Rapid formation of self-supporting polydimethylsiloxane sheets with periodic clusters of embedded nickel nanoparticles

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Abstract

The direct and rapid formation of a precise pattern of metallic NPs supported and/or embedded in a flexible polymeric substrate is not an easy task and represents a study focus due to the numerous applications that it follows. However, the development of simpler and more reliable procedures is still highly desirable. This paper presents an innovative technique simple, cheap and robust for producing a self-supported sheet of polydimethylsiloxane (PDMS) embedding periodic arrays of clusters of nickel NPs (NiNPs). The method uses the pyroelectric effect in a periodically poled lithium niobate (PPLN) crystal for producing a surface charge template able to address the patterning of the NPs by applying a simple thermal stimulation. The key advantages are rapidity, single-step and electrode-free operation. The reliability of the technique has been demonstrated for different geometries that we call here “dots” and “grid” and for three different periods 50 µm, 200 µm, 400 µm. The resulting sheets are attractive for both their flexibility and magnetic properties that could be used for detection, entrapment and/or patterning of micro and nanoparticles in various fields such as microfluidics and biomedicine.

Keywords: Metal nanostructures, Nickel nanoparticles, polymeric sheet, Lithium Niobate, pyroelectric effect.

1. INTRODUCTION

Metal nanostructures are attracting great interest due to their unique and extraordinary properties [1,2]. In fact, some unusual effects are generated when the size of metal particles is reduced to nanoscale [3-5]. Nowadays the metal nanoparticles (NPs) are likely to impact all aspects of physics, chemistry, biology, health sciences, and other interdisciplinary areas, as well described in many valuable reviews [6-10]. In particular, over the last few years, there is an increasing interest in
developing devices made of metal NPs supported and/or embedded into a flexible polymeric substrate, due to the exciting new applications offered by the ability to assume arbitrary shapes and geometries. In fact, this allowed the development of several flexible, stretchable and wearable devices consisting for example of sensors, light-emitting diodes and transistors [11-16].

Among the flexible substrates, polydimethylsiloxane (PDMS) is the elastomer most widely used in such systems [17]. PDMS is a silicone-based component, introduced the first time for rapid fabrication of microfluidic devices through the so-called ‘soft lithography’ [18,19]. The key advantages of PDMS include low costs, short fabrication and turn-around time, optical transparency, flexibility and bio-compatibility, thus making it a first choice in various fields such as microfluidics, lab-on-a-chip, micro-optics, microbiology and biomedical devices [20-23].

We can identify two main families of devices making use of metal NPs combined with PDMS substrates: (1) those with patterns of NPs on the surface of rubber-like PDMS substrates and (2) those with NPs embedded in the polymer matrix by appropriate mixing procedures prior to the cross-linking process. In the first case a wide variety of fabrication techniques has been proposed in literature. The most common ones make use of dry etching and lift-off procedures [24,25] which, even providing relatively high spatial resolutions, they still present different drawbacks in terms of complexity, time-consuming processes and expensive equipment. In addition, the solvents commonly used in these procedures are detrimental for the properties of PDMS. Alternative techniques include soft lithography [13, 26,27], where the fabrication of a separate mold is required for the pattern transferring, which also increases the complexity of the whole fabrication process. More recently also inkjet printing techniques have been presented in literature for printing successfully NPs-based inks [28,29] on the surface of PDMS substrates, but still their applications present different limitations due to nozzle-clogging drawbacks.

Concerning the family of embedded NPs usually they are used as fillers under a wide variety of varying conditions that include for example the surface functionalization, the shape and the concentration of the particles, in order to investigate the properties of the resulting composite material [30-32]. In particular, there is a field of research that focuses the attention on the fabrication of aligned structures of NPs embedded in PDMS substrates, in order to achieve composite materials with anisotropic properties. The most widely used means for aligning metal NPs in polymer matrices is an external magnetic field [33,34], especially in case of nickel (Ni) NPs.

In this wide framework of techniques, more or less well-established for fabricating PDMS structures reinforced with metal NPs, the development of easier and more reliable procedures is still highly desirable for patterning metallic NPs embedded in elastomer sheets. In the last decade we have proposed an innovative use of the pyroelectric effect for a new electrode-free version of electro-
hydrodynamics for different applications including dielectrophoresis [35], charge lithography [36], inkjet printing [37-39], electrospinning [40,41], biological manipulation [42-46] and biosensors [47-49]. The technique makes use of the spontaneous charge developed pyroelectrically on the surface of periodically poled lithium niobate (PPLN) crystals through an appropriate thermal stimulation.

