Electronic Supplementary Material (ESI) for ChemComm.
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Electronic Supplementary Information

Electrocatalytic water oxidation by Cu(II) ions in neutral borate buffer solution

Hai-Hua Huang, Jia-Wei Wang, Pathik Sahoo, Di-Chang Zhong and Tong-Bu Lu**

Experimental Section

General Methods.

$[Cu(bpy)(OH_2)_2](SO_4)_2$, $[Cu(en)_2](SO_4)_2$ and $[Cu(TMC)](ClO_4)_2$ were synthesized and characterized as reported.[1-3] All of other chemicals were commercially available and used without further purification. The purity of Argon is 99.999%. All solutions were prepared with Milli-Q ultrapure water (> 18 MΩ) unless otherwise stated. ITO glass (*R*s = 6-7 Ohms) was purchased from Zhuhai Kaivo Electronic Components Co., Ltd. UV–vis spectra were determined on a Shimadzu UV-3150 spectrophotometer. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) spectra were collected by field emission scanning electron microscope (Quanta 400). Electrochemical measurements were carried out using an electrochemical workstation CHI 760E. Unless otherwise stated, all potentials were reported versus normal hydrogen electrode (vs. NHE). Pt foil was used as counter electrode in the three-electrode system. For cyclic voltammetry (CV) measurement, the reference electrode was Ag/AgCl electrode (saturated KCl, +0.199 V vs. NHE), and the working electrode was 0.071 cm^2 glassy carbon (GC) electrode. For electrolysis measurement, the reference electrode was Ag/AgCl electrode (saturated KCl, 0.199 V vs. NHE) and the working electrode was ITO slides.

ITO Electrode: Prior to the experiments, the glass slides were cleaned by sonication in acetone, ethanol and Milli-Q ultrapure water for ~10 min, respectively.

Glassy Carbon Electrode (0.071 cm^2): Prior to experiments, the glassy carbon electrode was polished with 0.3 and 0.05 μm Al_2O_3 slurry for 60 s respectively, to obtain a mirror surface, followed by sonication in distilled water for ~60 seconds to remove debris, and was thoroughly rinsed with Milli-Q ultrapure water.

Cyclic Voltammetry. CV measurements were conducted under an air atmosphere unless otherwise stated. The working electrode and the counter electrode were in the same compartment. All experiments were performed at room temperature (25 °C).

Controlled-Potential Electrolysis. Controlled-potential electrolysis (CPE) was performed in a three-compartment, three-electrode cell (the volume for each cell is 18 mL) with a stirred solution. No *iR* compensation was used in these experiments. The counter electrode compartment, containing a platinum foil electrode, was separated from the working electrode compartment by a porosity frit. An Ag/AgCl reference electrode (sat. KCl) was placed in the third compartment, attached to the working

electrode compartment with a Luggin capillary. The gas product analysis was conducted by gas chromatography (Agilent 7820A-GC, molecular sieve columns, thermal-conductivity detector, TCD). The chromatographic response for O_2 was normalized to residual O_2/N_2 from ambient air.

Computational Section

Computational Details

All the calculations were performed with Gaussian 09 program.[4] The selected functional was M06-L.[5] The selected basis set was 6-31+G(d) for S, B, O and H, and SDD[6] for Cu. Solvation was introduced implicitly through the SMD model, with water as the solvent. All geometry optimizations were computed in solution without symmetry restrictions. We confirmed the nature of all computed stationary points as minima or transition states through vibrational frequency calculations. Free energy corrections were calculated at 298.15 K and 105 Pa pressure, including zero point energy corrections (ZPE). The concentration correction of 1.9 kcal/mol at room temperature (derived from the free-energy change of 1 mol of an ideal gas from 1 atm (24.5 $L \cdot mol^{-1}$, 298.15 K) to 1 M) was added for all species other than water and borate anion, for which the corresponding value are 4.3 kcal/mol as $[H_2O]$ are 55.6 M. The 3D optimized structure figures in this paper were drawn by CYL view visualization program.[7] Unless otherwise mentioned, all reported energy values are free energies in solution.

For the redox potentials calculation, the result was calculated by

(1)

where n is the number of electrons, F is the Faraday constant, is the free energy change of the redox process at standard conditions, which is composed of the free energy change in gas phase at standard conditions ( ) and the free energy change of solvation ( ), as shown in Equation (2). The and are from the results of DFT calculations.

00 (2)

For the proton-coupled electron transfer (PCET) process, the electron transfer is along with the proton transfer. Thus, the solvation energy of proton needs to be taken into consideration. The solvation energy of proton ( ) referenced to the experimental as -265.9 kcal/mol.[8] Considering the small correction of the gas–phase

Gibbs free energy of a proton (, -6.3 kcal·mol^{-1}), thus the standard free energy of a proton in solution can be calculated by

(3)

$$-(_{00})$$ (4)

Finally, since the experimental observed redox potential results were reported vs. NHE, the calculated redox potential is referenced to NHE by subtracting 4.24 V.[9]

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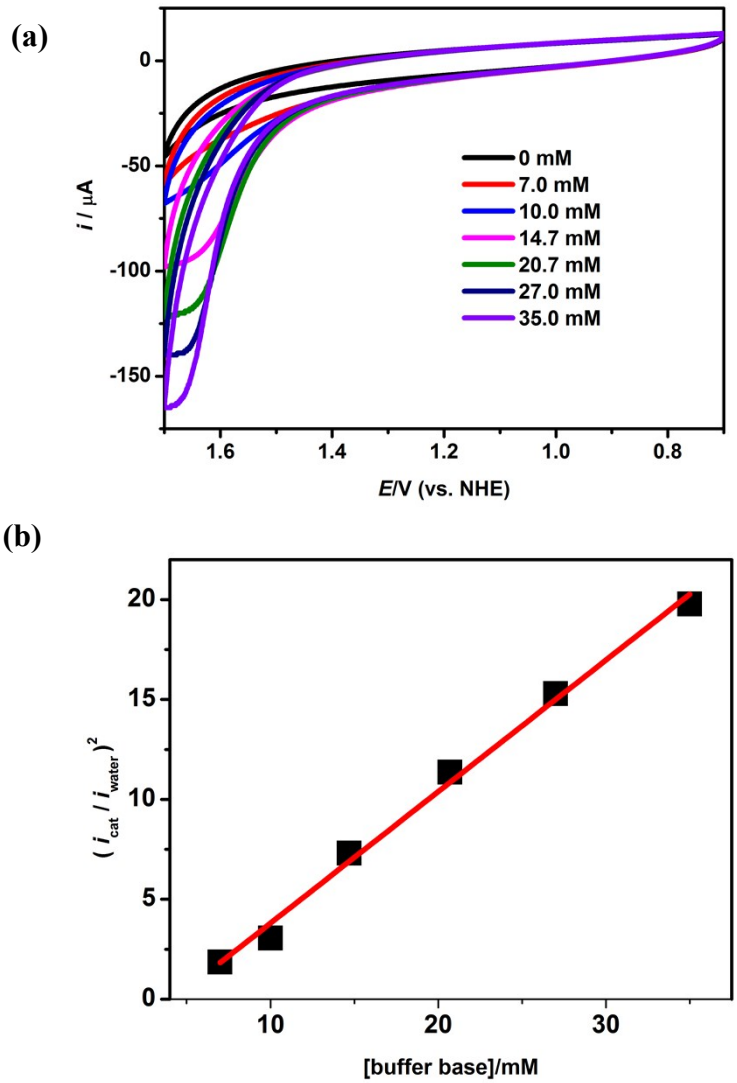

