SUPPORTING INFORMATION

Bioinspired *in-situ* repeatable self-recovery of the superhydrophobicity by self-reconstructing the hierarchical surface structure

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Abstract: Inspired by the wheat leaves self-recovery mechanism of superhydrophobicity, a new class of waxgel material with sustainable hierarchical surface micro-structures has been mimicked. After being damaged or removed, the waxgel material can self-reconstruct its surface layer both chemically and structurally, as well as successfully recovers its superhydrophobicity. In addition, it shows non-fluorinated composition, durability to severe mechanical challenges, and self-recoverable structures without external input of any kind, which distinguishes waxgel from any previous self-healing superhydrophobic systems.

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Experimental Procedures

Materials:

Long chain normal alkane hexatriacontane (C_{36}) is purchased from Sigma-Aldrich Corporation. Fatty alcohol eicosan-1-ol ($C_{20}OH$) is purchased from Tokyo Chemical Industry. Polydimethylsiloxane (PDMS) oligomer (Sylgard 184) and curing agent are purchased from Dow Corning. Tetrahydrofuran (THF) is purchased from Sinopharm Chemical Reagent Co., Ltd. Wheat plants (*Triticum aestivum*) are self-planted in a lab-based greenhouse.

PDMS rubber preparation:

PDMS oligomer is thoroughly mixed with the curing reagent by weight ratio of 10:1. After mixing, the resulting mixture is degassed under vacuum for 30 min, casted into the mould, and cured at room temperature for 12 h and then at 70ºC for 4 h. The cured PDMS film is then cut into desired sizes and immerged into the THF for at least 7 days to extract unreacted PDMS oligomers. The weight loss is monitored in every 24 h, followed by replacing with fresh THF. When there is no more weight loss, the PDMS matrix is taken out from the solvent, dried in oven at 80ºC for 12 hours to fully evaporate the THF. Then the PDMS matrices are used for subsequent processes.

Waxgel preparation:

Waxgel was prepared in a simple 2-sptes methods. First immerge the PDMS rubber into a bath of C_{36} + $C_{20}OH$ at a temperature 150ºC. After swelling for 6 h the PDMS rubber matrix is cooled down into the room temperature and remove the excess wax from the surfaces. Waxgel is then left at laboratory conditions for several hours and observe crystal growth on its surfaces.

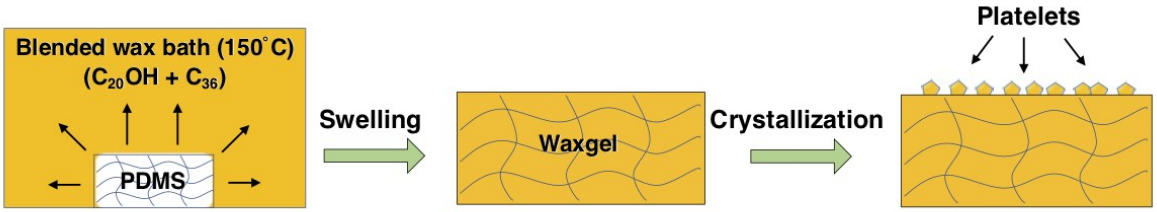

Figure S1. Preparation process of waxgel. PDMS is immersed in a blended wax bath of 150ºC and swelled for 6 h. After swelling, waxgel is cooled down at room temperature and remove the excess wax from surfaces. Leave it at laboratory condition for few hours, wax migrates on surface and form 3D crystal platelets.

A range of waxgels are prepared in a mixture of C_{36} and $C_{20}OH$ with various ratios (WG100-0 to WG0-100) shows in **Table 1**.

Table 1: Ratio of the C20OH and C36 in the bath during preparation of different waxgel samples

Sample Name	$C_{20}OH$ (wt%)	C_{36} (wt%)
WG100-0	100	0
WG90-10	90	10
WG75-25	75	25
WG50-50	50	50
WG25-75	25	75
WG10-90	10	90
WG5-95	5	95
WG2.5-97.5	2.5	97.5
WG1-99	1	99
WG0-100	0	100

Cyclic test on self-recovery of wax platelet structure and superhydrophobicity:

A piece of waxgel (3.0 × 3.0 × 0.35 cm^3) is kept at room temperature for a certain time to completely generation of platelets on its surface. CA is then measured and recorded with a Krüss Drop Shape Analyzer. Later, the platelets are carefully removed by adhesive tape followed by CA measurement. Then, the sample is again kept at room temperature for some time and CA is measured. For data reliability, all CA is taken at 10 different locations on a single sample surface, using 1-2 µL of water droplets.

