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Observing Catalysis through the Agency of the Participating Electrons: Surface-Chemistry-Induced Current Changes in a Tin Oxide Nanowire Decorated with Silver

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ABSTRACT

Conductometric measurements were performed on single tin oxide nanowires with and without Ag nanoparticle surface decoration, in flowing oxygen/ethylene mixtures of varying composition. Ag-decorated nanowires showed a significant ethylene effect, which we explain in terms of the modification of the Schottky junction formed between the Ag particles and the tin oxide, resulting from the surface chemical processes involving ethylene and oxygen occurring exclusively on the silver nanoparticles' surface. Assuming the observed temperature dependence of these ethylene-induced current decrements reflect changes in the steady-state concentration of ethylene, oxygen, and a surface intermediate that ultimately leads to ethylene oxide, one calculates the enthalpy for the production of the reaction intermediate to be approximately –4.6 kcal/mol, of the right order of magnitude as the calculated value reported in the literature for the formation of a putative ethylene oxametallacycle intermediate in the ethylene epoxidation reaction. Our results illustrate how fundamental catalytic processes occurring at metal nanoparticle surfaces can significantly influence the electronic properties of oxide nanowires used as metal particle supports.

Single-nanowire-based gas sensors configured as resistive elements or field-effect transistors (FETs) have been the subject of growing interest, with emphasis both on the fundamental understanding of the physics and chemistry underlying their operating principles and on the possible device applications of such nanosystems.[1,2] Nanostructures configured as FETs can also potentially serve as devices with which the catalytic processes occurring at the surface of the active medium can be tuned by varying the gate potential of the device.[3]

In this study we take a step toward electronic control of a catalytic process by showing that the chemical process occurring at the surface of metal nanoparticles deposited on the surface of a semiconducting nanowire measurably affects the source−drain current through the nanowire. The surface reaction chosen to demonstrate this effect is ethylene oxidation, for which the appropriate catalytic metal is Ag. Ethylene oxidation was chosen as the model process and SnO_2 nanowire as the substrate for several reasons: (1) Tin oxide itself is a poor catalyst for ethylene oxidation, and (2) although the conductance of a tin oxide nanowire is very sensitive to the presence of oxygen in the ambient, in the absence of silver the addition of ethylene to an oxygen stream over a tin oxide nanowire (at steady state) does not change its conductance appreciably. (Although in the absence of oxygen, ethylene does have a measurable effect on the conductance of a pristine tin oxide nanowire.) (3) Finally, the catalytic oxidation of ethylene (and other small olefins) is an industrially important process.[4] Accordingly, a considerable amount of literature exists devoted to that process from which a great deal is currently known regarding the mechanism of the silver-catalyzed epoxidation reaction.[5−7] For example, it is generally accepted that the surface oxygen that engages in ethylene epoxidation is a single ionic species (as opposed to a dioxygen species). Additionally, a number of recent papers have suggested that an oxametallacycle surface intermediate plays an important role in the formation of ethylene oxidation on Ag.[8]

The present study was motivated by the premise that investigating the consequent effect on the electronic properties of a semiconducting nanowire of a surface reaction such as ethylene oxidation taking place on the surface of metal particles deposited on the nanowire might lead to a more general tool for investigating the charge exchange processes accompanying catalysis on nanosystems, potentially down to single metal particles. Although only conductometric

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measurements were carried out in the present studies, they were carried out on a device that could be easily configured as a back-gated FET anticipating the much more difficult experiment in which the gate potential could be used to modify the surface processes occurring on the metal nanoparticles.

