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# Self-Catalyzed Sensitization of CuO Nanowires via a Solvent-free Click Reaction

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modification but also has demonstrated that surface Cu(I) can be obtained during the process and promote a surface-catalyzed click reaction without additional copper catalyst. Here, it is demonstrated that this surface-catalyzed chemistry can be performed on a surface of the CuO nanomaterial without a solvent, as a "dry click" reaction, as confirmed with spectroscopic and microscopic investigations with X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction, solid-state nuclear magnetic resonance, and scanning electron microscopy. Computational studies provided instructive information on the interaction between the surface prop-2-yonate and azide functional group to better understand the mechanism of this surface-catalyzed click reaction.

# INTRODUCTION

The two-step surface sensitization of metal and metal oxide materials has been demonstrated to be an efficient process allowing for selective attachment of a wide variety of target functionalities, including surface chromophores, with simultaneous preservation of intricate surface morphologies. Initially, both the first step, delivering a robust chemical "hook", such as an alkyne functionality, for example, to the surface, and the second step, that could conveniently use copper-catalyzed click chemistry<sup>1</sup> to deliver the desired surface functionality, were both performed in a liquid phase.<sup>2-6</sup> More recently, the first step was shown to be efficient and gentle toward metal oxide nanostructures, if performed by a gas-phase process.<sup>7-5</sup> Specifically, the alkyne functional group was delivered by gas-phase exposure of the target metal oxide nanomaterial to prop-2-ynoic acid (PA). Among the metal oxide materials, nanostructured copper oxides (NCOs) have found extensive use in a large variety of applications including sensing, catalysis, photoelectronics, and energy conversion. $^{10-12}$  Numerous NCO preparation methods have been developed and achieved tremendous success to devise a number of Cu<sub>x</sub>O nanostructures, including CuO nanowires grown via thermal oxidation, CuO/Cu<sub>2</sub>O nanoparticles fabricated by chemical vapor deposition (CVD), and  $Cu_2O$  nanocrystals synthesized via electrochemistry.<sup>11–13</sup> Surface sensitization of NCOs can expand this versatility even further, especially if the process can preserve the morphology of these often brittle nanostructures, which has significant impact on their applications.<sup>14–16</sup>

resulted in a successful morphology preserving chemical

Recently, it has been shown that Cu<sub>x</sub>O nanomaterials can be utilized as heterogeneous catalysts for alkyne-azide click cycloaddition,<sup>17-22</sup> in which possible reduction processes have been discussed to produce surface Cu(I) species desired for the catalytic cycloaddition process,<sup>23–25</sup> suggesting a possibility of designing surface functionalization schemes where the surface itself could serve as a catalyst. In this communication, we demonstrate that a convenient two-step sensitization of CuO nanostructures can be performed without any additional catalysts and without any solvents. The reaction scheme is performed by first exposing the CuO nanomaterial to gasphase PA, leading to the formation of surface carboxylate with an alkyne functionality and simultaneous reduction of Cu(II) to the necessary surface catalytic Cu(I) species. The second step of surface sensitization is demonstrated by gas-phase attachment of benzyl azide (BA) to this surface functionality in a solvent-free click reaction. The fact that no additional catalyst or solvent is needed allows for a detailed description of surface species formed in each step by spectroscopic methods and computational analysis.

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Scheme 1. Proposed Reactions of PA: Modification and Self-Catalyzed Cycloaddition on the CuO Surface<sup>a</sup>



<sup>*a*</sup>In the scheme, hydrogen atoms of aromatic structures are omitted for clarity.

Scheme 1 shows the protocol of this two-step functionalization process. Experimentally, carefully prepared CuO nanowires were exposed to the gas-phase PA under medium vacuum conditions following a simple pretreatment by preheating in vacuum to remove impurities weakly adsorbed on the surface. Our previous work on a variety of oxide materials<sup>9</sup> proposed that in the first step of gas-phase PA modification of CuO, a monodentate surface species shown in Scheme 1 is produced. This step produced fully morphologically preserved surfaces with reactive alkyne functional groups for further modification with azido-compounds by the click reaction, which was previously demonstrated on ZnO nanoparticles and Cu nanowires by reacting them with BA in a liquid phase.<sup>9</sup> In this work, to prove that this is indeed selfcatalyzed cycloaddition on the CuO surface, we compared the click reaction on the surface of two oxide materials, ZnO and CuO, with gas-phase BA, as a function of temperature, and then investigated the possible mechanisms of surface reactions spectroscopically and computationally.