Here we demonstrate for the first time a simple, inexpensive and robust technique based on a pyroelectric charge template for producing free-standing PDMS sheets which embed periodic arrays of nickel NPs (NiNPs) clusters. The particles are dispersed randomly in the elastomer base and spin coated onto a lithium niobate (LN) crystal sample micro-engineered with an array of reversed ferroelectric domains. We use here the pyroelectric effect for arranging the particles according to the template defined by the LN domain pattern through a rapid, single-step and electrode-free modality that makes use of an innovative electro-hydrodynamic effect generated by the surface charges on the surface of the LN crystal after a simple thermal stimulation. The PDMS composite with the microarray of NiNPs clusters is peeled-off from the crystal very easily and the same crystal can be re-used several times for producing different sheets, allowing us to avoid tedious replications of chemical and/or physical procedures. The high versatility and robustness of the technique allows us to fabricate microarrays with different periods ranging from 400 µm down to 50 µm. Moreover, we show how, after fabrication, the clusters can be magnetized easily, thus obtaining a freestanding sheet with microarrays exhibiting magnetic properties.

2. MATERIALS AND METHODS

2.1 Lithium niobate.

The LN crystals were bought from Crystal Technology Inc. in the form of both sides polished 500µm thick c-cut 3-inch wafers and were cut into square samples (2×2) cm2 sized by a standard diamond saw. It is well known that, at equilibrium, the spontaneous polarization $P_s$ of a c-cut LN crystal is fully compensated by screening charges from the environment, thus producing an electrically neutral system. According to the pyroelectric effect, a temperature change $\Delta T$ causes a variation $\Delta P_s \propto \Delta T$, which, neglecting the losses, builds up uncompensated surface charges, corresponding to a charge density $\sigma \propto \text{Pc} \Delta T$, where $\text{Pc}$ is the pyroelectric coefficient [50]. In other words, the temperature variation perturbs the equilibrium state generating uncompensated charges that, as a consequence, produce a high electric field on the crystal surface [39].

2.2 Electric field poling.

The LN crystal samples were subjected to electric field poling in order to fabricate (2×2) cm2 sized PPLN samples with a square array of ferroelectric domains with opposite orientation and hexagonal
The PPLN were obtained by standard electric field poling onto photoresist patterned samples [53]. Three square arrays of hexagons were considered: period 400 µm, period 200 µm and period 50 µm [52].

2.2 PDMS/Ni suspension.
The NiNPs were purchased from Sigma Aldrich powder, <1 µm, 99.8% trace metals basis. Their diameter falls in the range 300-500nm. They were cleaned via multiple cycles of centrifugation and, after removal of supernatant, they were precipitated and dried in a vacuum desiccator for 24 h. After that they were monodispersed in fresh nonpolar PDMS (Sylgard 184, Dow Corning Corp) at a concentration of 12% w/w and uniformed by magnetic stirring and ultrasound treatments for 5h. The PDMS was purchased in the form of two compounds, a pre-polymer and a cross-linker with a percentage of curing agent 1:10.

3. RESULTS AND DISCUSSION
We used c-cut wafers of LN with pyroelectric properties (see Materials and Methods). We fabricated PPLN crystals by electric field poling (see Materials and Methods for details) and Fig.1(a) shows the typical optical microscope image.

Figure 1. (a) Optical microscope image of a typical PPLN crystal where the hexagonal areas correspond to the ferroelectric domains with reversed polarization; (b,c) 3D schematic views of a typical PPLN crystal with the arrows indicating the orientation of the polarization in case of original face c- up and c+ up, respectively.
The hexagonal areas correspond to the ferroelectric domains with polarization reversed respect to the surrounding regions. **Figure 1(b)** shows the 3D schematic view of the PPLN crystal with the original $c$- face (i.e. before poling) positioned up and therefore with hexagons exhibiting $c^+$ polarity. Conversely, **Fig.1(c)** shows the schematic view of the PPLN crystal with the original $c^+$ face up and therefore with hexagons with $c^-$ polarity. At equilibrium conditions, these polarization charges are compensated by surface screening charges of opposite sign (not shown in the schemes) producing a neutral system. For example, in case of the hexagons with $c^+$ polarity (see **Fig.1(b)**) the polarization charge (+) into the hexagons is compensated by negative screening charges (-) provided by the environment and, the viceversa occurs in case of the hexagons with $c^-$ polarity (see **Fig.1(c)**).

