Zinc Oxide

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Catalytic Activation of a Solid Oxide in Electronic Contact With Gold Nanoparticles**

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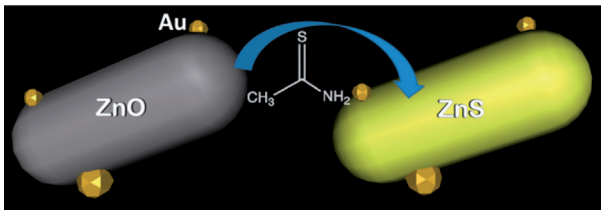
Abstract: *Although inert in its bulk form, nanostructured gold supported on oxides has been found to be catalytically active. In many cases, the oxide promotes the activity of Au. It is now shown that in turn, nanoscale Au particles can chemically activate the solid oxide. Specifically, it was discovered that 4 nm Au nanoparticles deposited on zinc oxide catalyze the transformation of the oxide into the sulfide in the presence of an organosulfur species. Contact of the oxide with Au nanoparticles lowers the activation barrier for the solid-state reaction by approximately 20 kJ mol^{-1}, allowing the reaction to be achieved closer to ambient temperatures. Electron transfer from oxygen vacancies to Au nanoparticles is proposed to generate acidic sites on the surface of the zinc oxide, resulting in the enhanced reactivity of the oxide. Knowledge of such electronic interactions between the noble metal and oxide can be exploited for engineering reactive heterostructures for low-temperature pollutant sorption and hydrocarbon processing.*

Owing to its electronic structure, gold is characterized by chemical nobility in its bulk form.[1] But Au dispersed on an oxide in the form of nanoparticles or nanoclusters is highly catalytically active.[2–10] For instance, bulk Au can neither chemisorb nor dissociate O_2 except at very high temperatures[11–13] whereas oxide-supported Au nanoparticles can bind and activate oxygen with significant binding energies.[14–16] Oxide-supported Au nanoparticles have been shown to catalyze a range of reactions, including the low-temperature oxidation of carbon monoxide and hydrogen,[3] methanol synthesis from syngas,[8] the water-gas shift reaction,[9] and selective oxidations of small organic molecules.[17,18]

Some early work attributed the catalytic activity exclusively to nanoscale size effects, including the favorable electronic interaction of gas molecules with the discrete semiconductor-like electronic states of Au clusters[19,20] and the prevalence of under-coordinated edge and corner atoms on small nanoparticles, which serve as high-energy adsorption sites.[21] However, many studies have since shown that the oxide support is critical to the surprisingly high activity of Au.[22–27] Oxides, particularly reducible ones such as TiO_2, MgO, or CeO_2, have been shown to promote the catalytic activity of Au when in contact with nanoscale Au.[28,29] One mechanism for such a promotion is that electrons from oxygen vacancies in the oxide transfer across the interface to form anionic Au species that can activate small molecules such as O_2.[22–30]

We show herein that the chemical interplay resulting from electronic contact between the oxide and Au nanoparticles is mutual. Just as the oxide can promote the catalytic activity of Au, we found that Au, in reciprocity, can chemically activate the oxide. Whereas the former activation has been a topic of intense investigation in Au/oxide heterostructures, the reactivity of the oxide itself[31–36] in such heterostructures has received less attention, possibly because of the deemed status of the oxide as a support, albeit a promoting one. We investigated how the chemical reactivity of the oxide is influenced by nanoscale Au particles, which may have an important role in the synergistic catalytic abilities of oxide-supported Au nanoparticles.

Specifically, we observed that contact with Au nanoparticles significantly enhanced the reactivity of the oxide towards small molecules (see Scheme 1). The enhanced reactivity originates from the generation of acidic sites on the oxide surface resulting from the transfer of electrons from the oxide to Au. Aside from implications for supported Au catalysis, the observed phenomenon can be exploited for rationally engineering highly reactive oxides that can undergo solid-state transformations and perform activated processes, such as reactive adsorption[33–35] and small-molecule transformations, closer to ambient temperatures.



