

Hydrophobic CuO Nanosheets Functionalized with Organic Adsorbates

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Characterization details

Contact Angle measurement. Water contact angles were measured by an optical tensiometer (OneAttention, Biolin scientific instrument) using the sessile drop method. A 3 μL DI water droplet was placed on the thin film sample and photographed using a digital camera. The left and right contact angles were determined from digital images with post-processing software (OneAttention software). Contact angle was observed as a function of time and the mean contact angle are reported. Films were prepared by adding a slurry of sample in ethanol to a glass slide and rolling using a Meyer rod. The surface was rolled back and forth multiple times to achieve increased smoothness.

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). SEM and TEM images were collected on a Hitachi SU-70 and FEI Tecnai Osiris, respectively. The acceleration voltage was 10 kV for SEM and 200 kV for TEM. For SEM, powder samples were pressed onto double-sided carbon tape, while TEM samples were dispersed in ethanol via sonication and then added dropwise to a holey carbon-coated gold grid. In both cases multiple spots were examined to ensure sample uniformity.

X-ray Diffraction. XRD patterns were collected on a Rigaku SmartLab X-Ray diffractometer using a Cu $K\alpha$ source with a beam energy of 8.04 eV ($\lambda = 1.5406\text{\AA}$). Powder samples were measured on glass slides and data analysis was performed using PDXL-2 Rigaku software.

Fourier Transform Infrared Spectroscopy (FTIR-ATR). Powder samples were measured using a Thermo Nicolet 6700 FTIR with a diamond ATR attachment and KBr beam splitter. Transmission measurements were conducted at room temperature using a deuterated triglycine sulfate (DTGS) detector and data analysis was performed using the Origin software package. Plots shown are the average of 64 scans collected over the range of 500-4000 cm^{-1} . An additional 8 scans were acquired as background before loading each sample. The noise region around 1900-2300 cm^{-1} is caused by the instrumental defects.

X-ray Photoelectron Spectroscopy. The XPS spectra were collected using a monochromatic 1486.7 eV Al $K\alpha$ X-ray source on PHI VersaProbe II X-ray Photoelectron Spectrometer with a 0.47 eV system resolution. The energy scale has been calibrated using Cu $2p_{3/2}$ (932.67 eV) and Au $4f_{7/2}$ (84.00 eV) peaks on a clean copper plate and a clean gold foil, respectively. Powder samples were pressed onto a double-sided scotch tape on a substrate. For region scan, high power (100u100W20kV_HP), 23.500 eV Pass Energy and 0.1000 eV step size were used, and each spectrum was swept for 10 times to improve the accuracy. Data analysis was performed with a software package in MultiPak and CasaXPS. Atomic concentrations were calculated as suggested by the following equation

$$AC_1(\%) = \frac{A_1/R.S.F}{A_1/R.S.F \dots + A_n/R.S.F} \quad (1)$$

where AC stands for atomic concentration, R.S.F is relative structural factor, n is the total number of different categorized atoms. Cu $2p_{3/2}$ associated peaks were chosen for peak integrations.

X-ray Fluorescence. XRF data was collected by Rigaku ZSX Primus II XRF machine. The Wavelength Dispersive X-ray Fluorescence (WDXRF) spectrometer adopts Rh $K\alpha$ source with a beam energy of 20.2161 keV, corresponding to an X-ray wavelength of 0.6147 \AA .

Proton-Nuclear Magnetic Resonance Spectroscopy (1H-NMR). $^1\text{H-NMR}$ spectra were measured on Varian Mercury-300 (300 MHz) spectrometers at ambient temperature. Chemical shifts are reported in parts per million (ppm or δ) and are referenced to the solvent (δ 7.26 for CHCl_3). Quantitative analysis was performed with Mnova software package by integrating the peak areas of interests.

Thermogravimetric Analysis. Thermogravimetric analysis was conducted by TGA in air atmosphere, TA Instruments Q50. The flow rate of air was 100 ml/min. 5-15 mg of sample was loaded into an alumina crucible and heated in the instrument to 40 $^\circ\text{C}$ for 1 hour. After 1 hour, the samples were heated at 10 $^\circ\text{C}/\text{min}$ to 600 $^\circ\text{C}$ and left to equilibrate for 1 hour before being allowed to cool to room temperature. Data analysis such as peak integration was conducted using Igor's multipack feature.

