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J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.7b11654 • Publication Date (Web): 03 Jan 2018

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Hydrophobic CuO Nanosheets Functionalized with Organic Adsorbates

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ABSTRACT: A new class of hydrophobic CuO nanosheets is introduced by functionalization of the cupric oxide surface with p-xylene, toluene, hexane, methylcyclohexane and chlorobenzene. The resulting nanosheets exhibit a wide range of contact angles from 146° (p-xylene) to 27° (chlorobenzene) due to significant changes in surface composition induced by functionalization, as revealed by XPS, ATR-FTIR spectroscopies and computational modeling. Aromatic adsorbates are stable even up to 250-350 °C since they covalently bind to the surface as alkoxides, upon reaction with the surface as shown by DFT calculations and FTIR and 1H-NMR spectroscopy. The resulting hydrophobicity correlates with H2 temperature programmed reduction [H2-TPR] stability, which therefore provides a practical gauge of hydrophobicity.

INTRODUCTION

Nanomaterials offer a versatile framework for engineering surfaces with specific functionalities,1-12 as required for applications with constraints on the chemical, mechanical, magnetic, electronic and optical properties of the materials. Traditionally properties of nanomaterial surfaces have been tuned by doping3-5 or by controlling the nanoparticle size,7, 10-11 shape,7, 10-11 dimension, and chirality1. Functionalization based on covalent binding of adsorbates to the material surface is becoming an increasingly popular strategy for tuning the properties of nanomaterials.4, 12 Compared to dopants that are often integrated into the lattice, functional groups are only chemically bonded to the surface. Nevertheless, they can dramatically affect the properties of the materials,4 particularly for nanosheets where a large fraction of the atoms are surface exposed. Here, we focus on functionalization of metal-oxide surfaces with hydrophobic adsorbates such as CuO nanosheets functionalized with p-xylene, toluene, hexane, methylcyclohexane and chlorobenzene.

Many studies have focused on functionalizing carbonaceous systems such as carbon nanotubes13-21 and graphenes2, 22-26 with oxygen, nitrogen, sulfur, boron, and other moieties to drastically change their properties. For instance, carbon nanotubes functionalized with sulfur groups showed increased mechanical strength due to denser packing.27 Functionalization of gold and silver nanoparticles typically involves thiol and amine groups.2-20-29 Nanowires have been functionalized with biologically relevant molecules for sensing or drug delivery.30 Surfactants and polymers have been employed as capping agents to enhance dispersibility and antimicrobial activity.31-32 Functionalization of metal oxides in particular is gaining increasing attention owing to their dynamic properties and extensive use in electronics,33 catalysis,34 and other applications. Silicon polymers have been explored to functionalize copper oxide and other metal oxides to increase hydrophobicity and photocatalytic activity.35-37 Superhydrophobic CuO is reported to be more corrosion resistant suggesting that reactions involving water may be controlled using functionalization.38 Though much has been done towards functionalizing metal oxides for superhydrophobicity, most of them involve the use of fluorinated compounds, which are highly toxic and environmentally hazardous.39 Still, large classes of molecules and materials remain unexplored, or poorly understood. Rigorous characterization and theoretical studies are needed to elucidate the nature of these surfaces and the binding modes of molecular adsorbates.

Reactions of small organic/aromatic molecules over inorganic materials have been studied for decades, including numerous reactions over copper oxide catalysts.40-43 Copper oxide is particularly attractive since it is a non-hazardous material composed of earth abundant
elements. For example, mesoporous CuMnCeO₃ with different CuO and MnOₓ doping contents were shown to catalyze chlorobenzene decomposition,⁴¹ while copper oxide on mesostructured silica was shown to dehydrogenate cyclohexane.⁴² Gaseous toluene was found to be oxidized over metal oxides, including copper oxide.⁴³ Most of these earlier reports focus on characterization of the reaction itself although in general they do not investigate how the reaction affects the catalytic surface as explored in our study.

Functionalization can be exploited to change the properties of the surfaces in a wide range of possibilities. We focus on hydrophobicity that can enhance stability under aqueous conditions. There is already a growing interest in inorganic hydrophobic materials such as copper oxide.⁴⁴-⁴⁷ Current technologies utilize coated or nanopatterned surfaces although they often involve environmentally hazardous materials, or economically demanding.⁴⁸ Copper oxides are attractive alternatives offering a valuable framework to investigate how changes in structure and composition affect hydrophobicity.⁴⁹ Except for a few studies which examined CuO functionalized with silicon polymers,⁵⁰ functionalization of CuO for hydrophobicity has remained unexplored.

We demonstrate that the hydrophobicity of copper oxide nanosheets may be tuned by functionalization the surface with small organic molecules such as toluene, p-xylene, hexane, methylcyclohexane, and chlorobenzene. We use an assortment of characterization tools and computations to show that these organic molecules become strongly bonded to the CuO surface as alkoxides without changing the nanostructure or crystal structure of the material. Experimental work is supported by DFT calculations exploring the binding process at the molecular level. Finally, we demonstrate the stability of these materials in both oxidative and reductive atmospheres.

**EXPERIMENTAL SECTION**

All chemicals used here were purchased from Sigma-Aldrich with purity ≥ 97%. Gases used were ultrahigh purity (UHP) grade purchased from AirGas.

