Supplementary Information

Effects of Copper on the Chemical Kinetics and Brown Carbon Formation in the Aqueous ·OH oxidation of Phenolic Compounds

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Section S1. Assessing the effectiveness of the EDTA addition to extracted sample aliquots

Previous studies added EDTA to their samples to quench reactions initiated by Cu-catalyzed H_2O_2 decomposition,[1, 2] but these studies did not specify the pH conditions of their solutions. We observed that the addition of EDTA alone to the extracted sample aliquots still led to substantial degradations of the PhCs. In contrast, the addition of EDTA acidified to pH 2 with H_2SO_4 to the extracted sample aliquots did not lead to substantial degradations of the PhCs even though the measurements took place after 18 h of storage at 4 °C. Here, 18 h was chosen as the threshold storage time in our tests after considering the typical wait times encountered to obtain access to the department's communal UPLC-PDA system for our PhC measurements. As shown in Figure S1, over our kinetics experimental timescale, the concentrations of the PhCs in experiments where acidified EDTA was added to the extracted sample aliquots and then analyzed after 18 h of storage at 4 °C were close to those of which the PhCs in the extracted sample aliquots were measured immediately without the addition of EDTA. Consequently, their $\frac{[PhC]_t}{[PhC]_0}$ values were pretty close regardless the reaction time. In contrast, the measured PhC concentrations were substantially lower when non-acidified EDTA was added to the extracted sample aliquot, thus resulting in substantially lower $\frac{[PhC]_t}{[PhC]_0}$ values. Thus, in photooxidation and dark experiments aimed at measuring the decay kinetics of the PhC in solutions containing $CuSO_4$ and H_2O_2, EDTA acidified to pH 2 with H_2SO_4 was added immediately to the extracted sample aliquots to quench the reaction prior to UPLC-PDA analysis. Additionally, the quenched extracted samples were analyzed within 18 h.

Section S2. SPE protocol

SPE was immediately performed on the extracted sample aliquots using SPE cartridges (HLB, 200 mg, 6 cm^3, 30 μm, Waters) to desalt the samples prior to UPLC-MS analysis: The SPE cartridge was first activated and conditioned by filling it with 2 mL methanol and 2 mL ultrapure water. After that, the extracted 3 mL sample aliquot was loaded to the SPE cartridge. Next, the cartridge was flushed by adding 9 mL ultrapure water and dried by flushing air through the cartridge using an air pump. Finally, the elution was conducted by the addition of 6 mL acetonitrile and dried with flushing air. The eluted acetonitrile with organic compounds was diluted with 6 mL purified water, filtered using 0.22 μm pore size FTPE filters (Tianjin

Jinteng Experiment Equipment Co., Ltd., Tianjin, China), and collected for UPLC-MS analysis.

Section S3. UPLC-MS measurements of 4-hydroxybenzoic acid

4-hydroxybenzoic acid was measured using an ultra-high performance liquid chromatography system (1290 Infinity LC, Agilent) coupled to a high-resolution quadrupole-time-of-flight mass spectrometer (Sciex X500R QTOF) equipped with an ESI source that was operated in negative mode. All the extracted 3 ml aliquots were desalted using the SPE procedure described in Section S1. A reverse phase Kinetex (Phenomenex) PS-C18 column (150 × 2.1 mm, 2.6 μm, 100 Å) equipped with a security guard and a PS-C18 pre-column was used for the UPLC-MS analysis. The temperatures for the column oven and the UPLC autosampler were set to 25 °C. A gradient elution program was used. The binary mobile phases consisted of eluent A (10 mM ammonium acetate) and eluent B (acetonitrile) delivered at a flow rate 300 μL min^{-1}. The sample injection volume was set to 10 μL. The following mobile phase gradient was used: 0 to 3 min 1% B, 3 to 5 min linear gradient to 80% B, 5 to 6 min 80% B, 6 to 6.5 min linear gradient to 1% B, 6.5 to 7 min 1% B. The following tandem MS conditions were used: −4500 V ESI ion spray voltage, −80 V declustering potential, −15 V collision energy, 25 PSI curtain gas, and 450 °C source temperature.

Section S4. UPLC-MS data processing and analysis of products from dark oxidation and photooxidation experiments

The raw UPLC-MS data first underwent preprocessing using the open-source HR-MS workflow R package, patRoon. The program uses the open-source software library, OpenMS, for the automatic identification of chromatographic peaks. The following feature finding settings were used: the noise intensity threshold ("noise_threshold_int") was set to 200, the signal to noise ratio was set to 5, and an allowed mass deviation of 10 ppm was set. The settings were selected based on a balance between quantity and quality of the extracted peaks, with consideration given to the total number of peaks while minimizing the effects from noise. Similar peaks that were found across samples were grouped. The resulting feature groups were filtered based on their peak intensities and ubiquitous presence in replicates. In addition, only peaks with signal intensities that were at least three times higher than those of the sample blanks were included. The molecular formulas for all the feature groups were calculated automatically, using the "generateMSpeakLists" function from the patRoon R package. This generated MS peak lists from the feature groups. This function utilized the mzR package to obtain the MS

and MS/MS spectra, which were then averaged and filtered. Candidate formulas were then calculated for the feature groups using the "generateFormulas" function, which relied on the open-source package, GenForm. GenForm generated molecular formulas for the high-resolution MS and MS/MS data by using the accurate mass of the feature groups to calculate candidate formulas. The candidate formulas were scored based on matched theoretical/measured isotopic patterns, and only formulas that met the basic chemical criteria were included. The formula calculations included C, H, and O atoms.

