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Electronic Supplementary Information (ESI)

*Effect of copper salts on hydrothermal oxidative decarboxylation: A
study of phenylacetic acid*

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22 I. EXPERIMENTAL SECTION

23 Materials

24 Benzyl alcohol (99%), benzoic acid (99%), benzaldehyde (>99%), phenylacetic acid
25 (99%), *p*-tolylacetic acid (99%), and *p*-fluorophenylacetic acid (98%) were obtained from Sigma
26 Aldrich and used as received. Copper (II) salts including copper chloride (99%), copper acetate
27 (98%), copper sulfate (98%), and copper trifluoromethanesulfonate (98%) were purchased from
28 Sigma Aldrich, whereas copper nitrate (>99%) was purchased from Fisher Chemicals. Magnesium
29 nitrate (>99%), zinc nitrate (98%), and nickel (II) nitrate (>99%) were all obtained from Sigma
30 Aldrich. Dichloromethane (99.9%) was obtained from VWR and *n*-dodecane (99%) was purchased
31 from Sigma Aldrich. Deionized water was obtained from a Barnstead Nanopure system with a
32 resistivity of 18.2 M Ω ·cm. Fused silica glass tubes were obtained from GM Associates, Inc. and
33 rinsed with dichloromethane before use.

34 Methods

35 Hydrothermal experiments were performed in fused silica glass tubes (2 mm inner diameter
36 and 6 mm outer diameter) using a previously developed method.¹ In short, 0.03 mmol of
37 phenylacetic acid was weighed and carefully transferred into the tube through a Pasteur pipette. A
38 0.3 mL aliquot of metal salts solution (0.2 molal in degassed and deionized water) was
39 subsequently added using a gas-tight micro-syringe, to reach a molar ratio of 1:2 between
40 phenylacetic acid and the divalent metal ions. In sodium salts experiments, the anions
41 concentrations were kept the same as those in copper salts experiments, with a molar ratio of 1:4
42 between phenylacetic acid and the sodium ions, except for sodium sulfate (1:2). The headspace air
43 in silica tubes was evacuated through three pump-freeze-thaw cycles and the tubes were sealed
44 with an oxyhydrogen flame under vacuum. The sealed tubes were then heated in a gas

45 chromatography (GC) oven at 200 °C for up to 6 hours. The pressure inside the tube was calculated
46 to be ca. 15 bar (P_{sat} at 200 °C) based on thermodynamics calculations using SUPCRT92.²

47 The hydrothermal experiments were quenched by submerging the silica tubes in a cold
48 water bath and the cooling process took less than one minute. The tubes were cut open and the
49 products were quickly transferred into a 3.0 mL dichloromethane solution with *n*-dodecane as the
50 GC internal standard. Reaction products were analyzed using an Agilent 7820 GC equipped with
51 an autosampler (Agilent 7650) and a flame-ionization detector, and the product identification was
52 verified by a GC-MS (Agilent 7890A/5975C). Product concentrations were quantified by GC
53 calibration curves that were generated with standard solutions. The GC oven was programmed to
54 start at 50 °C (hold 8 min), ramp at 10 °C min⁻¹ to 220 °C (hold 10 min), and ramp at 20 °C min⁻¹
55 to 300 °C (hold 5 min). The injector temperature was set at 300 °C.

56 The absorbance of dissolved copper (II) in solution before and after the hydrothermal
57 reaction was measured using a UV-Vis spectrometer (Agilent). To minimize oxidation of copper
58 (I) to copper (II) by air, the aqueous samples after the hydrothermal process were quickly extracted
59 with 3.0 mL DI water, filtered through a 0.45 µm-membrane filter, and transferred to a cuvette
60 before the spectroscopy analysis in a wavelength range of 500 to 900 nm. The absorbance of
61 copper (II) was measured at 799 nm, and the copper (II) concentration was determined based on a
62 calibration curve built with copper (II) standards. Concentration of copper (I) was not quantified
63 because of the low solubility of the copper (I) salts, and insoluble solids were observed after the
64 reaction, which are consistent with formation of copper (I) products.

65 Raman measurements were collected through the wall of sealed silica tubes using a Horiba
66 Xplora Plus Raman microscope, similar to a previous approach.³ In a typical measurement, the
67 laser was first focused on the top of the silica tube above a region containing fluid. The stage was

68 then raised 1500 μm to bring the focus of the laser ~ 500 μm within the tube. All Raman spectra
69 were acquired using a 473 nm laser with perpendicular polarization through a 50x long-working
70 distance objective (0.50 NA) with ~ 25 mW power at the sample surface, a 100 μm confocal
71 pinhole, a 100 μm monochromator slit, a 1200 groove mm^{-1} dispersive grating, 60 s acquisition
72 time, and 3 co-averaged scans. Each Raman spectrum was subjected to a 10th-order polynomial
73 smoothing algorithm following collection. Displayed spectra have had the water signal from a
74 CuCl_2 solution subtracted following smoothing. The phonon band at 520.7 cm^{-1} from crystalline
75 silicon was used to calibrate all Raman spectra.