**Functionalization of CuO nanosheets.** CuO nanosheets were synthesized via a soft templating method following the same protocols from our previous work.⁵¹ 200 mg of CuO nanosheets were dispersed in 100 mL organic solvents, including toluene, p-xylene, hexane, methylcyclohexane, or chlorobenzene depending on the treatment and refluxed for 24 hours. The solution was then filtered, and the precipitate was washed with additional solvent. After the filtration, samples were vacuum dried in a desiccator for two days and finely ground with mortar and pestle before further measurements.

Characterization details on contact angle measurement, scanning electron microscopy, transmission electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy-ATR, X-ray photoelectron spectroscopy, X-ray fluorescence, proton-nuclear magnetic resonance spectroscopy, thermogravimetric analysis, BET physisorption and H₂ temperature programmed reduction are given in the SI.

**Molecular Modelling.** DFT calculations with periodic boundary conditions were performed with the Vienna ab initio simulation package (VASP)⁵²-⁵⁵ version 5.4.1. The projector augmented plane wave (PAW) method⁵⁶-⁵⁷ together with the PBE exchange-correlation functional⁵⁸ were employed to describe the electron-ion interactions. The PBE + U method following Dudarev’s approach⁵⁹ was implemented to add on-site potentials to the d electrons of transition metals and properly describe the electronic states. Uₜot = U - J parameter of 7.5 eV was used to reproduce the experimental band gap of bulk metal oxides. A cutoff of 450 eV was chosen for the plane wave basis set and a 7 x 7 x 7 Monkhorst-Pack type k-point grid for bulk geometry optimization. A Gaussian smear was used with a σ = 0.1 eV. The energy convergence criterion was 10⁻⁵ eV per unit cell and the force convergence criterion was defined as 0.01 eV Å⁻¹ for geometry optimization. Supercells with dimensions of 9.38 Å x 6.86 Å x 25.26 Å with OH termination were used to model the CuO (002) surface that reproduce the experimentally observed band gap of CuO nanosheets. A 3 x 3 x 1 Monkhorst-Pack k-point mesh was used for all slab calculations. Dispersion interactions are important in the binding of small molecules to CuO surfaces, and they were treated with Grimme’s D3 version correction with Becke-Johnson damping function.⁶⁰-⁶¹ For small adsorbate molecules calculations, a supercell of 20 Å x 20 Å x 20 Å and a 1 x 1 x 1 Monkhorst-Pack k-point mesh was used. The reaction free energy changes were calculated as ΔG = ΔE + Δ(ZPE) − TΔS, where ΔE, Δ(ZPE) and ΔS are electronic energy, zero-point energy, and entropy difference between products and reactants. The zero-point energies of isolated and absorbed molecules were calculated from the frequency analysis performed by VASP. The entropies of isolated molecules were calculated with the PBE functional and the 6-31G(d) basis set,⁶² as implemented in Gaussian 09 software package (Revision E. 01).⁶³ Dispersion effects were again considered by Grimme’s D3 version with Becke-Johnson damping function. The entropies of absorbed species were calculated from the partition function by treating all degrees of freedom as vibrational. The quasiharmonic approximation, with vibrational frequencies lower than 60 cm⁻¹ raised to 60 cm⁻¹, was used in the calculation of partition functions to correct the well-known breakdown of the harmonic oscillator model for the entropy of low-frequency vibrational modes.⁶⁴ The visualization of structures were performed with VESTA software package version 3.⁶⁵

**RESULTS AND DISCUSSIONS**

**HYDROPHOBICITY.** Copper oxide nanosheets were synthesized and then functionalized by reflux in various solvents to increase their hydrophobicity. The solvents were selected to test the effects of different molecular structures. Hexane was selected for functionalization with a linear alkane, methylcyclohexane as a model cyclic hydrocarbon, toluene and p-xylene as aromatic rings, and chlorobenzene was selected to determine the influence of a
hydrophobic by drop testing in DI water (data not shown).  Bulk CuO was refluxed in toluene and found to be essential for functionalization. In addition, commercial contact angle for this sample, indicating that reflux is as a control, CuO nanosheets were immersed into toluene groups can limit the binding process. to bind to CuO nanosheets and how halo and alcohol ability to bind to CuO nanosheets and how halo and alcohol sections, we show how methylated benzene rings have the hydrophobicity of the resulting material. In subsequent hydrophobic effects were obtained with toluene and p-xylene treatments that increased the contact angle of the CuO nanosheets to 134° and 146°, respectively, Table S1. Surprisingly, functionalization with chlorobenzene increased the contact angle by only 27°, comparable to modest contact angles typically produced by functionalization with non-aromatic compounds (e.g., 29° for methylcyclohexane and 30° for hexane). Clearly, the chemical nature of the aromatic group plays an important role in determining the hydrophobicity of the resulting material. In subsequent sections, we show how methylated benzene rings have the ability to bind to CuO nanosheets and how halo and alcohol groups can limit the binding process.

As a control, CuO nanosheets were immersed into toluene without heating for 24 hours. We found no change in the contact angle for this sample, indicating that reflux is essential for functionalization. In addition, commercial bulk CuO was refluxed in toluene and found to be hydrophobic by drop testing in DI water (data not shown).