Figure S1. (a) CVs of 0.2 mM $CuSO_4$ at a GC working electrode at different concentrations of buffer base. Conditions: 1.0 M Na_2SO_4, pH 7, scan rate: 100 mV·s^{-1}. (b) Plot of $(i_{cat}/i_{water})^2$ vs. base concentrations for CVs of 0.2 mM $CuSO_4$ at various concentrations of buffer base. Other conditions include a GC working electrode, 1.0 M Na_2SO_4, pH 7 and a scan rate of 100 mV·s^{-1}.

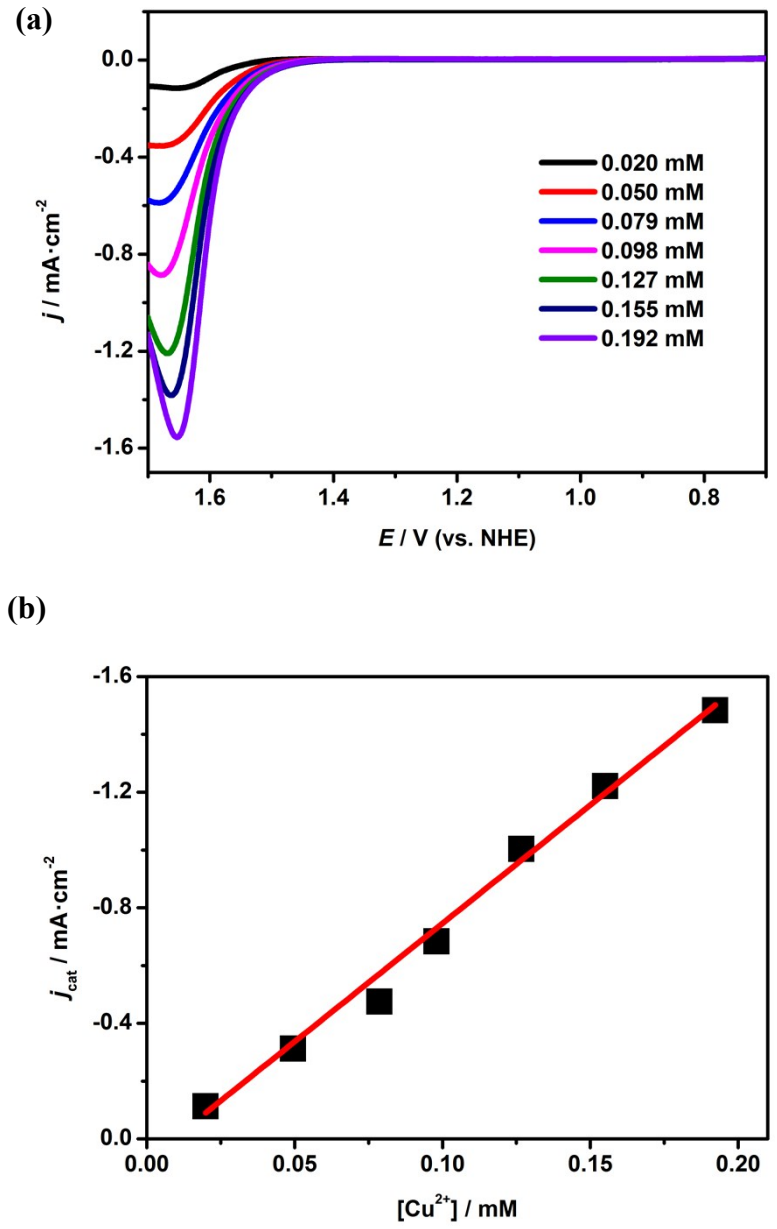

Figure S2. (a) CVs of various concentrations of $CuSO_4$ (background corrected). Returning currents are not shown for clarity. Other conditions include a GC working electrode, 0.45 M NaBi buffer, 1 M Na_2SO_4, pH 7 and a scan rate of 100 $mV \cdot s^{-1}$. (b) Plot of the catalytic peak current density (background corrected) for $CuSO_4$ vs. the catalyst concentrations.

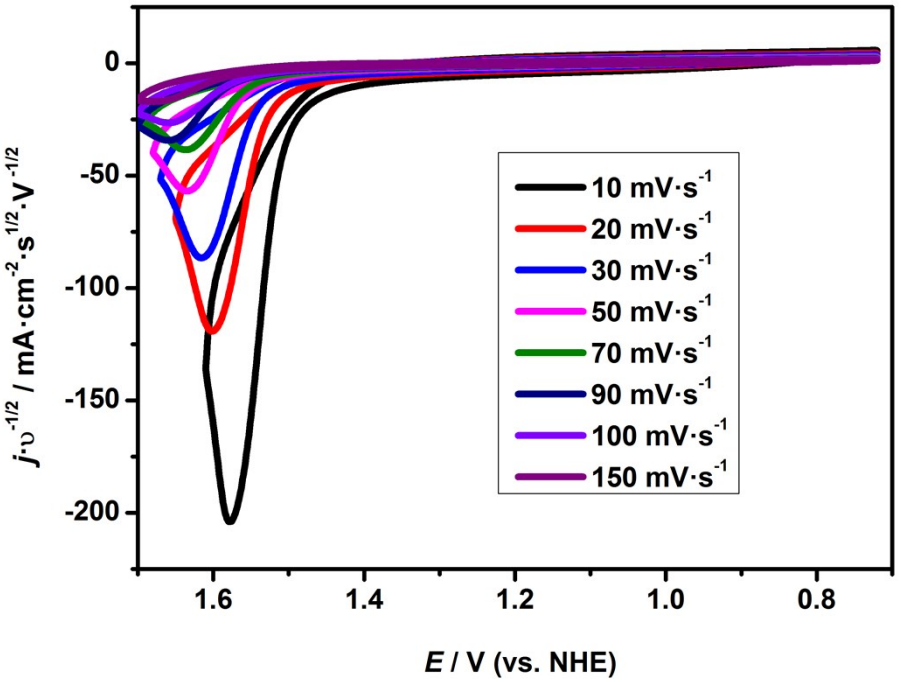

Figure S3. Normalized CVs ($i/v^{1/2}$) of 0.2 mM $CuSO_4$ in 0.45 M buffer solutions (pH 7, containing 1 M Na_2SO_4) at a GC electrode at different scan rates (v).