Swelling Ratio (Q):

Wax bath is set at 150 ± 2ºC in an oven and a piece of PDMS matrix is weighted (W_0) and immerged in the bath. After certain period of time, the matrix is taken out and allowed to cool down to room temperature. Measured the current weight (W_t) after removing excessive wax covering the waxgels. In results, the swelling ratio (Q) is calculated by the following formula:

$$Q = \frac{W_t - W_0}{W_0} \times 100\%$$

Scanning electron microscopy (SEM):

All specimens fixed to aluminum stubs by conductive carbon double-sided adhesive tape were coated with gold (ca. 20 nm) in a vacuum Sputter Coater SCD500 (Leica, Germany) and investigated by SEM (JSM-7500F, JOEL, Japan). Wheat leaves both fresh and after removing the epicuticular wax by adhesive tape were investigated under SEM to identify the epicuticular wax morphologies on intact and after peeling respectively. To confirm the epicuticular wax regeneration on the living plant, waxes were first carefully removed by adhesive tape, then after 72h the leaves were cut from the plant and investigated under the SEM.

Gas chromatography (GC) and mass spectra (MS):

To identify the chemical composition of the waxgels inside, a piece of pre-weighted PDMS rubber sample was swollen at a chemical ratio by the above-mentioned procedure. The as-prepared sample is immediately dipped into the toluene to extract the wax in the waxgel. After 24 hours, the PDMS matrix is taken out and dried in an oven at 80ºC for 12 h, then measure the weight loss. The process is repeated until it resumes to the initial weight. In case of the surface wax composition characterization, the wax is scraped off with a razor blade.

Results and Discussion

Determination of swelling ratio at different time at a typical temperature

Wax bath is set to a typical temperature (150 ± 2ºC) and a piece of PDMS matrix is weighted (W_0) and then immerged in the wax bath. After certain period of time, *t*; the PDMS matrix is taken out, allowed to cool down at room temperature. The excess wax is then carefully removed followed by weight measurement (W_t). The swelling ratio, Q, is calculated and plotted in a graph **(Figure S2)** for as swelling time by the following formula **(Equation 1)**;

$$Q = (W_t - W_0)/W_0 \times 100\% \qquad (1)$$

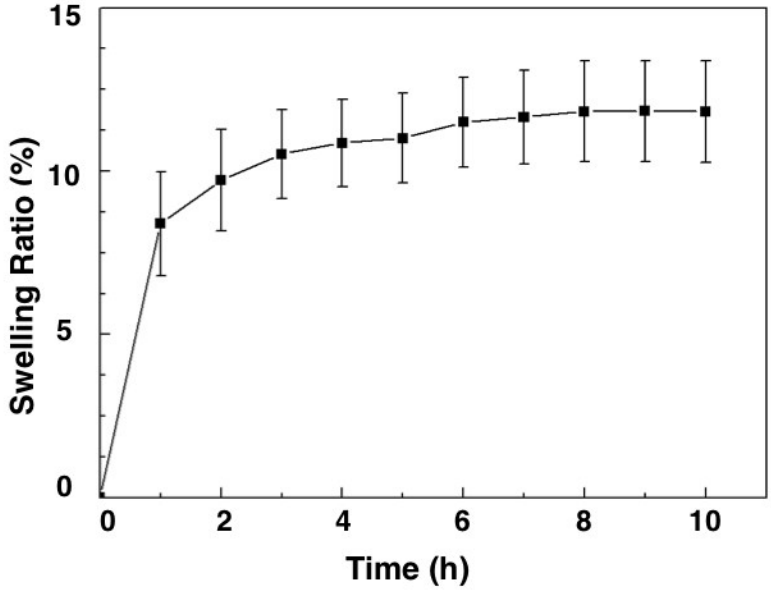

Figure S2. Time vs. swelling ratio curve shows that the swelling ratio of waxgel increases with the time until reaches a plateau in ~ 6 hours.

