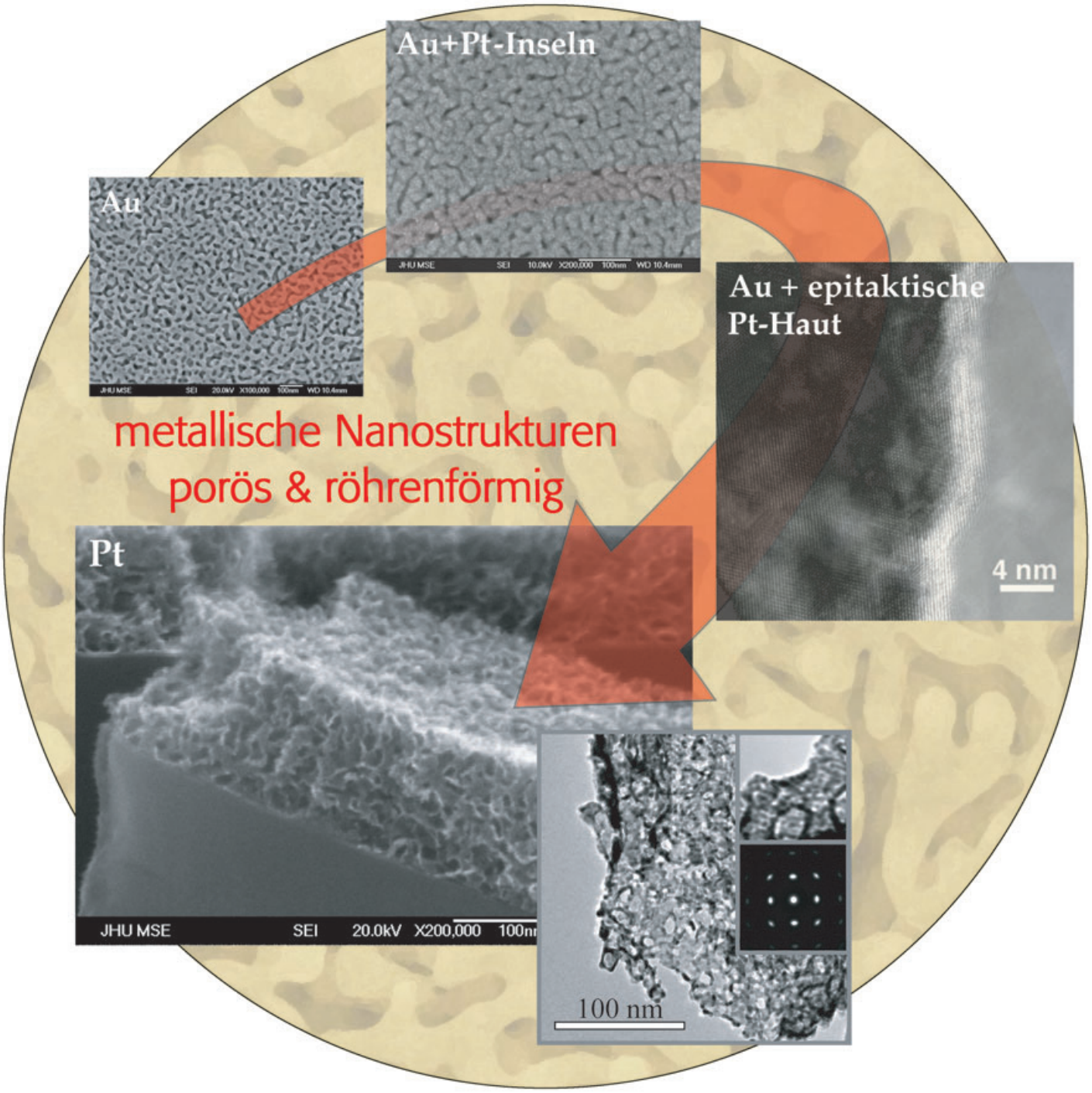
Zuschriften



Epitaktisches Gießen von Platin auf nanoporöse Goldmembran-Gussformen führt zur Bildung von mesoporösen Platin-Nanoröhren, einem neuen Material mit hoher mechanischer Stabilität und interessantem Kapillarverhalten. Mehr über die Synthese und die Eigenschaften dieses Netzwerks aus Platin-Nanoröhren finden Sie in der Zuschrift von J. Erlebacher et al. auf den folgenden Seiten.

