Rational Method of Monitoring Molecular Transformations on Metal-Oxide Nanowire Surfaces

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Supporting Information

ABSTRACT: Metal-oxide nanowires have demonstrated excellent capability in the electrical detection of various molecules based on their material robustness in liquid and air environments. Although the surface structure of the nanowires essentially determines their interaction with adsorbed molecules, understanding the correlation between an oxide nanowire surface and an adsorbed molecule is still a major challenge. Herein, we propose a rational methodology to obtain this information for low-density molecules adsorbed on metal oxide nanowire surfaces by employing infrared p-polarized multiple-angle incidence resolution spectroscopy and temperature-programmed desorption/gas chromatography–mass spectrometry. As a model system, we studied the surface chemical transformation of an aldehyde (nonanal, a cancer biomarker in breath) on single-crystalline ZnO nanowires. We found that a slight surface reconstruction, induced by the thermal pretreatment, determines the surface chemical reactivity of nonanal. The present results show that the observed surface reaction trend can be interpreted in terms of the density of Zn ions exposed on the nanowire surface and of their corresponding spatial arrangement on the surface, which promotes the reaction between neighboring adsorbed molecules. The proposed methodology will support a better understanding of complex molecular transformations on various nanostructured metal-oxide surfaces.

KEYWORDS: Metal-oxide nanowires, organic gas sensors, surface chemical reactions, infrared spectroscopy, gas chromatography–mass spectrometry

INTRODUCTION

Understanding the adsorption behavior of molecules on nanostructured metal oxide surfaces is a long-standing, important, and challenging issue for their applications, which include molecular sensors,¹² catalysts,³–⁵ batteries,⁶,⁷ and other devices.⁸ Various analyses of bulk powders, based on X-ray photoelectron spectroscopy (XPS), Raman and infrared (IR) spectroscopy, or other techniques,⁹–¹² have revealed many interesting and peculiar properties of the adsorbed molecules. For example, the key intermediates of various catalytic reactions on metal oxides were successfully observed by employing infrared spectroscopic techniques.¹³–¹⁷ However, the understanding of the chemical interactions between molecules and metal oxide surfaces is still not fully developed.⁸¹⁰ One of the issues is that typical nanostructured metal oxides contain various complex crystal surfaces, and the surface chemical reactivity strongly depends on the crystal planes on which molecules are adsorbed.¹⁸,¹⁹ For this reason, single-crystal metal oxide substrates have been extensively investigated because they provide well-defined platforms to elucidate the intrinsic molecular features of specific crystal planes.²⁰–²² It should be noted that surface science measure-
nonanal on single-crystalline ZnO nanowires. Detailed chemical transformation mechanisms and pathways of (temperature-programmed desorption/gas chromatography–mass spectrometry, IR pMAIRS) and mass-spectrometric (infrared p-polarized multiple-angle incidence reflection spectroscopy) pretreatments on the nanowires. A combination of spectroscopic, TPD/GC–MS analyses of the desorbed gas from nonanal-adsorbed ZnO nanowires (pretreated at 400 °C in air) upon heating at various temperatures.

Results and Discussion. Figure 1a–c shows the TPD/MS desorption profiles of nonanal from the ZnO nanowires, which were thermally pretreated at different temperatures (400, 500, 600, 700, or 800 °C) and atmospheres (air, 10 Pa O2, or vacuum) prior to the molecular adsorption. As can be seen in the figures, the nonanal desorption profiles show two distinct peaks: a low-temperature (low-T) peak around 120 °C (blue-shaded region) and a high-temperature (high-T) peak around 230 °C (pink-shaded region). This result implies that two different chemical species or adsorption states exist on the ZnO nanowire surface. In addition, the intensity ratio of the two peaks significantly changes when varying the temperature or atmosphere of the thermal pretreatments. The ratio of low-T peak intensity to high-T peak intensity decreases with increasing temperature or decreasing pressure of the thermal pretreatment (Figure 1d). These results indicate that the adsorption and desorption behavior of nonanal on ZnO nanowires strongly depend on the thermal pretreatment conditions of the nanowires.