Tin oxide nanowires were synthesized by chemical vapor deposition. Briefly, an alumina boat with SnO powder (99.9%, Alfa Aesar) was placed at the center of the quartz tube of a tube furnace. A 1 cm × 1 cm p-type Si(110) wafer covered by a 3.0 nm vapor-deposited Au film was placed downstream of the boat. The tube was evacuated, and an Ar carrier gas (50 sccm) containing traces of oxygen were introduced into and maintained at 130 Torr using a mechanical pump. The furnace temperature was increased to 900 °C and the reaction run for 20−60 min. The stoichiometry and morphology of the ensuing one-dimensional (1-D) nanostructures were verified by scanning electron microscopy (SEM), X-ray diffraction (XRD), and transmission electron microscopy (TEM).

The as-synthesized nanowires were transferred to a clean p-type silicon wafer covered with a 250 nm silica film, which served as an insulating layer for the nanowires (and can serve as a back-gate electrode in future experiments). Metallic Ti (20 nm)/Al (120 nm)/Ni (30 nm)/Au (50 nm) micropads were vapor deposited acting as the source (S) and drain (D) electrodes; however we found that Ti/Al/Ni/Au produces better ohmic contacts than Ti/Au. Accordingly, this pad material was used for most of the experiments reported in this study. Conductance measurements were carried out on isolated individual nanowires (Figure 1 upper-right inset) in a custom-built chamber in which the temperature and gas composition can be varied. The composition of gases was controlled by mass flow meters which can maintain gas partial pressure at 1−100 mTorr. Before any measurements were carried out, the samples were heated in vacuum ($\sim 10^{-6}$ Torr) for at least 1 h at 300 °C to help improve the ohmic contact between the nanowire and metallic micropads. Ag particles were deposited in situ in the chamber with a pressure of $\sim 10^{-6}$ Torr using a resistively heated silver filament as source (Alfa Aesar, 0.25 mm diameter 99.9%). The filament was outgassed under vacuum by annealing prior to the silver evaporation step. Metal decoration was carried out in situ so as to allow us to use a single nanowire in each experiment, thereby maximizing the probability that the observed changes with and without silver arose from the presence of silver rather than to the variation in the properties of the nanowires if multiple nanowires are used. As a result, all measurements of the changes in the source−drain current, I_{SD}, were carried out on the same nanowire, with the first set carried out prior to silver particle decoration and the second set subsequent to silver deposition with both sets run under similar conditions of temperature and ambient gas composition.

The SEM image indicates that in a typical synthesis SnO_2 nanowires cover the surface of the silicon substrate uniformly and compactly and that the average diameters are approximately 60−80 nm. One hour of growth typically results in nanowires ~ 100 μm in length. XRD analysis of the sample (Figure 1 inset) reveals the nanowires to have a tetragonal rutile SnO_2 structure with lattice constants $a = 4.68$ Å and $c = 3.15$ Å. An individual SnO_2 nanowire device and schematic view of FET structure with Ag-decorated SnO_2 nanowire was shown in parts a and b of Figure 1, respectively.

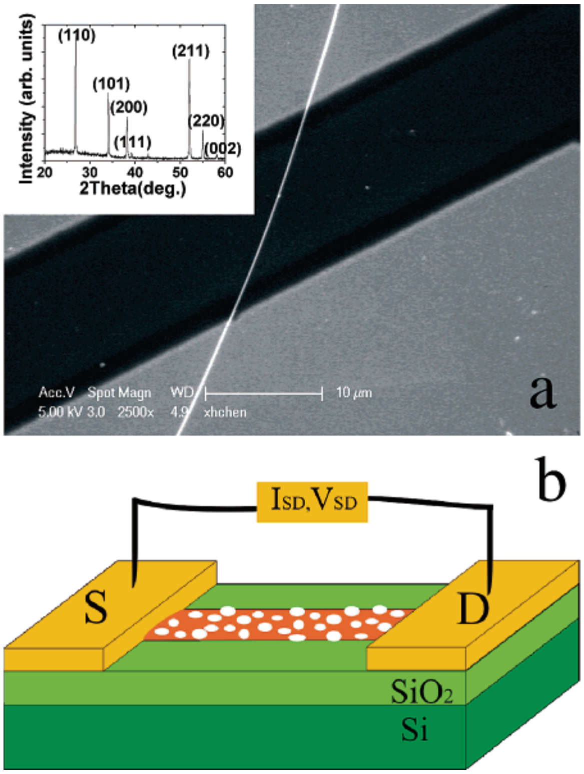

Figure 1. (a) SEM image of an individual SnO_2 nanowire device configured with appropriate ohmic contacts for electrical measurements in a gaseous atmosphere. Inset: XRD of as-grown SnO_2 nanowires. (b) Schematic view of FET structure with an individual Ag-decorated SnO_2 nanowire.