**Figure 1** Contact angle measurements of a) Untreated CuO nanosheets, b) Toluene treated (134°), c) p-Xylene treated (146°), d) Hexane treated (30°), e) Methylcyclohexane treated (29°), f) Chlorobenzene treated (27°).

**Figure 2** TEM images of a) Untreated CuO nanosheets, b) Toluene treated, c) p-Xylene treated, d) Hexane treated, e) Methylcyclohexane treated, f) Chlorobenzene treated. The red circles reveal the large defects.

NANO_STRUCTURE AND CRYSTAL_STRUCTURE. The hydrophobicity of a surface can increase with changes in nanostructure that increase the surface area and roughness. Jagged and sharp edges increase the hydrophobicity of hydrophobic materials as well as the hydrophilicity of hydrophilic surfaces. Our TEM and SEM analysis of treated and untreated CuO nanosheets, however, determined that our functionalization treatments did not alter the nanostructure (Figure 2 and S1). We found that for all of the surfaces investigated, the structure of the nanosheets was largely unperturbed. All materials, functionalized or not, were nanosheets ranging from 250-1000 nm in length and width. From AFM in previous work, we know that the nanosheets are 10-20 nm in thickness. Compared to the untreated sample, there are hardly any changes in the sharpness of the edges of the nanosheets. However, from visual inspection of the nanosheets, we see an increase in the number of large defects.

Surface area can change the contact angle observed for a material. However, increases in surface area would make a hydrophilic surface more hydrophilic and a hydrophobic surface more hydrophobic. In this work, we see a shift from hydrophilicity in the untreated sample—to the point where it absorbs water—towards more hydrophobicity in the treated samples. Additionally, there is no trend in surface area with hydrophobicity in the treated samples. Therefore, the changes in surface area cannot be solely responsible for the changes in contact angle.

Another factor that plays a critical role in hydrophobicity is the composition of the material. Cuprous oxide is well known for being hydrophobic, however its poor stability limits its utilization in many applications. XRD was performed to determine if the treatment converted any of the CuO materials into Cu$_2$O. Since CuO and Cu$_2$O have very distinct diffraction patterns, they are easily distinguishable in XRD. All samples, treated and untreated, were found to have diffraction patterns matching that of CuO (PDF Card No: 01-080-1268), Figure S2. No Cu$_2$O peaks were detected indicating that the crystallite and composition were that of CuO. The peak broadening found in all samples is consistent and expected due to nanosized crystallite domains. Calculations of the size of the
crystallite domains, based on Scherrer's equation, are consistent with the nanoscale observed in previous work. Based on this data, we conclude that the increases in hydrophobicity are not due to changes in nanostructure or bulk composition.

SURFACE CHEMISTRY. Having found no significant changes to the nanostructure or crystal structure, we turned our attention towards the surface composition. To determine how the functionalizing species bind to the surface, we first performed FTIR measurements (Figure 3). Though typically considered only a surface technique, the penetration depth of FTIR-ATR can range from 0.5-2.0 micrometers. Since the thickness of the CuO nanosheets is on the order of 10-20nm, this technique is likely probing tens to hundreds of nanosheets. Nevertheless, non-crystalline surface groups may still be detected using this technique.

The FTIR spectra of CuO nanosheets treated with hexane and methylecyclohexane are very similar. Both exhibit the characteristic CuO peaks as well as peaks in the 1100-1300 cm\(^{-1}\) range corresponding to C-O bonds, as for the C-O stretching of aromatic-treated samples. However, no peaks associated with aromatics are found, nor expected, since the precursors do not include aromatic functional groups. Differences also exist in the hydroxyl stretching regions at 3500 cm\(^{-1}\). While the peak intensity was drastically attenuated for toluene and p-xylene treated samples compared to the untreated CuO nanosheets, the hydroxyl region changed very little for MCH and hexane treated samples. In fact, as suggested by modeling analysis discussed in greater details in the following section, the C-O stretching peaks in these cases are more likely to be ascribed to the hydroxyl groups that formed in the carbon framework after being oxidized by the CuO nanosheets.

Turning our attention to the chlorobenzene treated CuO nanosheets, we find significantly fewer peaks in the FTIR spectrum compared to toluene or p-xylene treated nanosheets. The aromatic C=C stretching peaks were much more attenuated and many benzene structure related peaks have disappeared, including the benzene skeleton stretching at 1447 cm\(^{-1}\), unsaturated C-H stretching at 3067 cm\(^{-1}\), and C-H wagging peaks of aromatics at 704 cm\(^{-1}\) and 686 cm\(^{-1}\). Additionally, no C-Cl stretching signal (742 cm\(^{-1}\)) was detected after functionalization, indicating the abstraction of chlorine during the reaction, consistent with the earlier observation of chlorobenzene decomposition over mesostructured CuO catalysts. Though in that study chlorobenzene degradation occurs at a higher temperature (250°C), we find that CuO nanosheets are more reactive than their bulk counterparts. Therefore, we conclude that chlorobenzene has decomposed over the CuO nanosheets during reflux. This might indicate that the low contact angle observed for the chlorobenzene treated sample, compared to the toluene or p-xylene treated samples, is due to structural loss of the aromatic ring. Similar to the other samples, we find C-O stretching around 1250 cm\(^{-1}\), further indicative of oxidation of the functional groups.

