Complex gold nanostructures derived by templating from diatom frustules

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Diatom frustules have been used for the first time as templates for the fabrication of gold nanostructures; high-precision replicas featuring complex three-dimensional gold nanostructures from the nano- to the microscale were achieved.

Biological materials and processes are a relatively new source of inspiration for the design and fabrication of advanced nanostructured materials.[1] There are numerous examples of organisms capable of synthesising inorganic based structures into intricate architectures with ordered features from the micro- to the nanoscale.[2] One particularly intriguing process is the exceptional variety of patterned silica structures generated by aquatic microalgae known as diatoms.[3] Diatoms are single-celled photosynthetic microorganisms that possess intricate microshells (frustules) comprised of amorphous silica.[3] Each of the estimated 10^5 diatom species has a specific frustule shape decorated with a unique pattern of nano-sized features (pores, channels, ridges, spikes, spines *etc.*).

A plethora of potential applications for diatom frustules, including optics, biophotonics, electronics, biosensing, filtration, microfluidics, catalysis, lubrication and drug delivery have been proposed.[4] However, the conversion of the three-dimensional (3-D) bio structure of a diatom frustule into technologically more suitable materials is essential for many of these applications. To transform biosilica into ceramic (MgO, TiO_2, zeolites), semiconducting (Si–Ge) or organic scaffolds (polyaniline), several approaches have been demonstrated. These include gas/solid displacement, sol–gel synthesis, polymerisation and genetic/environmental manipulation.[5]

Here we describe a simple shape-preserving method for the fabrication of pure gold replicates of diatom frustule valves. Considerable interest has been devoted to gold nanostructures because of their attractive optical, chemical, electrochemical and electrical properties.[6] Among existing microfabrication technologies, template synthesis using biological materials offers a cheap and convenient alternative for the fabrication of complex spatially patterned micro-to-nano structures.[7]

The aims of this work are twofold; first, to demonstrate that templating by diatom frustules could be used as a generic approach for the fabrication of complex nanostructures and secondly, to fabricate gold structures with intricate and unique morphologies that are not accessible with conventional fabrication techniques. In comparison with previous studies,[5] the focus of this approach is on preserving the local 3-D structures of diatom frustule nanotopography rather than the curvature of the gross frustule valve. This approach is relevant to potential applications of gold structures, which rely on planar surfaces. The centric diatom *Coscinodiscus* sp was chosen for this study because of its large frustule (80–100 μm), its multiple centripetal layers and unique organisation of pores. The fabrication method is based on the deposition of gold by vacuum evaporation on the diatom frustule, followed by the stripping of the gold film.†

A series of representative scanning electron microscope (SEM) images of a cleaned *Coscinodiscus* sp. diatom frustules used as template is shown in Fig. 1(a)–(e). The images present the internal frustule valve, from which replication was initiated. The valve is circular in shape (Fig. 1(a)) and is composed of two levels of pores. Larger pores (foramen) of 1.2 μm are organised in lines radiating outwards from the valve centre and are arranged in hexagons with an interpore distance of about 500 nm (Fig. 1(b) and (c)). Below, separated from the foramen by silica chambers (areolae) resides a membrane with smaller pores (150–200 nm), the so-called cribrum,

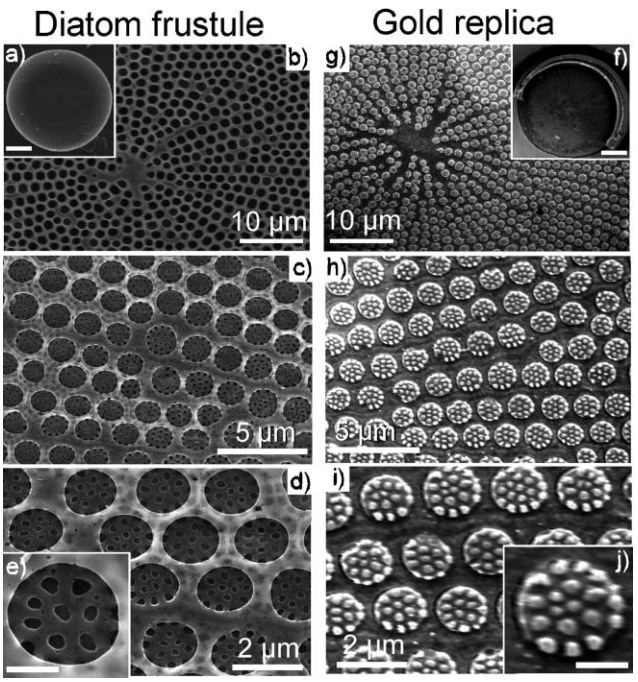

Fig. 1 SEM images (a)–(e) show the internal side of frustule valve (*Coscinodiscus* sp.), and images (f)–(j), show the gold structures replicated from the frustule. The scale bars are: (a) and (f) 20 μm, (e) and (j) 0.5 μm.

