Published in final edited form as:

Chem Mater. 2017 May 9; 29(9): 4063–4071. doi:10.1021/acs.chemmater.7b00747.

Chemical Protection of Material Morphology: Robust and Gentle Gas-Phase Surface Functionalization of ZnO with Propiolic Acid

Fei Gao[†], Soraya Aminane[‡], Shi Bai[†], and Andrew V. Teplyakov^{*,†}

[†]Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, United States

[‡]Université Pierre et Marie Curie, Paris Cedex 05 75005, France

Abstract

Chemical functionalization of ZnO surface with an alkyne functional group was successfully achieved by exposing ZnO nanopowder to gas-phase propiolic acid in vacuum, which left the alkyne group available for subsequent chemical modification via the azide–alkyne cycloaddition “click” reaction with benzyl azide. The highly selective formation of a bidentate carboxylate linkage and the reaction of benzyl azide were confirmed by solid-state nuclear magnetic resonance spectroscopy, Fourier-transform infrared spectroscopy, and X-ray photoelectron spectroscopy. Most importantly, scanning electron microscopy revealed that the surface morphology was perfectly preserved by this gas-phase modification, as opposed to the alternative protocols based on liquid phase processing. This simple and precise design can serve as a universal method for the modular functionalization of zinc oxide surface following the initial surface preparation and be further applied to thin films, nanostructures, and powders, where preserving surface morphology during chemical modification is especially important.

Graphical abstract

*Corresponding Author. andrewt@udel.edu. Phone: (302) 831-1969. Fax: (302) 831-6335.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b00747.

DFT description and models, additional IR and XPS investigations, full ref 29 (PDF)

The authors declare no competing financial interest.

1. INTRODUCTION

In the last decade, metal oxides have attracted increasing attention to benefit a number of applications including solid state lighting, hybrid organic–inorganic light-emitting diodes, and dye-sensitized solar cells.^{1,2} Among these materials, zinc oxide, with a wide band gap of 3.3 eV at room temperature and photoluminescence emission centered at ~287 nm,³ has commanded substantial interest, specifically targeting research on interfacing it with small molecules, dyes, or biomolecules,⁴ because the resulting organic–inorganic hybrids can be employed in devices such as solar cells and sensors.⁵ In fact, precise control and molecular-level understanding of the interface between ZnO and molecules have become fundamentally and technologically important challenges for a very wide range of possible future applications.

The most common approach to functionalize ZnO surface with small molecules usually utilizes wet chemistry reactions with functionalized carboxylic^{4,6–8} and phosphonic acids.^{8–12} Bishop et al. reported an approach to form stable, multidentate carboxylate linkages to a variety of metal oxide nanoparticles including ZnO, Fe₂O₃, TiO₂, and WO₃ while also enabling subsequent multistep chemistry via the Cu(I)-catalyzed “click” reaction.¹ Later, Cao et al. investigated ZnO nanorod films functionalized with carboxylic acid capped with an azide end group followed by copper-free “click” chemistry.⁴ More recently, Tudisco et al. obtained nanostructured ZnO fibers functionalized through the grafting of a bifunctional phosphonic linker with azide terminations, followed by the anchoring of a specific cavitand receptor having four alkyne groups via “click” reaction.¹² Although carboxylic and phosphonic acids do lead to the formation of stable linkages on ZnO surface, multiple species are always formed during the attachment process, which makes it difficult to apply further modification protocols to the resulting surfaces. More importantly, solution-based methods, despite sometimes being successful in applications to nanoparticles, alter the structures of thin films or nanostructured materials because ZnO is easily dissolved in a wide number of solvents and especially prone to dissolution in acids.^{13–15} This point is especially detrimental to chemical modification of delicate ZnO nanostructures that can be grown on a variety of substrates and possess a wide range of very attractive properties.^{16–18}

Despite recent advances in solution ZnO surface modification, even successful and carefully optimized conditions for processes utilizing wet chemistry methods are normally associated with some changes in material morphology caused by etching processes.¹⁹ Thus, an alternative method for surface modification must be developed that produces stable and robust surface linkages and at the same time does not dissolve (or influences the structure of) ZnO features. Hence, the necessity to develop a well-controlled interfacial strategy on ZnO surface is highly desired. Here we report a simple and precise method to achieve stable bidentate carboxylate linkage to ZnO surface, which has an azide group available for further modification that can be tested, for example, by “click” chemistry, as summarized in Figure 1. This alkyne–azide click reaction has been successfully explored under ultrahigh vacuum condition, where the azide is stable upon adsorption, yet maintains sufficient reactivity.²⁰

There are a number of advantages of the gas-phase modification as opposed to the solution-based chemistry. First, the preparation of the ZnO surface can be controlled much better compared to the solution methods since vacuum annealing and exposure to additional coreagents can provide a better set of conditions for a reaction with a selected adsorbate. Second, as will be shown below, the chemistry of the adsorbate can be controlled to deliver a perfectly preserved functional group to the surface and at the same time the adsorbate created can be anchored to the surface in a highly selective manner. Finally, the functional group delivered by this gas-phase exposure can be further modified either by subsequent exposures to a desired reagent in a gas phase or by wet-chemistry modification procedures, as the ZnO surface modified in the first step becomes structurally stable with respect to both of these approaches.

In this paper, to confirm the reaction of gas phase carboxylic acid with ZnO surface followed by azide–alkyne cycloaddition “click” reaction and to establish the structures of surface species produced, each step of modification was characterized by scanning electron microscopy (SEM), solid-state nuclear magnetic resonance spectroscopy (SSNMR), Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). Density functional theory (DFT) calculations were performed to propose a plausible mechanism of surface reaction and to produce a set of appropriate spectroscopic observables including vibrational spectra and core-level energies to compare with the results of experimental studies.