Easy cleaning properties of the as-prepared waxgel

As-prepared waxgel also shows easy cleaning of foreign contaminants such as sand can be easily washed off by water (**Figure S3)**

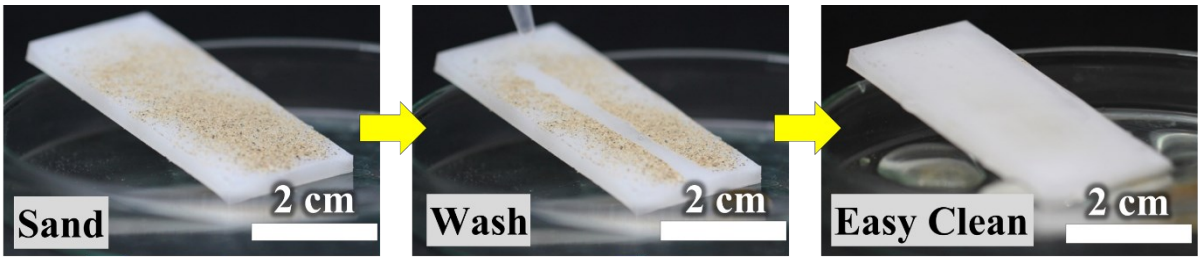

Figure S3. Demonstration of easy cleaning properties of a solid contaminant (sand).

Identification of the chemical composition present in different waxgel samples by GCMS

Figure S4-S8 show the detail GCMS results of wax composition in and on the waxgel. To identify the chemical composition of the waxgels inside, a piece of pre-weighted cured PDMS sample is swollen at a certain wax ratio by the above-mentioned procedure. The as-prepared sample is immersed in toluene to extract the wax content. After 24 hours, the PDMS matrix was taken out and dried in an oven at 80ºC for 12 h followed by weight measurement. The process was repeated until the PDMS weight returned to its original. In case of the surface, the wax was removed by scrapping with a razor blade for GCMS test.

For both cases, the sample was dissolved in toluene (1 mg/mL) and analyze by a GCMS brand Shimadzu, Model QP2010 Ultra with electron ionization (EI) detector. A high temperature capillary column RESTEK Rxi-5sil MS (30 m, 0.25 mm ID, 0.25 µm) was used. Each time 0.2 µL sample was injected at injection temperature 250ºC, at a purge flow 60 mL/min. Oven temperature was initially set to 150 °C for 1 min and increased to 300 °C at 10ºC /min and hold for 10-15 min. Helium gas (He) was used as a carrier gas with a constant flow of 1.4 mL/min. The interface temperature was set to 320ºC for EI detector. The results were recorded and analyzed with GCMS solution software.

