Supplementary Information

Precise 3D structure determination of Cu single atoms on α-Al_2O_3(0001) surface by polarization-dependent total reflection fluorescence X-ray absorption fine structure and first-principles calculations

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Table S1. Curve fitting results for Cu K-edge PTRF-EXAFS spectra of Cu/α-Al_2O_3(0001) (Figure S3(a)). Backscattering amplitude and phase shift for Cu-O shell are obtained from the EXAFS analysis of the Cu_2O reference compound. The quantity $k^3\chi(k)$ in the *k*-range of 30 to 80 nm^{-1} was Fourier transformed into *r*-space, and the peak in the transform was filtered (filtered *r*-range was 0.074 to 0.215 nm).

	Shell	Coordination number	r / nm [a)]	Energy shift (ΔE_0) /eV	$\Delta\sigma$ / nm [b)]	*R*-factor / %
s-pol	Cu-O	2.6±0.8	0.194±0.003	2.2±2.8	0.004±0.002	3.6
p-pol	Cu-O	2.4±0.5	0.193±0.002	-0.4±2.0	0.004±0.002	2.0
average	Cu-O	2.5±0.8	0.194±0.003	2.1±1.6	0.004±0.002	3.1

[a)] Bond distance

[b)] Debye-Waller factor, which is relative to the Debye-Waller factor of the Cu_2O reference compound.

Table S2. Atomic positions for Cu, O_1 and Al_2 (or Al_3) used for EXAFS simulation in Figure 5.

Atoms	H_1			H_2		
	x / nm	y / nm	z / nm	x / nm	y / nm	z / nm
Cu	0.000	0.000	0.143	0.000	0.000	0.148
O_1	0.000	0.151	0.000	0.000	0.155	0.000
O_1	0.130	-0.075	0.000	0.134	-0.078	0.000
O_1	-0.130	-0.075	0.000	-0.134	-0.078	0.000
Al_2 or Al_3	0.000	0.000	-0.124	0.000	0.000	-0.101

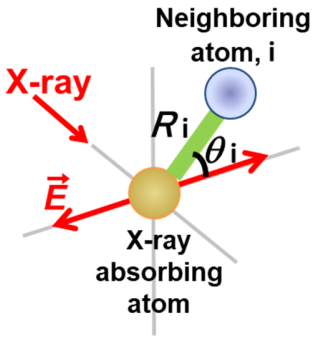
Table S3. Atomic positions for Cu, O_1, and Al_3 used for EXAFS simulation in Figure 6.

Atoms	Modified H_1		
	x / nm	y / nm	z / nm
Cu	0.000	0.000	0.116
O_1	0.000	0.155	0.000
O_1	0.135	-0.078	0.000
O_1	-0.135	-0.078	0.000
Al_3	0.000	0.000	-0.156

Analysis of the Cu K-edge PTRF-EXAFS spectra of the Cu/α-Al_2O_3(0001)

Our analysis of the PTRF-EXAFS spectra follows the procedure described below. Firstly, the polarization-dependent EXAFS spectra of the Cu/α-Al_2O_3(0001) for each orientation (see Figure 2(a)) were subjected to conventional curve-fitting analysis to estimate the preliminary structure of the Cu species. The bond distance, coordination number and Debye–Waller factor for the first shell (Cu-O interaction) were determined as shown in Table S1 and Figure S2. Secondly, in order to determine more accurate three-dimensional structure around the Cu atom, theoretical simulation of the polarization-dependent EXAFS spectra was conducted based on a real space model structure using FEFF8.04 code. In the simulation, the following input parameters are required: (1) atomic coordinates for Cu, O, and Al; (2) amplitude reduction factor and Debye-Waller factor for Cu-O and Cu-Al interactions; and (3) direction of the electric field of the incident X-ray beam. (2) were estimated by curve fitting analysis of reference compounds or calculated using the FEFF8.04 code. Therefore, theoretical polarization-dependent EXAFS can be simulated once (1) and (3) are known. In the simulation, three O and one Al atoms which are located within 0.3 nm around the Cu atom were considered because the contribution from the more distant atoms is small and negligible in the EXAFS oscillations.

