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**Heat-treated 3,5-diamino-1,2,4-triazole/graphene hybrid functions as an oxygen
reduction electrocatalyst with high activity and stability**

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Abstract

We synthesized a novel copper-based oxygen reduction electrocatalyst by heat treating a mixture of reduced graphene oxides and a copper complex of 3,5-diamino-1,2,4-triazole at 900 °C for only 45 s. Extended X-ray absorption fine structure and X-ray photoelectron spectroscopy analyses of the synthesized catalyst revealed that the nitrogen (N) atoms coordinated to copper (Cu) atoms were doped into the *sp*² networks of graphene. In neutral solutions, the catalyst exhibited efficient electrocatalytic activity for oxygen reduction, with an onset potential of 790 mV. More importantly, the catalyst possesses high stability due to the anchoring of active Cu-sites into the graphene substrate via the Cu-N coordination bonds.

Keywords:

Copper, Electrocatalyst, Graphene, Nitrogen, Oxygen reduction

1. Introduction

The electrochemical oxygen reduction reaction (ORR) occurs at the cathode side of various types of fuel cells. Although hydrogen-oxygen fuel cells generally operate under acid or alkaline conditions, the ORR in neutral solutions has also attracted much attention for application in enzymatic and microbial fuel cells [1-4]. At present, platinum (Pt) is generally used as the cathode electrocatalyst for accelerating the ORR. However, as Pt is expensive due to its scarcity, the use of earth-abundant materials as catalysts is considered to be an essential requirement for the further dissemination of biofuel cells. One promising strategy to develop cost-effective catalysts is to learn from natural systems. In living cells, copper (Cu)-containing enzymes, such as laccase and bilirubin oxidase, catalyze the four-electron ORR for respiration with lower overpotential than Pt in neutral pH conditions [1-3]. In these enzymes, modulation of the electronic state of the central Cu by coordination with nitrogen (N) atoms is believed to be a key factor for the high catalytic activity [5, 6]. For this reason, numerous studies have described the synthesis of Cu-based complexes with N-ligation that mimic Cu-enzymes [7-13]. For example, a dinuclear Cu complex of 3,5-diamino-1,2,4-triazole (Cu-DAT) supported on carbon black exhibited an onset potential of 0.73 V (vs. RHE) at pH 7 for the ORR, which is the highest value among Cu-based catalysts reported to date [8, 14]. In addition, Cu-DAT also served as the cathode catalyst in alkaline fuel cells [15]. Although Cu-DAT is therefore a promising platform for the development of low-cost ORR catalysts, its half-wave potential for the ORR decreased by about 140 mV after 100 cycles of cyclic

1 voltammograms (CVs) [8]. Thus, for the practical application of this catalyst, it is necessary to
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4 improve its stability.
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7 Carbon-based materials containing N and metals, such as iron (Fe) and/or cobalt (Co), are
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10 alternative candidates as ORR electrocatalysts because the stability of these catalysts is much
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13 improved compared to that of molecular catalysts [16-21]. We recently reported that stable graphene
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16 materials with Fe-N coordination bonds can be synthesized by the short-duration heat treatment (<
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19 60 s) of graphene oxides in the presence of an Fe-pentaethylenhexamine complex [22, 23]. Notably,
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22 the use of the short-duration heat treatment improved the stability of the prepared catalyst while
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25 maintaining Fe-N coordination. For this reason, it is worth investigating whether this synthesis
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28 method can be applied to Cu-DAT, which exhibits the highest performance among Cu-based
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31 complexes [8].
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39 **2. Experimental**