XPS was performed to further probe and compare the surfaces of treated and untreated CuO nanosheets (Figure 4). Experimental details are given in the SI. All the spectra were similar at Cu2p, displaying the characteristic peaks at 933.4 eV, 941 and 943.5 eV, 953.5 eV, and 962 eV corresponding to Cu2p\(_{3/2}\), Cu2p\(_{3/2}\) satellite peaks, Cu2p\(_{1/2}\), and also Cu2p\(_{1/2}\) satellite peaks, respectively. No peaks
were found corresponding to Cu\textsuperscript{1+} or Cu\textsuperscript{0} in any of the samples. This suggests that the treatments do not reduce the nanosheets to cuprous oxide or copper metal, which is consistent with the XRD and FTIR data. One difference is that qualitatively all of these peaks are lower in intensity in the functionalized samples compared to the untreated sample. The implications of this will be discussed quantitatively after examining oxygen and carbon.

More information can be gained from the C1s region of the spectra. Here the intensities of the peak at 284.8 eV are different, chlorobenzene treated CuO nanosheets has the largest peak intensity followed by toluene and p-xylene treated samples, then by the hexane treated sample, the methylcyclohexane treated sample and finally by the untreated sample with the lowest peak intensity. Interestingly, we see differences in the peak at 288.5 eV, which is typically associated with O-C=O. Here, the methylcyclohexane treated sample has the largest peak, followed by the toluene, then by the p-xylene and untreated sample, then by the chlorobenzene and hexane samples, which appear to have no signal in this region.

Shifts in binding energy relate to changes in the intramolecular atomic bonds. A shift to higher binding energies suggests that these bonds are becoming stronger and shifts to lower binding energies suggests these bonds are weakening. In the case of the treated samples, it would appear that some of the oxygen atoms in the CuO structure are binding more strongly. Interestingly, we do not see these shifts at Cu2p or C1s. As mentioned above, the binding energy of carbon is calibrated and fixed at 284.8 eV. Therefore, small changes in chemical bonds within the material may not be apparent at C1s. Cu2p, however is not as fixed. Indeed, others have shown that even small changes in the oxidation state of copper can significantly alter the peaks intensity and position at Cu2p.\textsuperscript{60} This leads us to conclude that functional groups are likely binding through lattice oxygen atoms rather than copper atoms.

A quantitative analysis of these spectra lends to more insights into the surface binding of these species, Table 1. In the untreated CuO sample we calculate that there is 15.4% carbon relative to oxygen and copper by atom. For functionalized samples, we find that this number grows to 24.9% in the toluene treated sample, 30.7% in the p-xylene treated sample, 19.1% in the hexane treated sample, 20.7% in the methylcyclohexane treated sample, and 36.6% in the chlorobenzene treated sample. In general, there is some relation between hydrophobicity and carbon content; toluene and p-xylene contain 5-10% more carbon than the hexane and methylcyclohexane sample. The

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\textbf{Atomic Concentration} & \textbf{C\%} & \textbf{O\%} & \textbf{Cu\%} & \textbf{Cu:O} & \textbf{C:O} \\
\hline
Untreated CuO & 15.43 & 41.70 & 42.88 & 1.03:1 & 0.37:1 \\
\hline
Toluene & 24.87 & 39.82 & 35.31 & 0.89:1 & 0.62:1 \\
\hline
p-Xylene & 30.65 & 37.85 & 31.50 & 0.83:1 & 0.81:1 \\
\hline
Hexane & 19.11 & 44.78 & 36.11 & 0.81:1 & 0.43:1 \\
\hline
MCH & 20.66 & 40.95 & 38.40 & 0.94:1 & 0.51:1 \\
\hline
CB & 36.57 & 33.44 & 29.99 & 0.9:1 & 1.09:1 \\
\hline
\end{tabular}
\end{table}
exception to the rule, is chlorobenzene-treated copper oxide, which has the highest carbon percent and a hydrophobicity only on part with hexane and methylcyclohexane treated copper oxide. Also of note, is that no chlorine was detected in any of the samples, including the chlorobenzene treated CuO nanosheets. This is consistent with the FTIR spectra for chlorobenzene treated CuO nanosheets that showed no C-Cl signals. Based on all of this evidence, we must conclude that the chlorobenzene is being decomposed by the CuO nanosheets during the functionalization treatment. The difference in hydrophobicity, therefore, cannot simply be a function of carbon surface coverage, but must also be due to the arrangement of carbon on the surface. This further supports the conclusions drawn based on the FTIR data that the presence of aromatic rings greatly enhances hydrophobicity.

Since the percent of carbon in all treated samples changed relative to the untreated sample, the oxygen and copper percentages also by necessity have to change. In all cases the percentage of these atoms decreased relative to the untreated sample, however not by the same amount. In the untreated sample, the copper to oxygen ratio is 1.03:1; in the toluene treated sample the ratio is 0.89:1; in the p-xylene treated sample the ratio is 0.83:1; in the hexane treated sample the ratio is 0.81:1; in the methylcyclohexane treated sample the ratio is 0.94:1; and in the chlorobenzene treated sample the ratio is 0.9:1. This ratio does not follow a trend in the hydrophobicity, nor does it correlate to overall carbon coverage. However, what is consistent is that all treated samples have less copper than oxygen.