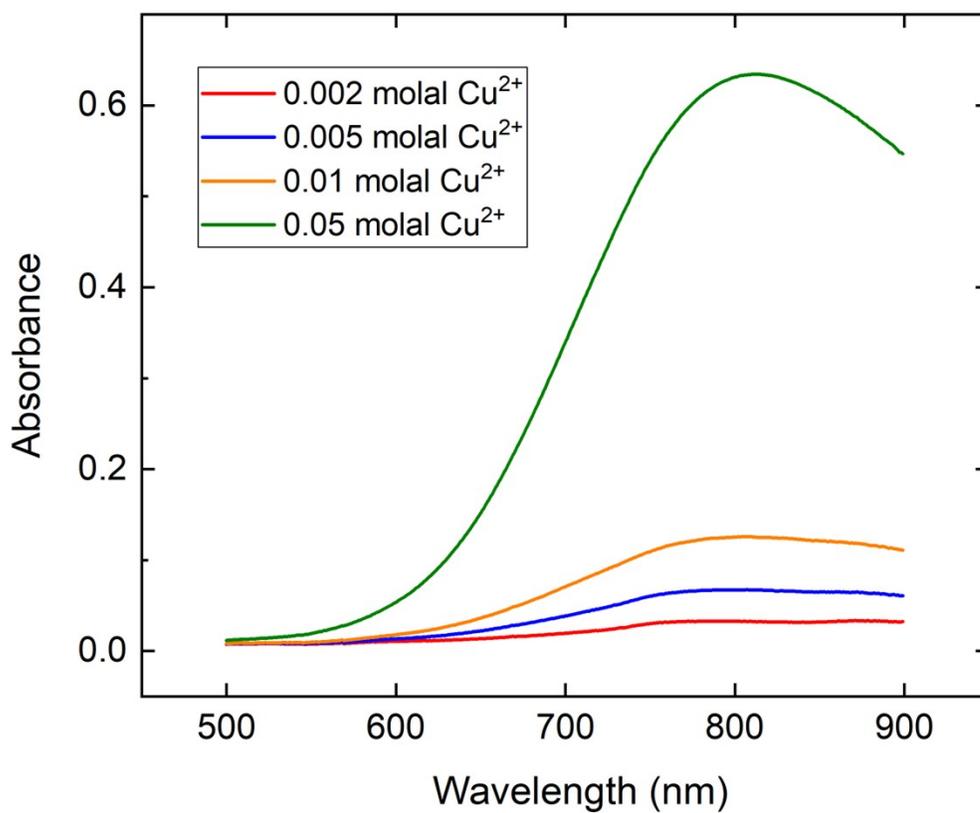
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78 **II. FIGURES AND TABLES**

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80 **Figure S1.** Absorbance of copper (II) in standard solutions with a concentration ranging from
81 0.002, 0.005, 0.01 to 0.05 molal.



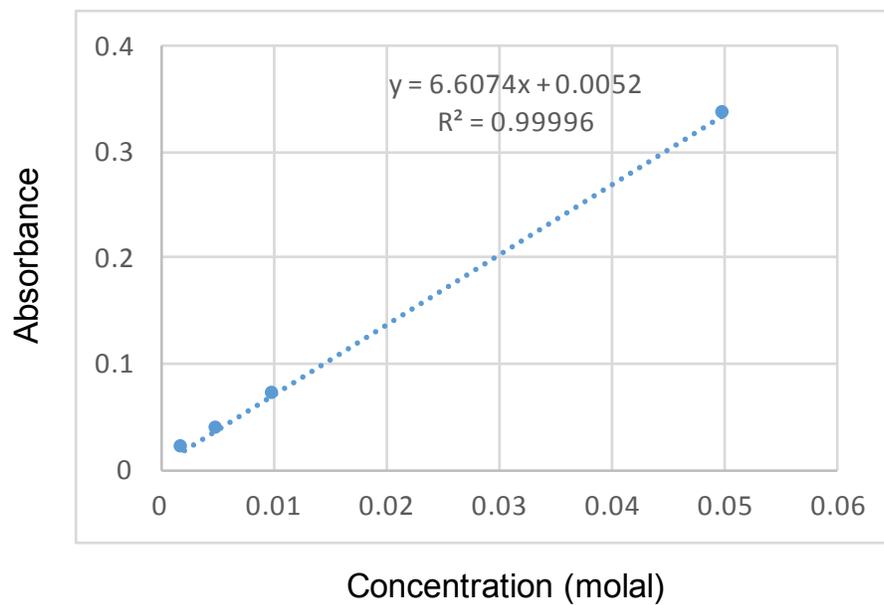
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85 **Figure S2.** Calibration curve built with copper (II) absorbance versus copper (II) concentrations.