40 41 42 *2.1. Materials.* 43 44

45 Reduced graphene oxides (r-GOs) were synthesized through the heat treatment (900 °C) of
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48 graphene oxides under an inert atmosphere, as detailed in our previous report [24]. It should be noted
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51 here that no metal residue was observed in the resulting r-GOs from X-ray photoelectron spectra.
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54 CuCl₂·2H₂O (114 mg; Wako) and 3,5-diamino-1,2,4-triazole (132 mg; TCI) were dissolved in 10 ml
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57 ultra pure water to form Cu-DAT complex in solution. A total of 200 mg r-GOs was added to 9.14
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1 ml of the Cu-containing aqueous solution, and the resulting mixture was dried. The obtained material
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4 was placed at the bottom of a half-closed quartz tube filled with argon and quickly inserted into a
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7 muffle furnace preheated to 900 °C. After heat treatment for 45 s, the tube was quickly removed
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10 from the furnace and immediately cooled under argon flow. The synthesized material was washed
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13 with 2 M H₂SO₄ at 60 °C for 3 h. The resulting catalyst was designated HT/Cu-DAT (HT: Heat
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16 treatment). The Cu-DAT complex supported on r-GOs (non-HT/Cu-DAT) was prepared on the basis
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19 of previous paper [8], except for the use of r-GOs as carbon supports. 20wt% Pt/C (Fuel Cell Earth)
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22 was also used as a reference sample.
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29 *2.2. Electrochemical measurements.*

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33 Oxygen reduction activities were evaluated using a rotating ring-disk electrode (RRDE) in a
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36 0.1 M phosphate-buffer solution containing 0.5 M NaClO₄ (pH 7.0). The counter electrode was a
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39 titanium wire. A Ag/AgCl/KCl sat. was used as the reference electrode and was calibrated with
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42 respect to a reversible hydrogen electrode (RHE = Ag/AgCl/KCl sat. + 0.198 V + 0.0591 x pH at
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45 25 °C). Working electrodes were first prepared by dispersing 5 mg of each catalyst in 437.5 µl
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48 ethanol and 47.5 µl of 5 wt% Nafion solution (Aldrich). The resulting catalyst inks were dropped in
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51 2.5-µl aliquots onto a glassy carbon electrode (0.196 cm²). Therefore, the amounts of loaded catalyst
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54 and Nafion were controlled to be approximately 0.13 mg·cm⁻² and 0.06 mg·cm⁻², respectively.
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58 The number of electrons was evaluated by using a RRDE and calculated based on the
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equation (1) [22].

$$n = 4 I_d / (I_d + I_r / N) \quad (1)$$

in which N ($= 0.41$), I_d and I_r are the collection efficiency, disk current and ring current, respectively.

The poisoned potential on the Pt ring was 1.2 V versus RHE. We also estimated the number of electrons from the Koutecky-Levich equation as follows:

$$j^{-1} = j_k^{-1} + (B\omega^{1/2})^{-1} \quad (2)$$

where j is the measured current, j_k is the kinetic-limiting current and ω is the electrode rotation rate.

The theoretical value of the Levich slope (B) was evaluated from the following relationship:

$$B = 0.62nFCD^{2/3}\nu^{-1/6} \quad (3)$$

where n is the number of electrons, F is the Faradic constant (96485 C mol^{-1}), C is the bulk concentration of oxygen ($1.13 \times 10^{-6} \text{ mol cm}^{-3}$), D is the diffusion coefficient of oxygen ($1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), and ν is the viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$).

The stability of catalysts was also evaluated using a rotating disk electrode (RDE). Rotation speed and scan rate were set at 1500 rpm and 250 mV s^{-1} , respectively, during 1000 CVs.

2.3. X-ray measurements.

Hard X-ray absorption measurements (XAFS) were performed using the hard X-ray beam line 01B01 at SPring-8, Japan. Transmission yield spectra were acquired using a double-crystal Si (111) monochromator. X-ray photoelectron spectroscopy (XPS) analyses (Axis Ultra, Kratos

Analytical Co.) were obtained using monochromated Al K α X-rays at $h\nu = 1486.6$ eV.