To identify the origin of the two distinct TPD/MS peaks in Figure 1, we conducted GC–MS analyses of the desorbed gas at each temperature. Figure 1e shows the GC–MS chromatograms of the desorbed gas at different desorption temperatures. Only a single peak at a retention time of 19.1 min is observed in the chromatogram at 100 °C (Figure 1e, blue line). Based on the mass fragment pattern, the peak is attributed to nonanal. However, the nonanal peak disappears and another peak appears at 35.7 min when the desorption temperature increases to 200 and 300 °C. These results suggest that the two distinct peaks observed in the TPD/MS plots in Figure 1 can be explained in terms of the reaction of nonanal on the ZnO surface. The largest m/z value of the new peak at 35.7 min is found to be 266, which matches the molecular weight of the product of the condensation reaction of two nonanal molecules. In fact, the retention time and the mass fragment pattern are in good agreement with those of pure (E)-2-heptyl-2-undecenal (Figure S4). This proves the formation of (E)-2-heptyl-2-undecenal on the surface, which indicates that aldol condensation of nonanal occurs on the metal oxide surface.

Figure 1. TPD/MS profiles of nonanal-adsorbed ZnO nanowires pretreated in (a) ambient air, (b) 10 Pa O2, or (c) vacuum (5 × 10⁻² Pa) at various temperatures (400, 500, 600, 700, and 800 °C). (d) Intensity ratios of low-T to high-T peaks plotted against the pretreatment temperatures of the ZnO nanowires. (e) GC–MS spectra of desorbed gas from nonanal-adsorbed ZnO nanowires (pretreated at 400 °C in air) upon heating at various temperatures.
nonanal molecules adsorbed on the ZnO nanowires is immediately converted to an \( \alpha,\beta \)-unsaturated aldehyde via aldol condensation, and (2) the degree of progress of the reaction is drastically enhanced when the thermal pretreatment is performed at higher temperature or lower pressure conditions.

Next, we examine the origin of the drastic change in the aldol reaction progress when varying the atmosphere of the thermal pretreatment of the nanowires. First, the variation in surface microstructure is considered as a possible factor in this change. The scanning electron microscopy (SEM) images in Figure S5a show the morphological changes observed on the ZnO nanowire surfaces upon thermal pretreatment at 400 °C in various atmospheres (air, 10 Pa O2, and vacuum). Although these three samples exhibit marked differences in the aldol condensation progress (as seen in Figure 1), no morphological changes are visible in the SEM images (Figure S5a). The transmission electron microscopy (TEM) and selected area electron diffraction (SAED) images of a ZnO nanowire treated at 400 °C in air (Figure S5b) show that the nanowire sidewall surface is composed of well-defined (10–10) crystal planes. This shows that the surface microstructure of the ZnO nanowires remains almost unchanged within the range of thermal pretreatment conditions employed. Therefore, the mechanism involving surface morphological changes induced by thermal pretreatment alone cannot explain the observed variation in the aldol condensation progress of nonanal on the ZnO nanowires.

Next, we consider the acid/base properties of the ZnO nanowire surfaces because it is well-known that aldol condensation is promoted by either acidic or basic inhomogeneous metal oxides, including ZnO.46 The density of hydroxyl groups (−OHs) on the ZnO nanowire surface is used as an indicator of the acidic ability of the surface. This is because the −OH group prefers capping bare Zn\(^{2+}\) ions,\(^{47}\) which can act as strong Lewis acids. Figure 2a shows the Fourier-transform infrared (FT-IR) spectra of ZnO nanowires pretreated at various temperatures in air. All spectra show two peaks (\( \nu(\text{OH}) \)) located at about 3716 and 3612 cm\(^{-1}\), which are attributed to surface −OH groups.\(^{47} \)\(^{-} \)\(^{49}\) The absorbance of the \( \nu(\text{OH}) \) peak is found to monotonically decrease with increasing pretreatment temperature (Figure 2b). XPS measurements were performed to further confirm the variation in the amount of the −OH groups on the ZnO surface,\(^{50}\) and Figure 2c shows the O 1s spectra of ZnO nanowires pretreated at different temperatures (ranging from 400 to 800 °C in air). The peaks at ~530.2 and 531.3 eV are assigned to lattice oxygen (O\(_{\text{(lattice)}}\)) and surface-adsorbed hydroxyl (O\(_{\text{(OH)}}\)) species, respectively.\(^{51} \)\(^{52}\) The area ratio of the O\(_{\text{(OH)}}\) to O\(_{\text{(lattice)}}\) peaks clearly decreases with increasing temperature or decreasing pressure of the pretreatment atmosphere (Figure 2d). Figure 2e shows the correlation between the relative amount of surface −OH groups estimated by XPS and the progress degree of the aldol condensation calculated from the TPD/MS results; a clear negative correlation is observed between the two terms. Because the coverage of surface −OH groups on the ZnO nanowires is correlated with the surface density of Lewis acidic Zn\(^{2+}\) sites exposed on the nanowire surface, the results in Figure 2e also indicate a positive correlation between the amount of exposed Lewis acidic Zn\(^{2+}\) sites and the degree of progress of the aldol condensation on the ZnO nanowires.