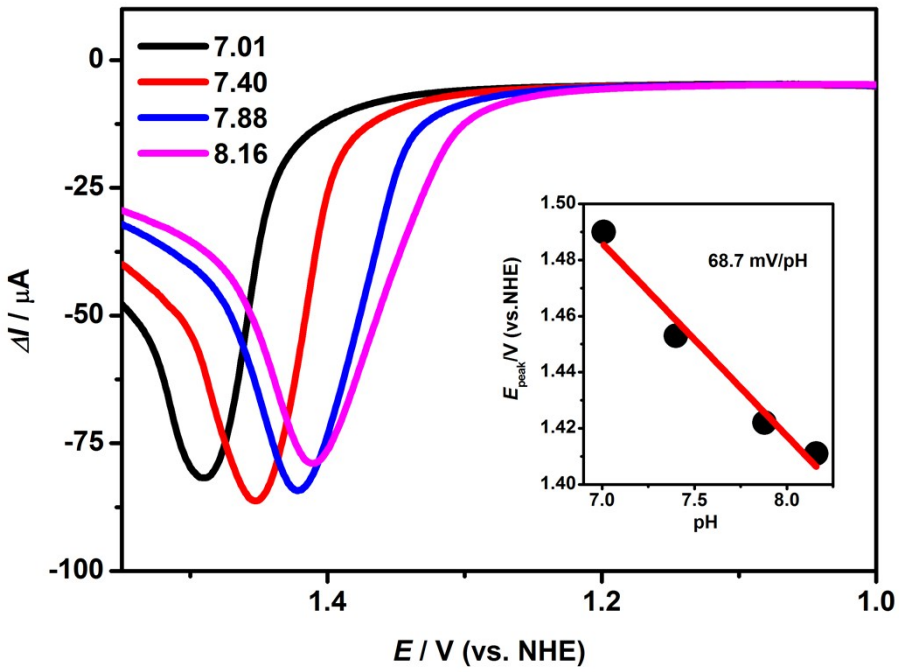

Figure S4. Differential pulse voltammetry (DPV) results of 0.2 mM $CuSO_4$ in 0.03 M borate anion (containing 1 M Na_2SO_4) at different pH values.

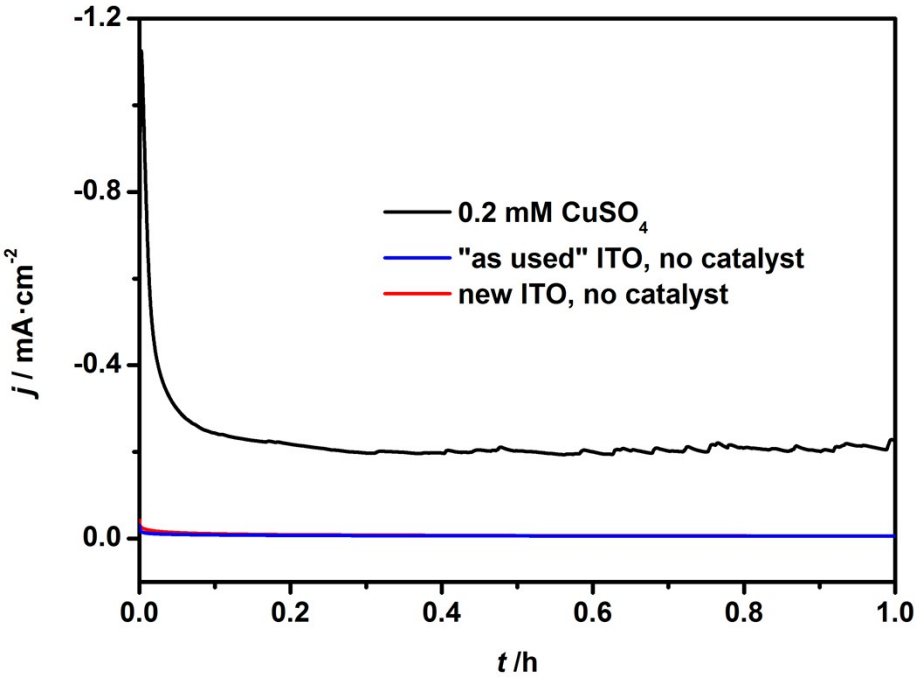

Figure S5. Current density profiles of CPE using an ITO electrode at 1.55 V for the borate buffer background (no catalyst, red), 0.2 mM $CuSO_4$ (black), and the borate buffer using the same used ITO working electrode after the CPE (blue), respectively. Conditions: 0.45 M borate buffer, 1 M Na_2SO_4, pH 7.

