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Colloidal Cu/ZnO catalysts for the hydrogenation of carbon dioxide to methanol: investigating catalyst preparation and ligand effects

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Contents

Characterisation techniques.

All manipulations were undertaken using a nitrogen filled glovebox or using a Schlenk line, unless otherwise stated. Stearic acid (Fluka, >97%) and $ZnEt_2$ (Sigma Aldrich) were used directly from suppliers. Dioctylphosphinic acid[1] and CuMes[2] were prepared using established literature routes (N.B. it was essential to filter and recrystallize the CuMes from toluene twice to isolate the compound as a very pale yellow powder without any impurities). $ZnEt_2$ is pyrophoric (caution!) and was added to samples in a nitrogen filled glovebox. As a liquid, all additions of $ZnEt_2$ were transferred by syringe (measured by negative weight of donor flask). Toluene was dried by refluxing over sodium and stored under nitrogen. Mesitylene was used as supplied but stored over molecular sieves. All dry solvents were degassed by three freeze-pump-thaw cycles and stored under nitrogen.

NMR spectra were recorded on Bruker AV-400 instruments, all chemical shifts reported in ppm.

Solid-state FTIR spectra under air were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer with a Universal ATR Sampling Accessory.

UV/visible spectra were collected using UV/visible spectra were collected using PerkinElmer Lambda 950 spectrophotometer from mesitylene solutions diluted with toluene to [Cu] = 1.2 mM. The UV absorption edge of ZnO can be used to estimate the particle size by the empirical relationship established by Meulenkamp.[3]

Oxidation profiles were obtained using UV/vis spectroscopy, the sample was exposed to air (20 s) and then shaken (30 s) twice before the initial measurement after 2 minutes.

Elemental Analysis was determined by Stephen Boyer at London Metropolitan University.

X-ray diffraction (XRD): was performed using an X'Pert Pro diffractometer (PANalytical B. V., The Netherlands) and X'Pert Data Collector software, version 2.2b. The instrument was used in the theta/theta reflection mode, fitted with a nickel filter, 0.04 rad Soller slit, 10 mm mask, 1/4° fixed divergence slit, and 1/2° fixed antiscatter slit. Air sensitive samples were prepared in a glovebox and sealed with polyimide tape. The diffraction patterns were analysed using Fityk (version 0.9.0; Marcin Wojdyr, 2010): the peaks were fitted to a SplitPearson7 function, and the crystallite size was calculated from the full-width half-maximum of the fitted curve using the Scherrer Equation to the most intense and not overlapped reflections; Cu: 43.5° (hkl= 111), ZnO: 47.5° (hkl= 102).

Scanning TEM images, conventional TEM images, and electron diffraction patterns were acquired on an FEI Titan 80-300 microscope operated at 300 kV. For air sensitive samples the sample solution was deposited on a 300 mesh gold holey carbon grid with an ultra-thin 3 nm thick carbon support (Agar Scientific AGS187-4), while in a glove box. The grid was then loaded into a Gatan environmental holder to prevent any exposure to air prior to TEM imaging. Annular dark field emission (ADF) and energy dispersive X-ray (EDX) mapping were performed with a JEOL JEM 2100F scanning transmission electron microscope operated at 200 kV, and equipped with a Oxford X-Max 80 SDD EDX detector.

Synthesis of ZnO@DOPA nanoparticles (NPs).

ZnO@DOPA NPs were produced by a previously reported route.[4] The representative procedure is given here: dioctylphosphinic acid (800 mg, 2.75 mmol) was added to a Schlenk flask with a stirrer bar, and any surface moisture removed under vacuum (~10 minutes). Dry toluene (92 ml) was added to the flask and then $ZnEt_2$ (1.7 g, 13.8 mmol) was added slowly to the solution, with the evolution of ethane gas being observed. The flask was left to stir for two hours. Deionised water (0.5 mL, 27.8 mmol) was added to acetone (69 mL, winchester grade) and this solution added dropwise to the Schlenk flask under a flow of N2. The mixture was left to stir for two hours before adding further acetone (~20 mL) to precipite the ZnO NPs. The suspension was centrifuged and the isolated particles washed and centrifuged twice more (toluene/acetone, then acetone). The isolated ZnO@DOPA NPs were dried in air overnight before grinding them to a powder and further drying under vacuum. The particles were stored under vacuum, as they may ripen if exposed to atmospheric moisture.5 The ZnO@DOPA NPs (1.75 g isolated) were fully characterised by XRD (2.0-2.3 nm by Scherrer equation), TEM (~2.5-3 nm), UV spectroscopy (2.8 nm by band edge)3, IR spectroscopy and elemental analysis (the $[DOPA]^-$:Zn ratio was determined from C% to be 0.17). A single batch of ZnO@DOPA was prepared for all catalytic runs to ensure an exact ZnO size is maintained throughout the study. This sample was stored under vacuum. The size of the ZnO NPs was monitored during the period of study, confirming no ripening occurs under these storage conditions.

Synthesis of Cu@DOPA NPs.

Dioctylphosphinic acid (11.7 mg, 0.04 mmol) was added to a Young's tap flask and the flask placed under vacuum to remove any moisture. CuMes (73.3 mg, 0.40 mmol) was added to the flask, in a glovebox, and then mesitylene added (11 mL) to make up the concentration to [CuMes] = 0.036 M. The solution was stirred for 10 minutes and was almost colourless. A freeze/thaw degas cycle was conducted to remove the N_2 atmosphere and the solution re-frozen and evacuated before addition of H_2 gas at 1 bar for 30 seconds (open to bubbler). By submerging ~2/3 of the flask in liquid N_2 during the addition of H_2 a pressure of ~3 bar can be achieved once the sealed flask is warmed to room temperature. After the flask had warmed to room temperature it was placed in an oil bath at 110°C and stirred for 2.5 hours resulting in formation of a deep red solution. After this period, the flask was left to cool and the H_2 gas was removed by 4 cycles of short vacuum/N_2, care was taken not to remove solvent during the degassing process. The samples were stored in a glovebox where they remained red and well dispersed for several weeks.

Synthesis of Cu_2O@DOPA NPs.

Dioctylphosphinic acid (11.7 mg, 0.04 mmol) was added to a Young's tap flask and the flask placed under vacuum to remove any moisture. CuMes (73.3 mg, 0.40 mmol) was added to the flask in a glovebox and then mesitylene (11 mL) added to make up the concentration to [CuMes] = 0.036 M. The flask was exposed to air, whilst stirring, and left for 3 days. The resulting yellow/brown solution was used directly in catalysis.

Synthesis of the CuMesZnO@DOPA.

ZnO@DOPA NPs (52.1 mg, 0.40 mmol Zn) were added to a Young's tap flask and the flask placed under vacuum to remove any moisture. CuMes (73.3 mg, 0.40 mmol) was added to the flask in a glovebox and mesitylene (11 mL) added to make up the concentration to [CuMes] = 0.036 M. The solution was stirred for 10 minutes and should appear almost colourless. A freeze/thaw degas cycle was conducted to remove the N_2 atmosphere and the solution re-frozen and evacuated before addition of H_2 gas at 1 bar for 30 seconds (open to bubbler). By submerging ~2/3 of the flask in liquid N_2 during the addition of H_2, a pressure of ~3 bar can be achieved once the sealed flask is warmed to room temperature. After the flask had warmed to room temperature, it was placed in an oil bath at 110°C and stirred for 2.5 h forming a deep red solution. After this period, the flask was left to cool and the H_2 removed by 4 cycles of short vacuum/N_2, care was taken not to remove solvent during the degassing process. The samples were stored in vials in a glovebox where they remained red and well dispersed for several weeks.

Samples with addition of extra ligand were prepared by adding the desired amount of dioctylphosphinic acid along with the ZnO@DOPA NPs. After this, the aforementioned procedure was conducted.

Synthesis of the CuZnO@St pre-catalyst colloid.

CuZnO@St was prepared according to a reported method.[5] Under an inert atmosphere, copper(II) bis(stearate) (252.2 mg, 0.4 mmol) and diethyl zinc (49.4 mg, 0.4 mmol) were mixed in dry toluene (10 mL) at room temperature. The resulting red/brown pre-catalyst colloid was stirred for 1 hour before being transferred to the reactor using air sensitive techniques. The solution consists of

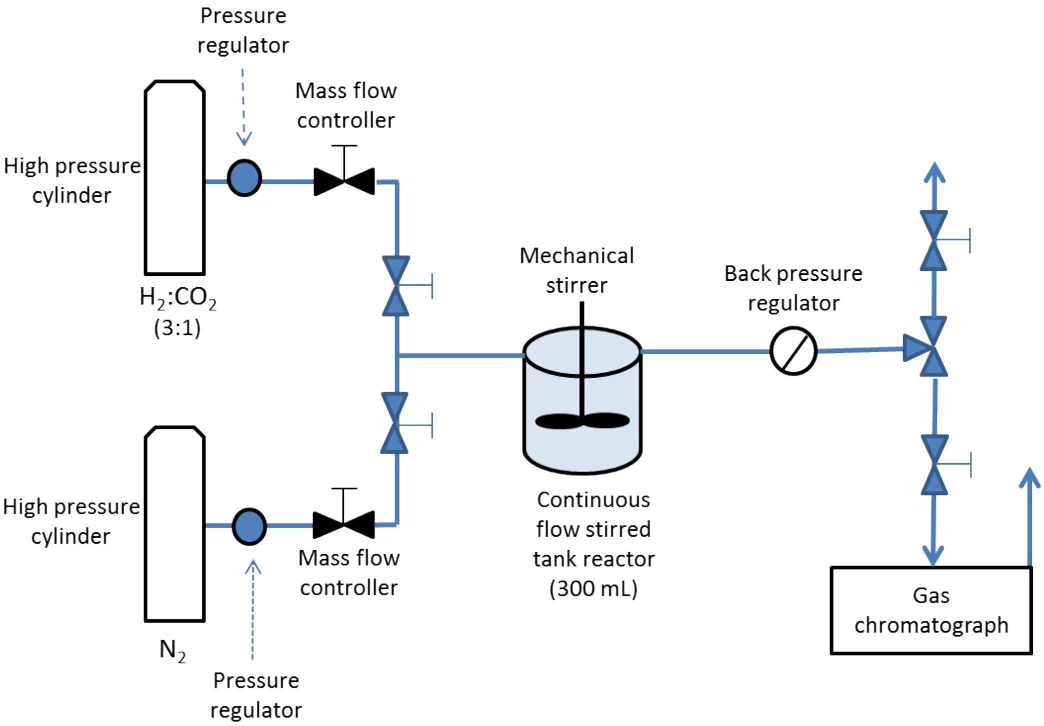
Cu@stearate NPs and Zn complexes, which are hydrolysed under the reaction conditions to form ZnO NPs.

Catalytic experiments.

The methanol synthesis experiments were performed in a 300 mL continuous flow stirred-tank reactor (CSTR, Parr) which was mechanically stirred at 1500 r.p.m. and with vertical baffles to ensure homogeneous mixing of the liquid and gas phase. Any air stable precursors, ZnO@DOPA as solid powders or Cu_2O@DOPA NPs colloidal solution, were added directly to the reactor vessel, and then, the reactor was filled with mesitylene up to a total volume of 100 mL. The solution mixture was subsequently stirred and degassed by flowing N_2 (400 $mL.min^{-1}$) for 30 minutes. Any colloidal solution of air sensitive precursors (e.g. Cu@DOPA NPs, CuMesZnO@DOPA or CuMesZnO@DOPA+x) were added by syringe under a flow of N_2, always giving a total reaction volume of 100 mL. 0.4 mmol each of Zn and Cu were added in all cases. Finally, the reactor was pressurized to 5.0 MPa using a gas mixture comprising 96 vol% of H_2:CO_2= 3:1 and 4 vol% Ar (used as internal standard for GC analysis), and heated to 210°C. The experiments were performed under 150 $mL.min^{-1}$ for 10 h.

The commercial CuO-ZnO-Al_2O_3 precursor of the methanol synthesis catalyst from Alfa Aesar (45776, mass composition CuO; 63.5%, ZnO; 25.1%, Al_2O_3; 10.1%, MgO; 1.3%), ground to a fine powder, was tested as a reference material. The choice of catalyst loading was dictated by normalisation considerations, making sure that the total moles of Cu and Zn metals was the same as in the Cu/ZnO colloids. Before any catalytic experiment was conducted, the reference catalyst was activated using a diluted H_2 stream (5 vol% H_2/N_2) at 0.45 MPa and 240°C (ramp 2°$C.min^{-1}$) for 3 h, according to a standard activation protocol for the ternary Cu-ZnO-Al_2O_3 methanol synthesis catalyst in slurry reactors.[6] Finally, the catalytic run was performed under the same conditions described before.