The successful functionalization of the ZnO surface by exposure to gas-phase propiolic acid apparently stabilizes the oxide surface so that further modification, for example, by “click” chemistry can be performed either in liquid phase or, again, by a gas-phase exposure to a probe azide. This universal method opens up new possibilities for working with a multitude of different modification schemes following the initial surface preparation and for developing new chemistries for ZnO-based nanomaterials and nanostructures.

2. EXPERIMENTAL SECTION

2.1. Materials

All ZnO powder samples (99.99% purity, Acros organics) were prepared as described previously^{21,22} and used as substrates for all other experiments and characterizations. All chemicals were reagent grade or as indicated: argon (Keen Compressed Gas, research purity), propiolic acid (Acros organics, 98%), benzyl azide (Alfa Aesar, 94%), tetrahydrofuran (THF) (Fisher, distilled from Na/benzophenone), copper(I) acetate (Sigma-Aldrich, 97%), methanol (Fisher, 99.8%), and acetonitrile (Fisher, 99.9%). The deionized water used to rinse the surfaces and containers was from a first-generation Milli-Q water system (Millipore) with 18 MΩ cm resistivity.

2.2. Experimental Details

2.2.1. Preparation of Propiolic Acid-Modified ZnO Surface—The ZnO samples in this study were prepared by pressing about 20 mg of ZnO powder on the tungsten mesh and then mounting it on a sample holder between two tantalum clamps that allowed for resistive

heating of the sample, as described in detail previously.²² To remove the adsorbed impurities, the ZnO sample was transferred into a high-vacuum chamber with a base pressure about 1×10^{-6} Torr and annealed to 850 K for 15 min. After it was cooled down to room temperature, the sample was exposed to propiolic acid at 1 Torr for 5 min. The propiolic acid-modified sample was kept in high-vacuum chamber under 1×10^{-6} Torr for at least 16 h to pump away nonchemically bound propiolic acid.

2.2.2. Click Reaction in Gas Phase—After gas phase benzyl azide was dosed into the system at 1 Torr, the propiolic acid-modified ZnO sample was exposed to the benzyl azide at 100 °C for 45 min to thermally activate the in situ copper-free click reaction.^{4,23} Following this procedure, the remaining reagent was pumped away.

2.2.3. Click Reaction in Liquid Phase—A propiolic acid-modified ZnO sample was removed from the high vacuum chamber, taken off the tungsten mesh, and transferred into a 25 mL round-bottom flask filled with 1.1 mg of copper(I) acetate, 0.2 mL of benzyl azide, and about 5 mL of THF.^{1,24} The mixture was then stirred gently for 24 h at 40 °C under Ar atmosphere. Upon reaction completion, the ZnO sample was rinsed gently with acetonitrile in water (v/v 1:1), methanol, and THF several times before characterization.¹

2.3. Characterization Techniques

2.3.1. Transmission Fourier Transform Infrared Spectroscopy (FTIR)—FTIR spectra in the range of 4000–650 cm^{-1} were collected in a high-vacuum chamber with a base pressure under 1×10^{-6} Torr interfaced with a Nicolet Magna 560 spectrometer with liquid nitrogen-cooled external MCT-detector.^{21,22} The entire optical path was purged by water- and CO_2 -free air. All spectra were collected with a resolution of 4.0 cm^{-1} and 512 scans per spectrum.

2.3.2. X-ray Photoelectron Spectroscopy (XPS)—XPS studies were performed on a K-Alpha+ XPS System from Thermo Scientific using Al Ka X-ray source ($h\nu = 1486.6$ eV) at a 35.3° takeoff angle with respect to the analyzer. The high-resolution spectra for spectral regions corresponding to Zn 2p, C 1s, O 1s, Cu 2p, and N 1s were collected over the range of 20 at 0.1 eV/step with the pass energy of 58.7 eV. The survey spectra were collected over the energy range of 0–1000 eV. CasaXPS (version 2.3.16) software was utilized to analyze all the raw data. The C 1s peak was set to 284.6 eV to calibrate all peak positions.^{25–28}

2.3.3. Nuclear Magnetic Resonance Spectroscopy (NMR)—All solid-state NMR measurements were carried out on a 11.7 T wide-bore Bruker Avance III solid-state NMR spectrometer, operating at a Larmor frequency of 500.13 MHz for ^1H and 125.77 MHz for ^{13}C . A 3.2 mm Bruker multinuclear HCN magic angle spinning (MAS) probe was used. The CP/MAS data were acquired at 25 °C with an MAS frequency of 14 kHz, controlled to within ± 3 Hz using the Bruker MAS controller. The typical 90° pulse length was 2.85 μs for ^1H and 3.3 μs for ^{13}C . For a typical measurement, a sufficient number of scans was collected for ^{13}C CP/MAS NMR spectra with a recycle delay of 3 s and a cross-polarization time of 2 ms until a spectrum with a reasonable signal-to-noise ratio was obtained. ^1H SPINAL-64 heteronuclear decoupling with field strength of approximately 100 kHz was

applied during the acquisition period. The solution ^{13}C NMR spectrum was obtained on a 400 MHz Bruker Avance III instrument.

2.3.4. Scanning Electron Microscopy (SEM)—The SEM images of the ZnO sample were collected on a Zeiss Auriga 60 scanning electron microscope in the W. M. Keck Electron Microscopy Facility at the University of Delaware. An accelerating voltage of 3 kV was used, and images were collected with a secondary electron (in-lens) detector at a working distance of 3.0 mm.

2.3.5. Density Functional Theory (DFT) Calculations—DFT calculations were carried out using Gaussian 09 software²⁹ with B3LYP functional^{30,31} and LANL2DZ^{32,33} basis set. To simulate the most common surface of ZnO powder, a $\text{Zn}_{20}\text{O}_{20}$ cluster model based on mixed-terminated $\text{ZnO}(1\bar{0}10)$ surface was used as a substrate.^{22,34} This representation described the surface that corresponds to approximately 80% of the ZnO surface in the nanopowder^{35,36} and is the key in chemical description of ZnO material interaction with carboxylic acids, as described in detail previously.^{37,38} The two bottom layers of atoms in the $\text{Zn}_{20}\text{O}_{20}$ cluster model are “frozen” at their bulk position to prevent unrealistic distortion of the model structures. Computational details and all the models used in this publication are provided in the Supporting Information (Table S1).

