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(54) **FABRICATION OF LENSES BY DROPLET FORMATION ON A PRE-HEATED SURFACE**

5/23; G02B 5/3033; G02B 21/02; G02C 7/104; G02C 7/108; G02C 7/12; G02C 2202/16; B29D 11/00009; B29D 11/00644; B29D 11/0073; B29D 11/00865; B29D 11/00913; B29D 11/00923; B29D 11/00653; B29D 11/00365; B29D 11/00442; B29K 2029/04; B29K 2104/16;

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G02B 1/04 (2006.01)
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G02B 21/02 (2006.01)
B29K 83/00 (2006.01)
B29K 105/16 (2006.01)

(52) **U.S. Cl.**

CPC **G02B 1/041** (2013.01); **B29D 11/0073** (2013.01); **B29D 11/00365** (2013.01); **B29D 11/00442** (2013.01); **B29K 2083/00** (2013.01); **B29K 2105/16** (2013.01);

(Continued)

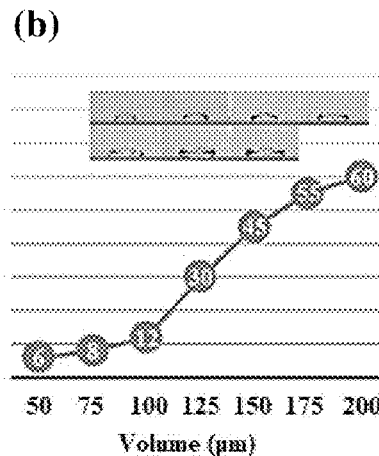
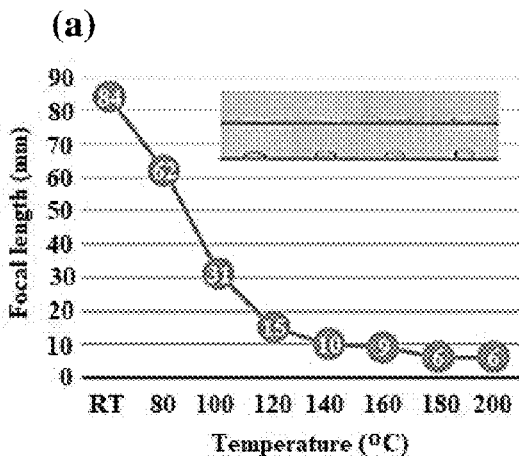
(58) **Field of Classification Search**

CPC . G02B 1/041; G02B 1/14; G02B 1/18; G02B 1/11; G02B 5/208; G02B 5/22; G02B

(57) **ABSTRACT**

A lithography-free, mold-free, single-step method of fabricating high quality optical lenses by curing polydimethylsiloxane (PDMS) droplets on a pre-heated smooth surface allows lenses with different focal lengths to be made by varying the droplet volume and surface temperature.

