

Electronic Supplementary Information (ESI)

Deprotonation of a dinuclear copper(II) complex of 3,5-diamino-1,2,4-triazole for high oxygen reduction activity

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Experimental section

Chemicals

All chemicals were used as received without further purification. $\text{Cu}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$, $\text{NaClO}_4 \cdot 5\text{H}_2\text{O}$ (Nacalai tesque), 3,5-diamino-1,2,4-triazole (Hdatrz, Aldrich), H_3PO_4 , and H_3BO_4 (Aldrich) were used. CH_3COOH , NaOH , and Nafion® dispersion (5 wt%, DE520CS) were purchased from Wako Pure chemical industries. Ketjen black ECP300 (KB) was provided by Lion Co. Vulcan was purchased from BASF. Mill-Q water was used in all experiments.

Preparation and analysis of the Cu-complex catalyst supported on KB

Synthesis of a Cu^{II} -Hdatrz catalyst on a carbon support of KB (Cu/KB) was based on the literature.¹ KB (1.00 g), $\text{Cu}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ (0.60 g, 1.8 mmol) and water (20 mL) were mixed and ultrasonicated to form a homogeneous dispersion. An aqueous solution of Hdatrz (0.48 g, 4.8 mmol; 10 mL H_2O) was added to the dispersion with continuous stirring. The mixture was stirred for 18 h. The solids in the dispersion were collected by suction filtration, dried in vacuo for overnight, and then, pulverized with a mortar pestle. The prepared Cu/KB was analyzed by N_2 adsorption measurement (ASAP2020, Micrometrics), XRD (RINT Ultima IV, Rigaku Co. Ltd.), and ICP-MS (Varian, 820-MS).

Electrochemical measurements

The typical electrode preparation method was based on the literature with some modifications.¹ The glassy carbon (GC) rod (Tokai carbon, $\phi 5$ mm) was successively polished with 0.3 μm and 0.05 μm alumina slurries. The GC rod was then mounted in RRDE (E6, Pine), the electrode was then cleaned in water and acetone using ultrasonic bath and dried. The Cu/KB catalyst in water was dispersed using an ultrasonic homogenizer and cast onto the GC disk of RRDE and dried in an atmosphere. The ethanol dispersion of 0.05 w/v% Nafion (4.5 μL) was cast onto the Cu/KB thin film on the GC disk and heated at 50°C for 1 h in an oven. The obtained electrode had 0.752 μg_{Cu} (3.83 $\mu\text{g}_{\text{Cu}} \text{ cm}^{-2}$). Electrochemical measurements were performed by a potentiostat (IVIUM CompactStat, IVIUM technologies) in a three-electrode configuration with a

platinum wire counter electrode (separated with glass filter) and a doubly junctioned Ag|AgCl reference electrode at room temperature. The potentials are presented as values vs. RHE. All electrochemical measurements were carried out using Britton-Robinson (B.R.) buffer solution and containing 0.1 M NaClO₄ as supporting electrolyte. The pH value of B.R. solutions was adjusted with 0.1 mol dm⁻³ NaOH.

In situ XAFS measurement

The catalyst was cast on an Au thin film electrode deposited on a Kapton film window for *in situ* XANES of Cu K α edge in a fluorescent mode at room temperature. The samples for *in situ* fluorescent XAFS were prepared as follows. A Kapton film was cut into a film with 50 \times 60 mm² and sonicated in acetone for 30 min. Then, the Kapton film was rinsed with water and carefully fixed on a glass plate. The Kapton film fixed on the glass plate was dried with an evaporator and etched by exposing to oxygen plasma (100 W) for 1 min in a plasma etching equipment (Samco). The clean Kapton window was immediately transferred to the chamber of a sputter coater (Emitec, Turbo Sputter Coater) and gold film with a thickness of 30 nm was deposited on the Kapton window with a circular pattern of 8 mm diameter through an aluminum mask. After the Ar plasma treatment (20 W, 1 min.) of the Au surface, a Cu/KB dispersion, which contained ca. 6 μ g of Cu, was cast on the Au-deposited Kapton window. The surface concentration of Cu in the sample was ca 10¹⁷ cm⁻², which was proper concentration for fluorescent XAFS measurements. After drying the Cu/KB film for one night, Nafion dispersion of 0.05 wt% diluted by ethanol was cast on the Cu/KB-deposited Au/Kapton window, and dried at 50°C for 1 h to cover the Cu/KB catalyst with a Nafion thin film of 50 nm thickness.

The Cu/KB-deposited Au/Kapton window, which was electrically connected to the PC-controlled potentiostat (Ivium, Compactstat) as the working electrode, was fixed on the home-built spectroelectrochemical flow cell (**Scheme S1**), in which the three electrode system was constructed with the Pt wire counter and the leak-free Ag|AgCl reference electrodes. The Cu/KB catalyst layer on the Au/Kapton window was exposed to the electrolyte solution flow inside the spectroelectrochemical flow cell and the potential was controlled by the potentiostat. For the electrolyte solution, Britton-Robinson buffered solution (pH = 7, 10 and 13) containing 0.1 M NaClO₄ was

continuously flown with N₂ and O₂ bubbling to obtain XAFS spectra in inert and ORR conditions, respectively.

