

Supplemental Tables and Figures

Diffuse reflectance data for P25 and composite ZnO/TiO₂ photocatalysts were acquired, and from these data, Tauc plots were prepared and used to estimate bandgaps for the materials.

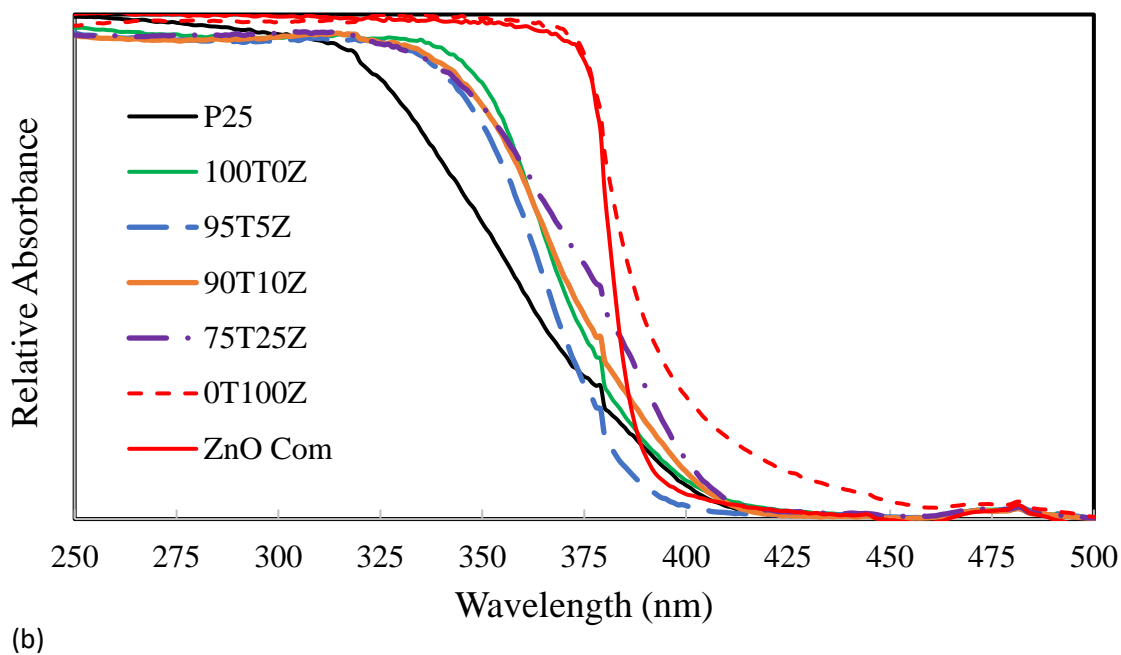
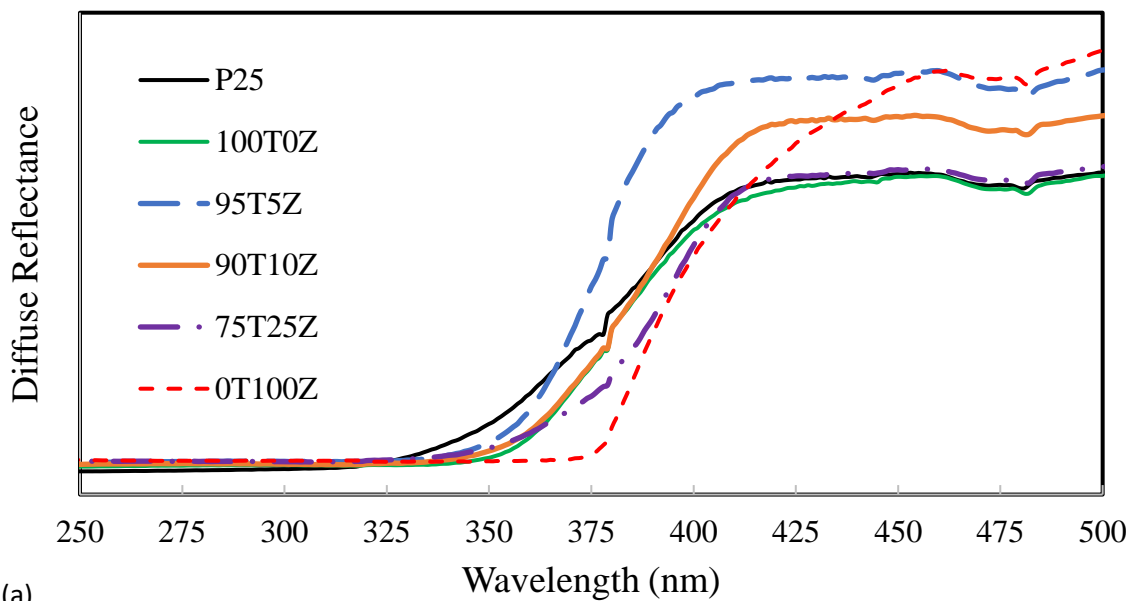


Figure S.1. Diffuse reflectance data. a) Diffuse reflectance vs wavelength. b) Light absorption vs wavelength for photocatalysts, derived from diffuse reflectance data.

The BET surface area analyses were based upon nitrogen adsorption isotherms at 77 K. Figure S7 shows the nitrogen adsorption isotherms for the photocatalysts used in this study. Noted is that the adsorption isotherms have hysteresis, which suggests that they are mesoporous materials.