3. Results and discussion

Cu K-edge extended X-ray absorption fine structure (EXAFS) analyses were first conducted to confirm that Cu-N coordination bonds remained in HT/Cu-DAT. Fig. 1 shows the Fourier transformation of k^3 -weighted EXAFS oscillation for HT/Cu-DAT, Cu phthalocyanine and Cu foil. The EXAFS spectra for HT/Cu-DAT and Cu phthalocyanine displayed peaks derived from the first coordination sphere at $R = 1.43$ Å and 1.50 Å, respectively, which were assignable to Cu-N bonds. The coordination number for N atoms was estimated to be 1.7 in HT/Cu-DAT. Cu foil had a peak corresponding to the first coordination sphere at $R = 2.16$ Å, which was ascribed to Cu-Cu bonds. Importantly, this peak was not observed for HT/Cu-DAT. In contrast, the EXAFS spectrum for the heat treated sample without the acid treatment (Fig. S1) shows both the Cu-N and Cu-Cu peaks. These results indicate that a certain portion of Cu-N bonds in Cu-DAT precursors indeed kept intact after the short-duration heat treatment, although the other Cu-N bonds were broken and aggregated as metallic Cu nanoparticles, which were removed through the acid treatment.

The catalytic activity of HT/Cu-DAT was compared to those of non-HT/Cu-DAT and 20wt% Pt/C by measuring current density (j) vs. potential (U) relationships in neutral solutions (Fig. S2: the curves in oxygen and argon, Fig. 2(a): the subtracted curves). From the curves, it was determined that HT/Cu-DAT generated a cathodic current with an onset potential (U_{onset} : the

potential value corresponding to a cathodic current of $-10 \mu\text{A cm}^{-2}$) of 0.79 V and exhibited the catalytic activity comparable to that of non-HT/Cu-DAT. Note that the U_{onset} of non-HT/Cu-DAT is essentially identical to the value which was previously reported [8]. To our knowledge, although the ORR activity is still lower than that of Pt/C (U_{onset} for Pt/C was 1.02 V vs RHE), the onset potential (0.79 V) of HT/Cu-DAT is the highest value reported to date among Cu-based ORR catalysts in neutral solutions. The number of electrons for HT/Cu-DAT was estimated from the yield of H_2O_2 to be approximately four over the entire potential range (Fig. 2(b)), which essentially coincides with the results of the Koutecky-Levich plots (Fig. S3). These results indicate that most dioxygen molecules would be reduced to water via a four-electron transfer pathway. We also measured the ORR activities in 0.5 M NaClO_4 without phosphate buffer as shown in Fig. S4, which shows that the slopes of the j vs U curves near the onset potential were much gentler than those in buffer solutions. This is likely because the local pH at electrode surfaces increased due to the consumption of proton by the ORR [25].

To evaluate the stability of HT/Cu-DAT, j vs. U curves were measured before and after 1000 CVs and compared with those of non-HT/Cu-DAT (Figs. 3(a) and (b)). Although the absolute current density value in the kinetic region (0.6 V vs. RHE) [26] after the CV cycling decreased by 81% (-0.72 to -0.14 mA cm^{-2}) for non-HT/Cu-DAT, it decreased only by 6% (-0.87 to -0.82 mA cm^{-2}) for HT/Cu-DAT (Fig. 3(c)). These results indicate that the stability of HT/Cu-DAT was enhanced by the heat treatment.

The elemental compositions of both catalysts before and after 1000 CV cycles were estimated by XPS analyses. Cu/C and N/C ratios before performing the CV cycles are presented in Table 1. After 1000 CV cycles, the Cu and N contents of non-HT/Cu-DAT decreased by 75% and 67%, respectively, whereas those of HT/Cu-DAT decreased only by 10% and 4%, respectively, as shown in Figs. 3(d) and (e). This finding clearly demonstrates that the desorption of Cu and N atoms was reduced in HT/Cu-DAT compared to non-HT/Cu-DAT. Thus, the observed deterioration of ORR activity (kinetic current densities) after 1000 CV cycles (Figs. 3(a) and (b)) corresponds to the decreased Cu and N content, indicating that the suppression of Cu and N atom desorption improves the stability of HT/Cu-DAT. Trial to achieve further improvement of the catalytic stability for practical use is under progress.