25 Claims, 6 Drawing Sheets



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Figure 1

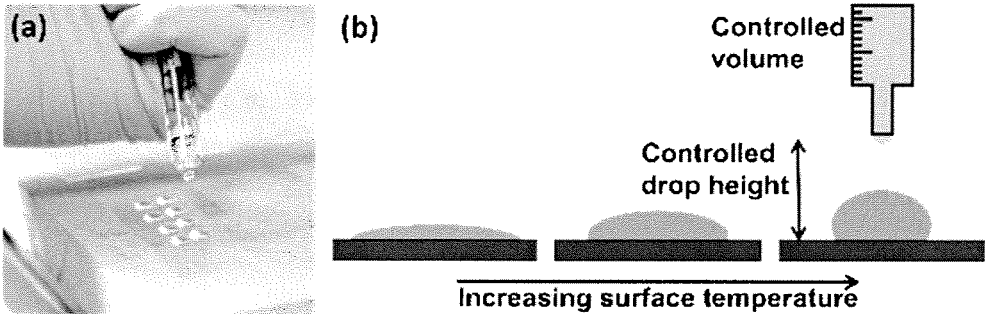


Figure 2

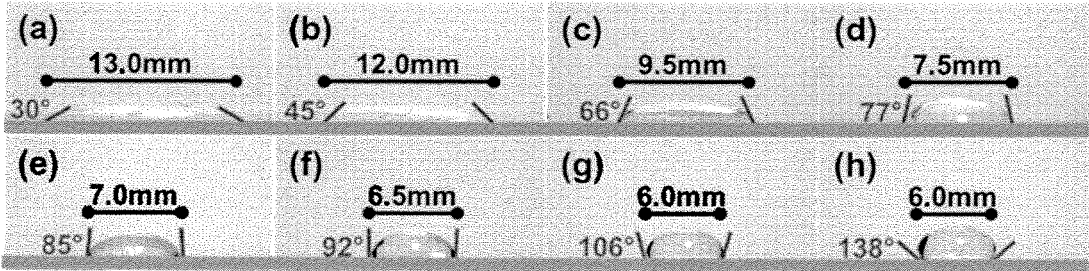


Figure 3

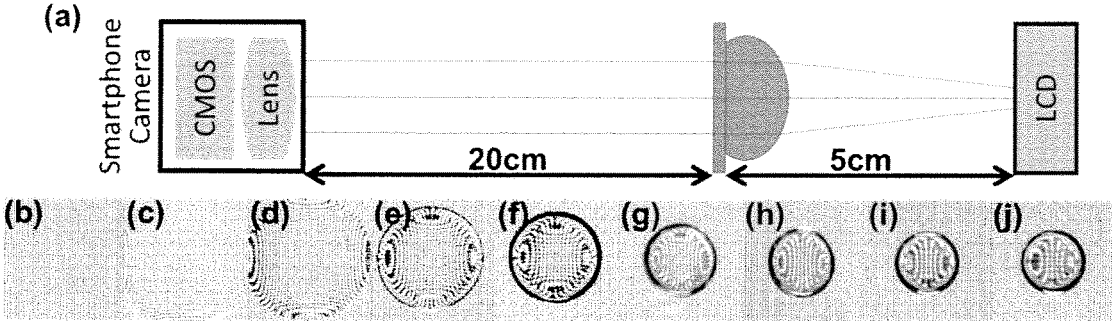


Figure 4

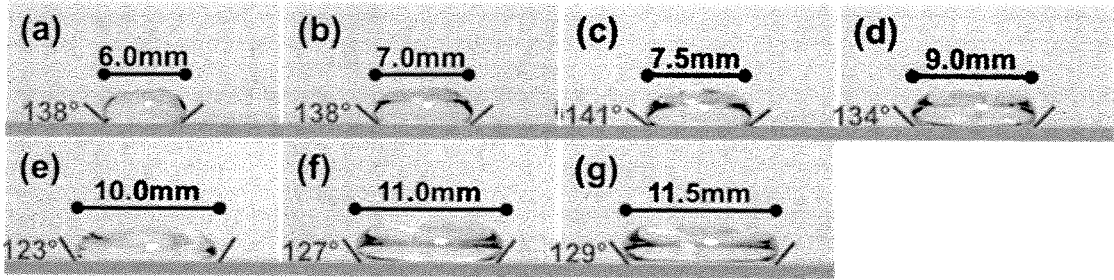


Figure 5

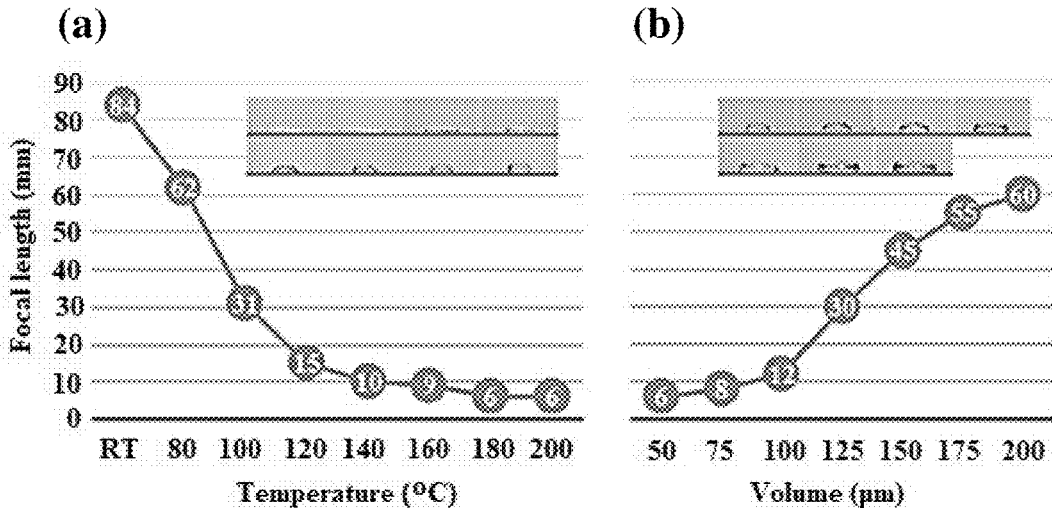
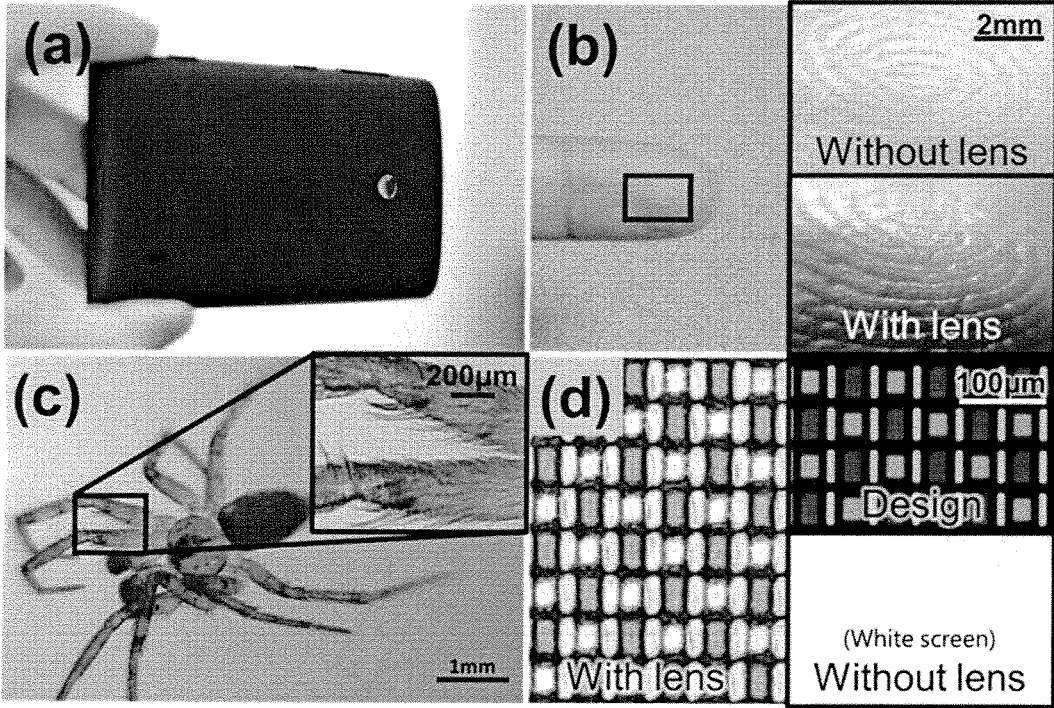


Figure 6



FABRICATION OF LENSES BY DROPLET FORMATION ON A PRE-HEATED SURFACE

This application claims priority to U.S. Provisional Patent Application No. 62/031,516, entitled "Fabrication of Lenses by Droplet Formation on a Pre-Heated Surface," filed on Jul. 31, 2014, the entire content of which is hereby incorporated by reference.

The present invention used in part funds from the National Science Foundation (NSF) CAREER Award No. CBET-1151154, the National Aeronautics and Space Administration (NASA) Early Career Faculty Grant No. NNX12AQ44G) and the Gulf of Mexico Research Initiative Grant No. GoMRI-030. The United States Government has certain rights in the invention.

BACKGROUND

This disclosure pertains to method for fabricating high quality optical lenses by curing liquid PDMS droplets on a pre-heated smooth surface.

Lenses are traditionally constructed with rigid materials such as glass or plastics by mechanical polishing or injection molding. High optical quality lens surface requires well-controlled fabrication parameters which increases complexity and reduces yield. Current demands for complementary metal-oxide semiconductor (CMOS) image sensors have resulted in the increase in fabricating small lenses ranging from 1 mm to 1 cm in diameter. In addition, emerging applications of flexible optoelectronics demand mechanically flexible lens materials. Fluidic lenses in particular is a simple method of creating small lenses of high quality without the requirement of molds or complex parameter control. However, an encapsulated fluidic lens requires a system to provide mechanical stability, and prevent evaporation. In contrast, lens formation due to surface energy minimization during polymer curing has provided an alternative method for making high quality, low-cost "fluidic" lenses that are independent components, flexible and robust.