The reaction products and unreacted material were monitored by an online gas chromatograph (Bruker 450 GC), equipped with a thermal conductivity detector (TCD), for the quantification of CO, CO_2 and Ar, and a flame ionization detector (FID), for the quantification of MeOH, and other oxygenates or hydrocarbons (if produced). To avoid any product condensation during the experiments, the lines from the reactor to the GC were heated to 180°C. An scheme of the reaction system can be found in the following scheme 1.All the experiments were conducted under differential conditions, with a CO_2 conversion always below 2%. Selectivities are given on a carbon basis. Repeat experiments (see Cu2OZnO@DOPA and Cu-ZnO-Al_2O_3) showed high reproducibility.



Scheme S1. *Reaction system used for conducting the catalytic experiments.*

Supporting Figures

ZnO@DOPA NPs *(Data reproduced from Pike et. al.[7] with permission of the authors)*

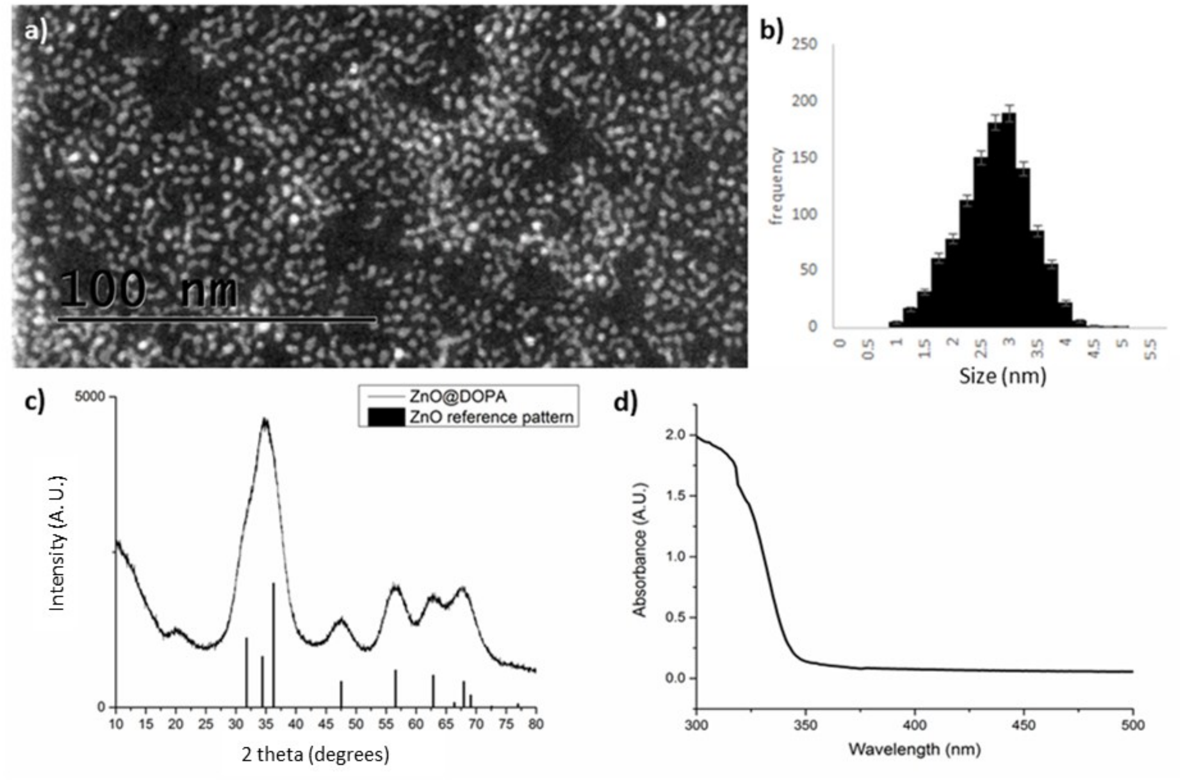


Figure S1. *a) Representative ADF-STEM image of ZnO@DOPA NPs; b) histogram showing size distribution of NPs from STEM image; c) powder XRD pattern of ZnO@DOPA NPs with Wurzite reference pattern; d) UV spectrum of ZnO NPs dispersed in toluene. Full characterisation details previously reported.*[7]

Cu@DOPA NPs *(Data reproduced from Pike et. al.* [8] *with permission of the authors)*

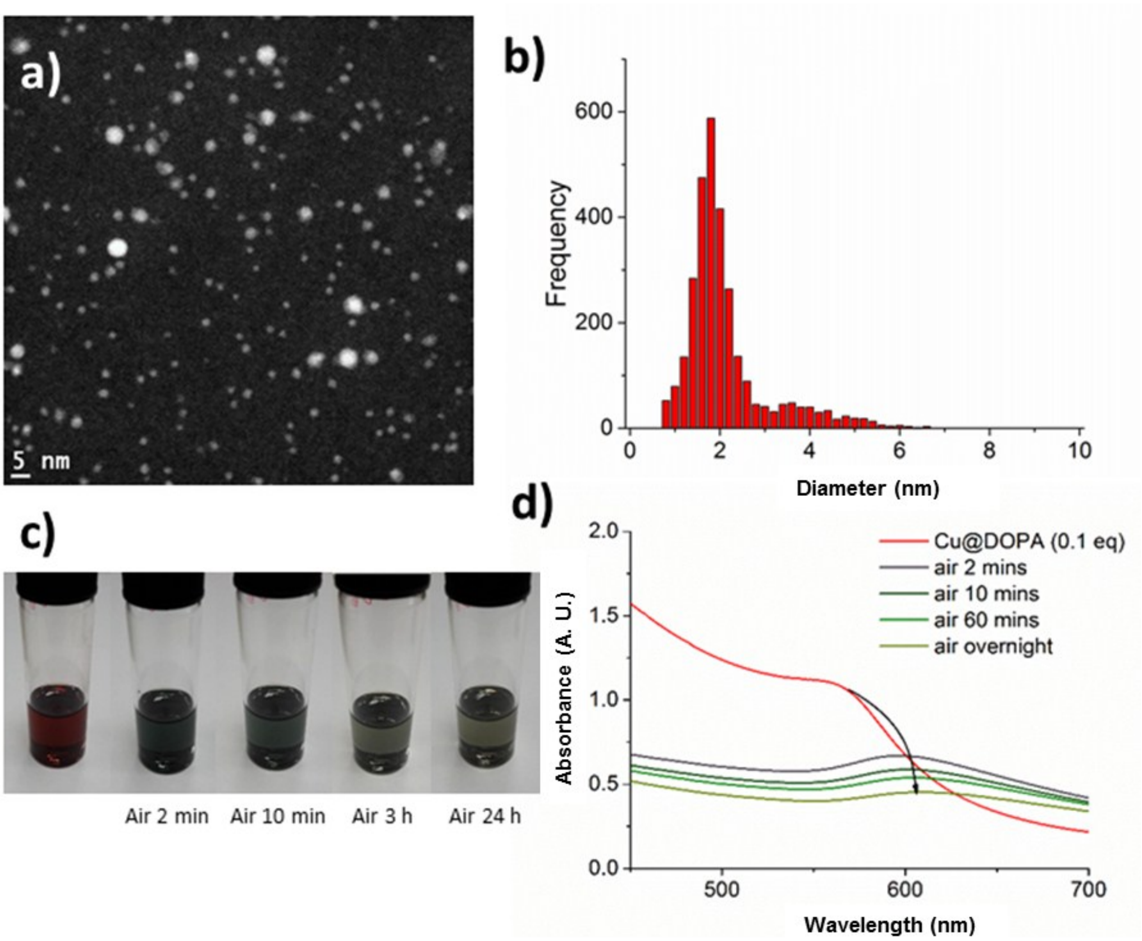


Figure S2. *a) Representative ADF-STEM image of Cu@DOPA NPs using a Gatan Vacuum Transfer Holder; b) related histogram showing particle size distribution; c) visible spectra of Cu@DOPA NPs and subsequent spectra after exposure to air. Full characterisation data previously reported;*[8] *d) photographs of a toluene solution of Cu NPs before and after exposure to air.*

Cu_2O@DOPA NPs *(Data reproduced from Pike et. al.* [8] *with permission of the authors)*

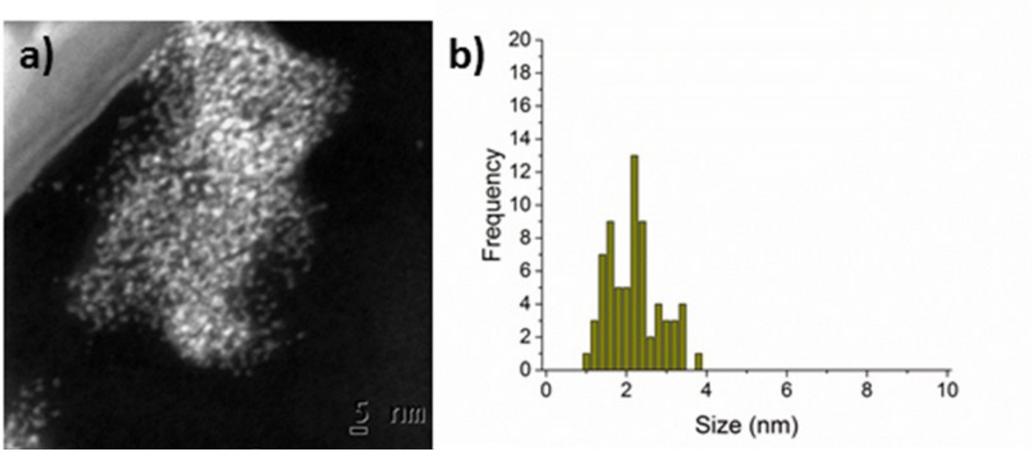


Figure S3. *a) Representative ADF-STEM image of Cu_2O@DOPA NPs; b) related histogram showing particle sizes (from (a));*

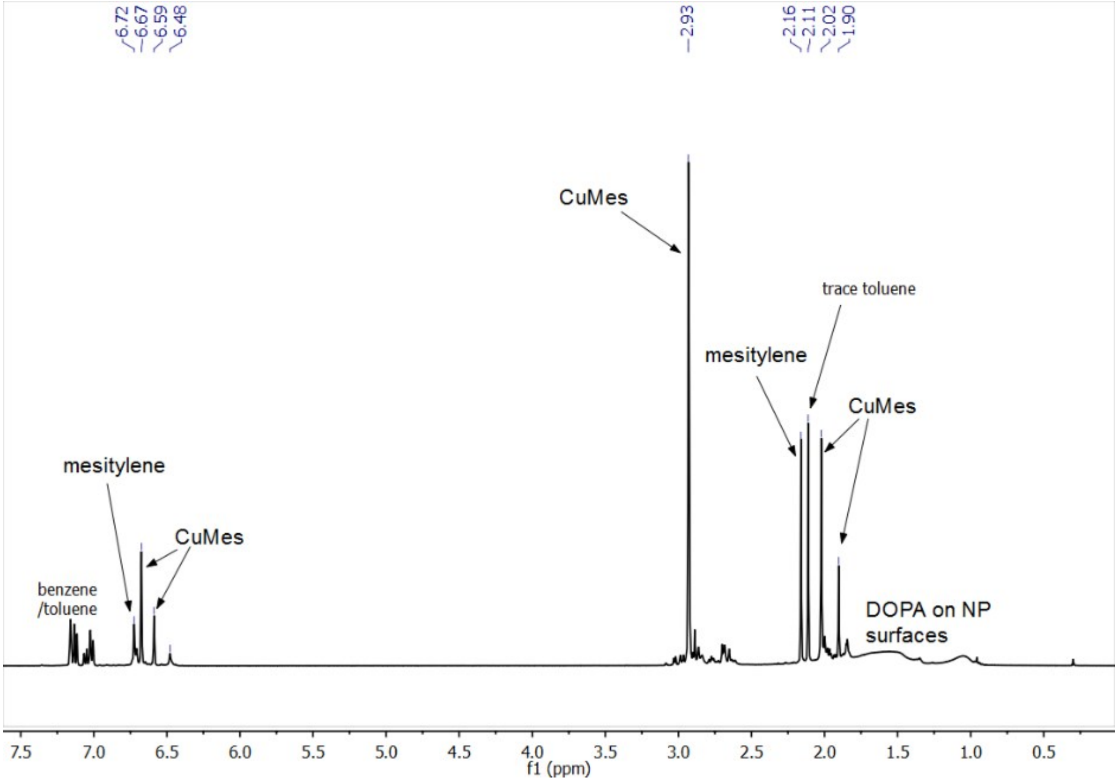


Figure S4. *^1H NMR spectrum of CuMes + ZnO@DOPA (1:0.17 metal:ligand molar ratio) (1:1 Cu:Zn molar ratio) in C_6D_6. Mesitylene evolved from reaction of CuMes with moisture of ZnO surface OH groups.*