86 The absorbance of copper (II) was measured at the wavelength of 799 nm.



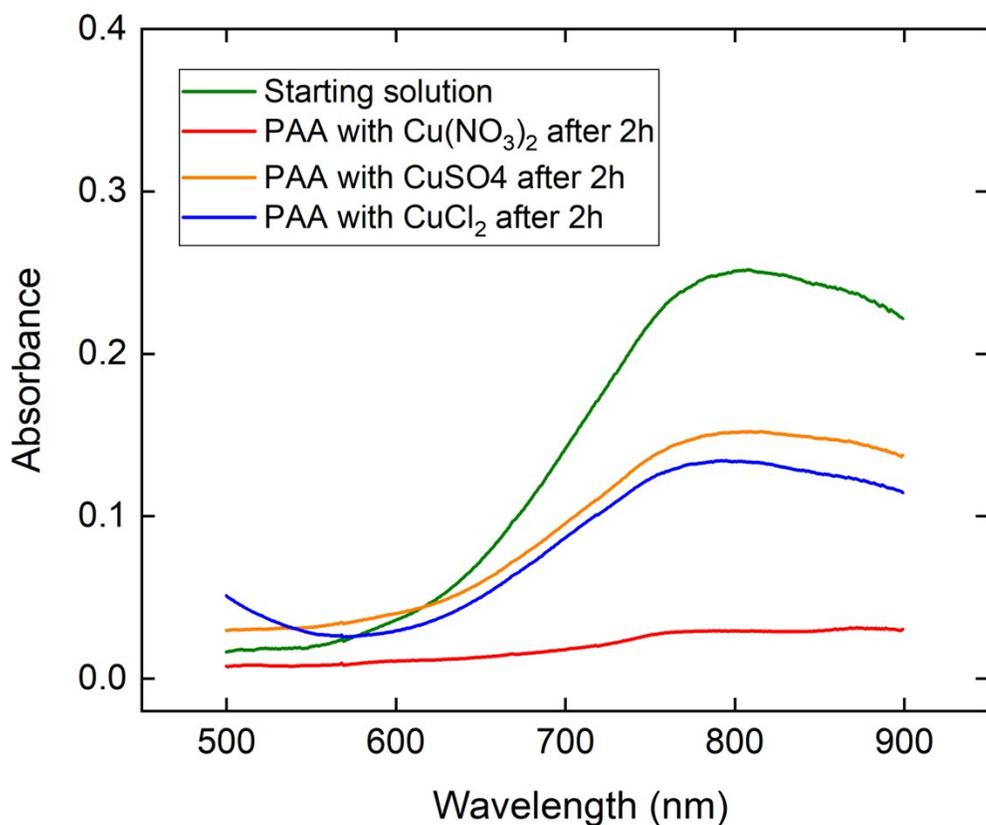
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91 **Figure S3.** Absorbance of copper (II) in solutions before (green curve) and after the hydrothermal
92 experiments of PAA with copper chloride (blue curve), copper sulfate (orange curve), and copper
93 nitrate (red curve) at 200 °C and 15 bar after 2 hours. The starting concentrations of PAA and
94 copper (II) were 0.1 and 0.2 molal, respectively. The samples were diluted 10 times before the
95 UV-Vis analysis to ensure the absorbance values were not higher than 1.



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98 **Table S1.** Major products concentration and reaction conversion of PAA with 2 and 4 equivalent
99 of copper (II) salts in H₂O at 200 °C and 15 bar after 2 hours. The starting concentration of PAA
100 was 0.1 molal. The initial concentrations of 2 and 4 equivalent of copper (II) were 0.2 and 0.4
101 molal, respectively.

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	Copper (II) salts	Copper (II)/PAA ratio	PAA decomposition (%)	Benzaldehyde (mmolal)	Benzoic acid (mmolal)	Remaining Cu ²⁺ (molal)
PAA	CuCl ₂	2	42.2	30.4	10.7	0.02
PAA	CuCl ₂	4	68.9	61.8	7.1	-
PAA	CuSO ₄	2	34.1	12.0	20.8	0.02
PAA	CuSO ₄	4	44.7	25.7	18.9	-
PAA	Cu(OAc) ₂	2	39.4	24.7	14.7	-
PAA	Cu(OAc) ₂	4	66.6	49.2	17.4	-
PAA	Cu(NO ₃) ₂	2	71.3	8.7	62.6	0.01
PAA	Cu(OTf) ₂	2	14.6	4.6	9.1	-
PAA	Cu(OTf) ₂ + NaNO ₃	2	53.7	10.9	42.8	-

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108 hydrothermal transformations. *JoVE* **2018**, (138), e58230.
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