

Surface-Stress Induced Macroscopic Bending of Nanoporous Gold Cantilevers

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ABSTRACT

We report the preparation of composite foils consisting of two layers, one solid gold and one nanoporous gold. Tip displacements of several millimeters are observed when the foils are immersed in aqueous electrolytes and the electrochemical potential varied. This suggests that nanoporous metals could be used as the active component in actuators, and it demonstrates for the first time that changes in the surface stress f of the metal–electrolyte interface can induce a macroscopic strain, orders of magnitude larger than the amplitudes which are reached in conventional cantilever bending experiments used to measure f .

Changes of the shape of liquid mercury electrodes in response to changes of the electrical potential have been observed as early as the 19th century. In 1872, Gabriel Lippmann invented his capillary electrometer in which small voltage differences can be measured by observation of the displacement of a mercury meniscus. The Lippmann equation relates the surface tension of a liquid electrode to the electrode potential, and it is also a good approximation for solids.¹ However, the surface stress f of a solid is not even approximately equal to its surface tension γ , and it exhibits a different (generally, stronger)² dependence on the potential.¹ Furthermore, due to the stiffness of solids, potential-dependent changes in the position or shape of solid surfaces are much smaller than those of liquid electrodes. Highly sensitive extensometers³ were used to monitor the strain, and in the past decade, surface stress changes have been measured using atomic force microscope type techniques: thin metal films on the cantilevers are used as electrodes, and techniques as, for instance, laser beam deflection allow the tip displacement (in the lower nanometer range, e.g., in ref 4) induced by changes in the surface stress to be measured.^{5–10} Because the surface stress in solids could hitherto only be detected in a laboratory environment using sophisticated equipment, it might be considered as an “exotic” phenomenon of little practical relevance. Even in thin film growth, where the

interface-induced stress may be large, its importance remains the subject to current research.¹¹

More recently, surface stress induced length changes of 1.5 μm have been observed in nanoporous mm-sized platinum cubes, an indication that the capillary effects can be enhanced by increasing the surface-to-volume ratio α ,¹² which takes on exceptionally large values in porous nanostructures. Since the pressure in the bulk required to balance the surface stress scales with α independent of the geometry of the microstructure,¹³ large volume changes and a considerable mechanical work density result from changes in the surface stress of the nanoporous metal.¹² Therefore, it has been suggested that such materials may be attractive for use as actuators.¹⁴ However, integration of the porous metal into a device requires that it can be precisely and reproducibly shaped, and that it can be bonded to the parts of the device that transmit displacement and load. It has not been demonstrated so far how this can be achieved using nanopowder compacts; furthermore, while powder compacts support a considerable hydrostatic pressure, their resistance to shear stress may be poor. Here, we show that nanoporous metals prepared by dealloying a bulk solid solution exhibit similarly large strain amplitudes as nanopowder compacts, and that the porous material can be joined to solid metal foils to form a composite cantilever beam actuator. The charge-induced expansion or contraction of the porous metal gives rise to a biaxial stress component that results in a large bending of the foil. In this way, the effect of the interface-induced stress is amplified so that the deflection becomes visible to the naked eye: the tip moves by 3 mm, an increase

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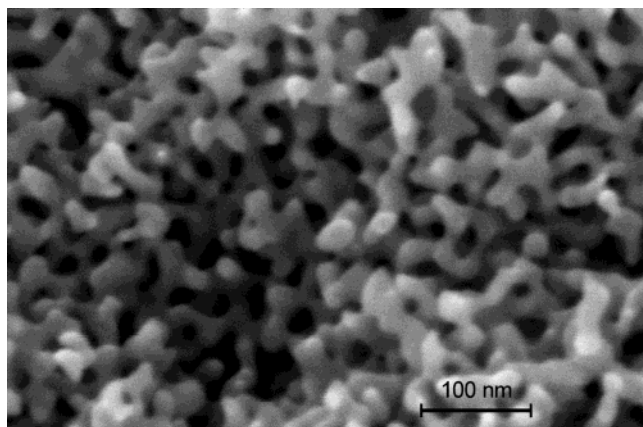