Brunau-Emmet-Teller (BET)- N_2 Physisorption. Surface area measurements were performed using a Quantachrome autosorb. Adsorption-Desorption isotherms were constructed using an 11 point Brunauer, Emmett and Teller (BET) measurements protocol with N_2 as the adsorbate. Typically, 50-100 mg of sample was used and outgassed at 200 $^\circ\text{C}$ for 12-18 hours. Measurements of each sample were performed in triplicate and their average and standard

deviation calculated.

H₂-Temperature programmed reduction. H₂-TPR was performed on powder samples using a flow reactor set up. Mass flow controllers were used to control gas flow rates and k-type thermocouples were used to control temperature. For each sample, 20 mg was loaded into a straight tube quartz reactor with a rough silica bed and controllably heated from 100-400 °C at 10 °C/min. Over this period, gas was flowed over the sample at a rate of 100 ml/min; the composition of the feed gas was 10% H₂ and 90% Ar. The outlet gas composition was measured using an SRS RGA 100 Mass Spectrometer.

Contact Angle values**Table S1 Contact angle values**

Samples	Contact angles
Untreated	--
Toluene treated	134.29°± 0.12°
p-Xylene treated	146.49°± 0.09°
Hexane treated	30.52°± 6.01°
Methylcyclohexane treated	29.24°± 1.06°
Chlorobenzene treated	26.93°± 0.15°
Benzyl Alcohol treated	33.60°± 0.78°

Scanning Electron Microscopy

SEM images suggest no significant structural loss after functionalization process.

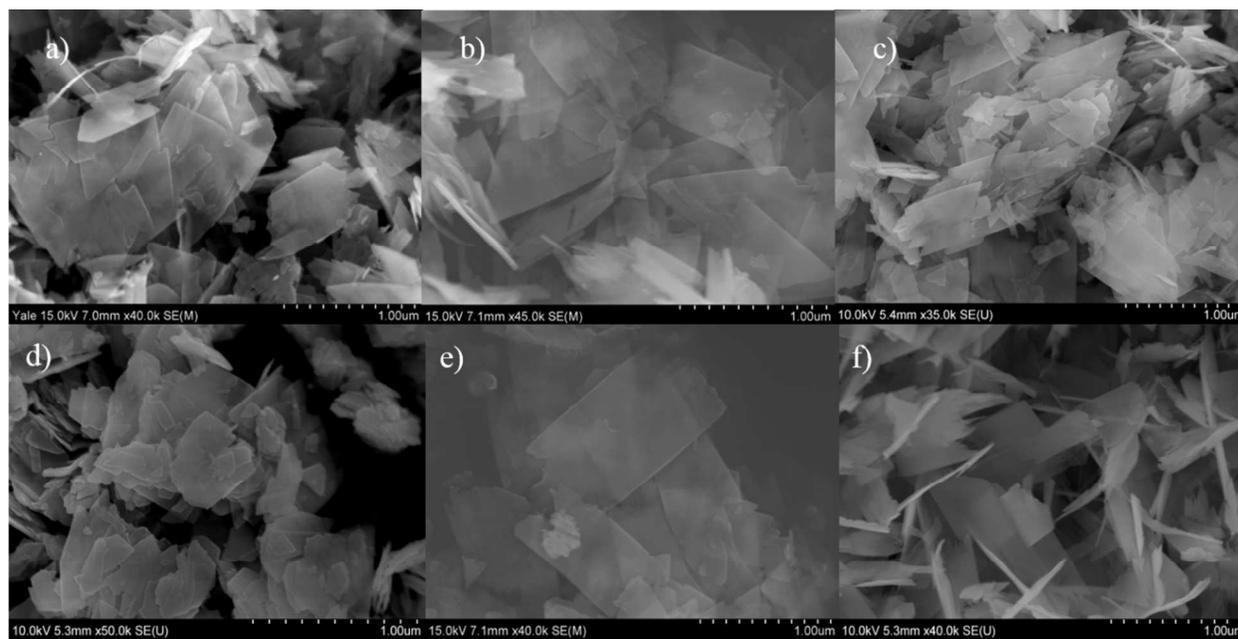


Figure S1 SEM images of a) untreated CuO nanosheets, b) Toluene treated, c) p-Xylene treated, d) hexane treated, e) methylcyclohexane treated, f) chlorobenzene treated.