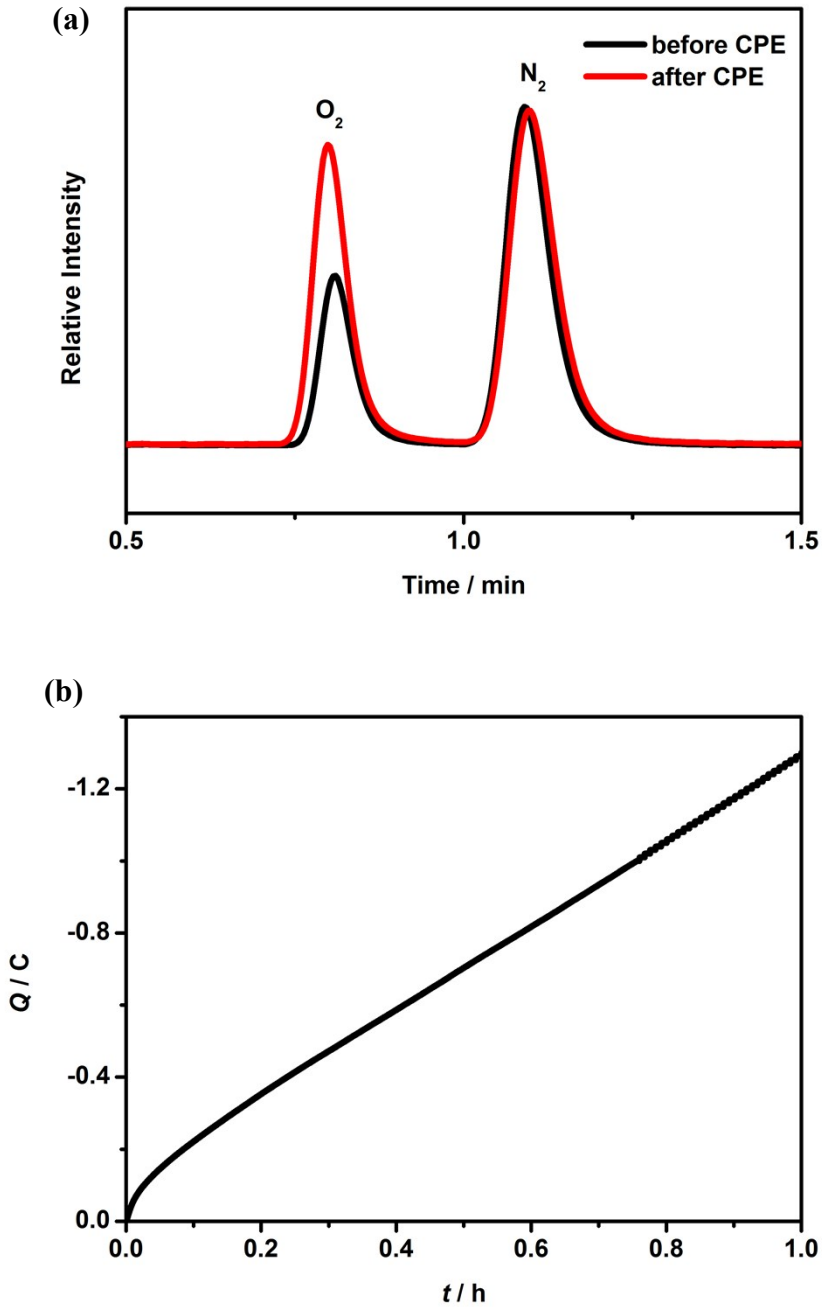

Figure S6. (a) Normalized GC traces from a representative CPE experiment. The black line shows the air background. (b) CPE with 0.2 mM $CuSO_4$ at an ITO electrode in 0.45 M borate buffer (pH 7) at 1.55 V vs. NHE.

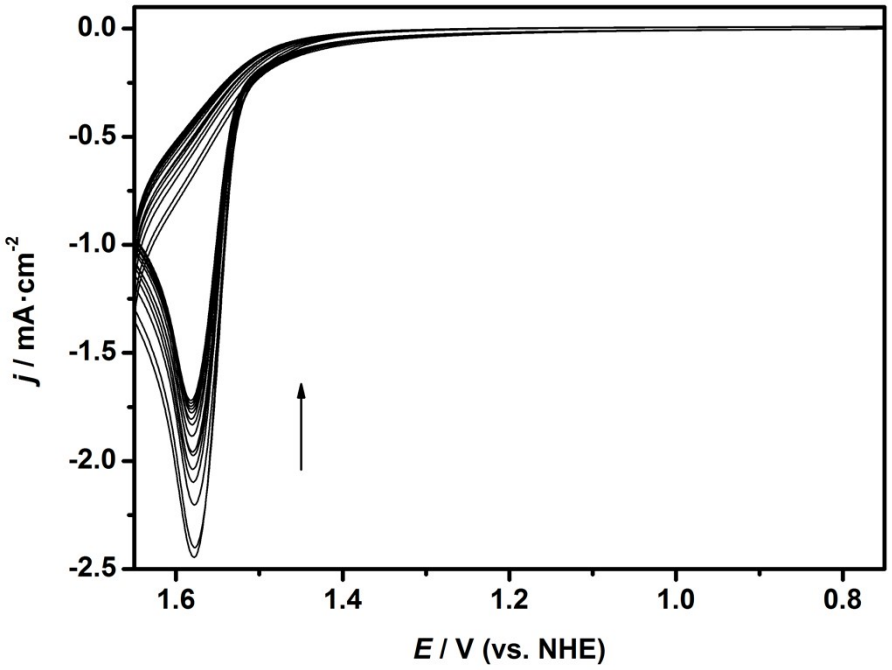

Figure S7. Repeated CV scanning of 0.2 mM $CuSO_4$ in 0.45 M pH 7 buffer solutions (containing 1 M Na_2SO_4) at a GC electrode; scan rate = 10 mV/s.

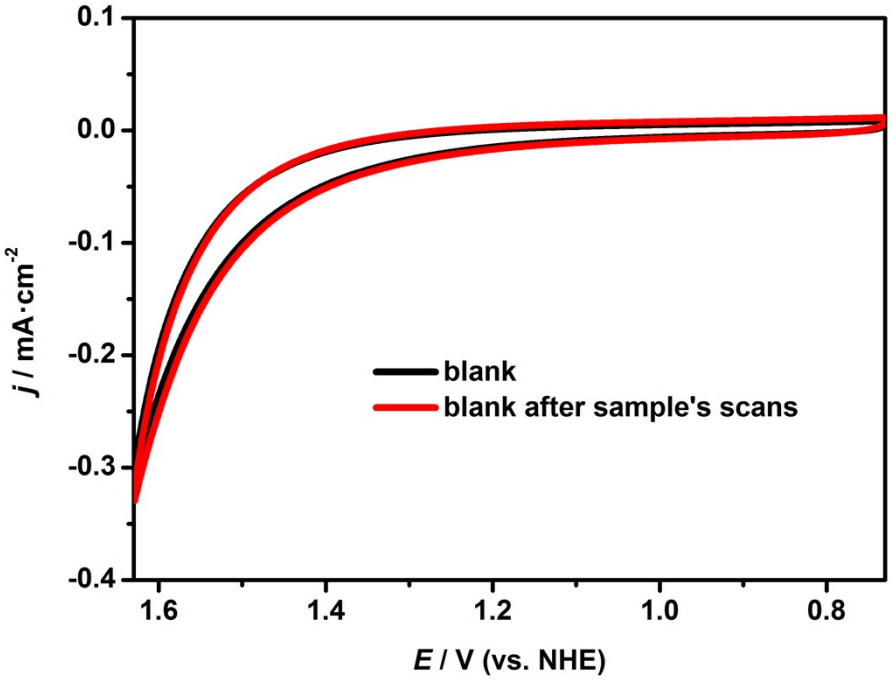

Figure S8. CVs of 0.2 mM Cu(II) in borate buffer using the fresh working electrode (black) and the working electrode after 30 segments of CV scans (red). Measurement conditions: glassy carbon working electrode, 0.45 M borate buffer, 1 M Na_2SO_4, pH 7, scan rate 10 $mV \cdot s^{-1}$.