3. RESULTS AND DISCUSSION

3.1. Morphology Change of ZnO Surface during Propiolic Acid Treatment and Following “Click” Reaction

In addressing any treatment approaches for solid state materials in powder or nanostructure form, it is always important to understand the effects of these treatments on the morphology of the material studied. Given that ZnO can easily dissolve in acidic solutions,^{13–15} and acidic surface modifiers including thiol, carboxyl, and phosphonate linkers have been observed to alter the surface chemistry and to etch the zinc oxide surface,¹⁵ it is critical to confirm that gas-phase exposure of this material to propiolic acid does not influence the surface morphology. A set of studies exploring this statement is presented in Figure 2, where the morphology of ZnO powder following various treatments is investigated by SEM to uncover any potential “etching” by a carboxylic acid. Following the exposure of pristine ZnO powder (shown in Figure 2a) to the gas phase treatment with propiolic acid at 1 Torr for 8 min, the structure of the material is fully preserved, as shown in Figure 2b. However, if the treatment is performed by the propiolic acid in liquid phase, the structure of the nanopowder is largely destroyed, as demonstrated in Figure 2e, meaning that further surface modification based on the surface shown in Figure 2e would definitely lead to a different morphology compared to the pristine surface. Most importantly, if the first step is the gas-phase exposure of ZnO nanopowder to propiolic acid (where the morphology is preserved), further chemical reactions, such as either gas-phase thermal “click” with benzyl azide (shown in Figure 2c) or the copper-catalyzed “click” process in the liquid phase (Figure 2d), do not appear to affect the morphology of ZnO material at all. Thus, the propiolic acid-functionalized ZnO surface formed in the first step is sufficiently stable to withstand the annealing and solution-based processing. In other words, such gas-phase modification of ZnO provides an alternative

pathway to modify the ZnO surface with a carboxylic acid at a high degree of control over the morphology, without any noticeable impact on the surface structure, offering a solution for the common challenge posed by acidic modifiers for ZnO functionalization.

3.2. Confirmation of Carboxylate Linkage to ZnO Surface by Infrared Investigation

Although structural integrity of the ZnO material studied is confirmed by SEM, to be practical, the modification schemes proposed must be verified spectroscopically. The initial assessment of the successful surface modification can be made based on in situ infrared investigations. Figure 3 summarizes the spectral region of 1000–3800 cm^{-1} for gas phase propiolic acid (Figure 3a), propiolic acid-functionalized ZnO surface (Figure 3c), along with DFT predicted vibrations of a single propiolic acid molecule chemisorbed on the model cluster representing ZnO surface (Figure 3b) provided for comparison. The chemical reaction between the gas-phase propiolic acid and ZnO can be confirmed by the disappearance of the hydroxyl group absorption at around 3600 cm^{-1} following the room-temperature exposure of ZnO powder to the gas-phase propiolic acid, as would be expected, since the most common reaction pathway would be the dissociation of the carboxylic group to form a carboxylate and a surface-bound hydrogen,¹⁵ with vibrational signature substantially different from the unreacted $-\text{COOH}$.^{37,38} At the same time, the produced adsorbate clearly exhibits the characteristic absorption features of the $\text{C}\equiv\text{C}$ stretching vibration around 2100 cm^{-1} and an obvious feature just above 3250 cm^{-1} corresponding to the $\text{C}-\text{H}$ stretching of the alkyne group. The spectrum in Figure 3c was recorded following extensive (16 h) pumping in vacuum to remove all the nonchemically adsorbed propiolic acid. Shortened pumping time leads to multiple species physisorbed on the ZnO surface including molecular propiolic acid, as observed by infrared spectroscopy in Figure S1 (shown in Supporting Information). The removal of physisorbed species by additional pumping will be further elaborated by SSNMR and discussed later to demonstrate that only one type of zinc carboxylate species is formed on a surface during gas-phase reaction with propiolic acid. The chemisorbed propiolic acid also exhibits a strong absorption peak at 1608 cm^{-1} and weaker split peaks centered at 1375 cm^{-1} , consistent with the asymmetric and symmetric stretches of a zinc carboxylate species.^{1,5,7,39,40} It also shows a relatively weak broad absorption feature around 1710 to 1685 cm^{-1} likely associated with the differences in $\text{O}-\text{C}-\text{O}$ vibrations in multiple structurally similar surface species present.^{1,41–43} The nature of the chemisorbed product is also confirmed by comparing the experimentally recorded infrared spectrum to that predicted computationally for a model proposed surface species shown in Figure 3b. On the basis of this comparison, the predicted spectrum is consistent with the experimental results for the signatures of $\text{C}\equiv\text{C}$, $\text{C}\equiv\text{C}-\text{H}$. A noticeable shift in the vibrations corresponding to the carboxylate linkage can be explained by the simplicity of the computational model used, as the realistic structures will be affected by their neighbors and by the likely interactions with available surface hydroxyl groups, affecting the vibrational frequencies of both species. Overall, this set of infrared studies confirms the $-\text{COOH}$ dissociation and the presence of $\text{C}\equiv\text{C}$, $\text{C}\equiv\text{C}-\text{H}$, and zinc carboxylate containing chemical groups following the reaction of gas phase propiolic acid with ZnO surface, forming a bidentate carboxylate linkage to ZnO.

