Journal of Visualized Experiments

Aesthetically Enhanced Silica Aerogel Via Incorporation of Laser Etching and Dyes

--Manuscript Draft--

Article Type:	Invited Methods Article - JoVE Produced Video
Manuscript Number:	JoVE61986R1
Full Title:	Aesthetically Enhanced Silica Aerogel Via Incorporation of Laser Etching and Dyes
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Additional Information:	
Question	**Response**
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Please indicate whether this article will be Standard Access or Open Access.	Standard Access (US$2,400)
Please indicate the **city, state/province, and country** where this article will be **filmed**. Please do not use abbreviations.	Schenectady, NY USA
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TITLE:

Aesthetically Enhanced Silica Aerogel Via Incorporation of Laser Etching and Dyes

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KEYWORDS:

silica aerogel, etching, laser engraving, etched aerogels, dye-doped aerogels, aerogel mosaics

SUMMARY:

This protocol describes a method for etching text, patterns, and images onto the surface of silica aerogel monoliths in native and dyed form and assembling the aerogels into mosaic designs.

ABSTRACT:

A procedure for aesthetically enhancing silica aerogel monoliths by laser etching and incorporation of dyes is described in this manuscript. Using a rapid supercritical extraction method, large silica aerogel monolith (10 cm x 11 cm x 1.5 cm) can be fabricated in about 10 h. Dyes incorporated into the precursor mixture result in yellow-, pink- and orange-tinged aerogels. Text, patterns, and images can be etched onto the surface (or surfaces) of the aerogel monolith without damaging the bulk structure. The laser engraver can be used to cut shapes from the aerogel and form colorful mosaics.

INTRODUCTION:

Silica aerogel is a nanoporous, high surface area, acoustically insulating material with low thermal conductivity that can be used in a range of applications from collecting space dust to building insulation material[1,2]. When manufactured in monolithic form, silica aerogels are translucent and can be used to make highly insulating windows[3–5].

Recently, we have demonstrated that it is possible to alter the appearance of a silica aerogel by etching onto or cutting through the surface using a laser engraving system[6,7] without causing bulk structural damage to the aerogel. This could be useful for making aesthetic enhancements, printing inventory information and machining aerogel monoliths into various forms. Femtosecond lasers have been shown to work for crude "micro-machining" of aerogels[8–11]; however, the current protocol demonstrates the ability to alter the surface of aerogels with a simple laser engraving system. As a result, this protocol is broadly applicable to the artistic and technical communities.

It is also possible to incorporate dyes into the aerogel chemical precursor mixture and thereby make dye-doped aerogels with a range of hues. This method has been used to fabricate chemical sensors[12,13], to enhance Cerenkov detection[14], and for purely aesthetic reasons. Here, we demonstrate the use of dyes and laser etching to prepare aesthetically pleasing aerogels.

In the section that follows, we describe procedures for making large silica aerogel monoliths, altering the monolith preparation procedure to incorporate dyes, etching text, patterns and images onto the surface of an aerogel monolith, and cutting shapes from large dyed monoliths to be assembled into mosaics.

PROTOCOL:

Safety glasses or goggles should be worn when preparing the aerogel precursor solutions, working with the hot press, and using the laser engraving system. Laboratory gloves should be worn when cleaning and preparing the mold, preparing the chemical reagent solution, pouring the solution into the mold in the hot press and handling the aerogel. Read Safety Data Sheets (SDS) for all chemicals, including solvents, prior to working with them. Tetramethyl orthosilicate (TMOS), methanol and concentrated ammonia, and solutions containing these reagents, must be handled within a fume hood. Dyes can be toxic and/or carcinogenic, so it is important to employ appropriate personal protective equipment (see the SDS). As noted in our previous protocol[15], a safety shield should be installed around the hot press; the hot press should be properly vented and ignition sources should be removed. Before using the laser engraver, ensure that the vacuum exhaust system is operational.

1. Obtain or fabricate an aerogel monolith

NOTE: Methods for making a 10 cm x 11 cm x 1.5 cm aerogel monolith in a contained metal mold via a rapid supercritical extraction method (RSCE)[15–18] are described here. This RSCE process removes the solvent mixture from the pores of the silica matrix without causing structural collapse. Because the precursor mixture fills the mold, this method involves supercritical extraction of a significantly smaller volume of alcohol (in this case, methanol) than other high-temperature alcohol supercritical extraction methods. Aerogels produced using this method have densities of approximately 0.09 g/mL and surface areas of about 500 m^2/g. For etching, the monolith can be of any size large enough to etch on and prepared via any appropriate method (i.e., CO_2 supercritical extraction, freeze drying, ambient drying). For dyed aerogels, these other methods may not be as suitable because the dye can leach out during solvent exchange steps. If using a monolith obtained from another source, skip to step 2.

1.1. Prepare the mold

NOTE: All solution preparations should be performed in a fume hood wearing gloves and safety goggles.

1.1.1. Obtain a three-part (4140 alloy) steel mold consisting of a top, middle, and bottom part with outer dimensions of 15.24 cm x 14 cm and a 10 cm x 11 cm cavity in the center (see **Figure 1**). The top part of the mold has fourteen 0.08-cm vent holes, seven on each side. This mold assembly will produce a 10 cm x 11 cm x 1.5 cm aerogel.

NOTE: A different size mold may be used; however, the parameters will need to be adjusted, as described in Roth, Anderson, and Carroll[20].

1.1.2. Use diluted soap and a rough textured sponge to scrub and clean the top, middle, and bottom part of the mold. Dry all parts of the mold using a clean paper towel.

1.1.3. Pour 20 mL of acetone into a 50 mL or larger beaker. Dip a disposable cleaning wipe into the acetone and wipe the mold using a new cleaning wipe for each part. Repeat until the cleaning wipe appears clean after wiping.

1.1.4. Lightly sand all surfaces with 2,000-grit sandpaper until the mold is smooth to the touch and any residue from previous uses has been removed. Pay extra attention to the inside of the middle mold where the aerogel is formed.

1.1.5. Flow compressed air through the vent holes in the top mold part to clear them.

1.1.6. Squeeze out approximately 2.4 mL of high-vacuum grease and manually apply a thick, even, 1–2 mm layer of grease to the entire (26 mm) top-connecting surface of the bottom mold (see **Figure 1**).

1.1.7. Squeeze out approximately 1.0 mL of high-vacuum grease and manually apply a thick, even 1–2 mm layer of grease to the outer half (13 mm) of the bottom-connecting surface of the top mold (see **Figure 1**).

1.1.8. Squeeze out approximately 0.5 mL of high-vacuum grease and manually apply a thin (less than 0.5 mm), even layer of grease to the inside surfaces of the top and bottom mold (those surfaces that will contact the precursor solution and resulting aerogel, see **Figure 1**).

1.1.9. Wipe away excess grease with a disposable cleaning wipe until the surface feels smooth and no stickiness from the grease is felt.

1.1.10. Squeeze out approximately 0.5 mL of high vacuum grease and manually apply a thin (less than 0.5 mm), even layer of grease to the inside surface of the middle mold (see **Figure 1**). Do not wipe away excess grease.

1.1.11. Place the middle mold part on top of the bottom mold part. Use a rubber hammer covered with disposable cleaning wipes (to protect the mold surface) and gently hammer the middle part into the bottom part until all sides are evenly sealed.

1.1.12. Using two 0.0005” (0.0127 mm) thick 16 cm x 15 cm pieces of stainless steel foil, and a 0.0625” (1.59 mm) thick 16 cm x 15 cm piece of flexible graphite sheet, make a bottom gasket consisting of the graphite sandwiched between two layers of stainless steel foil. Make a similar gasket for the top of the mold.

1.1.13. Place the bottom gasket on the lower hot press platen and then place the assembled middle and bottom mold pieces on top of the gasket (see **Figure 2**). Ensure that the mold assembly is placed in the center of the hot press platen and use the hot press to apply a 90 kN force to the mold for approximately 5 min to seal the two pieces.

1.1.14. Remove the mold from the hot press. Use a disposable cleaning wipe to remove excess grease that may have squeezed out between the middle and bottom pieces. Ensure that no debris is on the inside surface of the mold.

1.2. Prepare aerogel precursor mixture

NOTE: This recipe is for a TMOS-based silica aerogel that can be made in the mold described above in section 1.1. Any suitable silica aerogel recipe can be used so long as the precursor recipe gelation takes more than 15 min but less than 120 min at room temperature (see, for example, Estok et al.[19] for a suitable tetraethyl orthosilicate-based RSCE recipe). Aerogels can be prepared in native (step 1.2.1) or dyed form (step 1.2.2). All solution preparation work is performed in a fume hood using gloves and safety goggles.

1.2.1. Native aerogels

1.2.1.1. Gather the following reagents: TMOS, methanol, deionized water, and 1.5 M ammonia.

1.2.1.2. Use an analytical balance to measure 34.28 g of TMOS into a clean 250 mL beaker. Pour the measured TMOS into a clean 600 mL beaker and cover with paraffin film.

1.2.1.3. Use an analytical balance to measure 85.76 g of methanol into another 250 mL beaker. Pour the measured methanol into the 600 mL beaker containing TMOS and cover with paraffin film.

1.2.1.4. Measure 14.14 g of deionized water into a 50 mL beaker using an analytical balance. Use a micropipette to add 1.05 mL of 1.5 M ammonia to the water in the beaker. Stir gently.

1.2.1.5. Pour the water and ammonia mixture into the 600 mL beaker with the remaining reagents and cover with paraffin film. Place the beaker in a sonicator and sonicate for 5 min.

1.2.2. Dye-doped aerogels

NOTE: If a different procedure is used that involves solvent exchanges, a considerable amount of dye will be washed out during the exchanges; consequently, the colors of the resulting aerogels will not be as vibrant as those presented here.

1.2.2.1. Gather the following reagents: tetramethyl orthosilicate (TMOS), methanol, deionized water, 1.5 M ammonia and a suitable dye.

1.2.2.2. Use an analytical balance to measure 34.28 g of TMOS into a clean 250 mL beaker. Pour the measured TMOS into a clean 600 mL beaker and cover with paraffin film.

1.2.2.3. Use an analytical balance to measure 42.88 g of methanol into a 250 mL beaker. Pour the measured methanol into the 600 mL beaker containing TMOS and cover with paraffin film. Use an analytical balance to measure another 42.88 g of methanol into the 250 mL beaker.

1.2.2.4. Use an analytical balance to measure 0.050 g of fluorescein (to make a yellow-tinged aerogel) or 0.042 g of rhodamine B (to make a pink-tinged aerogel) or 0.067 g of Rhodamine 6 G (to make an orange-tinged aerogel) into a 10 mL beaker. Add the dye to the 250 mL beaker containing the methanol and gently mix until dissolved.

NOTE: These instructions are for aerogels used in the example mosaic design; the dye concentration can be altered to change the depth of color in the resulting aerogel (see **Table 1**).

1.2.2.5. Pour the dye solution into the 600 mL beaker containing TMOS and cover with paraffin film.

1.2.2.6. Measure 14.14 g of deionized water into a 50 mL beaker using an analytical balance. Use a micropipette to add 1.05 mL of 1.5 M ammonia to the water in the beaker.

1.2.2.7. Pour the water and ammonia mixture into the 600 mL beaker with the remaining reagents and cover with paraffin film. Place the beaker in a sonicator and sonicate for 5 min.

1.3. Perform rapid supercritical extraction

NOTE: This procedure uses a 30-ton programmable hot press equipped with a safety shield. Gloves and safety goggles should be worn.