BET Surface Area and Surface Coverage

Table S2 BET Surface Areas

Samples	BET surface areas/(m ² · g ⁻¹)
Untreated	19.96 ± 0.85
Toluene treated	24.56 ± 0.05
p-Xylene treated	22.83 ± 0.34
Hexane treated	22.29 ± 0.34
MCH treated	24.72 ± 0.90
CB treated	--

Surface Coverage calculations

$$\frac{M_f}{\sigma} = \tau \quad (2)$$

By employing this equation, we also make the assumption that the functional groups evenly coat the surface. Though we have no direct measure of this, this assumption can be made since the treatment process occurred over a long-time scale (24 hours) in a solution under reflux, which would evenly expose all parts of the sample to the treatment.

Values for surface area were obtained from BET N₂ Physisorption, as noted earlier. Since sample limitations prevented us from measuring the surface area of the chlorobenzene treated sample, we instead used the average surface area of all the treated samples for calculating the surface coverage of the chlorobenzene treated sample. This assumption of surface area can be made since we found no trend between treatment type and surface area except that all treatments increased the surface area relative to the untreated sample CuO nanosheets.

X-ray Diffraction Patterns

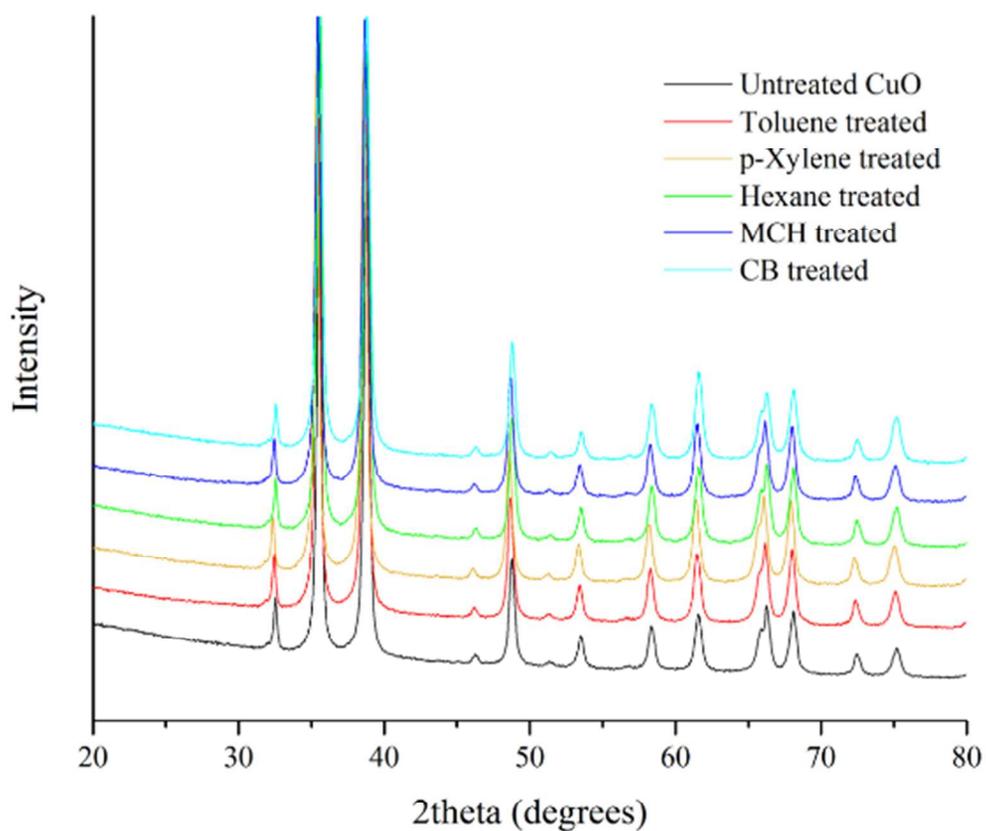


Figure S2 XRD patterns for all samples (PDF Card No.: 01-080-1268). XRD patterns reveal no change in the composition before and after functionalization processes.

