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Al-Azawi, Anas; Cenev, Zoran; Tupasela, Topi; Peng, Bo; Ikkala, Olli; Zhou, Quan; Jokinen, Ville; Franssila, Sami; Ras, Robin **Tunable and Magnetic Thiol-ene Micropillar Arrays**

Published in: Macromolecular Rapid Communications

DOI: 10.1002/marc.201900522

Published: 01/01/2020

Document Version Publisher's PDF, also known as Version of record

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Please cite the original version: Al-Azawi, A., Cenev, Z., Tupasela, T., Peng, B., Ikkala, O., Zhou, Q., Jokinen, V., Franssila, S., & Ras, R. (2020). Tunable and Magnetic Thiol-ene Micropillar Arrays. *Macromolecular Rapid Communications*, *41*(2), 1-6. Article 1900522. https://doi.org/10.1002/marc.201900522

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Tunable and Magnetic Thiol-ene Micropillar Arrays

Anas Al-Azawi, Zoran Cenev, Topi Tupasela, Bo Peng, Olli Ikkala, Quan Zhou, Ville Jokinen, Sami Franssila, and Robin H. A. Ras*

Tunable and responsive surfaces offer routes to multiple functionalities ranging from superhydrophobic surfaces to controlled adhesion. Inspired by cilia structure in the respiratory pathway, magnetically responsive periodic arrays of flexible and magnetic thiol-ene micropillars are fabricated. Omnidirectional collective bending of the pillar array in magnetic field is shown. Local non-contact actuation of a single pillar is achieved using an electromagnetic needle to probe the responsiveness and the elastic properties of the pillars by comparing the effect of thiol-ene crosslinking density to pillar bending. The suitable thiol-ene components for flexible and stiff magnetic micropillars and the workable range of thiol-to-allyl ratio are identified. The wettability of the magnetic pillars can be tailored by chemical and topography modification of the pillar surface. Low-surface-energy self-assembled monolayers are grafted by UV-assisted surface activation, which is also used for surface topography modification by covalent bonding of micro- and nanoparticles to the pillar surface. The modified thiol-ene micopillars are resistant to capillarity-driven collapse and they exhibit low contact angle hysteresis, allowing water droplet motion driven by repeated bending and recovery of the magnetic pillars in an external magnetic field. Transport of polyethylene microspheres is also demonstrated.

Extensive research on superhydrophobic surfaces led to improvement of performance and stability of water repellency by incorporating wide array of materials and fabrication

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The copyright line for this article was changed on 13 June 2020 after original online publication.

DOI: 10.1002/marc.201900522

Macromol. Rapid Commun. 2020, 41, 1900522

1900522 (1 of 6)

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schemes.^[1] Advancements in superhydrophobic surfaces can be accomplished by designing surfaces with enhanced properties like tunable non-wettability and responsive properties, which ultimately can lead to new avenues in applications and functionalities in microfluidic devices and cell handling.

Thiol-ene chemistry has emerged recently as a viable route toward polymer microfabrication due to its compatibility with existing microfabrication techniques and minimal requirement for investment.^[2] Thiol-ene refers to the UV-initiated click chemistry reaction that occurs between thiol and allyl groups in a mixture containing two chemical components in its simplest form, one with thiol groups and the other with allyl groups mixed together in liquid form at stoichiometric or off-stoichiometric ratio. It offers remarkable properties like fast curing where 2 mm thick thiol-ene layer is fully cured by UV dose of approximately 100 J m^{-2[3]} and the ability to

tune the mechanical properties of the material from low Young's modulus value of less than 11 MPa^[4] to high Young's modulus value of 1750 MPa^[2a] by controlling the crosslinking density. Furthermore, rapid and direct surface modification for adjusting the surface energy can be achieved with simple post-functionalization of hydrophobic groups.^[2] Thiol–ene is therefore a promising material for polymer-based functional materials including micropatterned responsive surfaces.

Magnetically responsive micropatterned surfaces actuated by external non-invasive stimuli allow instantaneous tuning of surface properties such as adhesion,^[5] structural coloration,^[6] and surface wettability.^[7] Notable applications of magnetic pillars that have been reported include tactile force sensing,^[8] liquid flow sensing,^[9] mixing in microfluidic devices,^[10] mixing of droplets,^[11] switchable adhesive surfaces,^[5a] cell analysis,^[12] directional wetting,^[13] real-time manipulation of light,^[6] micromanipulation of beads,^[14] and droplet transport.^[15] The fabrication schemes in the reported cases involve either magnetic particle self-assembly under magnetic field or replica molding with polydimethylsiloxane (PDMS) as the common soft elastomeric material. Thiol–ene based materials have not been explored yet for responsive superhydrophobic surfaces.