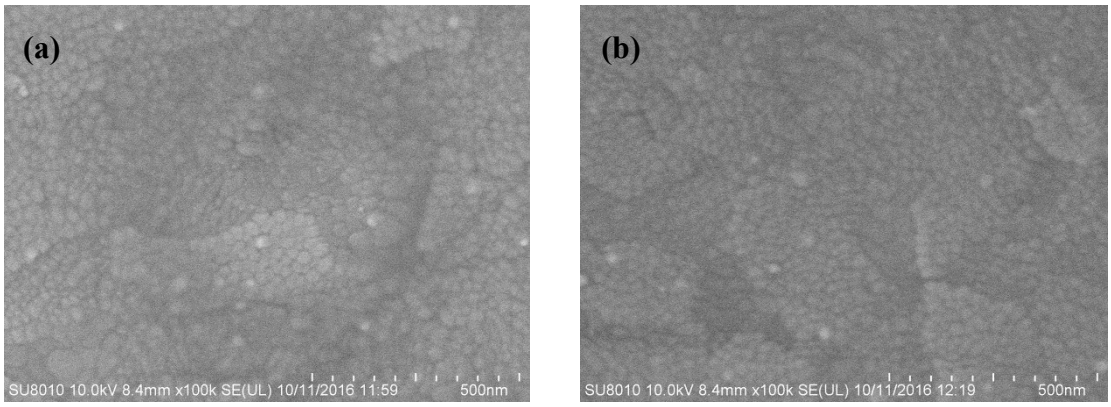

Figure S9. SEM images of ITO electrode before (a) and after (b) 1 h of CPE with 0.2 mM $CuSO_4$ in 0.45 M borate buffer and 1 M Na_2SO_4 solution.

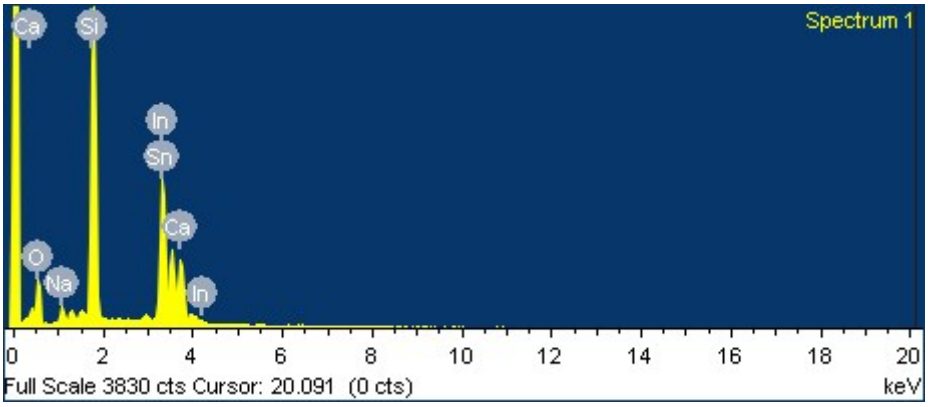

Figure S10. EDS histogram of the ITO after 1 h of CPE with 0.2 mM $CuSO_4$ in 0.45 M borate buffer and 1 M Na_2SO_4 solution, pH 7. (The signals of Ca, Na, K, Sn, Si, In and O were from the substrate).

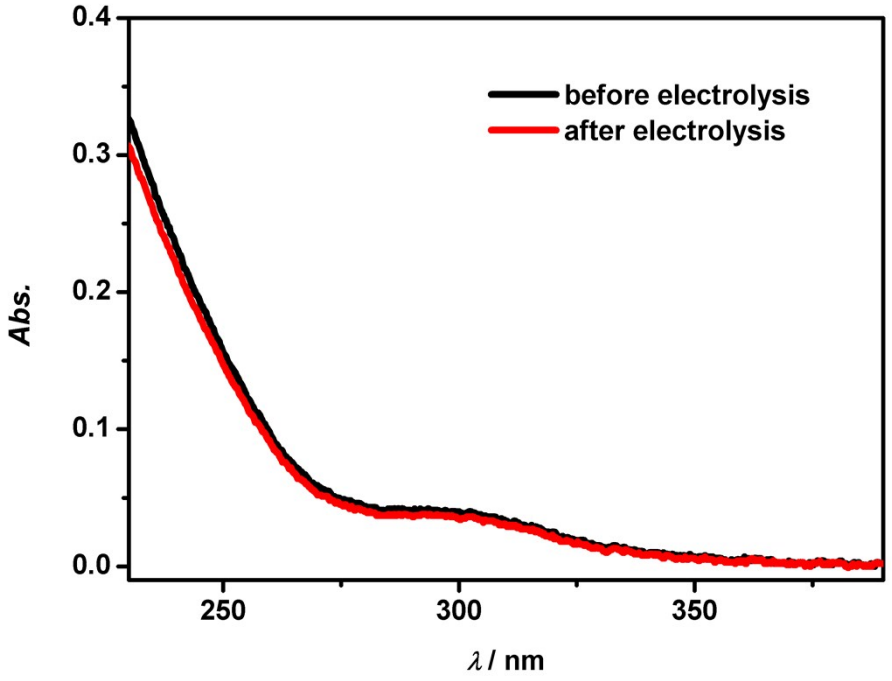

Figure S11. UV-vis spectra of 0.2 mM $CuSO_4$ in 0.45 M borate buffer solution before and after 1 h of CPE at an applied potential of 1.55 V.

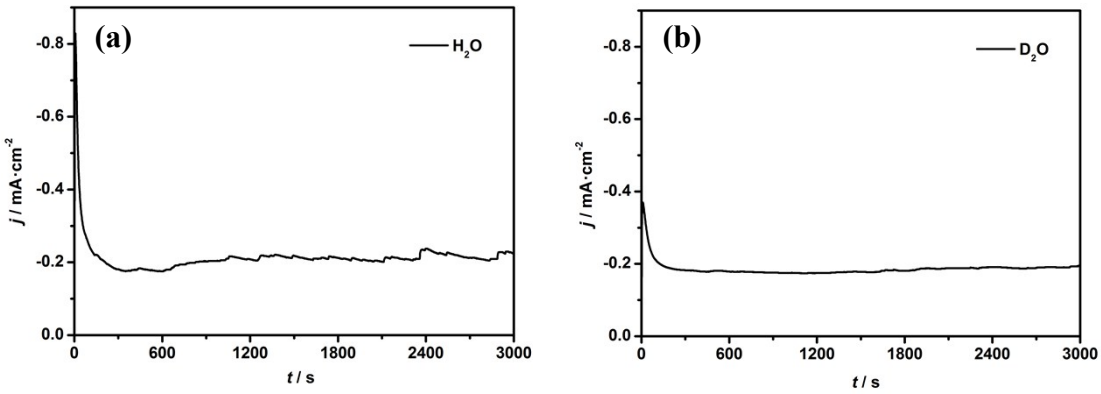

Figure S12. CPE at 1.55 V with 0.2 mM Cu(II) in 0.45 M borate buffer and 1 M Na_2SO_4 at pH/pD 7 at an ITO electrode in (a) H_2O and (b) D_2O, respectively.