The amplitude of the EXAFS oscillation ($\chi_i(k)$) originated from ith bond (R_i) follows a $3\cos^2\theta_i$ dependence, where θ_i is the angle between the R_i direction and the electric vector of the incident X-ray beam ($\vec{E}$) as illustrated in Figure S1 and the equation (1) in the manuscript. In our simulation, the Cu-O bond distance was fixed at 0.194 nm, a value determined by the curve fitting analysis (see Table S1), for the H_1 model in Figure 5(a). Therefore, the angle between each Cu-O bond and the electric vector $\vec{E}$ of the X-ray beam, as well as the Cu-Al distance, must be optimized in order to reproduce the observed EXAFS spectra for both *s*- and *p*-polarizations. We then used the d_1 and d_2 variables as the optimization parameters and simulated the corresponding polarization-dependent EXAFS spectra to calculate the R^2 values (see the equation (2) in the main text) for a given set of d_1 and d_2, as illustrated in Figures S4(a) and S4(b). The range of acceptable values of d_1 and d_2 was determined based on the R^2 values, which are less than 1 for both *s*- and *p*-polarizations (Figure S4(c)).



$$\chi_{pol}(k) = \sum_i 3\cos^2\theta_i \cdot \chi_i(k)$$

(Equation (1) in the main text)

Figure S1. Polarization dependence of EXAFS oscillation $\chi_{pol}(k)$. $\chi_i(k)$ is the EXAFS oscillation originated from the bond R_i.

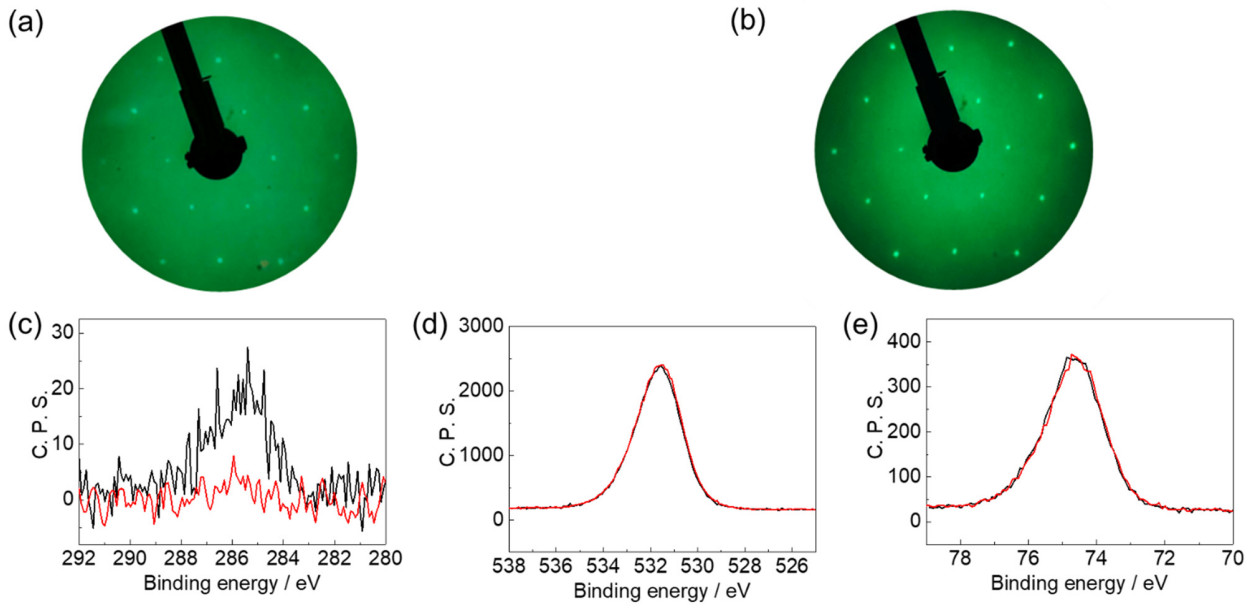


Figure S2. (a) and (b) LEED patterns of the α-Al_2O_3(0001) surface before and after surface cleaning by O_2 plasma. The incident electron energy was 163 eV. (c), (d), and (e) correspond to XPS spectra in C1s, O1s, and Al2p regions, respectively, where the black and red lines represent the spectra before and after O_2 plasma, respectively.