Here, we develop magnetic thiol–ene micropillar arrays that demonstrate fast responsiveness, suitable for droplet transport applications. The advantage of using thiol–ene is the tunability of elastic and surface properties. The elastic properties of the thiol–ene pillars are tuned by controlling the crosslinking





density, which is verified by local actuation of single magnetic pillars using an electromagnetic needle.

UV-assisted surface activation is utilized to decorate the surface of the thiol–ene magnetic micropillars with colloidal polyvinyltrimethoxysilane (PVTMS) micro- and nanoparticles. Thiol– ene pillars are rendered superhydrophobic by UV-grafting of hydrophobic self-assembled monolayers (SAMs) on the surface of the colloidal particles. The resulting magnetic pillars display a combination of robustness against collapse and superhydrophobicity enabling wide range of practical applications.

For this work, we selected two different thiol-ene systems: trimethylolpropane diallyl ether mixed with trimethylolpropane tris[3-mercaptopropionate] (diallyl:trithiol) and 1,3,5-triallyl-1,3,5-triazine-2,4,6 (1H,3H,5H)-trione mixed with trimethylolpropane tris[3-mercaptopropionate] (triallyl:trithiol). Superparamagnetic carbonyl iron particles (CIP) were used with size distribution ranging between 600 nm and 2.3 μm in powder form (Figure S1, Supporting Information). For pattern replication, two micropillared silicon surfaces were fabricated by photolithography and silicon etch (Figure S2, Supporting Information). Height of the cylindrical pillars is 63.0 µm for one of the micropillared surfaces and 70.2 µm for the other. The pitch is 40 μ m and the diameter of the pillars is 8.7 µm on both surfaces. PDMS mold was obtained from the micropillared silicon surface (Figure 1a,i) and was placed on top of a neodymium iron boron permanent magnet. Thiolene mixture without CIP was then poured onto the PDMS mold (Figure 1a,ii). Afterward, thiol–ene mixed with CIP was pipetted onto the immersed PDMS mold. To assist effective distribution of CIP in the thiol–ene filled PDMS cavities, the magnet below was moved back and forth followed by two sonication steps, first without magnet and then with the magnet fixed below the PDMS mold (Figure 1a,iii,iv). The sonication cycle was repeated three times before scraping the magnetic particles off the PDMS mold while it was still being placed on top of the magnet. The thiol–ene layer was fully cured by UV exposure (Figure 1a,v) before manually separating it from the PDMS mold in ethanol (Figure 1a,vi).

The thiol–ene mixture can be prepared as stoichiometric or off-stoichiometric with thiol or allyl excess. The stoichiometry of thiol–ene polymer network can be tuned by changing the ratio between allyls and thiols in the mixture (Figure S3, Supporting Information).

There is a workable range for the off-stoichiometry for successful replication of diallyl:trithiol thiol–ene from the PDMS mold. Composition of above 80% thiol excess did not fully cure (Figure S3, Supporting Information) and the adhesion between thiol–ene layer and the PDMS mold became high with 50–80% thiol excess causing the pillars to tear up during separation. The success of separating the thiol–ene pillar layer from the PDMS mold depends on multiple factors such as pattern density, aspect ratio, and the adhesion determined by thiol excess. The measured value of the maximum force of adhesion for flat diallyl:trithiol thiol–ene surface increased from 0.51 ± 0.14 mN for



Figure 1. a) Sketch of the thiol-ene magnetic pillars fabrication process. b) SEM inspection of thiol-ene magnetic pillars after separation and freeze drying showing two pillar arrays each with distinct value of aspect ratio (AR). c) Magnetic particle distribution inside the pillars is visible under the optical microscope.



Figure 2. Snapshot images of videos recorded by optical microscope showing actuation of the magnetic pillar sample immersed in ethanol using a permanent magnet. a) Top view (i) and side view (ii) of thiol–ene magnetic pillar array before actuation. b) Top view (i) and side view (ii) images of collective pillar bending enabled by the magnetic field.

stoichiometric thiol–ene to 1.05 ± 0.13 mN for off-stoichiometric thiol–ene with 50% thiol excess. Similarly, the work of adhesion increased from 43.5 ± 12 mJ m⁻² for stoichiometric thiol–ene to 86.5 ± 15.3 mJ m⁻² for off-stoichiometric thiol–ene with 50% thiol excess (Figure S4, Supporting Information). The adhesion measurement values were obtained from force–distance curves recorded when retracting an indentation probe from the surface of thiol–ene at a constant speed.