3.3. Confirmation of “Click” Reaction on Modified ZnO Surface by IR and XPS

To explore the possibility of performing multistep functionalization of the ZnO surfaces based on the initial chemisorption of a functionalized carboxylic acid, the propiolic acid-modified ZnO was exposed to gas-phase benzyl azide at elevated temperature to thermally activate copper-free click chemistry.^{4,23} Reaction with benzyl azide is expected to provide a phenyl group as an indicator of chemical modification for IR and XPS analysis. The spectral region of 1000–3800 cm^{-1} for gas phase benzyl azide (Figure 4a) and benzyl azide “clicked” propiolic acid-functionalized ZnO surface (Figure 4c) is presented in Figure 4. When benzyl azide is introduced into the reaction chamber, strong signatures of azide group and phenyl ring at 2110 and 3050 cm^{-1} , respectively, are clearly recorded for the gas-phase benzyl azide (Figure 4a). On the basis of the DFT prediction for a product of thermal “click” chemistry between the model ZnO cluster and benzyl azide (Figure 4b), the signature of this chemical modification should be very different from the gas-phase species. The spectrum recorded following this thermal “click” resulting from the gas-phase exposure of benzyl azide is shown in Figure 4c using propiolic acid-modified surface as a background. If this spectrum is compared with the spectrum of the propiolic acid-modified surface (spectrum Figure 4d) replotted from Figure 3, it is clear that this signature is a combination of the absorption features corresponding to the benzyl azide reaction and the decrease in intensity of the selected features corresponding to chemisorbed propiolic acid. Specifically, the decreased intensity of the 3250 cm^{-1} feature corresponds to the loss of the alkyne functionality. The decrease in intensity of several features corresponding to the very specific vibrations of the surface-bound carboxylate/ $\text{C}\equiv\text{C}$ such as the decreased intensity of the peaks at 1608 and 1375 cm^{-1} also suggests that the triple bond participates in a reaction with benzyl azide. At the same time, several key vibrations associated with the formation of a triazole ring and a successful “click” reaction are recorded to appear within the fingerprint vibrational region.^{44–46} The small peaks above 3000 cm^{-1} and around 1130 cm^{-1} corresponding to aromatic C–H are observed as the evidence of phenyl ring attachment. Two strong peaks at 1403 and 1228 cm^{-1} are the signature of C–N in the triazole ring as suggested by the DFT-predicted spectra. Thus, the infrared study of copper-free click reaction indicates the presence of phenyl groups and triazole linkage following the copper-free click reaction of benzyl azide with propiolic acid-modified ZnO surface. One question that is more difficult to address based solely on the infrared spectra is if some of the benzyl azide may directly react with the ZnO surface, forming a nitrene-type species and possibly displacing surface carboxylates. This question can be addressed using XPS. This technique could also help us in identifying the difference in gas-phase and liquid-phase modification processes following the initial gas-phase exposure of ZnO to propiolic acid.

The spectra of C 1s region of propiolic acid-functionalized ZnO surface and the surface following the “click” reaction with benzyl azide are presented in Figure 5. This figure also compares the results of the copper-free gas-phase “click” reaction and the copper-catalyzed azide–alkyne cycloaddition (CuAAC) reaction conducted using liquid phase benzyl azide with the propiolic acid functionalized ZnO surface.^{1,24} As shown in Figure 5, for all three samples, three peaks at 284.6, 286.3, and 288.6 eV are fit and assigned to C–C bonds, C–O/C–N bonds, and C=O bonds. It needs to be noted that the peak at 286.3 eV, associated with C–O/C–N bonds on propiolic acid functionalized ZnO surface, increases after copper-

free “click” reaction with gas phase benzyl azide and increases in intensity even more following CuAAC reaction with liquid phase benzyl azide, as a result of benzyl azide interacting with the propiolic acid-functionalized ZnO surface forming the triazole ring. This observation is also consistent with the expectation that CuAAC reaction is substantially faster than thermal attachment.⁴⁷ However, the most important observation is the peak at 292.1 eV, which corresponds to the $\pi-\pi^*$ shakeup in aromatic functional groups, confirming the presence of the aromatic entities on the modified surface following the “click” reaction with benzyl azide. Since this peak is not observed for propiolic acid functionalized ZnO surface, there is only one possible source of aromaticity in this sample: the presence of the phenyl ring from benzyl azide.

Another spectral region that should be very informative is the one corresponding to N 1s. Figure 6 shows the N 1s spectral region of propiolic acid-functionalized ZnO surface and benzyl azide “clicked” ZnO surface by two different methods, respectively, along with the DFT-predicted N 1s core level energies shown as solid bars for the models indicated in the figure. The N 1s experimental spectrum shown for the propiolic acid-functionalized ZnO surface in Figure 6a exhibits no feature of nitrogen containing species, as would be expected. In Figure 6b, following copper-free “click” reaction with gas phase benzyl azide, propiolic acid functionalized ZnO surface shows a strong and broad peak centered at 401 eV, which is discerned into three peaks attributed to the triazole ring.^{45,46,48} Furthermore, the experimental results match consistently the computational prediction of N 1s core level for the triazole model structure shown in Figure 6. Another comparison is given by the N 1s experimental spectra of propiolic acid functionalized ZnO surface “clicked” with benzyl azide through CuAAC reaction, as shown in Figure 6c. Although the features appear to be shifted slightly toward lower binding energy region, this spectrum shows a very similar strong and broad feature, fit with three peaks for the triazole ring as well.⁴⁶ According to the DFT calculation, the two possible isomers resulted from copper-free “click” reaction, as opposed to catalyzed liquid-phase process, would result in species differentiated by 0.8–0.9 eV in XPS spectra, which may explain the observed peak shift and the small differences in peak shape resulted from CuAAC reaction, which only leads to a single triazole-ring isomer produced.^{24,47} It is also worth pointing out that the results of gas-phase thermal “click” in Figure 6b and liquid phase copper catalyzed “click” attachment in Figure 6c exhibit low intensity broad shoulders in addition to the main features. Given the high reactivity of benzyl azide, a number of additional investigations summarized in Figure 6 were performed to evaluate the direct reaction of this compound with ZnO surface. On the basis of the DFT prediction of proposed models shown in Figure 6, the shoulders observed in Figure 6b and c are possible results of the direct attachment of a nitrene entity inserted into ZnO bond following the loss of N₂ by an azide molecule and other reactions occurring on surface defect sites. Other possible attachments appear to correspond to much higher binding energies than what is observed experimentally. To test this hypothesis, a control experiment for benzyl azide adsorbed directly on a ZnO surface is presented in Figure 6d. It shows a broad low intensity feature above 400 eV, likely corresponding to surface-bound nitrene species according to the comparison with the DFT models in Figure 6. The shape and intensity of the observed feature suggest that it is not the major species in the reaction of benzyl azide with the ZnO surface modified with propiolic acid. The XPS spectra of Cu 2p,