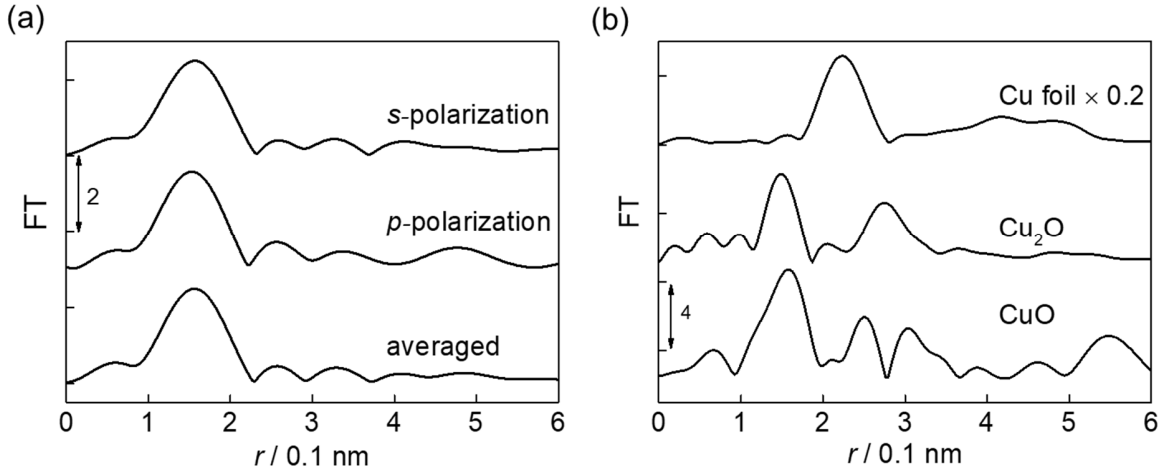


Figure S3. (a) Fourier transform (FT) of Cu K-edge $k^3\chi_{s-pol}(k)$, $k^3\chi_{p-pol}(k)$, and $k^3\chi_{avg}(k)$ EXAF spectra of the Cu/α-Al_2O_3(0001). $\chi_{avg}(k) = (2 \times \chi_{s-pol}(k) + \chi_{p-pol}(k))/3$. k-range: 30 to 80 nm^{-1}. (b) FT of Cu K-edge $k^3\chi(k)$ EXAFS spectra of the Cu reference compounds. k-range: 30 to 80 nm^{-1}.

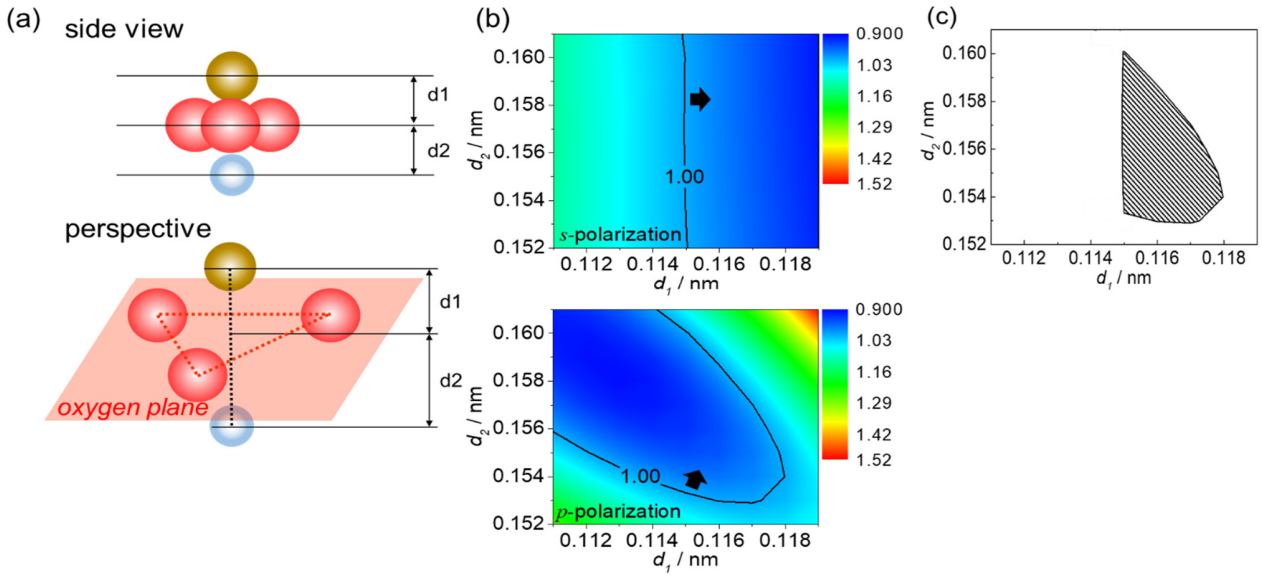


Figure S4. (a) illustrates the schematic of the atom positions used for their optimization to reproduce the observed PTRF-EXAFS spectra using the theoretical EXAFS simulation. Brwon, red, light blue spheres correspond to Cu, O and Al atoms, respectively. The Cu-O bond distance was fixed at 0.194 nm. d_1 and d_2 values were systematically changed and the correspond R^2 values (see equation (2) in the main text) for *s*- and *p*-polarization PTRF-EXAFS spectra were calculated. (b) The R^2 value maps against d_1 and d_2 values for *s*- and *p*-polarizations. The black curves and shaded region in (c) represent the range where the R^2 values for both *s*- and *p*-polarizations are less than 1.

