Electronic Supplementary Information for:

Hard-magnetic Cell Microscaffolds from Electroless Coated 3D Printed Architectures

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Experimental methods section:

Stereolithography 3D printing. All the 3D scaffolds were designed using Solidworks software (Dassault Systèmes, France) and printed with a commercial stereolithography machine, model DWS028J Plus produced by Digital Wax Systems (DWS systems, Italy). This machine mounted a monochromatic laser Solid State Bluedge BE-1500A/BE-1500AHR with galvanometer control, an emitting power of 30 mW, a wavelength of 405 nm, a beam spot diameter of 22 μm and a vertical (z-axis) resolution of 10 μm. Prior to the printing step, the 3D virtual models were processed with a dedicated 3D parametric software (Nauta+, DWS systems) and reoriented on the working platform to ensure the highest printing resolution. The resulting processed virtual models were subsequently sent to Fictor (DWS Systems), the software that directly controls the 3D printer, and numerically sliced according to the user-imposed building parameters. The laser speed was ranged between 250 and 4300 mm/s and the layer thickness between 25 and 10 μm. A commercial urethane-acrylate resin filled with 20% m/m silica-alumina powder (DL260 by DWS) was employed. According to technical specifications, such resin is characterized by E_c and D_p of 9.48 mJ/cm^2 and 0.079 mm, respectively. A unique cylindrical microscaffold design (visible in figure S1) was printed in two sizes, namely L (large) and S (small). Table S1 reports nominal measures for L and S samples. After the printing step, the samples were washed in ethanol to remove unreacted resin, dried with nitrogen and then post-cured by further exposition to UV radiation for 30 minutes (λ = 405 nm, Model S Ultraviolet Curing Unit, DWS®). The UV post-curing step is meant to crosslink any uncured liquid resin within laser-scanned adjacent lines and to accomplish the total polymer conversion.

Devices metallization. All the chemicals employed were purchased from Sigma Aldrich and used as received. The devices were cleaned for 4 minutes at room temperature in a solution containing 50 g/l sodium carbonate, 35 g/l sodium silicate, 3 g/l sodium dodecyl sulfate. No stirring was used during the cleaning. The devices were immersed in the solution and subsequently filtered out at the end of the cleaning step. After being washed with deionized water, the surface of the samples was etched for 30 minutes in a 200 g/l KOH solution at 45 °C. Also in this case, no stirring was used and the samples were filtered out of the solution to recover them. The surface was carefully washed with water and activated for electroless deposition using a Sn-free activation process comprising two steps: immersion in a Pd based commercial activator (Neoganth 834 by Atotech) and subsequent immersion in a reducing bath composed of 20 g/l $NaBH_4$. Activation was performed three times on the devices. The devices were not washed after the immersion in the Neoganth activator but they were rinsed after the passage in the reducing solution. A first copper layer was deposited using an alkaline electroless

bath having the following formulation: 20 g/l copper sulfate pentahydrate, 40 g/l trisodium EDTA, 10 mg/l 2, 2'-bipyridine, 10 mg/l potassium ferricyanide, 10.5 g/l glyoxylic acid solution (50 % wt.). Deposition was performed at 45 °C and pH 12 for 15 minutes. The microdevices were continuously suspended in the solution thanks to the vigorous agitation. At the end of the metallization they were recovered from the solution by filtering, washed in deionized water and dried with nitrogen. The active magnetic material, CoNiP, was applied using an electroless bath containing 39.3 g/l cobalt sulfate hexahydrate, 7 g/l nickel sulfate hexahydrate, 50 g/l trisodium citrate dihydrate, 30 g/l boric acid, 25 g/l sodium hypophosphite monohydrate. Deposition was performed at pH 9.5 and 45 °C for 3 hours. CoNiP was deposited also on planar Cu samples for 30 minutes in the same conditions to study its magnetic properties and microstructure. A square area of 1 cm × 1 cm was metallized with CoNiP. Figure 1a visually depicts the overall plating process followed to obtain the CoNiP metallized microdevices. A gold layer was deposited on some samples via ENIG to favor biocompatibility. After applying CoNiP, filtering, washing and drying the samples, a NiP layer was applied from the following solution: 32 g/l nickel sulfate hexahydrate, 20 g/l trisodium citrate dihydrate, 25 g/l ammonium chloride, 28 g/l sodium hypophosphite monohydrate. Deposition was carried out at 45 °C and pH 9 for 15 minutes. NiP constituted the first step of the ENIG process, which was completed with the immersion in a commercial solution (Aurotech by Atotech) to deposit gold on the surface by displacement.