Scheme 1. Au nanoparticles in contact with ZnO serve to catalytically activate the oxide and enhance the reactivity of the oxide towards organosulfur compounds.

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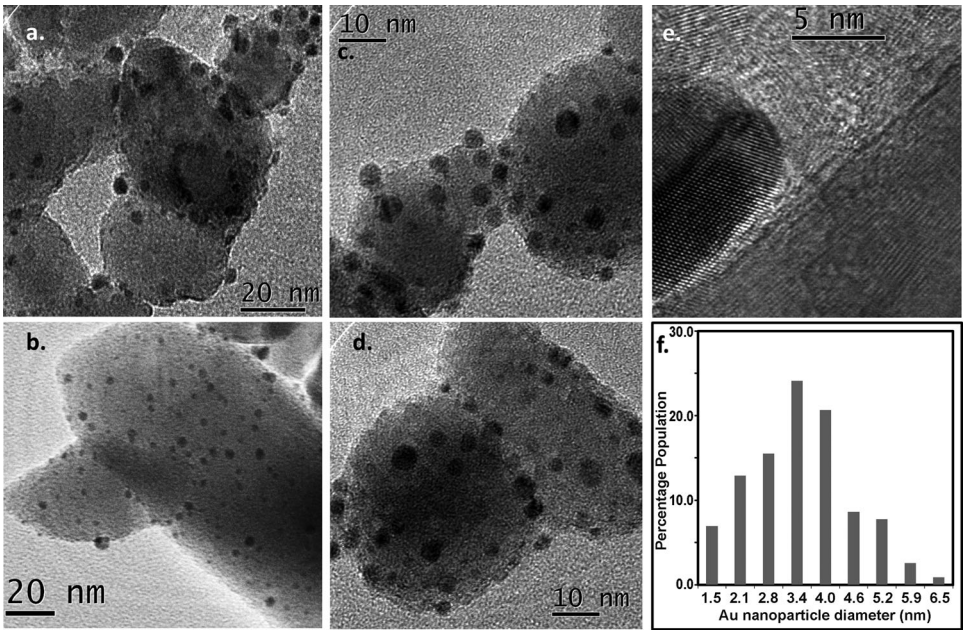
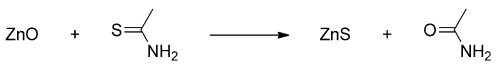


Figure 1. a–d) Representative transmission electron micrographs of the Au/ZnO heterostructures used for this study. The Au nanoparticles are identified by their higher contrast. e) The interfacial contact between Au and ZnO is shown in a magnified image. f) Size histogram of 116 Au nanoparticles, which have an average size of 3.8 ± 1.1 nm (sd).

Our investigation was performed on heterostructures of Au nanoparticles and zinc oxide (ZnO), a reducible oxide (Figure 1). The heterostructures were synthesized by in situ wet chemical reduction of Au salt in the presence of ZnO nanoparticles. This method ensured interfacial contact between the formed Au nanoparticles and ZnO (Figure 1e). The deposited Au nanoparticles were on average approximately 4 nm in size and constituted 2 wt % of the composite. The nanoparticulate nature of both ZnO and Au ensured a high specific area of interfacial contact between the oxide and Au.

We investigated the reactivity of ZnO towards a model organosulfur compound, thioacetamide. This choice was motivated by the use of oxides as solid-state adsorbents in desulfurization[37–40] and similar pollutant removal technologies. The reactivity of the oxide can be exploited for removing organosulfur compounds from hydrocarbon fuel streams by reactively adsorbing the organosulfur compound in the form of zinc sulfide (ZnS). In the present case, this took place as:



where the thioacetamide (C_2H_5NS) was stoichiometrically converted into acetamide (C_2H_5NO), which may further hydrolyze to acetic acid (CH_3COOH) and solvated ammonium ions. This reaction was not limited to the surface of the oxide, but progressed through the bulk of the solid, forming an extended zinc sulfide phase. The reaction conversion could thus be monitored by X-ray diffraction (XRD), which we employed to characterize the reactivity of the oxide with and without deposited Au nanoparticles (Supporting Information, Figure S1).