A summary of the measured source−drain current, I_{SD}, for a Ag-nanoparticle-decorated SnO_2 nanowire is shown in Figure 2 as a function of time, at various temperatures and for various flow rates (20, 15, and 10 sccm) of ethylene added to the background oxygen stream. The oxygen flow rate was kept constant at 0.1 sccm, so as to maintain a 2×10^{-4} Torr pressure in the chamber, in the absence of ethylene. When ethylene was flowing, the overall pressure in the chamber rose by approximately an order of magnitude for the highest ethylene flows. The Ag particles, which were determined by TEM to be no larger than 3−4 nm in diameter, are found to cover the surface of the nanowire densely (Figure 2b).

The data shown in Figure 2a indicate that as the temperature, T, is reduced, I_{SD} decreases following the expected relationship $I_{SD} = I_0 e^{-E_B/k_B T}$. Plotting the logarithm of the current versus the inverse absolute temperature produces a straight line with a slope that yields the value $E_B = 0.27$ eV. This value implies that under an oxygen ambient the tin oxide nanowire acts as a semiconducting channel which displays activated conductance with activation energy ~ 0.27 eV. This value, which is approximately half the value

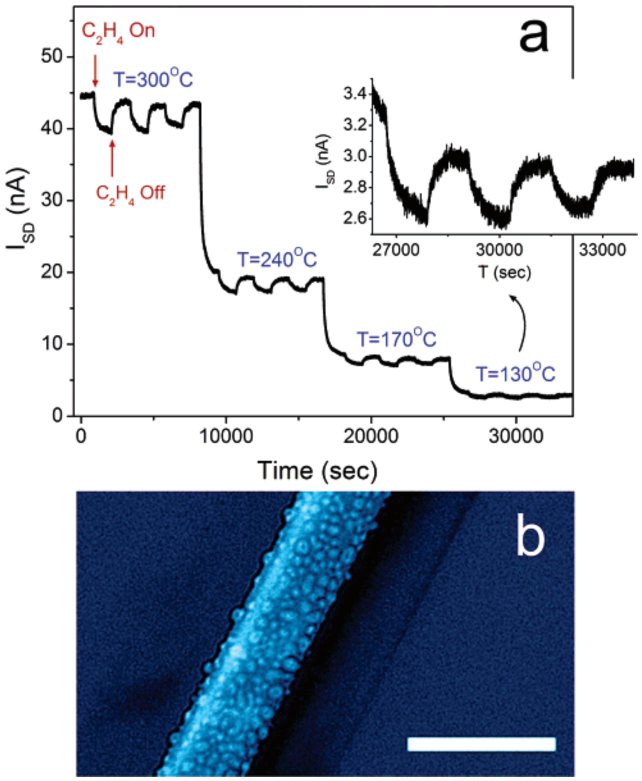

Figure 2. (a) Current response of a silver-nanopraticle-decorated SnO_2 nanowire sensor measured in an oxygen flowing atmosphere at temperatures: 300, 240, 170, and 130 °C and with ethylene flow rates 20, 15, and 10 sccm at each of the above temperatures. Inset: the magnified response curve at 130 °C. (b) TEM image of a silver-nanopraticle-decorated SnO_2 nanowire. The scale bar indicates 200 nm.

determined previously for pristine tin oxide nanowires,[3] is much lower than the ~3.6 eV band gap of bulk, stoichiometric SnO_2 due to the formation of shallow donor states resulting from surface oxygen defects.[9] This process has been thoroughly discussed in the literature.[9] The lowering of the activation energy for conduction following silver deposition might suggest that the silver nanoparticles deplete some of the tin oxide donor states, possibly by localizing the electrons on oxygen adsorbed on the silver.