Figure 1. Scanning electron micrograph of the nanoporous gold structure obtained by etching silver–gold alloy in perchloric acid.

by the factor 10^6 compared to previous cantilever bending experiments using a planar surface. This demonstrates that changes in the surface stress of nanoporous metals can be exploited to do work in cantilever bending, analogously to what was recently reported for carbon nanotubes,¹⁵ vanadium oxide nanofibers,¹⁶ and conducting polymers.¹⁷

Dealloying, the selective dissolution of the less noble component from a solid solution, is well-known to result in nanoporous structures.¹⁸ Dealloying is attractive as a technique for preparing nanoporous solids since it can be applied irrespective of the shape of the active part of a device – including, conceivably, lithographically shaped miniaturized

components. Our samples were obtained by the dealloying of $\text{Ag}_{75}\text{Au}_{25}$ master alloy sheets (see Methods). Figure 1 shows a scanning electron microscopy image of the nanoporous gold microstructure. The ligament size is ca. 20 nm.

Cuboids of porous gold of dimension $1.2 \times 1.2 \times 1 \text{ mm}^3$ were investigated in a commercial dilatometer equipped with an in-situ electrochemical cell. Figure 2A is the cyclic voltammogram (current vs potential curve) of a nanoporous gold sample immersed in 50 mM sulfuric acid, recorded in-situ in the dilatometer cell. The potential limits are given by the onset of hydrogen evolution (ca. -0.25 V) and gold oxidation (above 1 V). The voltammogram in Figure 2A is typical of a polycrystalline gold surface: The current is almost constant over the entire potential range, indicating a continuous capacitive double-layer charging and discharging, in agreement with the known tendency of SO_4^- anions to interact only weakly with Au.¹⁹

Figure 2B shows the change ΔL in sample length versus the time as the potential is cycled between -0.26 and $+1.05 \text{ V}$ in 50 mM H_2SO_4 . The length changes periodically and reversibly with the potential, with a small irreversible shrinking superimposed to that. When the reversible part of ΔL is plotted versus the potential (Figure 2C), it is apparent that the length of the sample can be changed reproducibly by controlling the potential, with a small hysteresis of 0.1 V (or $0.02 \mu\text{m}$). The charge was obtained by integration of the current of Figure 2A and by setting the potential of zero charge (pzc) to 0.25 V [compare ref 20]. The graph of strain versus charge (Figure 2E) is highly reversible and linear both

