There is an abundance of plant surfaces in nature, which inspires scientific community to replicate and prepare artificial superhydrophobic surfaces. However, most of these studies are limited to low-aspect-ratio structures as found in petals and leaves. In this study, the authors chose *Canna indica*, a garden plant belonging to Cannaceae family, as a model plant. The *C. indica* seedpods possess high-aspect-ratio multiscale structures and also show superhydrophobic behavior. These high-aspect-ratio hierarchical structures as found in *C. Indica* seedpod were then successfully replicated by replica molding in different polymers such as poly(dimethylsiloxane) (PDMS) and resorcinol–formaldehyde (RF)-based xerogel. These biomimicked polymer surfaces exhibit superhydrophobicity as confirmed by water contact angle measurement. The original seedpod shows water contact angle of 151°, while negative PDMS and RF gel replica with high-aspect-ratio structural patterns show water contact angle of 146 and 155°, respectively. Thus, the biomimetic approach depicted here not only allows the facile fabrication of high-aspect-ratio structures over a large area but also provides a low-cost alternative to produce superhydrophobic polymer surfaces.

**1. Introduction**

The surfaces with water contact angle more than 150° are commonly referred as superhydrophobic.1-3 Water droplets roll off these surfaces with little tilt that facilitates the removal of contaminants providing self-cleaning ability. Besides using as a self-cleaning material, superhydrophobic surfaces are now widely used in various other engineering applications such as paints, antisticking materials and microfluidics with reduced drag.4-6 As a result, there is a growing interest in the fabrication of superhydrophobic surfaces from last decade.1,2,4-6,17

Since the ‘Lotus effect’18,19 has been observed and explained in late 1990s, nature has been a continuous source of inspiration in the fabrication of superhydrophobic surfaces.20-33 Although a number of techniques, such as electrospinning,21,23,24 etching,23 electrodeposition,23,24 chemical vapor deposition,23 sol-gel emulsion,23,25 lithography23,24,36 and self-organization,37 are demonstrated in literature to fabricate the superhydrophobic surfaces, using the biological surfaces directly as template and mimicking their structures into polymers is still one of the preferred and inexpensive method.

Besides lotus leaf, various other plant surfaces such as taro leaf, rice leaf and *Canna indica* leaf show superhydrophobicity and self-cleaning ability.12,19,20,32 Recently, rose petal has also been used as a model surface to show superhydrophobicity; however, water droplet does not roll off due to large contact angle hysteresis.33 Furthermore, not only plant’s surface but also animal’s surfaces show superhydrophobic behavior such as leg of water strider and duck feathers.20,21,34 Most of these plant leaves, petals and animal surfaces exhibit superhydrophobic behavior because of low-aspect-ratio hierarchical structure present on their surfaces. However, to the best of the knowledge, there are only a few reports of mimicking the plant surfaces with high-aspect-ratio patterns except hairy surface leaves.27,28

In this study, *C. indica*, a garden plant belonging to Cannaceae family, has been chosen as a model plant. As mentioned above,
C. indica leaf shows superhydrophobicity and so also its seedpod. However, unlike the leaf, C. indica seedpod has high-aspect-ratio hierarchical structures on its surface. The authors used C. indica seedpod as a template to successfully replicate its high-aspect-ratio hierarchical structures first into an elastomer, poly(dimethylsiloxane) (PDMS), using replica molding followed by preparing a positive replica into an organic resorcinol–formaldehyde (RF) xerogel. Since RF xerogel is a polymer precursor to glassy carbon, these high-aspect-ratio hierarchical, biomimicked polymer structures could be converted into 3D glassy carbon structures on pyrolysis to enable their use in carbon-based microelectromechanical systems (C-MEMS). The authors later studied the wettability characteristics of these high-aspect-ratio hierarchical biomimicked polymer surfaces, which also exhibited superhydrophobicity similar to their original counterpart.

