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Spatiotemporally controlled electrodeposition of magnetically driven micromachines based on the inverse opal architecture

Chengzhi Hu[a,*], Fabian Aeschlimann[a], George Chatzipirpiridis[a], Juho Pokki[a], Xiangzhong Chen[a], Josep Puigmarti-Luis[b], Bradley J. Nelson[a], Salvador Pané[a]

[a] Multi-Scale Robotics Lab (MSRL), Institute of Robotics & Intelligent Systems (IRIS), ETH Zurich, Zurich 8092, Switzerland
[b] Institute of Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich 8093, Switzerland

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ABSTRACT

We describe a double template-assisted electrodeposition of porous metal microstructures. The method combines two-dimensional photolithography and electrophoretic assembly of polystyrene beads, in order to confine the electrochemical growth of a porous magnetic cobalt–nickel alloy within well-defined microscale boundaries. Polystyrene beads are electrophoretically deposited onto a sulfonate derivatized gold substrate where a patterned photoresist layer (first template) is applied. The polystyrene beads trapped in the first template act as the second template, and cobalt–nickel alloy is electrochemically grown through the voids between the beads. After removal of both templates, magnetic microstructures with well-defined shapes and porosity are successfully obtained. Additionally, we demonstrate the capabilities of these magnetic microstructures as wireless cargo microtransporters by loading their pores with a stimulus-responsive hydrogel. Magnetic manipulation experiments are also demonstrated.

1. Introduction

Micro and nanoporous metals are three-dimensional architectures consisting of interconnected metal filaments [1]. Because of their high porosity and large surface area, these porous materials have recently attracted attention in several areas of research and technology, including catalysis, sensing, fuel cells, plasmonics and magnetophotonics, among others [2–5]. There are several approaches to the synthesis of metal porous structures such as dealloying, sol-gel or hydrogen-evolution-assisted electrodeposition [6–8]. A facile approach to produce metallic porous structures involves the use of beads self-assembled on a substrate as templates. This fabrication strategy is known as colloidal lithography [9,10]. By electrodepositing a material inside the voids between the beads, inverse opal architectures can be easily manufactured. Additionally, the beads can be thermally treated to create a more disordered structure and tune the morphology of the final porous material [11].

While there are many ways of preparing inverse metallic opals, the batch production of porous metal micro- and nanostructures with well-defined shapes and geometries remains a challenge [12–14]. The main difficulties are associated with the colloidal assembly step. For instance, spin coating is a promising approach for the creation of good quality bulk templates. However, the thickness of the template depends on the position of the substrate with respect to the center of rotation. The centrifugal force on the suspension of beads causes differences in solvent evaporation, which in turn affects particle–surface and particle–-particle interactions. Vertical deposition leads to high-quality thin templates. However, the method is very slow and very sensitive to environmental conditions. In general, while most techniques can be used to manufacture relatively large colloidal templates, they do not easily permit the fabrication of inverse opals with well-defined architectures.

In this paper, we capitalize on our previously reported sequential fabrication method for the preparation of porous structures, which exploits electrophoresis to control the coverage and assembly of polystyrene beads on conductive substrates. Herein, we successfully combine two-dimensional photolithography and electrophoretic assembly of polystyrene beads in order to confine the electrochemical growth of porous metal magnetic microstructures within well-defined boundaries. The proposed method allows for the fabrication of porous two-dimensional microstructures with virtually any arbitrary shape with a width resolution determined by the resolutions of photolithography and colloidal templating. To prove the capabilities of our porous microplatforms, we have impregnated the cavities of the resulting microstructures with a stimulus-responsive hydrogel containing a fluorescent dye. Moreover, we demonstrate the use of the fabricated porous

* Corresponding author.
E-mail address: huc@ethz.ch (C. Hu).

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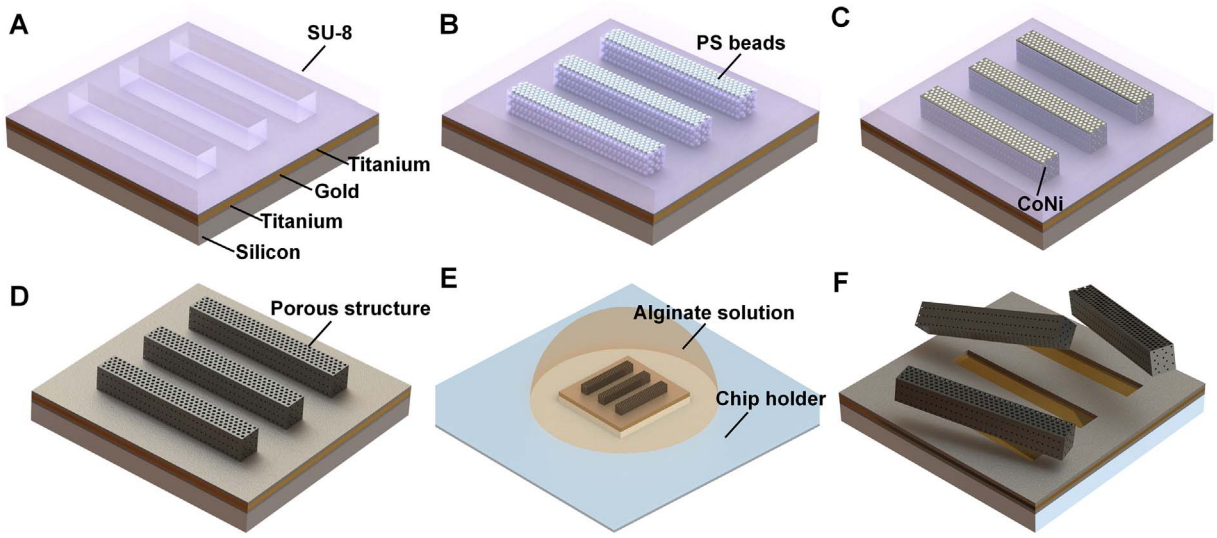