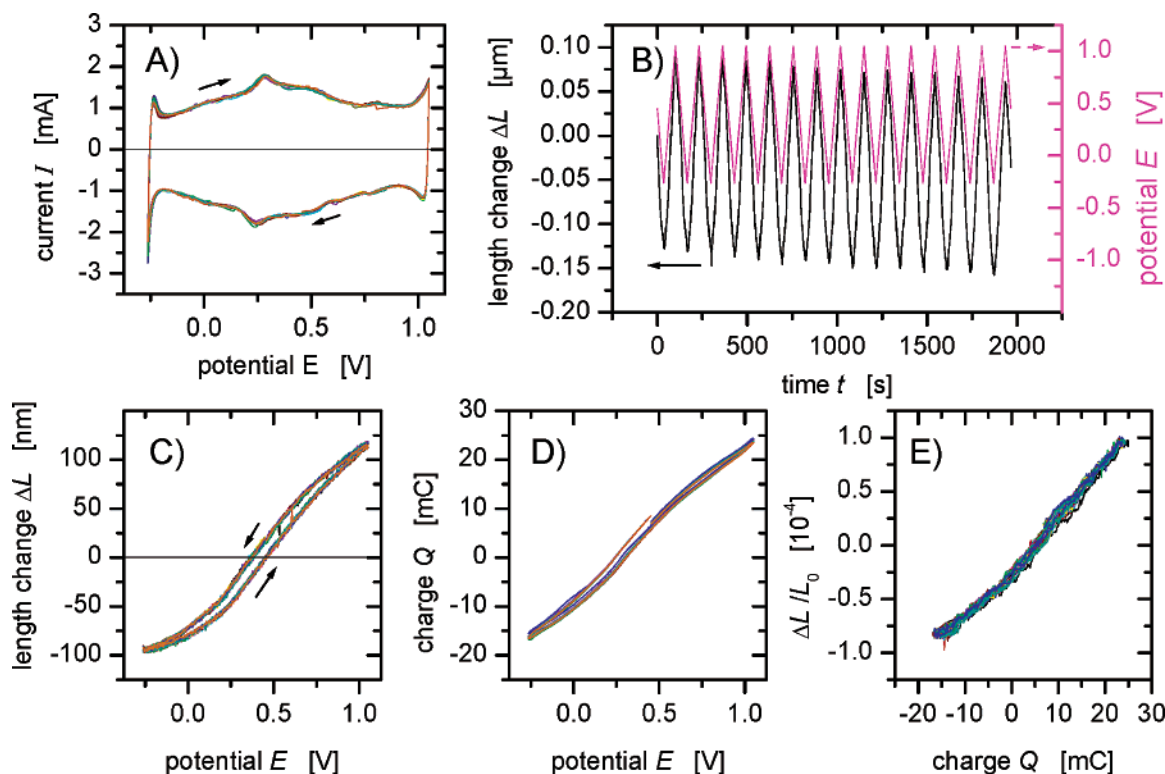


Figure 2. In-situ dilatometry using 15 successive cycles of the potential of a cuboid nanoporous gold sample in 50 mM sulfuric acid. (A) Cyclic voltammogram (current I versus the electrochemical potential E). (B) Length change ΔL versus time t during the 15 cycles of (A). (C) Reversible part of ΔL versus E , obtained by subtraction of a constant arbitrary value for each cycle. (D) Total charge Q versus E . (E) $\Delta L/L_0$ versus Q . (A) and (C)–(E) display results of all 15 cycles superimposed.

in the negatively and positively charged regimes; it exhibits a change in slope near the pzc. A similar linear correlation has been observed for a Au(111) surface by STM,^{21,22} but the break near the pzc of Figure 2E was not resolved there.

It is a matter of debate in how far the potential dependence of the surface stress reflects the details of the bonding of adsorbates to the surface (see ref 10 and references therein). We have carried out experiments using perchloric acid as the electrolyte, and found the results to be in qualitative agreement with Figure 2 (see Supporting Information). Since the ClO_4^- ion adsorbs even more weakly than SO_4^{2-} , this finding is compatible with the notion that the potential-induced strain does not intrinsically require the formation of the chemical bonds involved in specific adsorption; this would imply that the change in surface stress reflects the modified bonding in the space-charge layer within the metal surface.^{2,12} Two further observations in support of this notion are: (i) whereas we find Au to contract at negative potential, carbon nanotubes show the opposite effect, expansion upon negative charging,¹⁵ which indicates that the change in surface stress is strongly related to the nature of the bonding in the solid; and (ii) in-situ X-ray adsorption near edge spectroscopy (XANES) data show a significant change in d-band occupancy in Pt nanoparticles as the Pt-electrolyte interface is charged, confirming that the superficial electronic structure of the solid can be changed.²³ If the change in surface stress and the surface-induced strain in our samples are indeed a consequence of the modified bonding in the metal, then the results provide support for a more general concept:²⁴ by controlling the net charge in space-charge layers at metal surfaces, one can modify the electronic density of states and, thereby, the local properties of the matter at the surface. In nanomaterials, which have a large surface-to-volume ratio, this will result in changes of the overall properties, opening a way for tuning all those materials properties that depend on the density of states.