ZnO without deposited Au nanoparticles reacted with thioacetamide, but only when thermal activation was provided (Figure 2, ■). At room temperature, insignificant conversion was observed after two hours. Upon increasing the temperature to 41 °C (or 314.15 K), the conversion at two hours was only 11 %.

ZnO with deposited Au nanoparticles (Figure 2, ●) also showed no detectable conversion at room temperature, but the heterostructure was one order of magnitude more reactive than ZnO at elevated temperatures. For example, at 41 °C, almost 100 % conversion into the sulfide was achieved within two hours. This result is

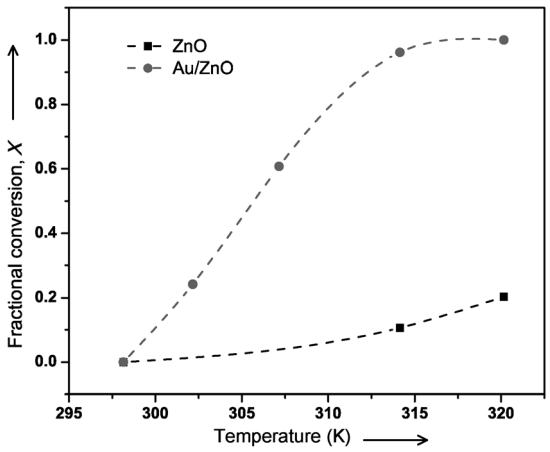


Figure 2. Au/ZnO heterostructures (●) are more reactive than ZnO (■) as seen from the fractional conversion of the oxide into the sulfide as a function of temperature. Dotted lines drawn to guide the eye.

remarkable considering that the observed transformation is essentially a complete anion exchange (S^{2-} replacing O^{2-}) of the entire solid oxide,[41] achieved at a fairly moderate temperature (i.e., only 16 °C above room temperature). Thus, Au nanoparticle deposition has been observed to enhance the reactivity of the oxide.

We quantified the observed enhancement by measuring the kinetics of the sulfidation reaction. The energy of activation for the solid-state reaction of ZnO was measured to be 65.2 kJ mol^{-1} (Figure 3b, ■). However, for ZnO in contact with Au, the energy of activation for the reaction decreased by almost 20 kJ mol^{-1} to 46.4 kJ mol^{-1} (Fig-