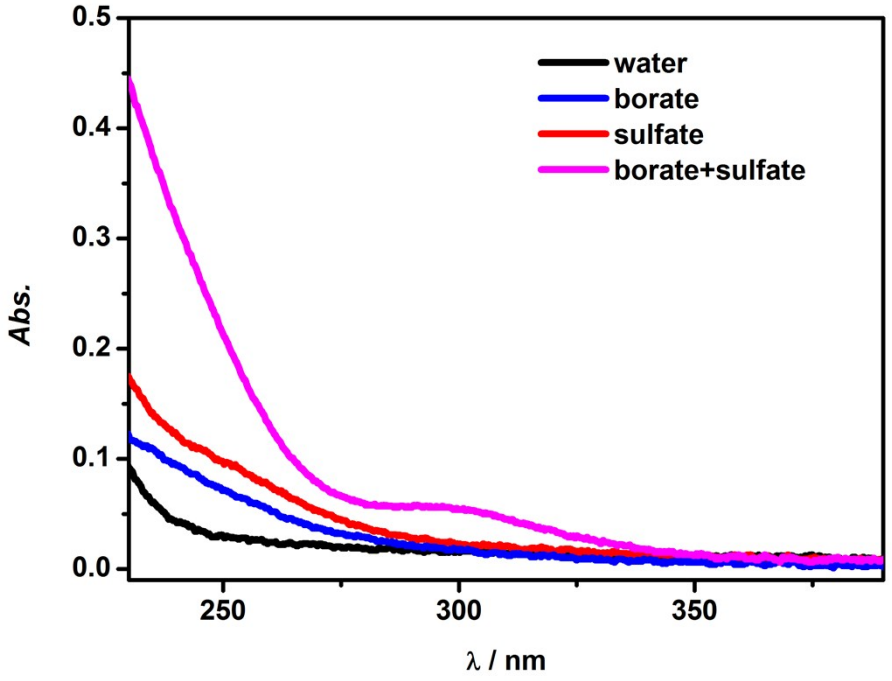

Figure S13. UV-vis spectra of 0.2 mM $CuSO_4$ in pure water, 0.45 M borate buffer (pH 7), 1.0 M sodium sulfate, and mixture of 1.0 M sodium sulfate and 0.45 M borate buffer (pH 7), respectively.

Discussion: *The starting molecular species in the catalysis was defined by UV-visible measurements. As shown above, a characteristic absorbance of Cu(II) was observed at 300 nm in sulfate and borate solution, while no absorbance appeared in the absence of either sulfate or borate. These results suggest the Cu(II) would coordinate with both sulfate and borate in the catalytic system, thus structure of the starting catalyst was proposed in Figure 2. It should be noted that the proposed compound is a simplified model for the catalyst. The real case is more complicated in the catalytic system.*

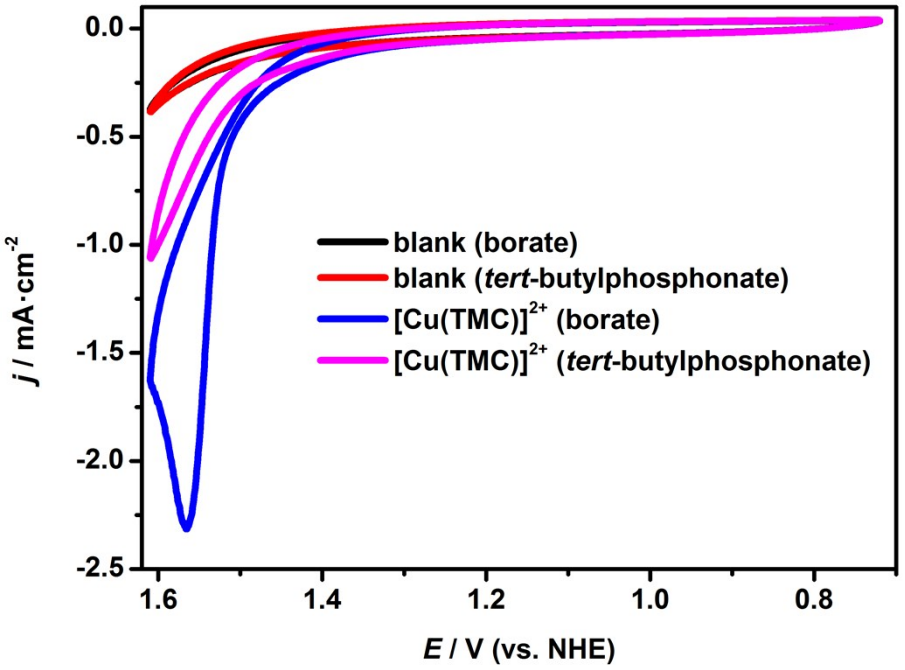

Figure S14. CVs of 0 mM and 1.0 mM $[Cu(TMC)]^{2+}$ in 0.45 M different buffer solutions (pH 7, containing 1 M Na_2SO_4) at a GC electrode; scan rate = 10 mV/s.