The action of the surface stress can be amplified by use of bilayer foils. Each of the foils consists of a layer of porous Au bonded to a layer of solid Au, see the cross-sections in Figure 3A. When the foil is immersed in an electrolyte, and its potential varied, then the porous layer will tend to expand or contract, whereas the solid layer will tend to maintain its dimensions. This will result in shear stress at the interface between the two layers, and in a bending of the foil, quite analogous to the effect of the differential thermal expansion used in bimetal thermometers. A similar arrangement has also been used to produce carbon nanotube actuators.¹⁵

To make the bilayer foils, a 2 mm thick sheet of silver–gold alloy was cold-welded to a 0.5 mm thick sheet of pure gold by rolling. After reducing the thickness of the stack to 30 μm by further rolling, the resulting foil was annealed for stress relief and strips 35–40 mm long and 2 mm wide cut from it. Dealloying resulted in a composite foil consisting of a 6 μm thick layer of solid Au covered with 24 μm of porous Au. Two foils were immersed in 1 M HClO_4 and wired as the working and the counter electrodes, respectively. Figures 3A and 3B show a schematic drawing and a photograph of the experimental setup. Both foils undergo a

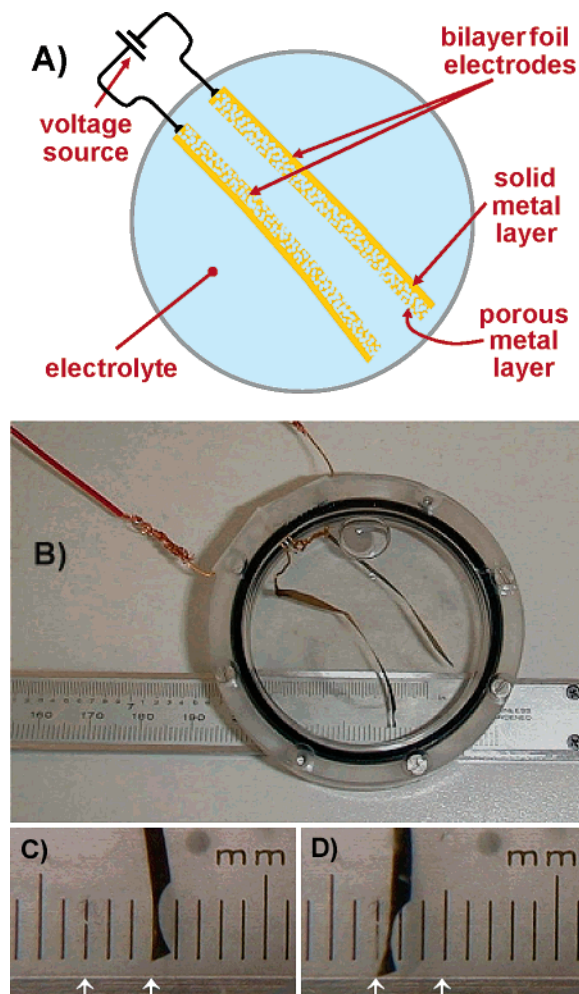


Figure 3. Illustration of the operation of the composite foils. (A) schematic cross-section through an electrochemical cell comprising two identical foils that serve (interchangeably) as working electrode and counter electrode. (B–D) photographs of an electrochemical cell with two bimetallic stripes (nanoporous gold on gold), similar to the schematic in (A). The electrolyte is 1 M perchloric acid. The lower scale of the ruler is calibrated in mm. (C, D) Two enlarged views of the cell in (B), showing the tip of one of the foils with two different voltages applied between the two foils, +1 V (C) and –1 V (D). It is seen, that when the voltage is inverted, the tip moves by ca. 3 mm. The arrows serve as reference markers, emphasizing the tip displacement.

reversible bending as the voltage is changed. Figures 3C,D show enlarged views of the tip of one of the foils before and after inverting the applied voltage. When the potential difference between the electrodes is switched from –1 V to +1 V, the tip moves by as much as 3 mm. Thus, compared to cantilever bending experiments using planar surfaces, the displacement resulting from surface stress changes has increased from few nanometers to the millimeter regime, that is, by about a factor of 10^6 . A video clip showing the actuator operation is displayed as Supporting Information. For the first time, the effects potential-induced changes of the interface stress, which had previously required sophisticated experimental equipment, have become visible to the naked eye.