On the surface, this result is quite surprising. Previously, we just concluded that lattice oxygen is binding these functional groups, and that these hydrocarbons can be oxidized by them. If one would predict atoms to be lost, one might expect it would be oxygen atoms, perhaps assuming that a portion of the oxidized hydrocarbons dissociate from the surface, leaving a copper rich, cuprous environment. Yet we find the opposite is true; that is, we find more oxygen atoms than copper atoms.

In the past, we have reported other treatments that have increased the ratio of oxygen relative to copper. In this work, however, we believe the mechanism to be completely different. In aqueous environments, copper is known to leach into the solution forming copper ions. Here, although the treatments occur in organic solvents, we suspect a similar process may be at play. X-ray fluorescence was used to test this theory, Figure 3. After treatment, the solution was filtered and the filtrate was collected and drop-cast onto filter paper in order to measure the presence of copper in solution. We detected a signal at 2θ equal to 45°, corresponding to Cu Kα edge at 8.040 keV. This suggests that the Cu atoms are leaching into the solvent during the functionalization treatment, possibly related to a redox reaction occurring at the surface. That is, after the solvent is oxidized, the remaining copper atom becomes less stable since it is coordinated by fewer oxygen atoms causing it to leach into solution. We conducted EPR measurements of the toluene solution after treatment, but could not detect any Cu$^{2+}$ (data not shown) suggesting that if copper is leaching then it is likely in the 1+ or 0 oxidation state. From XRD we know that the crystal structure of the material is unchanged, so this leaching must only be occurring on the surface resulting in defects observed during TEM. Finally, we also conclude that this is the cause behind the sub-stoichiometric ratio of Cu to O in the treated CuO nanosheet samples observed during XPS.

Further information can be gained by taking the ratio between carbon to oxygen atoms. Here, we find that the ratio of carbon to oxygen atoms in the chlorobenzene treated sample is the greatest with a value of 1.09:1, followed by the p-xylene treated sample with a value of 0.81:1, the toluene treated sample with a value of 0.62:1, the methylcyclohexane treated sample with a value of 0.50:1, the hexane treated sample with a value of 0.43:1, and finally by the untreated sample with a value of 0.37:1. Compared to the Cu:O ratio, the C:O ratio is a much better indicator of the material's hydrophobicity. The p-xylene treated sample is more hydrophobic than the toluene sample and has a greater C:O ratio and both are greater than the hexane and methylcyclohexane treated samples, which is consistent with the trend in contact angle. Lower C:O ratio, such as in the case of hexane and methylcyclohexane treated samples, may be due to increased oxidation of the functional groups leading to increased potential for hydrogen bonding in solution and consequently a lower hydrophobicity and contact angle. The outlier here seems to be the chlorobenzene sample, with the highest C:O ratio and the lowest contact angle. This indicates that while the C:O ratio can be a useful tool in predicting the hydrophobicity, it is not sufficient. Other factors, such as the retention of the aromatic ring, is necessary to consider when tuning the hydrophobicity of the surface.

BINDING MECHANISM. Our FTIR spectra suggested the presence of C=O bonds in all treated samples, consistent with previous studies which show that CuO catalyzes the oxidation of toluene and cyclohexane to PhCH$_2$OH$^+$ and cyclohexanol$^{32}$, respectively. In addition, Kaliszewski and Heuer$^{71}$ studied the interaction between ethanol and hydrox zirconia powders by FTIR spectroscopy and provided evidence of ethoxide formation, attributed to dehydration of CH$_3$CH$_2$OH and surface Zr-OH groups. Based on our FTIR spectra and previous studies, we proposed a functionalization mechanism shown in Figure 5a. The reaction involves partial oxidation of organic molecules (R-H) to alcohols (R-OH). The alcohols then dehydrate with the surface hydroxyl groups of CuO to form surface-bound Cu-O-R, responsible for the hydrophobicity of functionalized CuO nanosheets. Our DFT calculations support the proposed mechanism and rationalize the observed water contact angles and FTIR spectra of various treated CuO samples.

We considered five organic molecules, namely, toluene, p-xylene, hexane, methylcyclohexane and chlorobenzene. CuO nanosheets were modelled with the hydroxyl-terminated CuO (002) surface to be consistent with
previous XRD and band gap measurements,\textsuperscript{51} as well as FTIR spectra in the current study. The oxidation of all five molecules by oxygen to form alcohols is found to be thermodynamically favorable, with negative reaction free energies (See Figure S4). Thus, the reaction between R-OH and the Cu-OH surface to form Cu-O-R and H₂O is the most relevant step and the corresponding binding free energy (\(\Delta G_B\)) determines whether the hydrophilic Cu-OH surface can be modified by the hydrophobic R groups to form hydrophobic Cu-O-R surface. For toluene and p-xylene, the proposed alcohol intermediates are PhCH₂OH and CH₂⁻Ph-CH₂OH, respectively. Our calculated binding \(\Delta G_B\) of PhCH₂OH and CH₂⁻Ph-CH₂OH on the CuO (002) surface are -0.61 and -0.59 eV, respectively. Therefore, PhCH₂OH and CH₂⁻Ph-CH₂OH spontaneously bind to CuO surfaces and make it hydrophobic. Based on bond dissociation energies of primary, secondary and tertiary C-H bonds,\textsuperscript{72} the most likely partially oxidized alcohol intermediates for methylcyclohexane and hexane would be 1-methylcyclohex-1-ol and 2-hexanol. Direct binding of 1-methylcyclohex-1-ol and 2-hexanol to CuO surfaces to form hydrophobic Cu-O-R groups is unlikely due to the large steric repulsions between alkyl groups near the C-O bond and CuO surfaces, as indicated by the large positive \(\Delta G_B\) of 1-methylcyclohex-1-ol and 2-hexanol, 0.44 and 0.59 eV, respectively. In addition, a secondary aromatic alcohol \(\alpha\)-methylbenzyl alcohol model was computed to test this hypothesis, and results showed that the dehydration of \(\alpha\)-methylbenzyl alcohol on CuO surface has a positive free energy change of 0.10 eV (Figure S5) due to the large steric repulsion, indicating that the steric factor plays an important role in determining the hydrophobicity. Instead of dehydration, the partially oxidized intermediates (1-methyl-cyclohex-1-ol and 2-hexanol) and CuO surfaces could form hydrogen-bonding complexes with a negative free energy change of -0.17 and -0.28 eV (See Figure S6 in SI), which may slightly modify the water contact angles compared to the untreated CuO nanosheets.

