corresponding to Cu–Cu (0.22 nm) and Cu–O–Cu bonds (0.27 nm) were not detected, indicating Cu atoms in Cu-CTF were single isolated atoms. Figures 7c and 7d show j vs. U curves for Cu-CTF and CTF in neutral solutions and without and with O_2 , respectively. Although no redox peaks were observed for the CTF in Ar-saturated phosphate buffer solution, a single pair of redox peaks with a midpoint potential of 0.57 V vs. RHE was detected in the curves for Cu-CTF, which was ascribed to the Cu(II)/Cu(I) redox couple. The ORR onset potential for Cu-CTF was 0.81 V vs. RHE, as shown in Fig. 7d, and was 0.13 V higher than that for CTF, indicating that the Cu in Cu-CTF can exhibit catalytic activity toward the ORR.^{51,52} Notably, the ORR onset potential is consistent with the potential at which Cu(II) was converted to Cu(I), suggesting that the ORR was mediated by the Cu(I) species. The ORR onset potential (0.81 V vs. RHE) is one of the highest values reported for a synthetic Cu-based ORR catalyst. On the basis of the curve fitting of the EXAFS spectrum (Fig. 7a), the CN of the Cu site in Cu-CTF was calculated to be 3.4, which is lower than that in Cu

Figure 6. (a) j vs. U curves for 0.29 wt% Pt-CTF and CTF in H_2 -saturated 0.1 M $HClO_4$. Scan rate: 5 mV s^{-1} ; rotational rate: 2500 rpm. (b) Fuel cell output of membrane electrode assemblies. The anodes prepared with (red) 2.8 wt% Pt-CTF and (blue) 20 wt% Pt/C were loaded with 0.020 and 0.10 $\text{mg}_{\text{Pt}}\text{ cm}^{-2}$, respectively. (c) Chronoamperometric curves (solid line) 2.8 wt% Pt-CTF and (dashed line) 20 wt% Pt/C in 0.1 M $HClO_4$ at +0.6 V vs. RHE. The input gas was changed at 600 s (indicated by the arrow) from pure H_2 to a mixed gas consisting of H_2 and O_2 ($H_2:O_2 = 1:1$). Reproduced with permission from Ref. 36. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.

Figure 7. (a) Schematic of the Cu-CTF. (b) Fourier transformations of k^3 -weighted Cu K-edge EXAFS oscillations for Cu-CTF (red), Cu-TPP (black), and Cu metal (blue). (c, d) j vs. U curves under (c) Ar and (d) O_2 for Cu-CTF (red) and Cu-TPP (black) in phosphate buffer solution (pH 7). Reproduced with permission from Ref. 51. Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA.

macrocycles.^{40,48,53–55} Thus, as expected, the unsaturated coordination structure of Cu sites in Cu-CTF might strongly bind O_2 molecules, resulting in high ORR activity. The other important aspect of Cu-CTF is its high stability compared with that of Cu-based organometallic catalysts due to the rigid cross-linked covalent bonds in CTFs.

3.3 CO_2 reduction reaction by Ni-doped CTFs

We extended the application of *M*-CTFs to electrocatalysis of the CRR to CO. In general, Co- or Fe-based macrocycles are known to exhibit effective activity toward CO_2 reduction to CO.^{56,57} In contrast, Ni- or Cu-based macrocycles show inferior CO generation activity because of excessively weak adsorption with COOH, which is the key intermediate for CO.⁵⁶ Given that the adsorption energy of O_2 on Cu-CTF is larger than that on Cu-porphyrin, as previously described, we expected the unsaturated metal centers in CTFs to strongly interact with COOH. That is, CTFs may improve the performance of metal species which had been thought to exhibit no CRR catalytic activity. We therefore synthesized CTFs doped with 3d metal atoms (Co, Ni, and Cu) as electrocatalysts for CRRs.

EXAFS analysis confirmed that the obtained Ni-CTFs (CN = 3.4) and Co-CTF (CN = 3.2) have an unsaturated coordination structure in a similar manner with Cu-CTF (see section 3.2).⁵⁸ The potential dependences of the FEs for CO formation for *M*-CTFs and *M*-TPPs in neutral solutions are shown in Figs. 8a and 8b, respectively. Only Co-TPP exhibited CRR activity in *M*-TPPs; by contrast, not only Co-CTF but Ni-CTF effectively reduced CO_2 to CO. Ni-CTF exhibited the highest activity toward CO formation, with an FE exceeding 90 % at -0.8 to -0.9 V vs. RHE.^{58,59} Notably, H_2 was the other major product in all cases.

We subsequently studied the origin of the differences in the activities of the *M*-CTF and *M*-TPP using density functional theory (DFT) calculations. Figures 8c and 8d show free-energy diagrams for the conversion of CO_2 to CO on *M*-TPP and *M*-CTF. The overall

reaction pathway on the Co-TPP is exergonic, whereas the step to form the adsorbed COOH (COOH^*) is an endothermic reaction for the Cu- or Ni-TPPs. In contrast to *M*-TPPs, not only Co-CTF but also Ni-CTF exhibited exergonic COOH^* formation (Fig. 8d), which corresponds to their electrocatalytic activities (Fig. 8b). The low energy barrier to the formation of COOH^* for Ni-CTF resulted from the unsaturated coordination structures of metal centers in CTFs.⁵⁸

4. Conclusion

This comprehensive article presented an overview of our recent studies on robust heterogeneous electrocatalysts comprising single-atom sites with designed coordination structures. Molecular structures of metal precursors were retained in the resultant catalysts by the short-duration heat treatment of mixtures of graphene oxides and metal complexes. The obtained *M*-N-Grs exhibit both high catalytic activity and high durability for the ORR and CRR. In the case of SAC-COFs, because the electronic and geometric structures of the COFs can be modified at will due to the choice of the building blocks, coordination structures of SACs, such as CN and neighboring atoms, are easily tuned. Therefore, we anticipate that single-atom active sites with a designed coordination structure will be a new platform for heterogeneous electrocatalysts for various useful reactions. As our SACs feature both high stability and high design flexibility, they are expected to be loaded into various useful systems such as artificial photosynthesis systems and chemical batteries.

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Figure 8. (a, b) The faradaic efficiencies for CO production on (a) *M*-TPPs and (b) *M*-CTFs in a $KHCO_3$ electrolyte (saturated with CO_2) at pH 6.8. (c, d) Free-energy diagrams of the CO generation for (c) *M*-TPPs and (d) *M*-CTFs at (pale lines) 0 V and (dark lines) -0.87 V vs. computational hydrogen electrode. Reproduced from Ref. 58 under the CC BY 3.0 license.

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