

Feature article

Block copolymer template-directed synthesis of well-ordered metallic nanostructures

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ABSTRACT

3D nanostructured inorganic materials appear as promising candidates for various practical applications. Here we focus on metal nanofoams, a class of 3D nanomaterials uniquely combining the properties of metals and nanoporous materials, and review the recent developments in their preparation methods. Common approaches, such as dealloying, sol–gel synthesis, nanosmelting, combustion synthesis, *etc.*, render metallic nanostructures with highly disordered architectures which might have adverse effects on their mechanical properties. In contrast, block copolymers have the ability to self-assemble into bicontinuous ordered nanostructures that can be applied as templates for the preparation of well-ordered metal nanofoams. Several examples of block copolymer template-directed synthesis of continuous metallic nanostructures will be described and the prospects of this approach will be discussed.

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1. Introduction

To fulfill the constant quest for novel functional materials, the cooperation and development of research areas, such as material science, chemistry, physics, and biology, is required. Nowadays, much attention is given to the field of nanostructured materials that, by definition, have at least one dimension in the range from 1 to 100 nm. In comparison to macroscopic systems, nanomaterials have advanced properties arising from their nanoscale dimensions. Zero-dimensional (0D) nanostructures, nanoparticles, are widely applied in biology and medicine for probing of DNA structure [1], MRI contrast enhancement [2], tissue engineering [3,4], cancer therapy [5], *etc.* Furthermore, they find application in food packaging and food safety [6], as catalysts with enhanced performance [7], for hydrogen storage [8,9], data storage [10], *etc.* One-dimensional (1D) nanostructures (*e.g.*, wires, rods, tubes) are expected to play an important role as both interconnects and functional units in fabricating electronic, optoelectronic, electrochemical, and electromechanical nanodevices [11,12]. Several methods have been used to fabricate 1D nanostructures including template-directed synthesis, self-assembly of 0D nanostructures, size reduction of 1D microstructures, electrospinning and others. For example, Park et al.

demonstrated the preparation of metallic line patterns using functional block copolymer templates [13]. Polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) and poly(2-vinylpyridine)-*block*-poly(methyl methacrylate) (P2VP-*b*-PMMA) block copolymers were spin-coated onto Ag-coated silicon substrate and annealed under solvent vapor to achieve the desired surface morphology. Subsequently, porous block copolymers were obtained by either reconstruction of the P2VP block in ethanol or removal of the PMMA block by UV irradiation followed by rinsing with acetic acid. Finally, silver line patterns were generated using electrochemical etching or direct metal evaporation and lift-off processes. 2D nanostructures, like thin films, can be grown by vapor-phase (sputtering, chemical vapor deposition, atomic layer deposition, *etc.*) or liquid-phase deposition (electrochemical deposition, Langmuir–Blodgett films, self-assembled monolayers, *etc.*) [14–16]. Finally, 3D nanostructures represent the ultimate form factor for a number of materials. However, their creation is a rather delicate task [17]. The available top-down approaches are extremely challenging: lithography techniques allow precise patterning, but can only be implemented in an inherently 2D manner, whilst the available 3D microscale techniques cannot be easily translated to the nanoscale. Currently, the attention is focused on bottom-up approaches that are usually based on self-assembling processes often similar to those occurring in nature.

In this feature article we discuss 3D nanostructured metals. First, we describe the established methods for metal nanofoam preparation and their limitations in terms of ordering at the

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nanoscale. Then, we discuss the application of block copolymers and block copolymer based systems as precursors to metallic nanostructures and suggest the possibilities to overcome the aforementioned limitations with examples of block copolymer template-directed synthesis of metal nanofoams. Finally, we end with a brief outlook on the future trends in this research area.

2. Metal nanofoams: properties and preparation methods

A nanoporous metal foam is defined as a three-dimensional structure comprised of interconnected metallic features with a porosity greater than 50 vol% and in which sub-micron pores significantly contribute to the specific surface area of the foam [18]. Metal nanofoams have, on the one hand, properties characteristic of metals such as electrical and thermal conductivity, catalytic activity and ductility/malleability whilst, on the other hand, also display properties characteristic of nanostructured materials such as high surface area, ultralow density and high strength-to-weight ratio. Due to this unique combination, metal nanofoams appear as candidates for a number of technological applications. Several examples are described in the following paragraph.

Hydrogen is an environmentally friendly energy carrier and its storage is one of the key challenges in the hydrogen economy. It can be stored as pressurized gas, cryogenic liquid or solid fuel as a combination with other materials such as metal hydrides. Due to safety reasons, metal hydrides are the preferable option for hydrogen storage and it has been demonstrated that in comparison to bulk material, nanostructured metals significantly improve the reaction kinetics, reduce the enthalpy of metal hydrides formation, lower the hydrogen absorption and release temperatures [19–21]. Nanoporous metals and their derivatives can also be employed for the production of novel 3D-structured batteries. Open porous networks and thin ligaments enable fast diffusion of ions into and out of electrodes, thus, creating fast discharging and recharging batteries [22]. Due to the size-effect-enhanced catalytic properties, nanostructured metals, such as nickel, could be a low-cost substitution for precious-metal catalysts [18]. Furthermore, literature reports the tunability of the physical properties of nanoporous metals through an applied voltage [23,24]. Injection of the surface charges into a porous metal nanofoam enhances the surface stresses leading to its expansion or contraction. Actuation properties of metallic nanofoams have been proven experimentally [25]. A bilayer foil consisting of solid and nanoporous gold layer was immersed in aqueous electrolyte and the electrochemical potential varied. The nanoporous layer expanded or shrunk whilst the solid one maintained its original dimensions, and thus, the bilayer foil bent with a tip displacement of several millimeters. The observed strain was orders of magnitude larger than in conventional cantilever bending experiments. Metal nanofoams can also be applied as implant materials as they have a high strength-to-weight ratio and assist osseointegration. The high porosity and interconnected nanochannels enhance bone ingrowth and insure the long-term stability of the implant [26,27].