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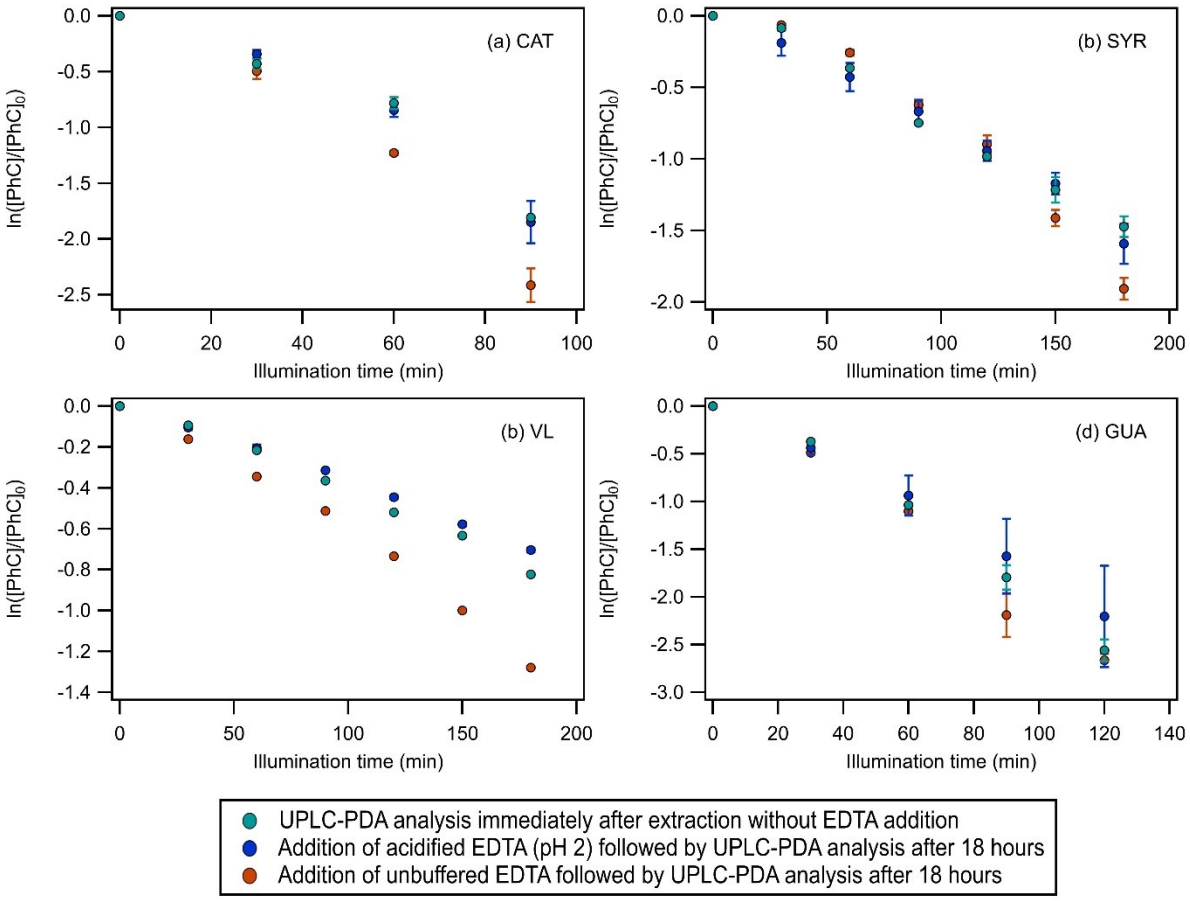

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117 **Figure S1.** Evaluation of the use of acidified EDTA to quench reactions during the
118 photooxidation of (a) catechol (CAT), (b) syringol (SYR), (c) vanillin (VL), and (d) guaiacol
119 (GUA) initiated by H_2O_2 decomposition in the presence of Cu(II). Error bars indicate standard
120 deviations from triplicate measurements.

