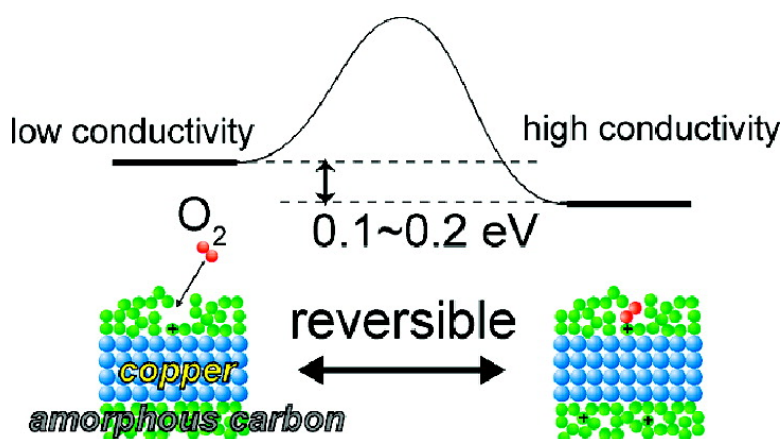## Communication

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Increased Electric Conductance through Physisorbed Oxygen on Copper Nanocables Sheathed in Carbon

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Adsorption of molecules onto solid surfaces can be classified into physisorption and chemisorption according to the binding energy.[1] Physisorbed molecules are so weakly bound to surfaces that adsorption and desorption can proceed reversibly even at room temperature. By contrast, chemisorption is accompanied by chemical bond formation, and higher temperatures are necessary for desorption in order to break the chemical bonds. Solid gas sensors, which are operated at high temperature,[2c,d] are normally based on chemisorption for modification of the electronic band conduction. Oxygen (O_2) is one of the most important gases related to combustion, respiration, oxidation reactions, and so on. Thus, sensing of O_2 has been widely investigated.[2] Recent advances in nanotechnology allow O_2 sensors to work at lower temperatures.[3] Here we show that copper nanocables sheathed in carbon can detect physisorbed O_2 at room temperature by just measuring electric resistance. The measurement of conductivity as a function of temperature and electron spin resonance (ESR) spectroscopy revealed that physisorbed O_2 activates localized holes in the copper acetylide (C_2Cu_2) nanocables into conductive hopping states.

C_2Cu_2 nanocables consist of metallic Cu nanowires sheathed in amorphous carbon layers. It is very simple to produce a sensor using C_2Cu_2 nanocables. The fabrication method for C_2Cu_2 nanocables, which involves bubbling acetylene (C_2H_2) gas into an ammonia solution of copper chloride (CuCl), has been described in detail elsewhere.[4] When the C_2H_2 reacts slowly, C_2Cu_2 molecules can self-assemble into nanowires 5 nm in diameter. Annealing of the precipitate at 80−90 °C for 1−5 days in vacuum transforms the C_2Cu_2 nanocables via a segregation reaction into elemental copper and carbon.[4a]

Figure 1a shows the transient conductivity on the C_2Cu_2 nanocables obtained by alternately exposing the nanocables to pure O_2 (100 kPa) and pure N_2 (100 kPa) gas. The conductance more than doubled during the 15 min O_2 exposures and recovered reversibly during the subsequent N_2 exposures. It must be noted that the reversible fluctuations in conductance were observed at room temperature. The fact that pumping out O_2 atmosphere and exposing to N_2 gas decreased the conductance in a similar fashion suggests that O_2 adsorption and desorption at room temperature influence the conductivity of the C_2Cu_2 nanocables. Detection of gas by a typical metal-oxide semiconductor is based on chemisorbed molecules. An O_2 molecule adsorbs on the surface by trapping an electron from the conduction band of the semiconductor. The presence of the charged species changes the semiconductor's Fermi level and the conduction of carriers.[5] However, reversible absorption and desorption cycles at room temperature are generally believed to involve physisorption of molecules. Physisorption of O_2, which is not accompanied by charge transfer, is extremely unlikely to modify the electronic band structure for sensing by conductance.