1.3.1. Program the hot press extraction program with the parameters shown in **Table 2**. Parameters are set to prepare a 10 cm x 11 cm x 1.5 cm aerogel in the mold described in step 1.1.1. If a different size mold is used, the parameters will need to be adjusted, as described in Roth, Anderson, and Carroll[20].

1.3.2. Place the middle/bottom mold assembly back on top of the bottom gasket in the hot press. Ensure that the mold is placed in the center of the hot press platen (see **Figure 2**).

1.3.3. Pour the aerogel precursor solution (native or dye-containing) into the mold until the solution is ~2 mm from the top. This will ensure that the mold is completely filled with the precursor solution when the top piece of the mold is added. There will be approximately 10 mL of mixture remaining in the beaker, which can be discarded or allowed to gel at room temperature.

1.3.4. Carefully place the top part of the mold in position on the middle/bottom mold assembly. Excess solution may come out of the vent holes on the top of the mold as it is placed on the middle mold. Wipe up the solution with a disposable cleaning wipe.

1.3.5. Place disposable cleaning wipes on top of the mold to protect the mold surface. Use a rubber hammer to lightly tap the top mold until it is evenly sealed on each side.

1.3.6. Place the top gasket on top of the assembled mold; close the safety shield and start the hot-press program. The precursor mixture gels as the system heats up. The entire process will take 10.25 h to complete for this size aerogel.

1.4. Remove aerogel monolith from mold

NOTE: Gloves should be worn when handling the aerogel monolith.

1.4.1. When the extraction process is complete, open the safety shield, remove the mold, and place it on a clean working surface.

1.4.2. Insert a flat-head screwdriver into the cavity between the top and middle mold (see **Figure 1**). Place a gloved hand on the backside of the mold and push down on the screwdriver to separate the top and middle mold parts.

1.4.3. Once the seal is broken, repeat step 1.4.2, going around the edges of the mold while pushing the screwdriver down to release the top mold part. Place the gloved hand wherever necessary to hold down the mold while opening it.

1.4.4. When all sides of the top mold are free from the middle mold, remove the top mold. Place the top mold to the side.

1.4.5. Obtain a lidded container large enough to hold the aerogel; remove the lid and place the bottom part of the container upside down on top of the middle mold with the container and mold cavity aligned. Flip the mold upside down; the aerogel should drop gently into the container.

1.4.6. Put the lid back on the container to protect the aerogel. The aerogel can be stored indefinitely before performing any etching or cutting.

2. Prepare laser engraver print file

NOTE: It is possible to print text, patterns, and images on the aerogel. Any suitable drawing program can be used. Images are interpreted in grayscale. The laser engraver will ablate the aerogel surface in locations where there is text or a pattern and varies the laser pulse density to achieve gray scale values. Etching occurs in locations where the printed image is non-white. Etching does not occur where the image is white. Separate instructions are included for text, pattern, or image files. All three can be combined in one file if desired[6].

2.1. Text files

2.1.1. Open up the drawing application and start a new document. Add the desired text of any size, linewidth, and style directly to the document.

2.1.2. Save the file.

2.2. Pattern files

2.2.1. Open up the drawing application and start a new document.

2.2.2. Add lines and shapes directly to the document using the desired linewidth.

2.2.3. To design a mosaic pattern that will be cut from (instead of etched onto) the aerogel monolith, use shapes and lines in the toolbox and set all line widths to hairline. See **Figure 3** for an example of a mosaic pattern.

2.2.4. Save the file.

2.3. Image files

2.3.1. Select an image and use any image-processing program to edit.

2.3.2. Use a software to remove non-white sections that are not to be printed from the image. See **Figure 4** for an example of this.

NOTE: Etching occurs in any non-white location.

2.3.3. Convert the image to grayscale for a visual indication of what the etched image will look like and adjust the contrast between image hues until satisfied that sufficient contrast exists to show the desired features (see **Figure 4**).

NOTE: The level of contrast needed will depend on the amount of detail in the image that the user desires to etch onto the aerogel. The drawing program should provide guidance, but the user may need to experiment with different contrast levels to achieve the desired outcome.

2.3.4. Open up the drawing application and start a new document. Upload an image to drawing program.

2.3.5. Save the file.

3. Etching procedure

NOTE: The following instructions are for a 50 W CO_2 laser engraver/cutter but can be modified to use with other systems. This system adjusts speed and power properties on a percent basis from 0% to 100%. Relevant laser engraver properties are included in **Table 3**. A vacuum exhaust system should be used to vent the laser engraver. Use gloves when handling the aerogel monolith.

3.1. Turn on the laser engraver, vacuum exhaust system, and the attached computer.

3.2. Measure the size of the aerogel monolith surface that will be etched (in the example above, the size is 10 cm x 11 cm).

3.3. Start the drawing program and open the previously saved file (from step 2.1, 2.2, or 2.3). Set the document's dimension/piece size to correspond to the measured aerogel monolith size.

3.4. Open the lid of the laser engraver. Using a gloved hand, place the aerogel (native or dyed) on the laser engraver platform as shown in **Figure 5**. Align the aerogel in the top-left corner so that the aerogel touches the top and left rulers.

3.5. Take the V-shaped magnet manual focus gauge attached to the laser and flip it upside down. Press **Focus** on the laser engraver.

NOTE: Because of the transparency of the silica aerogel monolith, it is necessary to manually set the focus parameters for etching. Do not use Auto Focus.

3.6. Place a disposable cleaning wipe on top of the aerogel monolith to protect it. Using the up arrow on the laser engraver control panel, move the laser engraver platform until the bottom part of the manual focus gauge just touches the aerogel.

3.7. Remove the disposable cleaning wipe and return the gauge to its original position. Close the laser engraver lid.

3.8. In the drawing program, click **File** and then **Print**. Choose the drawing program as the print location and open the **Properties** window.

3.9. Adjust the properties by selecting the **Raster** mode: a **DPI** of 600, a **Speed** of 100% (208 cm/s), and a **Power** of 55% (27.5 W). Confirm that the piece size matches the measured aerogel monolith size. Click **Apply** and then **Print**.

3.10. On the front panel of the laser engraver, click **Job** and select the corresponding file name. Click **Go**.

3.11. When the laser engraver finishes, click **Focus** and use the down arrow on the laser front control panel to lower the base. Using a gloved hand, gently remove the aerogel from the laser engraver platform and place it back in the container.

3.12. Purge the job from the laser engraver by clicking on the **Trash** button. Turn off the laser engraver and vacuum.

4. Cutting procedure

4.1. Turn on the laser engraver, vacuum exhaust system, and the attached computer.

4.2. Measure the size of the aerogel monolith surface that will be cut (in the example above, the size is 10 cm x 11 cm).

4.3. For general cutting, open the drawing program and start a new document. Enter the dimensions for the document/piece size to correlate with the measured aerogel monolith size.

4.4. Use the tools in the drawing program to create the shape or line that will be cut using a “hairline” line width. Locate the shape/line to match the desired cut location on the aerogel.

4.5. For mosaic patterns, import the previously saved file (from step 2.2) and adjust the size to match that of the aerogel monolith.

4.6. Obtain a 0.0005” (0.0127 mm) thick sheet of stainless steel foil large enough to cover the base of the aerogel monolith. Using a cleaning wipe, clean the stainless steel with acetone.

4.7. Open the lid of the laser engraver, place the stainless steel foil on the laser engraver platform to prevent residue on the platform from discoloring the aerogel during cutting and place the aerogel monolith on top of the foil. Align the aerogel and stainless steel foil in the top left corner with the aerogel touching the top and left rulers.

4.8. Follow steps 3.5–3.8 from the etching procedure above.

4.9. Adjust printing properties. Select the **Vector** mode: a **DPI** of 600, a **Speed** of 3% (0.27 cm/s), **Power** of 90% (45 W), and **Frequency** of 1,000 Hz. Make sure the piece size matches the measured aerogel size. The depth of the cut will vary with laser speed. See **Table 4** and **Figure 6**.

4.10. Follow steps 3.10–3.12 from the etching procedure.

4.11. Small pieces of ablated aerogel will be left on the face of the monolith that was in contact with the laser, as shown in **Figure 7**. To remove the particles, use a foam brush and gently wipe away the pieces.

5. Making aerogel mosaics

5.1. To yield a tri-color mosaic, prepare three different monoliths of the same thickness but with different dyes. (It is also possible to yield mosaics with three different shades, using different monoliths of the same thickness but with varying concentrations of the same dye, or to include native aerogel with dyed aerogel in mosaic patterns.)

5.2. Use the cutting procedure in section 4 with the mosaic design from section 2.2 to cut the mosaic patterns into three different colored aerogels of the same thickness.

5.3. Place the cut colored aerogels on a flat, clean surface.

5.4. Gently disassemble each single-colored aerogel and separate the components of the cut design using tweezers or a sharp knife to ease separation and prevent breakage.

5.5. Gently brush the sides of each shape with a foam brush to remove the excess white particles left by the laser cutting procedure.

5.6. Interchange the same shapes with different colors to produce multicolored mosaics (**Figure 8**) and assemble the cut shapes by compressing them together to form a complete mosaic-like tile, which can be placed within a glass frame.

REPRESENTATIVE RESULTS:

This protocol can be employed to prepare a wide variety of aesthetically pleasing aerogel monoliths for applications including, but not limited to, art and sustainable building design. Inclusion in the precursor mixture of the small amounts of dye employed here is only observed to impact the color of the resulting aerogel monolith; changes in other optical or structural properties are not observed.

Figure 8 shows an approach to preparing an aerogel mosaic from large silica monoliths. The same pattern (shown in **Figure 3**) is cut into three different dyed aerogel monoliths (**Figure 8a–c**). Aerogel pieces are then reassembled into a mosaic pattern (**Figure 8d–e**). To prepare a mosaic window, the aerogel mosaic can be sandwiched between two panes of glass or transparent plastic within a frame assembly. Use of a compression frame will eliminate gaps between the re-assembled pieces in the final mosaic assembly.

It is possible to etch designs on smaller monolithic pieces, following the same procedure outlined in section 3, in order to obtain visually interesting arrangements. **Figure 9** presents images of dyed, etched aerogel pieces under natural lighting conditions (**Figure 9a**) and under UV light (**Figure 9b**), highlighting the fluorescent nature of the dyes used here. Note that small monoliths of irregular size and shape were used to illustrate the feasibility of etching onto smaller pieces; the etching process did not cause them to break.

Figure 10 presents a montage of etched aerogels that illustrate different aesthetic effects that can be achieved using this protocol: native aerogels etched with patterns of various density (**Figure 10a–c**), aerogels with photographs printed onto the front surface of a planar surface (**Figure 10d**) and front and back of a curved surface (**Figure 10e**) as well as an etched fluorescein-dyed aerogel (**Figure 10f**). The montage illustrates the versatility of the etching and dying processes.

Etching results in changes to the surface of the aerogel, but visual observation, imaging and BET analysis demonstrates that it leaves the bulk structure intact[6,7]. Photographs in **Figure 5–Figure 9** illustrate that the unetched portions of the monolith are unscathed. The localized damage caused by etching can be imaged. **Figure 11** shows scanning electron microscope (SEM) images of etched silica aerogel. **Figure 11a** shows the interface between etched "lines" (upper right portion of image, with features in a venation pattern) and the un-etched nanoporous aerogel (which appears almost smooth at this magnification). Etching causes ablation of material from the surface and melting of some of the silica into filament-like structures hundreds of µm in length[7]. **Figure 11b** shows the effect of a single laser pulse in the aerogel.