Polymers have been generally utilized as a lens material by three categories of fabrication techniques: 1) lithographic methods, 2) surface-tension-driven methods, and 3) imprinting or embossing methods. These approaches demonstrate the feasibility of creating lenses with good optical characteristics and reproducibility; however, these techniques involve either time-consuming fabrication procedures typically measured in hours, or have high costs due to lithographic or molding equipment required, and generally limit the size of the lens to the micrometer scale. A recently introduced alternative method of creating a lens by droplet formation requires iterative drop-bake cycles to achieve a desired focal length. What is needed is a method for the production of high quality, inexpensive lenses with optimal focal length that requires minimal steps and is low cost.

SUMMARY

The present disclosure relates generally to a single-step method for fabricating lithography-free, mold-free, inexpensive, and high quality polydimethylsiloxane (PDMS) optical lenses by curing liquid PDMS droplets on a pre-heated smooth surface. Current methods for fabricating mold-free polydimethylsiloxane (PDMS) have relied on iterative gravity-assisted processes. These techniques can produce high quality lenses, but require iterative steps to provide optimal focal length. The present single-step method produces inexpensive, high quality optical lenses. The focal length of each

lens can be varied by changing the droplet volume and the temperature of the pre-heated surface. With this method a focal length as short as 0.5 mm and as long as 10 cm can be achieved. Furthermore, by attaching the lens on a smartphone camera, an imaging resolution of 10 μm , and as small as 2 μm , is possible. The single step process for fabricating an optical lens requires simply depositing a pre-selected volume of polydimethylsiloxane (PDMS) in liquid droplet form onto a smooth surface having a pre-selected temperature and allowing the PDMS to cure to solid form to create a lens having a diameter and a focal length. The pre-selected volume and the pre-selected temperature are selected to optimize the diameter and the focal length of the lens, and the single step process requires no further steps or iterations to produce the optical lens.

Polydimethylsiloxane (PDMS) is optically transparent ($T > 95\%$) in the visible spectrum with high refractive index ($n = 1.47 - 1.55$), and displays minimal yellowing over time. This disclosure relates to a method to manufacture lenses by curing PDMS drops on a pre-heated smooth surface. When PDMS is dropped onto a surface, interfacial surface energies allow the droplet to hold itself up into a droplet shape which naturally acts as a lens. By controlling the volume of the droplet and the surface temperature beneath the droplet, the speed of curing can be controlled, which allows the droplet to solidify while still retaining its large curvature, thus form lenses of different focal lengths. This method produces lenses having the ability to transform any mobile camera device into a microscope, or to add an area with additional magnification to a pair of eyeglasses. The strong, but non-permanent adhesion between PDMS and glass allows the lens to be easily detached or replaced after use without supporting structures. An imaging resolution of 10 μm , and an optical magnification of $\times 12$ has been demonstrated.

The quality of a lens depends on its geometry and surface smoothness. Fluidic lenses made by a droplet of solution can form very high quality lenses, as the surface tension distributes evenly on the droplet. Similarly, when uncured liquid PDMS is dropped onto a surface, it assumes a convex shape and can be used as a fluidic lens. However, its rheological properties causes the droplet to spread out onto the surface until equilibrium is attained between the interfacial surface energies and gravity, the subsequent lens is thin and wide, with a very large radius of curvature, and little lensing effect.

Because PDMS is a thermally curable elastomer, the flow of the droplet can be limited by decreasing the time allowed for the droplet to cure. A longer curing time allows more time for the PDMS to flow into a thin pancake-like structure, while a shorter curing time prevents excess flowing, as shown in FIG. 1. Two variables are important, the temperature of a pre-heated surface on which a drop of PDMS is deposited, and the volume of PDMS deposited. By controlling these variables, the geometry and focal length of the lens can be fine-tuned. In additional embodiments, dyes and nanoparticles can be incorporated into the PDMS prior to curing.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows (a) an image of droplets of polydimethylsiloxane (PDMS) deposited on a coverslip with a syringe and (b) a representation of how changing the temperature of the pre-heated surface modifies the geometry of a cured PDMS droplet;