2. Experimental section

2.1 Materials

C. indica flower and seedpod exists in different colors. The authors used green- and red-colored seedpod in this study as shown in Figure 1(a) and 1(b). Sylgard 184 prepolymer solution (consisting of silicone elastomer and a cross-linking agent) was purchased from Dow corning, Mumbai, India. Resorcinol (R; 99% purity), formaldehyde (F; 37–41% w/v), potassium carbonate (99.0% purity) and chloroform (99.5% purity) were obtained from Merck, Mumbai, India.

2.2 Fabrication of PDMS-negative and RF gel–positive replicas from C. indica seedpod

The Indian Canna seedpod was cut into small piece of 1 cm × 1 cm length by breath and dried at 40°C for 1 h to remove moisture. The dried seedpod was then fixed to a clean glass slide using a double-sided adhesive (Figure 2(a)). The PDMS solution with 10:1 weight ratio of Sylgard 184 silicone elastomer and cross-linking agent was prepared and poured on to seedpod piece as shown in Figure 2(b). The sample was then kept for deaeration in vacuum desiccator to remove the trapped air bubbles followed by curing at 80°C for 12 h in vacuum oven (Figure 2(c)). The cured PDMS sample was then immersed in chloroform for 1 h to allow the swelling of PDMS replica (Figure 2(d)), which eased the release of biotemplate (seedpod) forming a negative replica in PDMS. This PDMS replica with hole-like embedded structure was then dried slowly in ambient conditions (Figure 2(e)).

Further to make positive replica in RF xerogel, RF sol was prepared as reported elsewhere. First, R and F (R/F molar ratio 0.5) were mixed and stirred together continuously until clear solution was obtained. In another beaker, potassium carbonate (C) and deionized water (W) were mixed to maintain R/C and R/W molar ratios of 25 and 0.037, respectively. Both the solutions were then mixed with each other followed by magnetic stirring for 15 min to yield golden yellow-color RF sol.

RF sol thus prepared was then poured onto negative PDMS replica to fabricate positive replica (Figure 2(f)). However, before pouring RF sol, negative PDMS replica surface was treated with UV exposure for 15 min. PDMS replica sample with RF sol poured was then deaerated in vacuum desiccator followed by drying at room temperature for 12 h to undergo the gelation. Again, PDMS replica was allowed to swell in chloroform to separate it from RF xerogel replica (Figure 2(g)) followed by drying at 40°C for 12 h to yield positive replica of seedpod in RF xerogel (Figure 2(h)).

2.3 Characterization

Scanning electron microscopy (SEM; Model: Hitachi S-3400N, Dalla, TX, USA) was used to characterize the surface morphology of the original seedpod, negative PDMS and positive RF xerogel replicas. The samples were sputtered using JEOL fine coater JFC1100E (Tokyo, Japan) to coat a thin layer of gold to reduce the charging during imaging in SEM. The high-resolution confocal microscopy (Model: Olympus LEXT OLS4000, Tokyo, Japan) image was used to measure the aspect ratio of individual seedpod. The contact angle on original seedpod and biomimicked polymer replicas was measured using sessile drop method with goniometer (Model: VCA optima, Billerica, MA, USA). For each measurement, 10-µl droplet of deionized water was applied to the sample surface by automatic dispenser connected to the system. Still and video images of water droplet on different surfaces were captured by Canon digital camera (Model: EOS 550D, Tokyo, Japan).

3. Results and discussion

3.1 Aspect ratio measurement

The outer surface of the C. indica seedpod comprises a group of long and sharp tapered structures as shown in 3D confocal microscopic image of the top view of the seedpod (Figure 3(a)).
To calculate the aspect ratio for these structures, height and width was measured for minimum of ten structures using the 2D confocal microscopic image as shown in Figure 3(b). Furthermore, it was verified using 2D mapping of the seedpod. Average aspect ratio for seedpod structures was calculated to be 5.7 ± 1.1. For the individual tapered structure as shown in Figure 3(b), height was 2641.7 µm and average width was 444.3 µm giving an aspect ratio of nearly 6.