FIGURE AND TABLE LEGENDS:

Table 1: Information on the dyes. Information on dyes used for making yellow-, pink-, and orange-tinged aerogels and representative images. Different shades are achieved by diluting the methanol/dye stock mixture with additional methanol (as described in step 1.2.2.4.) prior to use in the precursor mixture. Images are shown for materials prepared with 0x dilution (stock solution, shown to the left), 2x dilution (50% methanol/dye + 50% methanol, shown in the center), and 6.67x dilution (15% methanol/dye + 85% methanol, shown to the right).

Table 2: Hot press parameters.

Table 3: Laser engraver properties.

Table 4: Laser cut depth as a function of laser head speed for a laser power of 100% (50 W) and frequency of 500 Hz.

Figure 1: Schematics of mold assembly. Schematics of the (**a**) top (with fourteen vent holes), (**b**) middle, and (**c**) bottom mold assembly. The blue surface (**d**) indicates the connecting surface of the bottom part (a similar one exists on the top surface) and the off-white surfaces (**e**) indicate

the inside surfaces of the middle and bottom mold (a similar one exists on the top surface). A three-part mold is used to facilitate removal of the aerogel, if needed.

Figure 2: Schematic showing mold placement in hot press. (**a**) Hot press platens, (**b**) graphite gasket, (**c**) stainless steel foil, (**d**) 3-part mold.

Figure 3: Example construction of a mosaic design. (**a**) square outline created, (**b**) diagonal lines added, (**c**) circle added, (**d**) inner diagonal lines removed, (**e**) hexagon added, and (**f**) final design. See **Figure 8** for aerogel mosaic constructed from this design.

Figure 4: Example adjustment of a cloud image. (**a**) Original image. (**b**) Inverted image with off-white background. (**c**) Original image with background removed and contrast adjusted to 40% to highlight features. (**d**) Photograph of aerogel etched with image shown in panel a. The low contrast level in the original image results in an indistinct etched pattern. (**e**) Photograph of aerogel etched with image shown in panel b. Here, the cloud is more visible but the off-white background results in less distinction. Note that the cracks observed were present on the monolith prior to etching and are not due to the etching process. (**F**) Photograph of aerogel etched with image shown in panel c. The adjusted contrast and removal of the background results in a more distinct cloud. In all the images, the cloud is approximately 2 cm high.

Figure 5: Laser engraver. (**a**) manual focus gauge, (**b**) laser and lens assembly, (**c**) aerogel and (**d**) platform.

Figure 6: Cut depth versus laser speed. Cut depth versus laser speed (100% leftmost cut, 3% rightmost cut) for a power of 100% (50 W) and a frequency of 500 Hz (see accompanying data in **Table 4**). This figure has been modified from Stanec et al.[7]. The arrow indicates the cut that penetrated the full depth of the aerogel.

Figure 7: Photograph of cut aerogel edge. Pieces of ablated aerogel can be seen on the leftmost surface.

Figure 8: Example of aerogel mosaic. The final pattern of **Figure 3** cut into (**a**) rhodamine-6G-dyed aerogel (orange), (**b**) fluorescein-dyed (yellow) aerogel, and (**c**) rhodamine-B-dyed (pink) aerogel (**d,e**) individual cut pieces reassembled to form tri-color mosaics.

Figure 9: Etched dyed aerogel samples. Etched dyed aerogel samples (**a**) under natural lighting conditions and (**b**) under UV light. Notes: the size of the largest aerogel piece (left side, middle) is approximately 3 cm x 3 cm x 1 cm. Dark spots observed are due to staining from the laser engraver platform or are loose particles, rather than an indication of inhomogeneity in dye distribution.

Figure 10: Photographs of etched aerogels. (**a**) view of geometric pattern etched on front and back of aerogel, (**b**) a dense etching pattern leaves the bulk structure intact, (**c**) flower pattern etching, (**d**) photograph (top) etched onto silica aerogel (bottom), (This figure has been modified

from Michaloudis et al.[6]) (**e**) photograph (top) of Kouros statue etched onto front and back of cylindrical aerogel of diameter 2.5 cm (note the original photo was inverted to create a white background before etching), and (**f**) image etched onto fluorescein-dyed silica aerogel of height 9 cm.

Figure 11: SEM images of a silica aerogel showing the effect of (**a**) etching lines on the upper-right side of the image and (**b**) a single laser pulse. (This figure has been modified from Stanec et al.[7].) The images show structural changes caused by the laser. The scale bar is 20 µm.

DISCUSSION:

This protocol demonstrates how laser etching and the inclusion of dyes can be employed to prepare aesthetically pleasing aerogel materials.

Making large (10 cm x 11 cm x 1.5 cm) aerogel monoliths requires proper mold preparation through sanding, cleaning, and grease application to prevent the aerogel from sticking to the mold and major cracks from forming. The parts of the mold in direct contact with the precursor solution/soon to be formed aerogel are the most critical. Reducing the surface roughness of the mold via machine polishing will improve performance. It is important to apply grease only to the outer perimeter (13 mm) of the top part of the mold so that when the hot press force is applied to the mold, grease does not seep into the cavity of the mold. If grease gets into the cavity, major cracks will form in the aerogel.

When using the laser engraver, the aerogel needs to be properly placed in the top-left corner of the laser engraver and the dimensions of the aerogel need to correspond with those of the drawing program document. The image to be etched must be properly prepared by removing the non-white background, adjusting contrast to get definition and highlight features in the image. Although it is possible to print dense patterns (see **Figure 8b**), if the pattern is too dense, the ablated material can separate from the bulk of the aerogel. When cutting through an aerogel the laser parameters should be adjusted to avoid discoloration[6,7]. High frequency, high power, and low speed settings will cause more damage. These settings will also affect the quality of the cut and the amount of damage at the cut surface. The guidelines provided here for laser power level, frequency and speed are for a typical silica aerogel of density 0.09 g/mL. Adjustments to these parameters may be needed for aerogels of different densities.

It is important to select dyes that can survive the RSCE aerogel fabrication process. They need to be thermally stable at 290 °C (550 °F) and they must not react with methanol. However, even if a dye meets these requirements, it may not work. In addition to the dyes described above, we tested Bismarck Brown, Indigo, Brilliant Blue and Congo Red (in an effort to satisfy Victorian Gothic aesthetics in the mosaic designs). These dyes did not survive the RSCE process and resulted in opaque cloudy white aerogels. The concentration level of dye affected the opacity of the aerogel but not the expected color. If aerogels produced from a precursor solution that includes dye show no color (indicating decomposition of the dye), the maximum processing temperature can be lowered to 260 °C, which is still above the supercritical temperature of methanol. Or an alternative aerogel preparation method (CO_2 supercritical extraction, ambient pressure drying, or freeze drying) can be used, although solvent exchange steps are likely to wash away a significant fraction of the dye. Another method for making colored aerogels is to incorporate metal salts into the precursor mixture. For example, cobalt, nickel, and copper salts can be used to produce blue[21], green[22] and red-brown aerogels[23], respectively, via the RSCE method; however, the resulting aerogels are opaque.

We are not aware of any other methods for etching or writing onto an aerogel surface. There are other methods for cutting aerogels including the use of mechanical saws[24]. Diamond saws can cut aerogel, but it is difficult to avoid cracking and excessive saw kerf. In applications to remove space dust from aerogels Ishii et al.[25,26] demonstrate the use of ultrasonic microblades to cut aerogel and minimize these issues.

The ability to dye and etch onto silica aerogels can be used to enhance the aesthetics of aerogel monoliths, which in native un-etched form often exhibit imperfections due to haze and light scattering. We are incorporating the resulting aesthetically enhanced aerogels into window prototypes and sculpture; however, it would be possible to use the methods described here in other applications, including printing inventory information and precise target patterns onto aerogel monoliths. The cutting and etching procedures also offer methods for machining silica aerogels into specific shapes.

ACKNOWLEDGMENTS:
The authors would like to acknowledge the Union College Faculty Research Fund, Student Research Grant program, and the summer undergraduate research program for financial support of the project. The authors would also like to acknowledge Joana Santos for the design of the three-piece mold, Chris Avanessian for SEM imaging, Ronald Tocci for etching onto the curved aerogel surface, and Dr. Ioannis Michaloudis for inspiration and initial work on the etching project as well as for providing the Kouros image and cylindrical aerogel.

DISCLOSURES:
The authors have nothing to disclose.