We fabricated three PPLN crystals which differ each other only for the period of the hexagonal domains: (1) 400 µm; (2) 200 µm; (3) 50 µm. We called them P400, P200, P50, for simplicity, and we investigated the reliability of the technique by using these three crystals under different conditions, as summarized in **Table 1**.

| PPLN CRYSTAL | PERIOD (µm) | TREATMENT                                      | PATTERN |
|--------------|------------|-----------------------------------------------|---------|
| P400         | 400        | • PDMS/Ni on $c^-$ - positive $\Delta T$ (heating) | dots    |
|              |            | • PDMS/Ni on $c^+$ - positive $\Delta T$ (heating) | grid    |
| P200         | 200        | • PDMS/Ni on $c^-$ - positive $\Delta T$ (heating) | dots    |
|              |            | • PDMS/Ni on $c^-$ - negative $\Delta T$ (cooling) | grid    |
|              |            | • PDMS/Ni on $c^+$ - positive $\Delta T$ (heating) | grid    |
|              |            | • PDMS/Ni on $c^+$ - negative $\Delta T$ (cooling) | dots    |
| P50          | 50         | • PDMS/Ni on $c^-$ - positive $\Delta T$ (heating) | dots    |
|              |            | • PDMS/Ni on $c^+$ - positive $\Delta T$ (heating) | grid    |

**Table 1**: Summary of the PPLN crystals and conditions used for the fabrication of the reinforced PDMS sheets. From the left, the first column indicates a short name chosen for each crystal, the second column the period of the hexagons, the third column indicates on which original face of the crystal the PDMS/Ni suspension was spin coated and the temperature variation applied, and finally the fourth column indicates the final pattern of Ni obtained. In the cooling experiments, the negative $\Delta T$ stands for $\Delta T = (-20^\circ C) - 25^\circ C$, while in the heating experiments the positive $\Delta T$ stands for $\Delta T = 170^\circ C - 25^\circ C$.

We prepared a suspension of PDMS with NiNPs, that we call PDMS/Ni, according to the procedure illustrated in the section **Materials and Methods**. Each of the three crystals was used for a first experiment with the suspension spin coated on the original $c$– face and, after solvent cleaning, for a second experiment with the suspension on the original $c^+$ face. The crystals P400 and P50...
experienced only the positive ΔT while in case of P200 we studied the effect of both positive and negative ΔT (see Tab.1). Figure 2 shows the schematic view of the fabrication steps.

Figure 2: Schematic view of the fabrication steps in case of positive and negative ΔT.

The hexagonal areas in the PPLN crystal correspond to the ferroelectric domains with polarization orientation reversed respect to the surrounding regions. It is noteworthy that they are not relief structures like the scheme makes them to appear. After standard solvent cleaning, the PPLN crystal was spin-coated at 7000 RPM with a thin film of the PDMS/Ni suspension (see Fig.2 (a)) and then subjected to the two types of experiments: (1) heating, starting from a room temperature condition (25 °C) the sample is heated up to 170°C on a digital hotplate for about 2 min (see Fig.2 (b)); (2) cooling, starting from a room temperature condition (25 °C) the sample is cooled down to -20°C in a refrigerator for about 5 min (see Fig.2 (c)).

Depending on the specific set of conditions illustrated in Tab.1 the final pattern can be of two types that we call here “dots” or “grid”. They are both periodic with the period corresponding to that of the hexagons underneath. The dots pattern consists of Ni clusters that, at microscopic scale, fill completely the hexagonal regions, assuming with high fidelity their shape. In other words, the edges of the Ni clusters correspond perfectly to those of the hexagonal domains. Conversely, the grid exhibits the complementary distribution with NiNPs filling the regions outside the hexagons. In the heating experiment it possible to have a contextually crosslinking of PDMS by adding the crosslink agent in the Ni /PDMS suspension. Since the cross-linking happens at 170 °C this feature is possible only in the heating experiment. After the crosslinking, the PDMS becomes solid, so that the NiNPs
pattern remains frozen into the PDMS layer that is then peeled-off the crystal easily. As a result, we obtain a freestanding PDMS sheet reinforced with a periodic pattern of Ni clusters (see Fig. 2(d)).