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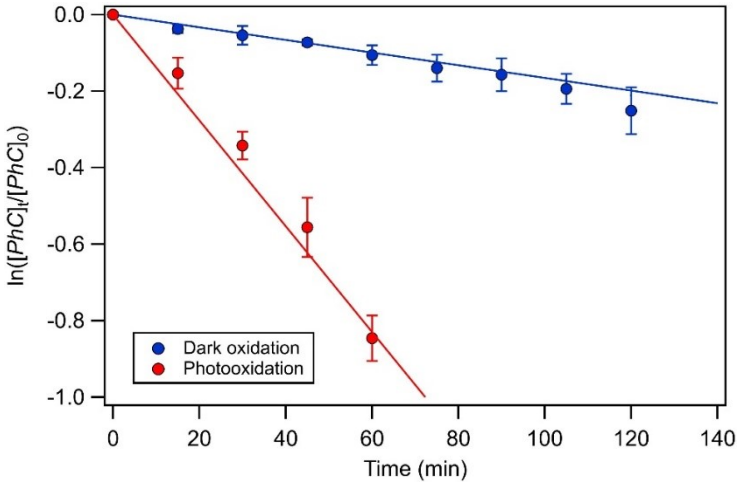
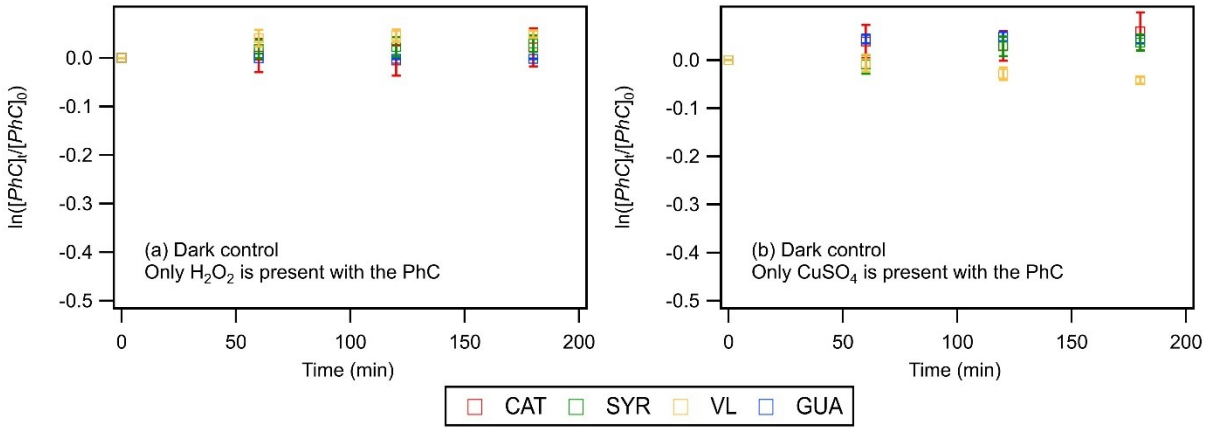


Figure S2. Decays of catechol in dark oxidation and photooxidation experiments utilizing solutions containing catechol, 50 μM of Cu(II), and 500 μM of H_2O_2 at pH 5.5. Lines show the exponential fits to the initial decays. Error bars indicate standard deviations from triplicate experiments and measurements. Similar kinetic analyses were conducted for the four PhCs. In dark experiments, time = 0 min is the time point at which Cu(II) was added into the solution. In photooxidation experiments, time = 0 min is the time point immediately before the solutions were exposed to light in the photoreactor. All the decays were fitted using equation (1).



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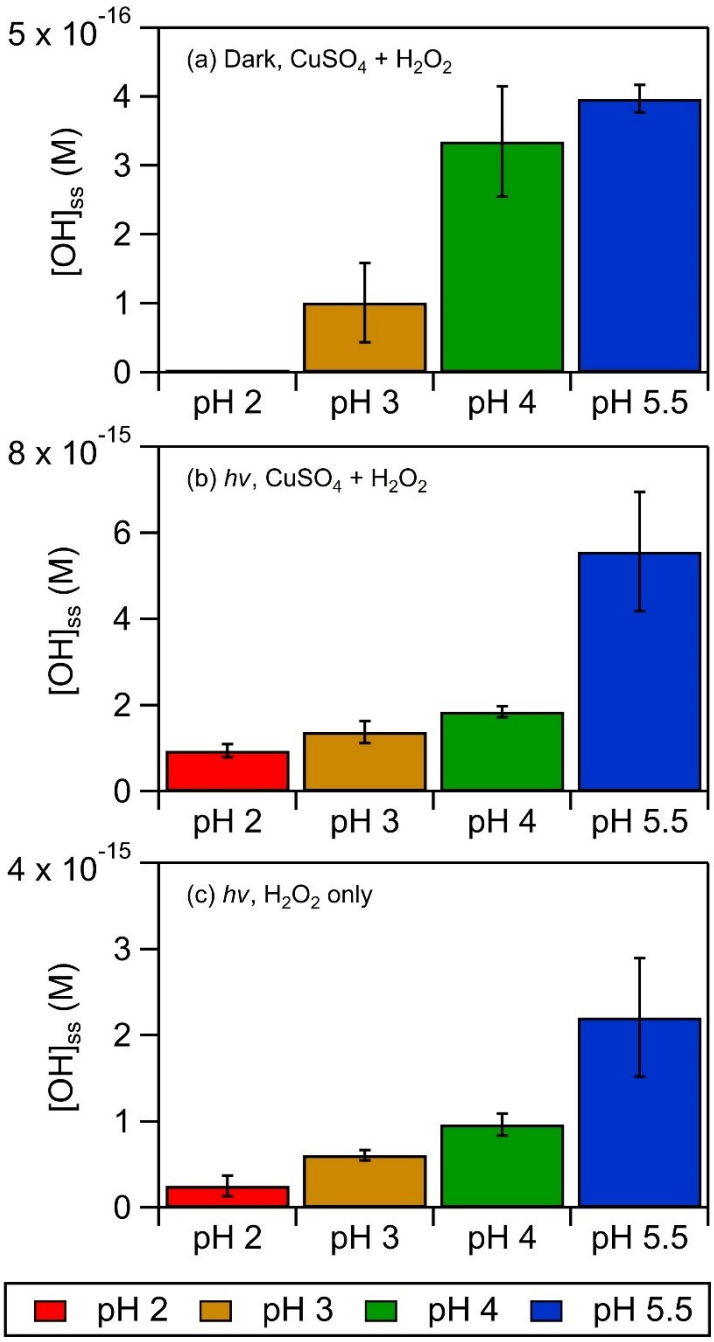
139 **Figure S3.** The $ln(\frac{[PhC]_t}{[PhC]_0})$ values for catechol (CAT), syringol (SYR), vanillin (VL), and
140 guaiacol (GUA) at pH 2 and 5.5 in dark control experiments where (a) only H_2O_2 was present
141 in solutions but not Cu(II), and (b) only Cu(II) was present in the solution but not H_2O_2. Error
142 bars indicate standard deviations from triplicate measurements. The $ln(\frac{[PhC]_t}{[PhC]_0})$ values were
143 close to 1 at the different time points, indicating that the PhC decays were insignificant in the
144 dark control experiments.