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Figure 1

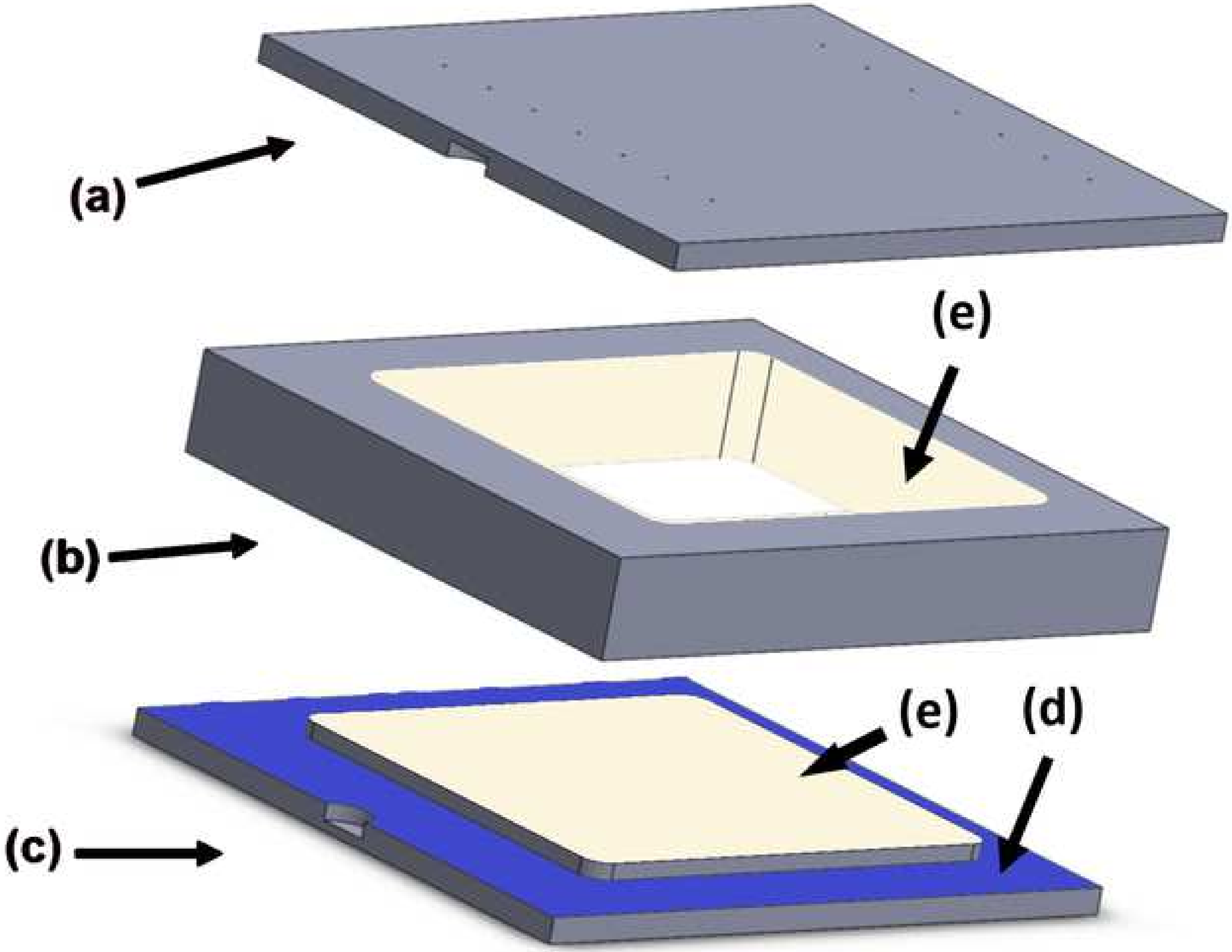


Figure 2

Click here to access/download;Figure;Figure 2.jpg

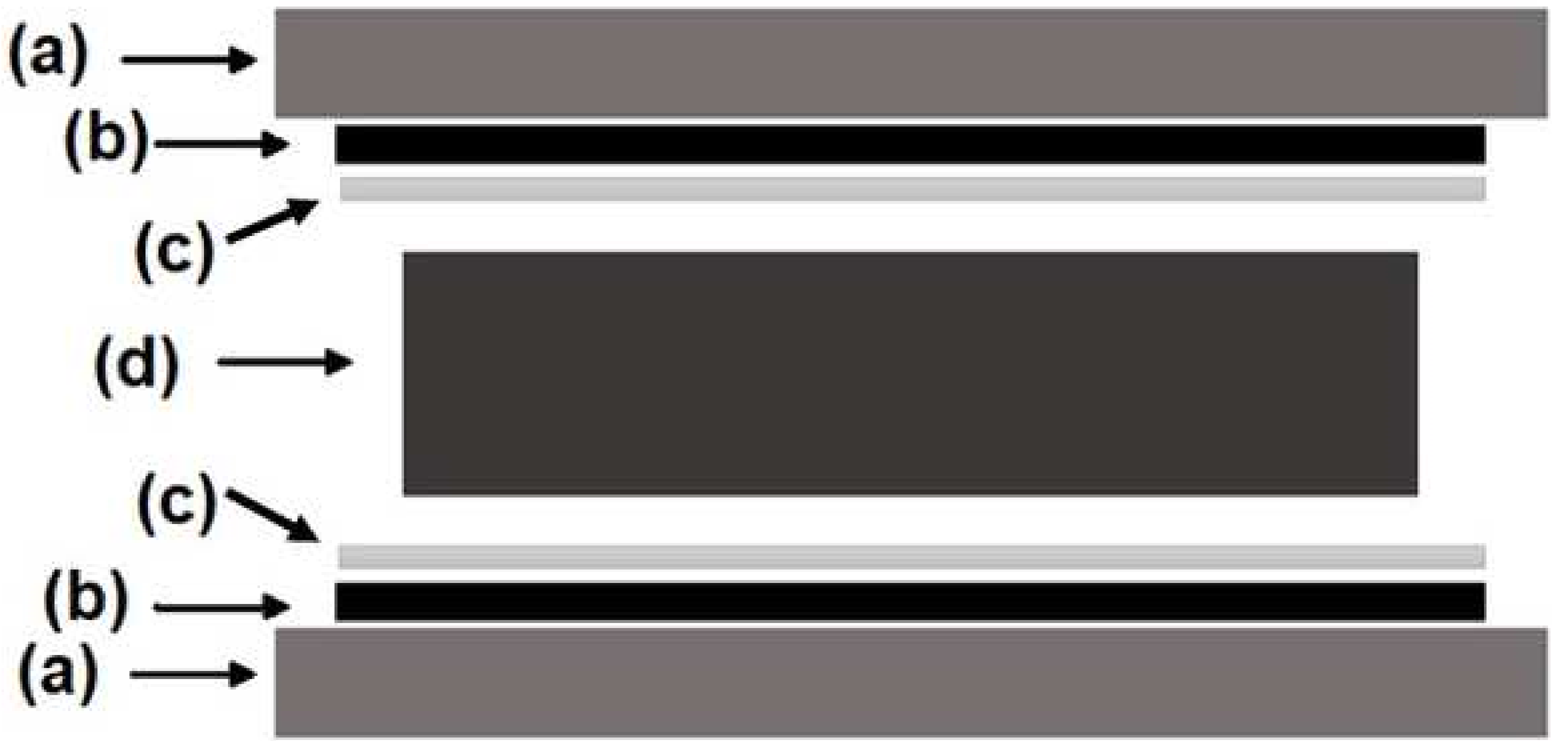


Figure 3

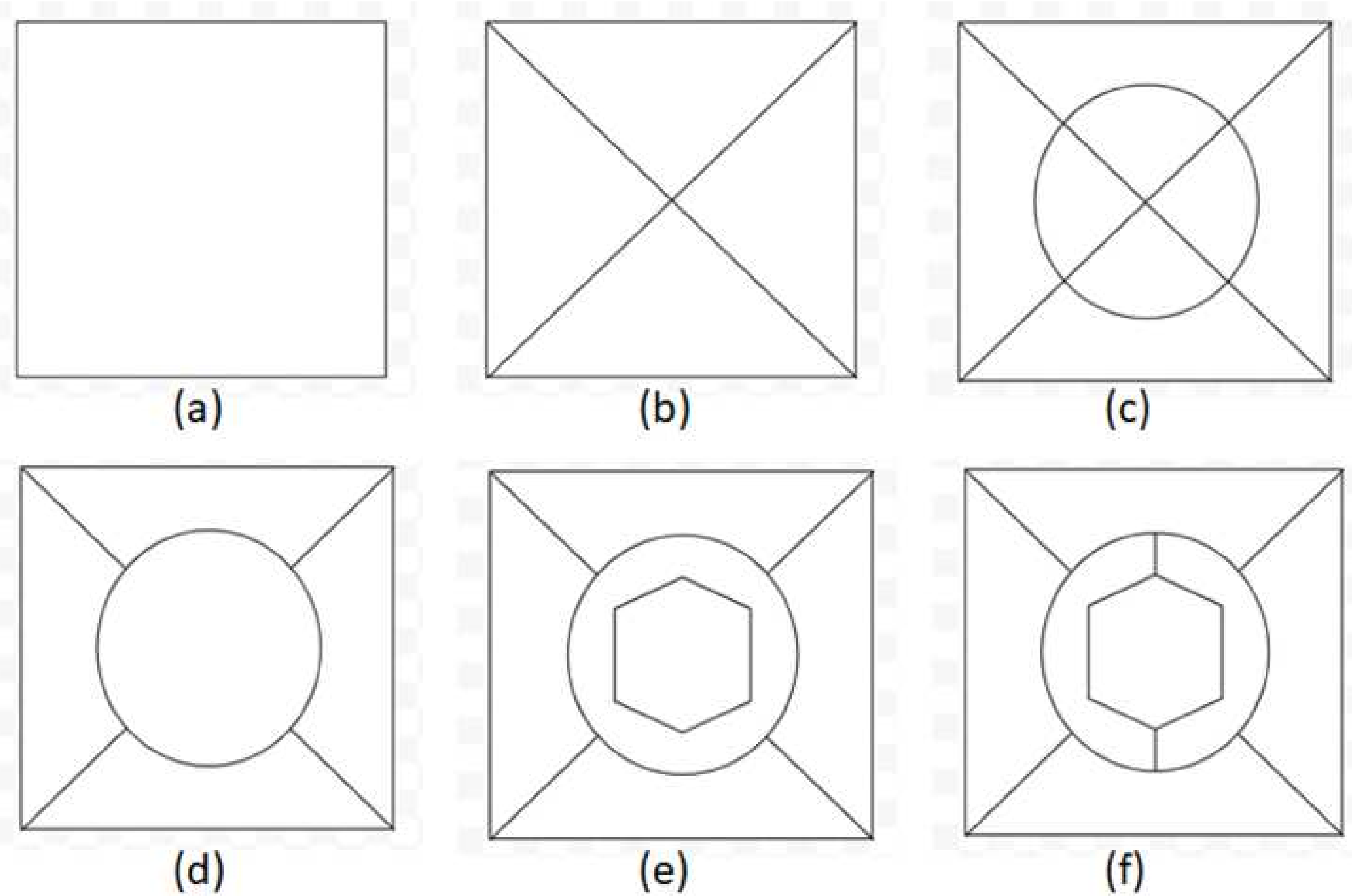
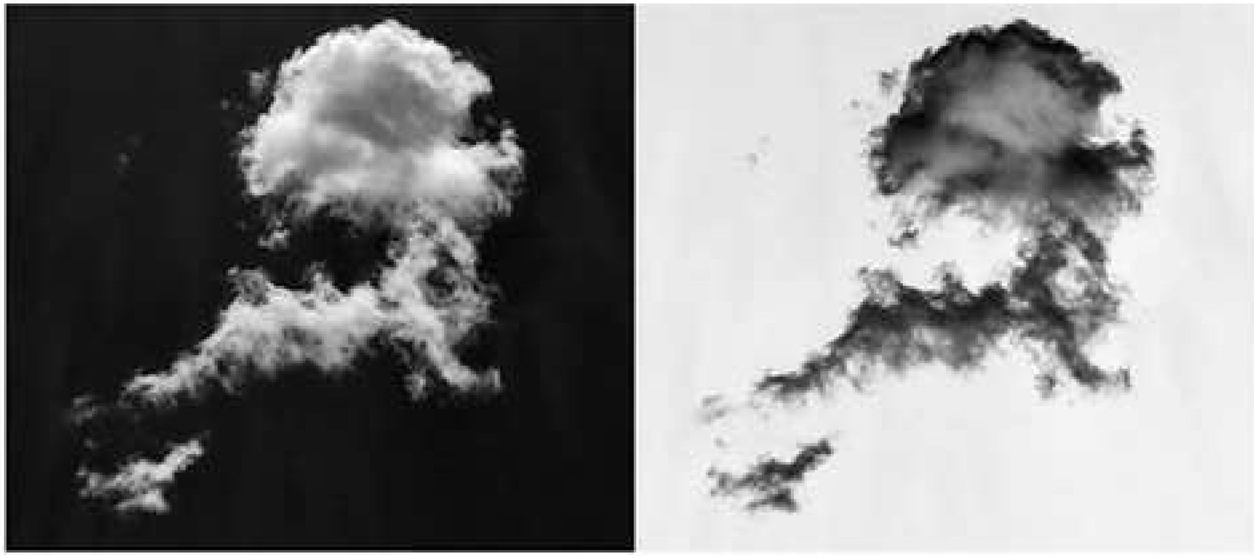


Figure 4

Click here to access/download;Figure;Fig 4.tiff



(a) (b) (c)

(d) (e) (f)