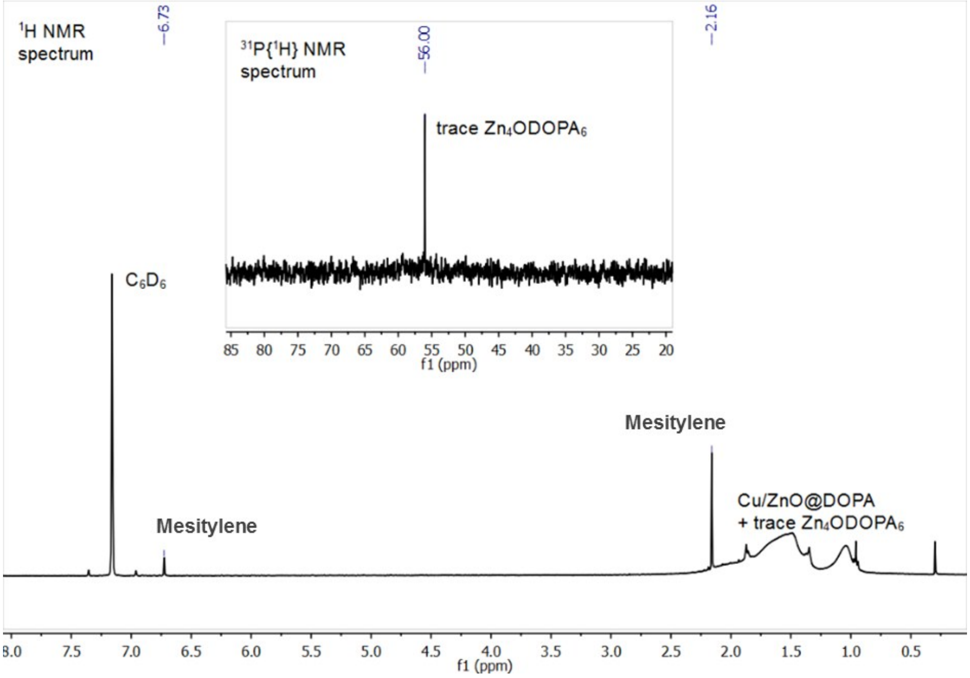


Figure S5. *^{1}H NMR spectrum of* ***CuMesZnO@DOPA*** *sample derived from the reduction (conditions: 3 bar H_2, 110° C, 2 hours) of CuMes + ZnO@DOPA (1:0.17 metal:ligand ratio) (1:1 Cu:Zn ratio) in C_6D_6. $^{31}P\{^1H\}$ NMR spectrum (inset) reveals a trace of $Zn_4O(DOPA)_6$ [δ = 56.0] but no other sharp signals, minor sharp signals between 0.8 and 2.0 ppm in ^{1}H NMR also consistent with $Zn_4O(DOPA)_6$.*[7]

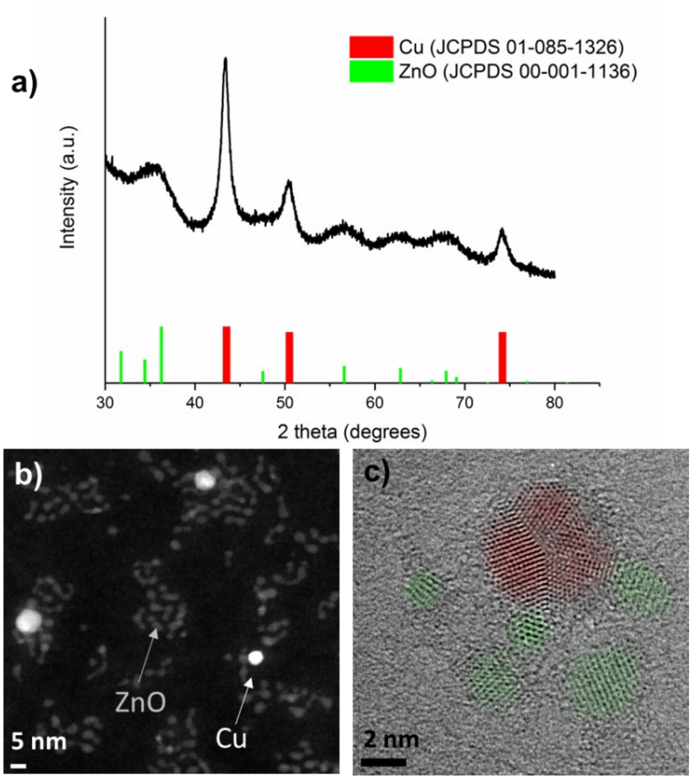


Figure S6. *Characterisation results of the pre-catalyst colloid* ***CuMesZnO@DOPA*** *a) Powder XRD spectrum of dried NPs analysed under air sensitive conditions b) Representative ADF-STEM c) HR-TEM image showing interfaces between crystalline Cu(0) (red) and ZnO (green) NPs.*

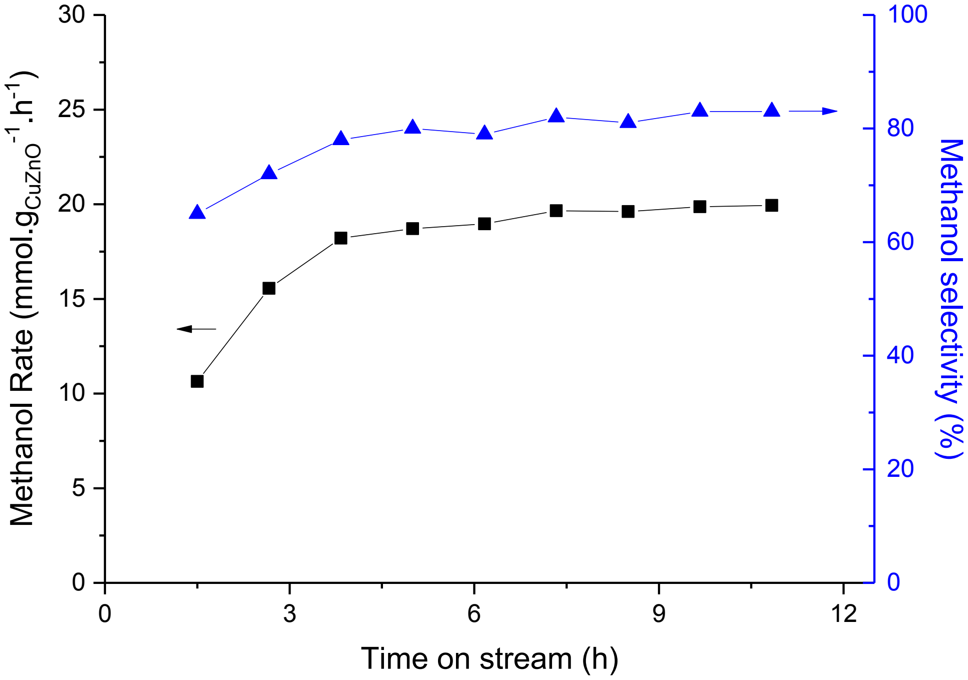


Figure S7. *MeOH rate and selectivity with time* ***CuZnO@DOPA****. Reaction conditions: 210°C, 50 bar, H_2:CO_2 molar ratio of 3:1.*

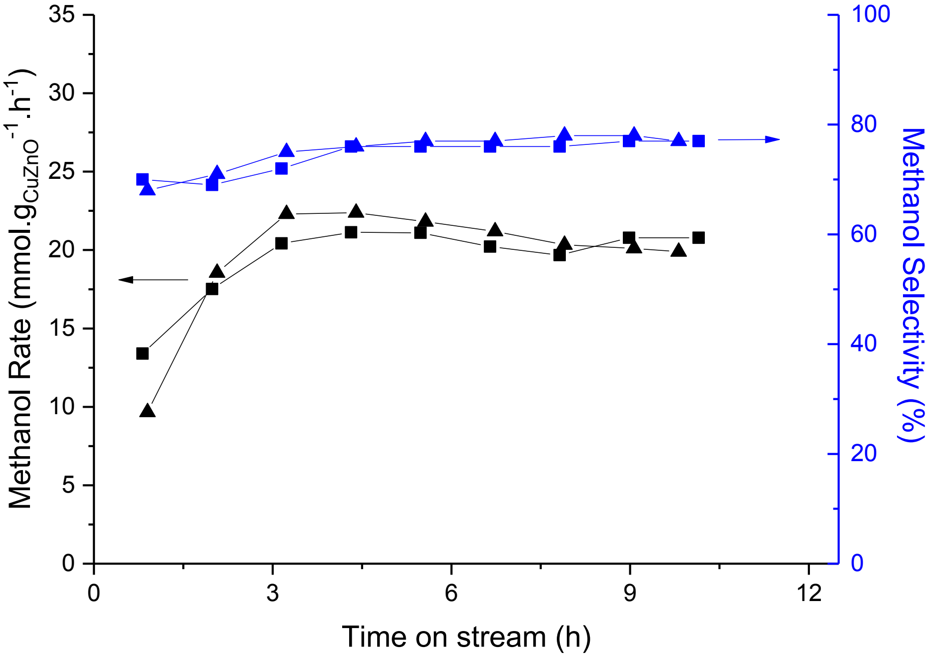


Figure S8. *MeOH rate and selectivity with time for* ***Cu_2OZnO@DOPA*** *and an identical repeat. Reaction conditions: 210°C, 50 bar, H_2:CO_2 molar ratio of 3:1.*

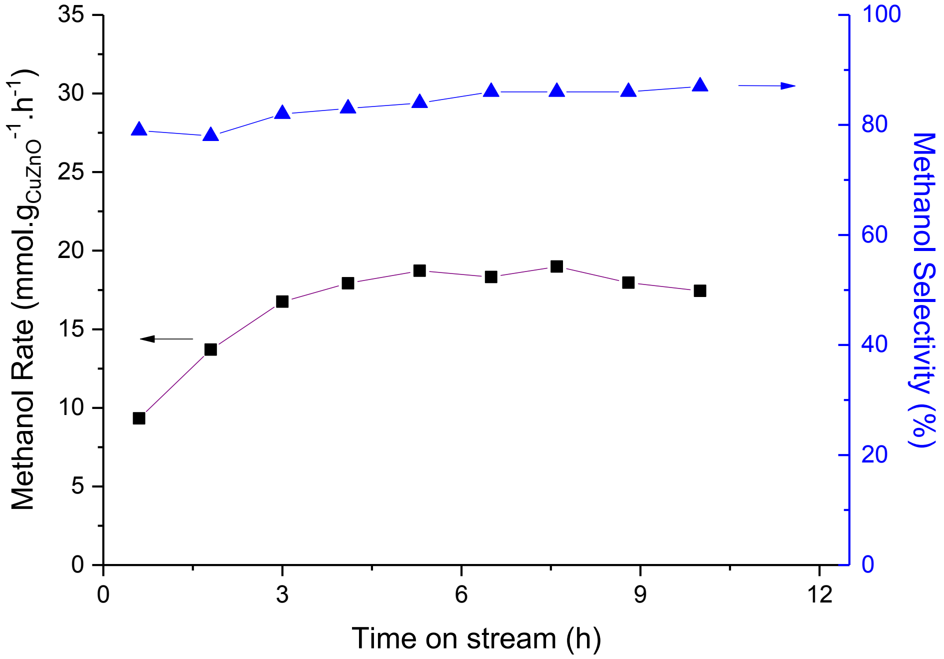


Figure S9. *MeOH rate and selectivity with time for* ***CuMesZnO@DOPA****. Reaction conditions: 210°C, 50 bar,* H_2*:*CO_2 *molar ratio of 3:1.*