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Materials Science

Epitaxial Casting of Nanotubular Mesoporous Platinum**

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Mesoporous precious metals (pore size 2–50 nm), especially platinum, are particularly sought after because of their immense technological importance in, for example, catalysis,[1] sensing,[2] and actuation.[3] A common approach to the fabrication of these materials is the replication of porous alumina[4] or liquid-crystal templates.[5,6] Templating generally offers a high degree of control over the pore size as well as microstructure periodicity, but most techniques in this class result in materials with one-dimensional porosity, such as an array of tubes. This characteristic is desirable for some optoelectronic applications, but for applications such as sensing or catalysis, materials with open porosity extending in all dimensions are favored to allow unlimited transport of the molecules of the medium;[1] in fact, the most useful materials often exhibit bicontinuous microstructures in which both the void space and the scaffold are completely interconnected, with the scaffold imparting mechanical stability and electrical pathways to catalytically active sites. Two important classes of bicontinuous mesoporous materials are aerogels[1] and nanoporous metals made by dealloying.[7]

Here we report the design and fabrication of nanotubular mesoporous platinum (NMP), a new material that can be described as a network of platinum nanotubes with diameters of about 15 nm and walls 1 nm thick that interconnect to form an open, doubly bicontinuous structure that may possess the highest surface area to volume ratio known (or possible) for a macroscopic sample of metal. NMP possesses a higher order of geometric complexity than most known porous materials in that the walls separate two distinct void spaces, one with predominantly negative curvature, the other with predominantly positive curvature. As such, the material exhibits interesting capillary behavior, and we envision application in nanofluidic systems as well as in ultrahigh surface area catalysis. Intriguingly, NMP exhibits structural characteristics of a macroscopic metal, in the sense that grains of micrometer size or larger are typical and that the nanotubular network within each grain exists as a single crystal with characteristic dimensions several orders of magnitude smaller.

The nanotubular mesoporous platinum is formed by epitaxial casting[8] using nanoporous gold (NPG) membrane molds. Our typical starting material is comprised of free-standing NPG membranes 100 nm thick for which the in-plane grain size is on the order of micrometers, but in principle this fabrication method is not limited to any particular size and shape of sample. NPG is a three-dimensional bicontinuous mesoporous metal with a tunable ligament size on the order 10–100 nm.[7] The crystallographic coherence of NPG extends to the scale of the grains of the Au/Ag alloy. In this sense, NPG is markedly different from most other nanoporous materials that are essentially controlled aggregates of nanoparticles.[9] Epitaxial casting is a new casting method in which an epitaxial skin of a second material coats a mold that is subsequently dissolved away. In previous work, we discovered that platinum could be grown epitaxially onto NPG by an electroless plating process,[10] which resulted in a composite core–shell nanoporous structure. More specifically, we found that a coating of Pt with an average thickness of about 1 nm took the form of a conformal coating of uniformly sized epitaxial islands on the NPG substrate. Past studies of Pt films on planar gold[11] exhibited a heteroepitaxial growth mode where initial layer-by-layer growth was followed by accommodation of misfit strain (4% in Pt/Au system) through injection of misfit dislocations (MD) at the interface. The critical thickness for injection of MDs was typically 1 nm. The presence of coherent islands with no MDs in the present case suggested that the approximately 5-nm radius of curvature allowed out-of-plane relaxation to occur by islanding, a characteristic feature of the Stranski–Krastanov growth mode. The presence of large epitaxial strains was confirmed during the course of this study by the behavior of the material after annealing at a moderate temperature (300 °C for 30 minutes), during which it was observed that the islands smoothed out to form a uniform coating with injection of misfit dislocations at the Pt/Au interface. At this point of processing, surprisingly, we found that we could completely dissolve the gold away in aqueous gold etchant (KI: 10 wt%, I_2: 5 wt%) to leave the 1-nm-thick Pt shell, still single crystalline within individual grains and retaining the bicontinuous void space of the original NPG but adding a second, tubular void region where the gold had been prior to etching.