For chlorobenzene, there is no position with methyl, secondary and/or tertiary C-H bonds to be oxidized, thus the functionalization of CuO surfaces with chlorobenzene is likely to undergo a different pathway. FTIR analysis and previous studies have suggested that chlorobenzene is decomposed into non-aromatic compounds over CuO nanosheets, thus resulting in only a slight increase in the water contact angle, similar in the cases of MCH and hexane functionalization.

Our computational results suggest that the hydrophobicity of CuO nanosheets treated with toluene and p-xylene comes from the reaction of surface hydroxyl groups with R-OH intermediates (R = PhCH₂ for toluene and R = CH₂⁻Ph-CH₂ for p-xylene), which changes hydrophilic Cu-OH surface groups into hydrophobic Cu-O-R groups. During the functionalization process, CuO nanosheets first catalyze the oxidation of toluene and p-xylene to PhCH₂OH and CH₂⁻Ph-CH₂OH, respectively. The \textit{in situ}-generated PhCH₂OH and CH₂⁻Ph-CH₂OH then react with the surface Cu-OH groups and bind as alkoxydes Cu-O-R. Our results suggest that we can use aromatic structures with oxidizable groups, such as toluene and p-xylene, directly to modify the CuO surfaces to make it hydrophobic. The resulting functionalization should also be applicable to other metal oxides.

Since the proposed mechanism suggests that the dehydration between –OH and Cu-OH leads to the hydrophobicity, one might think that similar chemistry would occur with other alcohol precursors. CuO nanosheets were functionalized with benzyl alcohol to test this hypothesis, however the contact angle of this material was found to be only 33°. Note that the reaction was kept at the boiling temperature of toluene instead of that of benzyl alcohol because under reflux conditions, benzyl alcohol showed the capability of fully reducing the CuO nanosheets into Cu metals. We suspect that benzyl alcohol is oxidized further to benzyl aldehyde leading to unfavorable reactivity with the surface.

Our DFT calculations show that benzyl aldehyde does not favorably bind to the surface. To further understand the underlying chemistry, we performed proton-nuclear magnetic resonance spectroscopy. The liquid phases before and after functionalization in toluene and benzyl alcohol systems were collected and analyzed using \(^1\)H-NMR. After refluxing for 24 hours, both samples exhibited significant changes in compositions as revealed by NMR spectra, Figure S7. Toluene was found to be partially oxidized into benzyl alcohol and benzaldehyde at trace quantities, given by the presence of additional peaks associated with benzyl alcohol and benzaldehyde in NMR...
after functionalization. These results are consistent with our DFT proposed mechanism and earlier work suggesting that CuO was capable of oxidizing gaseous toluene into benzyl alcohol, benzaldehyde, benzoic acid and other molecules.46

The conversion of benzyl alcohol to benzaldehyde in the liquid phase was found to be 6%, which is significant compared to the toluene functionalization case where the conversion to benzyl alcohol is less than 1%. This suggests that when reacting with CuO nanosheets, benzyl alcohol is more reactive than toluene and therefore can be more easily oxidized into benzyl aldehyde. Based on that observation, along with our calculations showing that the Gibbs free energy change of benzyl aldehyde binding to CuO nanosheets surface is not as favorable as that of benzyl alcohol, we conclude benzyl alcohol is oxidized into benzyl aldehyde in the functionalization process and therefore does not favorably bind to the surface, resulting in the small contact angle change, Figure S8.

1H-NMR studies suggest that redox chemistry is occurring between the solvent and the CuO nanosheets during functionalization and that oxidation of the solvent is essential for functionalization. The result of these reactions is key for determining the binding strength of the functional group, the chemical composition of the functional group, and the hydrophobicity of the resulting material.

STABILITY AND SURFACE COVERAGE. Thermogravimetric analysis (TGA) was performed in air to test thermal stabilities of treated and untreated CuO nanosheets, Figure S9. Absolute weight loss and derivative weight loss percent is graphed as a function of temperature. Compared to the untreated sample, all functionalized samples were found to have significant weight loss. This weight loss occurred way above the boiling points of the functional groups’ corresponding solvent, evidencing the claim that functional groups in the treated samples are strongly bonded to the surface of the CuO nanosheets. That being said, there are significant differences between the TGA plots of the various treated samples, Table 2.

