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ARTICLE

Bio-inspired HDPE-based dry adhesives and their layer-by-layer catechol modification on the surface for use in humid environments

Cite this: DOI: 10.1039/x0xx00000x

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Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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We applied thermal imprinting to fabricate gecko-foot-like nanostructures on HDPE films and modified those surfaces via dopamine and catechol to enhance their adhesion to wetted substrates. The dry adhesive was inspired by gecko feet, where multi-dimensional micro/nano structures on the surfaces can generate enough van der Waals force to hold a gecko's weight when it walks and presses on the surface to increase contact area. The other concept of catechol modification came from adhesion on a variety of surfaces by mussels, which are known to secrete a sticky liquid containing dopamine-related poly(aminoacid) to their enhance universal adhesion property in air, even in a humid or aqueous circumstance. Experimentally, polycarbonate sheets with nanoholes were used as templates to imprint general HDPE film surfaces to generate 400 nm diameter nanopillars. The demolding process was improved by using solvent replacement techniques to fabricate a practical and large-area gecko tape. The surface completeness was enhanced to 95%, and the tape with 400 nm diameter nanopillars showed 3170 nN adhesion force and was able to suspend 10.5 N per cm². In order to apply the adhesive in a humid environment, we introduced the catecholic functional group on the nanopillars using a two-step method to modify the surfaces with catechol groups. The surfaces were first modified with an acidic dopamine aqueous solution, and then they were modified with alkaline catechol aqueous solution. An additional microcontact printing technique was used to modify nanopillared domains with 1-dodocanethiol chains, showing an improvement of adhesion interaction in water due to hybrid contribution of both polar and nonpolar interaction with the substrate.

Introduction

The concept of biomimetic tape is derived from gecko feet, which have multiscale micro/nano structures containing some setae (30-130 μm wide) incorporated with very tiny spatulae (about 200 nm diameter) on their toe pads.¹ 6.5 million setae of a single tokay gecko attached maximally could generate 130 kg force.² Geckos' movements are thought to depend on repeatedly changing the direction of the setae to break the grip easily without sticky residues, tearing, or pressure necessary. Therefore, mimicking the setae or spatulae structures via micro/nano patterning techniques to produce synthetic gecko adhesives has received much attention.³ Synthetic gecko adhesives that exhibit dry adhesion have been fabricated from polymers with high aspect-ratio nanohairs,⁴ slanted structures,⁵ spatulate tips,⁶ and multiwalled carbon nanotubes with high aspect-ratio structures.⁷ Many studies focus on increasing the adhesion force. For example, Crosby and his coworkers developed an adhesive so strong that an index-card-size strip can have a shear loading capacity as high as about 29.5 N/cm².⁸ However, humid environments are known to reduce the effectiveness of dry adhesives, but the necessary improvements for usage of dry adhesives in a humid environment are relatively less attractive to researchers. Recently, a natural and universal glue, dopamine, was found to display adhesive

properties in a humid or wetted environment.⁹ Messensmith and coworkers provided a suggestion to mimic gecko feet and mussel adhesives.¹⁰ Their strategy employed arrays of gecko-mimetic nanopillars coated with a thin mussel-mimetic polymer film. It was reported that a hybrid biologically-inspired adhesive consisting of polymeric nanopillars was coated with a thin layer of dopamine-derivative copolymer to mimic the wet adhesive proteins found in mussel holdfasts. In their research, individual nanopillars showed excellent performance when tested with a cantilever, the authors' claim of 9 N/cm² adhesion force on surface area was an untested estimate based on extrapolation of the data for single nanopillars. In practical, nanopillars may buckle together and deform, reducing the effectiveness of the tape. Therefore, surface modification of nanopillars leaves for further exploration.

Dopamine treatment at pH 8.5 in tris-buffer solution was frequently applied; however, self-polymerization, isomerization, and oxidation reactions occurred simultaneously, leading to the formation of large aggregates and PDA nanoparticles.¹¹ Those derived particles might satisfy the requirement of a plain surface to display a certain extent of adhesion; however, they would block the nanopillars and cause the dry adhesives to lose their special nanostructures when in contact with nanopatterned surfaces. Accordingly, a surface modification technique with controllable thin-layer deposition should be developed.

