Capillary origami as a new method for obtaining folded structures with interior nanoparticle coating

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A B S T R A C T

We introduce capillary origami as a new method to obtain 3D enclosures with coated nanoparticles on their inner surfaces. When a liquid droplet that contains nanoparticles is placed on the surface of a thin and flexible membrane, the membrane folds around the droplet. As the droplet evaporates nanoparticles deposit on folded surfaces and eventually a 3D enclosure is obtained. In this study, both magnetic iron-oxide (Fe₃O₄) and gold (Au) nanoparticles are used and it is shown that with both types of nanoparticles the enclosures remain closed after the complete evaporation of the droplet. It is also demonstrated that the magnetic nanoparticles can be concentrated at a chosen location on the folded geometry by using a magnet during evaporation. The origami based coating method is applied on different geometries and distribution of nanoparticles depending on the surface orientation is quantified. As part of the study, the capillary origami behavior of liquids with and without nanoparticles is compared.

1. Introduction

Printing of nanoparticles on surfaces is an emerging technology where the final goal is to produce functional surfaces that can be used as sensors [1], flexible electronics [2] or drug delivery tools [3]. On the other hand, nanomaterials have unique characteristics due to their small size and large surface to volume ratio compared to bulk materials; therefore, there are several methods in literature to coat surfaces with nanomaterials [4]. In this work we introduce capillary origami as a new technique for coating 3D enclosures formed from surfaces with nanoparticles.

There have been interesting studies on using capillary forces to fold and wrap polymer surfaces around a liquid droplet in literature [5-6]. In these studies, researchers used water droplets to fold thin surfaces and named this process as capillary origami [7,8]. Among the other capillary origami work, Geraldi et al. showed that superhydrophobic surfaces can resist bending with this method [8]; Li et al. extended the mathematical model that was initially studied by Py et al. [7] and described a parameter for the criteria of spontaneous folding of thin films under capillary forces [9]; Rivetti et al. developed another theoretical model for this process and studied the interaction of droplets with an elastic beam under evaporation, impact and contact with heavy elastic strip [10]; Peraud et al. studied the effects of droplet volume, contact angle, geometry and surface material characteristics on folding [11]; Brubaker et al. introduced the first three dimensional mathematical model of capillary origami [12]. On the other hand, an interesting study by Pineira et al. used electric field to control the opening and closing of surfaces folded with capillary origami [13]. Capillary forces were also used to fold thin silicon membranes to obtain solar cells by Guo et al [14]; in which a thin film was coated with an adhesive and glass beads, and the structures remained enclosed after folding. As a different application, Li et al. showed the formation of 3D hydrogel constructs obtained by capillary origami, where they placed a hydrogel droplet on a thin polymer membrane and cross-linked it during evaporation which kept the structure folded after the process [15].

In this paper we utilize capillary origami to fold a thin polymer surface while coating it with nanoparticles. There are many studies for coating surfaces with nanoparticles and a great portion of this work is based on evaporation of solvents containing nanoparticles [16-20]; some of these surfaces are decorated with hydrophilic areas on which nanoparticles assemble [16, 17]. On the other hand, there are studies that focus on the coffee ring formation during the evaporation of nanoparticle solvent [18-20]. These studies were successful in coating flat surfaces; however, coating of folded surfaces or 3D enclosures with evaporative nanoparticle coating techniques remains as a challenge. In this work we show that capillary origami is a promising technique to address this challenge without using any externally applied force.

We used capillary origami to create enclosed structures that have
printed nanoparticles on their inner surfaces and demonstrated this method with both magnetic iron-oxide and gold nanoparticles. After the process, surfaces remained folded unlike the cases with DI water. As part of the study, we also showed the concentrated deposition of iron-oxide nanoparticles at a desired location with a magnet. We also investigated the parameters such as contact angle, surface tension, evaporation time and particle coating distribution based on orientation. We compared the capillary origami behavior of nanoparticle solutions with pure DI water. These folded polymer surfaces can later be used for applications such as drug or microorganism encapsulation.

2. Method

A droplet on a thin elastic membrane wraps the surface around it by applying capillary force and forms an enclosure as it evaporates which is demonstrated in Fig. 1. Whether the surface will fold or not can be pre-estimated by checking the critical length of the thin membrane on which the droplet is positioned. The surface tension, which causes the surface to fold, should overcome the opposing bending stiffness to form a folded structure. The main equation for the critical length was previously given by Py et al., and is shown below: [7]

\[ L_{EC} = (B/\gamma_0)^{1/2} \]  

\[ L_{EC} \] represents elasto-capillary length and depends on the bending stiffness and the surface tension between the droplet and the surface, \( B \) represents the bending stiffness, and \( \gamma_0 \) corresponds to the surface tension of the droplet. The length of the surface must be larger than \( c \times L_{EC} \) for the surface to wrap around the droplet where \( c \) is a constant that depends on factors such as the shape of the initial geometry [7] and surface wetting properties [21].