Devices and coatings characterization. For SEM characterization, a Zeiss EVO 50 microscope was employed. Such instrument was equipped with an Oxford Instruments Model 7060 EDS module used to study the composition of the deposited films. XRD was performed using a Philips X-pert MPD with CuK_{α} = 1.5406 Å. A Laica DMLM direct illumination microscope was used to analyze the section of the samples. Such section was obtained encapsulating a L scaffold in a reticulating epoxy resin. After 24 hours, the resin block containing the sample was cut along the axis of the scaffold and polished to mirror finish for the optical microscope observation. Thickness of the metallic layers observed in section was evaluated with ImageJ, an image analysis software. Hardness and elastic modulus of CoNiP was evaluated on a planar sample deposited on copper using a Fischerscope HCV in Vickers configuration with a load of 50 mN and 0.4 μm as indentation depth. The same instrument was employed to determine the elastic modulus of the DL260 resin. Magnetic properties of the materials were evaluated by mean of a Princeton Measurement Corp. MicroMag 3900 VSM system.

Magnetic actuation. Magnetic actuation was performed employing the Octomag manipulation system. Microscaffolds were premagnetized putting them in contact with a cylindrical NdFeB permanent magnet. The radius of the magnet was 2 cm, while its thickness was 1 cm. Samples were

left in contact with the center of the planar surface of the magnet for 1 minute and then carefully removed.

Biocompatibility tests. Biocompatibility was evaluated by mean of a standard MTT assay test. The cells used for biocompatibility tests were mouse 3T3 fibroblast (atcc) cultivated using standard methods, in 24-well flat bottomed tissue culture plates of good optical quality. The final volume of tissue culture medium in each well should be 0.1 mL, and the medium (DMEM) may contain up to 10% Fetal Bovine Serum to be at physiological conditions. The MTT Cytotoxicity study was conducted in well plates with 1×10^4 3T3 cells in culture medium (100 μL). They were incubated at 37° C for cleavage of MTT to occur. Optimal times may vary according to the assay, but four hours was suitable for the purposes of this work. At the end of this time, the MTT formazan produced in wells containing live cells appeared as black, fuzzy crystals on the bottom of the well. Cell medium was removed, and then cells were washed with PBS and exposed to microrobots. After 2 days of incubation, the supernatant was replaced by fresh media (100 μL) and supplemented with CTO2 MTT. After 4 h of incubation, isopropanol (100 μL) and HCl (0.04 M) were added to each well and they were mixed thoroughly by repeated pipetting with a multichannel pipettor. Finally, absorbance measurements were conducted in a microtiter plate reader (Tecan Infinite 200 Pro) at 540 nm and a reference wavelength of 630 nm

Figure S1 reports a dimensional scheme of the microscaffolds produced.

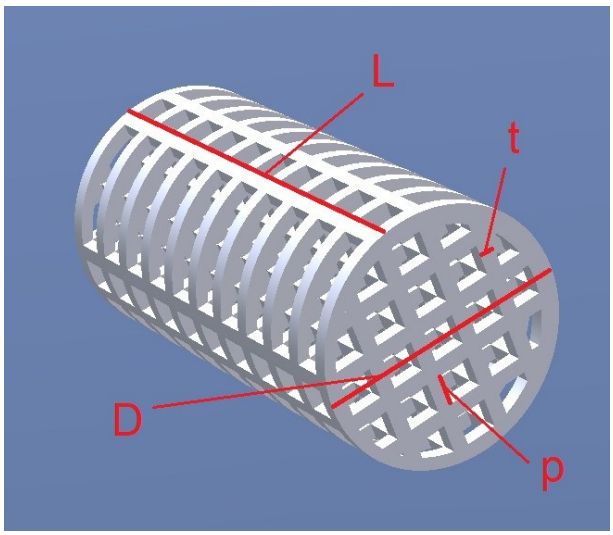

Figure S1. Scheme of a SLA printed microscaffold

Table S1 contains the nominal dimensions of the different features of the microscaffolds, as indicated in figure S1.