The energy of adhesion of the cured pillar to the PDMS mold is dependent on the work of adhesion and contact area of the thiol–ene pillars to the PDMS mold.^[16] Based on these considerations the optimized parameters of the thiol excess percentage is chosen to be below 40% for replication of the thiol–ene sample from the micropillared silicon surface with pillar diameter of 8.7 μ m, height 70.2 μ m, and pitch 40 μ m. On the other hand, it must be below 60% for pillars of 63.0 μ m height with the same values of diameter and pitch.

After UV curing, thiol–ene pillar layer was separated from the PDMS mold immersed in ethanol or isopropanol. However, the evaporation of ethanol causes the flexible pillars to deform laterally and adhere to each other due to the surface tension force associated with liquid/vapor menisci between the adjacent pillars.^[17] Therefore, the pillar sample must be immersed in liquid to avoid capillarity driven pillar collapse. Sonication can be utilized to recover collapsed pillars by immersing the dried thiol–ene sample in isopropanol. In contrast, separating the sample in ambient conditions causes unwanted pillar breakage and collapse due to adhesion and mechanical instability of the high aspect-ratio pillars.

UV activation of the magnetic pillar sample with 11-mercapto-1-undecanol, leads to thiol-allyl bonding and hydroxyl termination, allowing the sample to be immersed in water without pillar collapse. After water immersion, freeze drying the sample yields standing pillars in ambient conditions as shown in Figure 1b. Collapsing the pillars onto the bottom layer along a given direction was done by N₂ flow. Collapsed pillars in orderly fashion allow aspect ratio inspection using SEM (Figure S5, Supporting Information). In addition, the transparency of thiol–ene enables optical microscopy characterization of the magnetic particle distribution inside the pillars (Figure 1c).

Uniform and simultaneous collective bending of the micropillars in ethanol was achieved by changing the magnetic field gradient using a permanent magnet in close proximity to the sample (Figure 2, Movie S1, Supporting Information). The magnetic pillars exhibit omnidirectional bending in response to the direction and strength of the magnetic flux density without unwanted stickiness between adjacent pillars (Movie S2, Supporting Information).

Magnetic pillar actuation was also demonstrated in silicone oil (Figures S6 and S7 and Movies S3 and S4, Supporting Information).

Local actuation of single pillars with aspect ratio of 6.6 by an electromagnetic needle^[18] was used to determine the deflection and the responsiveness of the magnetic pillars immersed in water. The electromagnetic needle is oriented at ~45° at a fixed distance from the pillar and the tip of the needle is leveled with the pillar edge. Pillar bending with displacement δ was recorded after application of electrical current to the needle (**Figure 3**a). Starting with a current equal to 150 mA and followed by subsequent increase of 150 mA, it was noticed that displacement δ of diallyl:trithiol magnetic pillars increased accordingly with the supplied current at fixed separation distance of 25 µm between the pillar and the needle (Figure 3b; Movie S5, Supporting Information).

The effect of crosslinking density was verified using local actuation by employing the electromagnetic needle on







Figure 3. Single pillar actuation using an electromagnetic needle. a) Pillar bending sketch with not-to-scale dimensions showing displacement delta as a response to the force exerted by the needle. Both the needle tip and the pillars are immersed in water during the measurements. b) Top view images of stoichiometric thiol–ene pillars bending with increasing displacement as a result of increasing current through the needle. c) Top view images showing local actuation of thiol–ene magnetic pillars each with distinct crosslinking density. The current is 600 mA. Measured displacement as function of the supplied current to the needle separated at different distances from d) the stoichiometric thiol–ene pillars, e) off-stoichiometric thiol–ene pillars with 50% thiol excess, and f) stiff stoichiometric thiol–ene pillars.

thiol–ene pillars with three variations of thiol–ene chemistry, which are diallyl:trithiol stoichiometric thiol–ene, diallyl:trithiol off-stoichiometric thiol–ene and triallyl:trithiol stoichiometric thiol–ene. The characterization revealed that the stiffness of triallyl:trithiol stoichiometric thiol–ene pillars is significantly higher manifested by low displacement compared to diallyl:trithiol stoichiometric pillars (Figure 3c; Movie S6, Supporting Information). This is due to clear increase in the crosslinking density when diallyl is replaced with triallyl during the synthesis of the thiol–ene pillars. For diallyl:trithiol thiol–ene pillars, slightly larger displacement was noticed for off-stoichiometric thiol–ene pillars with 50% thiol excess.