#### EXPERIMENTAL SECTION

**Materials.** Unless otherwise specified, all the chemicals were of reagent grade or better and used as received without further purification. Copper foil (Alfa Aesar, 99.9%), PA (Acros organics, 99%), BA (Alfa Aesar, 94%), hydrochloric acid (Fisher, 37.3% certified ACS grade), sodium hydroxide (Fisher, 98%), Milli-Q water (first generation of Millipore), ethanol (Fisher, 299.8%), tetrahydrofuran (THF) (Fisher, distilled from Na/benzophenone), copper(I) acetate (Sigma-Aldrich, 97%), a horizontal tube furnace (Lindberg Blue M), and a homebuilt medium vacuum system were used. The ZnO nanoparticles were purchased from Acros Organics with a 99.99% purity and size distribution within 50-100 nm.

CuO Nanowire Preparation. The CuO nanowire samples were prepared using a two-step thermal oxidation of copper foil in air. The copper foil substrate was precleaned using an aqueous 1.0 M HCl solution for 1 min, followed by ultrasonic rinsing with ethanol and Milli-Q water for 2 min, respectively. The copper foil was then transferred to a solution made of 50 mg of sodium hydroxide and 25  $\mu$ L of ammonia dissolved in 10 mL of Milli-Q water for the 30 min pre-etching step. After rinsing with Milli-Q water and flow drying with nitrogen, the pre-etched copper foil was placed in a crucible boat and loaded into a quartz tube. The tube was placed in a furnace, which was heated and annealed at 500 °C in air under ambient pressure for 1 h. The color change from reddish to black during the growth process indicated the formation of CuO nanowires. Several sets of growth conditions have been tested including the concentration of sodium hydroxide in the preetching solution, annealing temperature, and annealing time. Confirmed by the scanning electron microscopy (SEM) investigation, the optimized growth condition was chosen as described.

**First-Step Modification with Gas-Phase PA.** The freshly prepared CuO nanowire sample was kept in the quartz tube, which was evacuated with a mechanical pump. A glass tube filled with

outgassed PA was connected to the other side of this quartz tube via a connector with a pressure gauge. Because the CuO nanowires were prepared by annealing at 500  $^{\circ}$ C, no additional preheating was performed. When the base pressure reached 0.3 Torr with the temperature of the tube below 55  $^{\circ}$ C, the valve to the pump was closed and the interior of the quartz tube was exposed to the gas-phase PA at a pressure of approximately 2 Torr, as confirmed by the pressure gauge.

**Second-Step Gas-Phase Click Reaction with BA.** After the first step of PA exposure, the valve to the pump was opened and the quartz tube was evacuated back to 0.3 Torr. Then, the valve was closed again and the sample connector was changed to the glass tube of outgassed BA, which was then dosed into the interior of the quartz tube at different reaction temperatures, standing for a 30 min gas-phase reaction before taking out the samples for further characterization.

Surface Characterization Techniques. X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) analyses were carried out on a K-Alpha+ XPS instrument from Thermo Scientific using Al K $\alpha$  radiation with a 35.3° takeoff angle. The pass energy used for the high-resolution spectra for each element was 58.5 eV over the range of 20 eV at 0.1 eV/step. Casa XPS (version 2.3.16) software was used for the data analysis. All peak positions and relative sensitivity factors were calibrated to the C 1s peak at 284.6 eV.

Scanning Electron Microscopy. SEM images were acquired on a Zeiss Auriga 60 scanning electron microscope in the W. M. Keck Electron Microscopy Facility at the University of Delaware. All the images were collected with a secondary electron (in-lens) detector using 3 kV as the accelerating voltage at a working distance of 4.0 mm.

*X-ray Diffraction*. X-ray diffraction (XRD) patterns were recorded on a Bruker D8-ADVANCE X-ray diffractometer operating in the reflection mode and equipped with Cu K $\alpha_1$  radiation isolated by the Vario monochromator at the X-ray tube. All the spectra were collected using The LynxEye position sensitive detector at a power level of 40 kV, 40 mA with an increase of 0.05° and a dwell time of 0.05 s.

Fourier Transform Infrared. Fourier transform infrared (FTIR) spectroscopy analyses were performed on a Nicolet Magna-IR 560 spectrometer with a liquid nitrogen-cooled MCT detector. The incident angle was  $60^{\circ}$  with respect to the incoming infrared beam. All the spectra were collected in the range 4000-650 cm<sup>-1</sup> with a resolution of 8 cm<sup>-1</sup> and 512 scans per spectrum.