Turning on the ethylene flow causes the current to decrease a little below its steady-state value under the oxygen-only ambient. When the ethylene flow was shut down, I_{SD} returned to its initial value. Repeating the experiment on different single SnO_2 nanowires gave reproducible results for the response of the system to oxygen and to ethylene. The current decrease was approximately linear in the ethylene partial pressure in the ambient stream, implying that the magnitude of current change is proportional to the ethylene concentration in the gas phase. In the absence of the Ag nanoparticles, turning on the ethylene flow at this point produced no significant change in the current for most of the nanowires investigated, although the occasional nanowire produced very small current changes upon adding ethylene to the oxygen flow. Plotting the incremental current decrease resulting from the addition of ethylene to the ambient as a function of temperature as an Arrhenius plot (Figure 3) produces a good

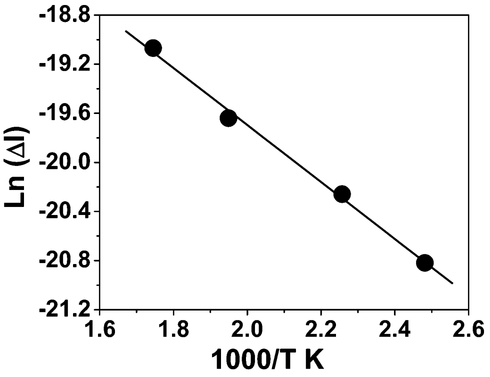

Figure 3. Arrhenius plot (Ln current changes vs inverse temperature) accompanying ethylene exposure (at a flow of 20 sccm) of an Ag-nanoparticle-decorated tin oxide nanowire.

straight line with a slope consistent with the equation $\Delta I_{Et} = \Delta I_{Et,0} e^{(-4.6 \mathrm{kcal/mol})/RT}$, in which ΔI_{Et} is the current decrement from steady state following the addition of ethylene and R is the gas constant. The fact that the current decreases when ethylene is added implies that the charge exchanges due to the chemical processes (and likely catalytic processes) occurring at surface of the silver nanoparticles affects the conductance of the tin oxide nanowire on which the nanoparticles are placed, a plausible account for which is presented below.

Placing a particle of a metal, such as silver, on the surface of a semiconductor, such as tin oxide, results in the formation of a localized Schottky junction which creates a charge depletion region in the nanowire in the vicinity of the nanoparticle (NP). The formation of the depletion region reduces the effective conductance channel through the nanowire. If the diameter of the nanowire is small enough, then even a single NP could, in principle, throttle off the current through the nanowire sufficiently to result in an observable current decrease. Consequently, a charge exchange reaction at the surface of the NP which affects the nature of the Schottky junction can result in an observable modulation of the current through the nanowire. Such an effect might seem unlikely with a metal NP on account of the large density of conduction electrons in metals; for a NP with a large enough surface-to-volume ratio, such as those used in this study, surface processes can affect the NP's electron density appreciably.

