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Reversible strain by physisorption in nanoporous gold

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Reversible strain amplitudes up to 0.02% in response to a 15% change in relative humidity were detected in nanoporous gold. We show that the mechanism involved in dimensional changes during physisorption is associated with changes in the surface stress when molecules are adsorbed from the vapor phase onto the metal interface. © *2011 American Institute of Physics.*
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Two types of vapor adsorption strains have been reported in nanoporous materials:[1,2] (1) at low coverage, reversible dimensional changes associated with changes in the adsorbate surface stress via van der Waals interactions and (2) at high coverage up to capillary condensation, dimensional changes associated with changes in the surface tension of the condensed liquid into the pores. This letter is aimed at showing that reversible strain amplitudes up to 0.02% in response to a 15% change in relative humidity were detected in nanoporous gold. In addition, we show that the dimensional changes attained during physical adsorption can be amplified using a bilayer strip configuration.[3,4] Further, it is shown that the physisorption strains are associated with changes in the adsorbate surface stress, rather than with capillary condensation.

A direct consequence of the high surface area-to-volume ratio for nanoporous metals is the macroscopic change in volume in response to changes in their surface stress,[5,6] i.e., the stress state at the ligaments-pores interface. These changes in the surface stress are usually driven by the electric charge transfer, either during ions electrosorption at the ligaments-electrolyte interface[5] or during chemisorption of atoms at the ligaments-gas interface.[6] The chemisorption process involves the irreversibly adsorption of gas molecules at the metal interface and the formation of reaction products, some of which are not always desirable. We have exploited the physical adsorption process, i.e., the reversible adsorption of gas molecules onto a solid surface, to achieve reversible dimensional changes in bulk nanoporous gold. Although the physical adsorption process initially involves the formation of a monolayer of adsorbate, extended adsorption of molecules from the gas phase onto the interface of nanoporous materials usually results in filling of the pores with condensed liquid, a phenomenon known as capillary condensation, which is also susceptible to give rise to pores expansion or contraction.[1,2]

Capillary condensation in the pores was investigated on bulk nanoporous gold samples with dimensions $\sim 2 \times 1 \times 1$ mm^3, synthesized by selective dissolution of silver from gold-silver alloys[7,8] with composition Au$_{25}$Ag$_{75}$ (at. %). A typical bi-continuous structure of a synthesized nanoporous gold sample is displayed by the scanning electron micro-

graph of Figure 1(a). Synthesized specimens have an average ligament diameter of ~ 20 nm, a porosity of $\sim 77\%$, and a specific surface area of ~ 10 m^2 g^{-1}, as deduced from a recent model for the determination of the specific surface area of nanoporous materials, based on their average ligament size.[8] The corresponding specific surface area-to-volume ratio is ~ 192 m^2 cm^{-3}. In our work, we exploit the polar water vapor molecules present in ambient air to cover the ligaments surface and by that way we generate changes in the surface stress. Although the enthalpy of condensation (-40.7 kJ mol^{-1}) and evaporation (40.7 kJ mol^{-1}) of water are equal, a characteristic of the physical adsorption process is the change in the Gibbs free energy, when water molecules interact with the ligaments surface. This change in free energy is associated with the loss (gain) of entropy during condensation (evaporation) and represents the input energy for dimensional changes.

Dimensional changes in the synthesized nanoporous gold were achieved by exposing a specimen to ambient air, and tuning the water vapor pressure in the pores by alternation of dry and humid air at constant temperature. At standard atmospheric conditions, water molecules are characterized by their dynamic equilibrium between the liquid and gas states. When the relative humidity is increased (exposure to humid air) or decreased (exposure to dry air) at constant temperature, a phase transition occurs and adsorption (desorption) takes place[9,10] at the ligaments-vapor interface, due to the permanent electric dipole moments[11] of water molecules. This reversible adsorption process gives rise to reversible changes in the surface stress and subsequently to reversible dimensional changes. Figures 1(b) and 1(c) display changes in the relative humidity as a function of the time (blue curves) and the corresponding dimensional changes (red curves) for long times exposure (~ 300 min per cycle) and short times exposure (~ 37 min per cycle), respectively. Dimensional changes up to 0.02% are measured when the ambient air relative humidity is lowered from $\sim 53\%$ to $\sim 36\%$.

As aforementioned, extended adsorption of water molecules from the vapor phase usually results in multilayer and meniscus formation, followed by the filling of the pores with condensed water. Therefore, the water content in the pores and the corresponding adsorbed-layer thickness were determined during desorption experiments. *In-situ* isothermal changes in mass of each nanoporous gold sample was

