



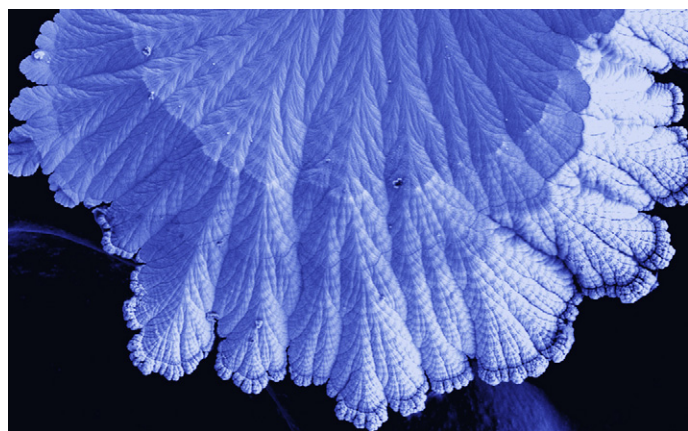
Uncovered

Coming out of its shell Biomimetic methods for metallic nanostructured mesoscopic model fabrication

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For several decades scientists have been trying to understand the laws of biological growth and morphogenesis, with materials scientists and engineers making models of wonderful natural creations in order to reproduce their functional properties. The fact is that millions of years of evolution have created materials with characteristics that are still unattainable for artificial materials. A well-known example is the lotus leaf phenomenon, i.e. the lotus leaf self-cleaning ability, which has been well studied and widely applied in technology. A number of papers are devoted to studies of the structure of the natural shells of molluscan shellfish, which exhibit mechanical properties that are currently unfeasible for synthetic materials. Among the unsolved problems of biomimetics is that of reproducing the structure of nacre exhibiting a phenomenal external load stability. An intensive search is

underway for materials capable of copying nature and the methods necessary to synthesize them, i.e., 'biomimetic' methods (as an example [1,2]). It has been found that the superior properties of natural materials are due to their architecture and their hierarchical structure. The creation of hierarchical structures in man-made materials, formed during synthesis, is crucial to biomimetic methods. Another important question is: is shape control of the model and their reproducible fabrication feasible?

At the Institute of Solid State Physics RAS, where materials science is one of the major research fields, we studied nanostructured metallic coatings and nanowires with magnetic and superconducting properties. In the course of nanowire growth by electrodeposition of metal on porous membranes, our attention was drawn to the meso-structures forming on the membrane. These structures grow on porous membranes by means of pulsed current electrodeposition if the electroplating is continued after the nanowires appear on the membrane surface. There are two scenarios possible for growing metal nanowires in porous membranes by means of pulse current electrodeposition. The first one is when nanowires, after they have appeared on the membrane surface, continue to grow separately. The second one, considered in the present discussion, is when nanowires form nanostructured 'vegetable' metallic meso-samples on the membrane surface. This occurs in the case of self-assembly of nanowires that appear on the membrane surface simultaneously with relatively small distances between the nanowires. Both methods were implemented by us.

The results presented show that pulse current electrodeposition on porous membranes ensures controlled growth of nanostructured metallic models of natural objects, plants and fungi, i.e., it is a biomimetic method of their synthesis. We have succeeded in preparing pores of definite configuration on a polymer membrane, which together with a precisely fixed regime of pulsed current electroplating, results in single type convex-concave structures resembling shells.

The architecture of the 'shells' was revealed by their fragmentation in an ultrasound bath and chemical etching. The self-organization of the metallic nanowires grown from the membrane gave rise to nanosize conical elements acting as 'bricks' to build a layered hierarchic structure at the nano-, micro- and meso-levels. Our models appear to replicate not only the exterior form of biological objects but also their hierarchical structure.

Structural diversity, controllable shaping and the remarkable resemblance to mushrooms, plants and shells, as well as the hierarchical structure suggest that pulse current electrodeposition on templates can be regarded as a biomimetic method for creating metallic structures. These arguments allow us to put forward the hypotheses that pulsed growth on templates is a tool of morphogenesis for most mushrooms and plants which is accompanied by self-organization of the growing clusters and fibers and fractal branching. By varying the pore size and pore pattern in a membrane, and by varying the electrolytes and the pulsed current parameters, an impressive manifold of metallic nanostructured mesostructures resembling natural objects (mushrooms and plants) was produced [3–5]. Nanostructured models have been grown from normal (Ag, Pd, Rh), magnetic (Ni, Pd–Ni, Pd–Co) and superconducting (Bi, Pb–In, Pb–Bi) metals and alloys which opens up prospects for their use in the creation of nanodevices. Nanostructured large surface models such as ‘silver wood’ and similar structures from other metals are of interest for applications including catalytic filters, batteries and supercapacitors.

This month’s cover image shows the mesostructure of a Pd–Ni alloy grown from specifically prepared pores. The image was captured using a SUPRA-50 VP scanning electron microscope. These delicate leaves are reproduced as a result of the self-organization of nanowires growing on the porous membrane over the course of pulse current electrodeposition. ‘Leaves’ start growing from the ‘root’ (‘bottom’) which is a stub-like site of layered fibers. The grown ‘leaves’ are an example of a metallic woven multilayer surface. The inner ‘leaf’ surface exhibits a nonuniform relief, a pronounced woven pattern; its lines directed from the ‘root’ to the

periphery. This relief is a manifestation of the inner architecture on the surface layer. Due to its technological simplicity, template growth of nanostructured metallic coatings may be used to fabricate superhydrophobic surfaces for practical applications.

Further reading

- [1] I. Corni, T.J. Harvey, J.A. Wharton, K.R. Stokes, F.C. Walsh, R.J.K. Wood, *Bioinspir. Biomim.* 7 (2012) 031001 (topical review).
- [2] X. Wang, B. Ding, J. Yu, W. Moran, *Nano Today* 6 (5) (2011) 510–530 (review).
- [3] G.K. Strukova, G.V. Strukov, E.Yu. Postnova, A.Yu. Rusanov, A.D. Shoo, With no color and scent: nanoflowers of metals and alloys arXiv:1108.4589.
- [4] G.K. Strukova, G.V. Strukov, A.Yu. Rusanov, S.V. Egorov, With no color and scent (Part II): Metal and alloy microstructures-handmade replicas of natural objects arXiv:1112.1894.
- [5] G.K. Strukova, G.V. Strukov, S.V. Egorov, With no color and scent (Part III): Architecture of metal ‘shells’ grown on templates by pulse current electrodeposition arXiv:1208.5546.



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