In order to observe in real time the formation of the NiNPs clusters, we used a conventional Peltier cell placed under the crystal on the stage of an upright optical microscope. In this way, the crystal experienced a rapid temperature variation that is positive in the heating experiment (1) and negative in the cooling experiment (2), both able to generate the pyroelectric effect (see Materials and Methods). At this stage, in about 10 s, the NiNPs appear to move rapidly in the liquid PDMS matrix until forming a well-defined periodic pattern which follows the geometrical template of the PPLN crystal. The supplementary movies S1 and S2 were captured under the optical microscope and show the formation of the dots pattern, as an example, in case of P200, with PDMS/Ni spin coated on the original c-face (i.e. hexagons with c+ polarity), positive AT and with two different concentrations of Ni. It is noteworthy how the displacement of the particles is so clear that the regions on the hexagons are completely full of Ni, while the surrounding ones are transparent with no residue of particles appreciable at microscopic scale.

Figure 3 shows the optical microscope images of the PDMS sheets, reinforced with different Ni patterns obtained by using the conditions illustrated in Table 1, while Fig. 4 shows the schematic view of the pyroelectric charge template arising after positive and negative AT. In particular, the images in Fig. 3(a,c,e) show the dots pattern obtained in case of the original c-face (e.g. hexagons with c+ polarity) for P400, P200 and P50, respectively, when using the positive AT. The temperature rise induces the pyroelectric effect, which decreases the net polarization inside the crystal. Correspondingly, the external screening charges loose partially the compensation from the polarization charge and become excessive. This means that the regions outside the hexagons exhibit a positive excess charge and viceversa for the regions inside the hexagons, as reported schematically in the insets of Fig. 3(a,c,e). The Ni clusters follow with high fidelity the shape of the hexagons underneath, thus generating a pattern with the same periodicity of the hexagons. The results are reproducible for all the three periods (400µm; 200µm; 50µm). Figure 3(b,d,f) show the images corresponding still to positive AT but in case of the original c+ face (e.g. hexagons with c- polarity) for P400, P200 and P50, respectively. As reported in the insets of Fig. 3(b,d,f), the charge exposed on the face c+ will be negative and the charge exposed inside the hexagon c- will be positive. In this case the clusters form a grid surrounding the hexagons of the PPLN crystal, again following with high fidelity the periodicity of the PPLN crystal. Also in this case, the process exhibits high reproducibility for all the three periods (400µm; 200µm; 50µm). Figure 3(g,h) show the images corresponding to P200 treated by a negative AT with PDMS on the original c- and c+ face, respectively. In correspondence with a negative AT, the increasing of the polarization charge leads to a state of a lack
of compensating charges on the surface of the crystal so that on the face $c^-$ (hexagons $c^+$) a net negative charge and opposite to that exposed inside the hexagons, will be exposed, viceversa happens on the $c^+$ face of the PPLN crystal.

Figure 3: Optical microscope images of the PDMS sheets reinforced with different Ni patterns before peeling off the crystal: (a) P400 PDMS/Ni deposited on $c^-$ (hexagon $c^+$) and heating experiment; b) P400 PDMS/Ni deposited on $c^+$ (hexagon $c^-$) and heating
Due to the pyroelectric effect the ferroelectric polarization of the crystal decreases when experiencing the positive $\Delta T$, thus leading to a temporary excess of screening charges leading to a temporary imbalance between the polarization charge and that of the screening charges (see Materials and Methods). This means that, in case of the original $c^+$ face, the positive $\Delta T$ generates a temporary excess of charge (+) in the areas of hexagons and of charge (-) in the surroundings. In other words, a pyroelectric charge template arises on the surface of the PPLN crystal. This is an alternation of charge (+) and charge (-) that leads to a pyroelectric field distribution which follows the geometry of the reversed domains and with the key innovation of being free from conductive coatings and external high voltage generators. The opposite charge distribution occurs in case of the original $c^-$ face, namely with hexagons exhibiting an excess of charge (-) and viceversa in the surroundings. Conversely, in case of negative $\Delta T$, the polarization charge increases in the ferroelectric domains, leading to a temporary imbalance between the polarization charge and that of the screening charges (see the pyroelectric effect in Materials and Methods). As a consequence, on the original $c^+$ face the pyroelectric charge template consists of hexagons with an excess of charge (-) and the surroundings with an excess of charge (+). The viceversa occurs in case of original $c^-$ face.