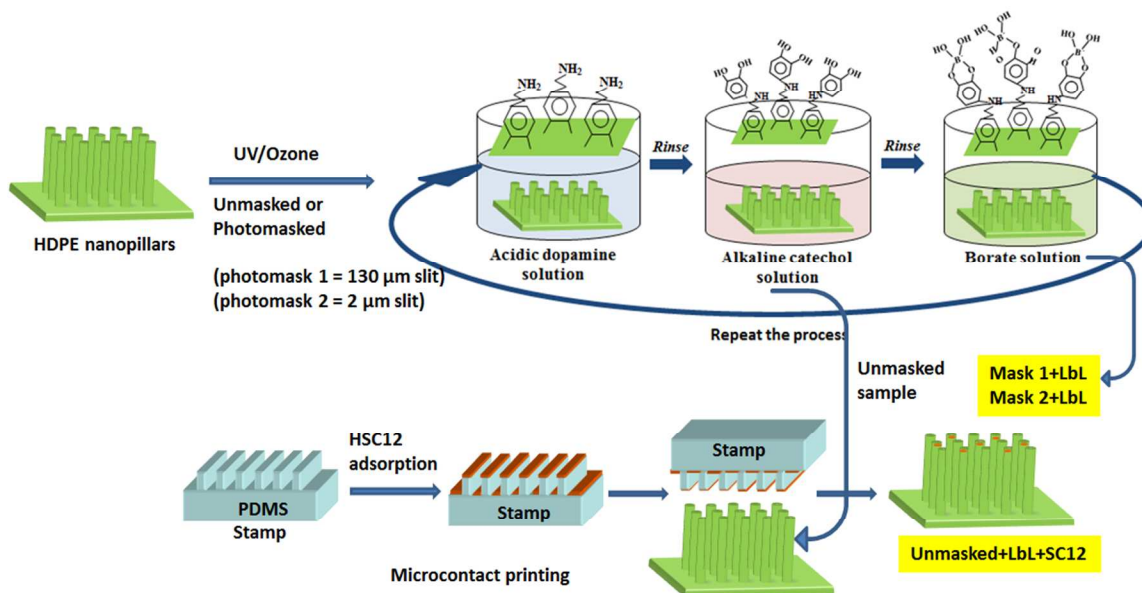


Figure 1. Schematic of partial surface modification on HDPE nanopillars via layer-by-layer and microcontact printing techniques.

In the study, we imprinted and transferred nanopillar patterns onto commercial HDPE surfaces to mimic gecko feet for preparation of dry adhesives with reduced nanopillar buckling. Furthermore, the superhydrophobic property of the HDPE dry adhesive was modified by using patterns and layer-by-layer (LbL) techniques to fabricate a partial domain on nanopillar surfaces to improve the adhesive's usability in a humid environment.

Experimental

Materials

Polycarbonate filter templates with 400 nm and 220 nm diameter nanopores were bought from Millipore Co. HDPE as a substrate was obtained from Aldrich Co. Surface modifiers and their related chemicals, such as 3-Hydroxytyramine hydrochloride (dopamine/HCl, 99%, Acros Co.), catechol (99%, Alfa Aesar), sodium tetraborate decahydrate (from J.T. Baker) and tris hydrochloride (ultra-pure, from MP Biomedicals), were used as purchased. Dichloromethane and absolute ethanol used to fabricate nanopillars were obtained from Tedia Co.. Poly(dimethyl siloxane) (PDMS) was fabricated using two precursor kits (Dow-Corning Co.) in a certain ratio (polymer/crosslinker = 10).

Preparation of HDPE nanopillar patterns

Two PC filter membranes with 400 nm and 220 nm diameter nanopores were used as templates to generate nanopillars. The PC membrane was placed on a clean glass slide and covered with an HDPE sheet and then another glass slide. The thermal imprint technique was applied to produce nanopillars at 145 °C for a 5 min initial period to melt the HDPE sheet, and then a 3 kg load was applied for 10 s to induce the melted polymer to flow into, but not through, the nanopores. The HDPE sheet was cooled at room temperature, dipped into dichloromethane for 15 min to remove the template, and then rinsed with deionized water and dried with nitrogen

blowing, giving an HDPE dry adhesive with nanopillars on the surface.

Layer-by-layer modification on the surface of the dry adhesive

A weak acidic solution (pH 4.5) consisting of 3.152 g tris-HCl dissolved in 200 ml deionized water was used as a 0.1M acidic tris-HCl buffer solution. Additionally, 3.152 g tris-HCl dissolved in 150 ml deionized water, mixed with 10 wt% NaOH aqueous solution to control pH value to 8.5, and then diluted to 200 ml with water, was used as a 0.1 M alkaline tris-HCl buffer solution. 0.02 g dopamine hydrochloride was dissolved into 20 ml 0.1M acidic tris-HCl buffer solution as the first step of surface grafting reactions, producing an acidic dopamine solution. After the HDPE nanopillar pattern was activated using a UV-ozone lamp to irradiate it for 10 min, it was immersed into the acidic dopamine solution for 30 min at room temperature, and then rinsed with deionized water, producing the 1st modified monolayer. 0.1 g catechol was dissolved in 20 ml 0.1 M alkaline tris-HCl buffer solution (pH 8.5) as the second step of grafting reactions, producing an alkaline catechol solution. The previous nanopillared HDPE with the 1st modified monolayer was dipped into the alkaline catechol solution for 30 min at room temperature, and then rinsed with deionized water several times, forming the 2nd modified layer on the nanopillar surface. Thereafter, the attached catechol layer was immersed into 4 wt% sodium tetraborate aqueous solution for 1 hr to connect vicinal hydroxide groups, producing the 3rd modified monolayer and exposing abundant B(OH)₂ structures. Through repeating the above three steps, multiple layers of dopamine and catechol molecules were established for the nanopillared HDPE surface.