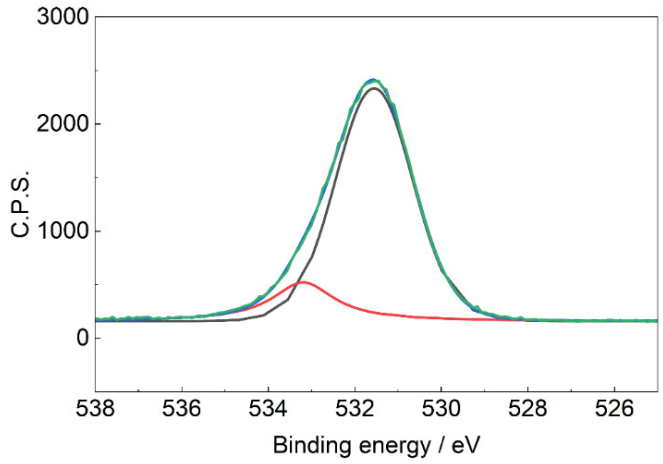


Figure S5. Deconvolution of the XPS O1s peak of the α-Al_2O_3(0001) surface after the UHV annealing (673 K, 1h) and O_2 plasma treatment. The red and the black peaks correspond to the O in OH species and the lattice O of the α-Al_2O_3(0001) surface, respectively.

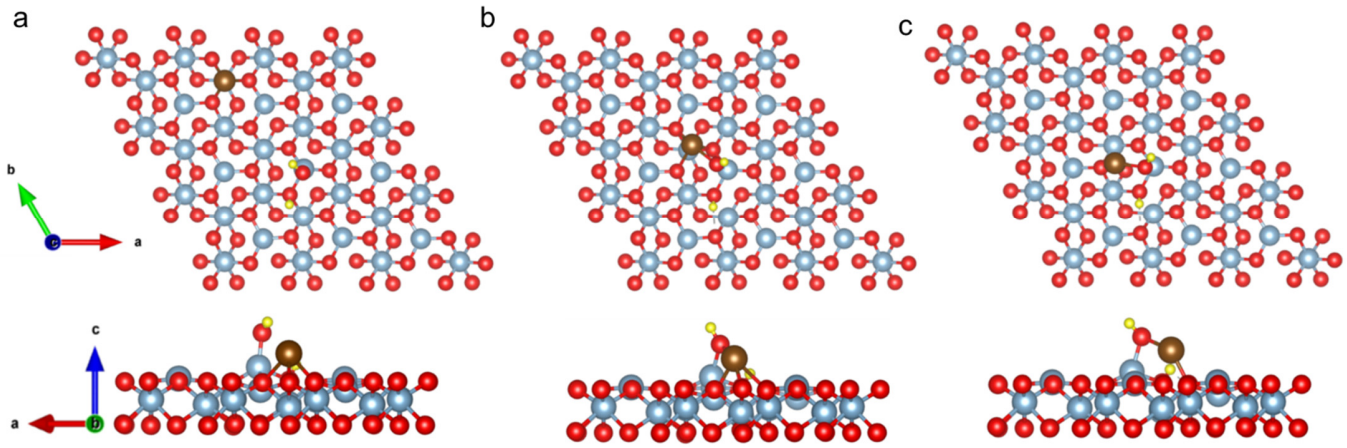


Figure S6. DFT-optimized structures of the Cu single atoms on the water-dissociated α-Al_2O_3(0001) surface. The OH coverage is 0.07 ML. (a) H_1 site, (b) T_1 site consisting of H_1 and O of Al_1-OH, (c) B_3 site bridging O_1 and O of Al_1-OH. The adsorption energies for the Cu atoms at the H_1, T_1 and B_3 sites were -2.59, -3.14 and -3.15 eV, respectively. Red, light blue, dark brown and yellow spheres represent O, Al, Cu and H atoms, respectively.