Electrochemical Assembly of Ordered Macropores in Gold**

By *Judith E. G. J. Wijnhoven, Stephan J. M. Zevenhuizen, Michel A. Hendriks, Daniël Vanmaekelbergh, John J. Kelly,* and *Willem L. Vos**

There is currently a great interest in the three-dimensional (3D) patterning of materials at length scales of μm and smaller. These materials are being investigated for a wide range of applications such as catalysis, separation technology, photonic crystals, or nano-electronics. Considerable advances are being made in the template-assisted assembly of macroporous materials (i.e., with pores of radii larger than 25 nm[1]); a 3D template is first assembled from a self-organizing material. The template is then impregnated with the desired solid material. Finally, the template is removed, resulting in an array of macropores that reflects the structure of the template. To deposit the solid material inside the template, several different routes have been chosen, namely liquid-phase reactions, sol-gel chemistry, chemical vapor deposition, deposition of small solid nanoparticles, or precipitation from a saturated solution.[2–18] This has resulted in a wide range of macroporous materials, including ceramics,[2–11] graphite and diamond,[12] CdSe,[13,14] polymers,[15] NaCl,[7] and metals.[16–18] In this work, we demonstrate electrochemical deposition as a new technique for patterning macropores. The possibility thus arises for fabricating macropores in II–VI semiconductors or in metals. The interest of the latter has been demonstrated in the recent observation of unusual optical properties of two-dimensional crystalline arrays of holes in silver.[19]

The starting material for the templates is a colloidal suspension of highly monodisperse silica or polystyrene spheres in ethanol. The silica particles are made by microemulsion polymerization[20] followed by further Stöber-like growing steps, and they have relative size variations of less than 2 %. The final particle radius is 113 nm, as determined by transmission electron microscopy. The polystyrene spheres were obtained from Duke Scientific and have an average radius of 322 ± 3 nm with a polydispersity of 1.9 % (as given by the supplier).

The templates were made by depositing a drop of colloidal suspension on a flat, conducting substrate (we used predominantly gold on glass slides). The spheres order on the surface through the capillary forces that occur during the evaporation, see e.g. Denkov et al.,[21] and form an artificial opal, a dry colloidal crystal. It is known that opals made in this way are fcc crystals.[22,23] Opals made of silica were heated to 600 °C to sinter the spheres.[24] Scanning electron micrographs (SEMs) showed that the distance between the spheres did not decrease noticeably nor did the sphere size itself. The substrates were partly covered with insulating tape in which a hole was left open for colloidal suspension (see Fig. 1). Care was taken to ensure that the opal covered all of the electrode surface exposed to the electrolyte. In this way the gold is deposited in the opal, instead of growing unimpeded outside the opal. The diameter of the samples was about 3 mm. The electrical connection was made to the uncovered part of the substrate above the solution.

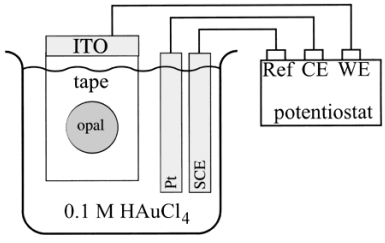

Fig. 1. Setup for electrodeposition of gold in an opal. A glass substrate with indium tin oxide (ITO) or gold on it is partly covered with non-conducting tape. In the hole in the tape an opal is grown. SCE = saturated calomel electrode, Pt = platinum electrode, Ref = reference electrode, CE = counter electrode, WE = working electrode.

To grow gold in the opals, the samples were suspended in a 0.1 M $HAuCl_4$ solution with a pH of 6. The counter electrode was Pt, and potentials were measured relative to a saturated calomel electrode (SCE). The cell was controlled with an EG&G 273A potentiostat. Before deposition, the gold electrode was pretreated by cyclic voltammetry between –0.2 V and 1.7 V. The deposition of gold was performed at a potential of 0.5 V vs. SCE. This is in the kinetic regime, as was determined by current–potential curves that were measured a priori on the same samples. Under these conditions, the amount of gold deposited is determined by the charge flowing through the system. The growth rates were varied between 3 C/h and 1 C/day (per 7 mm^2). The samples of Figure 2 were grown at rates of 1.8–3 C/h.

After the deposition of gold, the original opal material could be removed because the spheres touch. Opals made of silica were removed by etching with a 5 % solution of HF.[12,13] Opals made of polystyrene spheres were removed by gasifying and combustion at 450 °C. Dissolving the polystyrene in organic solvents causes damage to the crystal because of the swelling of the polymer before dissolution.