The p-xylene and toluene treated samples were found to be the most stable, showing no significant weight loss below 350 °C. Sharp peaks in the derivative weight loss percent can be seen at 356 °C and 350 °C for p-xylene and toluene treated samples, respectively. Importantly these are the only peaks found in these samples, indicating that a single species is decomposing or desorbing from the surface. The hexane, methylcyclohexane and chlorobenzene treated samples were found to be less stable, showing derivative peaks at 300 °C, 306 °C, and 325 °C, respectively. Unlike the toluene and p-xylene treated samples, these samples display broad peaks in their derivative plots. Additionally, these materials also show additional broad peaks over the range of 400-500 °C. This suggests that there are possibly multiple species on the surface and/or the decomposition of these species is a multi-step process. Qualitative inspection of the plots suggests that there is correlation between the shapes of these peaks and the hydrophobicity of the material. That is, the toluene and p-xylene treated samples have sharp single peaks with temperatures above that of the broad peaks of the hexane, methylcyclohexane, and chlorobenzene treated samples.

The untreated sample was found to have only a small, broad peak in the derivative plot spanning from 400-500 °C. It is difficult to conclude what this peak may be caused by. Though its position is similar to some of the other functionalized samples, its low intensity indicates that it is related to a separate process, such as oxygen exchange between the gas and solid phase.51 It is unlikely that any cuprous oxide is forming since the in air cupric oxide is more thermodynamically stable. A small baseline increase is found for all samples; this is an artifact of the instrument and is more pronounced when there is low absolute mass loss—as in the case of the untreated sample—or low sample loading, which was the case for the toluene treated sample due to sample constraints.

A quantitative analysis can be made by assuming that the mass loss in a sample is only a result of desorption of the functional groups. By doing so we can calculate the percent by mass of the functional groups for each sample, Table 2. The peaks in the derivative plots were integrated—and summed in cases where more than one peak was present—and we found that the functional groups mass percent ranged between 1-2% for all the treated sample. As a control, this calculation was also performed for the untreated sample; the mass loss calculated by this method for the untreated sample was found to be 0.34%, a factor of 3 less than any functionalized sample. The methylcyclohexane functionalized CuO nanosheets were found to have the greatest functional group mass percent with a value of 1.84%, the chlorobenzene treated sample had the second highest with a value of 1.65%, followed by the p-xylene treated sample with 1.38%, the hexane treated sample with 1.26%, and finally the toluene treated sample with a functional group mass percent of 1.08%.

### Table 2 Surface coverage calculated from BET and TGA

<table>
<thead>
<tr>
<th>Samples</th>
<th>Derivative Weight Peak location(°C)</th>
<th>Mass ratio (%)</th>
<th>Surface Coverage (mg/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated-</td>
<td>400-500</td>
<td>0.34</td>
<td>0.17</td>
</tr>
<tr>
<td>Toluene-</td>
<td>350</td>
<td>1.08</td>
<td>0.44</td>
</tr>
<tr>
<td>p-Xylene-</td>
<td>356</td>
<td>1.38</td>
<td>0.60</td>
</tr>
<tr>
<td>Hexane-</td>
<td>300</td>
<td>1.26</td>
<td>0.57</td>
</tr>
<tr>
<td>MCH-</td>
<td>306</td>
<td>1.84</td>
<td>0.74</td>
</tr>
<tr>
<td>CB-</td>
<td>325</td>
<td>1.65</td>
<td>0.70*</td>
</tr>
</tbody>
</table>

* The surface coverage of CB treated sample was calculated using the averaged surface areas of other samples due to the sample constraint.

Further information can be gained by combining these TGA weight loss results with BET surface area measurements discussed earlier. We can calculate the surface coverage of the functional groups on the treated samples using the equation below,
\[ \frac{M_f}{\sigma} = \tau \]  

(1)

where \( M_f \) is the mass fraction of the functional group compared to the overall sample (\( \frac{\text{g}_{\text{functional group}}}{\text{g}_{\text{total}}} \)), \( \sigma \) is the specific surface area of the sample (\( \text{m}^2/\text{g}_{\text{total}} \)), and \( \tau \) is the surface coverage (\( \text{g}_{\text{functional group}}/\text{m}^2 \)). More information on calculations can be found in the SI, page S6.

The values for surface coverage are reported in Table 2. Surprisingly, we find that the methylcyclohexane treated sample had the highest surface coverage with a value of 0.74 mg/m\(^2\), followed by the chlorobenzene, p-xylene, hexane, and toluene treated samples, with values of 0.70 mg/m\(^2\), 0.60 mg/m\(^2\), 0.57 mg/m\(^2\), and 0.44 mg/m\(^2\), respectively. For comparison, the untreated sample was calculated to have a surface coverage of 0.17 mg/m\(^2\), more than a factor of 2 less than any of the functionalized samples.

Most surprisingly, we find that contact angle is not correlated with a sample's functional group mass percent or its surface coverage. The toluene treated sample, which showed one of the highest contact angle, in fact showed the lowest surface coverage and functional group mass percent, and the hexane sample with a high functional group mass percent and the highest surface coverage showed only a small increase in contact angle compared to the untreated sample. This suggests that the surface chemistry plays a major factor in determining the hydrophobicity of the material. That is, surface aromatic groups lead to a higher hydrophobicity.