Although the results in Figure 2 highlight the strong correlation between the surface density of Lewis acid sites on ZnO and the acceleration degree of the aldol condensation, there are no experimental data clarifying how nonanal molecules interact with the ZnO nanowire surface. Therefore, the IR pMAIRS technique was employed to obtain data relative to the chemical transformation of nonanal on the ZnO nanowire surface, including insight into the chemical species generated on the surface and the reaction pathways during the molecular adsorption–desorption process. Figure 3a shows the typical IR pMAIRS spectrum of nonanal-adsorbed ZnO nanowires pretreated at 400 °C (blue line) and 800 °C (red line) in air. Both spectra show two separated peaks (\( \nu_1 \) and \( \nu_2 \)) in the 1650–1740 cm\(^{-1}\) region, generally associated with the \( \nu(C=O) \) vibration mode.\(^{53}\) Compared to the FT-IR spectrum of liquid-phase nonanal (1726 cm\(^{-1}\), Figure S8), both \( \nu(C=O) \) peaks (\( \nu_1(C=O) \) and \( \nu_2(C=O) \)) show distinct red shifts, indicating interactions between the carbonyl groups and the ZnO nanowire surface.\(^{57}\) Considering the extent of the red shifts, the two \( \nu(C=O) \) peaks correspond to two different adsorption states of nonanal: \( \nu_1(C=O) \) is assigned to nonanal
adsorbed via hydrogen bonding with a surface −OH, and ν2(C=O) to nonanal adsorbed by coordination to a surface Zn2+ (Figure 3b). The larger red-shift of the ν2(C=O) peak reflects the stronger Lewis acidity of Zn2+, compared to that of −OH. The present assignments of the ν1(C=O) and ν2(C=O) peaks are supported by theoretical calculations based on density functional theory (DFT). The peak wavenumbers are in good agreement with the theoretically calculated values (Figure S14). The larger out-of-plane/in-plane (OP/IP) ratio of ν2(C=O) compared to that of ν1(C=O) also supports the above assignments because the unsaturated Zn2+ coordination sites on the ZnO (10−10) plane are fixed at a slightly tilted angle along the c-axis.54 Notably, the ν2(C=O)/ν1(C=O) intensity ratio is significantly higher in the 800 °C- than in the 400 °C-treated sample. These results are also consistent with the lower amounts of −OH groups on the 800 °C-treated nanowire surface compared with those on the 400 °C-treated surface, as shown in Figure 2. In addition, Figure 3 shows the appearance of two additional peaks around 1590 and 1550 cm−1. The peak pattern is found to be identical to that observed in the spectrum of ZnO-adsorbed (E)-2-heptyl-2-undecenal (Figure S9). Therefore, these peaks derive from the aldol condensation product or from its reaction product on the surface. The peak at about 1636 cm−1 is assigned to the ν(C=C) mode of an enolate structure formed as an intermediate of the aldol condensation.53 Thus, the IR pMAIRS data demonstrate (1) the existence of two distinct adsorption states of the C=O groups of nonanal (bonded with −OH or Zn2+ species) on the ZnO nanowire surface, and (2) the correlation between the ratio of these two adsorption states and the ZnO nanowire surface states. It is worth noting that the amount of adsorbed nonanal was so small that no significant peaks were observed when a single-crystal ZnO (10−10) substrate was used instead of the ZnO nanowires (Figure S10). Furthermore, a very complex (and relatively harder to analyze) spectrum was obtained when ZnO powders (of ∼1 μm diameter and 99.99% purity) were used instead of the ZnO nanowires (Figure S11). This is likely due to the large variety of exposed surfaces on the ZnO powders. In addition, no significant changes in the spectral shape or the intensities in
the FT-IR spectra were observed within five-cycle repeated molecular adsorption and desorption processes (Figure S13). These findings clearly highlight the effectiveness of the single-crystal nanowire array as a platform for accurate FT-IR measurements of trace amounts of surface-adsorbed molecules.