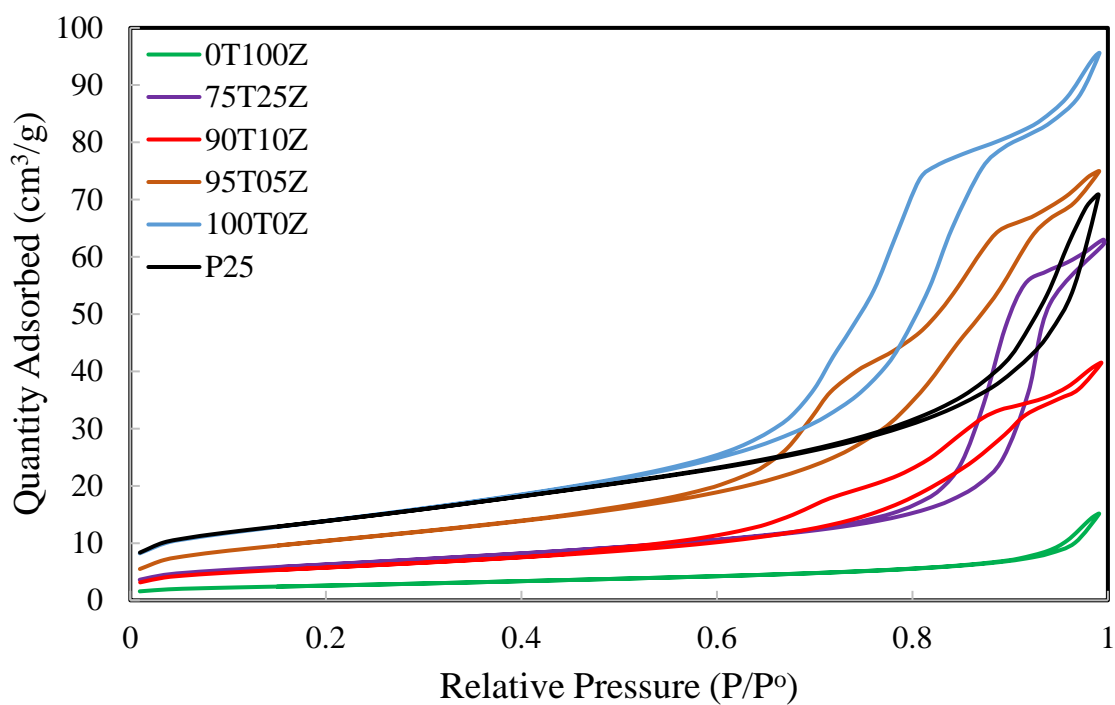


Figure S.2. Nitrogen adsorption isotherms at 77 K on the photocatalysts used in this study.

Adsorption studies were conducted to assess gas-phase adsorption of ethanol vapor on the photocatalysts. The data acquired is shown in Figure S5. Quantitative data on adsorption capacity of the catalysts was not obtained, since the system was not allowed to reach saturation for all photocatalysts. However, the breakthrough times are noted in Table S2, where breakthrough is defined here as 30% of the initial inlet concentration. The experimental trials were conducted at 110 cm³/min air flow rate with inlet ethanol concentrations between 80 and 110 ppm.

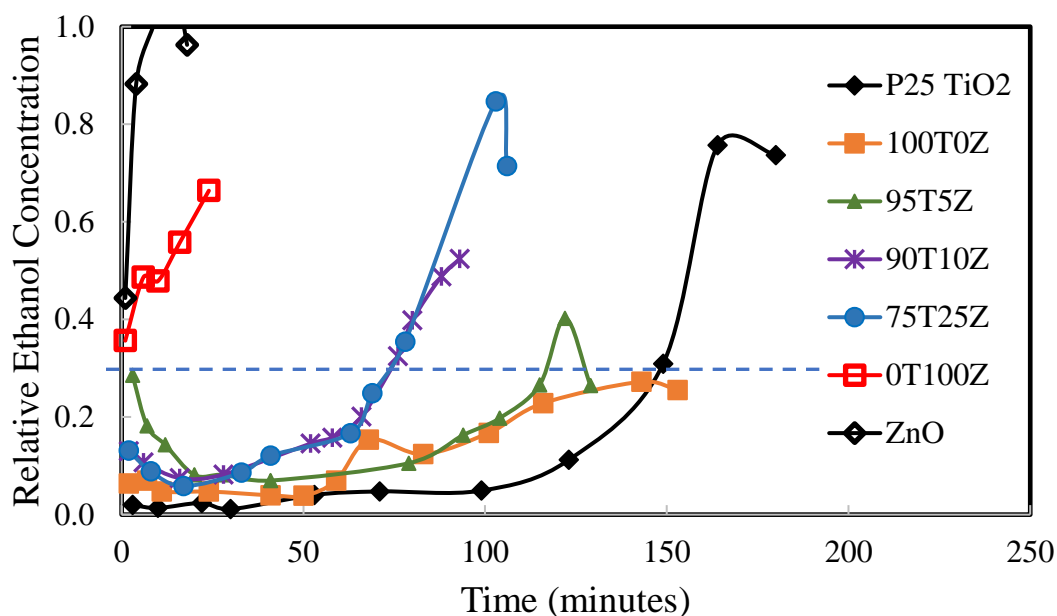


Figure S.3. Breakthrough curves for the adsorption of ethanol vapor on the photocatalysts in the UV LED photocatalytic reactor. The experimental trials were conducted at 110 cm³/min air flow rate with inlet ethanol concentrations = 100 (\pm 20) ppm.

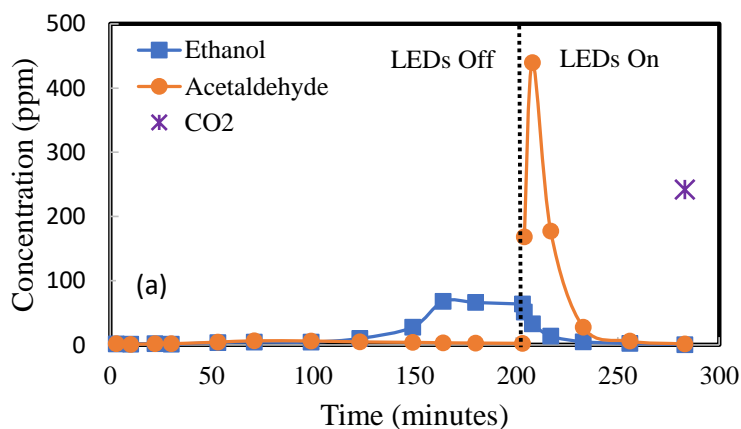
The dark adsorption experiments were followed by turning on the UV LEDs in the test system and monitoring the initial photocatalytic activity of the photocatalysts. Figures S3 (a-g) graphically show the data obtained. Noted is that as soon as the UV LEDs were turned on, acetaldehyde was formed and was emitted from the reactor. The concentrations of all organic vapors, however, decreased with time over the next 50 minutes, showing that all catalysts, except for 0T100Z and ZnO were active in our test apparatus. The ZnO-based photocatalysts showed very little activity in the UV LED photocatalytic test system used in this study, as indicated by the low conversions of ethanol vapor and low concentrations of acetaldehyde measured.