FIG. 2 shows images of 50 μL PDMS droplets dropped on a surface at temperatures of (a) 60° C., (b) 80° C., (c) 100°

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C., (d) 120° C., (e) 140° C., (f) 160° C., (g) 180° C. (h), 200° C., demonstrating the effect of speed-curing of PDMS to form lenses;

FIG. 3 shows (a) the setup for imaging an LCD with a smartphone camera with a PDMS lens positioned in between to demonstrate changes in lens magnification for PDMS lenses dropped on a surface at varying temperatures and the resulting magnification with (b) no lens and at temperatures of (c) 60° C., (d) 80° C., (e) 100° C., (f) 120° C., (g) 140° C., (h) 160° C., (i) 180° C., and (j) 200° C.;

FIG. 4 shows images of uncured PDMS dropped onto a surface of 200° C. with a volume of (a) 50, (b) 75, (c) 100, (d) 125, (e) 150, (f) 175, and (g) 200 μ L;

FIG. 5 shows change in focal length for PDMS lenses in response to variations in (a) surface temperature, and (b) droplet volume; and

FIG. 6 shows (a) an image of a PDMS lens directly and non-permanently bonded onto the lens element of a smartphone camera, (b) an image of a fingerprint with inset showing magnified image with and without lens, (c) an image of a spider with inset showing magnified portion of trichobotria, and (d) an image of a PenTile Matrix OLED screen with insets showing actual structure design, and the same structure taken without the lens.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present disclosure relates to a mold-free method of manufacturing lenses by curing PDMS drops on a pre-heated smooth surface. This single-step method allows lenses with different focal lengths to be made by varying the droplet volume and surface temperature. In an initial step, a pre-selected volume of polydimethylsiloxane (PDMS) in liquid droplet form is deposited onto a smooth surface having a pre-selected temperature. In a subsequent step, the PDMS is allowed to cure to solid form to create a lens having a diameter and a focal length, wherein the pre-selected volume and the pre-selected temperature are selected to optimize the diameter and the focal length of the lens.

In certain embodiments, the preferred droplet volume is between 0.1 μ L and 500 μ L, preferably about 50 μ L. Preferred surface temperature is between 60° C. and 300° C., preferably about 200° C. The diameter of the resulting lens is preferably 2 cm or less. The focal length of the resulting lens is between 0.5 mm and 10 cm, and preferably about 6 mm. An imaging resolution of 10 μ m, and an optical magnification of $\times 12$ has been demonstrated. The method can also be modified for parallel fabrication that may allow higher throughput. The material cost of the PDMS was calculated to be $< \$0.01$ USD for a 50 μ L lens, and can be conveniently attached to a mobile camera or any vision-enhancing lenses via the strong but non-permanent adhesion between PDMS and glass or plastic. The cured PDMS lens effectively acts as a supplemental lens that improves the magnification and performance of other lenses. Preferred embodiments include lenses for attachment to the mobile camera modules of any smartphones, tablets, smartwatches, or laptops, as well as lenses for attachment to any wearable products such as eyeglasses or enhanced “smart” glasses. For eyeglasses and wearable products, lenses that are larger work better. When the lenses are attached onto eye spectacles, they can provide the viewer a magnified view of a portion on the spectacle when the object is held at the focal length of the lens, 0.5 mm to 10 cm. No external accessories

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or attachments are required to obtain the increased magnification for any of the preferred applications, other than the lens itself.

In certain additional embodiments, prior to depositing and curing the PDMS droplet, selected particles, such as dyes or nanoparticles, can be incorporated into the liquid PDMS. The particles could include food coloring, such as Blue #1, Yellow #5, Red #40, and various mixture of two or more of these. All colors of food coloring can be incorporated into PDMS because the other colors are simply a mixture of these colors. These food colorings can either be water- or oil-based. In addition, titanium dioxide could be added to the PDMS. This will create a white opaque lens. Other exemplary particles are: Rhodamine 6G, which creates a fluorescent orange/green colored lens; Crystal Violet, which creates a purple colored lens; Methylene Blue, which creates a blue colored lens; Acridine Orange, which creates an orange colored lens; Gold nanoparticles, which create various colors depending on the diameter of the gold nanoparticles; and Iron powder, which creates a grey opaque lens. Additional examples include Cy3, Cy5, Cy7, Cy9, Alexa fluor dyes, silver nanoparticles, CdSe and ZnSe quantum dots, photochromic materials, and infrared transparent materials such as silicon particles, germanium particles, and chalcogenide compounds. All powdered or liquid dyes, as well as colored or opaque nanoparticles, quantum dots or other colored materials, could be added to the liquid PDMS prior to curing.