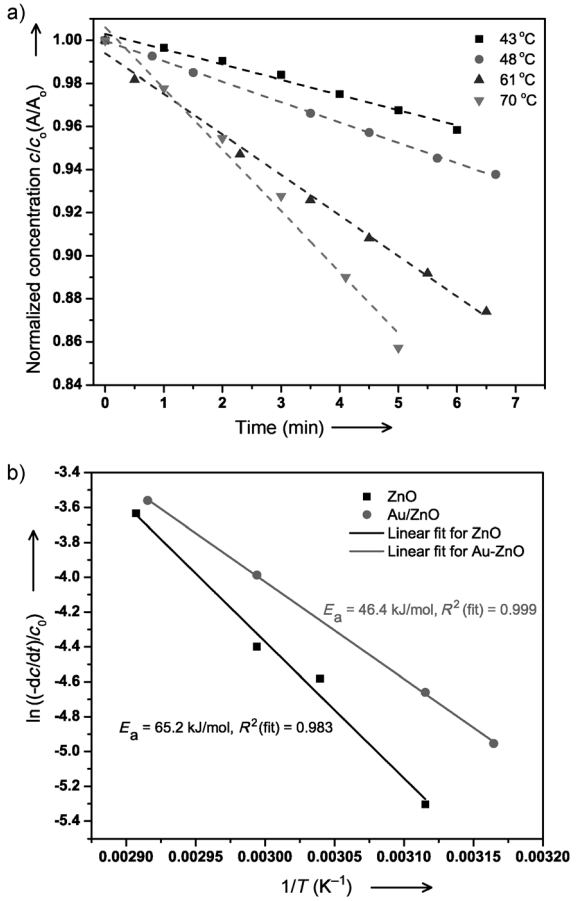


Figure 3. a) Sulfidation kinetics for Au/ZnO heterostructures at various temperatures obtained by monitoring the decrease in the excitonic absorbance of ZnO at early times in the reaction (Figures S2–S4). Assuming the reaction kinetics to be first order with respect to ZnO, we obtained an effective reaction rate constant $-\frac{1}{c_0}\left(\frac{\partial c}{\partial t}\right)_0$ from the slope of the linear fit for each temperature. b) Plot of ln(rate constant) versus $1/T$ for Au/ZnO heterostructures (●) and ZnO (■). From a linear fit (——), the energy of activation was determined to be 46.4 kJ mol^{-1} for Au/ZnO, which is approximately 20 kJ mol^{-1} lower than that for ZnO.

ure 3b, ●). Thus, Au nanoparticles cause significant catalytic activation of the oxide. Such activation would allow the oxide to be exploited for reactive adsorption processes without necessitating an energy-intensive high-temperature process.

To allow the observed catalytic effect to be optimized and exploited more rationally in future work, it is imperative to elucidate the mechanistic origin of the phenomenon, which we accomplished by structural and chemical characterization of the heterostructures. X-ray photoelectron spectroscopy (XPS) of the Au/ZnO heterostructures indicated the presence of Au with a $4f_{7/2}$ binding energy of 83.3 eV (Figure 4a). This value was shifted to a lower binding energy relative to the value of 84.1 eV observed for Au nanoparticles without the oxide (ca. 4 nm; Figure S5). This shift to a lower binding energy for Au/ZnO indicated that the Au has a partial negative charge[42] when it is in contact with ZnO. A similar effect has been seen for Au in contact with other reducible oxides, such as TiO_2 and MgO,[22,30] that are rich in oxygen vacancies, the location where Au typically binds.[43] Oxygen vacancies in ZnO are rich in electrons as their (double) ionization to form conduction band carriers requires significant activation (ca. 1 eV).[44] However, upon contact with Au, the electrons can transfer to Au, which has a high electron affinity and a Fermi level (−5.1 eV relative to vacuum) significantly lower than the oxide conduction band (−4.3 eV).[32] The situation is similar to TiO_2, the conduction band edge of which lies at −4.5 eV.

Electron transfer from an oxide to Au nanoparticles has in many cases played an important role in making Au nanoparticles catalytically active; however, this process also has a profound effect on the activity of the oxide, as we describe here. This electron transfer to Au results in the ionization of oxide vacancies, especially those at or near the surface closest to the interface with Au. Thus, surface Zn sites in the vicinity of ionized oxygen vacancies can take on a significant (Lewis) acidic character:

$$ZnO_{1-\delta/2} + \frac{\delta}{2}V_O{}^{x} + Au^0 \rightarrow ZnO_{1-\delta/2} + \frac{\delta}{2}V_O{}'' + Au^{\delta-} \rightarrow Zn^{\delta+}O_{1-\delta/2} + Au^{\delta-} \quad (1)$$

The suggested development of surface acidity is manifested in a vibrational analysis of the hydroxylated ZnO surface (Figure 4b). For ZnO without Au, diffuse-reflectance infrared Fourier-transform spectra (DRIFTS) of the hydroxy region of 3000–3800 cm^{-1} showed a broad band with a peak frequency of 3468 cm^{-1}. This frequency is characteristic of O–H stretches of surface-passivating hydroxy groups or water molecules adsorbed at a range of defect, edge, or mixed-facet sites prevalent on the ZnO nanoparticle surface.[45] However, for ZnO in contact with Au, the broad O–H stretching band developed an asymmetric shape with the appearance of a lower frequency peak at 3374 cm^{-1}. The reduced stretching frequency is indicative of O–H bonds that are weakened owing to their stronger coordination with surface Zn cations of significant acidic character.[46] Furthermore, in the prevalence of acidic (under-coordinated) Zn sites on the surface, hydroxy groups can coordinate to Zn sites in a bidentate fashion, which would also be consistent with the observation of a weakened O–H bond.[46] Aside from (Lewis) acidic Zn sites, hydroxy groups that are strongly bound to one or more electron-deficient Zn sites can become (Brønsted) acidic.[47]