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which are centripetal to the foramen openings and again follow hexagonal order (Fig. 1(d) and (e)).

A series of SEM images of gold structures obtained from the frustule templates are shown in Fig. 1(g)–(j). The shape, size and organisation of gold structures represents the negative of the porous frustule valve, confirming successful replica formation. The detailed surface morphology of the frustule and the gold replica is shown in AFM images (Fig. 2(a) and (b)). The profile analysis of both surfaces shows the high precision of this replication process. The gold replica films show a complex 3-D morphology on two levels: first large cylinders (Fig. 2(b), arrow 1, height 400–500 nm) corresponding to the foramen diameter and areolae chamber height (Fig. 2(a), arrow 1) and smaller cylindrical structures (height 100–150 nm) on the top (Fig. 2(b), arrow 2) conformal to the cribrum pores (Fig. 2(a), arrow 2). The SEM images show more details of the internal pore shape (Fig. 2(c)) and the replicated gold structures (Figs. 2(d)–(f)).

We noted that the individual gold cylinders could be removed from the gold film by gentle sonication (Fig. 2(d)–(f)). These unusual 3-D morphologies might be of use to nanotechnological pursuits requiring monodisperse gold particle regimes. Regarding the purity of the replica, energy-dispersive X-ray (EDX) analysis revealed only gold peaks (E = 2.12 keV) on the replica film (Fig. 2(g)).

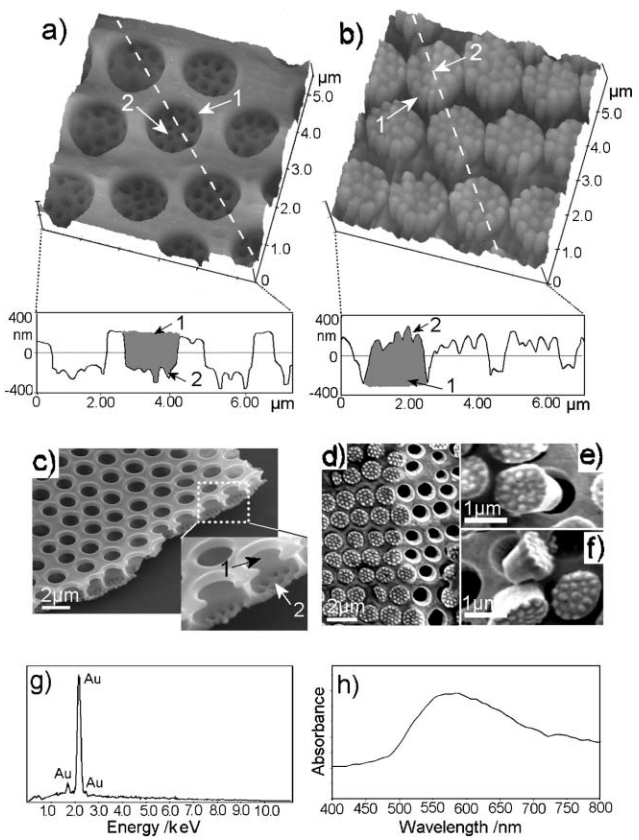

Fig. 2 AFM images (tapping mode) of (a) the internal frustule surface with profile graph and (b) replicated gold structures with profile graph. SEM images of (c) multilayered valve and (d)–(f) replicated gold structures partially removed from the gold film. EDX analysis (g) and UV/Vis absorbance spectrum (h) of the gold structures obtained from the gold replica.

Over the last two decades, optical properties of ordered metallic structures (mainly gold) have been the subject of many experimental and theoretical studies involving techniques such as surface plasmon spectroscopy (SPR) and surface enhanced Raman spectroscopy (SERS).[8] Our gold replicas have ordered features with dimensions comparable to optical wavelengths which tempted us to probe their optical properties. The localised surface plasmon resonance response of these gold structures is shown in Fig. 2(h). A broad peak is observed in the visible region between 525 and 640 nm (not seen on the flat gold film) and corresponds to the transverse plasmon absorbance band of the small gold cylinders (150–200 nm).[9] The well established chemistry of gold provides sufficient scope for further applications of these diatom gold replicas in order to exploit their potentially useful structural features.