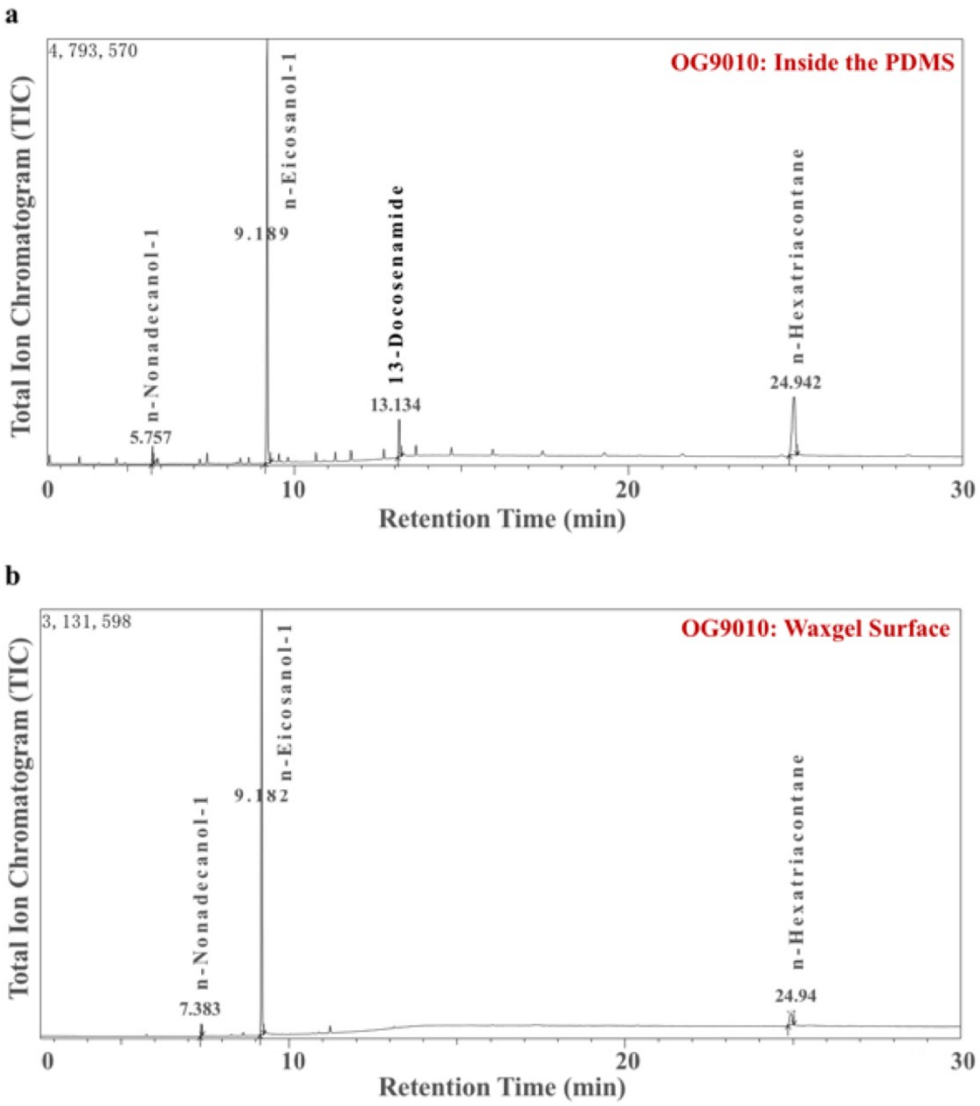

Figure S4. GCMS spectra of the wax presence (a) inside the PDMS matrix and (b) on waxgel surface for sample WG90-10.