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146 **Figure S4.** Estimated $[\cdot OH]_{ss}$ in separate (a) dark oxidation and (b) photooxidation experiments
147 conducted under different pH conditions using solutions containing 50 μM of benzoic acid (the
148 probe compound), 50 μM of Cu(II), and 500 μM H_2O_2. We were unable to measure 4-
149 hydroxybenzoic acid in dark oxidation experiments at pH 2 since its concentrations were below
150 the detection limit (0.13 μM) of the instrument. Thus, we were unable to estimate $[\cdot OH]_{ss}$ in
151 dark oxidation experiments at pH 2. Shown in (c) are the estimated $[\cdot OH]_{ss}$ in photooxidation
152 experiments conducted under different pH conditions using solutions containing 50 μM of
153 benzoic acid (the probe compound) and 500 μM H_2O_2 but no 50 μM of Cu(II). Error bars
154 indicate standard deviations from triplicate measurements.

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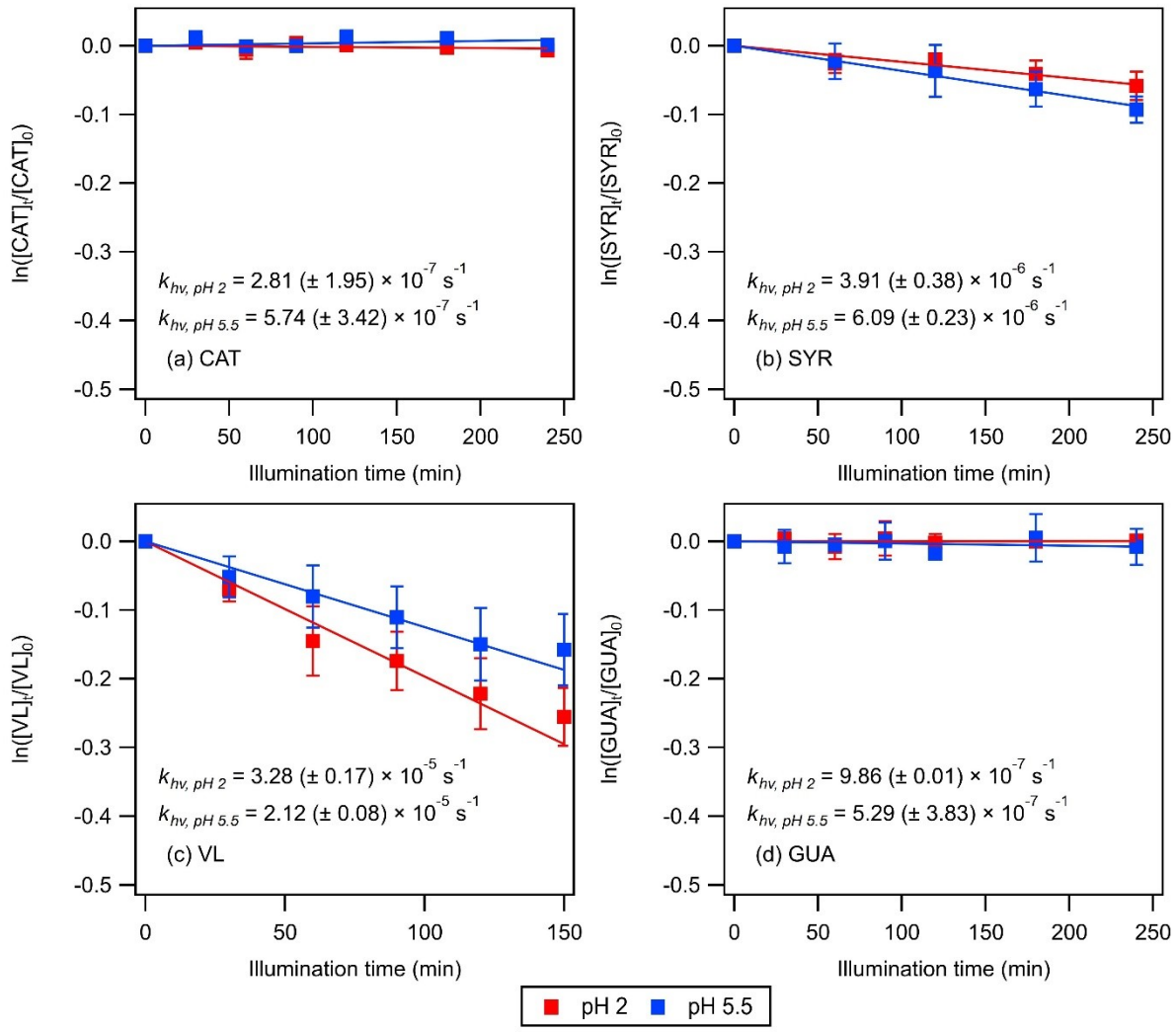