To investigate why the desorption of Cu and N was suppressed in HT/Cu-DAT, the electronic states of N atoms in HT/Cu-DAT and non-HT/Cu-DAT determined from N-1s XPS spectra were characterized and compared (Fig. 4). The N-1s XPS spectrum of HT/Cu-DAT can be deconvoluted into five peaks: pyridine-like N at 398.5 ± 0.2 eV, N atoms in the triazole ring or pyrrole-like N at 399.7 ± 0.2 eV, amine N bonded to the triazole ring at 400.4 ± 0.2 eV, graphite-like N at 401.0 ± 0.2 eV, and nitrogen oxide at 404.0 ± 0.2 eV [27-31]. The ratios of these components in HT/Cu-DAT were determined and are presented in Table 2(a). The total amount of pyridine-like N, pyrrole-like N and graphite-like N exceeded at least 65% of all N atoms in HT/Cu-DAT. Taken together, the XPS and EXAFS results suggest that N atoms coordinated to Cu atoms were doped into

the graphene network during the heat treatment (Fig. 5(a)). Thus, the anchoring of active Cu-sites into the graphene substrate through the covalent and coordination bonds resulted in the suppression of desorption of the active sites from electrodes [32]. In contrast, for non-HT/Cu-DAT, the peaks corresponding to N atoms in the triazole ring and amine N bonded to the triazole ring were observed at 399.5 ± 0.2 eV and 400.4 ± 0.2 eV, respectively [33-36]. The ratios of these components in non-HT/Cu-DAT are presented in Table 2(b). The XPS result suggests that Cu-DAT was only physically adsorbed onto r-GOs (Fig. 5(b)).

Let us discuss the ORR activity of HT/Cu-DAT. Thorum and colleagues reported that the closely spaced Cu centers in non-HT/Cu-DAT were essential for its high catalytic activity [8]. Kato *et al.* also suggested that the dinuclear Cu centers in non-HT/Cu-DAT activated dioxygen molecules [14]. Considering that molecular structures of precursors are retained in the resultant catalyst by the short-duration heat treatment, as demonstrated in our previous paper [22], we can speculate that the closely spaced Cu centers of non-HT/Cu-DAT remained in HT/Cu-DAT to some extent and worked as the active sites for the ORR. Another possible explanation for the high ORR activity of HT/Cu-DAT is that the heat treatment improved the electronic interaction between the active sites and the graphene substrate due to the introduction of active sites into graphene *sp*² networks. This assumption was supported by the N-1s XPS spectrum in Fig. 4 (doping of N atoms) and was reported in a number of previous reports [17, 37]. Further studies for identifying the molecular structure and the ORR mechanism are now in progress in our laboratory.

4. Conclusions

A novel Cu-based ORR electrocatalyst (HT/Cu-DAT) was successfully synthesized by the short-duration heat treatment of 3,5-diamino-1,2,4-triazole in the presence of r-GOs. The resultant hybrid material exhibited high stability and the best ORR activity in neutral solutions among the Cu-based electrocatalysts reported to date. XPS and EXAFS analyses revealed that Cu atoms coordinated by N atoms were introduced into the *sp*² networks of graphene via the heat treatment, leading to the improved stability of HT/Cu-DAT. We speculate that (1) the heat treatment was stopped before the complete breakage of active sites, thereby preserving the ORR activity of non-HT/Cu-DAT, and (2) the ORR catalytic activity can be further improved by the selection of an appropriate precursor. Further studies are required for clarifying the molecular structure of the active sites of HT/Cu-DAT.

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Figure and Tables Captions

Fig. 1. Fourier transformation (FT) of k^3 -weighted EXAFS oscillation for heat-treated (HT)/Cu-DAT after the acid treatment (red), Cu phthalocyanine (black) and Cu foil (gray).

Fig. 2. (a) j vs. U curves for HT/Cu-DAT (red) and non-HT/Cu-DAT (blue) in 0.1 M phosphate buffer solution (pH = 7.0). The inset shows the magnified curve for HT/Cu-DAT. These curves were obtained by subtracting the cyclic voltammeteries (CVs) in argon-saturated electrolyte solution from those obtained in O₂-saturated electrolyte solution. (b) Electron number for HT/Cu-DAT. Rotation rate: 1500 rpm; scan rate: 10 mV s⁻¹.

Fig. 3. j vs. U curves for (a) HT/Cu-DAT and (b) non-HT/Cu-DAT before (black) and after ((a) red, (b) blue) 1000 CV cycles in 0.1 M phosphate buffer solution (pH 7.0). Rotation rate: 1500 rpm; scan rate: 10 mV s⁻¹. The insets show magnified curves, and the arrows indicate the shift during 1000 CV cycles. Relative values of (c) current density at 0.6 V and the concentrations of (d) Cu and (e) N atoms after 1000 cycles of CV compared to the absolute values of each factor before the CV.