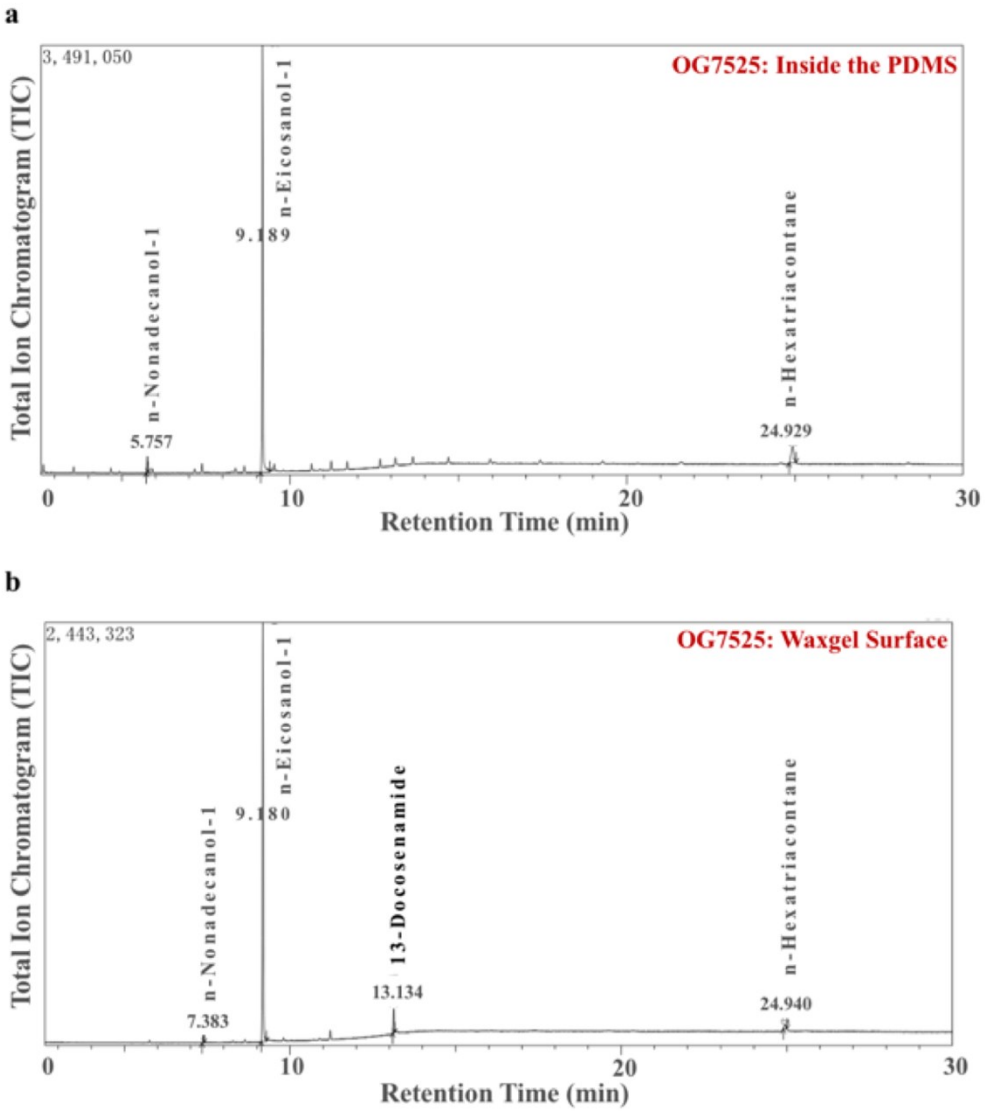

Figure S5. GCMS spectra of the wax presence (a) inside the PDMS matrix and (b) on waxgel surface for sample WG75-25.