The NiNPs were centrifugated before mixing with PDMS matrix and this process conferred a positive surface charge to the particles due to the triboelectric effect [54-56], while the PDMS is a nonpolar fluid with low dielectric constant and weak viscosity. In presence of the pyroelectric charge
template of the PPLN crystal, the Ni/PDMS suspension can be considered as an electrorheological suspension \[57\]. In particular, the motion and re-distribution of the NPs in the PDMS layer is determined by the net force \( F \) expressed by the following general formula \[58,59\]:

\[
F = F_{EP} + F_{DEP} = -qE + p(\nabla E)
\]

which is the combination of two prevalent forces acting on the NPs: the electrophoretic (EP) force \( F_{EP} \) and the dielectrophoretic (DEP) force \( F_{DEP} \). The first term describes the Coulombic interaction between the net charge \( q \) of the NPs and the homogeneous electric field \( E \) generated by the pyroelectric charges on the areas of the hexagons and of the surroundings, in other words far away from the hexagon edges. The second term arises from the interaction of the dipole moment \( p \) induced in the NPs by the gradient \( \nabla E \) of the electric field \( E \) developing across the borders of the hexagons, where the net charge on the surface jumps between (+) and (−). Approximating the shape of the NPs to a sphere, the net \( F_{DEP} \) can be quantified by the following general formula \[60\]:

\[
F_{DEP} = 2\pi r^3 \varepsilon_m \text{Re} \left( \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m} \right) \nabla E^2
\]

where

\[
\left( \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m} \right) = f_{CM}
\]

is known as the Clausius-Mossotti factor \[60\], \( r \) is the radius of the NPs, \( \varepsilon_m \) is the real permittivity of the medium (PDMS), \( \varepsilon_p \) and \( \varepsilon_m \) are the complex permittivities of the particles (Ni) and of the medium, respectively. A general complex permittivity is given by \( \varepsilon' = \varepsilon - j(\sigma/\omega) \) where \( \varepsilon \) is the real permittivity, \( \sigma \) the conductivity, \( j = \sqrt{-1} \) and \( \omega \) the angular frequency of the applied field. In this work the electric field is steady, which corresponds to a regime with \( \omega \to 0 \), and therefore

\[
\text{Re}(f_{CM}) = \frac{\sigma_p - \sigma_m}{\sigma_p + \sigma_m} \quad (\omega \to 0)
\]

meaning that the polarizability is governed by the conductivities. The conductivity \( \sigma_p \) of Ni (~1.4×10^7 S/m) is much higher than that \( \sigma_m \) of PDMS (~2.5×10^{-14} S/m). Therefore the real part of \( f_{CM} \) (see Eq.(4)) is positive and, as a consequence, the \( F_{DEP} \) is positive as well. This means that the NiNPs are attracted by the regions with high field gradient, such as the hexagon boarders. Moreover, a dipole-dipole interaction occurs between the NPs \[61\]. This causes neighboring particles to attract each other
and align themselves forming a network of head-to-head connections that leads to the aggregation of chain-like structures oriented along the field lines.

In summary, in the regions far from the hexagon boarders the electric field is homogeneous, so that the \( F_{EP} \) is prevalent and involves a simple Coulombic interaction which brings the particles close to (attractive force) or far away (repulsive force) from that region, depending on the sign of the polarities. This force is responsible for the clear filling or emptying of the hexagons that we observe in the dots and grid structures fabricated in this work (see Fig.3). At the same time, in the regions across the hexagon boarders we have a strong field gradient, so that the \( F_{DEP} \) is prevalent and the NiNPs are attracted by these boarders forming the above-mentioned chain-like structures oriented along the field lines. This effect is visible only at higher magnifications, such as in Fig.3(a,b,g).