These results have demonstrated that diatom frustules can be used as templates to fabricate gold structures with complex and unique morphologies. Here, gold is used as an example, but the technique could be applied to many other metals that can be subjected to vacuum evaporation. Notably, we have prepared replicas from other diatom species as well, such as from *Thalassiosira eccentrica*, which suggests that the method may be used as a general approach. Diatoms can be routinely grown in laboratory conditions and this strategy offers a cheap resource to an enormous number of desired templates. This approach is a good alternative to expensive lithographic procedures and results in complex 3-D nanostructures.

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Notes and references

† *Experimental*: The diatom species *Coscinodiscus* sp. was obtained from CSIRO, Marine Division (Hobart, TAS, Australia). The culture was maintained at 20 °C using a 12 h light/12 h dark cycle in GSE medium.[10] The live diatoms were harvested after 2–3 weeks of culturing and cleaned using concentrated sulfuric acid. Cleaned diatom frustules were stored in ethanol and used when required. Templating was performed using a similar procedure for fabrication of atomically flat gold described in our previous work.[11] One drop of cleaned frustule suspension was deposited on a piece of silicon wafer previously modified with 0.01% polylysine and dried in a stream of nitrogen. A gold film (thickness about 1 μm) was deposited on a frustule by vacuum evaporation. After evaporation, the gold film was glued onto a glass support and mechanically stripped off the silicon wafer. In most cases, the diatom frustules remained on the silicon wafer after stripping of the gold film. The remainder of the frustules adhered to the gold layer could be easily removed by treatment with 6% HF. Light and electron microscopy in combination with EDX was used to establish that the Au surface was free of diatomaceous remains. The samples with diatom frustules and their gold replicas were examined using SEM and AFM. A Philips XL 30, SEM fitted with a field-emission source and EDX was used. AFM imaging was performed using a Nanoscope IV, Multimode SPM (Veeco Corp., USA). Images were acquired using silicon probes in tapping mode in air. Both scanner "E" and "J" were used and images were acquired from 100 to 1 μm scan sizes. The absorbance spectra of the gold nanostructures were obtained using a microspectrophotometer consisting of a spectrometer (Ocean Optics, USB 2000, wavelength range 300–1000 nm) coupled through optical fibres with an optical microscope (40 × objective corresponding to an illuminated area of less than 50 × 50 μm). The UV/Vis spectra of a flat gold film was used as background spectrum and was subtracted from the absorbance spectrum of the gold replica.

1 M. Sarikaya, C. Tamerler, A. K.-Y. Jen, K. Schulten and F. Baneyx, *Nat. Mater.*, 2003, **3**, 577.
2 M. Srinivasarao, *Chem. Rev.*, 1999, **99**, 1935.

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3 F. E. Round, R. M. Craford and D. G. Man, *The Diatoms*, Cambridge, University Press, Cambridge, 1990.
4 (*a*) D. E. Morse, *Trends Biotechnol.*, 1999, **17**, 230; (*b*) R. W. Drum and R. Gordon, *Trends Biotechnol.*, 2003, **21**, 325; (*c*) C. E. Hamm, *J. Nanosci. Nanotechnol.*, 2005, **5**, 108; (*d*) T. Fuhrmann, S. Landwehr, M. E. Rharbi-Kucki and M. Sumper, *Appl. Phys. B*, 2004, **78**, 257; (*e*) N. L. Rosi, C. S. Thaxton and C. A. Mirkin, *Angew. Chem.*, 2004, **116**, 5616.
5 (*a*) M. R. Weatherspoon, S. M. Allan, E. Hunt, Y. Cai and K. H. Sandhage, *Chem. Commun.*, 2005, 651; (*b*) K. H. Sandhage, M. B. Dickerson, P. M. Huseman, M. A. Caranna, J. D. Clifton, T. A. Bull, T. J. Heibel, W. R. Overton and M. E. A. Schoenwaelder, *Adv. Mater.*, 2002, **14**, 429; (*c*) X. Li, C. Bian, W. Chen, J. He, Z. Wang, N. Xu and G. Xue, *Appl. Surf. Sci.*, 2003, **207**, 378.
6 A. N. Shipway, M. Lahav and I. Wilner, *Adv. Mater.*, 2000, **12**, 993.
7 F. C. Meldrum and R. Seshadri, *Chem. Commun.*, 2000, 29.
8 T. Vo-Dinh, *TrAC*, 1998, **17**, 557.
9 P. N. Bartlett, J. J. Baumberg, S. Coyle and M. E. Abdelsalam, *Faraday Discuss.*, 2004, **125**, 117.
10 R. R. L. Guillard and J. H. Ryther, *Can. J. Microbiol.*, 1962, **8**, 229.
11 D. Losic, J. G. Shapter and J. J. Gooding, *Langmuir*, 2001, **17**, 3307.

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