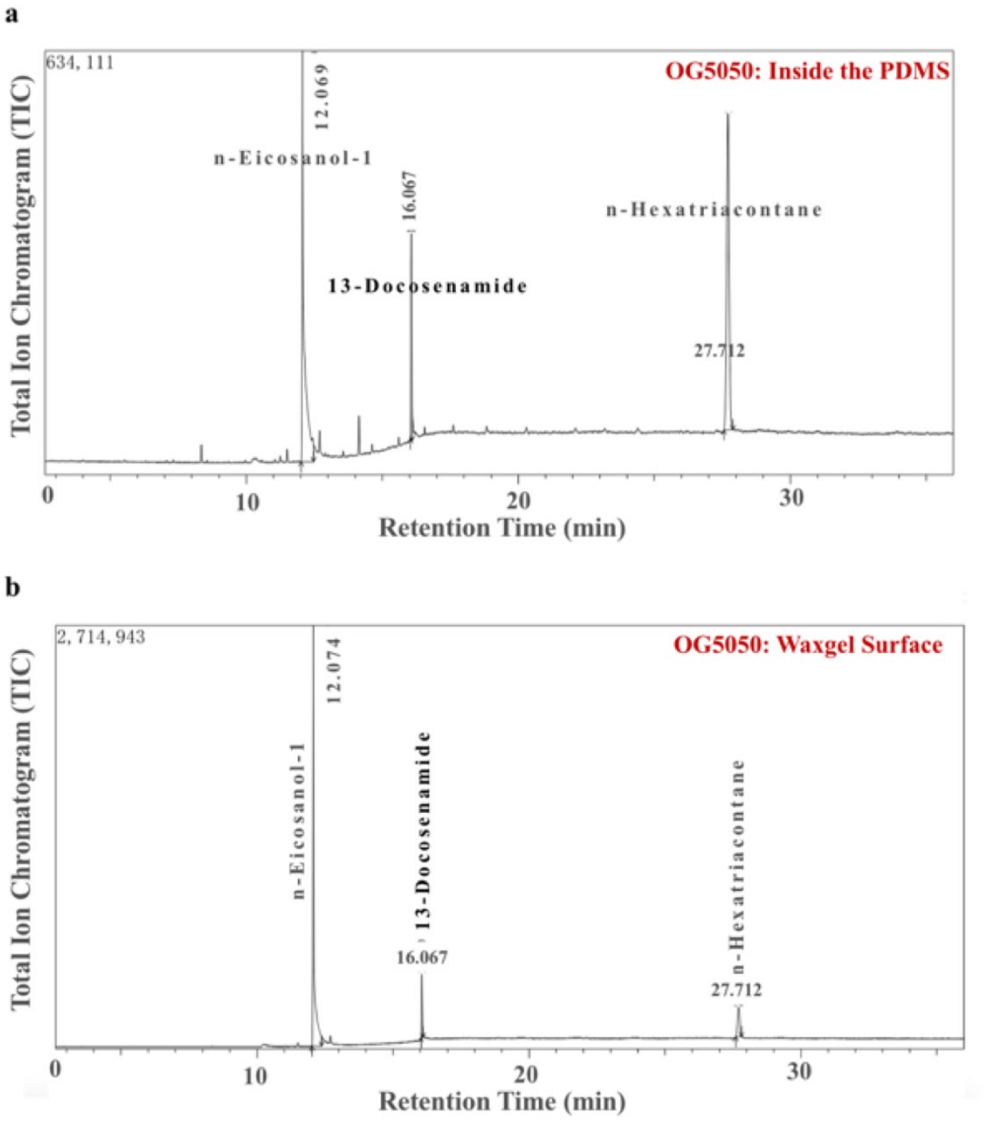

Figure S6. GCMS spectra of the wax presence (a) inside the PDMS matrix and (b) on waxgel surface for sample WG50-50.

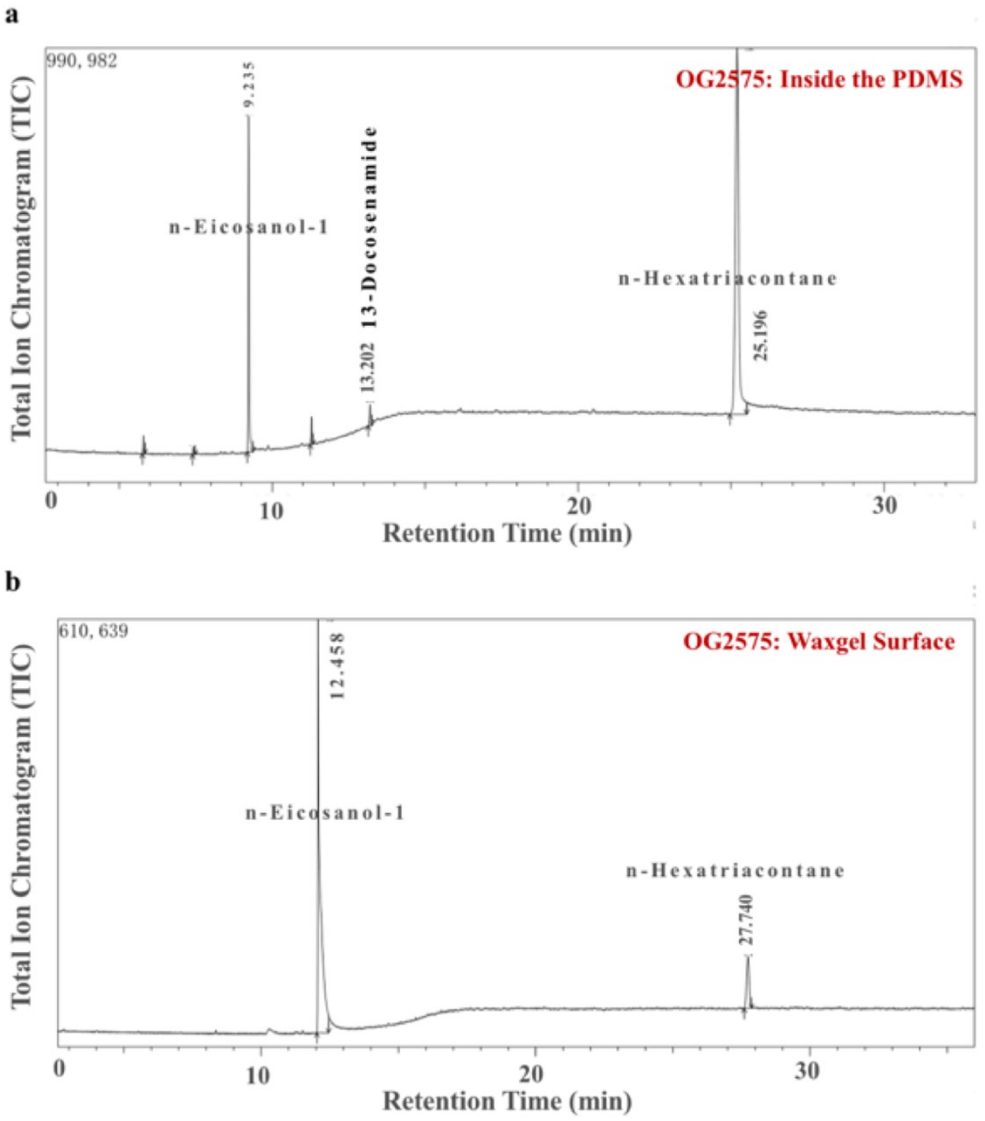

Figure S7. GCMS spectra of the wax presence (a) inside the PDMS matrix and (b) on waxgel surface for sample WG25-75.