Solid-State Nuclear Magnetic Resonance. The CuO nanowires were gently peeled off from the Cu foils and mixed with dry silica powder with an approximate ratio of 1:5 in weight. The well-dispersed CuO nanowires were then transferred into the zirconia rotor for the solid-state nuclear magnetic resonance (NMR) characterization.

Solid-state NMR measurements were recorded on a Bruker AVANCE III NMR spectrometer with 11.7 T wide bore using a 3.2 mm Bruker multinuclear HCN magic angle spinning (MAS) probe. All the <sup>13</sup>C cross-polarization (CP) MAS spectra were acquired under a Larmor frequency of 125.77 MHz at 25 °C. A Bruker MAS controller was used to control the MAS frequency to 14 kHz within  $\pm 3$  Hz and the 90° pulse length was set to 3.3  $\mu s$  for <sup>13</sup>C. A recycle delay of 3 s and a CP time of 2 ms were utilized to collect a sufficient number of scans for a reasonable signal-to-noise ratio. The solution

<sup>13</sup>C NMR spectrum of PA was obtained on a 400 MHz Bruker AVANCE III spectrometer.

**Computational Details.** The calculations for  $Cu_2O(111)$ structural optimization, the adsorption energy of PA, and the cycloaddition reaction with BA were carried out using the projector augmented wave method and density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP) code.<sup>26,27</sup> For the surface calculations, we constructed a five-atomiclayer  $Cu_2O(111)$  slab with 3 × 3 in-plane unit cells and a 15 Å thick vacuum layer. The top two layers of copper and oxygen atoms were allowed to relax until the force on each atom was less than 0.02 eV/Å, while the bottom three layers were fixed to simulate the underlying atomic layers in a bulk system. These settings are sufficient to investigate the bonding models of PA followed by the cycloaddition with BA on the optimized  $Cu_2O(111)$  surface. A cutoff energy of 400 eV for the plane-wave basis was employed with a 2  $\times$  2  $\times$  1 Monkhorst-Pack k-point mesh for integrations over the Brillouin zone. The transition states for the click 1,3-cycloaddition on a surface and in the gas phase were determined using the climbing-image nudged elastic band method<sup>28</sup> from VTST as implemented in the VASP code.<sup>29</sup> All the calculations include the Grimme D3 dispersion corrections.<sup>33</sup>

The adsorption energy was calculated using  $\Delta E_{ads} = E_{PA/slab} - [E_{slab} + E_{PA}]$ , where  $E_{PA/slab}$  is the total energy of the slab with adsorbate PA,  $E_{slab}$  is the total energy of the bare Cu<sub>2</sub>O(111) slab, and  $E_{PA}$  is the total energy of free gas-phase adsorbate PA. Thus, the more negative the  $E_{ads}$ , the stronger the adsorption it has to present a more stable bonding structure. The reaction energy ( $\Delta E_r$ ) was calculated using  $\Delta E_r = E_{FS} - [E_{IS} + E_{BA}]$ , where  $E_{IS}$ ,  $E_{FS}$ , and  $E_{TS}$  are the total energies of the initial state (IS), final state (FS), and reactant of free gas-phase BA. The details including selected bond lengths and angles of the obtained structures are listed in Table S1 in the Supporting Information section.

The gas-phase reaction of PA and benzylazide was also investigated by DFT calculations performed with the Gaussian 09 suite of programs<sup>30</sup> utilizing the B3LYP functional and 6-311+G(d,p) basis set<sup>31,32</sup> paired with Grimme D3 dispersion corrections and original damping function.<sup>33</sup> Transition states were determined using the synchronous transit-guided quasi-newton<sup>34,35</sup> method and confirmed by the presence of a single negative eigenvector (an imaginary frequency) in the corresponding frequency calculations. Once the transition state was determined, its nature was also confirmed by initiating a small displacement (approximately 0.05 Å) toward reactants or products and full convergence check.