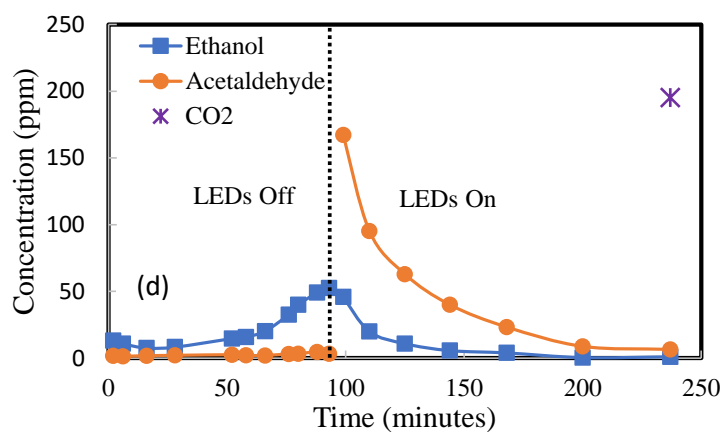
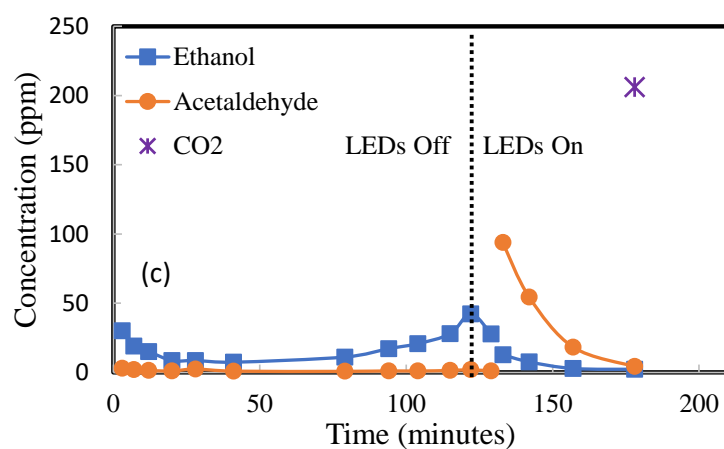
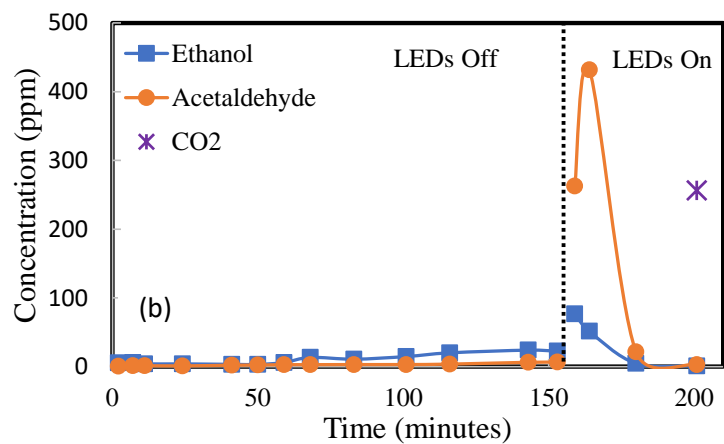
The data taken after >50 minutes following the UV LEDs being turned on (after the adsorption of ethanol) is provided in Table S1. The carbon balances on some tests are significantly greater than 1. This result is likely due to error in measuring the CO₂ concentrations. It is unknown how ethanol vapor affects the CO₂ sensor in the Amprobe CO₂ meter used in this study. In addition, the CO₂ collection system may not have come to steady-state before the final readings were taken.

Table S.1. Summary of experimental data acquired from photocatalytic oxidation of ethanol following adsorption experiments.

Photocatalyst	Adsorption	Inlet Ethanol (ppm)	Final Outlet Concentrations				C_{out} / C_{in}
	Breakthrough ^a Time (min)		Ethanol (ppm)	Acetaldehyde (ppm)	CO ₂ (ppm)		
P25	149	89.8	0.5	1.0	242		1.36
100T0Z	>153	88.7	1.2	2.3	256		1.48
95T5Z	117	105.2	2.2	4.1	206		1.04
90T10Z	74	105.2	1.0	5.9	195		0.99
75T25Z	73	97.1	2.0	2.9	174		0.95
0T100Z	<1	86.5	65.3	15.4	92		1.46
ZnO	<3	111.1	119.4	1.6	---		1.09

^aBreakthrough time for adsorption experiments was defined as 30% of initial concentration of ethanol.