Partial-area surface modification

As the intention of the study was to produce a surface covered in a mix of hydrophilic and hydrophobic nanopillars, not all nanopillars should be grafted with dopamine and catechol. Therefore, when the HDPE surface was pretreated by UV-Ozone irradiation in preparation for grafting, photomasks

were employed to control the area of irradiation. Two photomasks with uniform slits 130 μm and 2 μm in width, respectively, were employed to prevent irradiation and contact with ozone on parts of the surface. The partially-activated samples were then used for the above-mentioned multilayer modification. In addition, unmasked samples were also produced. After undergoing the above process without any photomask, the samples were stamped with a 320 nm-wide ruled PDMS stamp which was previously dipped into a 10 mM 1-dodcanethiol in alcohol solution for 30 min. The contact time was 10 min without any load. All the partial surface modification on HDPE nanopillars via layer-by-layer and microcontact printing techniques can be seen in Figure 1.

Characterization of surface modification

The pattern transfer and modified layer quality of all the samples were inspected with a scanning electron microscope (SEM, Hitachi S4800). Water contact angles on the pillar patterns were measured via a contact angle analyzer (Han-Kuang High Tech. Co. Taiwan) and their surface chemical bonds were analyzed via an X-ray photoelectron spectrometer (XPS, Ulvac-PHI PHI 1600). An atomic force microscope (AFM, NT-MDT Solver PRO-M) attached with a micro-Raman analyzer (NTEGRA Spectra) was employed to measure both the adhesive force and the functional group changes of the nanopillar domains. In order to explore the adhesion force between nano-domains of nanopillar patterns with a substrate, a cantilever without any tip probe was employed to imitate the situation of a flat surface in contact with bundles of nanopillars. The width, length, and force constant of the cantilever were 35 μm , 100 μm , and 11.5 N/m, respectively. The adhesion force between the cantilever and nanopillar bundles could be calculated via Hook's law: $F = k\Delta H$ with k as the force constant and ΔH as the deformation. A custom-built adhesion measurement system was used to measure the maximum shear adhesion force between those dry adhesives and a reference substrate. A gauge was connected to a nanopillared sheet which was previously fixed on a reference substrate with a 300 g preload. The force data was recorded using a camera with increasing pulling force until a complete detachment occurred.

Results and discussion

Fabrication of HDPE nanopillars and their evaluation of dry adhesion

Via adjustment of thermal imprint parameters at the temperature of 145 $^{\circ}\text{C}$, with pressure loading of 3 kg, and a processing time of 10 sec, the gecko-foot-inspired nanopillar structures were successfully prepared. The diameters of the nanopillars could be conformally replicated from nanopores of various sizes in the PC filters. Figure 2 shows the HDPE nanopillar patterns with 400 nm (Figure 2(a)) and 220 nm (Figure 2(b) and (c)) diameters. Those long nanopillars were completely transferred without severe buckling, entanglement, or collapsing (shown in Figure 2(c)). However, the 220 nm diameter nanopillar pattern displayed a relatively higher amount of deformation than the 400 nm one due to its high-aspect-ratio (near 40) structures lacking mutual support from lateral interaction. Another issue determining the quality of transfer was usage of the solvent replacement process, which used different solvents to stabilize nanopillars before drying. A large amount of ethanol was added to dilute the etching solution dichloromethane in the demolding process. After removing the

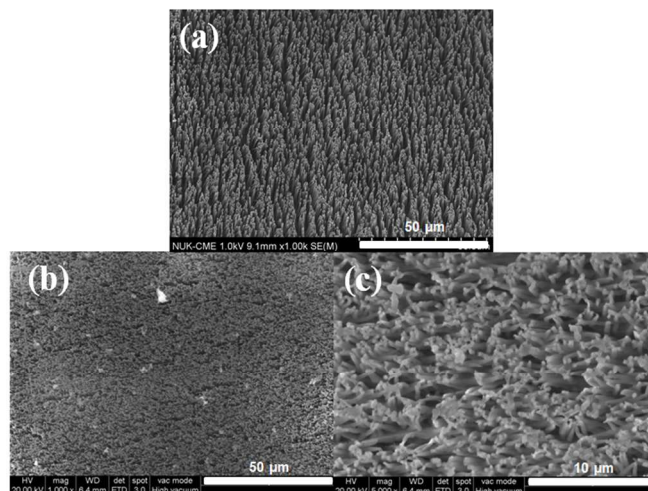


Figure 2. SEM images for HDPE nanopillar patterns (a) 400 nm in diameter and (b) 220 nm in diameter. (c) shows the higher magnification photo on the 220 nm nanopillars.