Conductance fluctuates during the 15 min gas exposures, as shown in Figure 1a. The conductance of the C_2Cu_2 nanocables reached a steady state in several hours. Surprisingly, the sensitivity
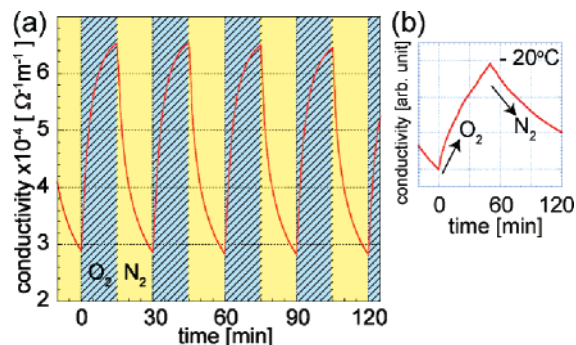

Figure 1. Reversible changes in C_2Cu_2 nanocable conductivity at (a) room temperature and (b) −20 °C. The resistance of the C_2Cu_2 nanocables decreased under O_2.

difference between the maximum and minimum stabilized conductance is more than 10 times for the C_2Cu_2 nanocables (Figure S1). The conductivity, sensitivity and responsivity depend upon the annealing conditions for the conversion to the C_2Cu_2 nanocables. The typical sensitivity of the C_2Cu_2 nanocables ranges between 2 and 20 times. It was reported that the conductance of carbon fibers decreases by 13% from vacuum to O_2 exposure.[6] The change in reversible resistance between air and vacuum for carbon nanotubes at room temperature is just 10−15%.[3a] The conductance changing by more than 10 times indicates an advantage for higher sensitivity in the C_2Cu_2 nanocable sensor.

In the steady state for conduction, a chemical equilibrium should be reached for O_2 adsorption/desorption reactions. When the chemical equilibrium of O_2 adsorption onto the C_2Cu_2 nanocables is analyzed, it is found that the O_2 partial pressure dependence of the conductance can be roughly fitted with the Langmuir's adsorption isotherm formula:[1,7]

$$\sigma/\sigma_0 = 1 + 13.9 \times bP/(1 + bP)$$

where σ/σ_0 is the relative conductance, P is the partial pressure of O_2, and b is a constant equal to 0.047 kPa^{-1}. This formula can be derived from a simple adsorption model between gas-phase molecules and adsorption sites of the solid. This means that a certain number of adsorbed sites exist for the changing conductance.

The heat of adsorption can be calculated by the temperature dependence of the rate constants of the simple adsorption reaction. Figure 1b shows the sensor sensitivity of the C_2Cu_2 nanocables in a freezer at −20 °C. Remarkably, reversible conductivity changes could be observed at such a low temperature. This clearly demonstrated that physisorbed O_2 affects the conductance of C_2Cu_2 nanocables. The reaction rate at −20 °C was much lower than that at room temperature. It should be noted that both the adsorption and desorption kinetics slowed down considerably. This means that there was a significant activation barrier for not only O_2 desorption but also O_2 adsorption. O_2 molecules were presumably trapped
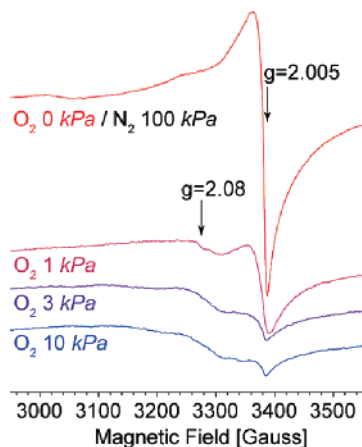
Figure 2. Variations in the ESR spectra with O_2 partial pressure. In the absence of O_2 gas (0 kPa), a sharp peak was observed at $g = 2.005$. When the C_2Cu_2 nanocables were exposed to O_2 gas, the peak at $g = 2.005$ weakened and a new broad peak emerged around $g = 2.08$ as a result of the adsorption of O_2 molecules.