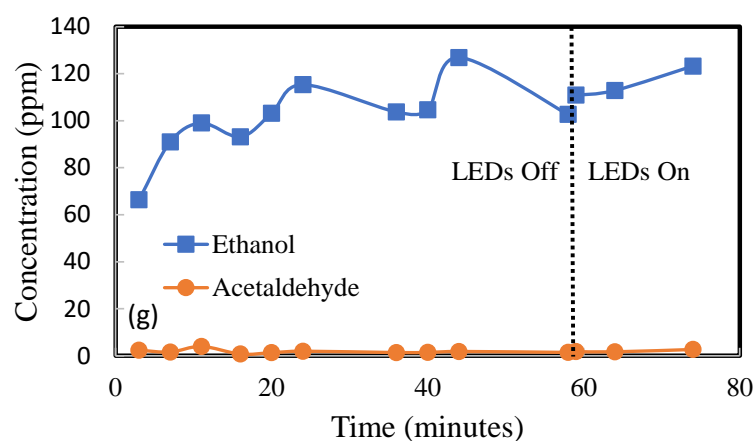
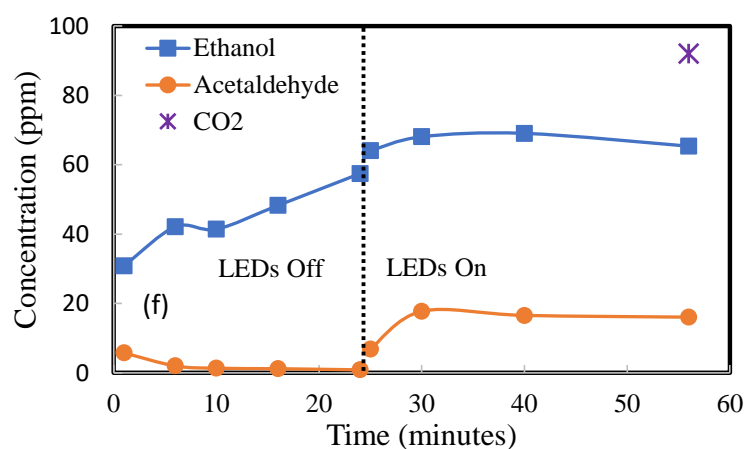
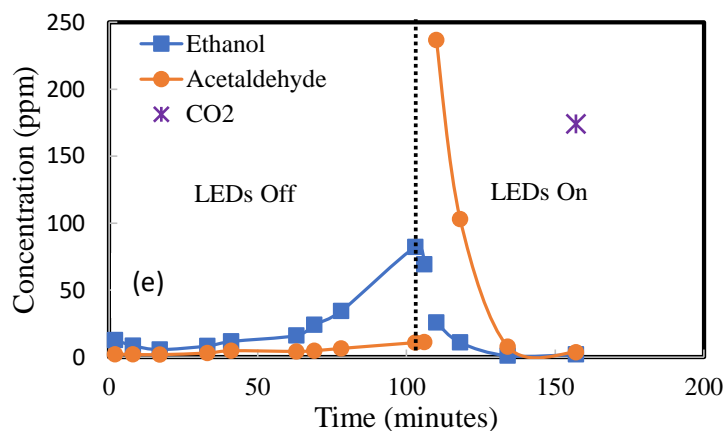
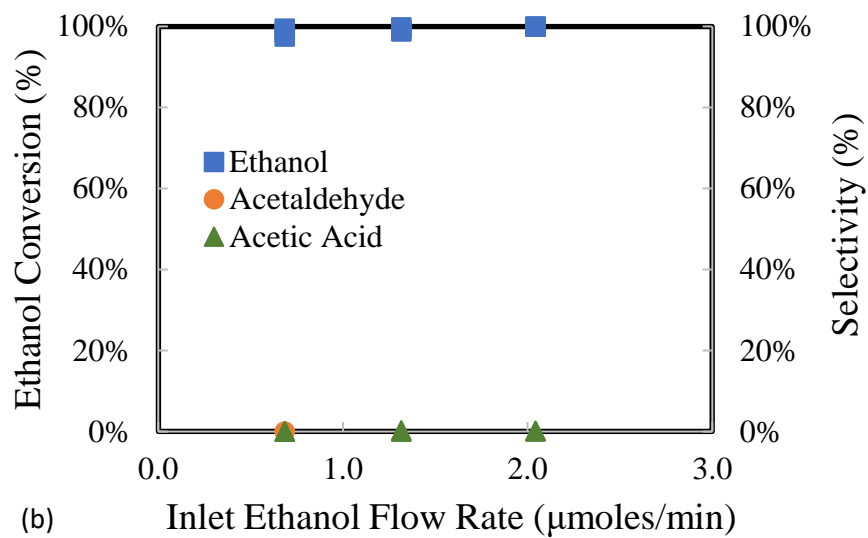
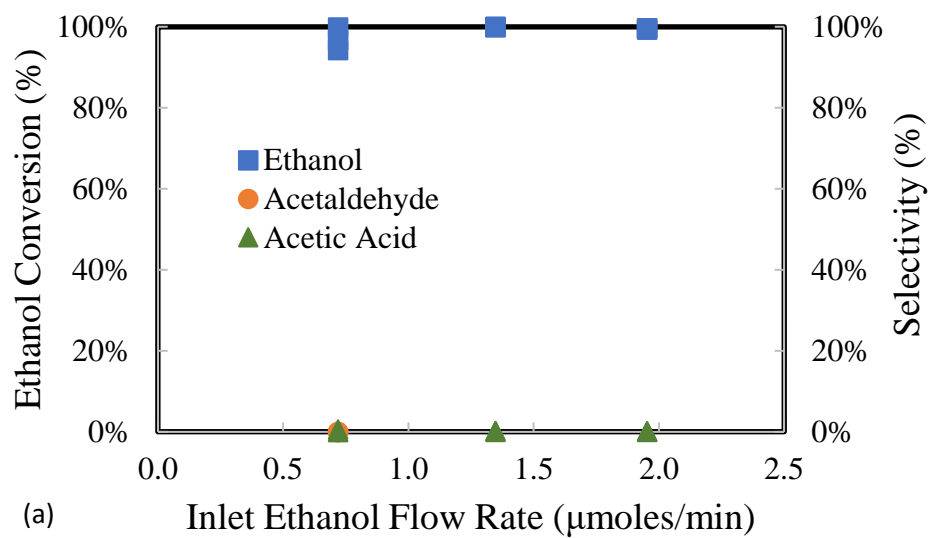