For actuator applications, the response time is important. Figure 4A shows the time-dependent ΔL during a series of

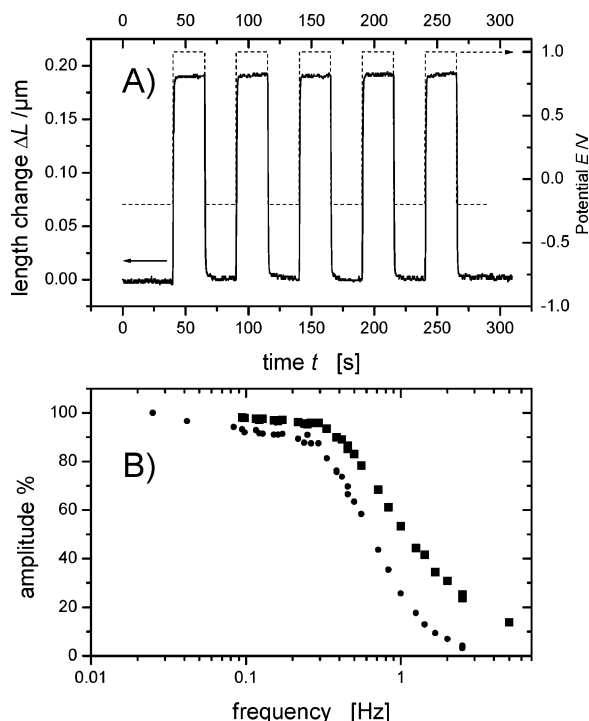


Figure 4. (A) Length change ΔL of the sample in 50 mM sulfuric acid versus time, measured in the dilatometer during a series of potential jumps from -0.2 to 1 V and back (dashed line: potential). (B) Frequency dependence of the amplitude during potential jumps (rectangular wave) in sulfuric acid. Large squares: Amplitude of the charge curve. Small circles: Amplitude of the length change as measured in the dilatometer. The dilatometer's maximum sampling rate of 10 s^{-1} limits the experimental strain amplitude at high frequency.

potential jumps from -0.2 V to 1 V and back. The half-times of the jumps in current and strain are 220 and 270 ms. Because of the limited sampling rate (10 s^{-1}) of the dilatometer, the time constant obtained from the charging curves is considered more accurate. The strain amplitude at a frequency of 0.3 Hz is almost identical to that during slower switching (Figure 4B), which is consistent with the response time given above. The bilayer foils react similarly fast, despite the drag of the electrolyte. The intrinsic time scale is given by the time constant of the charging current, which was determined as 25 ms, considerably faster than in the thicker dilatometer samples. This agrees qualitatively with the expectation that the drift of ions into the pores will be accelerated as the path is shortened.

The large mechanical response induced by changes in the surface stress predestines porous gold as an active component in sensors, especially if its surface is modified by adsorption, e.g., of molecules functionalized by thiol groups. These can be chosen to react selectively with specific molecules, for instance, antibodies; the reaction changes the surface stress, e.g., by steric repulsion of the product, and sensors detecting these changes have been proposed and tested.^{8,25–27} Their sensitivity may be significantly enhanced by using nanoporous layers instead of planar surfaces.

In addition to its performance as a simple actor producing reversible strain controlled by an applied voltage, the device

shown in Figure 3 can also be regarded as a primitive voltmeter. If the tip displacement was observed with an optical microscope as in Lippmann's device, it would be suited to measure small voltage differences. Thus, Lippmann's 19th century voltmeter based on changes of the surface tension of liquid mercury interface has found a modern equivalent based on changes in the surface stress of a solid metal.