The observation of current decreases on entraining ethylene in the gas flow over the Ag-decorated tin oxide nanowire (and the absence of an effect for pristine tin oxide nanowires) suggests that the ethylene chemistry taking place on the surface of the silver nanoparticles somehow alters the electron density in the underlying tin oxide nanowire. We showed such an effect previously with Pd-decorated SnO_2 and hydrogen chemisorption.[10] In that case, however, we argued that the effect due to spill over of H atoms onto the SnO_2 surface overwhelmed the purely electronic effect due to the modulation of the Schottky depletion region that we allude to above. That is, with Pd particles decorating the tin oxide nanowire and hydrogen flowing over the system, we interpreted the changes in the observed source−drain current to be primarily due to the fact that H_2 does not adsorb efficiently on the surface of tin oxide (other than at a few defect sites) whereas H atoms readily react at many sites on the surface of tin oxide to make species such as OH groups and water. Contrariwise, H_2 dissociatively chemisorbs efficiently on the surface of Pd nanoparticles and the resulting H atoms can migrate off the Pd and onto the tin oxide support. This in turn greatly affects the conductance of the tin oxide nanowire by creating low-lying filled surface states associated with the surface hydroxyls and water.

With ethylene the opportunity for spill over is greatly reduced, since none of the plausible reaction products or intermediates that are produced from the reaction of ethylene on silver are particularly stable surface species on the major portion of the tin oxide surface.[11] We therefore suggest that the small current changes shown in Figure 2 accompanying the introduction of ethylene into the flowing oxygen ambient result from the modification of the Schottky depletion region in the tin oxide near the point of contact with the silver nanoparticle.

The process envisioned operates as follows. In the absence of ethylene (but with oxygen flowing) a steady state is established (as suggested by the constancy of the source−drain current) in which many of the surface defect states on the exposed part of the tin oxide surface are occupied by oxygen; likewise, the surface of the silver nanoparticles is saturated with chemisorbed oxygen consistent with the ambient temperature and oxygen partial pressure. The Schottky junction that is established is therefore the one that is consistent with an oxygen-saturated (rather than a bare) Ag nanoparticle in contact with the SnO_2 nanowire, its work function, and electron density. The latter is presumably lower than it would be for a bare Ag nanoparticle since the electrons localized on the surface oxide species formed would likely come from the conduction band of the metal thereby depleting the electron density in the Ag nanoparticle. On turning on the ethylene some of the surface oxygens on the Ag would be used up to form the reaction intermediate in either or both the ethylene epoxidation or the ethylene combustion reactions and a new steady state would be set up wherein oxygen and ethylene are replenished on the Ag surface in proportion to the products that desorb from the Ag surface. Accordingly, in the new steady state the Ag nanoparticle surface would be covered with oxygen and ethylene as well as a steady-state surface concentration of the reaction intermediates, all consistent with the ambient temperature and partial pressures of oxygen and ethylene. Qualitatively, one would expect that by converting at least some fraction of the adsorbed oxygen to an oxygen/ethylene reaction intermediate a few electrons would be restored to the Ag nanoparticle which, in turn, would render it more metallic thereby increasing the Schottky depletion, further reducing the source−drain current through the tin oxide nanowire.

This picture can be quantitated somewhat; although because one is observing the surface chemistry on the silver nanoparticles entirely through the intermediacy of the source−drain current of the tin oxide nanowire, one cannot say a great deal regarding the precise nature of the surface intermediates involved. Fortunately, much is known about the surface chemistry of ethylene and oxygen on Ag.[12−14] Two major processes occur on the surface of Ag catalysts. The first leads to the formation of ethylene oxide which is thought to proceed through an oxametallacyclic intermediate.[14] This is an important industrial catalytic process. The second ultimately results in the combustion of ethylene to CO_2 and water. The overall picture for the ethylene oxidation results from a great deal of experimental evidence and more recently from high-quality computation, primarily using density functional theory. A recently published energy scheme for the ethylene oxidation reaction[15] is shown in Figure 4. Although this reaction path may not be complete and some discussion continues in the literature regarding the fine points of this fascinating and complex reaction, the scheme shown in Figure 4 suffices to account for our observations. The reaction pathway begins with gas-phase ethylene and oxygen which first adsorb to form initial adsorbed species. The adsorbed species can react to form a preliminary intermediate, and then the oxametallacycle intermediate which then desorbs as ethylene oxide.[16]