We performed \( \text{H}_2 \) Temperature Programmed Reduction (\( \text{H}_2 \)-TPR) to determine the stability of these materials (more information can be found in the SI, page S16). 20 mg of treated and untreated CuO nanosheets were heated in \( \text{H}_2 \) gas from 100 °C to 400 °C at 10 °C per min in a straight tube reactor. We used on-line mass spectrometry to monitor the outlet gas composition and observe \( \text{H}_2 \) consumption. Upon heating, CuO reacts with \( \text{H}_2 \) gas to form \( \text{H}_2\text{O} \) and Cu metal, as described by the following chemical equation,

\[ \text{CuO} (s) + \text{H}_2(g) \rightarrow \text{Cu} (s) + \text{H}_2\text{O} (g) \]  

(2)

In Figure 6, we find peaks for \( \text{H}_2 \) consumption located at different temperatures depending on the treatment. The untreated sample has the lowest peak \( \text{H}_2 \) consumption temperature at 235 °C. This is similar to previous work, though slightly lower, likely due to differences in sample loading (20 mg in this work versus 50 mg in previous work). A lower sample loading results in a lower signal to noise ratio, though was necessary for this work due to sample constraints.

Peak percent \( \text{H}_2 \) consumption peaks for the treated samples are located at 286 °C, 295 °C, 322 °C, 327 °C, and 286 °C for toluene treated, hexane treated, methylcyclohexane treated, Chlorobenzene treated. The peak location correlates with the hydrophobicity.
334 °C for the chlorobenzene, hexane, methylcyclohexane, toluene, and p-xylene treated samples, respectively. Therefore, the p-xylene treated CuO nanosheets are more stable than the toluene treated CuO nanosheets, which are more stable than the methylcyclohexane treated CuO nanosheets, followed by the hexane treated CuO nanosheets, then the chlorobenzene treated CuO nanosheets, and finally by the untreated CuO nanosheets. Interestingly, this trend seems to correlate very well with the trend in contact angles. That is, the more hydrophobic samples are more stable.

The location of H₂ TPR consumption peaks correlates with properties such as band gap that can be tuned with changes to the surface of the CuO nanosheets. Therefore, the trend we find with hydrophobicity is further evidence of property-property relationships likely linked to sensitive surface states in the CuO nanosheet system.

**CONCLUSION**

We have introduced hydrophobic CuO nanosheets by functionalization with hydrophobic organic molecules, such as toluene, p-xylene, hexane, methylcyclohexane and chlorobenzene. We found that these groups can increase the hydrophobicity of the nanosheets up to a contact angle of 146°. We showed that the functionalization treatments alter the properties of the surface without changing the nanostructure or crystal structure of CuO. Our experimental and computational tools determined that methylated aromatics (e.g. toluene and p-xylene) are first oxidized by CuO and then bind to the surface as alkoxides. Other chemicals, such as hexane and methylcyclohexane are oxidized as well, though their binding is weaker. We determined that the surface coverage of these species is not correlated with the hydrophobicity of the material; rather, aromatic groups on the CuO surface play a more significant role in introducing hydrophobicity. Through TGA and H₂-TPR we find these surface groups are stable up to 300°C. Hydrophobicity and H₂-TPR reactivity are correlated properties in this system. We determined that functional groups with methylated aromatic rings are ideal candidates for functionalizing CuO nanosheets. This strategy of small molecule functionalization has the potential to be applied to a wide range of metal oxides, for increasing their hydrophobicity and stability in various applications.

**REFERENCES**

Figure 1 Contact angle measurements of a) Untreated CuO nanosheets, b) Toluene treated (134°), c) p-Xylene treated (146°), d) Hexane treated (30°), e) Methylcyclohexane treated (29°), f) Chlorobenzene treated (27°).
Figure 2 TEM images of a) Untreated CuO nanosheets, b) Toluene treated, c) p-Xylene treated, d) Hexane treated, e) Methylcyclohexane treated, f) Chlorobenzene treated. The red circles reveal the large defects.
Figure 3  a) FTIR spectra of all samples in 2500~4000 cm⁻¹. b) Fingerprint region spectra from 650 to 1750 cm⁻¹. C-O bonds were observed in all functionalized samples indicating the oxidation of the organic adsorbates, c) Characteristic IR adsorption peaks for CuO at 610 and 480 cm⁻¹.
Figure 4 XPS regional spectra for all samples; a) C1s spectra; b) O1s spectra; c) Cu2p spectra; d) Color codes. All spectra were calibrated to C1s 284.8 eV. Compared to untreated CuO, all functionalized samples exhibited a higher C 1s peak, lower O1s and Cu2p peaks, indicating an increase in the carbon surface coverage.

332x295mm (96 x 96 DPI)
Figure 5  a) Proposed mechanism of surface functionalization of CuO treated by organic solvents. Structures and calculated binding free energies of b) toluene, c) p-Xylene, d) hexane and e) MCH treated CuO surfaces.
Figure 6 Temperature programmed reduction profile from top to bottom: Untreated CuO nanosheets, toluene treated, p-Xylene treated, hexane treated, methylcyclohexane treated, Chlorobenzene treated. The peak location correlates with the hydrophobicity.
TOC graphic

353x272mm (96 x 96 DPI)