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Supporting Information

Group 13 Lewis Acid Catalyzed Synthesis of Metal Oxide Nanocrystals via Hydroxide Transmetallation

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Figure S1. PXRD of a) Al^{3+} , b) Ga^{3+} , and c) In^{3+} catalyzed Cu_2O . Asterisks (*) in Al^{3+} data refer to peaks associated with Cu^0 .



Figure S2. PXRD of reaction products at 200 °C and 215 °C.



Figure S3. Digital photographs taken at the same time point (5 min 22 sec) for the injection of $Cu^{2+}-O_2CR$ with 5 mol% $Ga^{3+}-O_2CR$ catalysts at a) 200 °C and b) 180 °C. The yellow color for the 200 °C condition is visual confirmation of reduction from Cu^{2+} to Cu^+ . The blue-green color of the 180 °C condition shows lack of reduction at this temperature.



Figure S4. a) FTIR of copper (I) acetate and copper (II) acetate solids. b) UV-Vis of precursors synthesized from the exchange of copper (I) acetate and copper (II) acetate with oleic acid. Both solutions were made at 68 mM by dilution with oleyl alcohol.



Figure S5. PXRD of a) γ -Ga₂O₃ and b) In₂O₃ synthesized via continuous-injection of 2 mmol of M³⁺-O₂CR into oleyl alcohol at 200 °C under N₂.



Figure S6. SEM of Cu_2O nanocrystals synthesized with 1, 5, and 15 mol% Al^{3+} , Ga^{3+} , and In^{3+} catalysts.



Figure S7. Histograms for a) $Cu^{2+}-O_2CR$ only injection, b) 1-15 mol% Al^{3+} , c) 1-15 mol% Ga^{3+} , and d) 1-15 mol% In^{3+} . Size analysis was performed from SEM images.



Figure S8. a) TEM and b) EDS of Cu^{2+} reaction with 0 mol% catalyst. Unlabeled peaks near 2, 9, and 12 keV are due to Au (TEM grid).



Figure S9. a) TEM and b) EDS of Cu^{2+} reaction with 1 mol% Ga^{3+} catalyst. Unlabeled peaks near 2, 9, and 12 keV are due to Au (TEM grid).



Figure S10. a) TEM and b) EDS of Cu^{2+} reaction with 5 mol% Ga^{3+} catalyst. Unlabeled peaks near 2, 9, and 12 keV are due to Au (TEM grid).



Figure S11. a) TEM and b) EDS of Cu^{2+} reaction with 10 mol% Ga³⁺ catalyst. Unlabeled peaks near 2, 9, and 12 keV are due to Au (TEM grid).



Figure S12. a) TEM and b) EDS of Cu^{2+} reaction with 15 mol% Ga³⁺ catalyst. Unlabeled peaks near 2, 9, and 12 keV are due to Au (TEM grid).



Figure S13. a) TEM and b) EDS of Cu^{2+} reaction with 1 mol% In^{3+} catalyst. Unlabeled peaks near 2, 9, and 12 keV are due to Au (TEM grid).



Figure S14. a) TEM and b) EDS of Cu^{2+} reaction with 5 mol% In^{3+} catalyst. Unlabeled peaks near 2, 9, and 12 keV are due to Au (TEM grid).



Figure S15. a) TEM and b) EDS of Cu^{2+} reaction with 10 mol% In^{3+} catalyst. Unlabeled peaks near 2, 9, and 12 keV are due to Au (TEM grid).



Figure S16. a) TEM and b) EDS of Cu^{2+} reaction with 15 mol% In^{3+} catalyst. Unlabeled peaks near 2, 9, and 12 keV are due to Au (TEM grid).



Figure S17. a) HAADF TEM image of Cu_2O nanocrystals synthesized with 10 mol% Ga catalyst. EDS mapping of b) Cu and c) O of the nanocrystals imaged in a). EDS mapping shows a homogeneous distribution of Cu and O atoms throughout the nanocrystals, with no evidence of Ga doping.

Table S1. Summary of ICP-MS Analysis

mol% Al ³⁺	[Cu] / ppb	[Al] / ppb	[Al]/[Cu]
1 %	48.1(4)	0 ^a	0 %
5 %	41.2(5)	0 ^a	0 %
10 %	46.6(2)	0 ^a	0 %
15 %	49.2(2)	0 ^a	0 %
mol% Ga ³⁺	[Cu] / ppb	[Ga] / ppb	[Ga]/[Cu]
1 %	49.9(3)	0.00386(6)	0.0077(1) %
5 %	40.7(2)	0.0244(3)	0.0600(8) %
10 %	41.2(4)	0.339(4)	0.822(13) %
15 %	42.2(3)	0.0218(5)	0.0517(13) %
mol% In ³⁺	[Cu] / ppb	[In] / ppb	[In]/[Cu]
1 %	50.1(3)	0.0047(2)	0.0093(4) %
5 %	47.5(2)	0.0241(2)	0.0508(6) %
10 %	45.4(2)	0.0437(5)	0.0963(11) %
15 %	42.3(3)	0.186(1)	0.439(4) %

^aBelow detection limit



Figure S18. a) UV-visible absorbance spectra of $Cu^{2+}-O_2CR$ precursor in oleyl alcohol at controlled concentrations collected in a 0.2 cm path length cuvette. b) Beer-lambert plot for peak absorbance at 695 nm. Measured slope of 0.041 mM⁻¹ results in a calculated $\epsilon(695 \text{ nm}) = 205 \text{ M}^{-1} \text{ cm}^{-1}$.