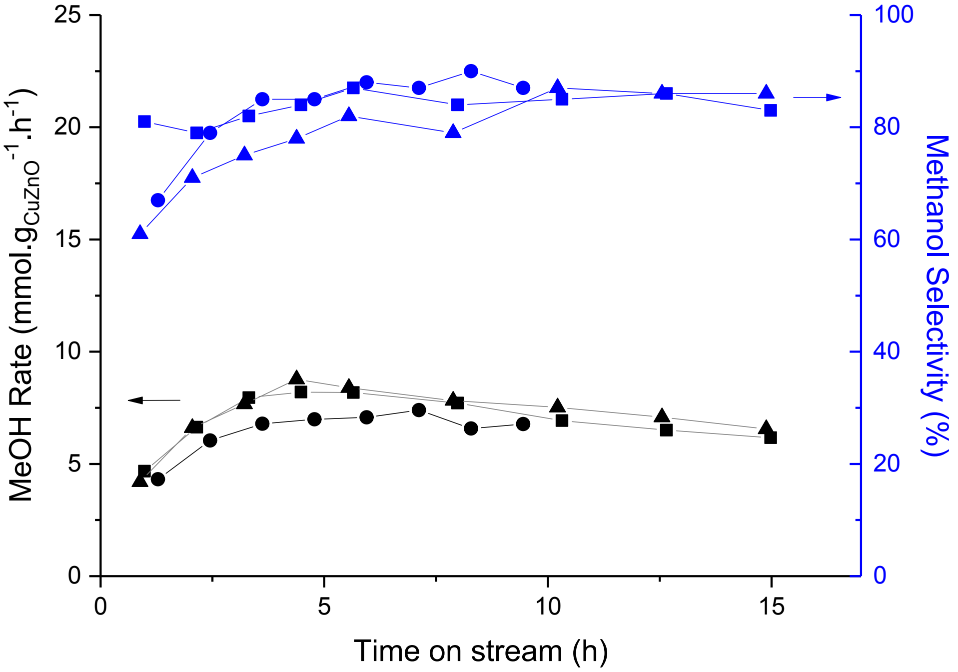


Figure S10. *MeOH rate and selectivity with for the conventional Cu-ZnO-*Al_2O_3 *catalyst and two identical repeats. Reaction conditions: 210°C, 50 bar,* H_2*:*CO_2 *molar ratio of 3:1.*

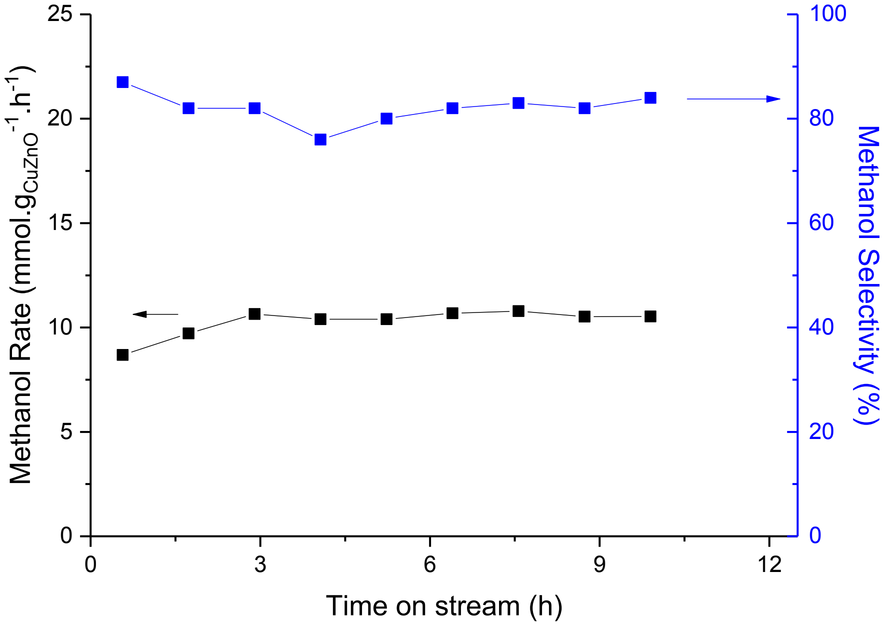


Figure S11. *MeOH rate and selectivity with time for* ***CuZnO@St****. Reaction conditions: 210°C, 50 bar,* H_2*:*CO_2 *molar ratio of 3:1.*

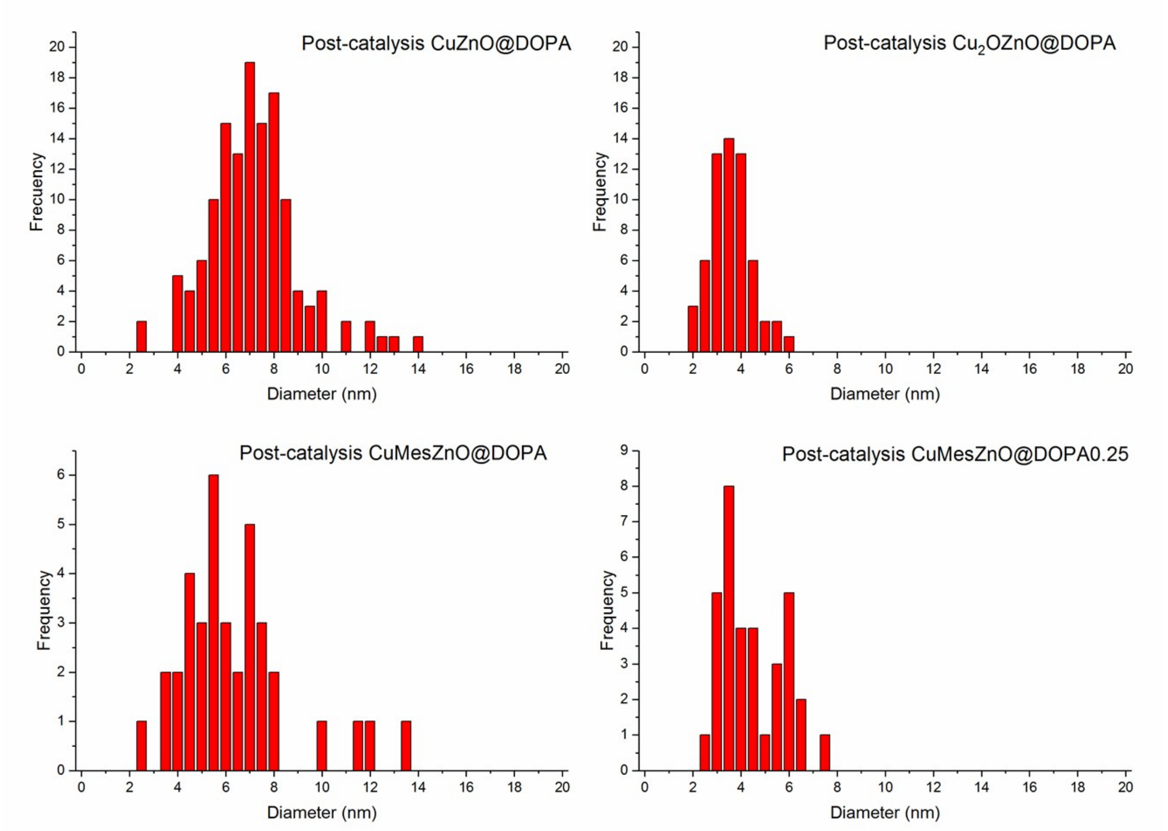


Figure S12. *Cu(0) NP size distributions for the post-catalysis CuZnO@DOPA,* Cu_2O*@DOPA, CuMesZnO@DOPA and CuMesZnO@DOPA+0.25.*

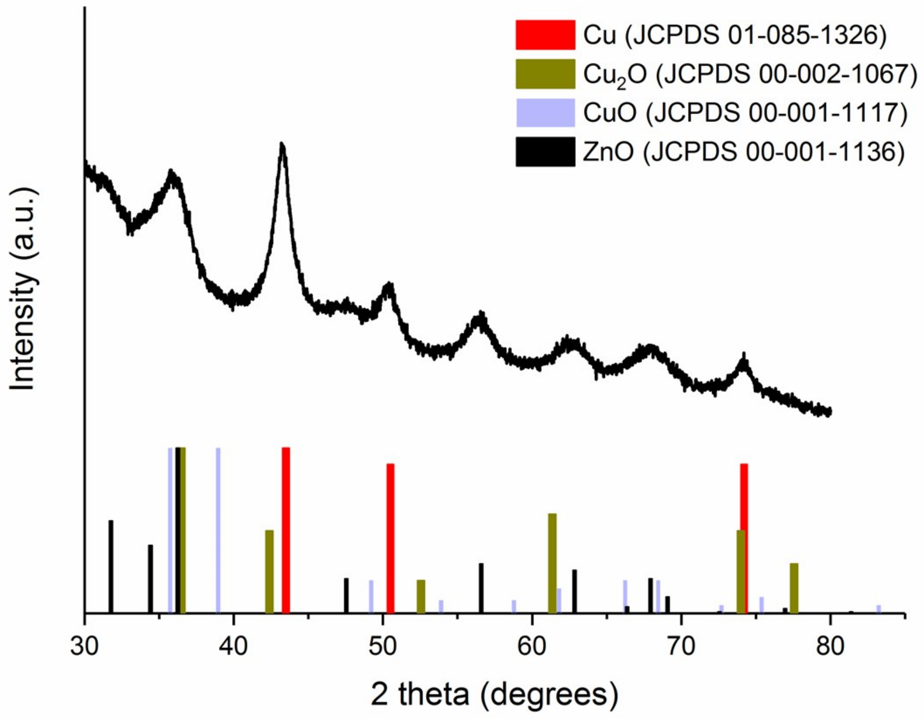


Figure S13. *Powder XRD pattern of dried post catalysis colloid* ***CuZnO@DOPA*** *under polyimide tape.*

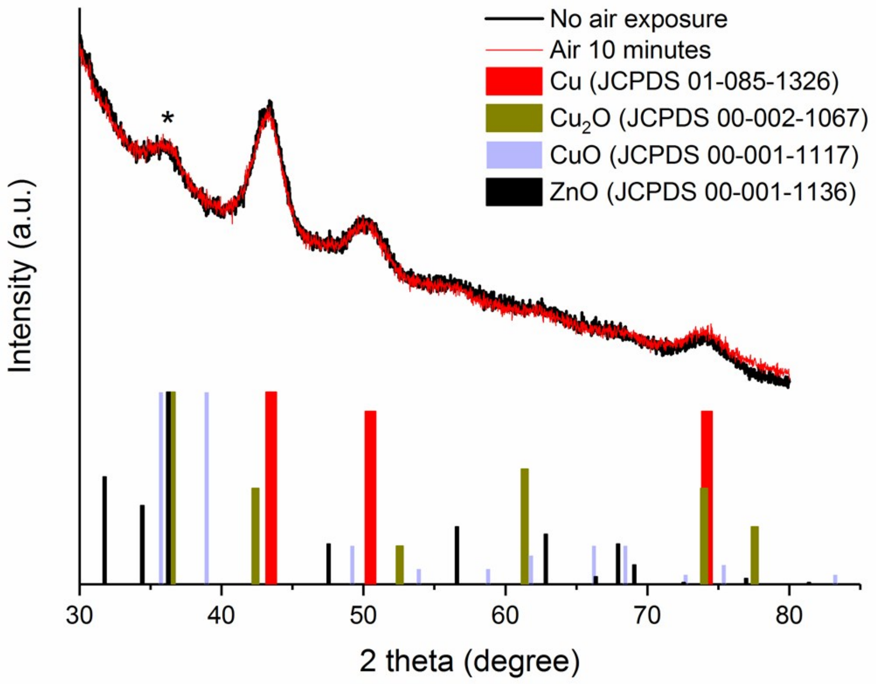


Figure S14. *Powder XRD patterns of dried post catalysis colloid* ***Cu_2OZnO@DOPA*** *under polyimide tape and after air exposure for 10 min. *Diffraction corresponding to the polyimide tape.*