Figure 5

Click here to access/download;Figure;Fig 5.jpg

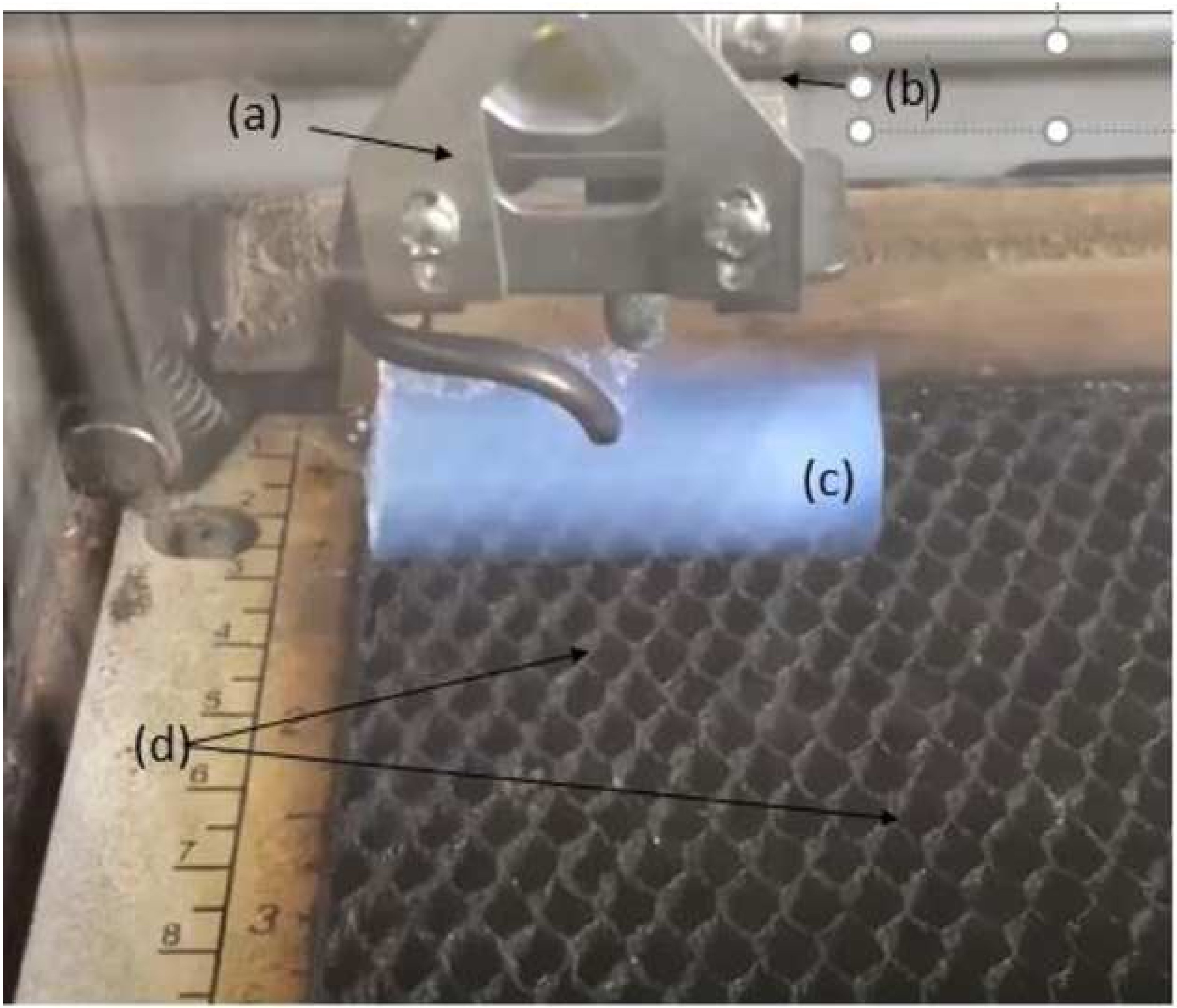


Figure 6

Click here to access/download;Figure;Fig 6.tiff

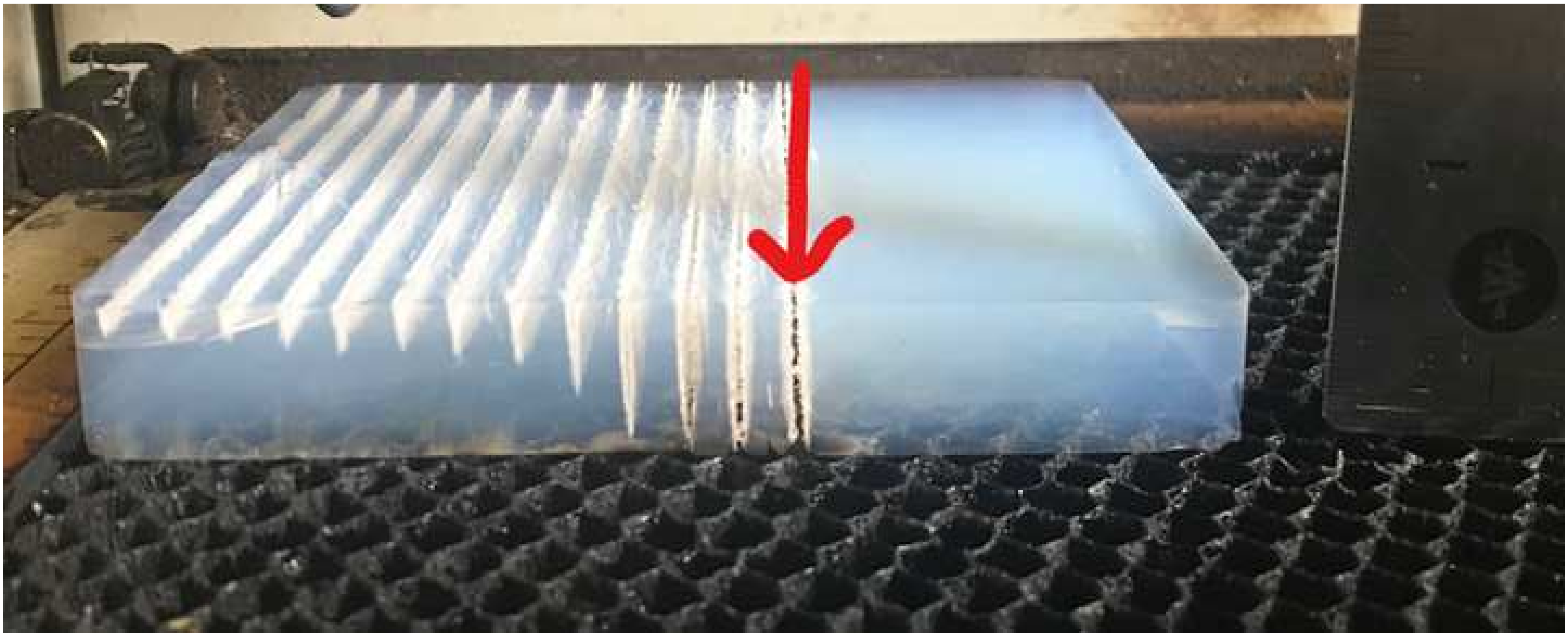


Figure 7

Click here to access/download;Figure;Fig 7.tiff

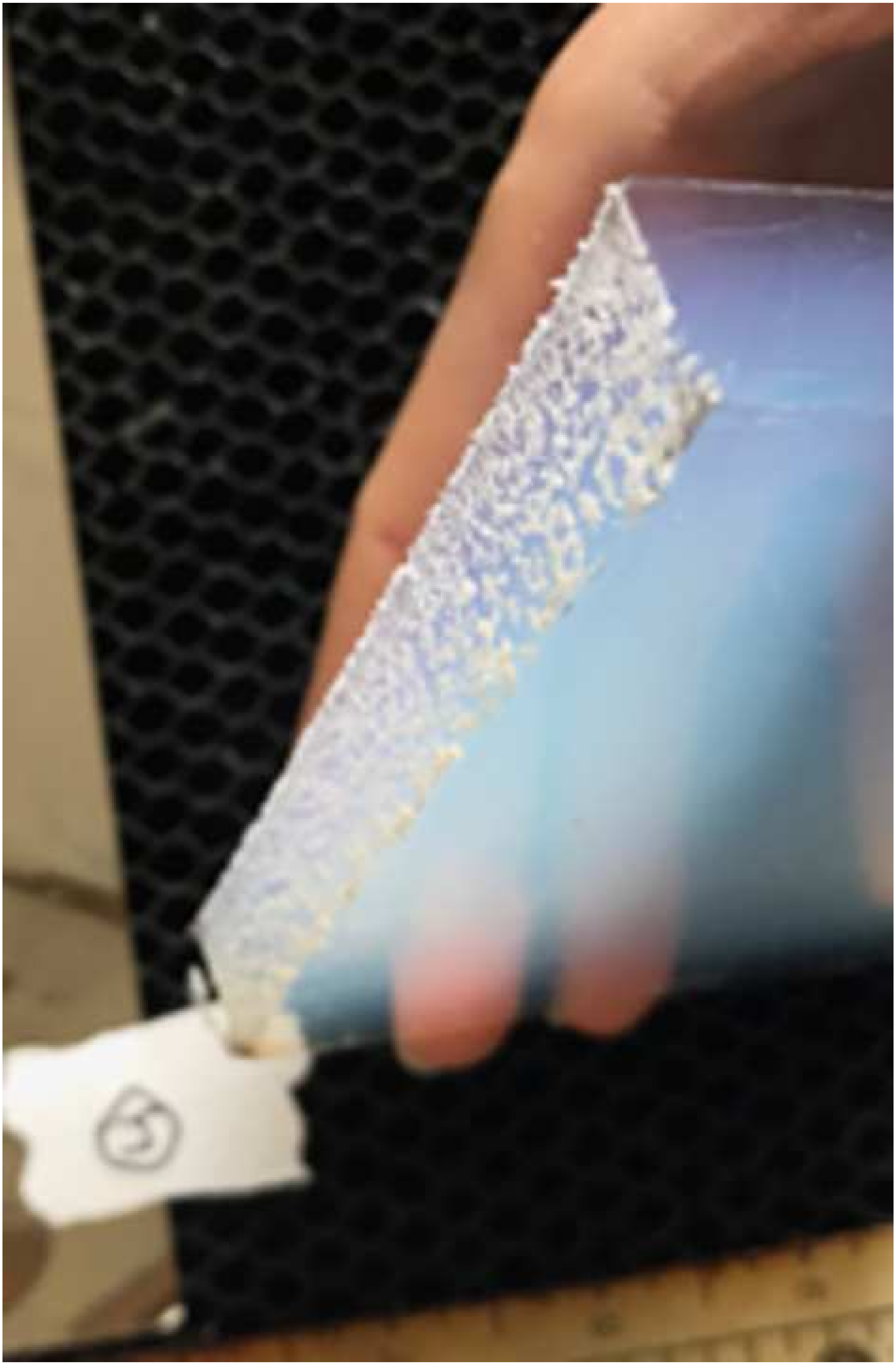
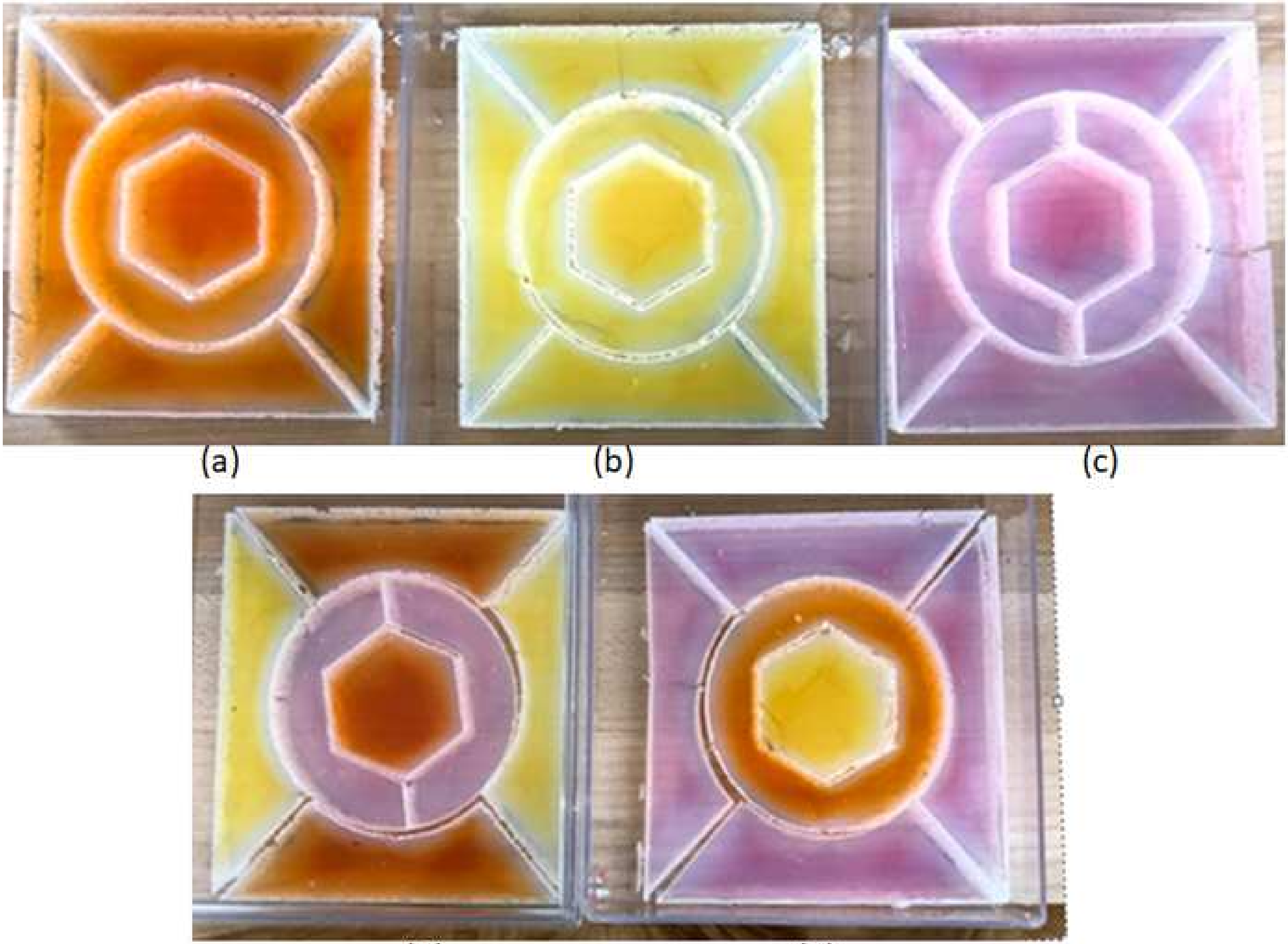