Recalling that we are measuring steady-state values, the latter portion of the overall reaction, which is what our current measurements are most sensitive to, can be summarized simplistically as follows

$$\mathrm{Et_{ads}} + \mathrm{O_{ads}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k_2} \mathrm{P}$$

Assuming steady production of the product, the three species $\mathrm{Et_{ads}}$, $\mathrm{O_{ads}}$, and I, which stand for adsorbed ethylene, adsorbed oxygen, and the final surface intermediate have steady-state concentrations on the Ag surface. Specifically, for steady state in the surface concentration of the intermediate I, the following condition obtains

$$0 = \frac{dI}{dt} = k_1 \mathrm{Et_{ads}} \mathrm{O_{ads}} - (k_{-1} + k_2)\mathrm{I} \tag{1}$$

where the symbols $\mathrm{Et_{ads}}$, $\mathrm{O_{ads}}$, and I stand for both the identity and their respective surface concentrations. This should produce no confusion since the context indicates which of these two meanings is appropriate.

Equation 1 can be rearranged to produce the quasi-equilibrium condition

$$\frac{\mathrm{I}}{\mathrm{Et_{ads}}\mathrm{O_{ads}}} = \frac{k_1}{k_{-1} + k_2} \equiv K = K_\mathrm{o} \exp(-\Delta H_\mathrm{E}/k_\mathrm{B}T) \tag{2}$$

We now make a few assumptions for heuristic reasons. We assume that the surface concentration of the intermediate I is much smaller than either $\mathrm{Et_{ads}}$ or $\mathrm{O_{ads}}$. Hence

$$\mathrm{Et_{ads}} + \mathrm{O_{ads}} = S \tag{3}$$

where S is the total number of Ag surface sites available for

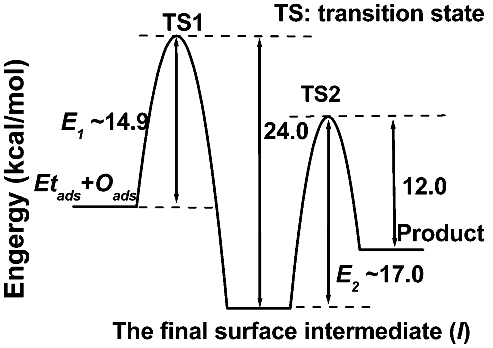

Figure 4. Reaction coordinate and putative transition states and intermediate for ethylene epoxidation on silver, based on ref 15. Energy units are kcal/mol.

either ethylene or oxygen. Substituting (3) into (2) so as to clear out Et_{ads} and solving for O_{ads}, one obtains the solution

$$O_{ads} = \frac{S + S(1 - (4I/S^2K))^{1/2}}{2} \tag{4}$$

Assuming further that the quantity $4I/S^2K$ is much smaller than unity so that the square root can be expanded, and only first-order terms are kept, one obtains the following expression

$$S - O_{ads} = \frac{I}{SK_o}\exp(\Delta H_E/k_BT) \tag{5}$$

The left-hand term in eq 5 corresponds approximately to the decrement in the surface oxygen concentration due to the addition of ethylene to the oxygen ambient, which we will assume to be proportional to the decrease in the source−drain current through the nanowire following ethylene exposure. This suggests that (at steady state) the reduction in the number of surface oxygens due to reaction with ethylene (together with the small quantity of reaction intermediate formed) results in a change in the electronic properties of the silver nanoparticles that appears as a proportional reduction in the charge depletion at the Schottky junction. This assumption is likely justified by the observation that the measured effects are small, and therefore that the correct (but unknown) function relating the charge depletion in the Schottky junction to the surface coverage on the silver particle can likely be expanded to first order without committing a large error.