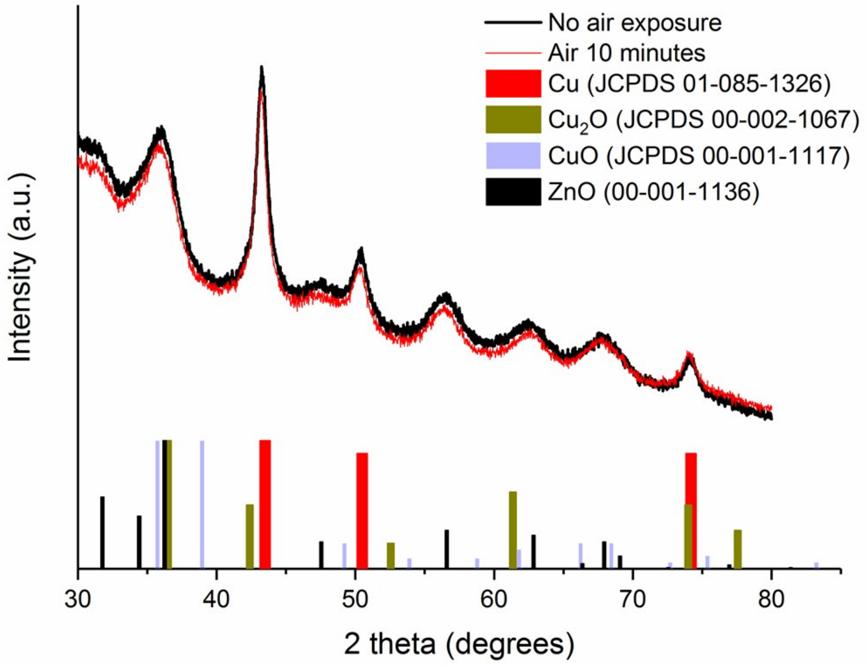


Figure S15. *Powder XRD patterns of dried post catalysis colloid* ***CuMesZnO@DOPA*** *under polyimide tape and after air exposure for 10 min.*

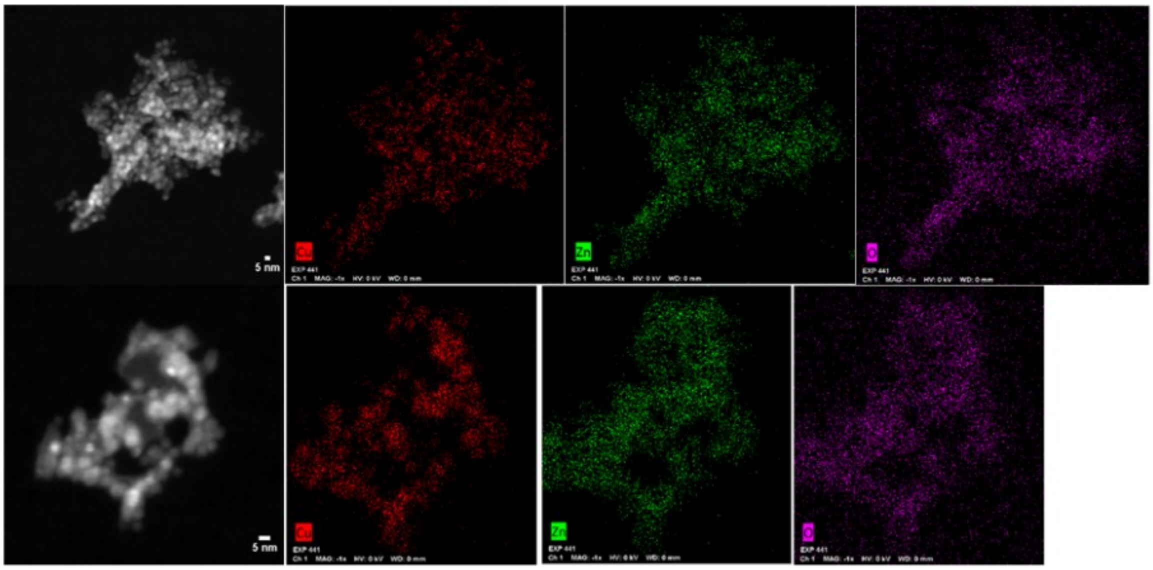


Figure S16. *Representative STEM images of the* ***Cu$_2$OZnO@DOPA*** *post catalysis sample. EDX images show the Cu, Zn and O contributions.*

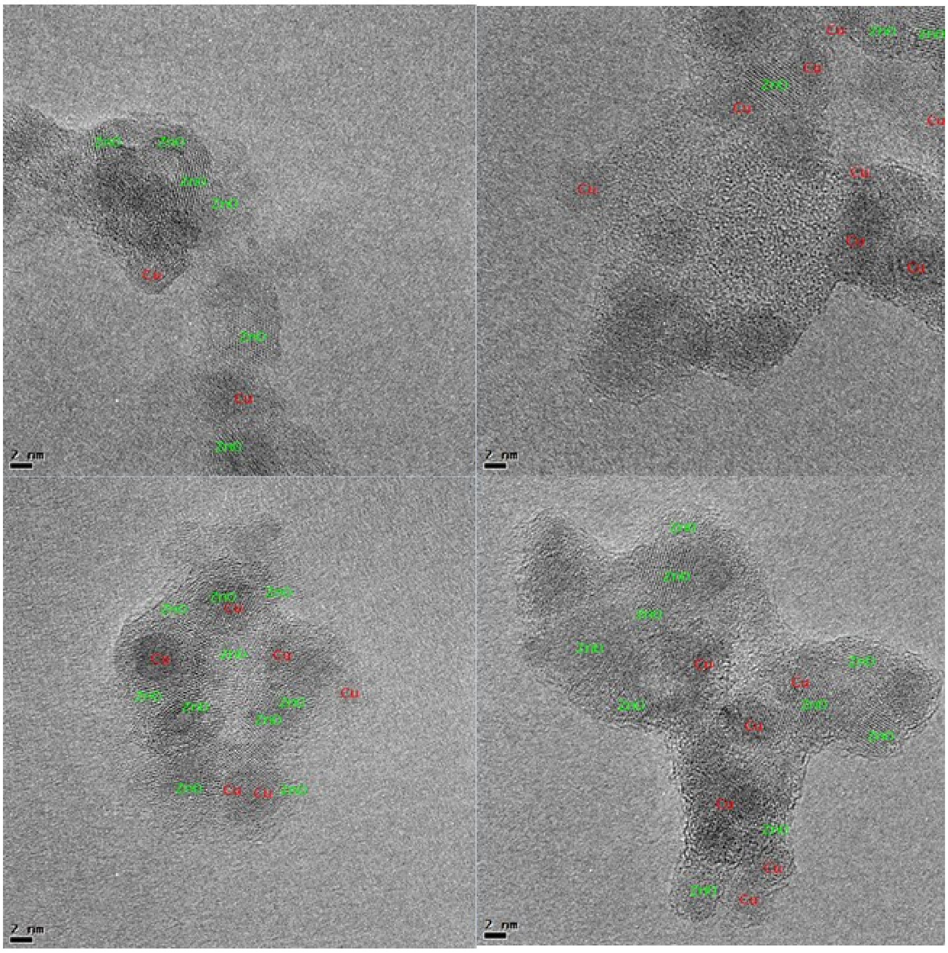


Figure S17. *Representative HR-TEM images of the* ***Cu$_2$OZnO@DOPA*** *post catalysis sample. Crystalline phases identified by lattice spacing analysis.*

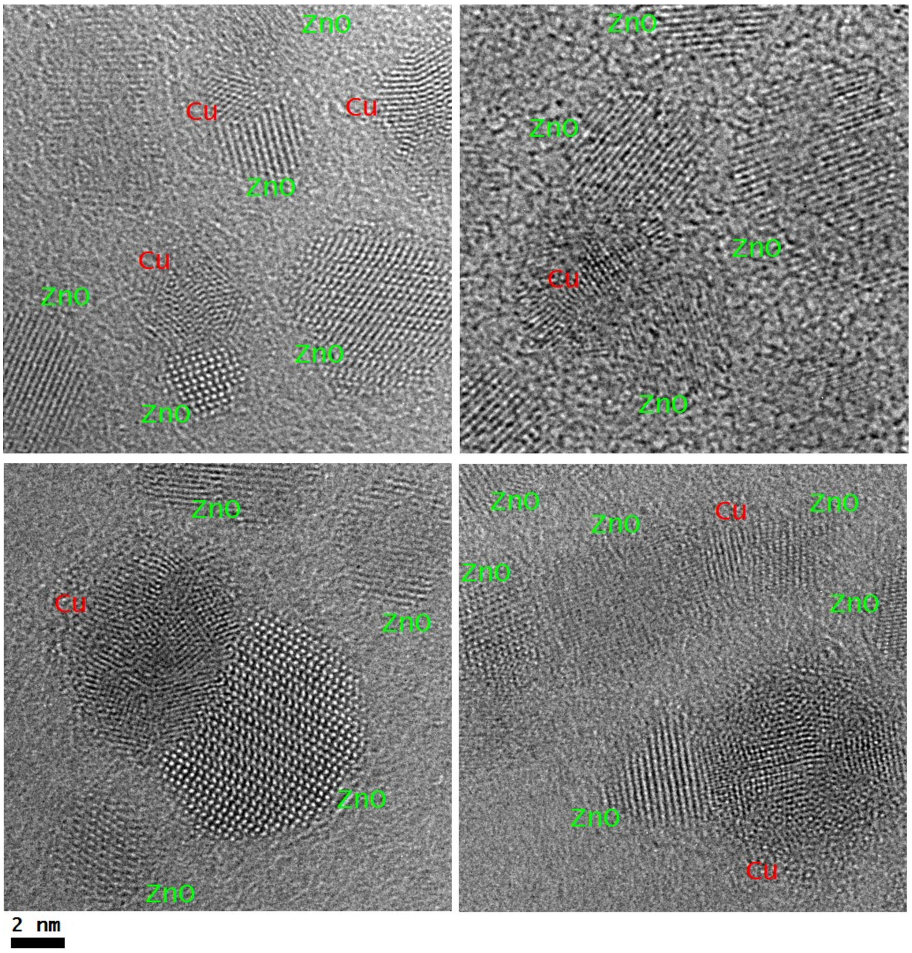


Figure S18. *Representative HR-TEM images of the* ***CuZnO@DOPA*** *post catalysis sample. Crystalline phases identified by lattice spacing analysis.*