Table S1. Nominal dimensions (with reference to figure S1) of the microdevices printed in the two sizes, L and S

Dimension	**Value (in µm; type L)**	**Value (in µm; type S)**
L	4500	3000
D	2400	1600
t	150	100
p	290	190

Figure S2 depicts the appearance of a L sample observed from the side (image left) and from the top (image right) with optical microscopy.

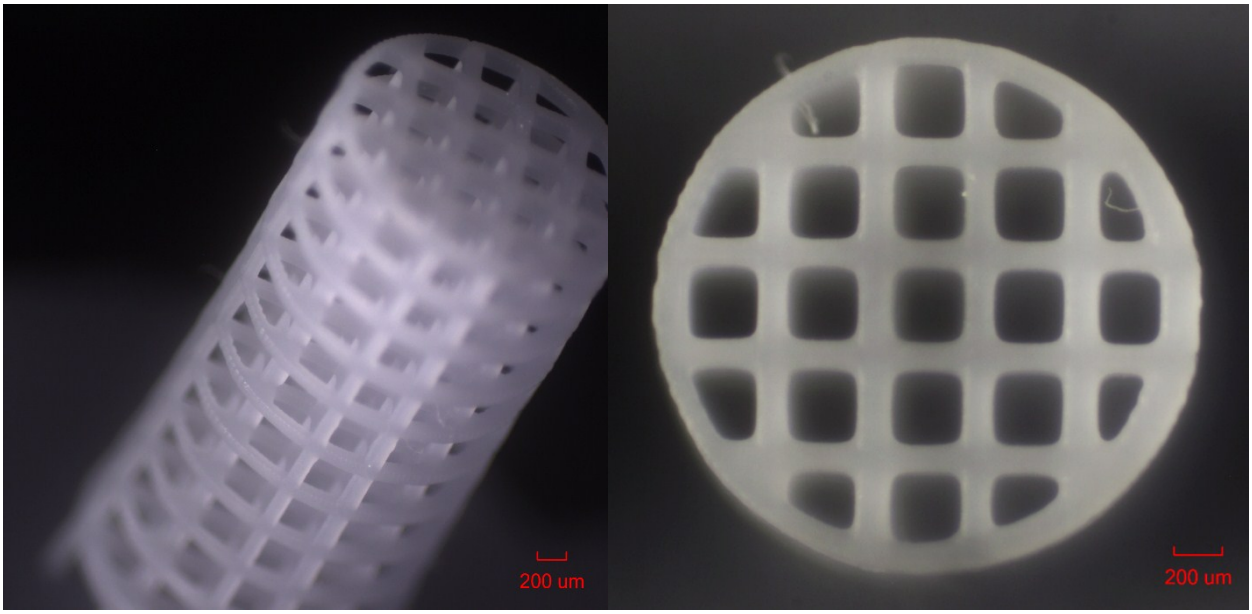

Figure S2. Optical image of a L sample after SLA printing: from the side (left image) and from the top (right image)

Figure S3 depicts the appearance of S samples with printing supports still present after SLA printing.

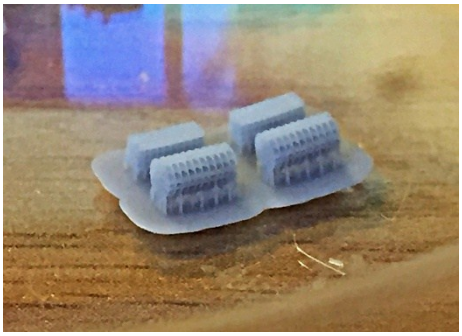

Figure S3. S samples after SLA printing

Figure S4 reports the VSM characterization of CoNiP plated on a planar Cu substrate.