mixed solution, ethanol was added to rinse the HDPE nanopillars and deionized water/ethanol was added to keep increasing the polarity of the rinse solution. Finally, a large amount of water was employed to rinse the patterns several times. The nanopillar patterns needed to stay “wet” throughout the process, before the final step of drying. The solvent replacement process reduced the buckling effect, which resulted from the aggregation of adjacent nanopillars when dichloromethane was directly evaporated out. High polarity of ethanol and water situated in and between nanopillars could separate them and extract all dichloromethane remaining in the surface of nanopillars, producing high completeness of vertically-aligned nanopillar patterns. Figure 3 (a) shows the buckling and aggregation phenomena, and Figure 3 (b) shows the improvement by solvent displacement method. Figure 3 (c) shows the cross-sectional view of the nanopillar pattern, and its estimated length was about 8 μm . A dry adhesive should contain countless nanopillars to generate enough van der Waals force between the pattern and a substrate. Therefore, the overall completeness of a pattern determines its utility of adhesion. The overall survey for the completeness of available pattern area was performed by using 30X magnification in SEM analysis and 5000X magnification on arbitrary spots of the pattern for examination of nanopillar structures, and by calculating the dark area using a program called Image-Pro Plus, detecting as high as 95% usable area (shown in Figure 3(d)).

Using the HDPE sample with a 400 nm-diameter nanopillar pattern allowed a simple suspension test. Half of the sample was attached onto a glass slide and the other half was stuck to a wall or to a weight, as shown in Figure 4. We used a custom-built adhesion measurement system to measure the maximum shear adhesion force. Shear stress was applied to increase deformation of nanopillars to give some bundles of lines contact, and also to lay nanopillars down to form a large contact surface. 10.5 N/cm² load was found to be the maximum load for the 400 nm diameter nanopillar pattern. Detachment of the tape using the tip of a pair of tweezers to pull away from the perpendicular direction could be easily performed in the detachment test, proving that the adhesion force matched the principle of gecko feet and displayed the characteristics of asymmetric adhesion force.¹² It was about the same as the shear adhesion forces supportable by other biomimetic gecko-foot

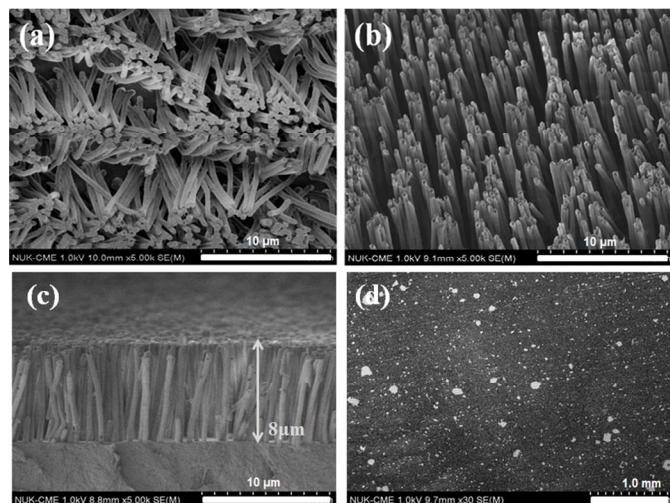


Figure 3. SEM images for 400 nm diameter nanopillars. (a) aggregated nanopillars, (b) improved by solvent displacement method, and (c) the cross-sectional view of nanopillar pattern. (d) shows the overall survey for the completeness of available pattern area.

tapes in previous literature,^{3,13} and deeply affected by some aggregation of nanopillars, density of nanopillars, and flexibility of HDPE. The adherence/detachment test was carried out at least ten times (the repeated cycle test was performed by hand with a preload of 500 g and will be applied using a robot arm in future designs), showing some durability of the nanopillars; however, it was still far beyond practical use. Here we focus attention on verifying the usage of nanopillar patterns on the commercial polymer HDPE. Another adequately-crosslinked UV resin has been designed and is currently under investigation for replacing the flexible HDPE via the same pattern. Preliminary data shows an increased shear load (15 N/cm²) and high durability compared to HDPE, but it needs to be explored further.

Surface modification with LbL catechol functional groups

The prime, unmodified HDPE dry adhesive displayed a superhydrophobic property on its surface, readily rejecting water molecules nearby and thus losing its adhesive property in

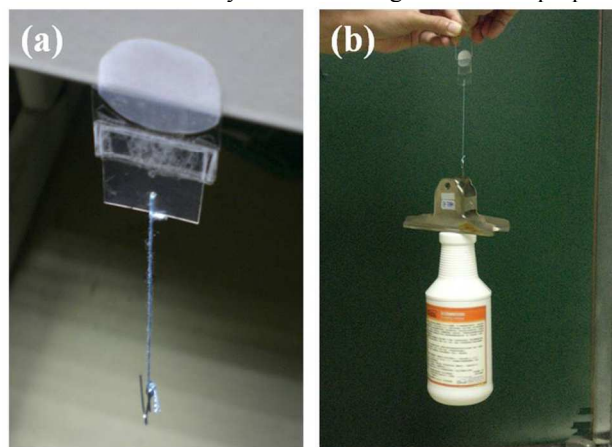


Figure 4. Photographs of suspension test. (a) The weight-bearing device attached on a wall and (b) its test for lifting a heavy object. The maximum load was 10.5 N/cm².