Displacement δ was measured for four values of the supplied current at a given pillar–needle separation and the measurements were conducted at four separation distances for diallyl:trithiol thiol–ene pillars. Measurments at the two separation distances furthest away from triallyl:trithiol thiol–ene pillars were disregarded because of barely noticeable displacement. The characterization results in Figure 3d–f, Figures S8 and S9, and Movie S7, Supporting Information, reveal how displacement of pillar bending increases with an increase in current or a decrease in pillar–needle separation. At pillar–needle separation of 25 μ m, the uncertainty in displacement value is highest as the effect of the variable distribution of magnetic particles inside the pillars becomes more significant at the closest pillar–needle separation.

For stoichiometric diallyl:trithiol pillars at pillar–needle separation of 30 μ m, displacement increased from 5.13 ± 0.56 to 13.8 ± 3.58 μ m for the current values of 300 and 600 mA, respec-

tively (Figure 3d). The corresponding values for off-stoichiometric pillars were 9.06 \pm 2.32 μm for 300 mA and 16.1 \pm 2.69 μm for 600 mA (Figure 3e). For comparison, displacement for triallyl:trithiol pillars is significantly smaller, 2.08 \pm 0.62 μm for 300 mA and 3.86 \pm 0.59 μm for 600 mA (Figure 3f).

These results confirm the effect of crosslinking density on the stiffness of the material. The value of Young's modulus measured using tensile test setup decreases from 7.58 ± 0.52 MPa for diallyl:trithiol at stoichiometric ratio to 1.17 ± 0.21 MPa for diallyl:trithiol at off-stoichiometric ratio with 50% thiol excess. The measured value of Young's modulus for triallyl:trithiol at stoichiometric ratio is 788 ± 72 MPa (Figure S10, Supporting Information).

The responsiveness of the magnetic pillars changes also with the thiol–ene chemistry. It decreases nearly three orders of magnitude from 1291 \pm 323 ms for triallyl:trithiol at stoichiometric ratio to 3.40 \pm 0.54 ms for diallyl:trithiol at stoichiometric ratio to 2.66 \pm 0.81 ms for diallyl:trithiol at off-stoichiometric ratio with 50% thiol excess obtained from electromagnetic needle measurements (Figure S11, Supporting Information).

Accessible allyl and thiol surface functional groups facilitate surface topography and chemical modification of the magnetic micropillars. Surface topography modification was realized by covalent bonding of allyl-terminated colloidal PVTMS microand nanoparticles to the surface of the pillars. This treatment will result in a secondary structure superimposed on the surface as the beads cover the pillars (**Figure 4**a). The number of covalently bonded PVTMS nanoparticles with average diameter of 547 nm shown in Figure 4a is higher than the number of







Figure 4. a) Thiol-ene micropillar arrays modified with allyl-terminated micro- and nanoparticles that are covalently bonded onto the pillar surface. Every subsequent image is a zoom-in from the previous image. b) Snapshot images of recorded video showing water droplet transport induced by the collective beat of superhydrophobic thiol-ene magnetic pillars immersed in silicone oil. Time elapsed: 16.1 s.

PVTMS microparticles with average diameter of 2.2 μ m. This is a result of both higher concentration of nanoparticles in the colloidal suspension and the directed self-assembly of particles by evaporation of the colloidal suspension before UV-assisted surface activation. The degree of surface roughness can therefore be tuned by the size and concentration of the particles.

The success of surface topography modification relies on easy and quick chemical modification. In order to bond the allyl-terminated PVTMS micro- and nanoparticles onto the thiol–ene pillars, allyl surface groups were modified to accessible thiol groups by UV-grafting of 1,6-hexanedithiol to facilitate bonding of PVTMS particles. In similar manner, chemical modification for lowering the surface energy was achieved by UV-grafting of SAMs to the surface of the pillars. Thiol groups were passivated by UV-grafting of 1*H*,1*H*,2*H*,2*H*-perfluorodecyl acrylate and allyl groups by 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol.

Based on the tunability of surface properties, superhydrophobicity was achieved without compromising flexibility and actuation ability. Magnetic pillars decorated with micro- and nanoparticles combined with chemical modification via UV-grafting of low energy SAMs exhibit low contact angle hysteresis (CAH), which is essential for the capability of the superhydrophobic magnetic pillars to achieve controlled motion of water droplets as shown in Figure 4b and Movie S8, Supporting Information. Contact angle measurement on thiol-ene micropillared surface decorated with PVTMS micro- and nanoparticles yielded 163° for advancing contact angle and 153° for receding contact angle (Figure S12, Supporting Information). Thiol-ene surface is inherently hydrophilic with advancing contact angle of 85° and receding contact angle of 39° measured on a flat surface after UV curing (Figure S13, Supporting Information). The secondary roughness of low surface energy gained by topography and surface energy tuning reduces solid-water contact fraction thus, achieving superhydrophobicity, which is a key point for enabling water droplet motion.