We also determined the surface acidity of Au/ZnO by means of a molecular probe, namely lutidine (2,6-dimethylpyridine).[47,48] On Au/ZnO treated with lutidine, significant surface adsorption of lutidine was detected by DRIFTS spectroscopy (Figure 4c) by the appearance of vibrational absorption bands at 1505 and 1553 cm^{-1}, which are attributable to ν_{8a} or ν_{8b} modes of adducts of basic lutidine with acidic surface species.[48,49] ZnO without Au exhibited no such adsorption of lutidine (Figure 4d). Although it is difficult to pinpoint at any particular acidic species on Au/ZnO, the frequency location of the bands (close to the 1580 cm^{-1} reported in literature)[49] is suggestive of hydrogen-bonded lutidine or lutidine bound to Lewis acidic sites (e.g., $Zn^{\delta+}$) or weakly Brønsted acidic sites (e.g., $H^{\delta+}\cdots O$). Although we cannot completely rule out the possibility of lutidine adsorp-

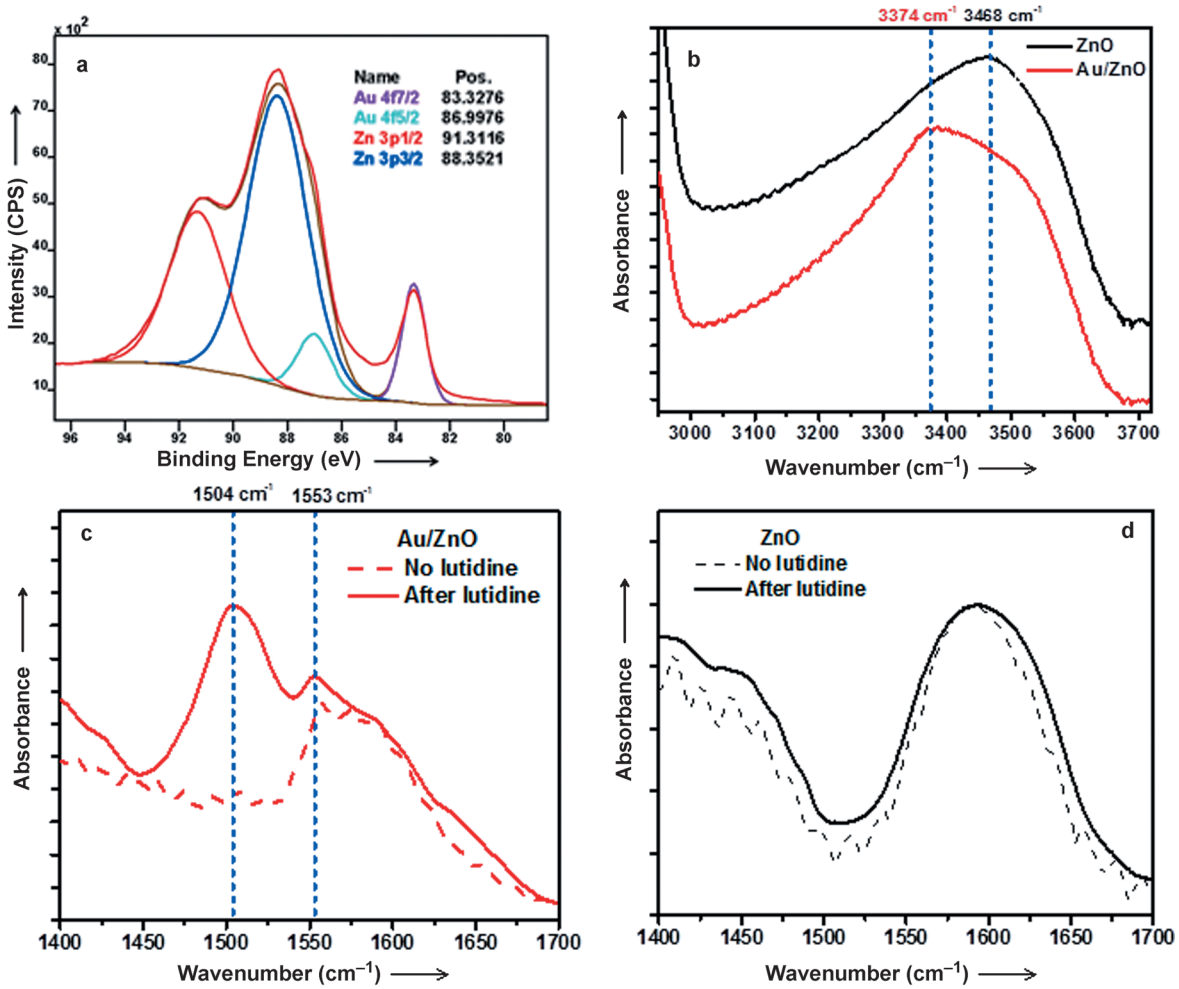
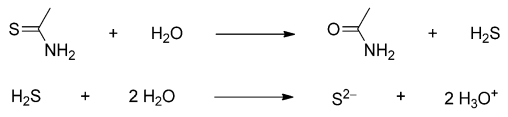