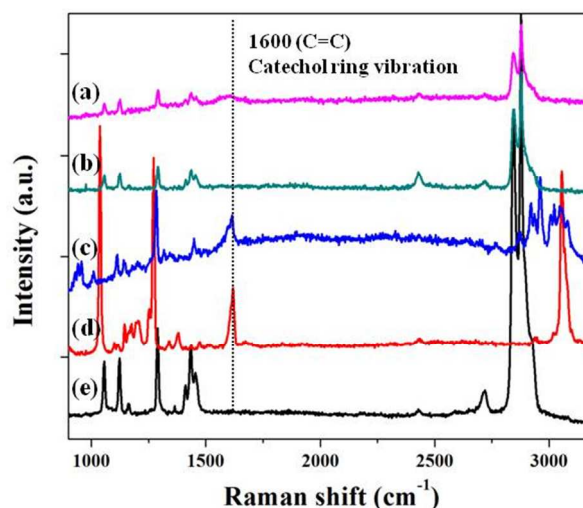


Figure 5. Raman spectra for multiple layers and their related chemicals. (a) HDPE-dopamine-catechol, (b) HDPE-dopamine, (c) dopamine, (d) catechol, and (e) prime HDPE.

humid environments. Modification with dopamine/polydopamine on the hydrophobic surface could increase its affinity toward water and surfaces with polar functional groups. Here we provide an unprecedented layer-by-layer modification process to introduce homogeneously attached catechol groups onto the surface, as can be seen from the schematic in Figure 1. In our modification process, the HDPE surface was oxidized via UV/O₃ irradiation to generate abundant hydroxyl groups on the surface. The first step of the two-step modification was carried out to attach a dopamine monolayer on the oxidized HDPE surface because the surface reaction proceeded in an acidic aqueous solution, instead of adopting traditional dopamine treatment in an alkaline tris-HCl buffer solution and forming PDA nanoparticles or aggregates. The primary amine group of dopamine should be protonated, reducing its nucleophilicity to auto-oxidation and self-polymerization, and dispersing its positive charge to eject PDA aggregates. The second step was employed to attach catechol groups on the dopamine-modified HDPE surface by adding catechol to have it attacked by protruding amine groups of attached dopamine in an alkaline aqueous solution; namely, a Michael type addition is performed. Terminated benzoquinone groups were then treated with a sodium tetraborate solution to interact with borate ions, leaving two unbound OH groups. Afterwards, the surface modification could be repeated from the first treatment using acidic dopamine solution, the second step using alkaline catechol solution, and then borate solution, creating a homogeneous multilayer surface.

By means of microRaman analysis, a thin catechol-enriched layer could be characterized at a peak of around 1600 cm⁻¹ in a spectrum. After the second catechol-modified layer was attached, the sample was verified to have an aromatic structure peaking at 1600 cm⁻¹ in a spectrum as compared to pure dopamine and polydopamine (shown in Figure 5). However, owing to the very thin outer layer, the laser in the microRaman spectrometer could not focus on a singular spot of the treated thin layer, leading to no apparent vibration peak being found. Using XPS analysis to characterize the surface elemental compositions, as can be seen in Figure 6, the first modified layer could be verified in accordance of appearance of N1s

peak and increment of O1s intensity. The second modified layer, based on the reaction of amino groups or dopamine at the aromatic ring of catechol groups, could also decrease N1s peak intensity and increase O1s intensity. The peak intensity ratio of O/N was increased after the second modification and could be used to confirm the catechol attachment, as listed in Table 1.

In order to balance the polar and nonpolar intermolecular interaction, another modification was performed to apply a patterned mask to the nanopillars when they were irradiated with UV/O₃, instead of complete treatment and modification with the hydrophilic polydopamine-like multilayer surface. The method using mask patterns with 130 μm and 2 μm wide slits left original HDPE chains on the concealed regions and grafted polydopamine-like molecules on the exposed regions, simultaneously maintaining both hydrophilic and hydrophobic properties on the nanopillars. Water contact angle (WCA) measurement on those various nanopillars with and without mask concealment and also before and after microcontact printing with hydrocarbon chains was carried out to evaluate the effects of layer-by-layer deposition. Figure 7 shows that the WCA was largely decreased from the very hydrophobic PE surface when the unmasked sample was grafted and fully covered with catechol groups on the nanopillar surfaces. Using photomask 1 (130 μm wide slits), a large surface area was exposed for modification, so the WCA was similar to that on the unpatterned flat PE surfaces. Using photomask 2 (2 μm wide slits) resulted in heterogeneous distribution of polar/nonpolar chains and a high contact angle even after dopamine and catechol treatment. WCA changes measured between each step in the layer-by-layer modification also verified the successful application of each layer. The unmasked nanopillar pattern was modified with a microcontact printing technique to print hydrophobic chains on a contact domain, due to a Michael addition of thiol groups with well-modified nanopillar surfaces with dopamine attached. A 320 nm-wide ruled pattern was chosen as a stamp to partially treat the surfaces, leading to an increase in WCA. However, there were still much more hydrophilic catechol groups protruding on the surface, compared to the original HDPE nanopillars.