We further monitored the dynamic variations of the surface molecular states during the molecular desorption processes using FT-IR spectroscopy. The FT-IR spectra of nonanal-adsorbed ZnO nanowires after treatment at various temperatures are shown in Figure 4. These measurements were conducted on two kinds of ZnO nanowires, pretreated at either 400 °C (Figure 4a,b) or 800 °C (Figure 4c,d) in air. We also monitored the spectra of (E)-2-heptyl-2-undecenal adsorbed on the 800 °C-pretreated ZnO nanowire to identify the spectral changes induced by the aldol-condensation product (Figure 4e,f). The experiments reveal the following spectral trends as a function of the temperature: (1) the intensities of the alkyl peaks in Figure 4a,c,e gradually decrease and then disappear above 300 °C, which indicates that aliphatic compounds adsorbed on the surface completely desorb below 300 °C; (2) the \( \nu_1(C=O) \) and \( \nu_2(C=O) \) peaks gradually decrease and completely disappear at 200 °C, which shows that surface-adsorbed nonanal completely desorbs or reacts to form other compounds below 200 °C; (3) the peak \( \nu_d \), which is originated from the vibration of C=O, C=C, or their mixture, first increases at temperatures below 100 °C and then decreases and eventually disappears below 300 °C. This result is considered to reflect the thermal activation of the aldol condensation followed by the thermal desorption and decomposition of the aldol condensation product. These results are clearly consistent with the GC–MS results shown in Figure 1e. Interestingly, Figure 4 shows that the intensity ratio of the peaks at around 1550 and 1590 cm\(^{-1}\) significantly increase with increasing temperature. The same trend is also observed in Figure 4c and d. It was frequently reported that carbonyl compounds adsorbed on metal oxides can be thermally oxidized to carboxylic acids, whose IR peaks appear around 1550 cm\(^{-1}\). Therefore, the peak around 1550 cm\(^{-1}\) is assigned to the \( \nu_{as}(COO) \) signal of carboxylate species derived from the thermal decomposition of the aldol condensation product. The high thermal stability of the \( \nu_{as}(COO) \) peak in Figure 4 also supports this assignment. It should be noted that the decrease ratio of the \( \nu_2(C=O) \) peak and the increase ratio of the \( \nu_1 \) peak from room temperature (RT) to 100 °C are markedly larger for the 800 °C-pretreated nanowires. These results suggest that the high-temperature pretreatment not only increases the amount of Zn\(^{2+}\)-activated nonanal molecules but also promotes the consumption of these activated species. This fact can be understood by assuming that both nonanal molecules involved in the aldol condensation must be activated by neighboring Zn\(^{2+}\) sites. In other words, the probability that an activated nonanal molecule has access to another activated nonanal is higher in the 800 °C-than 400 °C pretreated ZnO nanowires. Such a dual-activation mechanism is widely accepted for solution-phase aldol condensations.

Based on the results of the spectroscopy and mass-spectrometry experiments discussed above, we propose a possible mechanism for the chemical transformation process of nonanal on ZnO nanowires (Figure 5). (i) Nonanal molecules are coordinated at surface Zn\(^{2+}\) sites and are activated; (ii) the activated nonanal molecules are transformed into enolate-type intermediates and (iii) nucleophilically attack another activated nonanal, to form an aldol structure; (iv) the formed aldol structure is dehydrated and forms an \( \alpha, \beta \)-unsaturated aldehyde as condensation product; (v) the condensation product is oxidatively decomposed into carboxylic acids, which bind strongly to the ZnO surface.

Several conclusions can be drawn from the series of results discussed above. First, the enhancement of the aldol condensation by thermal pretreatment suggests a new strategy to discriminate structurally similar molecules using chemical sensors. This is because the reaction rates and products of aldol condensation are strongly affected by small structural differences in the starting compounds. Second, the use of the IR pMAIRS method for the aligned nanowire array enables the detailed identification of molecular states and orientations. For example, the pMAIRS analysis of the nanowires can distinguish between the two different adsorption states of C=O groups, either on −OH or Zn\(^{2+}\) sites, and determine their orientations and quantitative ratio (the orientations of the adsorbed molecules are further described in Figure S12 and Table S1). This spatial information will enhance our understanding of complex reaction mechanisms of molecules adsorbed on a solid surface.

**Conclusions.** In summary, we report a study of the chemical transformation mechanisms of an aldehyde on the ZnO nanowire surface, using nonanal as a model compound.
Besides the adsorption and desorption of nonanal, a large number of molecules were found to be chemically converted by aldol condensation and oxidation on the surface. The reaction rate was considerably enhanced by changing the conditions of the thermal treatment, i.e., by raising the temperature or reducing the pressure of the pretreatment atmosphere. Spectroscopic analyses revealed that the intrinsic variation behind this surface interaction should be linked to the exposed Zn\(^{2+}\) sites, acting as strong Lewis acids to promote the reaction. In addition, the dynamic changes in molecular bonding conformation and orientation were effectively analyzed by the IR pMAIRS technique. The present results provided a clear picture of the aldehyde transformation mechanism during the molecular adsorption–desorption process. The key for the success of this analysis was the well-defined and large-surface single-crystal structure of the ZnO nanowires, which enabled the use of a wide range of mass spectrometric and spectroscopic analyses. Further applications of the new combined analysis presented here will provide detailed insight into molecule–surface interactions, on which very limited information is available within the molecular sensing and inhomogeneous catalysis fields.