The structure of the samples was determined by SEM. Two different instruments were used: an ISI DS-130 microscope at the University of Amsterdam, and a Philips XL30S FEGSEM at the University of Utrecht.

Figure 2a shows a SEM picture of an opal of silica spheres after the deposition of gold. The spheres form well-

[*] Dr. J. E. G. J. Wijnhoven, Dr. W. L. Vos
van der Waals-Zeeman Instituut, Universiteit van Amsterdam
Valckenierstraat 65, NL-1018 XE Amsterdam (The Netherlands)
E-mail: wvos@wins.uva.nl
S. J. M. Zevenhuizen, M. A. Hendriks, Dr. D. Vanmaekelbergh, Prof. J. J. Kelly
Debye Instituut, Universiteit Utrecht
PO Box 80000, NL-3508 TA Utrecht (The Netherlands)

[**] We thank Petra de Jongh and Wijnand Takkenberg for help with electron microscopy and Ad Lagendijk for continuous encouragement. The work of JEGJW and WLV is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

  0935-9648/00/1206-0888 $ 17.50+.50/0

ADVANCED MATERIALS

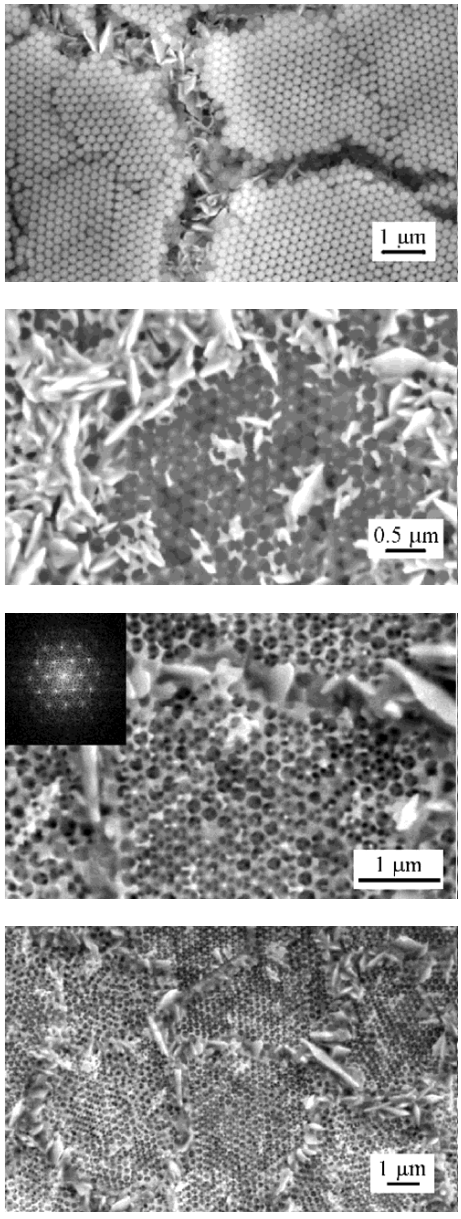

Fig. 2. a) SEM of an opal of silica spheres (radius 113 nm) filled with gold. In the empty space between the spheres gold is visible. In the opal, the gold has not reached the surface. b) SEM of an opal of silica spheres (radius 113 nm) impregnated with gold. Other area of the sample of Figure 2a; here gold has been grown to the surface of the opal. Dark circles are silica spheres, light colored material in between the spheres is gold. c) SEM of a crystal of air spheres (radius 111 nm) in gold, made with a silica template. The inset is a Fourier transform of the SEM image. The same sample as Figure 2a or 2b, after etching. d) SEM of crystals of macropores (radius 111 nm) in gold, made with a silica template. Overview of Figure 2c.

ordered crystal domains with dimensions of several micrometers. Between the crystallites, there is some empty space due to shrinkage during drying: A wet colloidal crystal has a volume fraction of spheres of 50–60 %[23] whereas an opal has a volume fraction of 74 %.[22] In the space between the as-grown crystallites, several well ordered layers of spheres can be seen, which confirms that the opal is 3D, and not a single layer. After deposition of the gold, flat gold flakes of about 1 μm length are seen here.

The enlarged SEM picture of another area of in the sample (Fig. 2b) reveals thin gold structures (light) of less than 50 nm thickness that have grown between the spheres (dark circles). These structures are the gold frameworks that build up the final structure of crystalline air spheres in a gold matrix. Because of non-uniform nucleation the gold grows at different rates at different spatial positions: at some positions it has reached the top of the opal, while at other positions it has not. Above the opal surface, the gold grows again in flakes similar to those in the opal grain boundaries, that is, with long axes of ~1 μm and short axes of ~100 nm. For comparison, gold that is deposited in the absence of opals shows disordered polycrystalline layers.