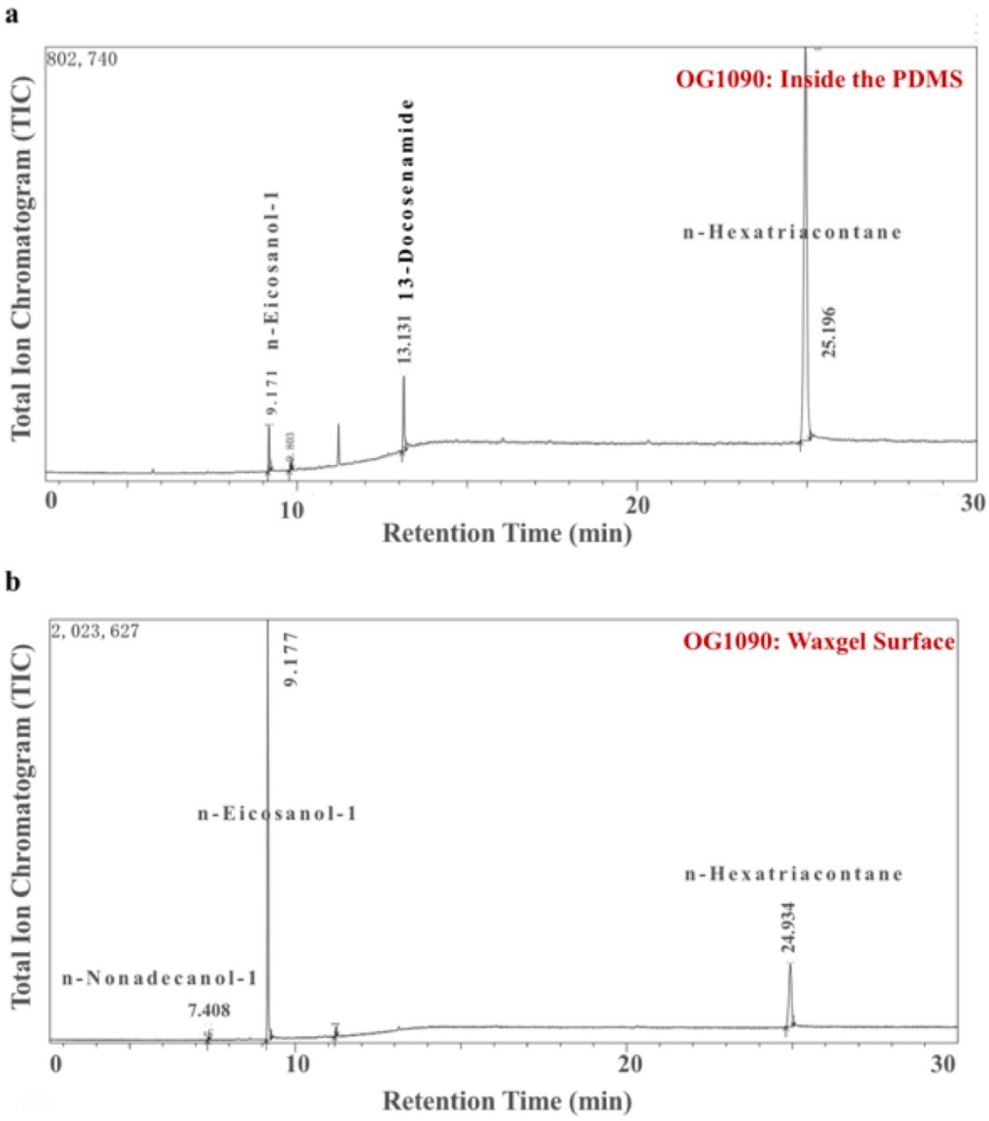

Figure S8. GCMS spectra of the wax presence (a) inside the PDMS matrix and (b) on waxgel surface for sample WG10-90.