Figure 1b shows a representative scanning electron microscopy (SEM) image of NMP. The average diameter of the tubular ligaments is about 15 nm, which is consistent with the ligament size of the NPG template (Figure 1a). Tube openings (see inset to Figure 1c) are frequently seen at the sample edges, and the shell thickness of the tubes is estimated to be around 1–2 nm. This thickness may be adjusted by varying the amount of platinum plated onto the NPG mold. A 1-nm-thick shell is only 4–6 atoms thick, which is smaller than the diameter of typical Pt nanoparticles by more than a factor

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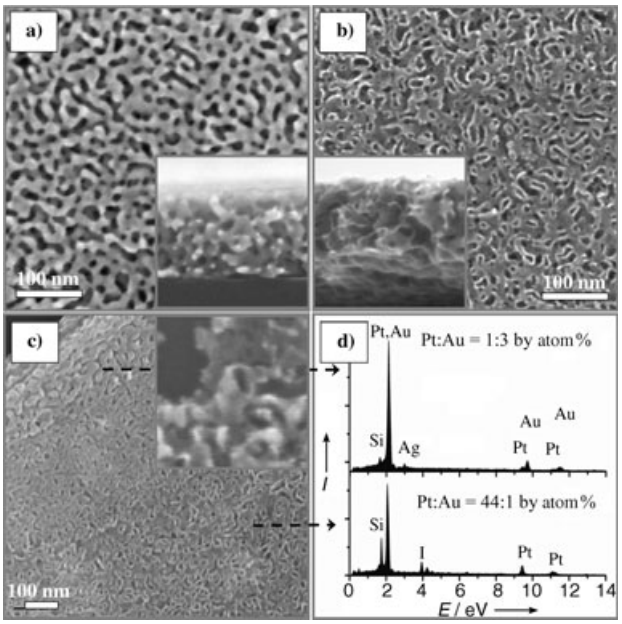

Figure 1. a) Plan-view and cross-section (inset) SEM images of NPG. b) Plan-view and cross-section (inset) SEM images of NMP. c) SEM image of a Pt-coated NPG sample within which gold has been only partially removed; the inset shows a tube opening of NMP. d) EDS analysis indicates a gradual structure transition from Pt/NPG to NMP. The NPG mode was made by dealloying white gold leaf in nitric acid for 10 minutes. The NPG surface was coated with platinum by electroless plating. Typical plating time is on the order of minutes, and thicker platinum layers may be formed with longer plating times. Experimental details have been reported in Ref. [10]. SEM images were acquired on a JEOL JSM-6700F SEM, equipped with a EDAX Genesis 4000 microanalysis system, under an accelerating voltage of 20 kV.

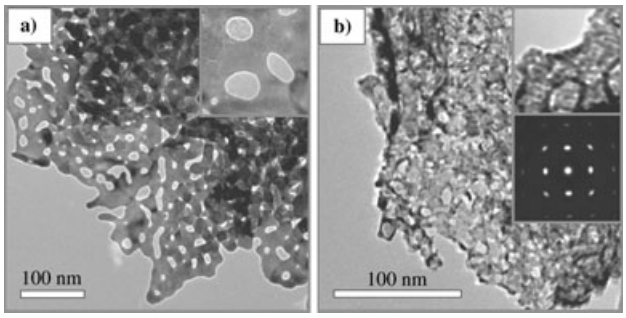

Figure 2. Bright-field TEM images of: a) NPG and b) NMP. The insets in (a) and (b) show three-way junctions of solid and tubular ligaments, and the electron-diffraction pattern shown as a lower inset in (b) indicates that NMP is a single crystal over a scale that is orders of magnitude greater than the pore size.

of two.[12,13] Note that all the tube edges of the structure show brighter contrast, a characteristic feature of tubular morphologies when observed by SEM. Figure 1c shows a Pt-coated NPG sample within which gold has been only partially removed. In this image, a gradual structure change from Pt/NPG to NMP can be clearly seen. Energy dispersive spectroscopy analysis (EDS) confirms this change. A Pt/Au ratio of 1:3 is found in the Pt/NPG region (Figure 1d), while the gold concentration is on the order of the detection limit of the instrument (ca. 1 atom%) in the NMP area and indicative of the nearly complete removal of the gold backbone.[14] If it is assumed that Pt/NPG has the idealized structure of coaxial cylinders with a diameter of 15 nm, one can calculate the shell thickness of the platinum layer to be about 1.1 nm (4 atomic layers), which is consistent with the SEM observation. We have also performed a virtual experiment (computer simulation) of coating a simulated NPG structure made by using literature methods[7], and then removing the porous gold substrate. The simulated morphology shows the original porous channels and hollow ligaments, and is remarkably similar to the experimental morphology (see the Supporting Information).