Figure 2c is a SEM picture of the remaining structure when the silica is etched away from a filled template. Spherical voids in between the gold structures are clearly visible. This confirms the observation in Figure 2b that gold does grow in between the colloidal spheres. The inset in Figure 2c is a Fourier transform of the SEM picture; the sharp peaks confirm that long-range order is present in the image and that the sample is indeed a crystal of air spheres in gold and not an irregular structure. The hexagonal pattern of the air spheres, typical of the face-centered cubic (fcc) (111) planes, is clearly reflected in the Fourier transform. Through the top layer of air spheres, the next layer of voids is visible, because each neighboring pair of air spheres is connected. Similar structure was observed in air-sphere crystals in titania.[7] Such holes appear because the impregnating solid material cannot grow at the contact area of a neighboring pair of colloidal spheres in the opal template. The average distance between the air spheres is 222 nm, which corresponds to a radius of close-packed air spheres of 111 nm, which is in excellent agreement with the radius of the original 113 nm silica spheres (Fig. 2a). This result demonstrates that the gold structure does not shrink during the etching of the template, hence that the radii of the macropores are controlled by the radii of the colloidal spheres in the template. For comparison, ceramic air-sphere crystals shrink considerably, by about 30 %, relative to the parent structure.[3,6,7] The likely explanation for the absence of shrinkage in the present case is the fact that the patterned gold has already reached the final crystal structure and volume fraction right after the electrochemical deposition in the opal. In contrast, ceramics made by liquid-phase or sol-gel chemistry have at this stage not yet fully reacted and thus not reached their final volume fraction. The role of the template material or of subsequent heating of opal plus impregnated material can be excluded, because shrinkage was not observed in either silica or latex templates (see below).

Figure 2d shows that the domains of air-sphere crystals extend over tens of sphere diameters, similar to the original opal. This indicates that the gold deposition does not disrupt the long range order of the opals. In between the crystal domains, large gold flakes are visible, similar to the opal filled with gold (Fig. 2a). This differs from our experience with titania, which tends to form shells around the colloidal spheres, but does not grow in the grain boundaries.[7,10] It is

  0935-9648/00/1206-0889 $ 17.50+.50/0

clear that electrochemical deposition results in so-called volume-templated structures,[12,25] as opposed to the surface-templated structures that are obtained by liquid-phase chemistry, sol-gel chemistry, or chemical vapor deposition. In volume-templated structures, the material grows both in the void space between the building blocks of the template, as well as on their surface. The advantage of volume-templated structures is that a higher volume fraction of solid material is obtained compared to surface templated structures.[12]

Figure 3 is a SEM picture of a gold layer deposited in a latex opal which has subsequently been removed. The gold has grown in the form of flakes that clearly carry the imprints of the original colloidal spheres. The configuration of imprints reveals an intriguing hierarchical order: the moulds are ordered on length scales of several sphere radii within each flake, but disordered on length scales from one flake to another. Apparently, the gold has a complex growth pattern: The gold forms flakes similar to those in Figure 2a, that mould to the template. The flakes are then able to push away latex particles. The latex particles have not—in contrast to the silica particles—been sintered before the electrodeposition. It is concluded that the surface tension of the gold is larger than the van der Waals forces between the latex particles. The radii of the spheres within each flake are about 330 nm. This is in good agreement with the value of 326 nm of the original spheres.

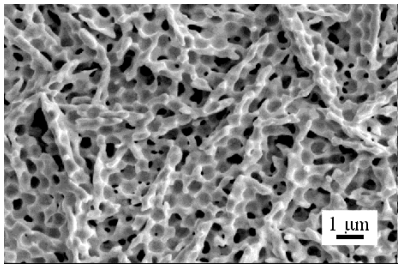

Fig. 3. SEM of macropores (radius 322 nm) in gold, made with a latex template. The structure has short-range order, but no long-range order.

We have demonstrated that electrochemical deposition is a successful method for forming nanostructures by impregnating artificial opals with a solid. The template can be removed by etching or calcination, which results in macropores in the electrochemically deposited material. For opal templates made of sintered silica colloids, the macroporous gold is an excellent replica of the template, and gives rise to a crystal of air spheres in gold. A structure with short range order and long range disorder was obtained from templates of latex spheres.

Received: January 11, 2000
Final version: March 17, 2000

[1] The International Union of Pure and Applied Chemistry (IUPAC) definition is that micropores are pores with radii $r < 1$ nm, mesopores have $1 < r < 25$ nm, and macropores have $r > 25$ nm.