Generally speaking, in order to incorporate powdered particles into the liquid PDMS, the first step is to dissolve the particles in water, or ethanol, or another solvent that does not interfere with the particles. If the particles are already liquid-based, such as either water or oil-based, this step is not necessary. The particle-liquid mixture is then mixed into uncured liquid PDMS and degassing of the mixture is performed. Then, the same procedure is followed as with un-modified liquid PDMS. The formation of colored lenses facilitates the use of these lenses in not only magnification, but also measuring colorimetric changes in samples of objects. The lenses allow for wavelength selective electromagnetic wave filtering. For example, differently colored lenses can be used to observe the same microscopic samples and obtain relative enhancement or inhibition of different wavelengths.

Example 1. Temperature Characterization

PDMS solution (SYLGARD® 184, Dow Corning) was prepared by mixing manufacturer recommended proportions of PDMS base and curing agent by a weight ratio of 10:1. After mixing and vacuum bubble removal, a syringe was used to deposit PDMS on the surface.

To prepare a pre-heated surface, a coverslip was cleaned and placed on top of a hotplate set to 60° C., and an infrared camera was used to verify that the coverslip glass reaches equilibrium temperature. 50 μ L of PDMS was dropped on the coverslip from a 2 cm height with the syringe. PDMS cures at room temperature, but exhibits accelerated curing with increasing temperatures. The procedure was repeated with the hotplate temperature set to 80° C., 100° C., 120° C., 140° C., 160° C., 180° C., and 200° C. respectively, with the resulting figures and properties of the droplet shown in FIG. 2. In each case, an infrared camera was employed to verify the coverslip has reached equilibrium temperature.

At 60° C., the PDMS droplet requires > 5 minutes to cure, the longer curing time allows the PDMS to spread across the surface to form a very thin, flat lens with negligible mag-

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nification. With increasing temperature, the curing time decreases, thus limiting the flow of the droplet and creates a smaller diameter lens. The focal length decreases due to the increase in surface curvature, which increases the magnification of the lens. At a higher temperature of 200° C., the PDMS droplet requires <5 seconds to cure, the droplet cures shortly on contact and exhibits a very high radius of curvature and enhanced magnification. It is significant to note that at this high temperature, no burning or charring was observed.

The optical power of a convex lens is the degree to which it converges light, and can be expressed by the equation $P=1/f$ where P is the power of the lens, and f is the focal length. FIG. 3 demonstrates the relationship between the optical power of the lens and the curing temperature, the lens is placed on a coverslip glass and positioned between a computer LCD monitor displaying a white screen, and a smartphone camera capturing the image. It is seen that with increasing temperature of curing, the optical power increases as the focal length decreases.

Example 2. Volume Characterization

To investigate the effect on the focal length and magnification on the drop volume, the hotplate was set to a constant temperature of 200° C. and different volumes of PDMS were dropped onto the surface, with all other conditions remaining identical to those described in Example 1 above. Volumes of 50, 75, 100, 125, 150, 175, and 200 μL were used respectively, with the resulting figures and properties shown in FIG. 4.

As the droplet volume increases, the lens diameter increases, however the contact angle only varies within $\pm 4.4\%$. The center region of the lens is found to exhibit decreasing curvature, and the focal length is found to increase slightly between 50 μL and 100 μL , from 6 mm to 8 mm respectively, and increases significantly between 100 μL and 200 μL , from 12 mm to 60 mm respectively. This can be shown that as the size of the droplet increases, the radius of curvature near the center of the lens no longer increases, and with an increasing volume of the PDMS droplet, the center portion will eventually become flat. This limitation makes it difficult using this method to create practical lenses larger than 2 cm in diameter.