O 1s, and Zn 2p regions are provided in Figures S2–S4 of the Supporting Information. It should be noted that the copper catalyst was removed following the CuAAC “click” reaction, as shown in Figure S2 and also confirmed by SEM/EDX measurements.

Thus, the XPS results confirm that both CuAAC and copper-free “click” reactions are successfully performed on the propiolic acid-functionalized ZnO surface and the results of both “click” approaches appear to be essentially the same.

3.4. Multistep Functionalization of the ZnO Surfaces Followed by NMR

Although the IR and XPS confirmed the modification of ZnO with gas-phase propiolic acid and also confirmed that the resulting surface can be further functionalized by “click” chemistry, they did not answer the question of why the liquid phase reaction with propiolic acid is so different from gas-phase exposure and also whether there is any difference between the anchoring of propiolic acid onto ZnO in liquid and gas phase attachment. NMR spectroscopy will help us address these questions.

Figure 7 displays the ^{13}C solid-state NMR spectra for gas phase propiolic acid-functionalized ZnO surface (Figure 7a), ZnO powder reacted with liquid phase propiolic acid (Figure 7b), and gas-phase benzyl azide “clicked” propiolic acid-functionalized ZnO surface (Figure 7c). To better interpret the results, solution ^{13}C NMR spectrum of propiolic acid in D_2O (Figure 7d) is shown for comparison. Despite the anisotropic broadening effect, these studies clearly show the signature of alkyne group at 79 ppm for the propiolic acid-functionalized ZnO surface (Figure 7a), fully consistent with that of propiolic acid in solution (77.5 and 73.9 ppm for alkyne carbons; Figure 7d). A sharp peak is recorded at 161 ppm (Figure 7a), corresponding to zinc bidentate carboxylate linkage.⁴⁹ These observations support the success of propiolic acid modification of the ZnO surface. When the ZnO powder is directly exposed to the liquid phase propiolic acid (Figure 7b), two additional peaks are observed at 165 and 169 ppm. These two peaks can be attributed to zinc monodentate carboxylate linkage and the physisorbed propiolic acid molecule;⁵⁰ the peak at 169 ppm is noticeably sharper, likely indicating that the mobility of this physisorbed propiolic acid is much higher than that of the species corresponding to the features of 161 and 165 ppm. This set of studies is extremely important in that it uncovers the main differences in liquid phase versus gas phase modification of ZnO. The gas phase modification offers a much better control of the surface, when the ZnO powder (and by extension many thin films or nanostructures) can be annealed in vacuum prior to exposure to propiolic acid. Thus, a single type of anchoring, the carboxylate formation, is dominant. However, if the ZnO modification is performed in ambient conditions or in a solution, the presence of surface hydroxyl groups and the possibility to form a physisorbed layer of propiolic acid prevent one from preparing well-defined surface with a single type of functionality. Thus, further modification processes are applied not only to the target carboxylate groups on a ZnO surface, but also to other functionalities and possibly surface defects, leading to the formation of a much less well-defined mixture of surface species.

What about the “click” chemistry confirmation by NMR? After being “clicked” with benzyl azide, the propiolic acid-functionalized ZnO surface (Figure 7c) shows the characteristic peaks of phenyl group and triazole ring at 128 and 135 ppm, clearly showing that the “click”

reaction occurred.⁵¹ It must be pointed out that the alkyne carbons at 79 ppm and zinc bidentate carboxylate linkage at 161 ppm do not completely disappear following the click reaction. The former is likely caused by the relatively low efficiency of copper-free “click” reaction and a low apparent yield of gas phase “click” chemistry.²⁰ The latter confirms that the bidentate structure is preserved on the surface following the click reaction. Thus, the ¹³C NMR spectroscopy studies strongly confirm the reaction of propiolic acid with ZnO surface forming a single type of a bidentate carboxylate linkage on ZnO, and the occurrence of the following “click” reaction with benzyl azide.

Thus, the solid state NMR study reinforces the conclusions reached in SEM, FTIR, and XPS investigations. The SEM study suggests that the ZnO surface morphology is preserved during the gas-phase surface modification process with propiolic acid and all the reactions following this initial functionalization. The FTIR study proves the formation of zinc carboxylate linkage capped with an alkyne group which enables the following “click” reaction. The XPS study indicates the formation of a triazole ring as a result of successful azide–alkyne cycloaddition with the propiolic acid-functionalized ZnO surface. Finally, the solid state NMR study provides a strong signature for each surface modification step.

4. CONCLUSIONS

A simple and precise method to modify the zinc oxide surface with gas-phase propiolic acid in vacuum at room temperature is described. The SSNMR, FTIR, and XPS results prove the formation of a stable bidentate carboxylate linkage to ZnO surface, and the alkyne group on the surface enables subsequent azide–alkyne cycloaddition “click” reaction with benzyl azide. This approach avoids the utilization of carboxylic acid solutions, preserving the surface morphology for further modification protocols, as confirmed by detailed microscopy investigations. This design can serve as a universal method for the modular functionalization of zinc oxide surface following the initial surface preparation. Since this gas phase interfacial engineering strategy allows for preserving surface structure and morphology of the modified surface from the “etching” effect of acidic modifier, it is an important method for surface modification of ZnO thin films, nanostructures, and nanopowders.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also supported by the National Science Foundation (CHE 1057374). We acknowledge the support of NSF (9724307; 1428149) and the NIH NIGMS COBRE program (P30-GM110758) for research activities in the University of Delaware Surface Analysis Facility and W. M. Keck Center for Advanced Microscopy and Microanalysis.