Figure 8

Click here to access/download;Figure;Fig 8.tif



(a) (b) (c)

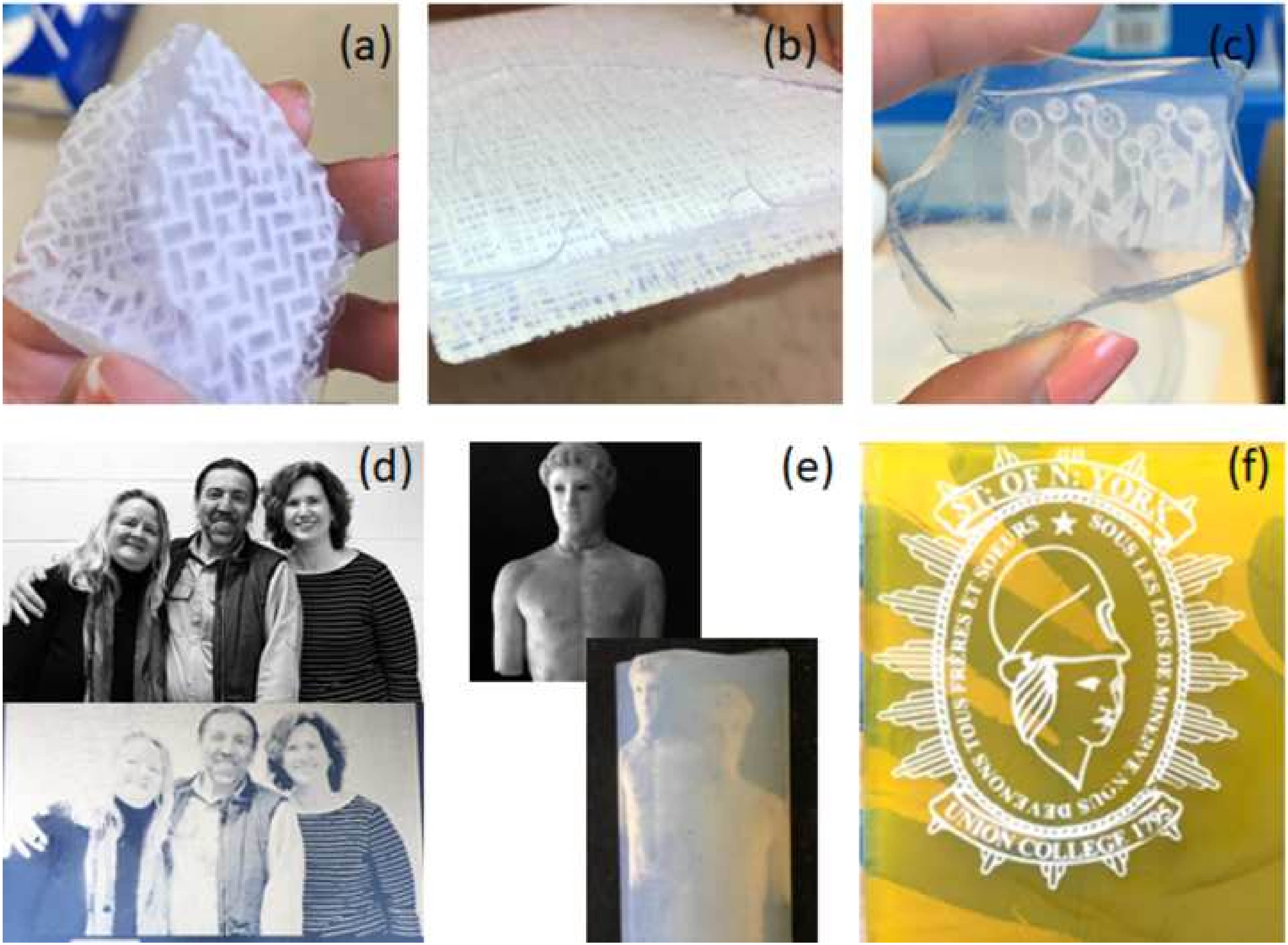
(d) (e)

Figure 9

(a)

(b)

Figure 10


(a)
(b)
(c)
(d)
(e)
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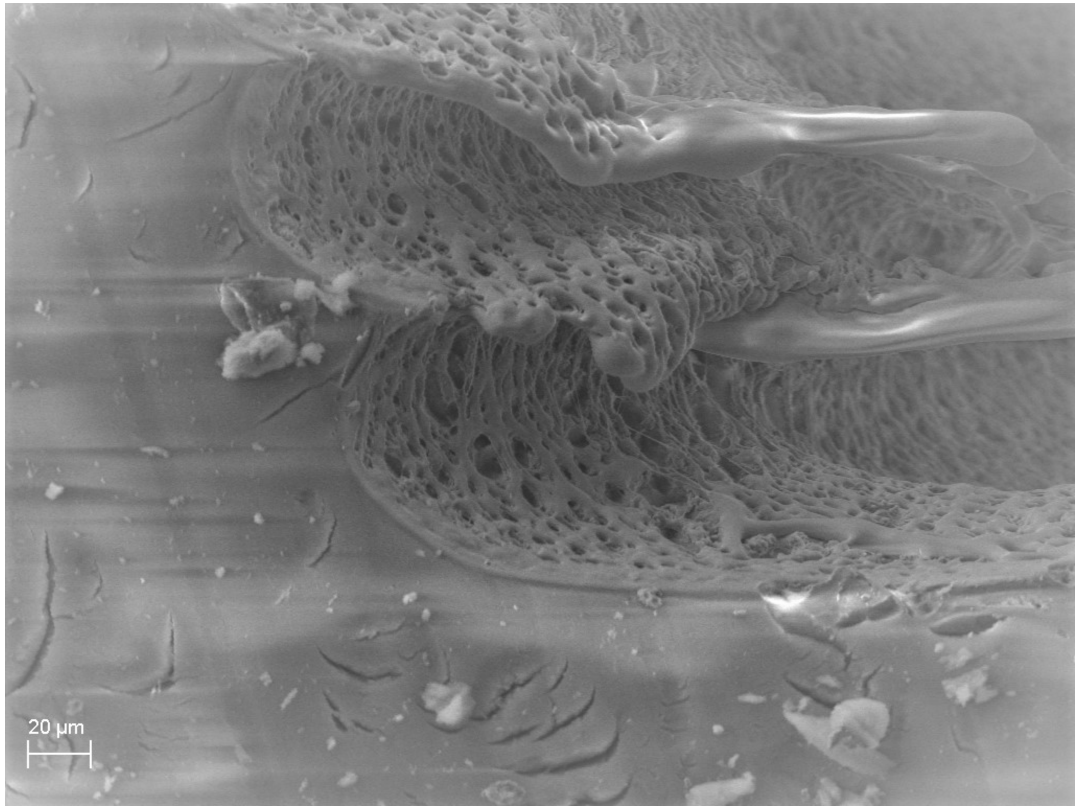
UNION COLLEGE 179

Figure 11

(a)



(b)

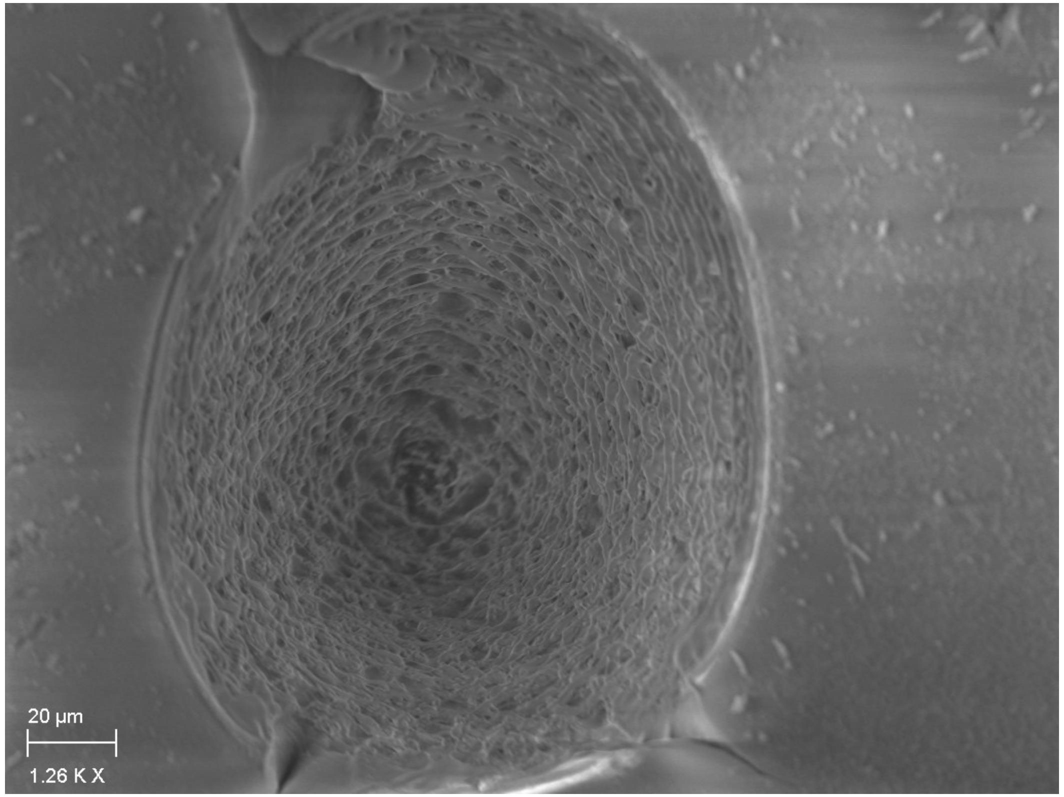


Table 1

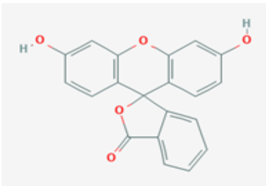
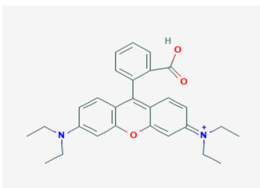
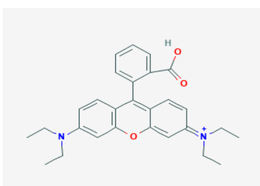
Dye & Structure	Melting Point (°C)	Mass ratio (Dye/Methanol) in stock solution	Images of Resulting Aerogels
Fluorescein 	315	0.05% g /g	
Rhodamine B 	165	0.075% g/g	
Rhodamine 6G 	290	0.16% g/g	