Figure 3 shows that (with the above assumption) eq 5 fits the observed dependence of the current decreases accompanying the addition of ethylene, with a value of $\Delta H_E \sim -4.6$ kcal/mol. If I is identified provisionally with the oxametallocyclic intermediate, then according to ref 15 and Figure 4, k_1 is the rate constant for the process that converts $Et_{ads} + O_{ads}$ to I which has a calculated barrier of 14.9 kcal/mol.[15] The calculated rate constants k_2 and k_{-1} have barriers (Figure 4) of 17 and 24 kcal/mo,l respectively. Because the barrier to the reverse reaction (whose rate constant is k_{-1}) is so much larger than that of the forward reaction described by k_2, the denominator in the equation defining K (eq 2) is approximately equal to k_2 so that $K \approx k_1/k_2$, from which one determines ΔH_E to be -2.1 kcal/mol. The value we determine experimentally (-4.6 kcal/mol) is of the correct sign and in the right ballpark as the computed values[15] if one accepts the assumption that the results we report arise primarily from epoxidation. In view of the assumptions made, the observed agreement is reasonably good.

Although we have accounted plausibly for the observed dependence of the source−drain current through the Ag-nanoparticle-decorated tin oxide nanowire on temperature following the addition of ethylene, relating it to catalytic processes on the silver, we need to amplify our explanation for the observation that the current decreases upon ethylene addition.

The effect of the finite size of the metal and/or the semiconducting phases forming a Schottky junction on the ensuing charge depletion has been considered by several authors.[17,18] Specifically, the charge transfer to a metallic nanoparticle semi-imbedded in TiO_2 (which, as a material, displays some parallels with tin oxide) was considered in ref 18. Not unexpectedly it was shown that the charge transfer to the metal decreases with decreasing nanoparticle radius (although the charge per metal atom increases) resulting in a commensurate reduction in charge depletion in the semiconductor. Additionally, these theories predict (as is also true for Schottky junctions between bulk phases) that as the work function of the metal decreases the electron depletion in the nanowire is reduced.

Because the chemisorption of oxygen on a silver particle localizes electrons on the adsorbate that had previously been conduction electrons in the tin oxide, a silver particle covered by a layer of adsorbed oxygen will act either as a particle with a smaller radius than the pristine Ag particle or as a particle with a lower work function or both. Consequently, exposure to ethylene, which is expected to reduce the quantity of adsorbed oxygen by virtue of the ensuing surface reaction, will bring about an effect which appears as an increase the effective radius either of the Ag particle or of its work function or both. This will, in turn, increase the charge depletion in the tin oxide nanowire resulting in a decrease in the current flowing through it, as observed.

Conclusions. Conductometric measurements were performed on single tin oxide nanowires with and without Ag nanoparticle surface decoration, in flowing oxygen into which ethylene was mixed at various concentrations. In the absence of Ag surface decoration (but in the presence of oxygen) the introduction of ethylene into the gas flow produced virtually no conductance change. When decorated with Ag, the current through the tin oxide nanowire decreased approximately proportionately to the ethylene partial pressure. The results are explained in terms of the establishment of a Schottky junction between the Ag nanoparticles and the tin oxide nanowire with an associated charge depletion in the tin oxide and the consequent modulation of that charge depletion resulting from chemical processes involving ethylene and oxygen occurring on the silver nanoparticles' surface.

The temperature dependence of the ethylene-induced current decrements follows an Arrhenius form. Interpreting this result to reflect the steady-state concentration of ethylene, oxygen, and a surface intermediate that ultimately leads to ethylene oxide, one calculates the enthalpy for the production of the reaction intermediate to be approximately −4.6 kcal/mol, which is of the correct sign and of the right order of magnitude as the calculated value reported for the formation of the putative ethylene oxametallacycle intermediate in the ethylene epoxidation reaction.[15] While our results cannot be ascribed unequivocally to the formation of that intermediate, they illustrate how fundamental catalytic processes occurring at metal nanoparticle surfaces can be investigated conductometrically, by using oxide nanowires as metal particle supports, and point to the plausibility that configuring the decorated nanowire as field-effect transistors could lead to a device in which the catalytic process may be modified by applying an appropriate gate potential.

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