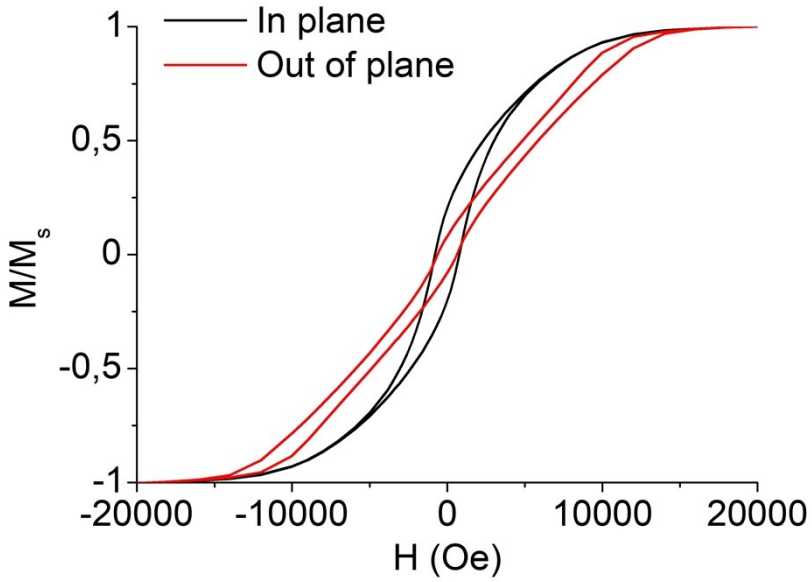

Figure S4. VSM characterization of electroless CoNiP on Cu

Figure S5 represent the visual appearance of some L samples, coated with either Cu/CoNiP or Cu/CoNiP/NiP/Au.

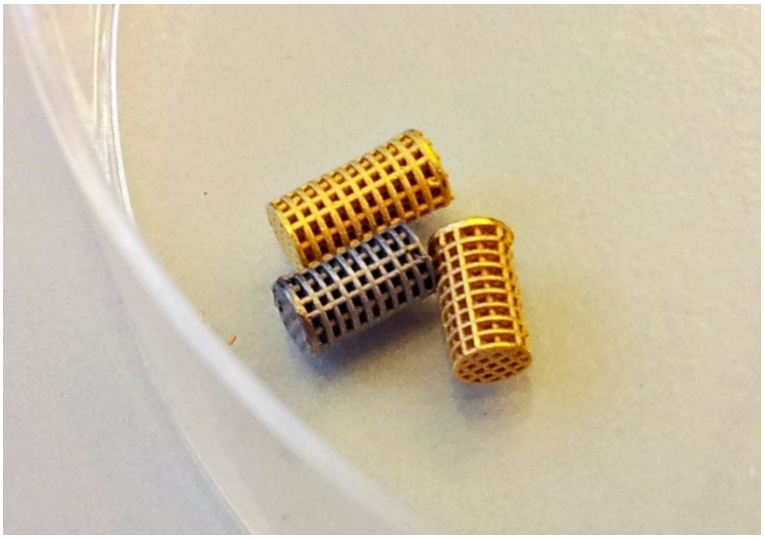

Figure S5. Visual appearance of three L samples, coated with either Cu/CoNiP (grey) or Cu/CoNiP/NiP/Au (yellow)

Figure S6 shows the section of a L sample embedded in an epoxy resin, cut with a diamond blade and polished with sand papers to mirror-like finish. Half of the image was obtained observing the sample at the stereomicroscope, while the remaining half was acquired using a metallographic optical microscope.