X-ray Photoelectron Spectroscopy details

Survey data pointed to three major regions of interest: binding energy in the range of 925-970 eV, corresponding to Cu2p; 524-546 eV, corresponding to O1s; and 280-300 eV, corresponding to C1s. All spectra were aligned to the C1s peak, set to 284.8 eV, which is attributed to C-C hydrocarbon bonds; this peak, present in a multitude of materials, is associated with adventitious carbon physically adsorbed to the surface. The penetration depth of XPS is on the order of 10 nm. As noted previously, the thickness of an untreated CuO nanosheets is approximately 10-20 nm, and thus this technique is likely probing the composition of only one nanosheet.

X-ray Fluorescence

XRF analysis shows that copper ions exist in the solution after functionalization.

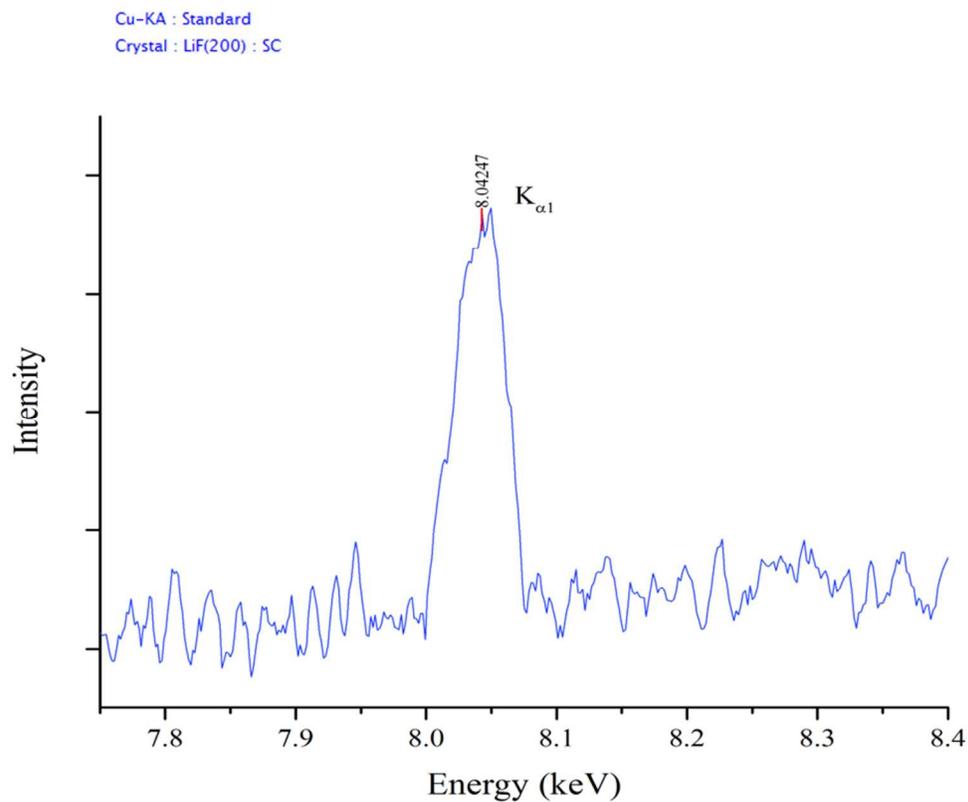


Figure S3 XRF spectrum of liquid phases after functionalization. Copper K_{α} line at 8.04 keV is detected indicating the presence of copper ion in the solution.