The Amsterdam density functional (ADF) approach,<sup>36</sup> in which the relativistic effects for the electron states of heavy atoms such as copper atoms can be implemented, was used for the chemical shielding calculation. The relativistic effects were treated as allelectron zeroth-order regular approximation and the scalar approximation was utilized for the <sup>13</sup>C chemical shielding calculation. The revised Perdew–Burke–Ernzerhof functional and the Slater-type basis sets (TP2Z) were used for all atoms. The <sup>13</sup>C chemical shift of the optimized models was calculated using  $\delta = (\sigma^{\text{TMS}} - \sigma)/(1 - \sigma^{\text{TMS}}) \approx$  $(\sigma^{\text{TMS}} - \sigma)$ , where  $\sigma^{\text{TMS}}$  (184.2 ppm) is the calculated <sup>13</sup>C isotropic shielding constant of tetramethylsilane (Si(CH<sub>3</sub>)<sub>4</sub>). The geometry of tetramethylsilane was optimized based on a single crystal structure (the CDS code: TIVWOL) using the same computational procedure. The calculated chemical shift was then calibrated by the relative deviation between the simulated chemical shift of PA and the experimental result.

#### RESULTS AND DISCUSSION

**Confirmation of Morphology Preservation and Surface Cu(II) Reduction.** The two-step modification illustrated in Scheme 1 was characterized by SEM to confirm the morphology preservation. As shown in Figure 1A, the pristine CuO nanowires have a diameter of less than 20 nm and a very uniform distribution of the nanowires over the substrate. This morphology is fully preserved following the gas-phase reaction



Figure 1. (A) SEM images of the pristine CuO nanowires before surface modification. (B) SEM images of the CuO nanowires modified with gas-phase PA. (C) SEM images of CuO nanowires in (B) following the surface-catalyzed click reaction with gas-phase BA. (D) Summary of XRD investigations of CuO nanowires before (a) and after (b) PA modification, with specific peaks corresponding to Cu<sub>2</sub>O and CuO materials indicated.

with PA, confirmed by images in Figure 1B, which shows no aggregation or noticeable etching or dissolution of the CuO nanowires. This preservation of nanowires can be contrasted with the dramatical changes observed for the CuO nanowires exposed to the diluted solution of PA in THF (see Figure S1 in the Supporting Information section). In that case, the nanowires appear to be covered by an aggregated netlike structure, which is very likely to be the polymeric product of a reaction between CuO and PA in solution. Figure 1C presents the morphology preservation of copper nanowires following the gas-phase reaction with BA. XRD patterns were recorded for the CuO nanowires before and after the propiolic acid modification shown in Figure 1D. The diffraction lines for the typical CuO crystalline surface can be observed before modification (black line). It is interesting to note that pronounced features corresponding to Cu<sub>2</sub>O appeared after the gas-phase reaction of CuO nanowires with PA, as shown in Figure 1D (red line). Signals corresponding to  $Cu_2O(110)$ around 28° and (200) around 42° were clearly recorded, indicating that the surface Cu<sup>2+</sup> was partially reduced to Cu<sup>+</sup>. At the same time, the intensity of the characteristic pattern line of CuO(110) around 32° and (111) around 39° decreased. This observation is fully consistent with the previously reported XPS spectra suggesting that upon this modification step, the surface of CuO nanowires becomes predominantly composed of the Cu(I)-containing layer.

**Confirmation of Surface Cu(I) Self-Catalyzed Click Reaction.** Given that the same overall results can be reached by thermal attachment as by the copper-catalyzed click process, to confirm the success of self-catalyzed cycloaddition on CuO nanowires, spectroscopic analysis has been utilized to monitor the two-step reaction on the CuO surface, as compared with the ZnO surface (noncatalyzed addition) prepared via CVD in our previous work.<sup>8,9</sup> According to the XPS studies summarized in Figure 2A,B, no surface nitrogen (and thus no alkyne–azide addition) was observed for ZnO samples following the attempted cycloaddition procedure without additional copper catalyst at room temperature. Only after



**Figure 2.** (A) N 1s XPS investigation of CuO nanowires following gas-phase PA exposure and click reaction with BA. (B) N 1s XPS investigation of ZnO nanowires following gas-phase PA exposure and click reaction with BA. In (A) and (B), spectra (a) show pristine starting nanomaterials, (b) show the same materials modified by gas-phase PA, (c–e) show the same materials exposed to gas-phase benzylazide at 25, 50, and 100 °C, respectively, and spectra (f) show the result of a traditional liquid-phase Cu(I)-catalyzed click process. (C) FTIR spectra of CuO nanowires following gas-phase PA exposure and click reaction with BA. Computationally predicted spectra of (a) PA and (b) the same acid reacted with BA are compared with the experimental spectra of the pristine CuO nanomaterial (c), the same material reacted with gas-phase PA (d), and the result of full two-step gas-phase sensitization of CuO without additional catalysts or solvents (e). (D) Liquid-phase NMR spectrum of PA in D<sub>2</sub>O provided as a reference (a) and computationally predicted isotropic <sup>13</sup>C chemical shift of a bidentate surface intermediate (b) corresponding to the ZnO modification with PA (d) and a monodentate intermediate (c) corresponding to the CuO modified with PA (based on the Cu<sub>2</sub>O model) (e).