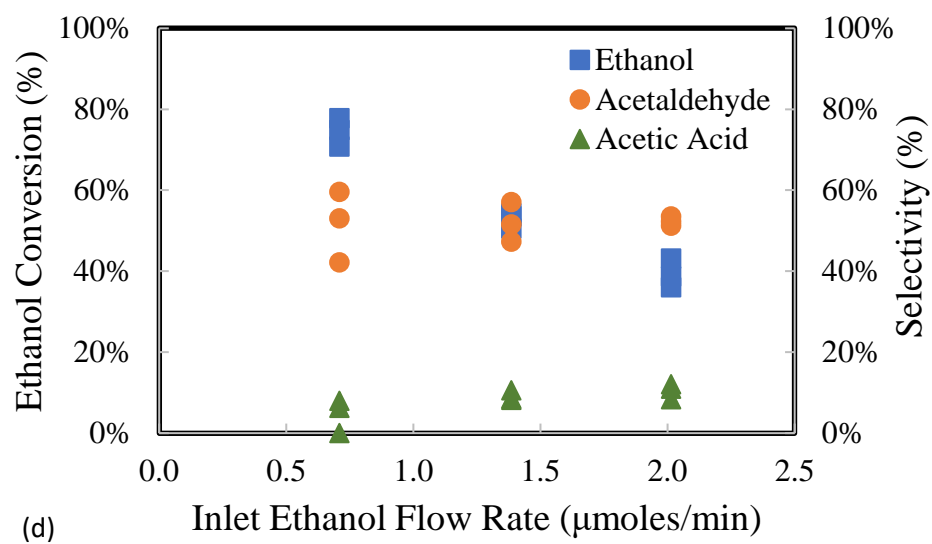
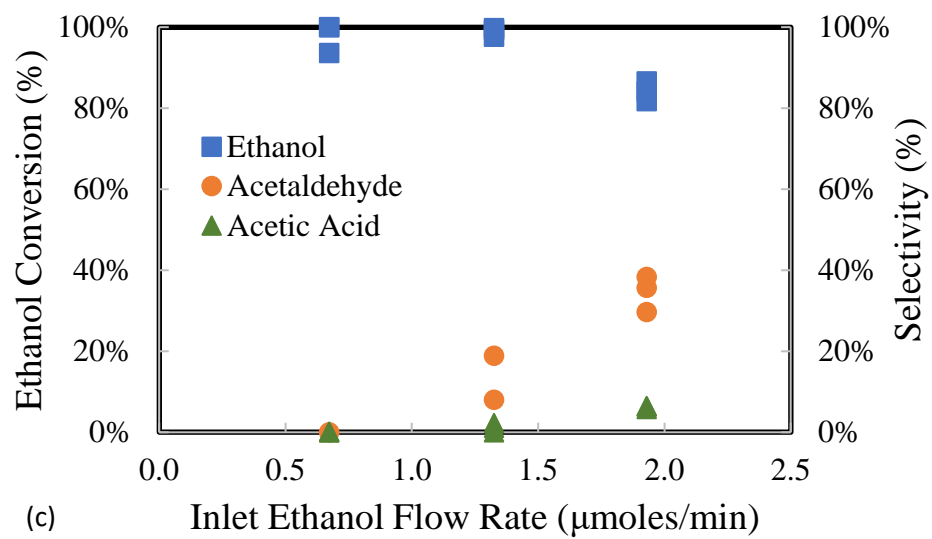
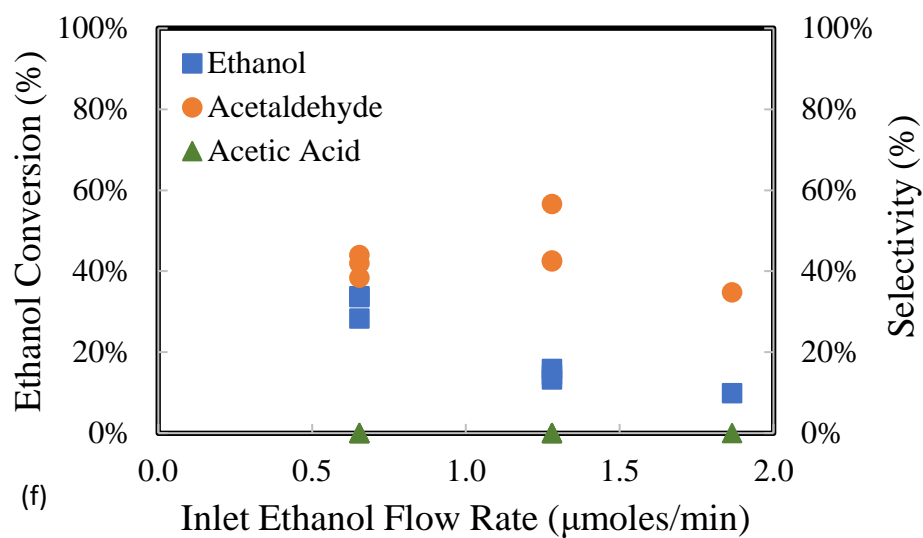
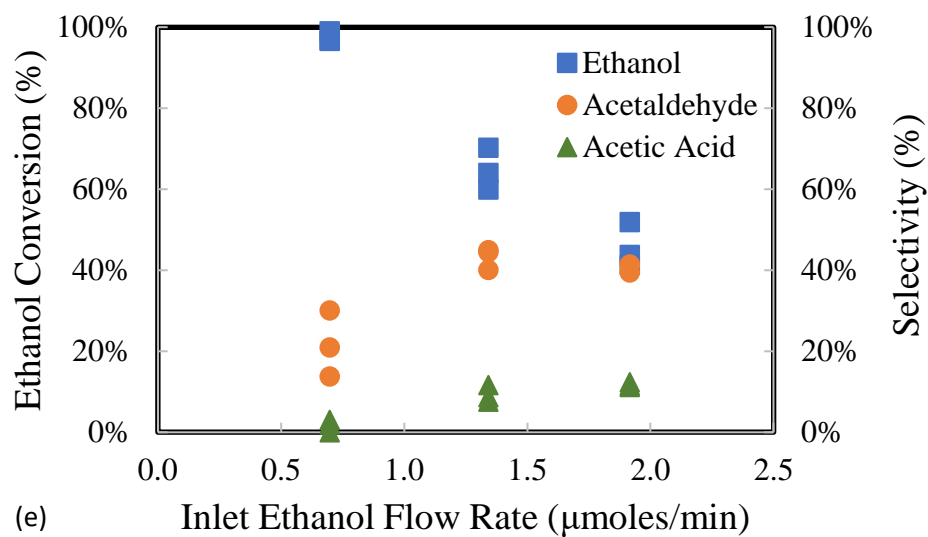