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157 **Figure S5.** Decays of (a) catechol (CAT), (b) syringol (SYR), (c) vanillin (VL), and (d)
158 guaiacol (GUA) in solutions that did not contain Cu(II) and H_2O_2 at pH 2 and 5.5 under
159 illumination conditions. Error bars indicate standard deviations from triplicate measurements.
160 Also shown are the k_{hv} values for the four PhCs.

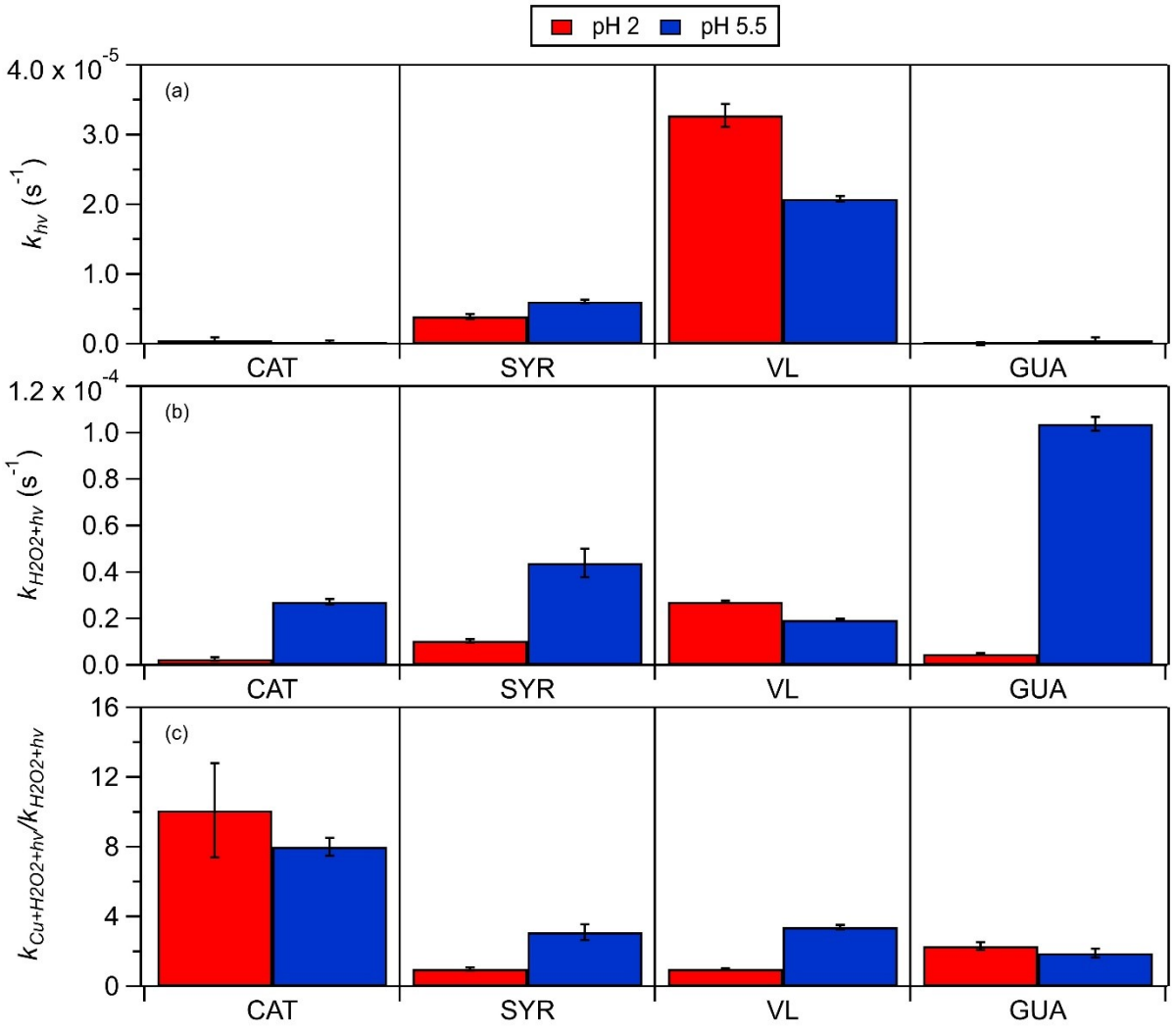
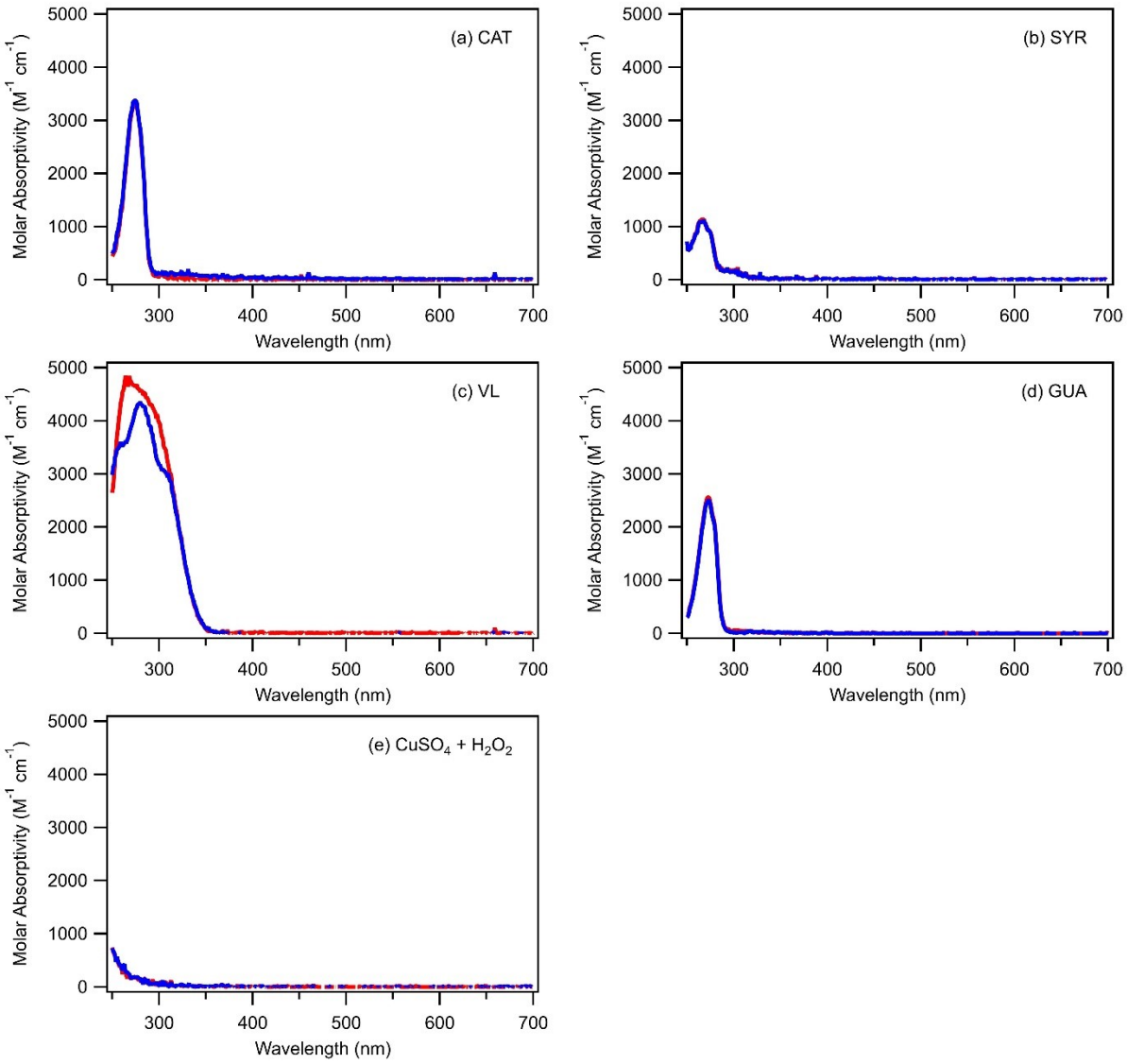


Figure S6. Comparison of the reaction rates ($k_{h\nu}$ and $k_{H2O2+h\nu}$) for catechol (CAT), syringol (SYR), vanillin (VL), and guaiacol (GUA) at pH 2 and 5.5 in (a) direct photolysis experiments (solutions did not contain Cu(II) and H_2O_2), and (b) ·OH photooxidation experiments where Cu(II) was absent (solutions did not contain Cu(II)). Panel (c) shows the ratios of reaction rates ($k_{Cu+H2O2+h\nu}/k_{H2O2+h\nu}$) obtained from photooxidation experiments that utilized solutions containing Cu(II) and H_2O_2 (Figure 2b) and photooxidation experiments that utilized solutions containing H_2O_2 only (Figure S4b). Error bars indicate standard deviations from triplicate experiments and measurements.