Calculated Gibbs free energies for oxidation reactions

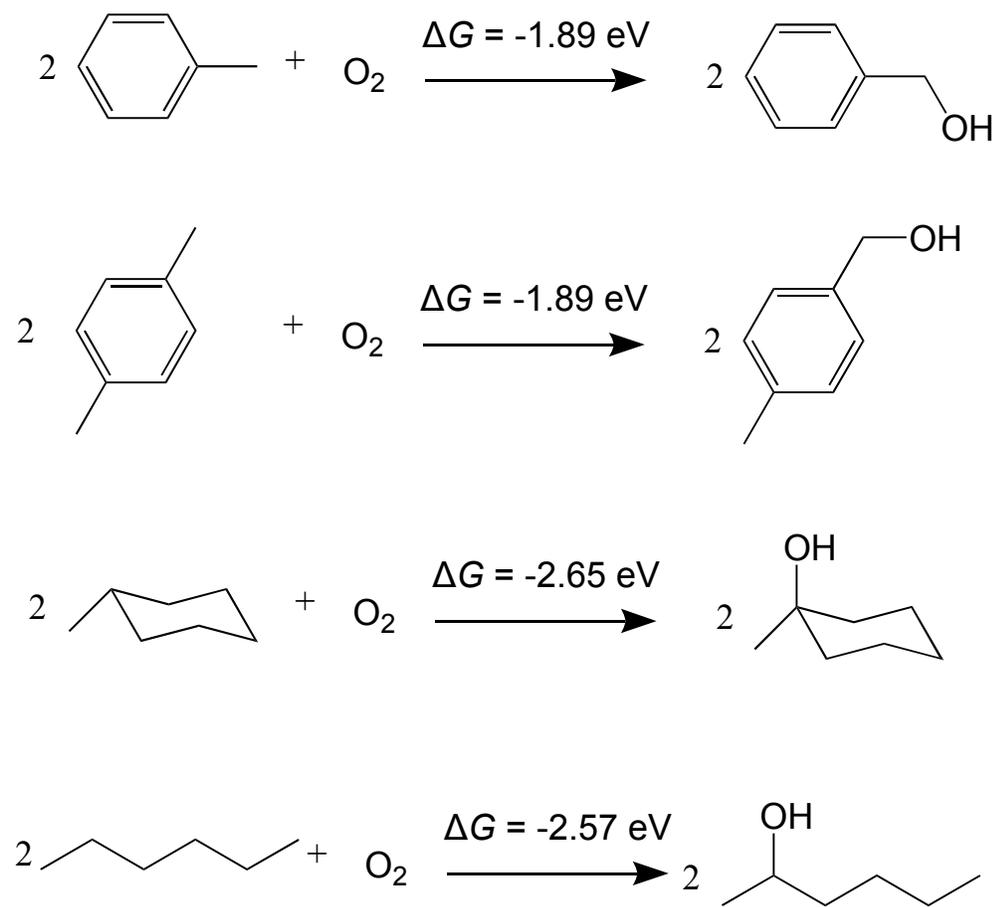


Figure S4 Calculated Gibbs free energies for oxidation reactions

Calculation model on α -methylbenzyl alcohol

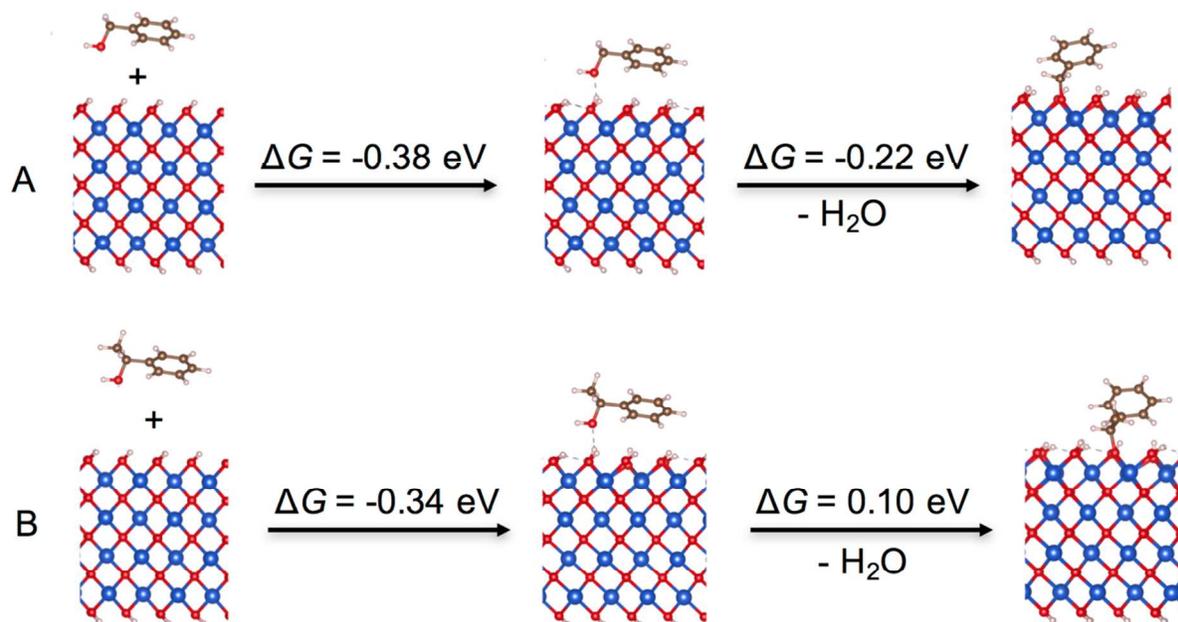


Figure S5 Hydrogen-bonding model vs dehydration calculations on A) benzyl alcohol; B) α -methylbenzyl alcohol. The binding energy of α -methylbenzyl alcohol through dehydration is positive due to the steric repulsion, consistent with our proposed mechanism in Figure 5.

Calculated binding free energies of hydrogen bonding complexes

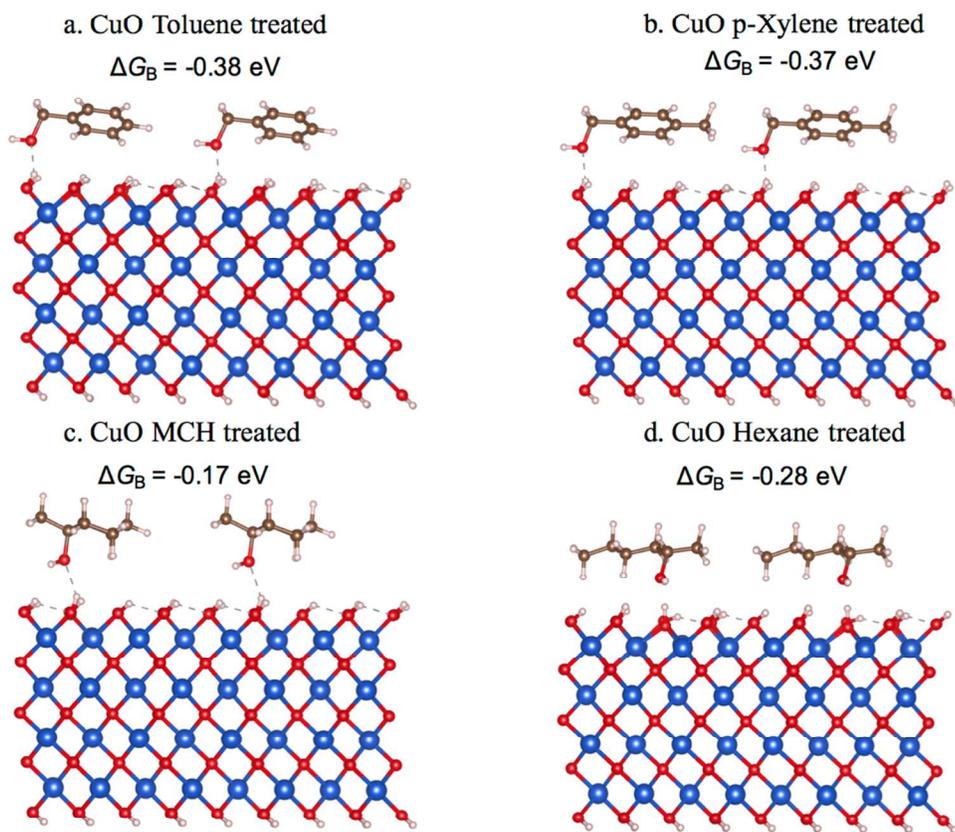


Figure S6 Structures and calculated binding free energies of hydrogen bonding complexes of a) toluene, b) MCH, c) hexane and d) p-Xylene treated CuO surfaces.