The properties of the lens are determined by its geometric parameters. Since the curing temperature of PDMS determines the speed of curing, and thus the contact angle and diameter of the lens droplet, the focal length of the lens can be accurately tuned in a single-step. As with fluidic lenses, mechanical defects on the curved surface are eliminated with this mold-free process, as the droplet experiences uniform surface forces from all sides during curing. FIG. 5 shows the change in focal length with response to (a) surface temperature, and (b) droplet volume.

Example 3. Numerical Aperture

From the preceding examples, it is shown that the lens created with a 50 μL volume droplet size, cured at 200° C. is most suitable for short-ranged imaging due to its short focal length. This example attempts to characterize the numerical aperture of this particular lens. The focal length of the lens is found to be 6 mm by focusing a white light onto a white plastic board. A 1-watt white LED flashlight source was positioned 1 m away from the lens, and a white plastic board on the other side of the lens was moved slowly towards the lens until a focused image was observed. The

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maximum usable curvature of the 6.0 mm diameter lens was found by superimposing a curve-fitted ellipse and taking the length where the lens outline is within $\pm 1\%$ of the ellipse, which yields a maximum usable curvature of roughly 3.8 mm. The numerical aperture of a lens is expressed as $NA=n \sin \theta$, where n is the index of refraction of the medium in which the lens is working ($n_{air}=1$), and θ is the half-angle of the maximum cone of light that can enter or exit the lens. For a focal length of 6 mm, and an effective radius of 1.9 mm, the half-angle is found to be 17.571°, and the numerical aperture is found to be 0.422.

Example 4. Use of Lenses with Smartphones

Add-on accessories to turn a smartphone into a magnifying device are widely available; however, most of these attachments significantly increase the bulk of the device. To demonstrate a practical application, the PDMS lens (50 μL cured at 200° C.) was attached to a Nokia Lumia 520 budget smartphone camera (Microsoft, Redmond, Wash., USA) with a 5-megapixel camera as shown in FIG. 6(a). The adhesive property of PDMS on glass and plastic surfaces allows the PDMS lens to bind non-permanently onto the camera lens without supporting structures, and is not prone to falling off.

Images taken from the smartphone with no further image processing are shown in FIG. 6(b)-(d). FIG. 6(b) shows an image of a finger taken with the camera without PDMS lens, and the inset taken with the PDMS lens attached clearly showing sub-millimeter fingerprint structures including sweat pores. FIG. 6(c) shows an image of a spider taken with the PDMS lens attached, and the inset shows a digitally magnified portion of the image. The thinnest thricobotria structures on the legs of the spider, measure roughly 15 μm in width. FIG. 6(d) shows an image of an organic light emitting diode (OLED) display with a PenTile matrix pixel geometry on a Nokia Lumia 800 smartphone displaying a white screen. The inset shows the actual geometry of the pixel matrix, the larger pixel measuring 20 μm in width, the smaller pixel and gaps measure 10 μm in width. A minimum discernible resolution of roughly 10 μm was achieved.

The magnification of the lens was found to be 12 \times by comparing the observed size of an arbitrary structure in a clearly focused image taken with the smartphone, and with a commercial microscope (Olympus IX-70, Olympus Corp) with 200 \times total magnification. The magnification of the smartphone with PDMS lens can be further enhanced by combining software based digital magnification.

Example 5. Use of Lenses with Eyeglasses

A 300 microliter lens was prepared at 200° C. as described above in Example 1, with a resulting magnification of 3 \times . The lens was attached to a pair of eye spectacles via the natural adhesion of PDMS to the spectacle lens. The spectacle wearer was able to view items clearly in focus with a 3 \times magnification when looking through the spectacle with the attached PDMS lens at any object when held at roughly 5 cm away from the spectacle.

Example 6. Focal Length

A 1 microliter lens was prepared at 200° C. as described above in Example 1, with a resulting focal length of 0.5 mm. A 1 mL (1000 μL) volume lens as also prepared at 200° C. as described above in Example 1. In this case, the resulting lens was completely flat in the middle with an infinite focal

length. This lens did not distort or change the direction of light and is actually useless as a lens. Although it is possible to construct any range of focal length, up to an infinite focal length, the maximum usable range is approximately 10 cm. 10 cm is the maximum effective usable range for viewing microscopic samples.