3.2 Surface morphology

Figure 4 summarizes the SEM observation of surface morphology of the original seedpod and polymer replicas. Figure 4(a)–4(d) shows the surface features at various magnifications of the original seedpod. Figure 4(a) shows the high-aspect-ratio tapered structures, whereas Figure 4(b) magnified the complex-subsurface-folded-like structures on an individual tapered bump. The average height of these tapered pillars was 2.5 mm, while on top of each tapered pillar, the authors observed surface-folded patterns with average width of 184 µm. At further higher magnification (Figure 4(c) and 4(d)), submicron spikes were found on individual tapered bump structure with average feature size of 287 nm. The complex nature of surface patterns on the seedpod can be well understood with feature size varying almost four orders of magnitude. Figure 4(e)–4(h) shows the images of negative PDMS replicas consisting of pores with surface patterned thoroughly inside their walls. The average width of these pores was 488 µm (Figure 4(e)), while another layer of patterns on inner surface walls of these pores (Figure 4(f)) consists of average feature size of 64 µm. Figure 4(g) and 4(h) shows the inner view of the pores at higher magnification with protrusions feature size appearing in submicron range (contrast was not good to image inner view at higher magnification). Figure 4(i)–4(l) shows the surface morphology of the positive RF xerogel replica.
observed in Figure 4(i) and 4(j), the authors were able to replicate the high-aspect-ratio (average height 2·1 mm) tapered structures with patterns on its surface with average length of 118 µm. Further magnified view as shown in Figure 4(k) shows the inner patterns with feature size of 47 µm. Figure 4(l) shows high-magnification image of these patterns and reveals that on each feature, there are signatures of submicron protrusions.

These results clearly illustrate the replica molding in controlled environment as a powerful tool to fabricate such complex hierarchical patterns having features that span over nearly four orders of magnitude (from millimeter to submicron range). The swelling of PDMS replica in chloroform was important to separate the original seedpod without losing the features. Later, the UV treatment of PDMS replica assisted in full penetration of RF sol inside the porous structures of PDMS replica and thus to capture the finer features successfully.

3.3 Wettability behavior

After successful replication of multiscale surface features in the biomimicked polymer replicas, water contact angle was measured to be 151° (Figure 5(b)). In case of PDMS replica having holes, water droplet touches the surface with slightly more contact area (Figure 5(c)), which is also evident in contact angle value. It was measured to be 136° as shown in Figure 5(d). Interestingly, the authors were able to retain the similar superhydrophobic behavior for positive RF xerogel replica that consists of similar high-aspect-ratio tapered patterned structures. Figure 5(e) shows the water droplet touching the tip of these structures and reveals that on each feature, there are signatures of submicron protrusions.

These results clearly illustrate the replica molding in controlled environment as a powerful tool to fabricate such complex hierarchical patterns having features that span over nearly four orders of magnitude (from millimeter to submicron range). The swelling of PDMS replica in chloroform was important to separate the original seedpod without losing the features. Later, the UV treatment of PDMS replica assisted in full penetration of RF sol inside the porous structures of PDMS replica and thus to capture the finer features successfully.

4. Conclusions

The uniqueness of C. indica seedpod structure provides an inspiration to fabricate an array of high-aspect-ratio hierarchical
patterns in polymers. The robustness of the method to mimic the complex features over a large area adds the prospects of biomimicking to be considered as a powerful and low-cost alternative tool in polymer microfabrication. The fabrication of such a high-aspect-ratio hierarchical structure in polymers and thus in carbon, using polymer precursors, may be used as 3D electrode arrays for energy storage devices and in C-MEMS. These biomimicked hierarchical polymer surfaces were then demonstrated exhibiting superhydrophobicity similar to the original seedpod. This further paves the way to their potential use in various engineering applications such as self-cleaning materials and low-friction surfaces for microfluidics.

Acknowledgements
The authors gratefully acknowledge seed research grant from IIT Hyderabad and also acknowledge Anulekha, ARCI Hyderabad, for her help with SEM imaging.

REFERENCES


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