**Experimental Section. Growth of ZnO Nanowires.** An hydrothermal method was employed to grow ZnO nanowires on a double-side polished Si(100) wafer (2 cm \(\times\) 4 cm) substrate. A 5 nm Ti buffer layer and a 100 nm ZnO thin film were sequentially deposited on the Si substrate using a conventional sputtering technique. The substrate was dipped into 200 mL of aqueous solution containing 25 mM zinc nitrate hexahydrate (Zn\((\text{NO}_3\))\(_2\)·6H\(_2\)O, Wako, 99.0%), 25 mM hexamethylenetetramine (HMTA, Wako, 99.0%), and 2.0 g branched polyethylenimine (PEI, \(M_n = 1800\), Aldrich, 50 wt % in H\(_2\)O). The solution was kept at 95 °C for 24 h to grow the ZnO nanowires, followed by rinsing with water. The as-grown ZnO nanowires were thermally treated at various temperatures (ranging from 400 to 800 °C) for 3 h in various atmospheres: (1) ambient air, (2) O\(_2\) (10 Pa), and (3) vacuum (5 \(\times\) 10\(^{-2}\) Pa).

**Characterization of ZnO Nanowires.** SEM images were acquired using a JEOL JSM-7610F instrument. X-ray diffraction (XRD) data were collected on a Philips XPert diffractometer, using a Cu K\(_\alpha\) source (45 kV, 40 mA) at a wavelength of 1.54 Å. TEM images and SAED patterns were collected on a JEOL ARM-200F microscope. XPS measurements were conducted on a Kratos AXIS-165 spectrometer. The SEM images (Figure S1a) confirm that the grown ZnO nanowires exhibit hexagonal columnar structures (diameter of ~94 nm and length of ~6.5 \(\mu\)m). The strong diffraction peak at 34.43° in the XRD patterns (Figure S1b) corresponds to the (002) plane, which indicates that the ZnO nanowires have a single wurtzite structure with the prism (10–10) plane as the main face.\(^{58,59}\)

**Molecular Adsorption Process.** A thermally pretreated ZnO nanowire array was placed in a bottle filled with saturated nonanal vapor and left undisturbed for 30 s. The molecular adsorbed ZnO nanowire was then used for the subsequent measurements.

**TPD/MS Analysis of Desorbed Gas.** Desorption spectra were recorded by GC–MS (Shimadzu GC-MS-QP 5050A) using a capillary column (length of 1 m and internal diameter of 0.1 mm) without stationary phases to connect the inlet and the mass spectrometer unit. The sample temperature in the inlet port was varied from 35 to 500 °C at a heating rate of 0.5 °C/s using a multishot pyrolyzer (Frontier Lab EGA-PY-3030 D). The detailed temperature program is shown in Figure S2. We monitored the changes in the total ion current (TIC) values with increasing inlet temperature.

**GC–MS Analysis of Desorbed Gas.** A Shimadzu GC-MS-QP 5050A instrument (equipped with a Supelco SLB-IL60 capillary column and an OPTIC-4 inlet temperature control system) was used to analyze the desorbed compounds at each temperature. The sample was heated for a short time (2 min) at each temperature (100, 200, 300, 400, and 500 °C) and immediately cooled to 35 °C. The desorbed gas at each temperature was analyzed by GC–MS. The measurements for each temperature were conducted sequentially (from 100 to 500 °C) without removing the sample from the inlet port. The detailed temperature program is shown in Figure S3.

**IR pMAIRS Measurements.** FT-IR spectra were measured on a Thermo Fisher Scientific Nicolet iS50 spectrometer equipped with a mercury–cadmium–telluride (MCT) detector. A series of eight single-beam sample measurements were carried out at angles of incidence from 9 to 44° at 5° steps and with a resolution of 4 cm\(^{-1}\). The test room was always purged with dry air. After collection of the sample data, the OP and IP spectra were automatically calculated with the pMAIRS software (Thermo Fisher Scientific). The theoretical details of the IR pMAIRS analysis can be found in the literature.\(^{60–62}\)

**FT-IR Monitoring of the Surface Reaction Progress upon Heating.** The nonanal-adsorbed ZnO nanowires were heated at a given temperature for 5 min and cooled to room temperature. The FT-IR spectra of the nanowires were then recorded at room temperature on a Thermo Fisher Scientific Nicolet iS50 FT-IR spectrometer equipped with a MCT detector.
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