Example 7. Color Effects

A red lens and a green lens were prepared according to Example 1 above, except that red and green dyes were incorporated into the liquid PDMS for each lens prior to curing. The xylem/phloem of a plant histological cross section was observed with both lenses. With the red lens, the green objects (xylem) appeared enhanced, while the red objects (phloem) appeared suppressed. With the green lens, the opposite occurred. Thus these lenses are useful as an image filter for enhancing/suppressing desired wavelengths of light for easier identification of features and measuring of colorimetric changes.

What is claimed is:

1. A method for fabricating an optical lens, comprising: heating a smooth surface to a pre-selected temperature between 60° C. and 300° C. to produce a heated smooth surface; depositing a pre-selected volume of polydimethylsiloxane (PDMS) in liquid droplet form onto the heated smooth surface; and allowing the pre-selected volume of polydimethylsiloxane (PDMS) to cure to solid form to create an optical lens having a diameter and a focal length, wherein the pre-selected volume and the pre-selected temperature are selected to optimize the diameter and the focal length of the optical lens.
2. The method of claim 1, wherein the pre-selected volume is between 0.1 μ L and 500 μ L.
3. The method of claim 1, wherein the pre-selected volume is 50 μ L.
4. The method of claim 1, wherein the pre-selected temperature is 200° C.
5. The method of claim 1, wherein the diameter of the lens is 2 cm or less.
6. The method of claim 1, wherein the focal length of the lens is 0.5 mm to 10 cm.
7. The method of claim 1, wherein the focal length of the lens is 6 mm or less.
8. The method of claim 1, wherein the pre-selected volume is 50 μ L, the pre-selected temperature is 200° C., and the focal length of the lens is 6 mm.
9. The method of claim 1, wherein the pre-selected volume of polydimethylsiloxane (PDMS) in liquid droplet form further comprises particles incorporated into the PDMS.
10. The method of claim 9, wherein the particles are dyes, nanoparticles, quantum dots, infrared transparent materials, or mixtures thereof.
11. The method of claim 9, wherein the particles are dyes and the optical lens is colored.
12. An optical lens prepared by the method of claim 1.

13. A method for increasing the magnification of a lens with a supplemental lens, comprising:

- heating a smooth surface to a pre-selected temperature between 60° C. and 300° C. to produce a heated smooth surface;
- depositing a pre-selected volume of polydimethylsiloxane (PDMS) in liquid droplet form onto the heated smooth surface;
- allowing the pre-selected volume of polydimethylsiloxane (PDMS) to cure to solid form to create a supplemental lens having a diameter, a focal length, and a magnification; and
- adhering the supplemental lens to the lens, wherein the pre-selected volume and the pre-selected temperature are selected to optimize the diameter and the focal length of the supplemental lens, and wherein the adhering comprises placing the supplemental lens directly on the lens without additional adhesive or attachments.

14. The method of claim 13, wherein the pre-selected volume is between 0.1 μ L and 500 μ L.

15. The method of claim 13, wherein the pre-selected volume is 50 μ L.

16. The method of claim 13, wherein the pre-selected temperature is 200° C.

17. The method of claim 13, wherein the diameter of the supplemental lens is 2 cm or less.

18. The method of claim 13, wherein the focal length of the supplemental lens is 0.5 mm to 10 cm.

19. The method of claim 13, wherein the focal length of the supplemental lens is 6 mm.

20. The method of claim 13, wherein the magnification of the supplemental lens is $\times 12$.

21. The method of claim 13, wherein the pre-selected volume is 50 μ L, the pre-selected temperature is 200° C., the focal length of the supplemental lens is 6 mm, and the magnification of the supplemental lens is $\times 12$.

22. A method for fabricating an optical lens, comprising: incorporating particles into liquid polydimethylsiloxane (PDMS) to produce modified PDMS;

heating a smooth surface to a pre-selected temperature between 60° C. and 300° C. to produce a heated smooth surface;

depositing a pre-selected volume of the modified PDMS in liquid droplet form onto the heated smooth surface; and

allowing the pre-selected volume of the modified PDMS to cure to solid form to create an optical lens having a diameter and a focal length,

wherein the pre-selected volume and the pre-selected temperature are selected to optimize the diameter and the focal length of the optical lens.

23. The method of claim 22, wherein the particles are dyes, nanoparticles, quantum dots, infrared transparent materials, or mixtures thereof.

24. The method of claim 22, wherein the particles are dyes and the optical lens is colored.

25. An optical lens prepared by the method of claim 22.

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