Table 2

Step	Temperature (°F, °C)	T-Rate (°F/min, °C/min)	Force (Kip, kN)	F-Rate(Kip/min,	Dwell (min)	Step Duration
1	90, 32	200, 111	55, 245	600, 2700	30	30
2	550, 288	2, 1.1	55, 245	--	55	285
3	550, 288	--	1, 4.5	1, 4.5	15	70
4	90, 32	2, 1.1	1, 4.5	--	0	230

Parameter	Values
Maximum Speed	8.9 cm/s (vector mode) 208 cm/s (raster mode)
Maximum Power	50 W
Frequency Range	1 - 5000 Hz
Print Resolution	75 - 1200 DPI

Speed (cm/s)	Cut Depth (mm)
0.27	12.8
0.45	12.2
0.71	10.4
0.89	10.2
1.78	7
2.67	6.2
3.56	5.2
4.45	4.6
5.34	4.3
6.23	3.7
7.12	3.4
8.01	2.8
8.9	3

Name of Material/ Equipment	Company	Catalog Number	Comments/Description
2000 grit sandpaper	Various		
50W Laser Engraver	Epilog Laser		Any laser cutter is suitable
Acetone	Fisher Scientific www.fishersci.com	A18-20	Certified ACS Reagent Grade
Ammonium Hydroxide (aqueous ammonia)	Fisher Scientific www.fishersci.com	A669S212	Certified ACS Plus, about 14.8
Beakers	Purchased from Fisher Scientific		Any glass beaker is suitable.
Deionized Water	On tap in house		
Digital balance	OHaus Explorer Pro		Any digital balance is suitable.
Disposable cleaning wipes	Fisher Scientific www.fishersci.com	06-666	KimWipe
Drawing Software	CorelDraw Graphics Suite		CorelDraw
Flexible Graphite Sheet	Phelps Industrial Products	7500.062.3	1/16" thick
Fluorescein	Sigma Aldrich www.sigmaaldrich.com	F2456	Dye content ~95%
Foam paint brush	Various		1-2 cm size
High Vacuum Grease	Dow Corning		
Hydraulic Hot Press	Tetrahedron www.tetrahedronassociates.con	MTP-14	Any hot press with temperatu
Laser Engraver	Epilogue Laser	Helix - 24	50 W
Methanol (MeOH)	Fisher Scientific www.fishersci.com	A412-20	Certified ACS Reagent Grade,
Mold	Fabricated in House		Fabricate from cold-rolled ste
Paraffin Film	Fisher Scientific www.fishersci.com	S37441	Parafilm M Laboratory Film
Rhodamine-6GRhodamine-6gFlouresceinRhodami	Sigma Aldrich www.sigmaaldrich.com	20,132-4	Dye content ~95%
Rhodamine-BRhodamine-6gFlouresceinRhodamin	Sigma Aldrich www.sigmaaldrich.com	R-953	Dye content ~80%
Soap to clean mold	Various		
Stainless Steel Foil	Various		.0005" thick, 304 Stainless Ste
Tetramethylorthosilicate (TMOS)	Sigma Aldrich www.sigmaaldrich.com	218472-500G	98% purity, CAS 681-84-5
Ultrasonic Cleaner	FisherScientific FS6	153356	Any sonicator is suitable.
Vacuum Exhaust system	Purex	800i	Any exhaust system is suitable
Variable micropipettor, 100-1000 µL	Manufactured by Eppendorf, purchased from	S304665	Any 100-1000 µL pipettor is su

N, 28.0-20.0 w/w%

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ıre and force control will work. Needs maximum temperature of ~550 F and maximum force of 24 tons.

≥99.8%
el or stainless steel.

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ıitable.

The authors are grateful for the detailed, constructive comments provided by the Editor and Reviewers. We have made a number of changes to the manuscript in response to these suggestions, as detailed in the tables provided here. These changes have, in our opinion, improved the manuscript considerably.

Note: In the accompanying manuscript we have used blue text to indicate significant changes to the text.

Editorial comments:

Changes to be made by the Author(s):

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues.	We have read the revised manuscript carefully and corrected the few spelling and grammar issues that we found.
2. For in-text formatting, corresponding reference numbers should appear as numbered superscripts after the appropriate statement(s), but before punctuation.	The in-text reference numbers have been corrected throughout the manuscript.
3. 1.1.12: Please show a diagram of the gasket and how it fits with the mold if you will not film this part.	We have added Figure 2 and the accompanying figure caption.
4. JoVE cannot publish manuscripts containing commercial language. This includes trademark symbols (™), registered symbols (®), and company names before an instrument or reagent. Please remove all commercial language from your manuscript and use generic terms instead. All commercial products should be sufficiently referenced in the Table of Materials and Reagents. For example: CorelDraw	All commercial language has been removed and specific information has been added to the table of materials.
5. Please sort the Materials Table alphabetically by the name of the material.	The Materials Table has been ordered alphabetically.

Reviewer #1:
I enjoyed reading the manuscript, which describes cutting, engraving and dyeing silica aerogels, and I am looking forward to watching the full video. Previously published works already discussed cutting aerogels with lasers and colorful silica aerogels can be bought at http://www.buyaerogel.com/aerogel-gift-guide/ but still providing a full video presentation of these processes can benefit many workers in the aerogel community. The video presentation should present also the rapid drying technique, which is unique to this lab. The rapid drying technique is especially important for this publication because dyes which are alcohol soluble will not remain the gel when super critical drying with CO2 is conducted.

Authors' response: We are pleased that the reviewer enjoyed the manuscript and appreciate the suggestions provided. We note that a video protocol of the rapid supercritical extraction method has been previously published in *JoVE* (reference #15), which is why we have not chosen to emphasize that process in this video protocol manuscript.

Reviewer #1 Comments	**Response**
1. It is not clear why parts of the protocol are colored in yellow. Please clarify this.	The highlighted text is that which will be used in the video recording.
2. It should be emphasized that the dyes which are soluble in alcohol will not stay in the monolithic aerogel if washing is required and if supercritical drying with CO2 is performed. For comparison, pink aerogels offered for sale by buyaerogel.com are made by a different technique due to this limitation.	The following text has been added after 1.2.2. Note: If a different drying procedure is used that involves solvent exchange, a considerable amount of dye will be washed out during the exchanges; consequently, the colors of the resulting aerogels will not be as vibrant as those presented here.
3. In figure 1 the different parts of the mold are not specified in the figure caption.	We do not understand this comment. The parts of the figure are described in the caption. We have added Figure 2 which includes the gasket setup.
4. It is not specified what is the final roughness of the mold surface.	The text in blue has been added to 1.1.4 Lightly sand all surfaces with 2000-grit sandpaper until the mold is smooth to the touch and any residue from previous uses has been removed.

5. It is not clear how is the grease applied evenly on the surface of the mold.	The word "manually" has been added to 1.1.6-1.18 and 1.10.
6. How is the mold sealed? Is there an additional o-ring? Silicone? Anything else?	The mold is sealed by using the hotpress to apply a force. The vacuum grease helps maintain the seal.
7. At the end of the drying process, the aerogel is taken out of the mold without disassemble of the bottom and frame. Why is it necessary to make these pieces separate?	The bottom piece is separate to make it easier to remove the aerogel. Text has been added to the figure caption to indicate this.
8. The authors should discuss if the addition of dyes to the silica sol has any effect on the physical structure or optical, or mechanical properties of the final product.	We have no evidence that the very small amount of dye significantly changes the properties. We have added the following text to the Representative Results section: Inclusion in the precursor mixture of the small amounts of dye employed here is only observed to impact the color of the resulting aerogel monolith; changes in other optical or structural properties are not observed.
9. If the mold has venting holes at the top, then you would expect to have gel in the holes too. How do you drain the sol from the holes? If not drained, then you would expect to obtain aerogel spikes at the top of the sample.	The vent hole size was studied and this size was chosen because it does not affect the aerogel.
10. It is not clear if gelation occurs before the drying process starts or simultaneously.	The gelation occurs as the chemicals are heated. The following text was added to 1.3.6: The precursor mixture gels as the system heats up. The entire extraction process will take 10.25 h to complete for this size aerogel.
11. In Figure 3: pictures (d) and (e) are not clear. In picture (f) a scale bar should be added.	Pictures d and e cannot be reproduced so text was added to the caption to explain them. The size of the images has been indicated in the caption.

12. Figures 2 and 7 should be presented one after the other.	We did not reorder the images but refer the reader to Figure 7 (now 8) in the manuscript when we introduce Figure 2 (now Figure 3).
13. In figure 4 Please add titles to each part of the system. It is not clear what is shown.	Figure 4 has been updated to label the different parts.
14. From Figures 5, 6 and 10, it is clear that the laser actually melts the silica. With the aid of SEM (a good picture at the right angle) the depth of melted silica into the bulk should be estimated. For any further applications, this information is important.	The laser cutting/etching results in both ablation and melting. The extent of damage to the surface depends on the power and speed employed. Additional studies are underway but we consider those to be beyond the scope of the present study, which focuses on the use of laser etching and cutting to produce aesthetic effects in silica monoliths.
15. Another phenomenon that you can notice in figure 7 is that also the dye is affected by the heat of the laser. Close to the edges of each piece the color fades.	Laser cutting may result in some thermal or photodegradation of the dye in the portion of the monolith adjacent to the cut surface.. Alternately, the apparent gradation in color may be due to scattered (white) light from the rough surface. We will be undertaking a study of this; however, we consider it to be beyond the scope of this manuscript..
16. Figure 9 is a nice demonstration for the fluorescence of the dye, which is still active even after the extreme conditions of the drying process. A measurement of the actual spectrum compared to a reference dye solution could demonstrate this more accurately and quantitatively.	Indeed, we have ongoing studies focused on investigating the spectral properties of and lightfastness of dye-doped silica aerogel monoliths. That study is beyond the scope of this manuscript..
17. In addition, it is not clear why the dye is not homogeneously dispersed in the aerogel samples. You can see dark dots on almost all samples in figure 9.	The dyes are homogeneously dispersed in the material. We note that the pieces shown are irregular in shape, so some gradations in tone seen in the photo are due to different path lengths through the samples. The dark spots are not from the dye. Some are due to staining from the laser base, others are loose particles. We have added text to the figure caption.