completely in the amorphous carbon layers. The heat of adsorption, subtraction of the adsorption barrier from the desorption barrier by the Arrhenius plot of rate constants, could be calculated at less than 0.2 eV (20 kJ mol^{-1}), which can be assigned to a slightly high physisorption energy.[1]

The temperature dependence of conductance was investigated to determine the energy dynamics of the conductive carriers. Thermoelectric power measurement indicates that hole carriers play the dominant role in electrical conduction (Figure S2), and the temperature dependence of conductivity (Figure S3) obeys the Mott three-dimensional variable-range hopping equation closely:

$$\sigma = \sigma_0 \exp\{-(T_0/T)^\gamma\}, \gamma = 1/4$$

As in a disordered system,[8] the electric states of holes in the C_2-Cu_2 nanocables are localized in the band gap. Conduction occurs by hopping with phonon-assisted tunneling between electric localized states centered at different positions. Thus, the temperature dependence of the conductance differs from that of a conventional activated semiconductor ($\gamma = 1$). The hopping conduction of localized carriers in the C_2Cu_2 nanocables contrasts with the band conduction of typical metal-oxide semiconductors used for gas sensing, where the chemisorbing gas molecules interact with electrons in the conduction and valence bands.[5]

ESR spectroscopy is one of the most powerful tools to probe a localized carrier having an unpaired electron. Figure 2 demonstrates the ESR spectra of freshly annealed C_2Cu_2 nanocables under various O_2 partial pressures. In the absence of O_2 gas, a sharp, slightly asymmetric peak was observed at $g = 2.005$. When the C_2Cu_2 nanocables were exposed to O_2 gas, the ESR signal decreased dramatically. Instead of the peak decrease at $g = 2.005$, an additional broad peak appeared around $g = 2.08$. Under the O_2 atmosphere, the ESR signals broaden because of the spin dipole–dipole interaction.[6] However, the decrease at $g = 2.005$ is much more marked than the peak broadening induced by the O_2 spin interaction. Thus, we conclude that O_2 adsorption transformed the ESR peak at $g = 2.005$ into the broad $g = 2.08$ peak. The asymmetry of the peak at $g = 2.005$ was actually enhanced by O_2 adsorption. This is explained by overlapping unresolved ESR peaks transforming from $g = 2.005$ to $g = 2.08$.

The change of the ESR pattern in Figure 2 is reflected by the conductance increase. The relationship between the changes in the conductance and the ESR signal show that the spin states at $g = 2.005$ are not related to hopping conduction. On the other hand, the spin states at $g = 2.08$ are linked to the conductivity and should be localized but accessible to another localized state by hopping conduction. The coexistence of the two spin states is consistent with the Langmuir's adsorption isotherm model.[7] The vacant sites correspond to the spin states at $g = 2.005$, and the O_2 adsorption produces the occupied sites observed as a broad peak around $g = 2.08$ in the ESR measurement. The shift of the g value in ESR suggests that O_2 adsorption perturbs the chemical environment of the pre-existing spins in the C_2Cu_2 nanocables. Hopping conduction can be strongly influenced even by small changes in the orbital energy and/or spatial dimension of localized states.[8a] Thus, the weak interaction of O_2 on the C_2Cu_2 nanocables can greatly enhance the hopping conductance.

Hopping is one of the most important conduction mechanisms in nanomaterials, where charge carriers are localized in individual nanoislands. Many metal-oxide nanomaterials have been fabricated for gas sensors owing to their large surface-to-volume ratio. However, most of these are based on chemisorption of gas molecules modifying electrons in conduction and valence bands. There is no significant difference between nanomaterials and bulk-sized sensors in terms of the sensing principle. The present O_2 sensor can open an avenue for the detection of physisorbed gaseous molecules through nanospecific hopping conduction. This different mechanism enables the operation of C_2Cu_2 nanocables at extremely low temperature.

Supporting Information Available: Figures S1−S3 and a description of the experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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