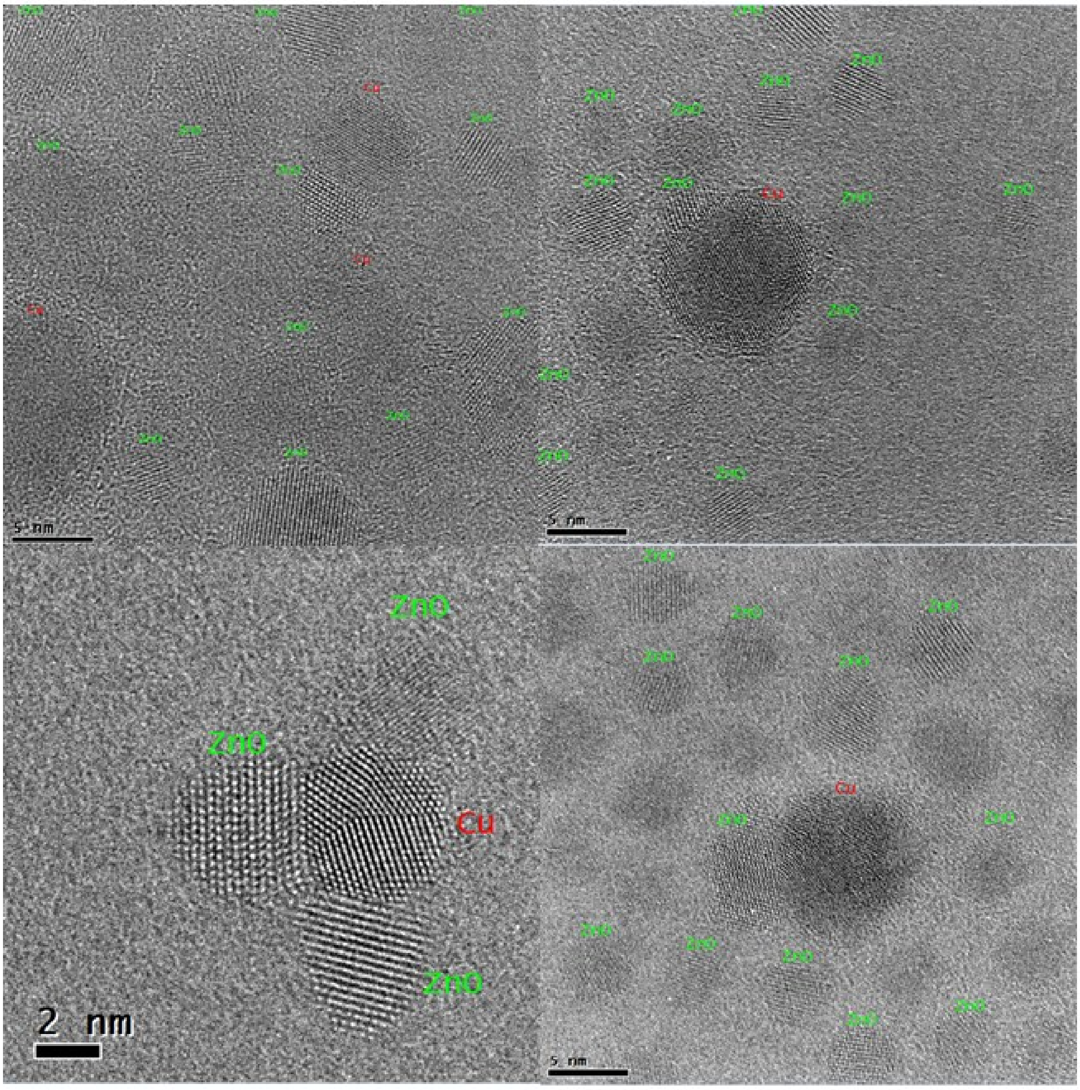


Figure S19. *Representative HR-TEM images of the* ***CuMesZnO@DOPA*** *post catalysis sample. Crystalline phases identified by lattice spacing analysis.*

Table S1*. Number of Cu(0) particles identified with a clear interface to ZnO for* ***CuZnO@DOPA****,* ***CuMesZnO@DOPA*** *and* ***CuMesZnO@DOPA+0.25*** *samples before and after catalysis.*

Sample	Cu particles with a clear interface to ZnO (sample size)
Pre-catalysis **CuZnO@DOPA**	0 (200)
Post-catalysis **CuZnO@DOPA**	109 (238)
Pre-catalysis **CuMesZnO@DOPA**	175 (201)
Post-catalysis **CuMesZnO@DOPA**	11 (13)
Pre-catalysis **CuMesZnO@DOPA+0.25**	0 (6)
Post-catalysis **CuMesZnO@DOPA+0.25**	13 (312)

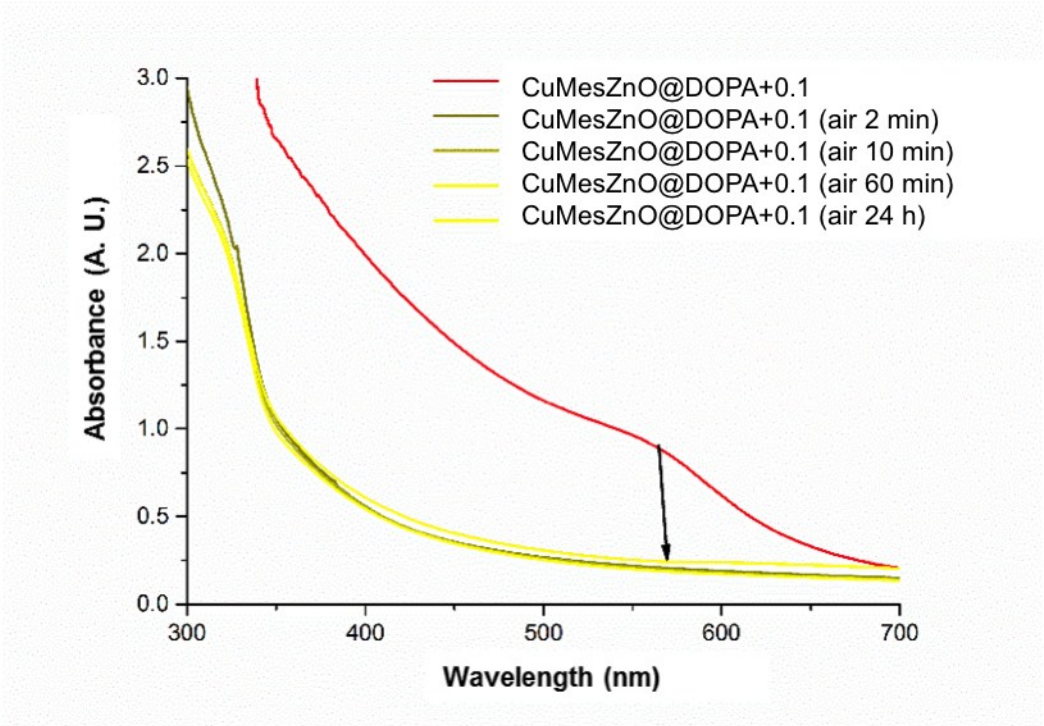


Figure S20. UV/Visible spectra of CuMesZnO@DOPA+0.1 colloidal solution, and subsequent spectra after exposure to air.

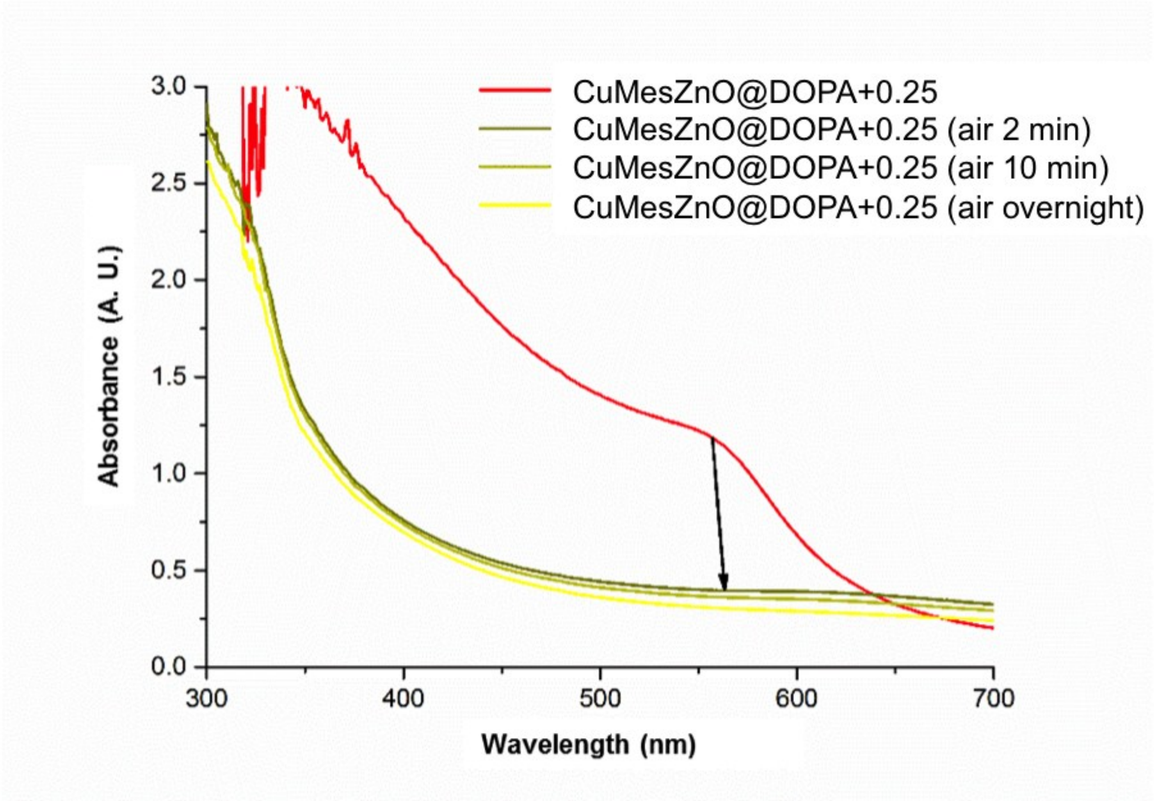


Figure S21. UV/Visible spectra of CuMesZnO@DOPA+0.25 colloidal solution, and subsequent spectra after exposure to air.

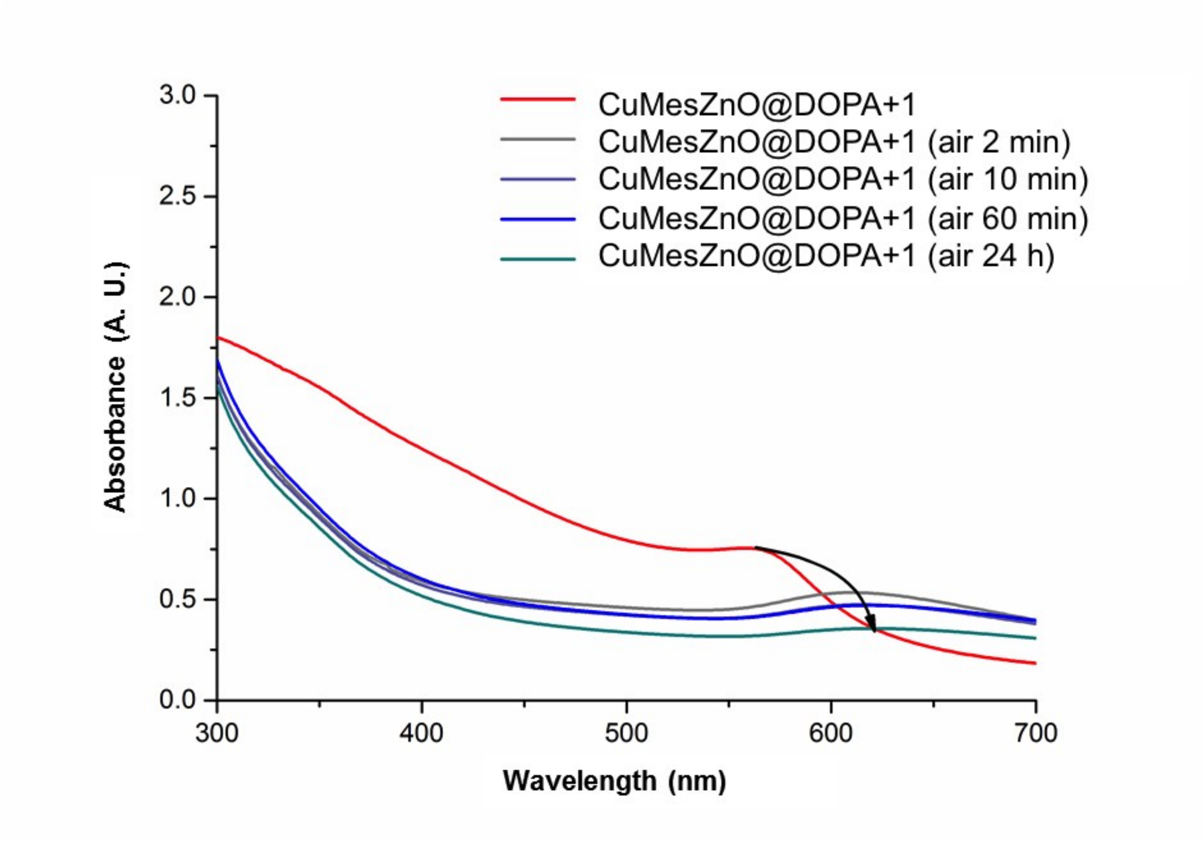


Figure S22. UV/Visible spectra of CuMesZnO@DOPA+1 colloidal solution, and subsequent spectra after exposure to air.