Fig. 1. Fabrication of porous magnetic microswimmers containing hydrogels. (A) Schematic illustration of the working surface (or seed layer) used for electrophoretic deposition. The patterned microcavities are also illustrated. (B) The working surface after the electrophoretic deposition of PS beads inside the microcavities. (C) Illustration showing the working surface after electrochemical plating of the CoNi alloy, and (D) after etching of the SU-8 and PS beads. (E) Drawing showing the filling process used to load the pores of the magnetic microstructures with alginate. (F) Illustration of the release of the porous magnetic microstructures achieved by sonication.

microstructures as wireless magnetic micromachines, thus showing the potential of these microstructures for applications in microrobotics, microfluidics, drug delivery and smart porous microsystems.

2. Experimental section

The procedure for fabricating porous magnetic microstructures is illustrated schematically in Fig. 1. First, Si (111) substrates with evaporated Ti (10 nm)/Au (100 nm)/Ti (10 nm) are prepared. The first Ti layer acts as an adhesion layer between Au and Si; Au acts as the conductive layer; while the second Ti layer acts as a photoresist adhesion promoter. Subsequently, the negative photoresist, SU-8, is applied and microcavities are patterned to define the shape of the final porous microstructure (i.e. the first template has been generated). The exposed second layer of Ti is then etched away using a Ti-etchant solution (TFTN, Transene Company, Inc.) revealing the conductive Au layer (Fig. 1A). To make the Au layer more hydrophilic, and thus to enhance the adhesion of polystyrene (PS) beads, the patterned silicon wafers are immersed in an aqueous solution containing sodium 3-mercapto-1-propansulfonate (40 g/l) for 1 h at 50 °C. Electrophoretic deposition (EPD) is then carried out at room temperature in a custom-made apparatus with a platinum-coated titanium counter-electrode. An ethanol/water mixture (3:1) containing PS beads (3 v/v%) is prepared for EPD. Beads of different sizes (0.5, 3 and 6 μm in diameter) are tested. The electrophoretic deposition of PS beads is performed by applying an electric field of 120 V cm^{-1} for 5 min, where the chip acts as an anode. To evaporate the remaining EPD solution and also to stabilize the PS beads, the substrate is then heated up to 90 °C for 30 min on a hotplate (Fig. 1B). Next, the electrodeposition of a cobalt–nickel (CoNi) alloy is performed (Fig. 1C) using a previously optimized electrolyte [15]. The electrochemical experiments are conducted using an Autolab potentiostat (Metrohm, PGSTAT204) at room temperature. All samples are fabricated by galvanostatic pulse electrodeposition at -40 mA/cm^{-2} with a 5 ms pulse on time and a 10 ms pulse off time. The electrodeposition conditions are selected to ensure a homogeneous CoNi deposition with smooth surface morphology. In the last fabrication step, the SU-8 photoresist is removed by resist remover RR-41 and the PS beads are etched away by immersing the chip in chloroform for 3–4 days (Fig. 1D). The morphology and chemical composition of the structures generated are investigated employing scanning electron microscopy (SEM, Zeiss ULTRA) and energy dispersive X-ray (EDX) spectroscopy (NVision 40, Zeiss), respectively, where quantification is done using K lines at 15 kV for 50 s. A cross-section analysis of the final porous magnetic microstructures is performed under SEM after breaking them with a micromanipulator. The magnetic properties of the structures are investigated by a vibrating sample magnetometer (VSM, MicroSense EZ9). The magnetization was calculated taking into account the plated area, the thickness of the structure and a random close-packed porosity value of 0.64. Afterwards, 1 wt% of alginate sodium solution mixed with 10 v/v% of fluorescent latex beads solution (L5155) is loaded on top of the chip (Fig. 1E). A vacuum is applied to facilitate the penetration of the hydrogel solution into the pores. The surplus alginate solution is removed by dipping the silicon wafer into water. Crosslinking of the entrapped alginate solution in the microstructure is achieved by immersing the rinsed silicon wafer in a 0.5 M calcium chloride ($CaCl_2$) solution [16]. Finally, the microstructures are released from the substrate by sonication (Fig. 1F). All the chemicals used in this study were purchased from Sigma-Aldrich and used as received. The carboxylated PS beads came from Polysciences.

3. Results and discussion

3.1. Fabrication and characterization of porous magnetic microstructures

EPD is a cost-effective and versatile technique for coating conductive substrates with particulates, regardless of their shape or texture [17,18]. The negatively charged PS beads, which are homogeneously dispersed in a solvent of water and ethanol, are allowed to migrate towards the positively charged gold layer of the chip via electrophoresis under an applied electric field. Once the particles reach the electrode, they coagulate to form a deposit. Fig. 2A shows SEM images of the porous magnetic microstructures fabricated from confined microcavities of various shapes present in the conductive working surface. The microstructures obtained have vertical walls, which conform to the photopatterned microcavities. Careful observation of the microstructures with SEM clearly shows that the micropores generated are well-ordered, fairly uniform, and open throughout the entire microstructure (Fig. 2B). The height of the final magnetic microstructure can be accurately controlled by varying the electrodeposition time. The size of the micropore is determined by the diameter of the PS beads used during the EPD process, which in the present case is 3 μm. Careful investigation of cross-sectional SEM images, such as the one shown in