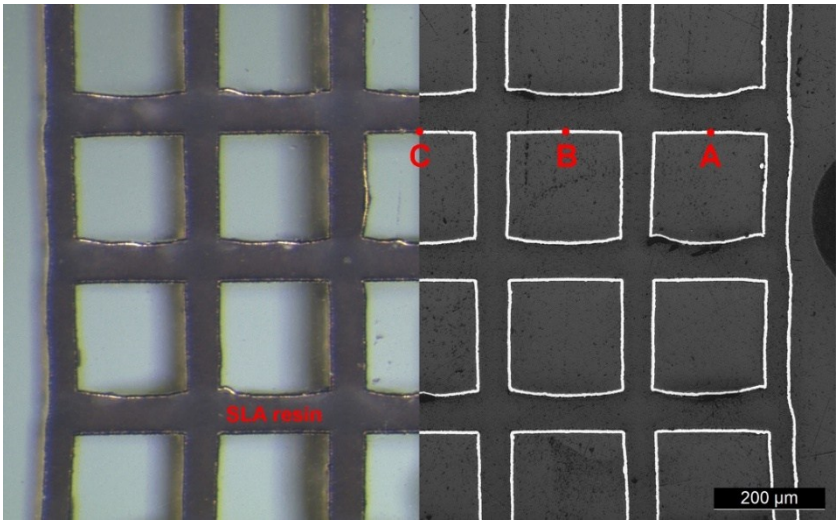

Figure S6. Section of a L microdevice with three zones (A, B and C) highlighted; the image is a composition of a stereomicroscopy picture (left) and an optical microscope operated in reflection (right)

Figure S7 depicts a S sample observed using SEM.

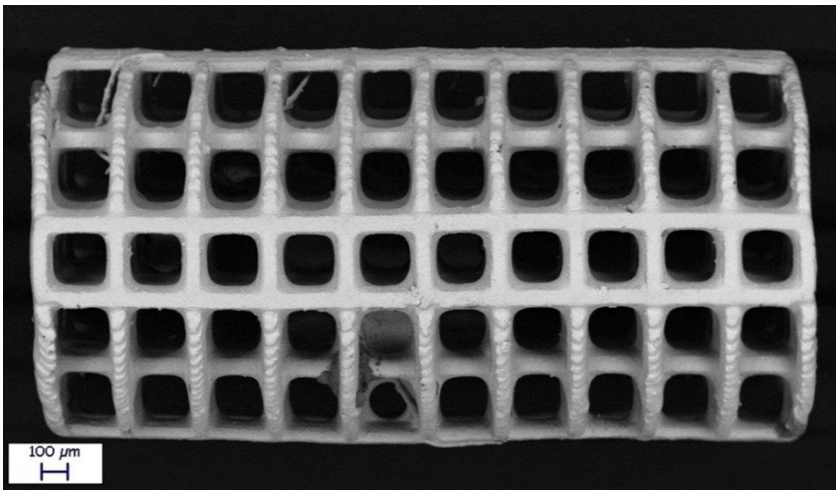

Figure S7. SEM image of a S microdevice metallized with Cu/CoNiP/NiP/Au

Figure S8 shows the appearance of the surface of a L sample after the biocompatibility test. Such sample was obtained prolonging the ENIG deposition for 5 hours.

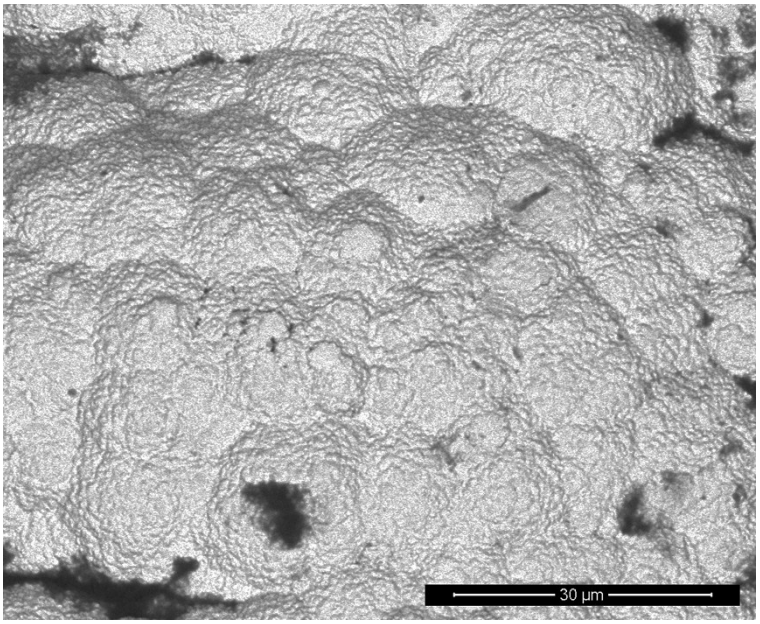

Figure S8. Surface of a L sample (Au 5h) after the biocompatibility test

Figure S8 was obtained exploiting the backscattered electrons signal. Black spots are organic residues resulting from the biocompatibility test.