[2] S. A. Davis, S. L. Burkett, N. H. Mendelson, S. Mann, *Nature* **1997**, *385*, 420.
[3] A. Imhof, D. J. Pine, *Nature* **1997**, *389*, 948.
[4] D. Velev, T. A. Jede, R. F. Lobo, A. M. Lenhoff, *Nature* **1997**, *389*, 447.
[5] M. Antonietti, B. Berton, C. Göltner, H. P. Hentze, *Adv. Mater.* **1998**, *10*, 154.
[6] B. T. Holland, C. F. Blanford, A. Stein, *Science* **1998**, *281*, 538.
[7] J. E. G. J. Wijnhoven, W. L. Vos, *Science* **1998**, *281*, 802.
[8] P. Yang, T. Deng, D. Zhao, P. Feng, D. Pine, B. F. Chmelka, G. M. Whitesides, G. D. Stucky, *Science* **1998**, *282*, 2244.
[9] O. D. Velev, T. A. Jede, R. F. Lobo, A. M. Lenhoff, *Chem. Mater.* **1998**, *10*, 3597.
[10] B. T. Holland, C. F. Blanford, T. Do, A. Stein, *Chem. Mater.* **1999**, *11*, 795.
[11] J. S. Yin, Z. L. Wang, *Adv. Mater.* **1999**, *11*, 469.
[12] A. A. Zakhidov, R. H. Baughman, Z. Iqbal, C. Cui, I. Khayrullin, S. O. Dantas, J. Marti, V. G. Ralchenko, *Science* **1998**, *282*, 897.
[13] Y. A. Vlasov, N. Yao, D. J. Norris, *Adv. Mater.* **1999**, *11*, 165.
[14] P. V. Braun, P. Wiltzius, *Nature* **1999**, *402*, 603.
[15] S. A. Jenekhe, X. L. Chen, *Science* **1999**, *283*, 372.
[16] P. Jiang, J. Cizeron, J. F. Bertone, V. L. Colvin, *J. Am. Chem. Soc.* **1999**, *121*, 7957.
[17] O. D. Velev, P. M. Tessier, A. M. Lenhoff, E. W. Kaler, *Nature* **1999**, *401*, 548.
[18] H. Yan, C. F. Blanford, B. T. Holland, M. Parent, W. H. Smyrl, A. Stein, *Adv. Mater.* **1999**, *11*, 1003.
[19] T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio, P. A. Wolff, *Nature* **1998**, *391*, 667.
[20] F. J. Arriagada, K. Osseo-Asare, *Adv. Chem. Ser.* **1994**, *234*, 113.
[21] N. D. Denkov, O. D. Velev, P. A. Kralchevsky, I. B. Ivanov, H. Yoshimura, K. Nagayama, *Langmuir* **1992**, *8*, 3183.
[22] H. Míguez, F. Meseguer, C. López, A. Mifsud, J. S. Moya, L. Vásquez, *Langmuir* **1997**, *13*, 6009.
[23] W. L. Vos, M. Megens, C. M. van Kats, P. Bösecke, *Langmuir* **1997**, *13*, 6004.
[24] H. Míguez, F. Meseguer, C. López, A. Blanco, J. S. Moya, J. Requena, A. Mifsud, V. Fornés, *Adv. Mater.* **1998**, *10*, 480.
[25] D. Vanmaekelbergh, A. Koster, F. I. Marin, *Adv. Mater.* **1997**, *9*, 575.

An Enhanced CVD Approach to Extensive Nanotube Networks with Directionality**

By *Nathan R. Franklin* and *Hongjie Dai**

There has been much interest in carbon nanotubes and their interesting electrical and mechanical properties.[1] However, several long-standing issues remain in nanotube growth. First, it is desired to obtain structurally perfect nanotubes with high yield and at a large scale. Second, growing defect-free nanotubes continuously to macroscopic lengths has proven challenging. Third, although progress has been made in growth of oriented multiwalled nanotubes at controlled locations,[2–4] significant further work is required to obtain ordered single-walled carbon nanotube (SWNT) architectures by direct synthesis approaches. Finally, there is the seemingly formidable task of controlling the chirality of SWNTs by any existing growth method.

Our group has been making concerted effort to gain control over the above issues.[5] In terms of SWNT architec-

[*] Prof. H. Dai, N. R. Franklin
Department of Chemistry
Stanford University
Stanford, CA 94305 (USA)

[**] HD acknowledges financial support from DARPA/ONR, NSF, the Lucille Packard Foundation, and SRC.

  0935-9648/00/1206-0890 $ 17.50+.50/0