Fig. 4. N-1s XPS spectra for HT/Cu-DAT (upper) and non-HT/Cu-DAT (lower). Measured data

(open colored squares), fitted curve (black line) and deconvoluted curves (gray lines).

Fig. 5. Schematic illustrations of the active sites for ORR in (a) HT/Cu-DAT and (b) non-HT/Cu-DAT.

Table 1. Cu/C and N/C ratios for HT/Cu-DAT and non-HT/Cu-DAT before performing 1000 CV cycles calculated from XPS spectra.

Table 2. Relative ratios of various nitrogen components in (a) HT/Cu-DAT and (b) non-HT/Cu-DAT calculated from decomposed N-1s XPS spectra.

Figure 1

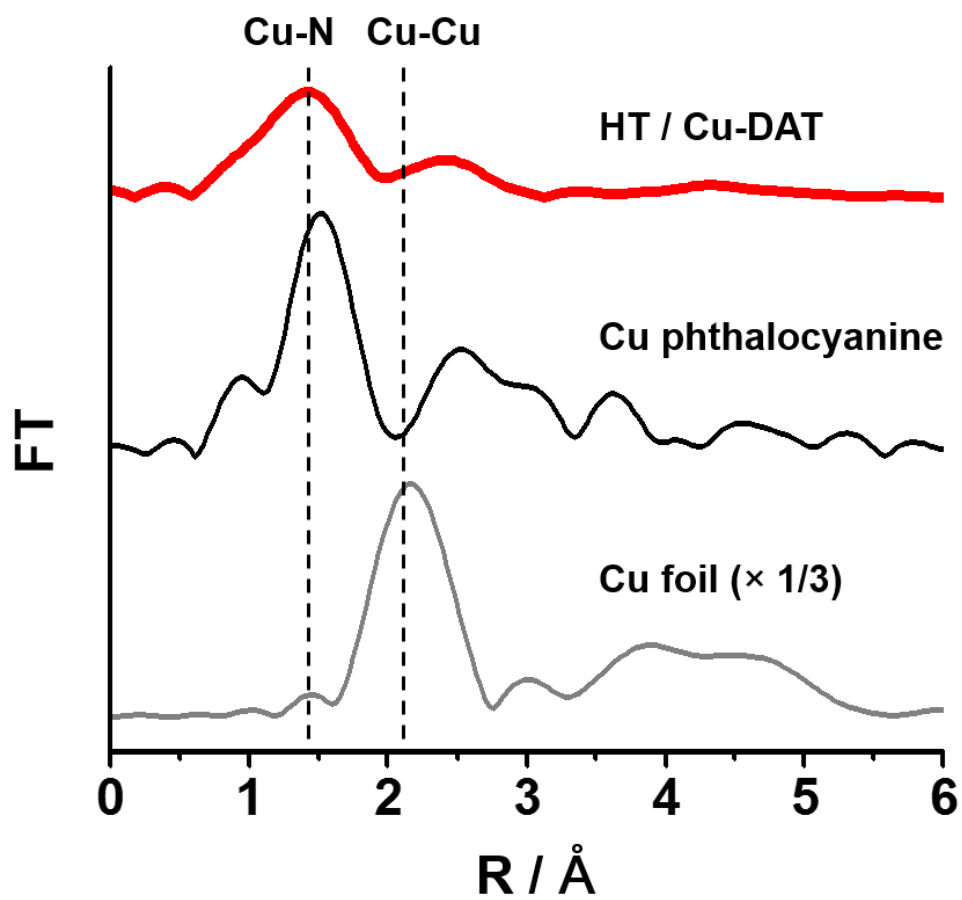


Figure 2

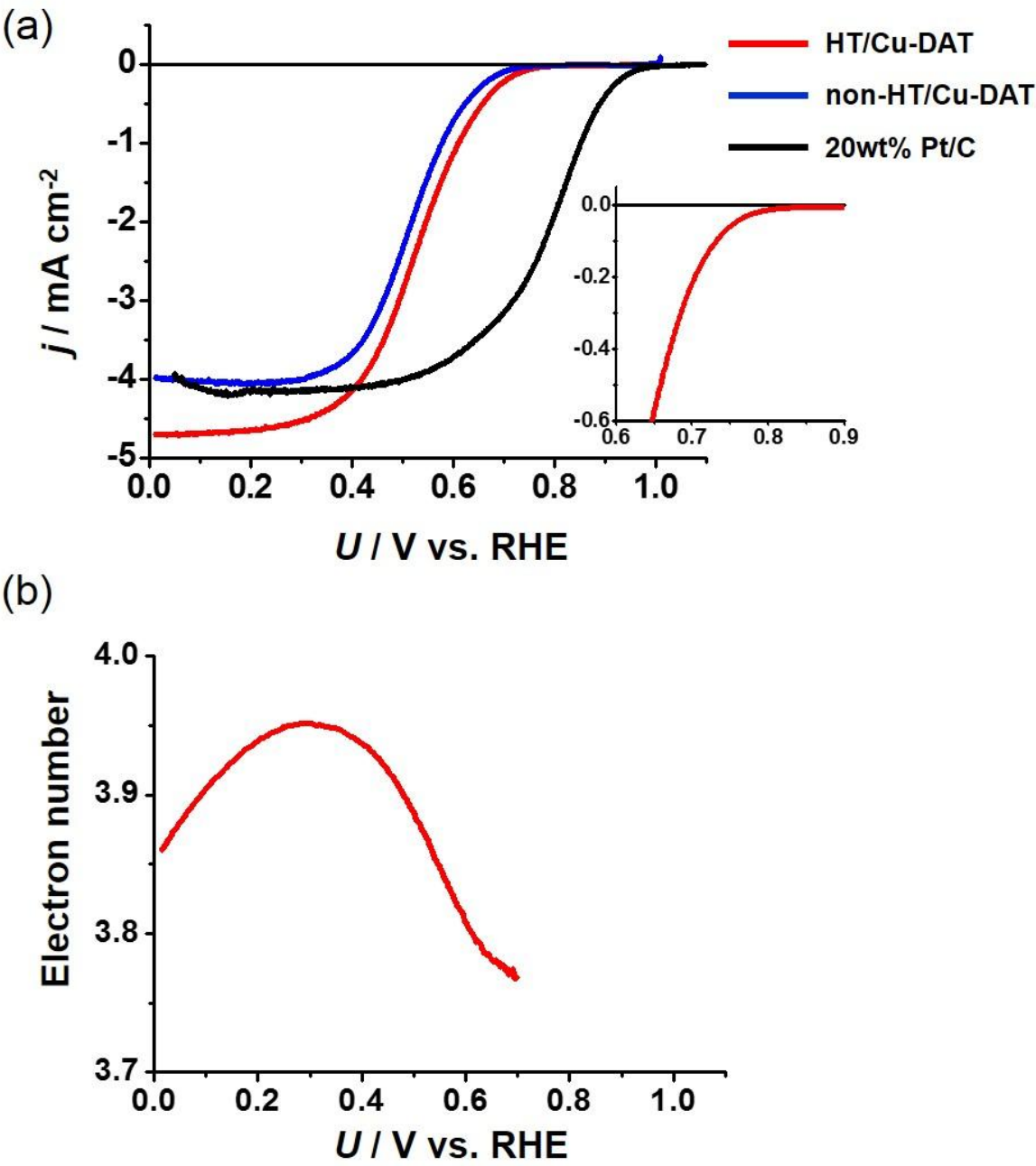


Figure 3

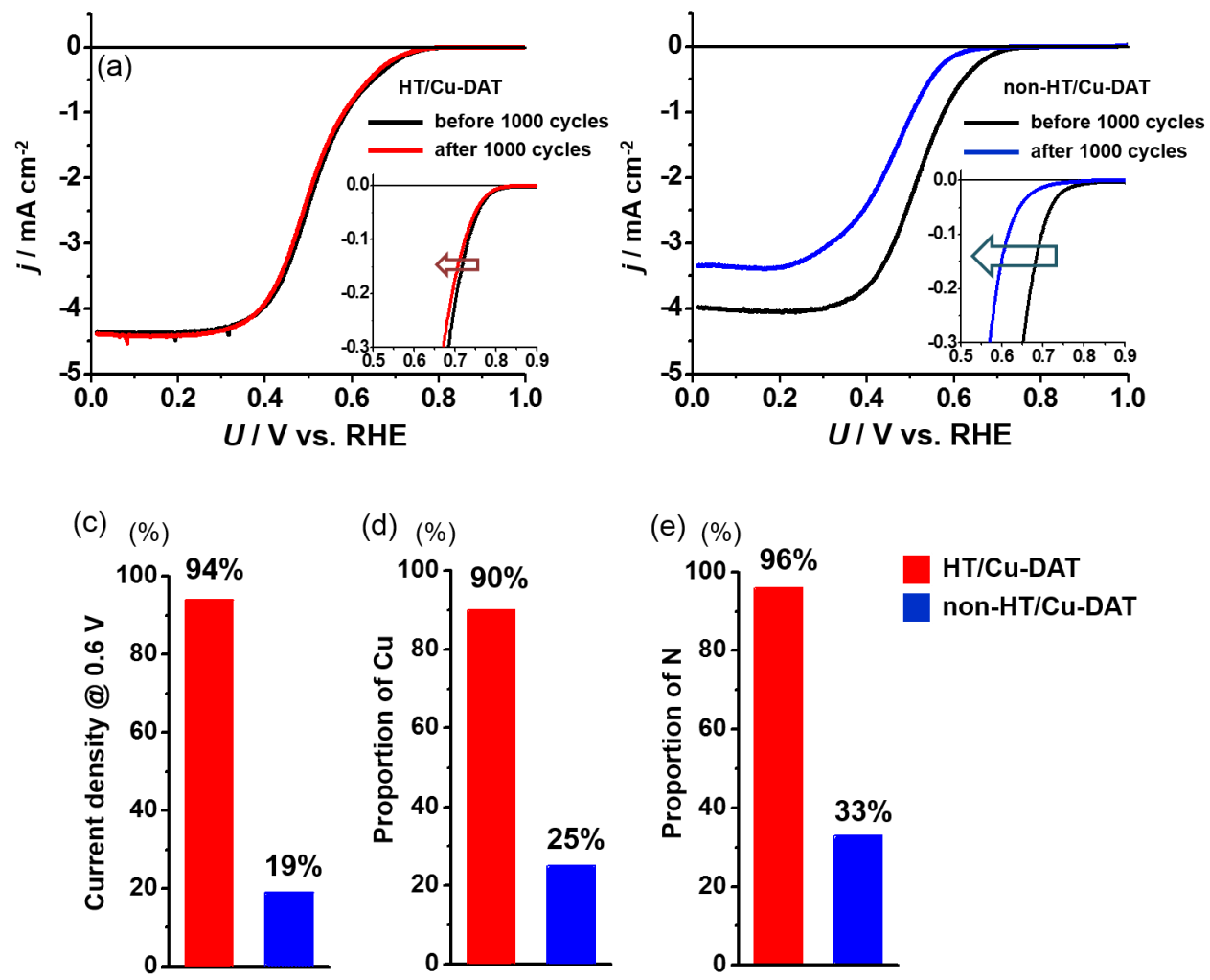


Figure 4

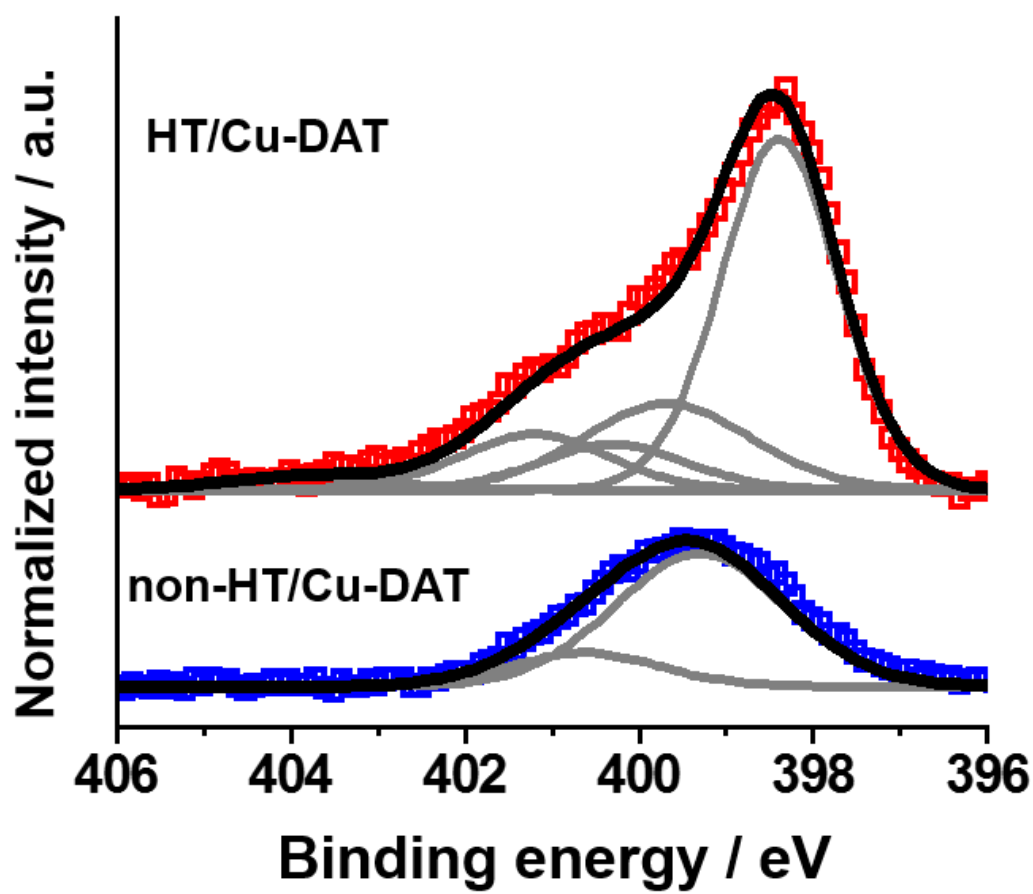