Table 1. Surface compositions of HDPE nanopillars and their modification via XPS analysis.

Sample	C (%)	N (%)	O (%)	O/N
PE	98.42	-	1.13	-
PE-dopamine	91.34	1.51	7.15	4.73
PE-dopamine-catechol	91.52	0.55	7.93	14.42

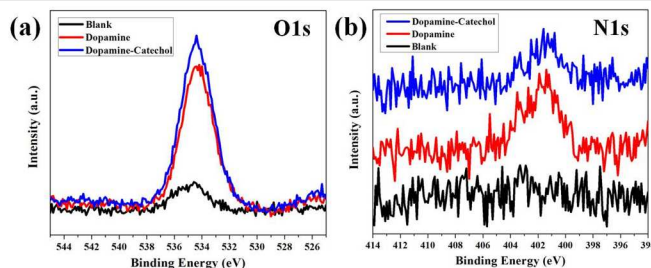


Figure 6. XPS spectra for (a) O1s and (b) N1s elements on the surfaces of prime and modified HDPE nanopillars.

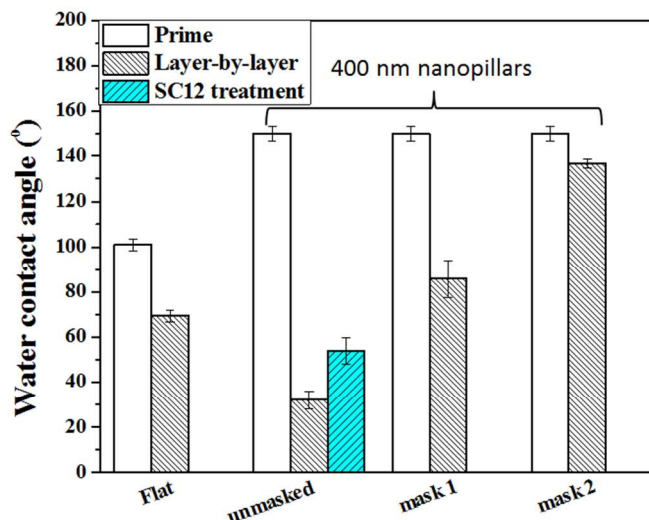


Figure 7. Water contact angles for 400 nm nanopillar surfaces treated with dopamine and then catechol (layer-by-layer method), with or without photomask; and unmasked surfaces produced via contact printing with SC12. “Flat” is the unmodified control surface.

Adhesion force measurement for surface-modified samples via AFM and in a humid environment

AFM is a powerful tool for evaluating the adhesion force on micro/nano domains. In order to mimic the nanopillars' attachment on a flat surface, a 35 μm -wide tipless cantilever with a modulus of 11.5 N/m was employed to measure the force-distance curve of the modified layers of the nanopillar patterns. For bendable and flexible nanopillars interacting with a relatively non-deformable flat cantilever, the adhesion force is mainly caused by the van der Waals force and capillary force between the nanopillars and the cantilever surface. The amount of adhesion force between the cantilever surface and modified nanopillars was estimated via calculating the deformation ΔH . Figure 8(a) shows a representative set of retraction force-distance curves obtained from various samples. In the figure, the vertical axis is the force experienced by the cantilever due to interactions between the cantilever surface and the sample. The horizontal axis is the displacement of the cantilever produced by the piezoelectric actuator to which the cantilever is attached. The cantilever usually rebounds once it snaps back, and then the pull-off force causing detachment between the sample and the cantilever surface is measured as the adhesion force. Adhesion is then determined as the maximum pull-off force noted in the force-distance curve. Figure 8 (b) shows that the nano-domain of the tape with 220 nm diameter nanopillars displayed up to 5882 nN adhesion force, while the tape with 400 nm diameter nanopillars showed 3170 nN adhesion force. A higher aspect-ratio pattern supplied larger contact area caused by PE bending and more van der Waals force than a lower one. However, the buckling effect between nanopillars rendered the 220 nm diameter nanopillar surface useless, but the 400 nm one was able to suspend 1.05 kg per cm^2 . The surface of the two samples after two-step modification displayed low adhesion force toward the cantilever surface. This was due to the polar catechol groups being able to bridge hydrogen bonding with a polar surface but losing non-polar London force with a surface. Using a mask to recover some extent of nonpolar interaction could readily increase adhesion force, showing the contribution of polar and nonpolar

interaction. The sample treated with photomask 2 was found to display 1635 nN adhesion force toward the cantilever surface and enhance the adhesion force by 99.7% when compared to unmasked modified nanopillars after the two-step treatment. Furthermore, long hydrocarbon chains introduced via microcontact printing with SC12 were found to enhance adhesion force in air, displaying about 2322 nN partly due to contribution of nonpolar interaction. Figure 9 shows the adhesive in water. As expected, the prime HDPE slipped away from a substrate under water due to its superhydrophobic property (Figure 9(a)). However, both unmasked and masked dopamine-treated nanopillared surfaces were found to attach on a substrate under water but without significant adhesion force (Figure 9(b)). Only the unmasked samples imprinted with hydrocarbon chains were found to suspend a relatively high load in water (Figure 9(c)), resisting shear adhesion force of 0.12 N/cm^2 in water and 0.2 N/cm^2 in air (Figure 10). The results evidenced the mussel-inspired dopamine treatment might provide catecholic polar and hydrogen bonding, but not van der Waals force. Microcontact printing with hydrocarbon thiol groups might be an improved method to supply both polar and nonpolar interaction for usage in water. The results also inspired us to design mixed hydrophobic/hydrophilic nanodomains to develop a “universal tape,” which we plan to research in the future.