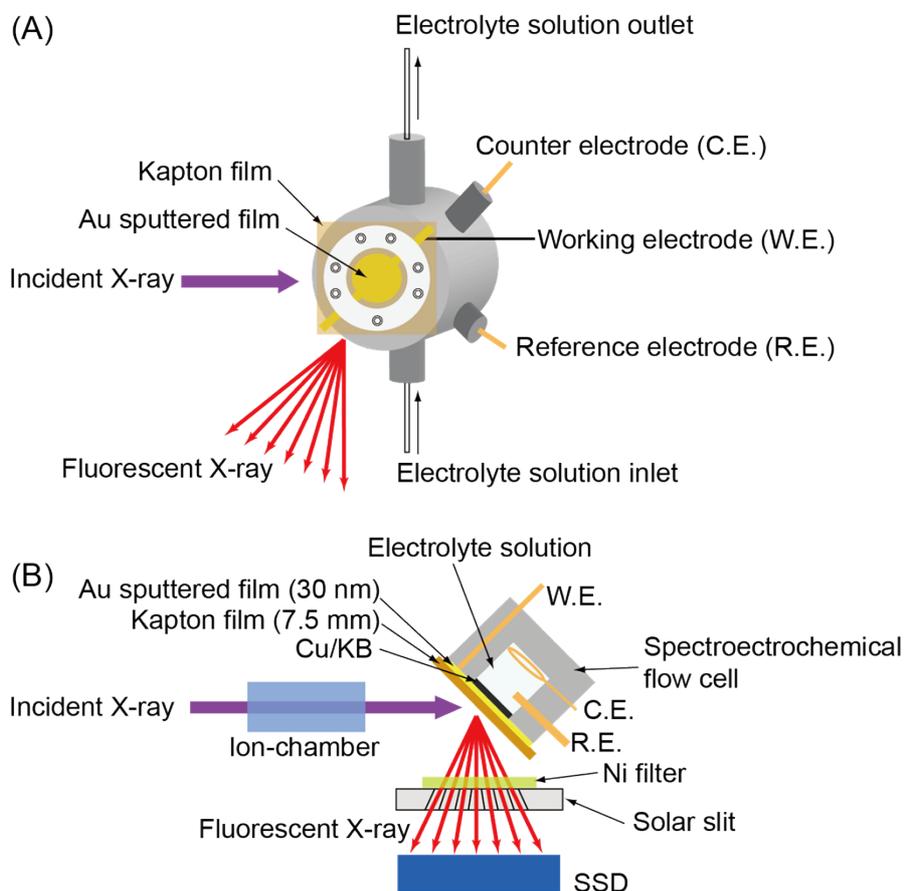
All the electrochemical XAFS measurements were carried out at the Photon Factory (Beamline 12C), the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-IMSS-PF). The incident X-ray was introduced from the backside of the Kapton window with the incident angle of 45° and the fluorescent X-ray from the Kapton window was detected by a multi-channel solid state detector cooled by liquid nitrogen, which was placed in the perpendicular direction to the incident X-ray axis. A nickel filter and a solar slit were placed in the front of the fluorescent detector to remove the elastic scattering and to extract the fluorescent X-ray from Cu-species. The intensity of incident X-ray, I_0 , was obtained by an ion-chamber placed before the sample (**Scheme S1**). XANES measurements were performed under potentiostatic conditions with monitoring the potential and current to be stable and were started 10 min after the potential change. When the atmospheres under N₂- and O₂-saturated conditions were changed, the electrolyte solution inside the tank was bubbled by N₂ and O₂, respectively, for 1 hour with keeping the solution flow.

Data analysis of the XANES spectra.

All XANES spectra obtained were analyzed using the REX2000 software package (Rigaku). Background removal and normalization were carried out using standard methods. Linear combination fitting analysis of the XANES spectra was performed to calculate the amounts of Cu^I.

Reference

1. M. S. Thorum, J. Yadav and A. A. Gewirth, *Angew. Chem. Int. Ed.*, 2009, **48**, 165-167.



Scheme S1 Schematic representation of (A) the home-built spectroelectrochemical flow cell and (B) a set-up for *in situ* XAFS measurements.

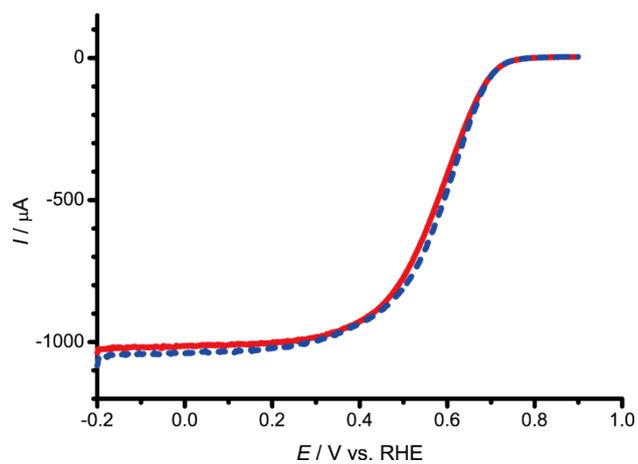


Fig. S1 Linear sweep voltammograms of Cu-Hdatrz on KB (the solid line in red) and on Vulcan (the dashed line in blue), recorded in a Britton-Robinson buffered aqueous solution (pH 7) at a rotating rate of 1600 rpm under oxygen.