18. The engraving of curved surfaces (as shown in Figure 9) should be described in more details.	When etching on the curved surface we used the method described in the protocol.
19. It is not clear if the authors succeeded to engrave samples in the center of monoliths. More information on these experiments are required. What is the spot size of the laser? How deep in the aerogel can you focus the light (considering refraction by the porous silica)?	We did not attempt to engrave on the centers of the monoliths.
20. Figure 9 is missing scale bars. This is specifically important for picture f which presents engraving with seemingly fine lines.	Size information has been added to the figure caption for 10e and f.
21. Table 1 on page 29 is missing description of the samples presented on the right column. Please indicate concentration differences of samples. In addition, please correct column "Dye to methanol ratio" because it can not be that one ratio was used for all three samples that are shown.	The dye-to-methanol ratio is for the stock solution. We have updated Table 1 and the text that refers to this table, accordingly. As indicated in the table caption, the leftmost image is for aerogels made with the stock solution, the next is for those prepared with a 2x dilution and the third for a 6.67x dilution.
22. Tables have no numbers and captions are required.	The captions are included in the manuscript text.
23. Pages 31-35 are cut.	We believe this is an artifact of the pdf construction.
24. Please include the foam brush in the list of materials and equipment.	This has been included.
25. In step 4.6, please explain why is the stainless-steel foil needed?	The following blue text has been added to step 4.7. Open the lid of the laser engraver, place the stainless steel foil on the laser engraver platform to prevent residue on the platform from discoloring the aerogel during cutting and place the aerogel monolith on top of the foil.

26. Figure 8 presents mainly broken aerogel pieces. Does this mean that the dye weakens the aerogels? Are the colored aerogels more fragile?	Small monoliths of irregular size and shape were used to illustrate the feasibility of etching onto smaller pieces of aerogel. The aerogels were intentionally broken up before etching; the etching process did not result in fracture. We have added text to the Representative Results section to explain this.
27. Please check lighting conditions in figure 8. A purple hue is seen at the top of picture (a).	Photos were taken in the laboratory under ambient (room) lighting. The authors would have no objection if the editors chose to crop the photos shown in Figure 8a and 8b.

To summarize, the manuscript is presenting a refreshing view of silica aerogels, not practical application. It can be improved if the authors could suggest other applications which may relate to material science.

Authors' response: We can envision a number of practical applications of aesthetically enhanced silica areogels in art and in sustainable building design. We have added some text to the first paragraph of the Representative Results section to emphasize this.

Reviewer #2: The authors demonstrate laser etching and dye incorporation to aesthetically enhance silica aerogel monoliths. The manuscript is generally clear, well-written, and easy to follow with the figures. The following comments are offered to strengthen the quality of the final manuscript.

Reviewer #2 Comments	**Response**
Step 1.1.1. Recommend a Note to indicate that molds of any suitably large dimensions may be used. May be helpful to recommend minimum HxLxW.	We had noted (in step 1.3.1) that different sized molds could be employed, and cited a reference for this. We have added a similar note to Step 1.1.1 in the revised manuscript.
Step 1.1.12. It may be helpful to show (or clarify) the gasket formation as part of Figure 1 or an additional figure.	FIgure 2 has been added to include this information.
Step 2.3.3. Recommend adding a Note, or Discussion to indicate what a good level of contrast is, or how fine a level of contrast can be achieved with the laser etch. While it may be difficult to assess the qualitative perception of the laser etched contrast, offering a practical perspective on % difference in image processing that results in effective contrast on the aerogel may be helpful for those attempting image printing.	The required level of contrast will depend on the detail included in the image to be printed and the desired outcome. The following text was added to Step 2.3.3: Note: the level of contrast needed will depend on the amount of detail in the image that the user desires to etch onto the aerogel. The drawing program should provide guidance but the user may need to experiment with different contrast levels to achieve desired outcome.
Line 413: For "etch designs on smaller monolithic pieces" it may be helpful to describe practical size limits.	We have added size information to the Fig. 9 caption.
Line 424-428: Comment/describe the changed structure relative to the native aerogel structure? Does the dye change the native structure (affect BET)?	We have added text addressing these comments to the first and fifth paragraphs in the Representative Results section.

Line 508-509: There is an interesting possible heat transfer, heat capacity, melting temp, fusion modelling study as a follow-on project.	We thank the reviewer for this suggestion for future study.
Line 510-512: Are the laser etching speed, power, frequency guidelines generalizable or instrument/machine specific? It may help to clarify one way or the other.	The speed and power numbers should be generalizable to any instrument.
Line 521: 260 is missing a degree symbol.	This has been corrected.

Reviewer #3:

Reviewer #3 Comments	**Response**
Title- enhancing of what ??? Please write the appropriate title.	We respectfully disagree with the reviewer that the title is unclear. As phrased, it indicates aesthetic enhancement of the silica aerogel itself.
Although the work is interesting but authors could not explain the procedure clearly.	Without more detail, we could not ascertain which portion of the procedure the reviewer found to be unclear.
Silica aerogels have drawback to crack easily, I am surprise they get the monoliths without any cracks.	We have developed a rapid, high-temperature, confined-mold method (references 15-20) that allows us to make large silica monolithic aerogels.
Authors also did not explain why they choose only these dyes, is there any specific reason?	As described in the discussion we selected dyes that were known to be thermally stable, because the aerogel fabrication process employed uses high-temperature and high-pressure conditions of our process. Some dyes tested (as noted in the discussion) did not survive the process.
Page 29, table units are not correct %/g/g. Please correct.	These units are correct for fabrication of the aerogels presented in the table.
Additionally, there are many grammatical errors.	We have reviewed the paper and corrected the few grammatical errors that we found.

Reviewer #4:

The authors have clearly presented a procedure for preparing aesthetically pleasing silica aerogels through a specialized supercritical extraction method. The method is straightforward and very useful. The video demonstration of the procedure will be very helpful since there are so many steps to this process, and industries interested in aerogel materials will find it useful. The procedural steps are detailed and helpful. It is quite impressive the effect that the image processing can have on how clear the etching turns out to be as shown in Figure 3. Please see below for a few specific comments for improvement.

Review #4 Comments	**Response**
The first paragraph of the introduction lists some applications, but more applications could be mentioned such as battery applications, fuel cell applications, and capacitor applications for instance.	Aerogels are, indeed, remarkable materials with a host of applications, including those we mentioned in the introduction and discussion sections and the others noted by the reviewer. The citations we have provided in the introduction are to sources that give much more detail.
Under Step 1 of the Protocol, 'Obtain or Fabricate an Aerogel Monolith' the first paragraph describes the rapid supercritical extraction method. Please indicate that methanol is supercritically extracted from a sol-gel to produce an aerogel with this method. This would be helpful to the reader since CO2 supercritical extraction is mentioned further down in the paragraph, and so it would be helpful to specify the type of extraction used in RSCE to distinguish this method from others.	The following blue text was added to Step 1: Methods for making a 10 cm x 11 cm x 1.5 cm aerogel monolith in a contained metal mold via a rapid supercritical extraction method (RSCE)[15-18] are described here. This RSCE process removes the solvent mixture from the pores of the silica matrix without causing structural collapse. Because the precursor mixture fills the mold, this method involves supercritical extraction of a significantly smaller volume of alcohol (in this case, methanol) than other high-temperature alcohol supercritical extraction methods.
In the same paragraph of Step 1 of the Protocol as mentioned above, the authors state that a monolith could be obtained from another source. It would be helpful to the reader who may have access to a laser engraver, but not to the necessary equipment to produce aerogels to know where to obtain aerogels. Some sources might be referenced to help the reader.	We are not allowed to add list commercial sources as per JoVe publishing guidelines.

In step 1.4.4, 'the' can be removed from 'When the all sides of...'	This has been corrected.
Under Representative Results, it would be helpful to clarify more of the description of Figure 10 either here in the Representative Results section or the Discussion section. When it is mentioned that the bulk structure is intact, please indicate that the reader can view this in Figure 10 a and b by viewing the porous structure exposed by the engraving, if that is the case of what is indeed being observed. Otherwise, please describe what the reader should be noticing in terms of an intact structure. In addition, when it is mentioned that the etched portion appears 'melted', please specify more clearly that the authors are referring to the one 'drip' on the top of the Figure 10b image and the two 'drips' on the bottom if that is the case of what is being referred to as this is a bit confusing since the majority of the image simply shows intact porous structure.	We have added clarifying blue text to the Representative Results section of the manuscript: Etching results in changes to the surface of the aerogel, but visual observation, imaging and BET analysis demonstrates that it leaves the bulk structure intact[6,7]. Photographs in Figures 6-10 illustrate that the unetched portions of the monolith are unscathed. The localized damage caused by etching can be imaged. Figure 11 shows scanning electron microscope (SEM) images of etched silica aerogel. Figure 11a shows the interface between etched “lines” (upper right portion of image, with features in a venation pattern) and the unetched nanoporous aerogel (which appears almost smooth at this magnification). Etching causes ablation of material from the surface and melting of some of the silica into filament-like structures hundreds of µm in length.[7] Figure 11b shows the effect of a single laser pulse in the aerogel.
In the Table 1 legend, the different dilutions referred to might be more clearly stated by giving grams used instead of percentages. As in the protocol steps of 1.2.2.3 and 1.2.2.4, grams of the dyes and the methanol are given. Or maybe it can be specified that the 50% methanol/dye + 50% methanol is referring to the amounts used in protocol steps 1.2.2.3 and 1.2.2.4. If this is not the case though, please specify more clearly as this is confusing to understand. In addition, within Table 1 it is not clear what is meant by the numbers given in the Dye to Methanol Ratio column. How do these correspond to what is given in steps 1.2.2.3 and 1.2.2.4 or to any of the dilutions mentioned in	The protocol instructions are for the mosaic sample, whereas the values in the table refer to the sample made in initial dye studies. To clarify, we have added the blue text to section 1.2.2.4, and to the table title/legend: Use an analytical balance to measure 0.050 g of fluorescein (to make a yellow-tinged aerogel) or 0.042 g of rhodamine B (to make a pink-tinged aerogel) or 0.067 g of Rhodamine 6G (to make an orange-tinged aerogel) into a 10-mL beaker. Add the dye to the 250-mL beaker containing the methanol and gently mix until dissolved. Note: these instructions are for aerogels

the legend? Please clarify these parts of Table 1.	used in the example mosaic design; the dye concentration can be altered to change the depth of color in the resulting aerogel (see Table 1). **Table 1.** Information on the dyes used to make yellow-, pink-, and orange-tinged aerogels and representative images. Different shades are achieved by diluting the methanol/dye stock mixture with additional methanol (as described in step 1.2.2.4.) prior to use in the precursor mixture. Images are shown for materials prepared with 0x dilution (stock solution, shown at left), 2x dilution (50% methanol/dye + 50% methanol, shown in center) and 6.67x dilution (15% methanol/dye + 85% methanol, shown at right).
In Table 2, units should be given for Force.	These have been added.
In the Figure 8 legend, it is stated that the aerogel pieces in this figure are not any bigger than 3 cm by 3 cm by 1 cm. It would be helpful to the reader if a small section of the discussion might be devoted to discussing how etching such small pieces differs from the larger examples given in the protocol and that are focused on more throughout the manuscript. It seems these small, variously sized pieces would be more difficult to work with and arrange for engraving, but perhaps this is not the case. However, if there are any special steps that should be taken when working with small samples, they would be helpful to mention.	It is surprisingly easy to etch on small pieces of monolithic aerogel. The same procedure is followed as for larger pieces. We have added clarifying text to the manuscript: It is possible to etch designs on smaller monolithic pieces, following the same procedure outlined in section 3, in order to obtain visually interesting arrangements.
In the fourth paragraph of the Discussion concerning the dyes a minor correction is that on line 525, it should state 'metal salts' instead of 'metals salts'.	This has been corrected.

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