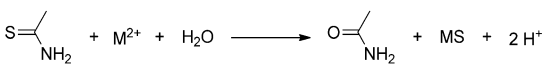
Figure 4. a) The X-ray photoelectron spectrum of Au/ZnO with fits to the observed peaks shows that Au has a $4f_{7/2}$ binding energy of 83.3 eV. This value, which is lower than that of 84.1 eV measured for Au nanoparticles without ZnO (Figure S5), indicates that the Au is negatively charged when in contact with ZnO. b) Diffuse-reflectance infrared Fourier-transform spectra (DRIFTS) of the hydroxy region of 3000–3800 cm^{-1} show that whereas in ZnO, surface hydroxy groups and adsorbed water exhibit a broad O–H stretching band at 3468 cm^{-1}, Au/ZnO exhibits a broad O–H band with a peak at 3374 cm^{-1}. The reduced peak frequency indicates that the O–H bonds are weakened by coordination with acidic surface sites. c) The surface acidity of Au/ZnO was detected by the adsorption of the basic probe lutidine. Upon lutidine adsorption on Au/ZnO, peaks appear at 1504 and 1553 cm^{-1} in the DRIFTS spectrum, which are characteristic of the vibrational modes of adducts of lutidine with Lewis/Brønsted acid sites on the surface. d) No such lutidine adsorption was detected in a DRIFTS measurement of ZnO without Au. Note that all DRIFTS spectra were normalized to an arbitrary absorbance scale for the purpose of comparison.

tion on Au, the low weight percentage of Au in the heterostructure makes such a process less likely.

Therefore, we deduce that the acidity of the surface of ZnO in contact with Au is responsible for the enhanced reactivity of the oxide towards thioacetamide. Thioacetamide is known to hydrolyze in water to give reactive S^{2-} ions:



This reaction typically requires heating to moderate temperatures, but it is also known to be catalyzed by acids, where the rate of hydrolysis is proportional to $[H^+]$. Alternatively, direct reactions with metal cations (e.g., Pb^{2+}) are also possible:



In both cases, electrophilic (H_3O^+ or M^{2+}, respectively) attack on the S atom is responsible for activating the C=S bond. Similar activation processes are expected to occur at either Brønsted acidic hydroxy sites or Lewis acidic (under-coordinated) Zn sites generated on the ZnO surface upon contact with Au nanoparticles. Whereas fully coordinated Zn in stoichiometric ZnO likely requires significant thermal activation to react with thioacetamide (or its decomposition product H_2S), $Zn^{\delta+}$ is expected to be more active for direct

reactive adsorption of thioacetamide or for the reaction with H_2S or S^{2-} formed by hydrolysis at Brønsted sites.