Several approaches for the preparation of nanoporous metal foams have been established. Erlebacher et al. reported the formation of nanoporous gold by the dealloying process from a binary alloy of silver and gold [28]. Silver, as a less-noble metal, can be etched away either electrochemically or by using acid, resulting in a nanoporous gold network with a ligament spacing of *ca.* 10 nm (Fig. 1). The morphology of nanoporous gold in terms of sizes of ligaments and pores can be controlled by varying the dealloying potential [29]. An interesting approach in which the dealloying is combined with templating to render hierarchically porous gold has been reported by Nyce et al. [30] First, Ag–Au alloy was electroless plated onto micron-sized spheres of polystyrene and then the

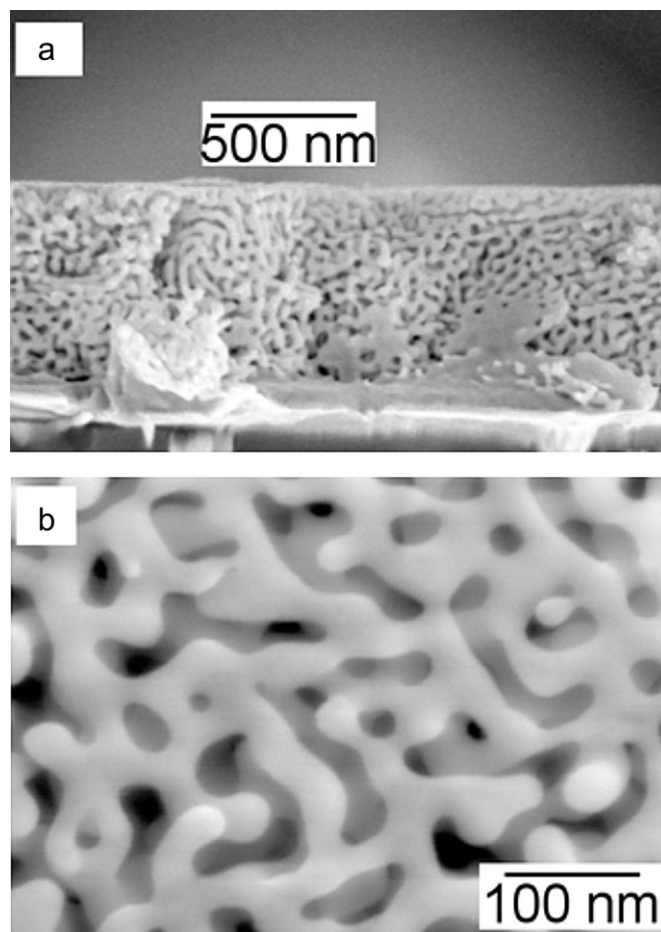


Fig. 1. Scanning electron micrographs of nanoporous gold obtained from Ag–Au alloy by selective Ag etching in nitric acid: (a) Cross-section of dealloyed $\text{Ag}_{32\%}\text{Au}_{68\%}$, (b) Plan view of dealloyed $\text{Ag}_{26\%}\text{Au}_{74\%}$ (atom%). Adapted from Ref. [28].

polymer was removed by pyrolysis. Finally, silver was etched away from Ag–Au alloy using nitric acid leaving behind hierarchically porous gold.

Sol–gel techniques are well-developed for the synthesis of metal nanoparticles, but their applicability to assemble nanoparticles into metal foams appears to be very challenging. It has

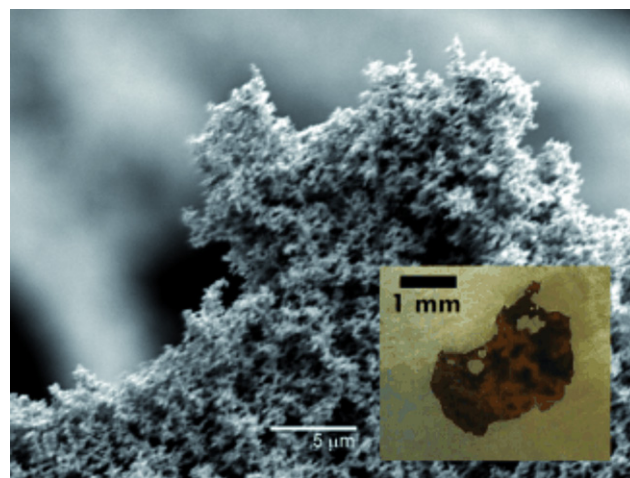


Fig. 2. Scanning electron micrograph of nanoporous gold obtained from sol–gel approach. Reprinted from Ref. [18].

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