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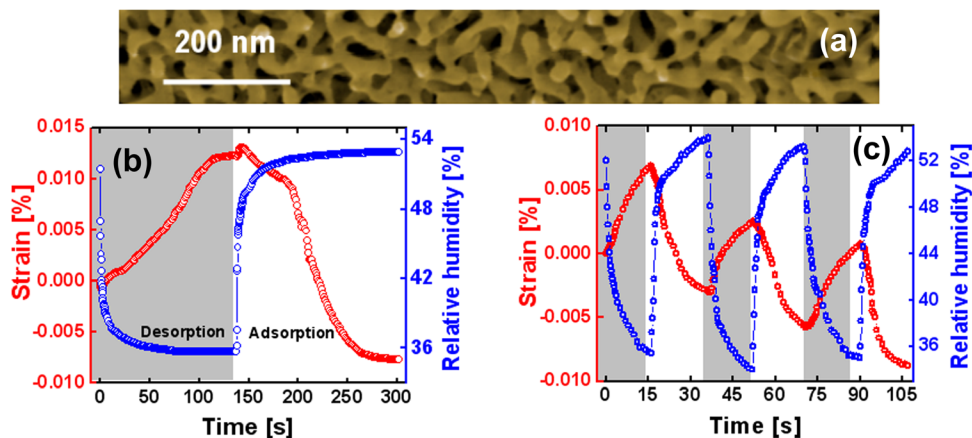
FIG. 1. (Color online) (a) Scanning electron micrograph of nanoporous gold synthesized by dealloying process. Ligament diameters are about 20 nm. (b) Changes in relative humidity versus time for short alternations of dry and humid air (right ordinate, blue curve) and corresponding strain versus time (left ordinate, red curve). (c) Changes in relative humidity versus time for long alternations of dry and humid air (right ordinate, blue curve) and corresponding strain versus time (left ordinate, red curve).

measured, when a specimen was brought from a relative humidity of ~47% to a lower relative humidity of ~25% in the measuring chamber of an ultra-precise microbalance. Figure 2(a) displays measurements of the loss of weight performed independently on three different samples (left ordinate) and the corresponding dimension changes under similar conditions (right ordinate). The recorded loss after 10 min is up to ~30 μg. The corresponding adsorbed-layer thickness deduced from the specimen specific surface area is ~0.3 nm (~1 monolayer of water). The thickness of the water layer in the pores is very small compared to the average pore size (~20 nm), meaning that the measured dimensional changes are not associated to the filling of the pores with condensed water.

The maximum water content inside the pores of each sample was determined. This maximum loss of weight for each specimen evaluated from thermogravimetric analysis (TGA) was found to vary between ~70 μg and ~90 μg as shown in Figure 2(b). The water content corresponds to ~5.8% of the total void space of a specimen. The low water content clearly indicates that the pores are not filled under our experimental conditions. Therefore, possible meniscus formation can only be local and not representative for the entire porous network. This means that the dimensional changes due to capillary condensation can be neglected.

The interaction between the adsorbed water film and the gold surface can be quantified by the excess pressure in the wetting water film, generally known as the Derjaguin's disjoining pressure.[12–15] Knowing the relative vapor pressure at the begin (RH$_1$ ~ 36%) and at the end (RH$_2$ ~ 53%) of each adsorption experiment as displayed in Figures 1(b) and 1(c), the disjoining pressure Π between these two equilibrium states can be evaluated by:[12–14]

$$\Pi = -\frac{RT}{V_m} \ln\left(\frac{RH_1}{RH_2}\right),\qquad(1)$$

where R is the gas constant (8.3 J K^{-1}mol^{-1}), T is the temperature (293 K), V$_m$ is the molar volume of water (18 mL.mol^{-1}). Equation (1) gives a change in disjoining pressure of Π ~52 MPa. The change in disjoining pressure Π was compared to the change in pressure ΔP from the Hooke's law of elasticity, required to generate the measured dimensional changes.[5,6]

$$\Delta P = K \frac{\Delta V}{V}.\qquad(2)$$

In Eq. (2), K represents the bulk modulus (180 GPa for gold), $\Delta V/V$ is the volumetric strain. For an isotropic material, $\Delta V/V = 3\ \Delta L/L$; where $\Delta L/L$ is the measured linear strain amplitude which is in the order of 0.01% (See Figures 1(b) and 1(c)). The change in pressure associated to that strain is $\Delta P \sim 54$ MPa. ΔP and Π are very comparable. This indicates that the measured dimensional changes are generated by surface forces associated to the interactions of the
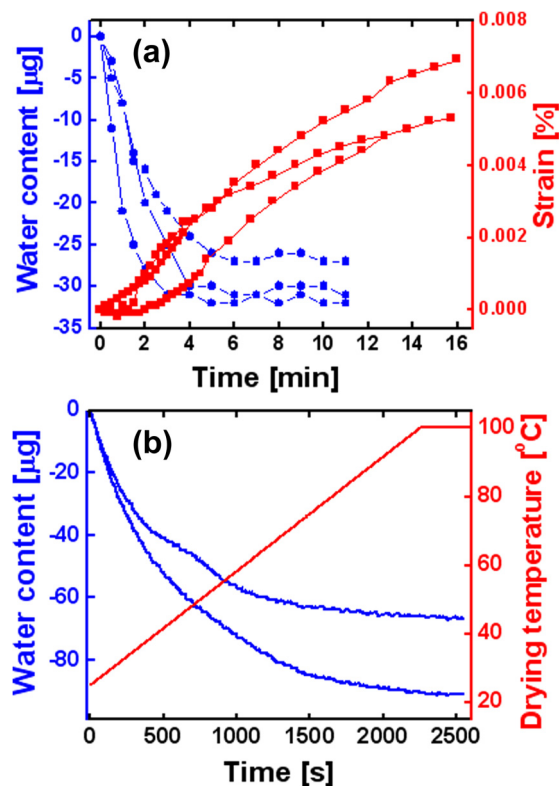