Complementary structural information is given by transmission electron microscopy (TEM) images and selected-area electron diffraction patterns (Figure 2). NPG and NMP appear as very complicated morphologies under TEM because of a 3D to 2D projection of highly interconnected wires (for NPG) and tubes (for NMP). The insets of Figure 2 show areas of three-way junctions of solid and tubular ligaments. NMP shows darker edges along the edges of its tubular ligaments than nanoporous gold. These darker edges correspond to electron attenuation by wall features parallel to the electron beam. As mentioned above, the epitaxial relationship between Pt and the NPG substrate mold suggests that large (approximately micrometer) grains of NMP are retained upon etching away the gold. The selected-area electron diffraction pattern shows this is indeed the case, as illustrated in the inset of Figure 2b, which shows a single-crystal square lattice recorded from a $\langle 001 \rangle$ zone axis of face-centered cubic (fcc) Pt. The stretched diffraction spots indicate minor lattice distortion possibly resulting from surface stresses or simply sample preparation.[3,15] Further characterization of epitaxial casting leading to NMP formation is given by high-resolution electron microscopy (HREM) images. The micrograph in Figure 3a clearly shows the epitaxial relationship between the annealed Pt overlayer and the NPG substrate. EDS analysis using an electron beam of about 1 nm shows that the bright area with a thickness of 5–8 atomic layers is a platinum skin. After removing the Au backbone, the Pt nanotubules with thin shells and nanosized holes can be clearly seen in HREM images. Figure 3b shows an example of this tubular structure, where a tubule appears to slightly tilt out of the plane as shown schematically in the insert in Figure 3b. The internal diameter of the tubule is around 10 nm, close to the ligament size of NPG. One side of the tubule was imaged along a $\langle 111 \rangle$ orientation of fcc Pt. The thickness of the sheet was estimated by simulating the atomic image, and the best match between the HREM and simulated images was obtained at a sample thickness of about 2 nm, which is consistent with the thickness of tubular shells observed in the cross-sectional image (Figure 3a). The HREM images also clarify the geometry of the tubular ligaments which are seen not to be single-valued in surface curvature; instead, they are more like hyperboloids of revolution for which each point is a saddle, thus possessing both positive and negative principal curvatures.

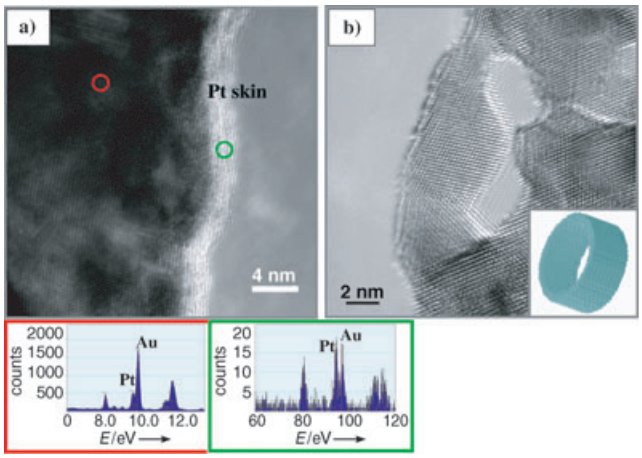

Figure 3. HREM images of Pt/NPG and NMP. a) A uniform skin of heteroepitaxial Pt on nanoporous gold was made by platinum deposition followed by thermal annealing at 300 °C for 30 minutes. The bright area with a thickness of 5–8 atomic layers is the platinum skin, as demonstrated by EDS analysis. The observation of gold in the shell region arises from sample drifting during imaging. b) Side-view of a tube opening of NMP. Lattice distortion and dislocations are observed. The inset is an atomistic model consistent with the projection of the tube opening shown in (b). TEM analysis was performed on a 300 kV, field-emission Philips CM300FEG in the Electron Microscopy Center at Johns Hopkins University.