By using Eq. (1), critical length of bending with water is calculated as \( 1.32 \times 10^{-5} \) mm where \( B \) is calculated according to the following expression: [22]

\[ B = \frac{E h^3}{12(1 - \nu^2)} \]  

where \( E \) is Young’s modulus, \( \nu \) is Poisson’s ratio and \( h \) is the thickness of the membrane.

3. Materials

Iron-oxide nanoparticles used in the experiments were synthesized by following the method by Karaagac et al. where an aqueous solution of ferrous chloride tetrahydrate and ferric chloride hexahydrate were mixed with ammonium hydroxide to obtain precipitates of iron-oxide nanoparticles [23]. Droplets of the synthesized iron oxide in aqueous solution with 0.01 M were used in the experiments.

Gold nanoparticles were synthesized by following the method proposed by Britto Hurrodo et al.; where aqueous solutions of gold (III) chloride trihydrate and ascorbic acid with sucrose are prepared separately and later mixed to obtain gold nanoparticles [24]. All chemicals were obtained from Sigma Aldrich.

Surfaces coated with nanoparticles were prepared by spin coating of polydimethylsiloxane (PDMS) (Dow Corning Sylgard 164 silicone elastomer) on a silicon wafer. After the curing of PDMS, it was cut with a CO₂ laser to obtain small surfaces to be used in experiments. Silicon wafer was initially coated with a perfluorinated polymer to reduce the adhesion of PDMS to Silicon to facilitate its removal after curing.

4. Experimental results and discussion

4.1. Experiments and results with DI water

Our initial experiments were carried out with deionized (DI) water droplets on 15 µm thick PDMS surfaces that have an average 4 mm² area. The droplet is placed such that it touches each corner of the membrane. The surface folds as the water droplet evaporates. The schematic showing the placement of the droplets in different geometries before folding is shown in Fig. 2 and bending of the surface around water droplet with a triangular initial geometry is shown in Fig. 3. Experiments with water showed that the surfaces unfold after the water droplet evaporates since there is not any force left to keep them closed.

Fig. 1. Schematic representation of folding surface.

Fig. 2. Geometries of surfaces used in the experimental studies and positions of the droplets placed on each surface (shown as black circle).

Fig. 3. Deformation of a triangle PDMS surface throughout the evaporation of the water droplet.
4.2. Experiments and results with iron-oxide nanoparticles

In order to coat the inner side of the folded enclosures with nanoparticles, droplets of aqueous solutions of Au and Fe$_3$O$_4$ nanoparticles were used. Coating of surfaces with iron oxide nanoparticles were accomplished with placing droplets with 0.23 M and 4-10 µL volume at the center of a PDMS surface cut by a laser tool. Evaporation of a droplet took approximately 20 minutes and surfaces remained closed after the evaporation of the water in the solution. Fig. 4 shows the capillary origami process with Fe$_3$O$_4$ droplets on a square surface and the resulting shape of the enclosure.

Formation of pyramid and cubic forms coated with iron oxide nanoparticles inside were also demonstrated and formation of these structures are shown in Fig. 5 and the image of a cubic form after the complete evaporation is given in Fig. 6. All these surfaces coated with iron oxide nanoparticles remained closed after the evaporation of the solvent as nanoparticles settled at the edges of the surface behaved like glue and kept the surface folded unless an external disturbance breaks their integrity.

Experiments were also conducted to determine the minimum
concentration that would form an enclosure and it was found that 0.5 M is the minimum concentration that would keep the structures closed. Fig. 7 shows the formation of an enclosure with minimum concentration.

During the experiments conducted with aqueous Fe$_3$O$_4$ nanoparticle solution, nanoparticles were also moved within the droplet without distorting the capillary origami process by using a magnet. By this way, the location of deposition can also be controlled. Fig. 8 shows the movement of the Fe$_3$O$_4$ particles inside the droplet during evaporation. It was also demonstrated that the accumulation of iron oxide nanoparticles in a single location by a magnet is possible. Fig. 9 shows this process before and after the evaporation of the droplet. After the full evaporation of the droplet, particles directed to a position by a magnet remained at that location as verified under the scanning electron microscope (SEM).