Figure S19. UV-visible absorbance spectra of post-reaction solutions for a) Al^{3+} , b) Ga^{3+} , and c) In^{3+} catalysts (0.2 cm path length). The peak at 695 nm is indicative of unreacted $Cu^{2+}-O_2CR$ precursor remaining in solution. Absorbance was corrected for oleyl alcohol with the reaction efficiency indicated in the legend ($\eta_{rxn} = 1 - [Cu^{2+}]_{unreacted}/[Cu^{2+}]_{total}$). [Cu²⁺] concentration calculated using $\epsilon_{695} = 205 \text{ M}^{-1} \text{ cm}^{-1}$ determined in **Figure S16**. [Cu²⁺]_{total} = 68 mM.



Figure S20. FTIR absorbance spectra of post-reaction solutions of a) In^{3+} and b) Al^{3+} catalyzed Cu_2O synthesis.



Figure S21. a) FTIR absorbance spectra of oleic acid dissolved in oleyl alcohol at controlled concentrations. Spectra are background corrected for oleyl alcohol. (b-c) Beer-Lambert plots for absorbance at 1710 and 1738 cm⁻¹ with slopes of 0.16 and 0.04 M⁻¹, respectively. Despite not knowing the path length associated with the ATR-FTIR measurement, the linearity in these plots indicates a constant path length across different samples. Therefore, the slopes were used directly as apparent extinction coefficients for oleic acid in oleyl alcohol such that $\varepsilon_{app}(1710 \text{ cm}^{-1}) = 0.16 \text{ M}^{-1}$ and $\varepsilon_{app}(1738 \text{ cm}^{-1}) = 0.04 \text{ M}^{-1}$.



Figure S22. a) FTIR absorbance spectra of $Cu^{2+}-O_2CR$ dissolved in oleyl alcohol at controlled concentrations. Spectra are background corrected for oleyl alcohol. b) Beer-Lambert plot for absorbance at 1620 cm⁻¹ with a slope of 5.6 x 10⁻⁴ mM⁻¹. Despite not knowing the path length associated with the ATR-FTIR measurement, the linearity in these plots indicates a constant path length across different samples. Therefore, the slope was used directly as an apparent extinction coefficients for $Cu^{2+}-O_2CR$ in oleyl alcohol such that $\varepsilon_{app}(1620 \text{ cm}^{-1}) = 0.56 \text{ M}^{-1}$.



Figure S23. a) FTIR Δ Abs spectra of oleic acid dissolved in oleyl alcohol and heated to 230 °C. Time dependent spectra were generated by removing small aliquots from solution over the course of the reaction. Δ Abs data were generated by subtracting all spectra from the initial 0 min at 25 °C condition. Inset shows raw absorbance data. b) Δ Abs at 1710 and 1738 cm⁻¹ plotted versus time of reaction. The final time point at 165 min, representing complete conversion from acid to ester, was used to calculate apparent extinction coefficients for oleyl oleate ester based on the equation Δ Abs(\tilde{v}) = $\Delta \varepsilon(\tilde{v})$ [Ester] where [Ester] = 1.27 M and $\Delta \varepsilon(\tilde{v}) = \varepsilon_{ester}(\tilde{v}) - \varepsilon_{acid}(\tilde{v})$. Resulting values were $\varepsilon_{app}(1710 \text{ cm}^{-1}) = 0.018 \text{ M}^{-1}$ and $\varepsilon_{app}(1738 \text{ cm}^{-1}) = 0.20 \text{ M}^{-1}$.



Figure S24. Time-dependent FTIR ΔAbs spectra for a) Cu²⁺-O₂CR only injection, b) 1 mol% Ga³⁺, 10 mol% Ga³⁺, 5 mol% Al³⁺, and 5 mol% In³⁺ catalyzed reactions. ΔAbs spectra generated by subtracting the initial spectrum at t = 0 min.



Figure S25. Time-dependent UV-visible absorbance spectra for a-d) 0-10 mol% Ga^{3+} , e) 5 mol% Al^{3+} and f) 5 mol% In^{3+} catalyzed reactions.



Figure S26. Comparison of FTIR ester peak absorbance at 1738 cm⁻¹ measured over time for 5 mol% a) Al³⁺, b) Ga³⁺, and c) In³⁺ with and without (*i.e.* control) the presence of Cu²⁺-O₂CR precursor.



Figure S27. TEM HAADF image of In_2O_3 nanocrystals produced with 100 mol% injection of $In^{3+}-O_2CR$ into oleyl alcohol at 200 °C.