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171 **Figure S7.** Absorption spectra of (a) 50 µM catechol (CAT), (b) 50 µM syringol (SYR), (c) 50
172 µM vanillin (VL), and (d) 50 µM guaiacol (GUA), (e) 50 µM Cu(II) mixed with 500 µM H_2O_2
173 solutions at pH 2 (red) and pH 5.5 (blue) at reaction time = 0 min.

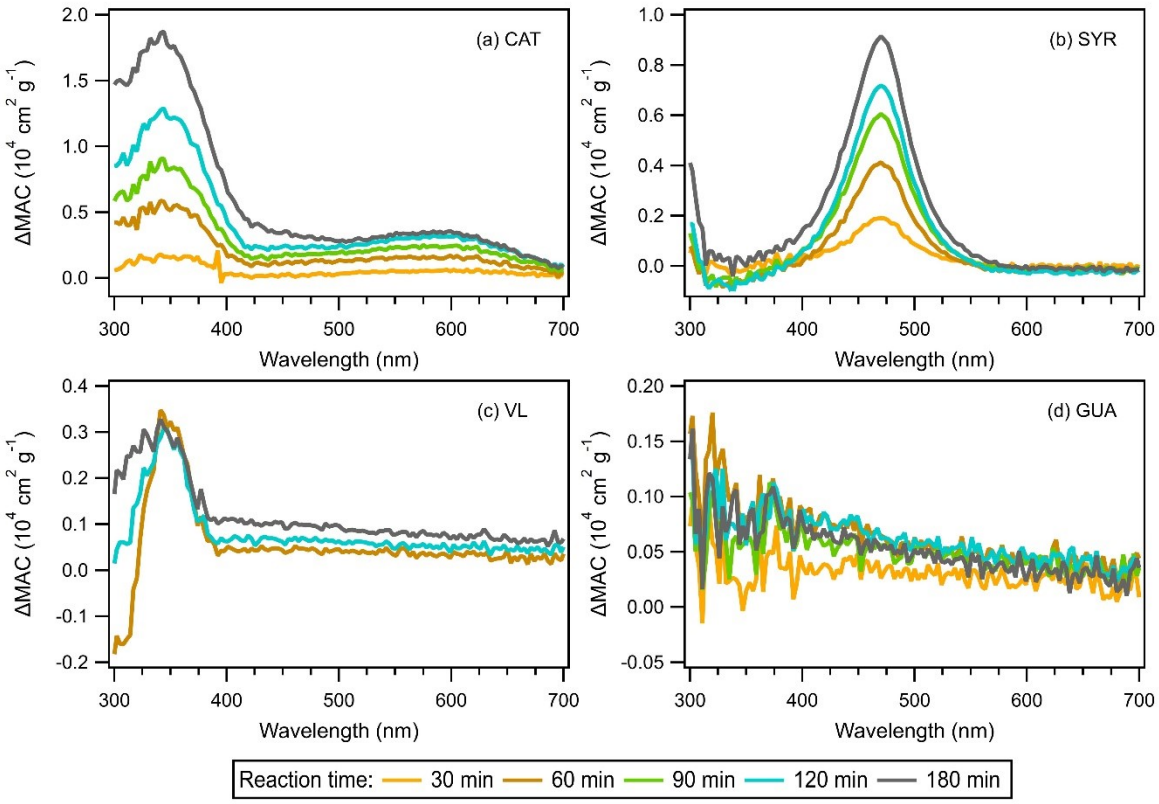

Figure S8. Background-subtracted MAC values in the near-UV and visible wavelength range (i.e., $\Delta MAC = MAC_t - MAC_{2\,min}$) for (a) catechol (CAT), (b) syringol (SYR), (c) vanillin (VL), and (d) guaiacol (GUA) under dark oxidation conditions at pH 5.5. All the solutions contained Cu(II) and H_2O_2. Note that measurements were only taken at reaction times = 0 min, 60 min, 120 min, and 180 min for vanillin.