4.3. Experiments and results with gold nanoparticles

To show the versatility of this method in particle coating, enclosures coated with gold nanoparticles were also demonstrated. The same experimental protocol was followed for coating enclosures with gold nanoparticles where this time a droplet of 0.56 M aqueous solution of gold nanoparticles were used. Experiments that were conducted with gold nanoparticles have similar results except that less amount of particle agglomeration was observed. Complete process and the evaporation took 12-20 min depending on the droplet volume and the solution molarity. In Fig. 10 the droplet of an aqueous solution of gold nanoparticles can be seen on a thin PDMS membrane. After the evaporation of the droplet a cubic geometry was obtained and remained folded as in the case for magnetic nanoparticles. SEM image of the cubic structure coated with gold nanoparticles shows the coffee ring effect obtained after the evaporation at the surface on which the droplet was placed initially. (The surface was unfolded by a tweezer to observe the pattern under the SEM.)

4.4. Characterization of coated surfaces

The distribution of nanoparticles on folded surfaces is also characterized by utilizing image processing and a comparative study is carried out to obtain data of nanoparticle amount versus the orientation of the folded structures. This study was carried out for both a square and a cubic geometry by re-opening them after the evaporation and processing their high-resolution images obtained by an optical microscope. Image processing procedure was conducted by using a k-means clustering algorithm. Implemented algorithm takes the pixels of an RGB image, groups the pixels into k clusters (which is taken as 128 for the presented study), and outputs the clustering vectors as well as the labels of the clustered pixels. Then the clusters are ordered based on their RGB values. Clusters are compared and normalized with each other by color intensities, 1 being the highest intensity and 0 being the lowest (corresponding to no nanoparticle occurrence). Intensities were processed over three different locations on the same area. An empty surface was first processed to obtain the default noise level and related data is shown in Fig. 11.

**Fig. 7.** Cubic enclosure formed by iron oxide nanoparticle solution with 0.5 M, which is the lowest concentration to maintain the structure enclosed.

**Fig. 8.** Movement of Fe$_3$O$_4$ droplets in square PDMS surface under the magnetic field.

**Fig. 10.** The droplet of an aqueous solution of gold nanoparticles can be seen on a thin PDMS membrane.
For a square surface, nanoparticles distributed symmetrically with respect to the center line at which the surface folds, at the center line there is less amount of nanoparticle whereas on both sides there is uniform distribution. Results are given in Fig. 12 for three locations of the surface.

The same procedure was followed for a cubic structure. As expected, the surface at the bottom of the cube has the greatest number of nanoparticles due to gravitational forces and less amount on the top surface. For the side surfaces, the distribution of nanoparticles was similar but less than the bottom side of the cube. Results are shown in Fig. 13 where the data was obtained for three locations for each side of the cube.

5. Conclusion

In conclusion, it can be stated that capillary origami is new and promising technique for nanoparticle coating of inner surfaces of 3D structures without using any external force. The study showed that after

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Fig. 9. (a-b) Nanoparticle manipulation with magnetic force, (c) SEM image of the surface with accumulated magnetic nanoparticles during evaporation. For SEM imaging, surface is forced to open. (The magnetic field produced by the sample affects the beam trajectory which eventually decreases the quality of imaging.)
the origami process, the surface remains folded and keeps its 3D shape due to the nanoparticles settled at the edges. Using magnetic forces to manipulate iron-oxide nanoparticles and concentrate them at a desired location gave extra control in the process. Image analysis was used to quantify the distribution of nanoparticles on surfaces forming the enclosure. It was observed that when no external force is applied, the distribution of nanoparticles on surfaces of the 3D structure was not uniform which can be explained by gravitational affects. Nanoparticles settled at the bottom surface of the cubic structure the most, and they were much dilute on folded regions. Overall this is the first attempt to form 3D structures while coating them with nanoparticles without using external forces. The method is versatile and can be further

![Fig. 10. a) Droplet containing gold nanoparticles on a thin surface before folding, b) Cubic enclosure produced by capillary origami c) SEM image of deposited gold nanoparticles on the unfolded cubic structure.](image_url)
improved to be used in applications where drug or microorganism carrying structures are necessary.

Declaration of Conflict of Interest

None.

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Fig. 12. (a) Schematic of the folding of a square membrane and its centerline. (b) Nanoparticle distribution after the coating with capillary origami. Line ’0’ corresponds to the center of the surface.
Fig. 13. a) Surface labels of a cubic geometry b) Nanoparticle distribution on each surface of the folded cube. Dashed lines on surface images indicate where distribution data is taken from.
References