¹H-NMR calculation details

¹H-NMR spectra were measured on Varian Mercury-300 (300 MHz) spectrometers at ambient temperature. Chemical shifts are reported in parts per million (ppm or δ) and are referenced to the solvent (δ 7.26 for CHCl₃). Quantitative analysis was performed with Mnova software package by integrating the peak areas of interests.

In benzyl alcohol, the hydrogen atoms from the aromatic ring, the methylene and hydroxyl group give the chemical shifts at δ 7.38- 7.33, δ 4.75, and δ 2.55-2.20, respectively. Similarly, chemical shifts at δ 10.01 and δ 7.58-7.42 can be assigned to the hydrogen from the aldehyde group and benzene ring of benzaldehyde, respectively. For toluene, benzyl alcohol and benzaldehyde, the hydrogen atoms on the methyl group (δ 2.41 s), the methylene (δ 4.67 s) and the aldehyde group (δ 10.01 s), respectively, were chosen as the objects of study or standards.

The conversions can be calculated by the following equation

$$\text{conversion}(\%) = \frac{A_r}{A_s/n} \quad (1)$$

where A_r is the peak area of interest relative to the standard; A_s is the peak area of the standard; n refers to the number of hydrogen atoms associated with the standard. For simplicity, values for A_s were set equal to n, therefore giving rise to the correlation that

$$\text{conversion}(\%) = A_r \quad (2)$$

Note that this method only gives a rough estimate of product to reactant ratio; to be more accurate, internal standard substance should be applied. However, the accuracy is beyond the scope of our discussion here. This estimation is appropriate for a semi-quantitative calculation.

For toluene to benzyl alcohol, $\text{conversion}(\%) = \frac{0.01}{3.00} = 1\%$ (Note: a peak area that's smaller than 0.01 will also give 0.01 due to the resolution limit)

For benzyl alcohol to benzyl aldehyde, $\text{conversion}(\%) = \frac{0.06}{2.00} = 6\%$

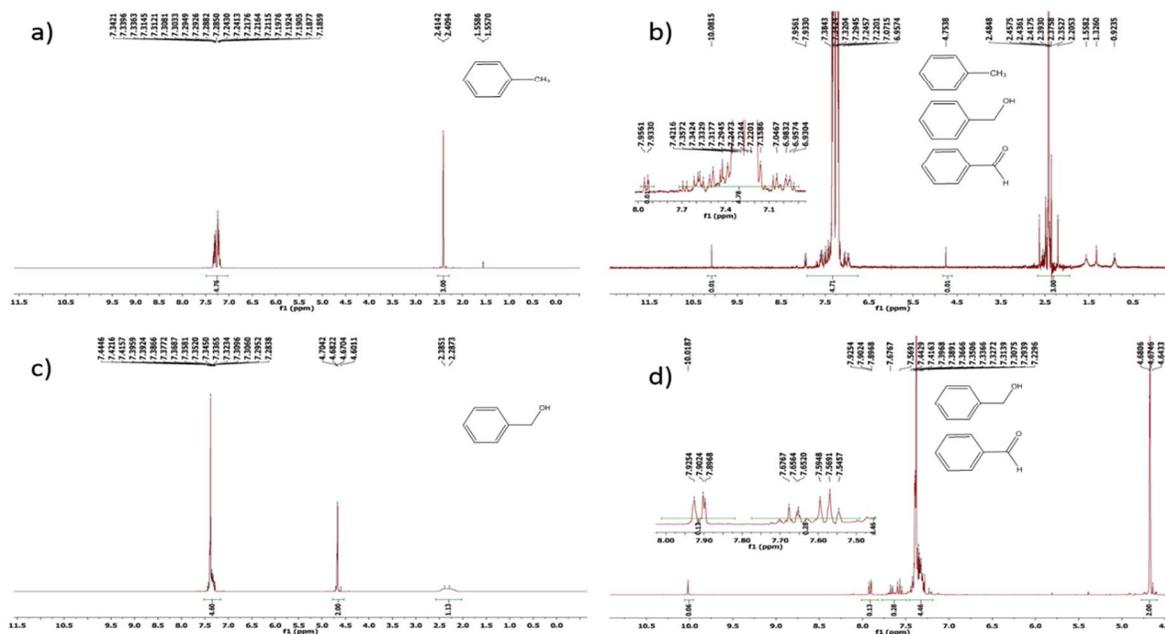
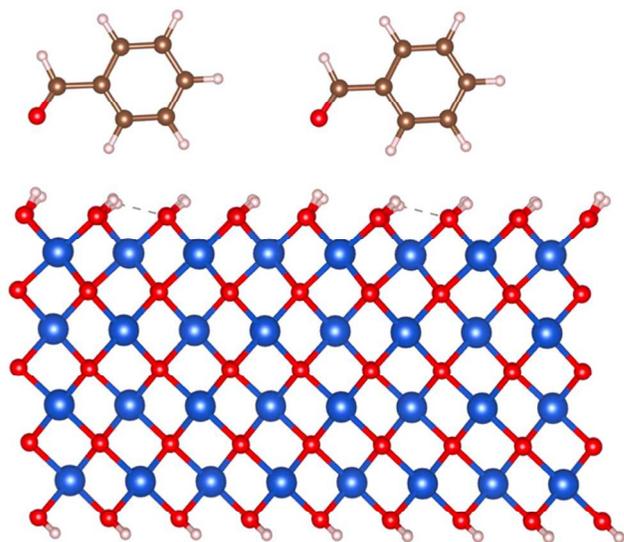