Figure S.4. Dark adsorption experiments followed by turning the LEDs on. Photocatalyst mass in the reactor = 0.5 g (\pm 0.08) g. (a) P25 TiO₂; (b) 100T0Z; (c) 95T5Z; (d) 90T10Z; (e) 75T25Z; (f) 0T100Z; (g) ZnO. Inlet ethanol concentration = 100 ppm (\pm 20 ppm) at 110 cm³/min air flow rate.

The following figures (Figure S4 a-f) show the experimental trials for the photocatalysts after 24 hours of reactor operation. Acetaldehyde and acetic acid were detected as partial oxidation by-products.







Figures S.5. Ethanol conversion and selectivity of acetaldehyde and acetic acid for the various experimental trials conducted in this study. a) P25 TiO₂; b) 100T0Z; c) 95T5Z; d) 90T10Z; e) 75T25Z; f) ZnO. 0T100Z is not included in this set of figures because the conversion of ethanol was < 10% in the first experimental trial, and further trials with it were not conducted.

Aqueous-phase ethanol photocatalytic degradation.

Quantitative data were obtained to show that all photocatalyst samples had photocatalytic activity for degrading ethanol in water. Qualitative data in this study showed that ZnO was just as effective as TiO₂ for decolorizing a methylene blue solution. Reasons why ZnO is an active photocatalyst in the liquid phase but not as active in the gas phase were discussed based upon published literature and experimental observations.

The liquid-phase photocatalytic oxidation of ethanol was investigated to assess whether the photocatalysts used in this study were active in aqueous-phase experiments. Continuously stirred aqueous (deionized water) solutions (50 mL) containing 180 mg/L of ethanol and 0.5 g/L of photocatalyst were placed under 2 Phillips 15W black lamps. The measured emission from the lamps at 365 nm (Omega UVA light sensor) was 3.2 ± 1.3 mW/cm².

Table S.2 summarizes the apparent first-order degradation rate constants for each photocatalyst. Figures S1 a-c graphically show the experimental ethanol concentrations in the solutions with time. Noted is that all photocatalysts perform better than the control, and therefore, they have apparent photocatalytic activity in the water phase. P25 TiO₂ performed the best of all photocatalysts investigated. ZnO, although relatively inactive in the gas-phase experiments, showed significant photocatalytic activity in the liquid phase.

Table S.2. Summary of apparent first-order rate constants, k_{appt} , for the photocatalytic oxidation of ethanol in water.

Photocatalyst ID	Apparent 1 st -order rate constant, k_{appt} (min ⁻¹)	Coefficient of Determination (R^2)
Control (no photocatalyst)	1.41×10^{-3}	0.876
P25 TiO ₂	6.57×10^{-3}	0.990
100T0Z	6.25×10^{-3}	0.970
95T5Z	4.34×10^{-3}	0.979
90T10Z	2.09×10^{-3}	0.873
75T25Z	5.24×10^{-3}	0.996
0T100Z	5.13×10^{-3}	0.928
ZnO	3.84×10^{-3}	0.971

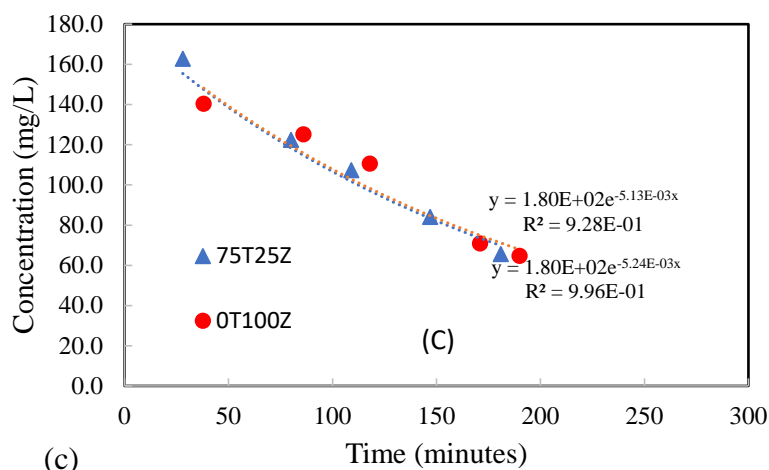
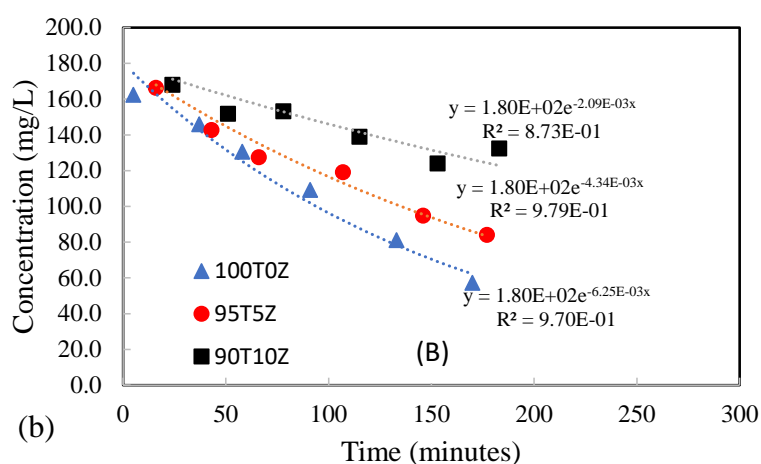
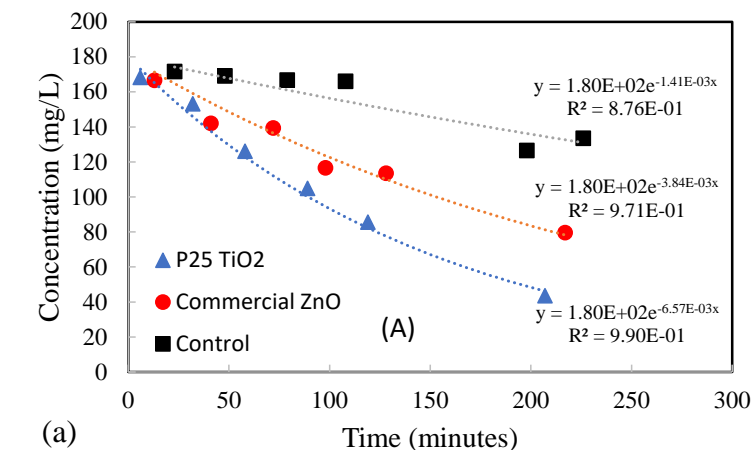