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Supporting Information Available: Experimental details, two additional Figures (S1, S2), and a video showing the movement of the bilayer foils. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Lipkowski, J.; Schmickler, W.; Kolb, D. M.; Parsons, R. *J. Electroanal. Chem.* **1998**, *452*, 193–197.
- (2) Schmickler, W.; Leiva, E. *J. Electroanal. Chem.* **1998**, *453*, 61–67.
- (3) Lin, K. F.; Beck, T. R. *J. Electrochem. Soc.* **1976**, *123*, 1145–1151.
- (4) Haiss, W.; Sass, J. K. *J. Electroanal. Chem.* **1995**, *386*, 267–270.
- (5) Ibach, H. *Surf. Sci. Rep.* **1997**, *29*, 195–263. Ibach, H. *Surf. Sci. Rep.* **1999**, *35*, 71–73.
- (6) Raiteri, R.; Butt, H.-J. *J. Phys. Chem.* **1995**, *99*, 15728–15732.
- (7) Miyatani, T.; Fujihira, M. *J. Appl. Phys.* **1997**, *81*, 7099–7115.
- (8) Ibach, H.; Bach, C. E.; Giesen, M.; Grossmann, A. *Surf. Sci.* **1997**, *375*, 107–119.
- (9) Raiteri, R.; Butt, H.-J.; Grattarola, M. *Electrochim. Acta* **2000**, *46*, 157–163.
- (10) Friesen, C.; Dimitrov, N.; Cammarata, R. C.; Sieradzki, K. *Langmuir* **2001**, *17*, 807–815.
- (11) Cammarata, R. C.; Trimble, T. M.; Srolovitz, D. J. *J. Mater. Res.* **2000**, *15*, 2468–2474.
- (12) Weissmüller, J.; Viswanath, R. N.; Kramer, D.; Zimmer, P.; Wüschum, R.; Gleiter, H. *Science* **2003**, *300*, 312–315.
- (13) Weissmüller, J.; Cahn, J. W. *Acta Mater.* **1997**, *45*, 1899–1906.
- (14) Baughman, R. H. *Science* **2003**, *300*, 268–269.
- (15) Baughman, R. H.; Cui, C.; Zakhidov, A. A.; Iqbal, Z.; Barisci, J. N.; Spinks, G. M.; Wallace, G. G.; Mazzoldi, A.; De Rossi, D.; Rinzler, A. G.; Jaschinski, O.; Roth, S.; Kertesz, M. *Science* **1999**, *284*, 1340–1344.
- (16) Gu, G.; Schmid, M.; Chiu, P.-W.; Minett, A.; Frayssé, J.; Kim, G.-T.; Roth, S.; Kozlov, M.; Muñoz, E.; Baughman, R. H. *Nature Mater.* **2003**, *2*, 316–319.
- (17) Baughman, R. H. *Synth. Met.* **1996**, *78*, 339–353.
- (18) Erlebacher, J.; Aziz, M. J.; Karma, A.; Dimitrov, N.; Sieradzki, K. *Nature* **2001**, *410*, 450–453.
- (19) Kolb, D. M. *Prog. Surf. Sci.* **1996**, *51*, 109–173.
- (20) Kramer, D., Thesis, University of Ulm, Germany, 2000.
- (21) Haiss, W.; Nichols, R. J.; Sass, J. K.; Charle, K. P. *J. Electroanal. Chem.* **1998**, *452*, 199–202.
- (22) Nichols, R. J.; Nouar, T.; Lucas, C. A.; Haiss, W.; Hofer, W. A. *Surf. Sci.* **2002**, *513*, 263–271.
- (23) Mukerjee, S.; Srinivasan, S.; Soriaga, M. P.; McBreen, J. *J. Electrochem. Soc.* **1995**, *142*, 1409–1422.
- (24) Gleiter, H.; Weissmüller, J.; Wollersheim, O.; Wüschum, R. *Acta Mater.* **2001**, *49*, 737–745.
- (25) Berger, R.; Delamarche, E.; Lang, H. P.; Gerber, Ch.; Gimzewski, J. K.; Meyer, E.; Güntherodt, H.-J. *Science* **1997**, *276*, 2021–2024.
- (26) Chen, G. Y.; Thundat, T.; Wachter, E. A.; Warmack, R. J. *J. Appl. Phys.* **1995**, *77*, 3618–3622.
- (27) Fritz, J.; Baller, M. K.; Lang, H. P.; Strunz, T.; Meyer, E.; Güntherodt, H.-J.; Delamarche, E.; Gerber, Ch.; Gimzewski, J. K. *Langmuir* **2000**, *16*, 9694–9696.

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