the Cu(I) catalyst was added into the liquid phase, was the reaction confirmed. The thermal uncatalyzed gas-phase reaction was confirmed on ZnO under these conditions only if the reaction temperature was increased to 100  $^{\circ}$ C.

However, for CuO, XPS shows the presence of nitrogen from the gas-phase BA reacted with surface alkyne functionality to form a triazole ring, according to Scheme 1 even at room temperature. Three different nitrogen peaks can be identified in Figure 2A, and this assignment is fully consistent with previous XPS work on the alkyne–azide click reaction of surfaces supported by computational predictions.<sup>9,37,38</sup> The apparent atomic ratio of N/Cu can be acquired from the peak areas of the XPS spectrum with the appropriate sensitivity factors, which is approximately 8.6% for the liquid-phase click reaction and 7.9% for the gas-phase click reaction. These numbers indicate that the surface densities of adsorbates are similar in both cases, which is also consistent with the high efficiency of the self-catalyzed gas-phase click reaction.

Furthermore, Figure 2C shows the infrared study of CuO nanowires following gas-phase PA exposure and click reaction with BA, in which the vibrational signal of  $-C \equiv C$  around 2100 cm<sup>-1</sup> can be observed after the gas-phase reaction with PA<sup>9,34</sup> and significantly reduced after the second step of the reaction with BA. At the same time, the vibrational signal of the phenyl ring around 3000 cm<sup>-1</sup> can be observed on the resulting CuO surface.<sup>34</sup> In this panel, Figure 2C, the assignment of the key observed vibrational features, alkyne and phenyl, is supported by computational predictions in spectra (a) and (b). The key vibrational signatures of the

carboxylate group overlap with the intense features of the CuO material. That is why, to further investigate the surface intermediates on CuO produced by a reaction with PA, Figure 2D compares the <sup>13</sup>C ss-NMR spectra of CuO nanowires, ZnO nanorods, and PA in D<sub>2</sub>O with the model spectra predicted by ADF calculations. According to this comparison, it is very clear that a downfield shift predicted for a monodentate carboxylate ligand on the CuO surface compared to the bidentate ligand on the ZnO surface is fully consistent with the experimental results. In addition, the two alkyne carbons on the ZnO surface, these carbons are clearly very different in <sup>13</sup>C chemical shift, again fully consistent with the experimental observation and with the reaction proposed in Scheme 1.

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**Computational Investigation.** The fact that the new process is catalyst- and solvent-free allows for a detailed computational analysis of the proposed reactions, specifically of the surface species formed following the reaction of PA with CuO. According to a comparison summarized in Figure 3,



Figure 3. Adsorption energy comparison of monodentate (left) and bidentate (right) species of PA stabilized on the simulated  $Cu_2O$  surface.

where the surface is mimicked by a Cu<sub>2</sub>O slab consistent with the experimental observations (see Computational Details section above), a possible monodentate species formed by PA on a simulated Cu<sub>2</sub>O (confirmed to be present by XRD and XPS) surface is stabilized by a surface significantly (more stable by approximately 337 meV) compared to a possible bidentate ligand. Given that the spectroscopic investigation presented above suggests that the monodentate ligand is indeed the one present on a surface, this structure (left structure in Figure 3) is the subject of further investigation. However, in order to uncover the catalytic potential of the surface, its chemistry is compared to the gas-phase (thermal, noncatalyzed) reaction of PA and benzylazide. It is expected that the carbon-carbon triple bond would behave similarly in a gas-phase (uncatalyzed) process and for the bidentate ligand, where the triple bond is located far away from the surface. This comparison is summarized in Figure 4.