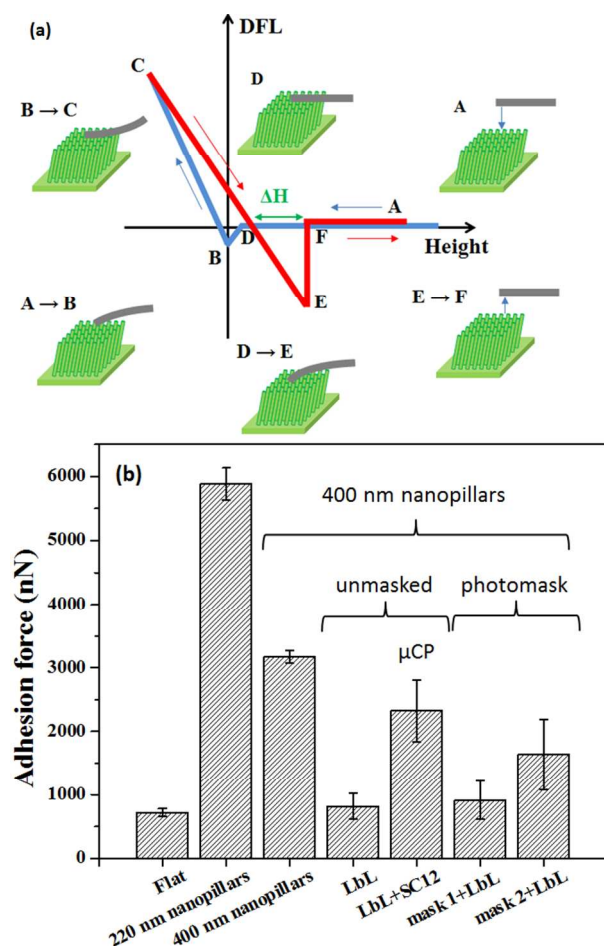


Figure 8. (a) Force-distance curves of dry adhesive surfaces detected with a tipless cantilever in AFM measurement. (b) shows the measured adhesion forces in air (averages obtained from at least 10 different spots for each sample).

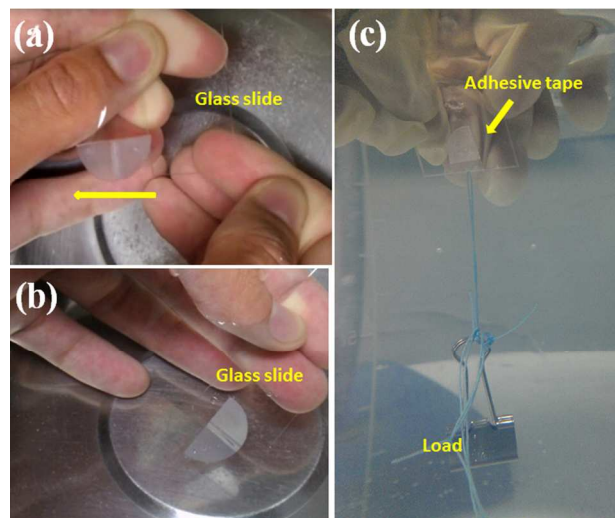


Figure 9. Photographs for adhesives usage tests under water. (a) prime nanopillared HDPE sheet. The arrow shows the sheet slipping away from the glass slide. (b) HDPE sheet treated with dopamine and catechol. (c) Suspension test in water on a partially-modified adhesive to suspend a load.

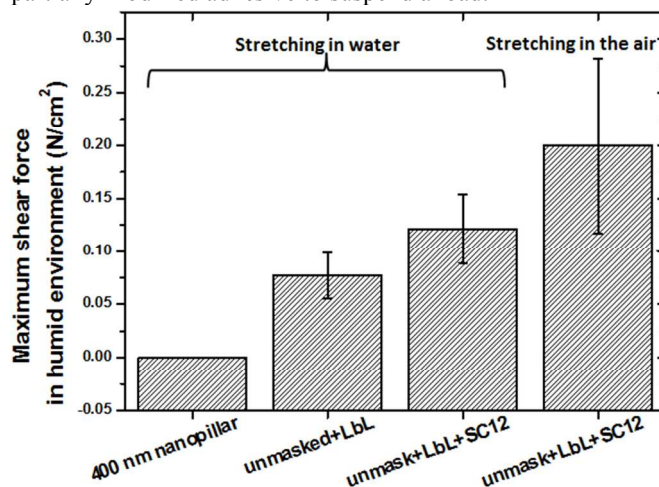


Figure 10. Maximum shear force measurement for unmasked nanopillars after partial surface modification. All attachments were carried out in water and the shear force measurements were taken in water or in air with gradual increment of force.