References

1. Bishop LM, Yeager JC, Chen X, Wheeler JN, Torelli MD, Benson MC, Burke SD, Pedersen JA, Hamers RJ. A Citric Acid-Derived Ligand for Modular Functionalization of Metal Oxide Surfaces via “Click” Chemistry. *Langmuir*. 2012; 28:1322–1329. [PubMed: 22145802]

2. Law M, Greene LE, Johnson JC, Saykally R, Yang P. Nanowire Dye-Sensitized Solar Cells. *Nat. Mater.* 2005; 4:455–459. [PubMed: 15895100]
3. Özgür Ü, Alivov YI, Liu C, Teke A, Reshchikov MA, Doğan S, Avrutin V, Cho S-J, Morkoç H. A Comprehensive Review of ZnO Materials and Devices. *J. Appl. Phys.* 2005; 98:041301.
4. Cao Y, Galoppini E, Reyes PI, Lu Y. Functionalization of Nanostructured ZnO Films by Copper-Free Click Reaction. *Langmuir.* 2013; 29:7768–7775. [PubMed: 23688020]
5. Keis K, Bauer C, Boschloo G, Hagfeldt A, Westermark K, Rensmo H, Siegbahn H. Nanostructured ZnO Electrodes for Dye-Sensitized Solar Cell Applications. *J. Photochem. Photobiol., A.* 2002; 148:57–64.
6. Rossini JE, Huss AS, Bohnsack JN, Blank DA, Mann KR, Gladfelter WL. Binding and Static Quenching Behavior of a Terthiophene Carboxylate on Monodispersed Zinc Oxide Nanocrystals. *J. Phys. Chem. C.* 2011; 115:11–17.
7. Taratula O, Galoppini E, Mendelsohn R, Reyes PI, Zhang Z, Duan Z, Zhong J, Lu Y. Stepwise Functionalization of ZnO Nanotips with DNA. *Langmuir.* 2009; 25:2107–2113. [PubMed: 19199718]
8. Liu D, Wu W, Qiu Y, Yang S, Xiao S, Wang Q-Q, Ding L, Wang J. Surface Functionalization of ZnO Nanotetrapods with Photoactive and Electroactive Organic Monolayers. *Langmuir.* 2008; 24:5052–5059. [PubMed: 18370437]
9. Zhang B, Kong T, Xu W, Su R, Gao Y, Cheng G. Surface Functionalization of Zinc Oxide by Carboxyalkylphosphonic Acid Self-Assembled Monolayers. *Langmuir.* 2010; 26:4514–4522. [PubMed: 20146498]
10. Hotchkiss PJ, Malicki M, Giordano AJ, Armstrong NR, Marder SR. Characterization of Phosphonic Acid Binding to Zinc Oxide. *J. Mater. Chem.* 2011; 21:3107–3112.
11. Na HB, Lee IS, Seo H, Park YI, Lee JH, Kim S-W, Hyeon T. Versatile Peg-Derivatized Phosphine Oxide Ligands for Water-Dispersible Metal Oxide Nanocrystals. *Chem. Commun.* 2007:5167–5169.
12. Tudisco C, Fragalà ME, Giuffrida AE, Bertani F, Pinalli R, Dalcanale E, Compagnini G, Condorelli GG. Hierarchical Route for the Fabrication of Cavitand-Modified Nanostructured ZnO Fibers for Volatile Organic Compound Detection. *J. Phys. Chem. C.* 2016; 120:12611–12617.
13. Greenwood, NN., Earnshaw, A. *Chemistry of the Elements.* 2. Butterworth-Heinemann Limited; Oxford, UK: 1997.
14. Ferracane, JL. *Materials in Dentistry: Principles and Applications.* Lippincott Williams & Wilkins; 2001.
15. Hewlett RM, McLachlan MA. Surface Structure Modification of ZnO and the Impact on Electronic Properties. *Adv Mater.* 2016; 28:3893–3921. [PubMed: 26936217]
16. Park JB, Oh H, Park J, Kim N-J, Yoon H, Yi G-C. Scalable ZnO Nanotube Arrays Grown on CVD-Graphene Films. *APL Mater.* 2016; 4:106104.
17. Rusli, NI., Abdulgafour, H., Hassan, Z., Yam, FK., Ali, NK., Hashim, AM., Mahmood, MR., Nayan, N. In ZnO Nanostructures Grown on Porous Silicon Substrate without Catalyst; 2012 International Conference on Enabling Science and Nanotechnology; Jan 5–7. 2012 p. 1-2.
18. Schmidt-Mende L, MacManus-Driscoll JL. ZnO – Nanostructures, Defects, and Devices. *Mater. Today.* 2007; 10:40–48.
19. González-Moreno R, Cook PL, Zegkinoglou I, Liu X, Johnson PS, Yang W, Ruther RE, Hamers RJ, Tena-Zaera R, Himpsel FJ, Ortega JE, Rogero C. Attachment of Protoporphyrin Dyes to Nanostructured ZnO Surfaces: Characterization by near Edge X-ray Absorption Fine Structure Spectroscopy. *J. Phys. Chem. C.* 2011; 115:18195–18201.
20. Bebensee F, Bombis C, Vadapoo S-R, Cramer JR, Besenbacher F, Gothelf KV, Linderöth TR. On-Surface Azide–Alkyne Cycloaddition on Cu(111): Does It “Click” in Ultrahigh Vacuum? *J. Am. Chem. Soc.* 2013; 135:2136–2139. [PubMed: 23360358]
21. Wingrave JA, Teplyakov AV. Infrared Spectrometer Attachment Assembly for Use with Vacuum and High-Pressure Cells. *J. Vac. Sci. Technol., A.* 2003; 21:1800–1801.
22. Kung H, Teplyakov AV. Formation of Copper Nanoparticles on ZnO Powder by a Surface-Limited Reaction. *J. Phys. Chem. C.* 2014; 118:1990–1998.