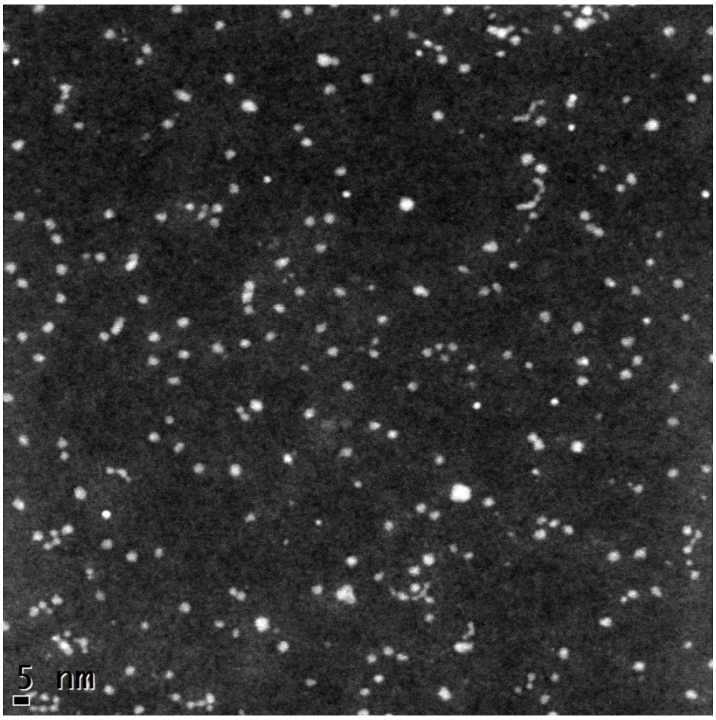


Figure S23. a) HR-TEM and b) STEM image of the **CuMesZnO@DOPA+0.25** colloidal solution.

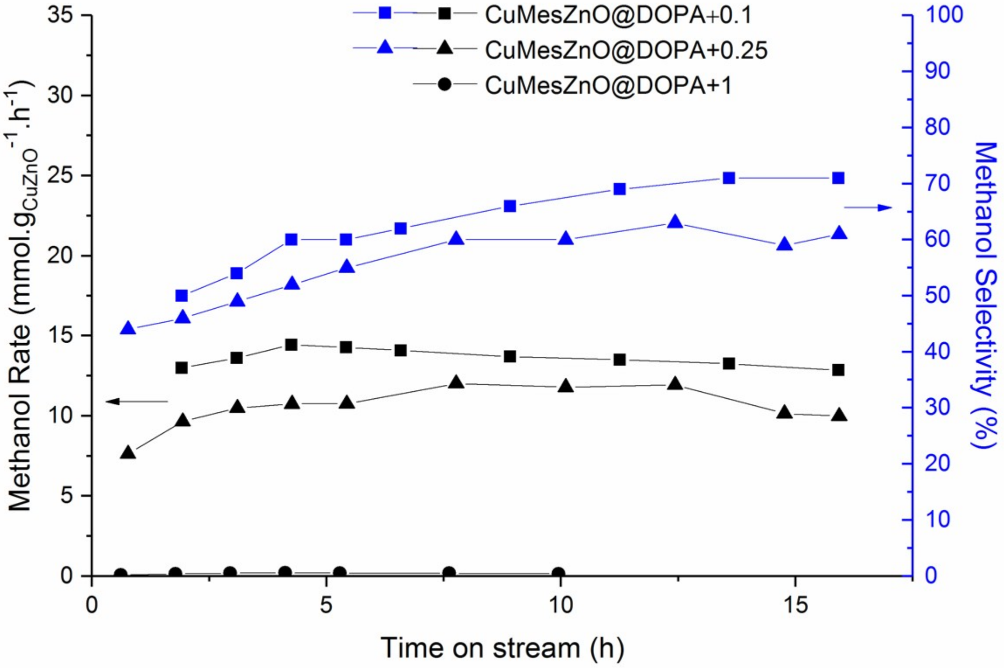


Figure S24. *MeOH rate and selectivity with time for CuMesZnO@DOPA+x with different ligand loadings. Reaction conditions: 210°C, 50 bar, H_2:CO_2 molar ratio of 3:1.*

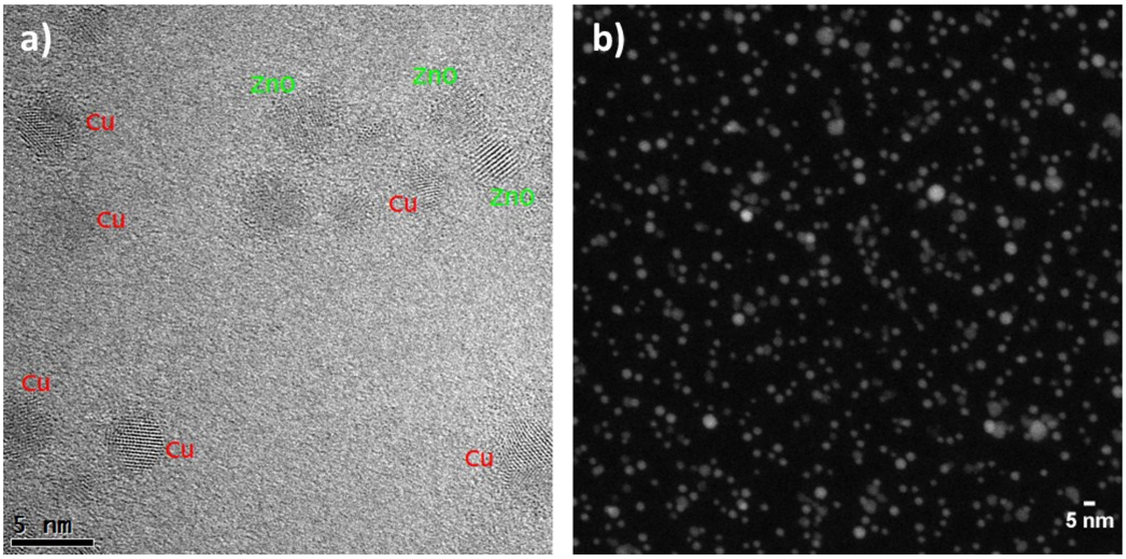


Figure S25. Representative a) HR-TEM and b) STEM images of **CuMesZnO@DOPA+0.25** post-catalysis

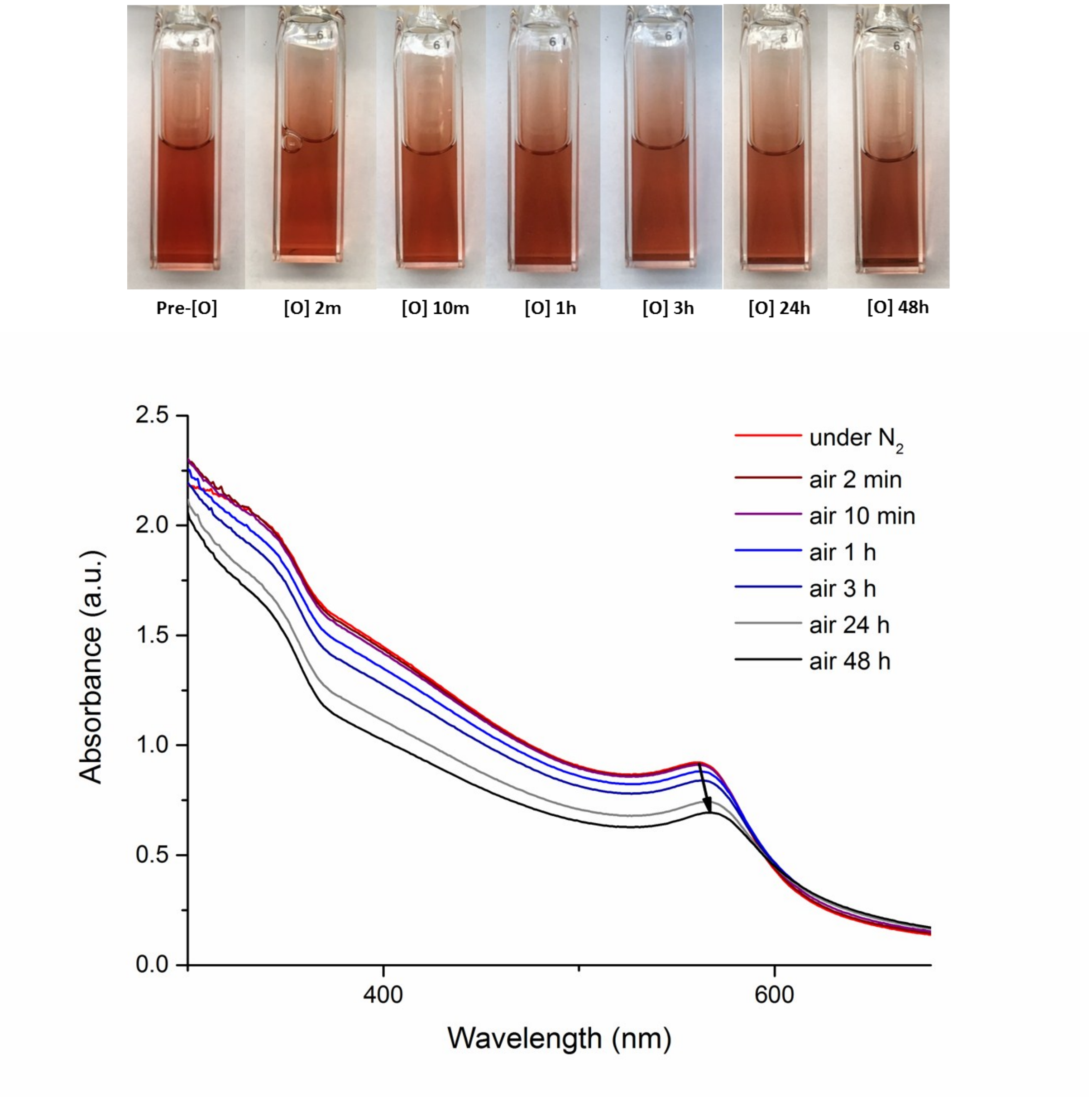


Figure S26. *Photographs of the post-catalysis* ***CuZnO@DOPA*** *dilution (diluted x3 with toluene) before and after exposure to air. UV/visible spectrum of solutions after catalysis and spectra after exposure to air over 3 days.*

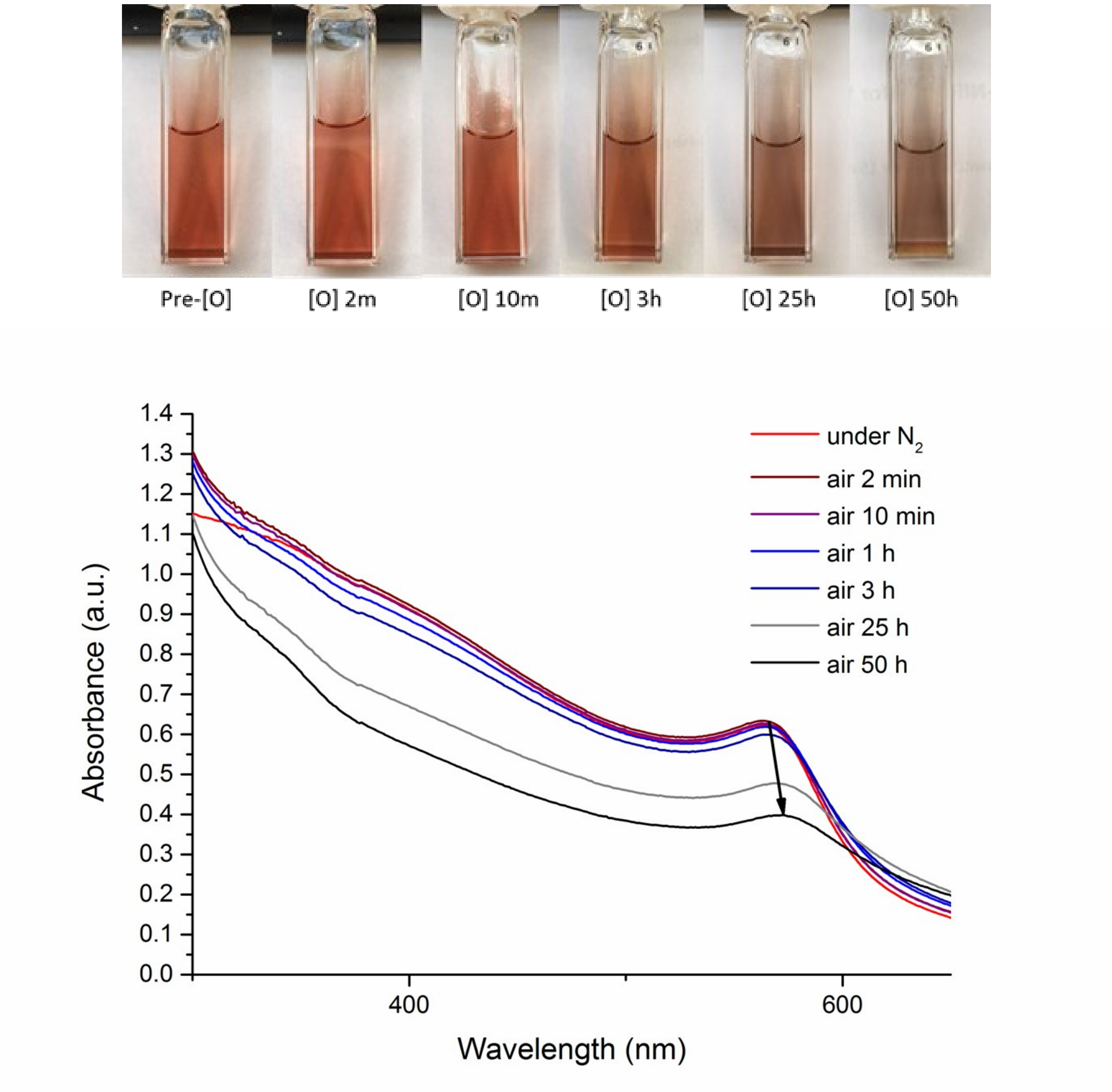


Figure S27. *Photographs of the post-catalysis* ***Cu_2OZnO@DOPA*** *dilution (diluted x3 with toluene) before and after exposure to air. UV/visible spectrum of solution after catalysis and spectra after exposure to air over 3 days.*