Since NMP has atomically thin tube walls it has a very high surface area and total surface free energy. This situation imparts an intrinsic metastability to the material which could potentially lead to morphological coarsening, a problem akin to the sintering problems plaguing nanoparticle-based catalysts. The likely mechanism for such coarsening in NMP at moderate temperatures is surface diffusion, for which the characteristic coarsening time t depends on the characteristic length scale l of the structure material according to the relationship $t \approx l^4$; [16] thus, NMP with $l \approx 1$ nm should coarsen 10^{12} times faster than 1-μm-sized solid platinum grains should sinter. We do know, however, that platinum surface self-diffusivities are three to four orders of magnitude slower than gold,[17] and NPG does coarsen at room temperature, particularly in certain electrolytic environments.[18] To examine this stability problem for nanotubular mesoporous platinum we studied the morphological stability of NMP by annealing it at elevated temperatures (see the Supporting Information). It was found that NMP is stable at 125 °C for at least 24 h. At 150 °C, the tube walls start to deform, and eventually evolve into Pt nanoparticles (Pt-NPG, in contrast, is stable at these temperatures). This behavior indicates that NMP may be useful for catalytic reactions at moderate temperatures, such as in a H_2/O_2 fuel cell.

The thermal stability of NMP is also interesting from the standpoint of fundamental thermodynamics. It has been predicted that the melting point of small particles is suppressed relative to that of bulk particles.[19] We estimate for Pt that a suppression of the melting point below 300 °C requires a radius of curvature less than approximately 1 nm. The principal curvatures of the network are greater than this (ca. 7–10 nm), so we expect NMP to be stable with regards to this instability. However, small pinholes in the tubular network may occasionally open up which may locally melt and then resolidify when the mass of the melted regions increases to the point that the solid is again thermodynamically stable. In this context, it is interesting to note the similarity of the NMP sample annealed at 300 °C to a network of solidified droplets.

The whole network and each individual tubular segment in NMP are essentially one crystallographic lattice. This characteristic feaure enhances the mechanical rigidity of the material, and one may be able to use this interconnected 3D channel structure as a model system with which to study nano-/microfluidic transport phenomena or confined reactions on the nanoscale.[20] To further develop this concept, we have made a platinum–palladium bicontinuous mesoporous composite structure by refilling the tubes of NMP[21] with palladium chloride. Samples were made by touching the edge of a sample of NMP with a drop of concentrated $PdCl_2$ solution. Strong capillary forces drove the liquid into the tube channels, an effect that caused a change in the appearance that was visible to the naked eye, and then the samples were subsequently dried and imaged by SEM. Figure 4 shows the structure of such a sample at the filled/

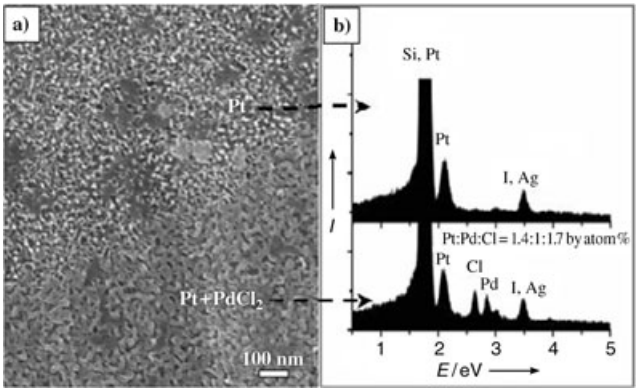

Figure 4. a) SEM image of NMP that has been partially filled with $PdCl_2$. b) EDS analysis showing the difference in pore composition between unfilled and refilled regions.

unfilled boundary. The area with $PdCl_2$ looks very similar to the morphology of unetched Pt/NPG, that is, the edge contrast arising from the tubular morphology disappears and the region in the upper section of the micrograph is clearly unfilled. Compositional analysis from both areas (Figure 4b) supports this view. It is interesting to find that liquid transport occurs preferentially through tubes rather than pores, possibly because of the much stronger capillary forces of tubes, which have very high negative curvature.

The surprising mechanical stability imparted by the nanostructure of NMP enables it to be produced in macroscopic quantities (membrane samples on the order of one square centimeter are routinely made). This feature should enable its easy integration into technologies for catalysis, nano-/microfluidic transport, as well as supplying a new

material to probe the nanoscale limits of materials research focusing on structural, physical, and mechanical properties.

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