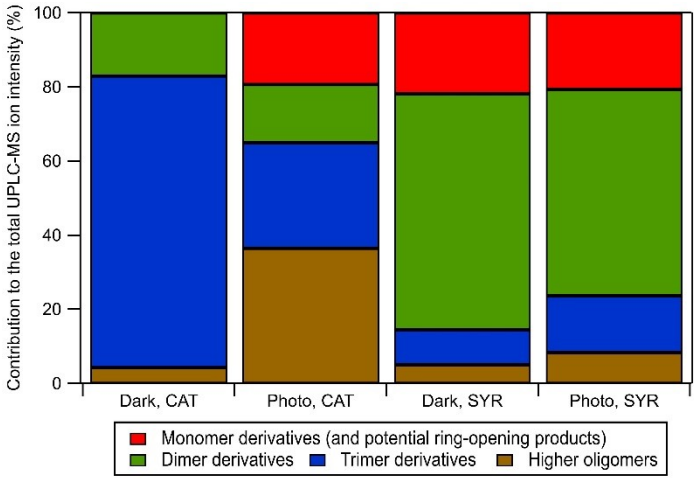

Figure S9. Comparison of the total UPLC-MS ion signals contributed by different product classifications for catechol (CAT) and syringol (SYR) under dark oxidation and photooxidation conditions at pH 5.5. All the solutions contained Cu(II) and H_2O_2. UPLC-MS measurements were taken at the time points at which the background-subtracted integrated MAC (300 to 700 nm) peaked.

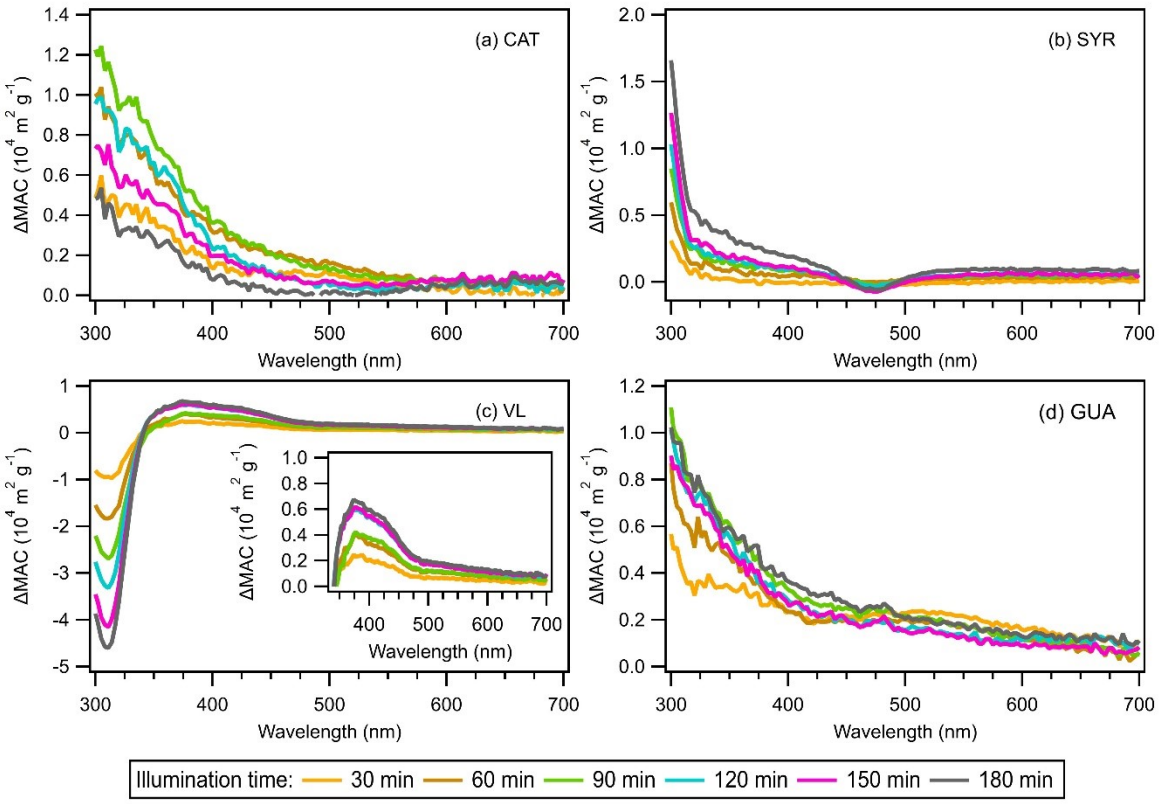

Figure S10. Background-subtracted MAC values in the near-UV and visible wavelength range (i.e., $\Delta MAC = MAC_t - MAC_{0\,min}$) for (a) catechol (CAT), (b) syringol (SYR), (c) vanillin (VL), and (d) guaiacol (GUA) under photooxidation conditions at pH 5.5. Also shown is the magnified view of the background-subtracted MAC values from 340 to 700 nm for syringol. All the solutions contained Cu(II) and H_2O_2.

References

1. H. Lee, H.-J. Lee, D. L. Sedlak and C. Lee, pH-Dependent reactivity of oxidants formed by iron and copper-catalyzed decomposition of hydrogen peroxide, *Chemosphere*, 2013, **92**, 652-658.
2. H.-J. Lee, H. Lee and C. Lee, Degradation of diclofenac and carbamazepine by the copper(II)-catalyzed dark and photo-assisted Fenton-like systems, *Chemical Engineering Journal*, 2014, **245**, 258-264.