Figure S.6. Liquid-phase photocatalytic oxidation of ethanol in deionized water. Initial ethanol concentration = 180 mg/L. Photocatalyst concentration = 0.5 g/L. Light intensity = 3.2 ± 1.3 mW/cm². (a) P25, ZnO, Control; (b) 100T0Z, 95T5Z, 90T10Z; (c) 75T25Z, 0T100Z.

P25 and ZnO were used to decolorize methylene blue solution to qualitatively show that ZnO has apparent photocatalytic activity for removing dyes from water. The qualitative experiment is shown to verify that the ZnO used in this study can decolor dye solutions rapidly and as well as (if not better than) P25 TiO₂. As shown in Figure S2, continuously stirred solutions (50 mL) containing 0.01mM of methylene blue in deionized water and 0.5 g/L of photocatalyst were placed under 2 Phillips 15W black lamps. The measured emission from the lamps at 365 nm (Omega UVA light sensor) was 3.2 ± 1.3 mW/cm². The solutions were decolorized within 15 minutes, but no quantitative data were obtained, as shown in Figure S3.



Figure S.7. Photograph of experimental tests showing the decolorization of 0.01 mM methylene blue solution in deionized water. Photocatalyst = 0.5 g/L. Light intensity = 3.2 ± 1.3 mW/cm².

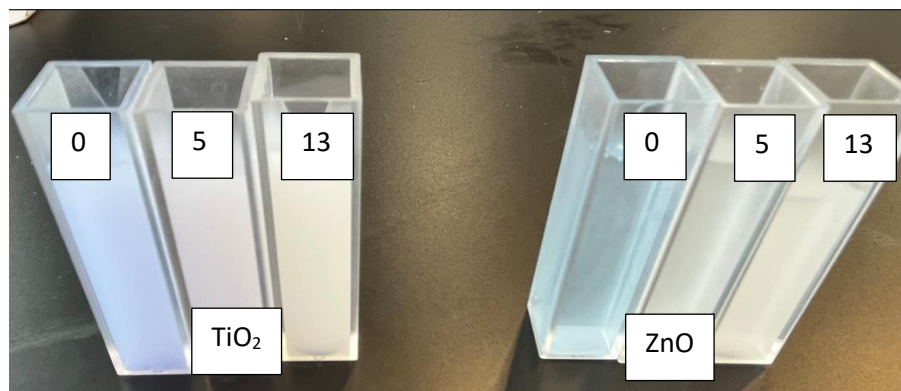


Figure S.8. Qualitative image of the decolorization of 0.01 mM methylene blue in deionized water at (from left to right) 0 minutes, 5 minutes, and 13 minutes. Samples on the left are P25 samples. Samples on the right are ZnO samples.

The light intensity as a function of distance away from the UV LEDs and position on the cover is shown in Figure S8. In our test system, the depth of the reactor was approximately 1.9 cm, and so the light intensity on the surface of the photocatalyst was approximately 4.5 mW/cm².