FIG. 2. (Color online) (a) Isothermal mass loss during desorption experiments, performed independently on 3 different nanoporous gold samples using an ultra-precise microbalance. When the relative humidity decreases from ~47% to ~25%, specimens release ~30 μg water (left ordinate, blue curve). Changes in dimension of a specimen under similar conditions (right ordinate, red curve). (b) Investigation of the maximum water content in the pores by TGA. Each specimen releases 70 to 90 μg water (left ordinate, blue curve), when the temperature is increased from 20 °C to 100 °C at a rate of 2 °C per minute (right ordinate, red curve).

adsorbed water film with the metal surface. The corresponding mean change in the surface stress $\langle \Delta f \rangle$ associated to measured strain amplitudes of $\sim 0.01\%$ was computed from the generalized capillary equation of solids[16,17] that relates the mean change in pressure $\langle \Delta P \rangle$ on an arbitrary microstructure to its mean change in surface stress $\langle \Delta f \rangle$:[5,6]

$$3V\langle \Delta P \rangle = 2A\langle \Delta f \rangle. \qquad (3)$$

In Eq. (3), V and A are the volume and interface surface area of the nanoporous gold. The mean change in the surface stress was found to be $\langle \Delta f \rangle \sim 0.3$ N m^{-1}. This value is comparable to the one reported during double-layer charging experiments at a gold-electrolyte interface.[18] Indeed, a measured strain of 0.02% in the capacitive charging interval was associated to a mean change in the surface stress of 0.5 Nm^{-1}. This proportionality between changes in the surface stress and changes in dimension provides supplementary confirmation that the measured dimensional changes are associated to the specific properties of the adsorbent surface, including changes in its surface stress during adsorption.

During physical adsorption, sample displacements up to 200 nm were measured over a sample size of 1 mm. This corresponds to strain amplitudes up to $\sim 0.02\%$, which is relatively small compared to the $\sim 0.1\%$ (or higher) measured during ions electro-adsorption or chemical adsorption. Nanoporous gold samples with bulk volume $\sim 2 \times 1 \times 1$ mm^3 were used to achieve these displacements. This suggests that a porous bulk volume of about $50 \times 1 \times 1$ mm^3 will be required for larger displacements up to 10 μm. Using a large volume of material to achieve large displacements is not efficient. Here, we address this drawback by showing that one can use a relatively smaller porous bulk volume of ~ 4 mm^3 to achieve sample displacements up to 10 μm during physical adsorption. This is done by exploiting a bilayer strip configuration to enhance the displacements.[3,8] A 60 mm-long and 20 μm-thick bilayer strip was made. This cantilever consists of a thick nanoporous gold layer (~ 14 μm) with porosity $\sim 85\%$ and a thin solid gold layer (~ 6 μm). A reversible cantilever bending was measured when the relative humidity was alternately varied between $\sim 33\%$ and $\sim 55\%$. The red curve in Figure 3 displays the typical cantilever displacements, measured at half-way (30 mm) from the cantilever edge. The reversible displacement at that point is about 5 μm (see red curve in Figure 3), when the relative humidity varies between $\sim 33\%$ and $\sim 55\%$ (See blue curve Figure 3). The corresponding displacement of the cantilever edge is ~ 10 μm. This indicates that larger displacements are achievable during physical adsorption-induced dimensional changes.

In summary, we have shown that it is possible to generate and control reversible macroscopic dimensional changes in nanoporous gold specimens exposed to ambient air by varying the water vapor content in air. The very small thickness of the water layer in the pores compared to the average size of the pores, the low water content in the pores compared to the total void space, and the value of the change in the surface stress during physical adsorption indicate that the
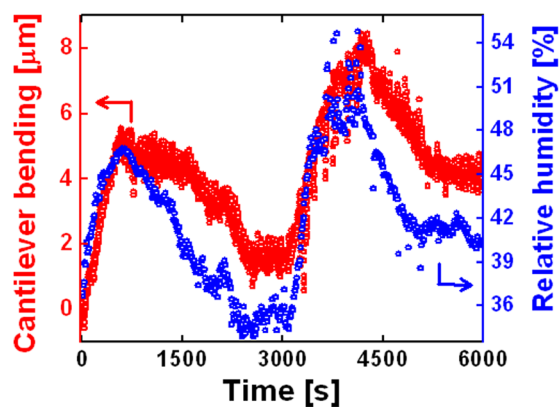

FIG. 3. (Color online) Bending of a bilayer gold foil (left ordinate, red curve) upon variation of the relative humidity (right ordinate, blue curve). The bilayer with a total thickness of 20 μm consists of a thick nanoporous gold layer and thin solid gold layer.

dimensional changes are associated to changes in the ligaments surface stress during adsorption. In addition, we have shown that the sample displacements can be enhanced using a bilayer strip configuration.

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