23. Baskin JM, Prescher JA, Laughlin ST, Agard NJ, Chang PV, Miller IA, Lo A, Codelli JA, Bertozzi CR. Copper-Free Click Chemistry for Dynamic in Vivo Imaging. *Proc. Natl. Acad. Sci. U. S. A.* 2007; 104:16793–16797. [PubMed: 17942682]
24. Rostovtsev VV, Green LG, Fokin VV, Sharpless KB. A Stepwise Huisgen Cycloaddition Process: Copper(I)-Catalyzed Regioselective "Ligation" of Azides and Terminal Alkynes. *Angew. Chem., Int. Ed.* 2002; 41:2596–2599.
25. Haber JA, Lewis NS. Infrared and X-ray Photoelectron Spectroscopic Studies of the Reactions of Hydrogen-Terminated Crystalline Si(111) and Si(100) Surfaces with Br₂, I₂, and Ferrocenium in Alcohol Solvents. *J. Phys. Chem. B.* 2002; 106:3639–3656.
26. Bansal A, Li XL, Yi SI, Weinberg WH, Lewis NS. Spectroscopic Studies of the Modification of Crystalline Si(111) Surfaces with Covalently-Attached Alkyl Chains Using a Chlorination/Alkylation Method. *J. Phys. Chem. B.* 2001; 105:10266–10277.
27. Gammon WJ, Kraft O, Reilly AC, Holloway BC. Experimental Comparison of N(1s) X-ray Photoelectron Spectroscopy Binding Energies of Hard and Elastic Amorphous Carbon Nitride Films with Reference Organic Compounds. *Carbon.* 2003; 41:1917–1923.
28. Tan X, Fan Q, Wang X, Grambow B. Eu(III) Sorption to TiO₂ (Anatase and Rutile): Batch, XPS, and EXAFS Studies. *Environ. Sci. Technol.* 2009; 43:3115–3121. [PubMed: 19534122]
29. Frisch, MJ., Trucks, GW., Schlegel, HB., Scuseria, GE., Robb, MA., Cheeseman, JR., Scalmani, G., Barone, V., Mennucci, B., Petersson, GA., Nakatsuji, H., Caricato, M., Li, X., Hratchian, HP., Izmaylov, AF., Bloino, J., Zheng, G., Sonnenberg, JL., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, JA., Jr, Peralta, JE., Ogliaro, F., Bearpark, M., Heyd, JJ., Brothers, E., Kudin, KN., Staroverov, VN., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, JC., Iyengar, SS., Tomasi, J., Cossi, M., Rega, N., Millam, JM., Klene, M., Knox, JE., Cross, JB., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, RE., Yazyev, O., Austin, AJ., Cammi, R., Pomelli, C., Ochterski, JW., Martin, RL., Morokuma, K., Zakrzewski, VG., Voth, GA., Salvador, P., Dannenberg, JJ., Dapprich, S., Daniels, AD., Farkas, O., Foresman, JB., Ortiz, JV., Cioslowski, J., Fox, DJ. Gaussian 09, revision B.01. Gaussian, Inc; Wallingford, CT: 2009.
30. Lee CT, Yang WT, Parr RG. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1988; 37:785–789.
31. Becke AD. A New Mixing of Hartree–Fock and Local Densityfunctional Theories. *J. Chem. Phys.* 1993; 98:1372–1377.
32. McLean AD, Chandler GS. Contracted Gaussian Basis Sets for Molecular Calculations. I. Second Row Atoms, Z = 11–18. *J. Chem. Phys.* 1980; 72:5639–5648.
33. Krishnan R, Binkley JS, Seeger R, Pople JA. Self-Consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wavefunctions. *J. Chem. Phys.* 1980; 72:650–654.
34. Kung H, Duan Y, Williams MG, Teplyakov AV. Transmetalation Process as a Route for Preparation of Zinc-Oxide-Supported Copper Nanoparticles. *Langmuir.* 2016; 32:7029–7037. [PubMed: 27351220]
35. Shao X, Fukui K-I, Kondoh H, Shionoya M, Iwasawa Y. Stm Study of Surface Species Formed by Methanol Adsorption on Stoichiometric and Reduced ZnO(10 $\bar{1}$ 0) Surfaces. *J. Phys. Chem. C.* 2009; 113:14356–14362.
36. Wöll C. The Chemistry and Physics of Zinc Oxide Surfaces. *Prog. Surf. Sci.* 2007; 82:55–120.
37. Gao J, Teplyakov AV. Surface Species Formed During Thermal Transformation of Ethanol on ZnO Powder. *J. Catal.* 2013; 300:163–173.
38. Gao J, Teplyakov AV. Chemical Transformations of Acetone on ZnO Powder. *J. Catal.* 2014; 319:136–141.
39. Taratula O, Galoppini E, Wang D, Chu D, Zhang Z, Chen H, Saraf G, Lu Y. Binding Studies of Molecular Linkers to ZnO and MgZnO Nanotip Films. *J. Phys. Chem. B.* 2006; 110:6506–6515. [PubMed: 16570948]
40. Keis K, Lindgren J, Lindquist S-E, Hagfeldt A. Studies of the Adsorption Process of Ru Complexes in Nanoporous ZnO Electrodes. *Langmuir.* 2000; 16:4688–4694.