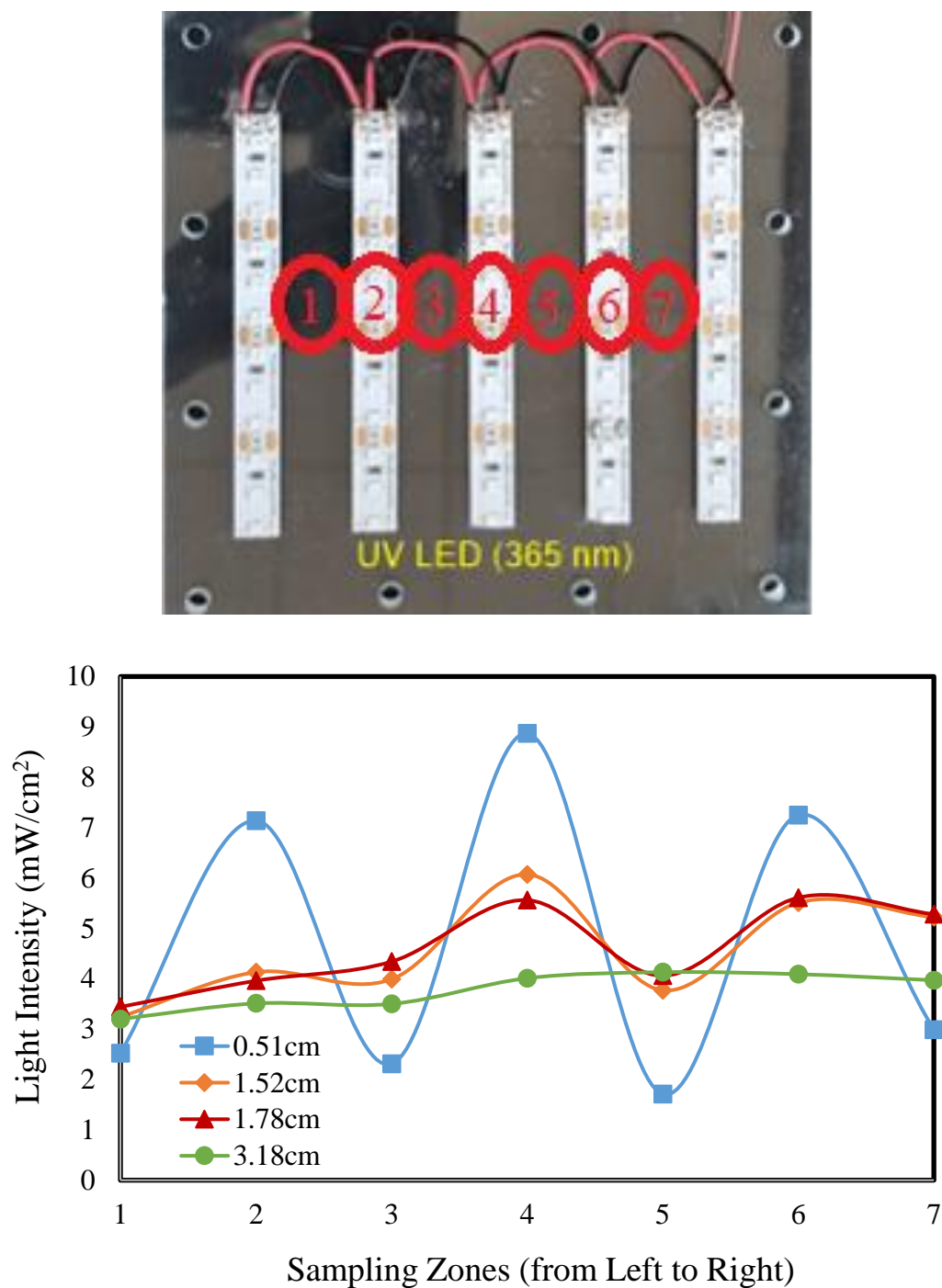


Figure S.9. Light intensity as functions of placement and distance away from the UV LED cover.

Gas-phase calibration of the GC/FID for ethanol.

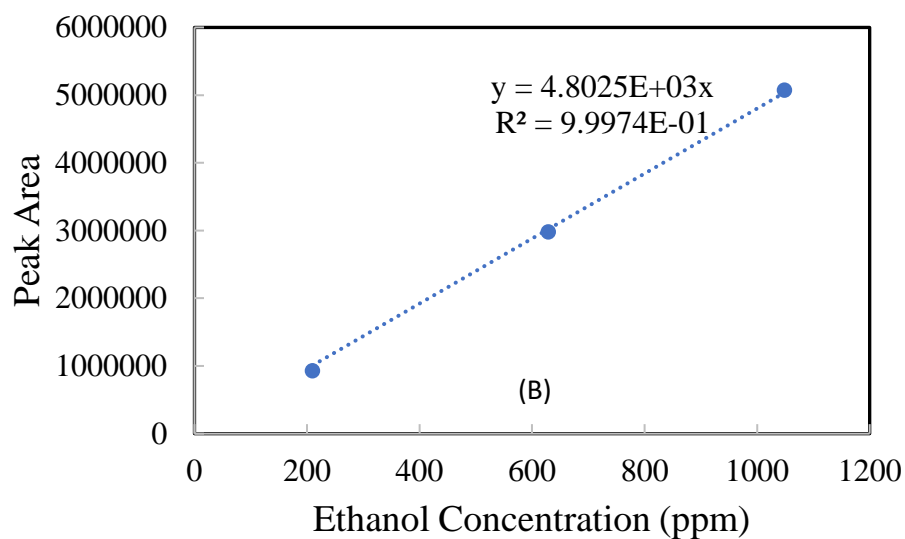
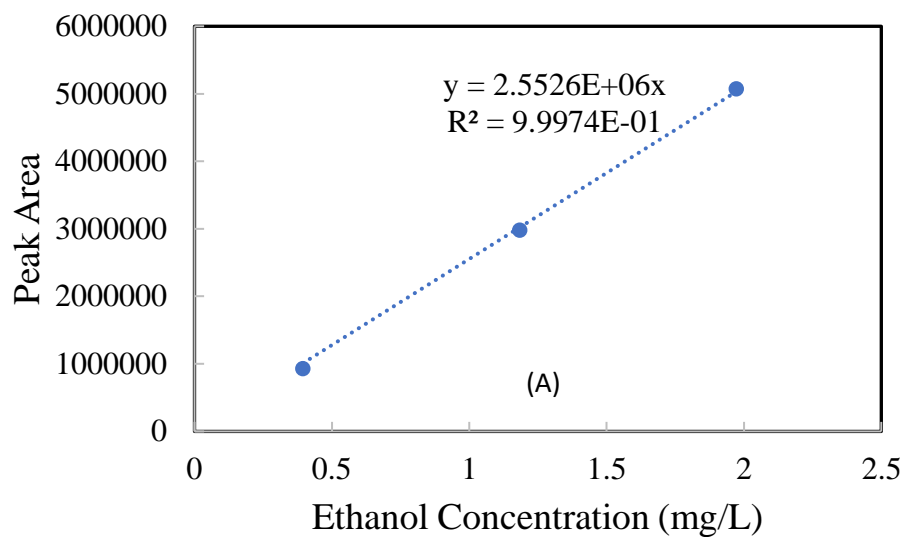


Figure S.10. Gas-phase calibration of the GC/FID for ethanol vapors. (A). Peak area as a function of ethanol concentration in mg/L. (B). Peak area as a function of ethanol concentration in ppm. 250 μ L injections of gas-phase samples.