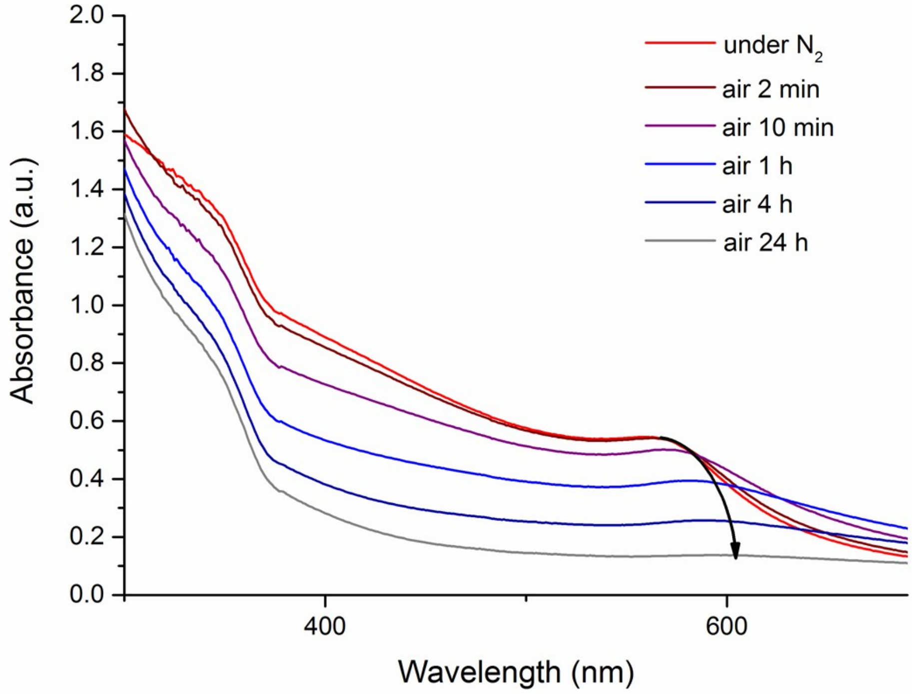


Figure S28. *UV/Visible spectra of post-catalysis* ***CuMesZnO@DOPA+0.1*** *solution and subsequent spectra after exposure to air.*

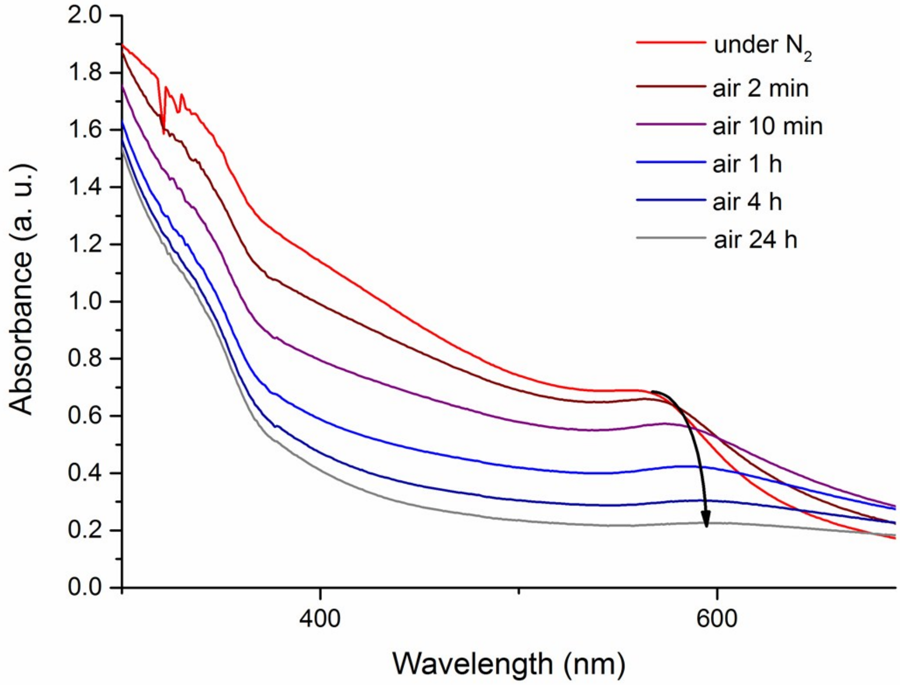


Figure S29. *UV/Visible spectra of post-catalysis* ***CuMesZnO@DOPA+0.25*** *solution and subsequent spectra after exposure to air.*

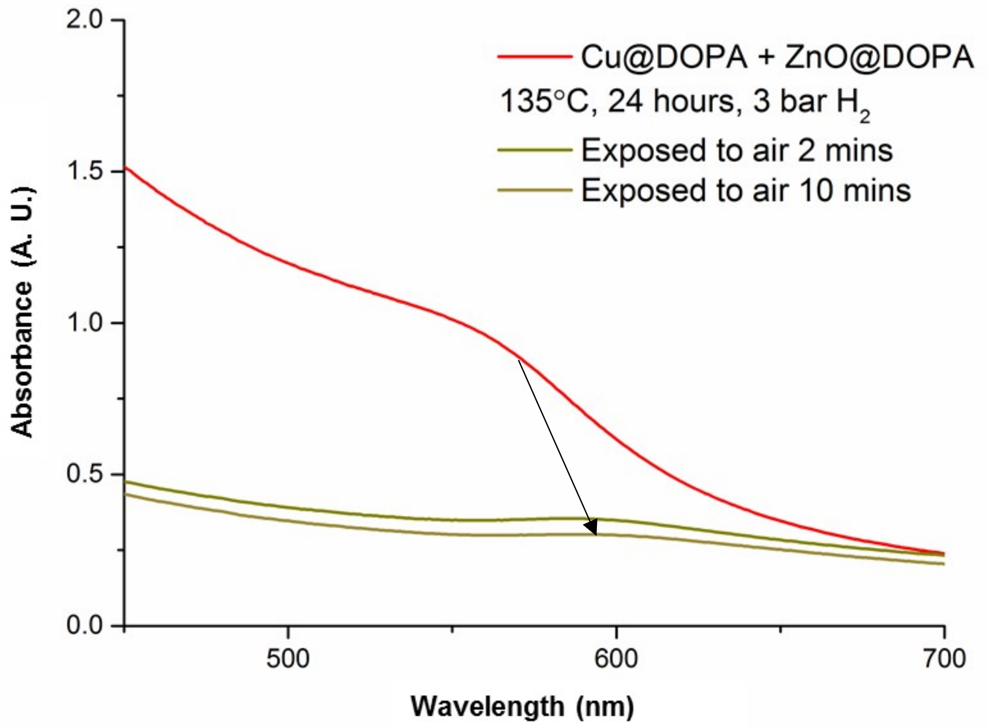


Figure S30. *UV-vis spectrum of a solution of Cu@DOPA + ZnO@DOPA which had been heated under 3 bar H_2 to 135°C for 24 h. Subsequent spectra shown after exposure of the solution to air.*

Supporting Note 1

During preliminary studies, catalysts prepared with stearate ligands were used, in all these cases evidence of the production of an alcohol (likely octadecanol) was observed after catalysis by a signal at ($HOC\mathbf{H_2}R$, $\delta = 3.64$) by ^1H NMR spectroscopy, consistent with previous studies using the stearate ligand.[4] This signal was never observed in cases where $[DOPA]^-$ was used as the ligand.

Supporting Note 2

When isolated ZnO@DOPA (1:0.17 Zn:ligand ratio) nanoparticles are dissolved in organic solvents (e.g. $CDCl_3$ or d_8-toluene) a broad signal (~52 ppm) is observed in the ^{31}P NMR spectra corresponding to the phosphinate ligand coordinating to the nanoparticle surface. Over time a sharper signal also grows in (32.9 ppm, $CDCl_3$), consistent with the known cluster $Zn_4O(DOPA)_6$,[7] by comparing the integrals of the NMR signal and an internal standard the quantity of $[DOPA]^-$ ligand incorporated into $Zn_4O(DOPA)_6$ clusters is estimated to be around 20% after 24 hours at room temperature, and further cluster formation is slow. It appears that the cluster can be released from the nanoparticle surface. This process is likely to also occur during the solution based synthetic and catalytic procedures involving ZnO@DOPA NPs in this report, and the cluster was identified in all post-catalysis solutions.

Addition of a further 0.2 equiv. of DOPA-H to a solution of the ZnO@DOPA (1:0.17 Zn:ligand ratio) NPs initially forms an approximately quantitative amount of $Zn(DOPA)_2$ (identified using ^{31}P NMR spectroscopy with an internal standard) as the acid etches the ZnO surface. Over 24 hours the $Zn(DOPA)_2$ coverts into $Zn_4O(DOPA)_6$ clusters, presumably through further reaction with the ZnO surface.

Supporting Note 3

HR-TEM images were used to determine the independent size distributions of Cu and ZnO for samples containing both phases. In each HR-TEM image, the fast Fourier transform was calculated over a region containing a single nanoparticle. The lattice spacings were measured, and compared with the known lattice spacings for Cu and ZnO to determine the phase. The size was then measured by taking the average of two orthogonal measurements of the nanoparticle diameter. This process was repeated for all nanoparticles across many high-resolution images to obtain the reported size distributions. Unlike the automated size analysis of STEM images (e.g. Figures S1-3) which only measures the combined size distribution, this method allows the determination of separate size distributions in mixed samples.

Supporting Note 4

In order to calculate the approximate ligand coverage (relative to available surface area) and the turnover frequency per m^2(Cu) it was necessary to calculate the surface area per gram of colloidal solution. The following procedure was followed using the sizing data obtained from TEM analysis

Assumptions: All particles are spherical and contain a pure phase with the same density as the bulk phase.

Surface Area of sample (m^2) = surface area of particle diameter r (m) x frequency of size particle (r ± 0.1 nm) in sample set

Volume of sample (m^3) = volume of particle diameter r (m) x frequency of this size particle (r ± 0.1 nm) in sample set

Surface area (m^2/g) = Surface Area of sample / (Volume of sample x density (g/m^3))

Molar surface area (m^2/mol) = Surface area * mass of repeat unit (e.g. for ZnO = 83.4, Cu = 63.5 and $CuO_{0.5}$ = 71.5)

Molar surface areas of CuZnO can then be obtained by adding the molar surface area of Cu with that of ZnO

Surface area taken up by a single $[DOPA]^-$ ligand = 0.244 nm^2.[2] Therefore one mole of $[DOPA]^-$ occupies an area of 147000 m^2. From this and the molar surface areas the required molar equivalents of $[DOPA]^-$ can be calculated to form a complete monolayer and this can be compared with the available ligand to give a ligand coverage percentage.

The turnover frequency is calculated from the catalytic activity (in this case defined as mmol(MeOH)/g(Cu).h) divided by the copper surface area (m^2/g)

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