After creating the structures shown in Fig.3 we used a scalpel for detaching gently the cross-linked PDMS layer from the crystal, obtaining free-standing elastomer sheets reinforced with various periodic Ni structures. Figure 5(a) shows the scanning electron microscope (SEM) image of the NiNPs (that appear quite monodispersed and of poliedrical shape with an average size of ca. 500 nm) while Fig.5(b-h) show some SEM images of the elastomer sheets under different points of view. In particular, keeping in mind the summary of crystals and conditions illustrated in Tab.1, Fig.5(b-d) refer to the sheet obtained by using the crystal P50 generating the dots pattern. The image in (b) shows the surface of the sheet and how the NiNPs form well defined clusters in correspondence of the hexagons, even at submicron resolution. The cross-section in (c) was captured at high magnification in correspondence of a single cluster. It shows that the particles are all aggregated in proximity of the PDMS surface that was in contact with the crystal, filling a depth of about 6 \( \mu \)m. Even at submicron resolution no particles are dispersed far from the hexagons, thus demonstrating the efficiency in particles capturing by the pyroelectric field. The image in (d) is another view of the cross-section at a lower magnification in order to demonstrate the stability of the structure even under sheet bending. Figure 5(e,f) show the surface of the sheet obtained by using the crystal P200 producing the dots pattern, under two different magnifications. Also, in this case of 200 \( \mu \)m period, the aggregation of the particles into the hexagonal region is clear at submicron resolution with no particles observable outside the hexagons. We analysed the image in (e) by ImageJ (open-source image processing program developed at the National Institutes of Health (NIH)), in order to evaluate the average distribution of the particles in the PDMS sheet and the Figure 5(i) shows the resulting values. In average 95 \% of the particles form the hexagonal clusters, leaving only 5\% in the surroundings, thus demonstrating the high efficiency of the pyroelectric charge template in displacing the particles according to the dots pattern. Fig.5(g,h) show the surface of the sheet obtained by using the crystal P200 producing the grid pattern, under two different magnifications. Also, for the grid
structure the particles appear to aggregate into a well-defined pattern, leaving the hexagons well empty with no residual particles. This is confirmed by the quantitative data in Fig.5(j) where we show the results of the ImageJ analysis on the image in (g). In average, only the 3% of the particles are located inside the hexagonal regions and 97% fill completely the surroundings. The red lines in (h) show clearly the chain-like structure formed across the hexagon edges by the dipole-dipole interaction mentioned previously.

Figure 5(k,l) show two large view images of a typical free-standing sheet with the dots pattern, standing on the stage and supported by a couple of manual tweezers, respectively. The structure is well defined and repeatable over an area of about 340 mm² and exhibits a good stability even under slight bending.

Figure 5: SEM images of (a) the NiNPs (a drop of alcoholic suspension was cast on a grid and dried a room temperature); (b) sheet obtained by using the crystal P50/c-; (c) cross section of sample P50 generating the dots pattern at high magnification in correspondence
of a single cluster; (d) cross section of sample P50 generating the dots pattern at a lower magnification under sheet bending; (e,f) surface of the sheet obtained by using the crystal P200 producing the dots pattern, under two different magnifications; (g,h) show the surface of the sheet obtained by using the crystal P200 producing the grid pattern, under two different magnifications; (i) ImageJ analysis on the image in (e) relating to the distribution of the particles in the PDMS sheet; (j) ImageJ analysis on the image in (e) relating to the distribution of the particles in the PDMS sheet; (k,l) large view images captured with Axio Zoom microscope of a typical free-standing sheet with the dots pattern. The red lines in (h) show the chain-like structure formed across the hexagon edges by the dipole-dipole interaction.

After peeling-off the crystal the reinforced elastomer sheets were subjected to a magnetization process by approaching a permanent magnet (iron boron neodymium) for about 1 min, in order to have a magnetic field gradient generated around the clusters of nickel. The supplementary movies S3 shows a typical reinforced sheet prior magnetization, while the supplementary movie S4 shows the same sheet that, after magnetization, retains a residual magnetic field capable of reacting to the proximity of a ferrous material such as the metal tweezers.

4. CONCLUSION

We have presented a direct and rapid approach for forming free-standing elastomer sheets reinforced by periodic clusters of NiNPs. We demonstrated the reliability of the technique in case of two different patterns, dots and grid, and for three different periods, 50 µm, 200 µm, 400 µm. The technique is free from time consuming and expensive mold-based and/or lithography-based procedures, thus appearing very promising for large scale and cost-effective production of elastomers with periodic reinforcement. It makes use of the pyroelectric charge template generated onto the surface of a PPLN crystal by a simple thermal treatment without using conductive coatings and high voltage generators. The technique is very rapid and robust and the Ni patterns follow with high fidelity the geometry of the PPLN crystal that can be re-used many times. Finally, the magnetization process demonstrates that the technique could open the route to the development of flexible magnetic microdevices to be used for a wide variety of new applications in the fields of sensing and recording, for example for sorting and/or capturing magnetic species at microscale. Anyway, the ability of the proposed strategy in forming reliable polymer membrane embedding period clusters of metallic nanoparticles opens the route for its useful exploitation in many advanced fields of material sciences, microfluidics, biotechnology and medicine.

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