Figure S7 ¹H-NMR (300 MHz, referenced to CDCl₃) spectra of a) Toluene before treatment b) Toluene after treatment c) Benzyl alcohol before treatment d) Benzyl alcohol after treatment.

Calculated Benzyl aldehyde binding free energy



$$\Delta G_B = -0.17 \text{ eV}$$

Figure S8 Structures and calculated binding free energies of benzyl aldehyde on CuO (002) surface.

Thermogravimetric Analysis

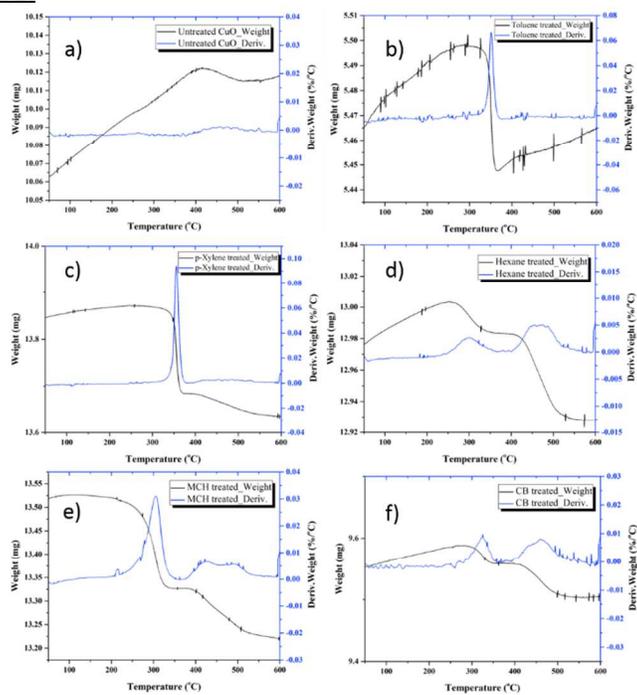


Figure S9 Thermogravimetric analysis of a) untreated CuO nanosheets, b) Toluene treated, c) p-Xylene treated, d) Hexane treated, e) Methylcyclohexane treated, f) Chlorobenzene treated. Color codes: Black-Weight, Blue-Deriv.Weight.

Temperature Programmed Reduction

Compared to the TGA experiments, which were conducted in an oxidative atmosphere (i.e. air), these TPR results were obtained in a reductive atmosphere (i.e. 10% H₂ in Ar). Therefore, these experiments probe the stability of the overall material, and not just the stability of the surface functional groups. Since this completely degrades the CuO materials, this process is simply used as an analytical technique, and not a preparative procedure.