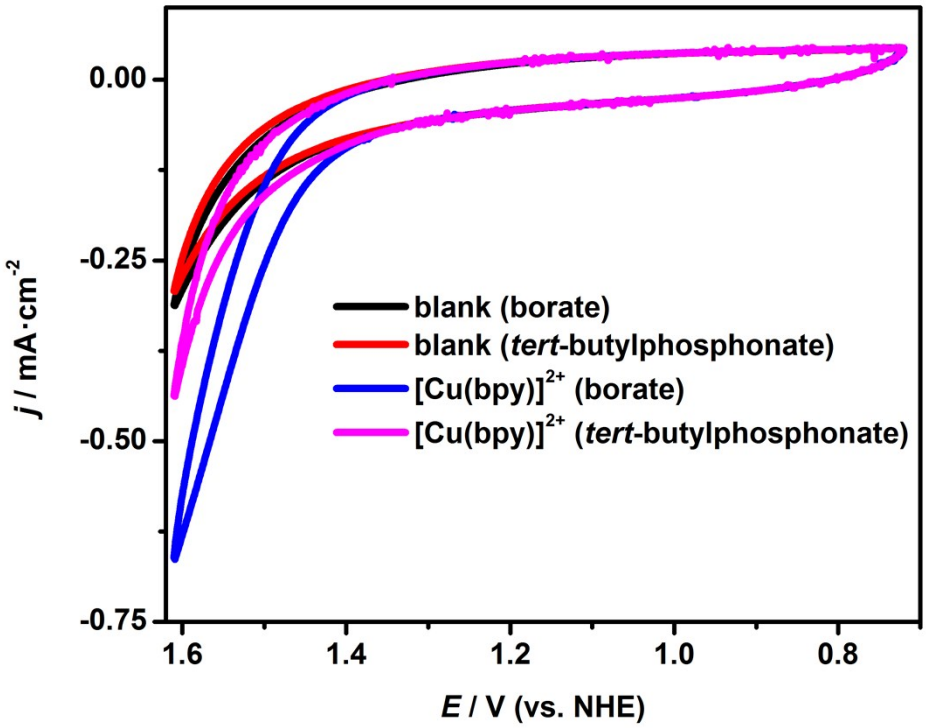

Figure S15. CVs of 0 mM and 1.0 mM $[Cu(bpy)]^{2+}$ in 0.45 M different buffer solutions (pH 7, containing 1 M Na_2SO_4) at a GC electrode; scan rate = 10 mV/s.

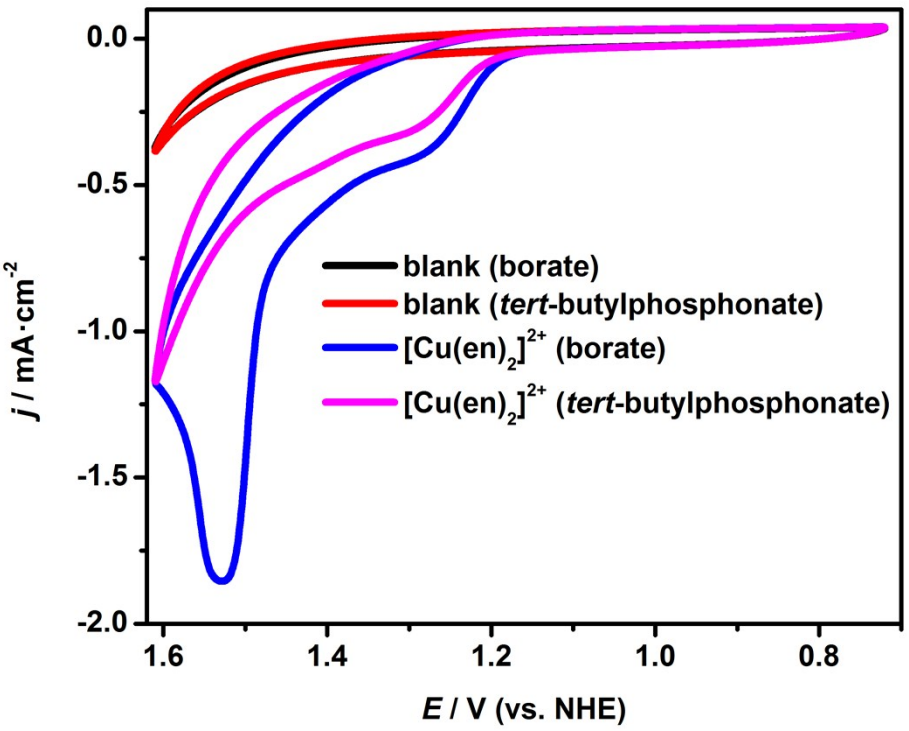

Figure S16. CVs of 0 mM and 1.0 mM $[Cu(en)_2]^{2+}$ in 0.45 M different buffer solutions (pH 7, containing 1 M Na_2SO_4) at a GC electrode; scan rate = 10 mV/s.

Optimized coordinates (xyz) in Figure 2

1

Cu	0.04921400	0.45753400	-0.24815000
O	-1.59919400	-0.35934500	-0.95484000
H	-1.33478800	-1.24064600	-1.26147300
O	-0.94586000	2.16563600	0.12179000
O	1.33284200	-1.08147800	-0.50983200
O	1.85358900	1.05135900	0.38698900
O	3.60047400	-0.13423400	-0.94314600
O	3.02664100	-0.94548200	1.31658800
S	2.53881800	-0.30454800	0.07401600
H	-1.88447000	1.81773300	0.22363000
H	-0.68069300	2.44405800	1.01452800
B	-2.72008300	-0.51120200	0.08250300
O	-3.25476900	0.86248300	0.13598000
H	-3.77603600	0.97308500	0.94331200
O	-2.20981100	-0.87304800	1.39462000
H	-2.01292400	-1.81961900	1.42046900
O	-3.65215100	-1.52607500	-0.38266100
H	-3.97306000	-1.29283200	-1.26480100

2

Cu	0.05127500	0.34666800	-0.18754100
O	-1.51175100	-0.50223300	-0.79347400
H	-1.27340600	-1.44812300	-0.81984800
O	-0.85850700	1.83626000	0.15571700
O	1.32137800	-1.08984600	-0.41231500
O	1.72033900	1.07693500	0.33401000
O	3.50316300	-0.03204800	-1.03061000
O	3.11313100	-0.76142400	1.30333400
S	2.54297000	-0.23860600	0.05791000
B	-2.80206900	-0.33693900	0.09682200
O	-3.22860200	1.04047800	-0.10091400
H	-2.90182300	1.58743500	0.62933700
O	-2.39366900	-0.68318200	1.43347300
H	-3.15629900	-0.65849000	2.02784600
O	-3.75207400	-1.27429700	-0.45676500

H	-4.13989200	-0.91696100	-1.26897800

3

Cu	0.00456600	0.22034200	-0.15135600
O	-1.58472000	-0.86181900	-0.75759500
H	-1.35565500	-1.79099400	-0.59671500
O	-1.21154300	1.66078600	0.25226700
O	1.47726900	-1.06989400	-0.53143200
O	1.72412300	1.06299900	0.47893700
O	3.54562100	0.23869800	-1.01377600
O	3.23568300	-0.78015500	1.21438400
S	2.58399700	-0.14922800	0.04370200
B	-2.74200700	-0.46843100	0.04942000
O	-2.55182100	1.19863800	-0.18631400
H	-3.13702500	1.66171900	0.44555700
O	-2.58277600	-0.76903300	1.41486900
H	-3.42818700	-0.71589400	1.88267200
O	-4.02743800	-0.71089600	-0.47798300
H	-4.04067500	-0.56952200	-1.43539900