The mechanism responsible for the water droplet motion is the collective beating of the magnetically driven superhydrophobic micropillars that generates a driving force acting at the triple contact line during magnetic actuation (Movies S8 and S9, Supporting Information).

Assuming a point force load perpendicular to the free end of the cylindrical pillar of height *h* and diameter *d*, the relation between pillar deflection δ and the force is given by $F = (3EI/h^3)\delta$ (Figure S14, Supporting Information),^[19] *E* is the Young's modulus and *I* is the second moment of area. The driving force exerted on the droplet is defined as the elastic recoiling of the magnetic micropillars during recovery from bending. The driving force is countered by CAH force (F_{CAH}) of the pillars given as $F_{CAH} = (24/\pi^3)\gamma D(\cos\theta_R - \cos\theta_A)$.^[20] Repeated bending and recovery of the decorated thiol–ene pillars along a given direction induces droplet motion along the same direction as a result of the low value of CAH exhibited by the pillars (Movie S8, Supporting Information) enabling the driving force of the superhydrophobic pillars to overcome F_{CAH} .

Droplet motion was demonstrated in silicone oil (Figure 4b) to avoid droplet evaporation. Contrary to unmodified thiol–ene pillars presented in Figure 2 that only can be actuated while immersed in solvents or oils, decorated thiol–ene pillars of low surface energy exhibit resistance to collapse and thus have the ability to actuate in air (Figure S15 and Movie S10, Supporting Information).

The fast response time of 3.4 ms for the diallyl:trithiol magnetic pillars combined with ease of omnidirectional bending enabled the magnetic pillars to be applied for controlled motion of solid beads. Polyethylene microbead motion in ethanol was achieved by repeated bending and recovery of thiol–ene pillars decorated with PVTMS nanoparticles (Figure S16 and Movie S11, Supporting Information). Additionaly, controlled motion of 150–200 μ m glass beads in ethanol was demonstrated (Figure S17 and Movie S12, Supporting Information).

In conclusion, we present a facile approach for fabrication and application of large arrays of magnetic thiol–ene micropillars. Superhydrophobicity and robustness against pillar collapse are remarkable properties obtained by surface modification of the thiol–ene pillars through UV-grafting of colloidal micro- and nanoparticles. The tunability of the magnetic pillars



is successfully demonstrated at the bulk and surface levels. The elastic properties are tuned by controlling the crosslinking density. Tuning the surface property was achieved by UV-grafting of colloidal micro- and nanoparticles and SAMs. Besides tunability, the thiol–ene material exhibits low permeability to common solvents. Additional properties like bonding to different substrates can be acquired by adding epoxy monomers to thiol–ene. This is what sets thiol–ene apart from other materials like PDMS. Actuation with fast response time to the magnetic field combined with superhydrophobicity of the pillars enabled water droplet motion, which was demonstrated in silicone oil using small droplets (500 μ m diameter). The versatility of thiol–ene as a material manifests itself by ease of surface modifications.

Therefore, this work represents a new pathway for advanced applications. The reported magnetic thiol–ene pillar arrays can potentially be integrated on top of a giant magneto impedance sensor for miniaturized tactile and flow sensing elements.^[8,9] Another potential application is within point-of-care and small volume elastic hemostatic essays.^[21] Here our flexible magnetic thiol–ene pillars may be used as a micro-elastomer correlating the stiffness of blood clots as they form with the applied force needed for pillar deflection.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the European Research Council ERC-2016-CoG (725513-SuperRepel) and the Academy of Finland (Centres of Excellence Programme (2014-2019) and projects #256206, #266820, #296250, #297360, #263560, #304843, and #317018). This work made use of the Aalto University Nanomicroscopy Center premises and the cleanroom facilities of Micronova Nanofabrication Center. The authors would like to thank BASF for generously providing the magnetic particles. They are grateful to Dr. Christoph Hörenz for his assistance in tensile tester measurements.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

microdroplet transport, micromanipulation, self-assembly, superhydrophobicity, thiol-ene elastomers

Received: September 30, 2019 Revised: October 26, 2019

Published online: November 28, 2019



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