41. Mudunkotuwa IA, Grassian VH. Citric Acid Adsorption on TiO₂ Nanoparticles in Aqueous Suspensions at Acidic and Circumneutral Ph: Surface Coverage, Surface Speciation, and Its Impact on Nanoparticle–Nanoparticle Interactions. *J. Am. Chem. Soc.* 2010; 132:14986–14994. [PubMed: 20919713]
42. Buchholz M, Xu M, Noei H, Weidler P, Nefedov A, Fink K, Wang Y, Wöll C. Interaction of Carboxylic Acids with Rutile TiO₂(110): Ir-Investigations of Terephthalic and Benzoic Acid Adsorbed on a Single Crystal Substrate. *Surf. Sci.* 2016; 643:117–123.
43. Knurr BJ, Weber JM. Structural Diversity of Copper–CO₂ Complexes: Infrared Spectra and Structures of [Cu(CO₂)_n]– Clusters. *J. Phys. Chem. A.* 2014; 118:10246–10251. [PubMed: 25317936]
44. Upadhyay AP, Behara DK, Sharma GP, Bajpai A, Sharac N, Ragan R, Pala RGS, Sivakumar S. Generic Process for Highly Stable Metallic Nanoparticle-Semiconductor Heterostructures via Click Chemistry for Electro/Photocatalytic Applications. *ACS Appl. Mater. Interfaces.* 2013; 5:9554–9562. [PubMed: 24018108]
45. Williams MG, Teplyakov AV. Building High-Coverage Monolayers of Covalently Bound Magnetic Nanoparticles. *Appl. Surf. Sci.* 2016; 388(Part A):461–467. [PubMed: 27789916]
46. Liu Y, RamaRao N, Miller T, Hadjipanayis G, Teplyakov AV. Controlling Physical Properties of Iron Nanoparticles During Assembly by “Click Chemistry”. *J. Phys. Chem. C.* 2013; 117:19974–19983.
47. Liang L, Astruc D. The Copper(I)-Catalyzed Alkyne-Azide Cycloaddition (CuAAC) “Click” Reaction and Its Applications. An Overview. *Coord. Chem. Rev.* 2011; 255:2933–2945.
48. Ciampi S, Böcking T, Kilian KA, James M, Harper JB, Gooding JJ. Functionalization of Acetylene-Terminated Monolayers on Si(100) Surfaces: A Click Chemistry Approach. *Langmuir.* 2007; 23:9320–9329. [PubMed: 17655337]
49. Jacobsen, FE. *Bioinorganic Tools and Zinc Selective Inhibitors for Matrix Metalloproteinases.* ProQuest: University of California; San Diego: 2007.
50. Ye B-H, Li X-Y, Williams ID, Chen X-M. Synthesis and Structural Characterization of Di- and Tetranuclear Zinc Complexes with Phenolate and Carboxylate Bridges. Correlations between ¹³C NMR Chemical Shifts and Carboxylate Binding Modes. *Inorg. Chem.* 2002; 41:6426–6431. [PubMed: 12444787]
51. Creary X, Anderson A, Brophy C, Crowell F, Funk Z. Method for Assigning Structure of 1,2,3-Triazoles. *J. Org. Chem.* 2012; 77:8756–8761. [PubMed: 22894557]

Figure 1. Reaction scheme for ZnO surface modification with propiolic acid followed by benzyl azide test reaction via gas phase and liquid phase modification.

Figure 2.

SEM studies of ZnO surface modification. (a) Clean ZnO nanopowder; (b) gas phase propiolic acid-functionalized ZnO surface; (c) propiolic acid functionalized ZnO surface depicted in panel b followed by copper-free gas phase "click" reaction with benzyl azide; (d) propiolic acid functionalized ZnO surface depicted in panel b followed by copper-catalyzed liquid phase "click" reaction with benzyl azide; (e) ZnO powder directly exposed to liquid phase propiolic acid.

Figure 3.

Infrared spectroscopy studies of propiolic acid reaction with ZnO surface. (a) Gas phase propiolic acid; (b) computationally predicted infrared spectra for the cluster model schematically represented in the figure (frequencies are scaled by a common scaling factor of 0.94); (c) propiolic acid-functionalized ZnO surface (molecularly adsorbed propiolic acid is removed following extended pumping time). Clean ZnO surface is used as a background for spectrum c.

Figure 4.

Infrared spectroscopy studies of copper-free "click" reaction with propiolic acid functionalized ZnO surface. (a) Gas phase benzyl azide; (b) computationally predicted infrared spectra for the considered cluster model shown (frequencies are scaled by a common scaling factor of 0.94); (c) benzyl azide reacted with propiolic acid-functionalized ZnO surface; (d) propiolic acid-functionalized ZnO surface (same as Figure 3c). Propiolic acid functionalized ZnO surface is used as a background for spectrum c.

Figure 5.

High-resolution XPS spectra of C 1s region for (a) gas phase propiolic acid-functionalized ZnO surface; (b) copper-free “click” reaction of gas phase benzyl azide with propiolic acid-functionalized ZnO surface; (c) copper-catalyzed “click” reaction of liquid phase benzyl azide with propiolic acid functionalized ZnO surface.

Figure 6.

High-resolution XPS spectra of N 1s region for (a) gas phase propiolic acid-functionalized ZnO surface; (b) copper-free “click” reaction of gas phase benzyl azide with propiolic acid functionalized ZnO surface; (c) copper-catalyzed “click” reaction of liquid phase benzyl azide with propiolic acid functionalized ZnO surface; (d) benzyl azide adsorbed directly onto ZnO surface. The core level energy shifts predicted by DFT for the model systems presented in the figure are shown as solid bars.

Figure 7.

¹³C NMR spectroscopy studies of the reaction of propiolic acid with ZnO surface and the following copper-free “click” reaction. (a) Gas phase propiolic acid-functionalized ZnO surface; (b) liquid phase propiolic acid-modified ZnO powder; (c) benzyl azide reacted with propiolic acid-functionalized ZnO surface; (d) liquid phase propiolic acid.