4

Cu	0.05349200	0.34608500	-0.19735500
O	1.61045600	-0.90955500	-0.80604100
H	1.85790300	-0.82635200	-1.74097600
O	1.01240000	1.90763700	0.24301800
O	-1.35441300	-1.05897000	-0.57272200
O	-1.75219800	1.03063600	0.49399700
O	-3.07428000	-0.95060300	1.22883800
O	-3.53657300	0.08283300	-0.96584500
S	-2.50922500	-0.24318000	0.05350800
B	2.70310900	-0.93556600	0.05376100
O	2.42825200	1.79869300	-0.08638700
O	3.95506100	-1.05685400	-0.47361300
H	4.63814700	-1.09109700	0.21328500
O	2.48705100	-0.90368600	1.40280200
H	1.54828500	-0.77626900	1.61779500
H	2.83040500	1.70491600	0.79587700

5

Cu	0.08032600	0.32596400	-0.18804200
O	1.66880900	-0.83383300	-0.83573900
H	1.92617200	-0.69646400	-1.76170500
O	1.08019100	1.93116300	0.23668900
O	-1.37671300	-1.08799200	-0.59294600
O	-1.70134600	1.00088600	0.51723300
O	-3.09219300	-0.94632300	1.21000300
O	-3.51077900	0.14495800	-0.96567400
S	-2.49550900	-0.24232300	0.04656900
B	2.75022700	-0.88952800	0.03921500
O	2.36704100	1.86656300	0.08084800
O	4.01135400	-0.94277900	-0.47563400
H	4.68519500	-1.00315500	0.21852100
O	2.51223800	-0.95259800	1.38299900
H	1.56737900	-0.86887800	1.59299400

6

Cu	0.11318200	0.49676100	-0.16212200
O	-1.53819300	-0.33613900	-0.95000700
H	-1.20449200	-0.96623000	-1.60814300
O	-0.55600300	2.20309600	0.37580300
O	1.36502000	-1.07414700	-0.53938600
O	1.98375400	1.00553000	0.43759000
O	3.64157800	-0.17026000	-1.00642400
O	3.11793300	-1.06828000	1.23250900
S	2.60376900	-0.35562500	0.03688600
B	-2.42492900	-1.05018100	-0.01142100
O	-3.15674900	0.24328500	0.68035000
H	-3.07854300	0.19367000	1.64952700
O	-1.70628900	-1.74151900	0.99925200
H	-2.26604800	-2.41005100	1.41798500
O	-3.43460700	-1.83578800	-0.62890500
H	-3.89703600	-1.32616300	-1.30952000
O	-1.93919500	2.45463600	-0.02504300
H	-2.70910500	1.11311600	0.41051000
H	-1.88070000	2.48716400	-0.99780400

7

Cu	0.09305300	0.48259000	-0.24513800

O	-1.56344300	-0.37038800	-0.98756900
H	-1.23136000	-1.04578700	-1.59966300
O	-0.53304900	2.30552100	0.05193600
O	1.36480900	-1.14108000	-0.47328200
O	1.94761700	1.01771200	0.35018200
O	3.64957100	-0.26149200	-0.94532900
O	3.06377400	-0.97810400	1.34285600
S	2.58028500	-0.37152200	0.07733800
B	-2.44318500	-1.00495600	0.00918200
O	-3.29034800	0.33696000	0.44422800
H	-3.57917500	0.27705100	1.37243600
O	-1.71900200	-1.47706200	1.13505200
H	-2.26795700	-2.06320100	1.67449400
O	-3.37994300	-1.93884800	-0.50068000
H	-3.85799800	-1.57161100	-1.25753800
O	-1.80497200	2.53341900	0.23837800
H	-2.71080700	1.16444300	0.38979200

TS1

Cu	0.04970400	0.26167800	-0.14660400
O	-1.54025300	-0.69592200	-0.73435700
H	-1.32362200	-1.63577700	-0.60822200
O	-1.02244600	1.66556300	0.20189100
O	1.42788300	-1.12177800	-0.42375400
O	1.70866300	1.08099400	0.35540200
O	3.51935900	0.09136900	-1.05281600
O	3.21152000	-0.68884600	1.27350600
S	2.57647600	-0.19057900	0.04235000
B	-2.77754600	-0.34929300	0.05713900
O	-2.85415300	1.15589500	-0.21197300
H	-3.23411400	1.59987200	0.56631000
O	-2.58595000	-0.67344700	1.43674000
H	-3.43946300	-0.80194800	1.87296800
O	-3.95332400	-0.96886700	-0.48586100
H	-4.07048400	-0.71476700	-1.41306500

TS2

Cu	-0.00921900	0.25383100	-0.14780800
O	-1.60474700	-0.83055000	-0.80723800

H	-1.29193100	-1.74862900	-0.74772100
O	-1.12525200	1.75157400	0.22987100
O	1.44563500	-1.06098300	-0.55233600
O	1.73135900	1.02865300	0.54126700
O	3.51764900	0.24801300	-1.01402600
O	3.23327500	-0.85884500	1.17488000
S	2.56762100	-0.17342000	0.04250500
B	-2.75347900	-0.62926700	0.03287000
O	-2.51278500	1.35096700	-0.06556300
H	-2.97689000	1.66964400	0.73172700
O	-2.57355300	-0.91554400	1.37413700
H	-3.41399700	-0.91254600	1.85543800
O	-4.02949100	-0.69954100	-0.49860500
H	-4.02109800	-0.55847200	-1.45655000

TS3

Cu	0.12294700	0.47803900	-0.21255800
O	-1.48424100	-0.29119500	-0.98340900
H	-1.13334400	-0.94514000	-1.61156000
O	-0.67278200	2.00501200	0.35014000
O	1.41334600	-1.01939600	-0.59064500
O	1.82960800	1.05398100	0.45942000
O	3.64218700	0.05686800	-0.93601300
O	3.09418300	-0.94797800	1.25479500
S	2.59461300	-0.25854000	0.05180900
B	-2.32851000	-1.04866400	0.08111000
O	-3.29983500	-0.01952400	0.48904200
H	-3.53808400	-0.13603200	1.41981000
O	-1.52868500	-1.43308600	1.22158800
H	-0.96315100	-2.18395300	0.99247500
O	-2.90293200	-2.21055800	-0.56723900
H	-3.48492900	-1.93556300	-1.28957700
O	-2.47837800	2.40625900	0.06260300
H	-2.80757700	1.45112200	0.24499700
H	-2.40940200	2.46331600	-0.90870900