Conclusions

Using hot embossing techniques incorporated with nanoporous molds could allow one to successfully prepare patterned HDPE with 400 nm and 220 nm diameter nanopillars. In order to reduce the buckling of nanopillars, the gradual solvent exchange technique was employed, resulting in vertically-aligned and large-area nanopillar patterns, with 95 % completeness. 1 cm^2 of dry adhesive (400 nm diameter nanopillars) could support a 1.05 kg weight on a flat substrate. In order to improve the applications of the dry adhesive to a humid environment, surface modification with dopamine was employed to increase the secondary polar interaction. The photomasks with $2 \mu\text{m}$ wide slits could be used to partially activate nanopillar surfaces and graft them with multilayer surfaces treated with dopamine and catechol. However, hydrocarbon chains attached on dopamine groups on top of nanopillars seemed essential due to contribution of van der

Waals force. Partially-treated nanopillars with multilayer dopamine/catechol surfaces showed improved adhesion under water or in a humid environment. Therefore, the treatment could give promising applications for biomedical purposes, sea-water-durable objects, bandages, and so on.

Acknowledgements

We thank the National Science Council of R.O.C. for financial support under Contract No. NSC 101-2221-E-390 -002 -MY3 and the proof-reading work of Mr. Bryan Van Biesbrouck, who has been working in editing for years.

Notes and references

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Electronic Supplementary Information (ESI) available for short videos: (1) Adhesion test for the dry adhesive and its report in press. (2) Adhesion test under water for prime HDPE. (3) Adhesion test under water for LbL multilayer modified adhesive. See DOI: 10.1039/b000000x/

- 1 H. Yao and H. Gao, *J. Mech. Phys. Solids*, 2006, **54**, 1120.
- 2 K. Autumn and A. M. Peattie, *Integr. Comp. Biol.*, 2002, **42**, 1081.
- 3 H. E. Jeong and K. Y. Suh, *Nano Today*, 2009, **4**, 335.
- 4 A. K. Geim, S. V. Dubonos, I. V. Grigorieva, K. S. Novoselov, A. A. Zhukov and S. Y. Shapoval, *Nature Mater.*, 2003, **2**, 461; M. Sitti and R. Fearing, *J. Adhes. Sci. Technol.*, 2003, **17**, 1055; M. T. Northen and K. L. Turner, *Nanotechnology*, 2005, **16**, 1159.
- 5 T.-I. Kim, C. Pang and K. Y. Suh, *Langmuir*, 2009, **25**, 8879.
- 6 J. Davies, S. Haq, T. Hawke and J. P. Sargent, *Int. J. Adhes. Adhes.*, 2009, **29**, 380; A. del Campo, C. Greiner, I. Alvarez and E. Arzt, *Adv. Mater.*, 2007, **19**, 1973.
- 7 B. Yurdumakan, N. R. Raravikar, P. M. Ajayan and A. Dhinojwala, *Chem. Commun.*, 2005, **30**, 3799; L. Qu, L. Dai, M. Ston, Z. Xia and Z. L. Wang, *Science*, 2008, **322**, 238; S. Hu, Z. Xia and L. Dai, *Nanoscale*, 2013, **5**, 475.
- 8 D. B. Michael, A. B. Croll, D. H. King, B. M. Paret, D. J. Irschick and A. J. Crosby, *Adv. Mater.*, 2012, **24**, 1078.
- 9 E. Faure, C. Falentin-Daudré, C. Jérôme, J. Lyskawa, D. Fournier, P. Woisel and C. Detrembleur, *Prog. Polym. Sci.*, 2013, **38**, 236; L. Guo, Q. Liu, G. Li, J. Shi, J. Liu, T. Wang and G. Jiang, *Nanoscale*, 2012, **4**, 5864; B. P. Lee, P. B. Messersmith, J. N. Israelachvili and J. H. Waite, *Annu. Rev. Mater. Res.*, 2011, **41**, 99.
- 10 H. Lee, B. P. Lee and P. B. Messersmith, *Nature*, 2007, **448**, 338.
- 11 C.-C. Ho and S.-J. Ding, *J. Mater. Sci. Mater. Med.*, 2013, **24**, 2381; T. Shalev, A. Gopin, M. Bauer, R. W. Stark and S. Rahimipour, *J. Mater. Chem.*, 2012, **22**, 2026.
- 12 J. Yu, S. Chary, S. Das, J. Tamelier, N. S. Pesika, K. L. Turner and J. N. Israelachvili, *Adv. Func. Mater.*, 2011, **21**, 3010.
- 13 D. Sameoto and C. Menon, *Smart Mater. Struct.*, 2010, **19**, 103001.