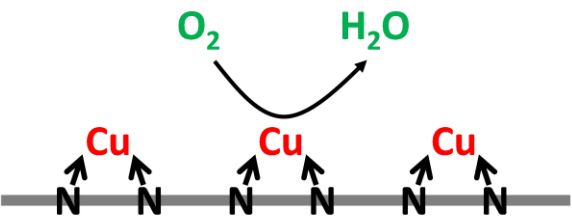


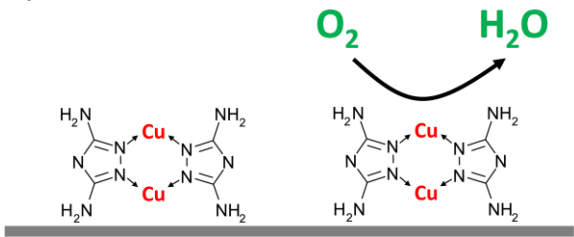
Figure 5

(a)



HT/Cu-DAT

(b)



non-HT/Cu-DAT

Table 1

	Cu/C	N/C
HT/Cu-DAT	0.012	0.085
non-HT/Cu-DAT	0.0032	0.033

Table 2

(a)

	pyridine N	N in triazole ring / pyrrole N	amine N	graphite N	N oxide
HT/Cu-DAT	56	20	9	12	3

(b)

	N in triazole ring	amine N
non-HT/Cu-DAT	81	19

Highlights

- The mixture of reduced graphene oxides and Cu-DAT was heat treated at 900 °C for 45 s.
- N atoms coordinated to Cu atoms were doped into graphene through the heat treatment.
- The resulting catalyst exhibited the efficient ORR activity in neutral solutions.
- The onset potential (790 mV vs RHE) is the highest among Cu based electrocatalysts.
- The stability of the catalyst was enhanced by the heat treatment.