One of the major challenges in understanding the reaction pathway for the click reaction catalyzed by a surface is determining the structure of the weakly interacting complex of benzylazide and PA (either free or chemisorbed on a surface). In the gas phase, there are a number of different possible arrangements close in energy for an azide and an alkyne to coordinate in a weakly bound state, and the presence of a surface makes the assessment even more difficult. In order to address this further, accurate calculations for the gas-phase reaction without the surface were performed using Gaussian 09 suite of programs utilizing the B3LYP functional and 6-



**Figure 4.** Comparison of the reaction pathway and transition states for the click reaction catalyzed by a  $Cu_2O$  surface with the catalyst-free reaction between BA and PA.

311+G(d,p) basis set paired with Grimme D3 dispersion corrections and original damping function, as described in the Computational Details section.

VASP calculations show that benzylazide weakly bound to the gas-phase PA is stabilized by 107 meV. Gaussian calculations predicted this stabilization to be 306 meV. The structure obtained with Gaussian calculations provided the geometry used for VASP optimization of the equivalent surface species. The full optimization of this weakly adsorbed molecule on a surface precovered with dissociated PA would require high coverage analysis of the species, which is beyond the scope of this work. The assumption is that saturating the surface monolayer with PA does not leave space for benzylazide to interact with the surface directly, consistent with the spectroscopic investigations above. It is expected that multiple weakly bound configurations would be very similar in energy; however, what is more important is to compare the structure and energy of the transition state for the click 1,3cycloaddition on a surface and in the gas phase. As shown in Figure 4, the transition state for this process is only 54 meV on a surface compared to 219 meV in the gas phase (with respect to unreacted benzylazide and a free or adsorbed PA). In other words, the click addition catalyzed by the surface has a very low barrier, while for the gas-phase process, it is calculated to be four times higher. Both barriers are relatively small; however, such a substantial difference is very important for comparing the catalytic and thermal processes that occur close to room temperature. Of course, the exact numbers may be somewhat different because the Gaussian investigation suggests that the transition state for the gas-phase process is even higher, 537 meV compared to the  $2\overline{19}$  meV obtained with VASP. Further research will be necessary to make the comparison more quantitative. Nevertheless, it is important to note that the reaction without the presence of the surface requires several times more energy compared to the surfacecatalyzed process. In addition to the differences in the transition-state energy, the surface process also stabilizes the final product by about 0.75 eV compared to the gas-phase result. Thus,  $\mathrm{Cu}_2\mathrm{O}$  surface catalysis shows both kinetic and thermodynamic driving forces.

The key geometric comparison of the points depicted in Figure 4 is provided in Table S1 in the Supporting Information section. It is interesting to note that the only substantive difference between the surface and gas-phase process is the length of the carbon-carbon triple bond of the transition state calculated on the surface. However, this small difference translates in a noticeable difference of the transition-state energy compared to that of the unreacted alkyne and aside entities, confirming the catalytic nature of the surface process. It appears that the length of the end C-H bond is not altered substantially during the formation of the surface intermediate despite its participation in the overall chemical process. Thus, further detailed investigations of the weakly bound and transition states for this surface catalytic processes would be necessary; however, the observed surface Cu<sub>2</sub>O arrangement seems to provide a perfect template for sequential binding of the monodentate prop-2-ynoate, carbon-carbon triple bond, and the end hydrogen, making the reactive species akin to the ones proposed for the liquid-phase copper-catalyzed click reaction available for cycloaddition with an azide, 39-41 a reaction that is overall very much thermodynamically favorable, according to the findings summarized in Figure 4.

# CONCLUSIONS

In this work, we have investigated a catalyst- and solvent-free surface sensitization process for CuO nanowires. We have demonstrated that the first step of the surface reaction, a gasphase dosing of PA, produced the "clickable" copper oxide surface with the morphology fully preserved. In this surface reaction, the  $-C \equiv C$  functionality was introduced onto the copper oxide surface through the carboxylic anchor. The same reaction step led to surface reduction of CuO to Cu(I)containing species. This surface arrangement was demonstrated to be a perfect template to interact with the prop-2yonate and accommodate the  $-C \equiv C$ -functionality and the end hydrogen atom and work as a surface catalyst that facilitates the click reaction when the azide is introduced. The gas-phase introduction of BA in the second step has been used to test the success of the surface sensitization. This work provides a new approach to catalyst- and solvent-free sensitization and also initiates further discussion of the solvent-free mechanism for the click process.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.0c02262.

Additional SEM images, computational structures, and structural parameters (PDF)

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#### Notes

The authors declare no competing financial interest.

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