Once the sulfidation reaction has been initiated at an interfacial $Zn^{\delta+}$ site, the reaction can propagate through the bulk of the solid through hopping of S^{2-} anions and/or oxygen vacancies. It is possible that similar to other ion exchange reactions,[50] sulfidation at an initial surface/defect site is rate-limiting in the solid-state process. In this case, nanoparticulate Au, despite its low loading of 2% and its chemical contact with only a small fraction of the ZnO units, would be able to provide a net enhancement in ZnO reactivity through the activation of the Au/ZnO interface, where rate-limiting nucleation of sulfidation takes place.

It must also be noted that electron transfer to the metal can have a long-range, delocalized effect on the electronic structure of the supporting oxide itself.[51] For instance, in Au/TiO_2, it has been shown that the charge left behind on the oxide is not localized on the Ti atoms where Au is bound, but rather that the charge is spread over several atomic layers in the oxide.[52] Thus, apart from the enhancement of interfacial reactivity, a modification of the bulk reactivity of the oxide, resulting from electronic interactions with Au, cannot be ruled out. Under-coordinated Zn cations, at sites of ionized oxygen vacancies within the bulk lattice, are also expected to require less activation for reactions with S^{2-} anions. Moreover, the ionization of existing oxygen vacancies by electron transfer to Au can perturb the defect equilibrium in the bulk of the oxide in favor of the generation of additional oxygen vacancies.[32] A higher density of lattice oxygen vacancies can enhance solid-state diffusion[53] of incoming S^{2-} and outgoing O^{2-}, facilitating anion exchange throughout the solid at moderate temperatures. Future work may be able to elucidate the contribution of such bulk solid-state mechanisms distinctly from the effect of enhanced reactive adsorption at the Au/ZnO interface. In this context, it may also be worth resolving the atomic identity of the active site/s where the reaction is initiated.

An alternative explanation for the enhanced reactivity of Au/ZnO is that Au serves as the site for reactive decomposition of thioacetamide and supplies S^{2-} to the oxide. For instance, in the process of hydrodesulfurization with Ni/ZnO, it has been found that the organosulfur molecules decompose on metallic Ni, and the extracted sulfur is stored in the form of nickel sulfide (Ni_3S_2 and Ni_3S_4).[54] However, we found no such evidence for sulfidation of Au either by XRD (Figure S1) or by XPS of sulfided Au/ZnO nanoparticles (Figures S6 and S7). The Au nanoparticles remain chemically unaffected by sulfidation. However, we cannot rule out that a short-lived Au sulfide intermediate is formed by the reactive dissociation of thioacetamide on Au. This metastable Au sulfide intermediate can serve as a source of reactive sulfide for the sulfidation of nearby ZnO. Future work may be undertaken to resolve the role and relative contribution of this alternate mechanism of activation.

In summary, we have observed that electronic contact with Au nanoparticles enhances the reactivity of ZnO and facilitates its solid-state transformation. In past studies, oxide reactivity has been described to be modified upon doping with metal ions or another metal oxide;[37–39,54] however, the catalytic activation of the oxide by contact with a noble-metal nanoparticle presents a unique perspective. Whereas the current paper presents an example of one type of heterostructure and one reaction, it may be possible to explore similar chemical enhancements in other metal/metal oxide systems and apply them to a range of small-molecule reactions (relevant for hydrocarbon processing) and phase transformations in oxide materials (relevant to solid-state devices such as batteries). The results also point to the possibility of employing noble-metal nanoparticles for controlled nanoscale patterning of the surface acidity on an extended surface. The mechanism identified herein goes hand-in-hand with the well-known promotion of gold nanoparticles by oxide supports. In light of this, it is worth revisiting the role of the oxide support[31] in small-molecule activation and photoactivation.[55]

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