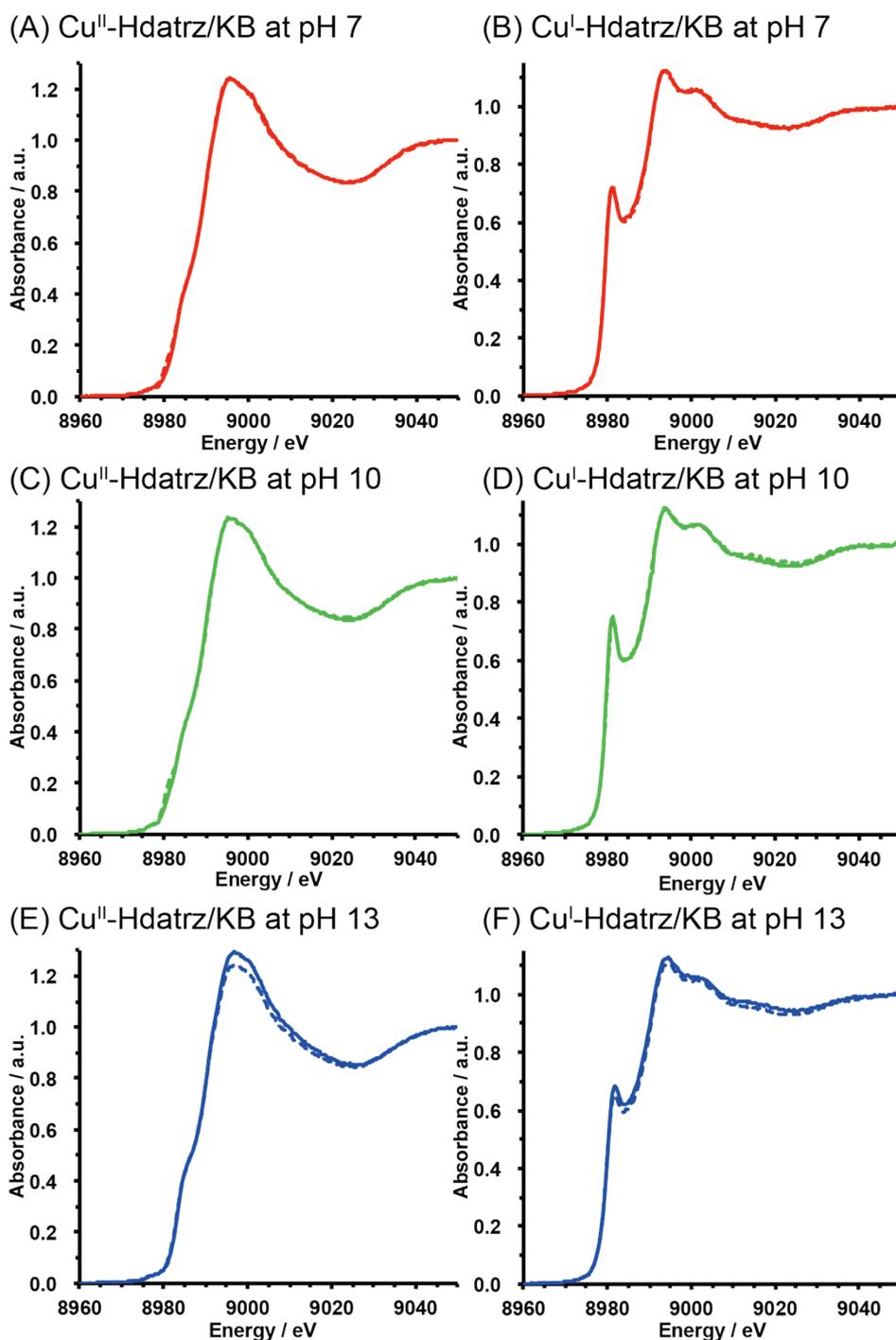


Fig. S2 XANES spectra of (A) Cu^{II} -Hdatrz at +0.95 V vs RHE at pH 7, (B) Cu^{I} -Hdatrz at -0.25 V vs RHE at pH 7, (C) Cu^{II} -Hdatrz at +1.11 V vs RHE at pH 10, (D) Cu^{I} -Hdatrz at -0.08 V vs RHE at pH 10, (E) Cu^{II} -Hdatrz at +1.29 V vs RHE at pH 13 and (F) Cu^{I} -Hdatrz/KB at +0.09 V vs RHE at pH 13. The solid lines and dashed lines indicate the XANES spectra recorded under nitrogen and oxygen, respectively.