Formation of ultra-flexible, conformal, and nano-patterned photonic surfaces via polymer cold-drawing

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We report a lithography-free method for large-area plasmonic nano-patterning on ultrathin plastic films through a polymer cold-drawing process. We further transfer the ultra-flexible nano-patterned films onto curved surfaces of plant leaves and apples to work as conformal SERS sensors.

1. Introduction

The ability to pattern materials into precisely defined geometries with nano-scale feature dimensions enables a broad range of studies and applications in the fields of photonics,^{1–4} electronics,^{5,6} and optoelectronics.^{7–10} To date, standard top-down nano-fabrication technologies, namely E-beam lithography (EBL),¹¹ focused ion beam (FIB),¹² and nano-imprint lithography (NIL)¹³ have dominated the fabrication of micro/nano-structures with controlled shapes and sizes. However, in an effort to keep up with the increasing needs towards practical applications, these conventional technologies are fundamentally limited by their complicated procedures, long processing time, low process throughput, and high fabrication cost.¹⁴ Thus, several robust methods have been developed to achieve nano-patterned surfaces in large-scale areas with low cost. For instance, the inherent nano-patterns such as nanoporous anodic aluminum oxide (AAO) membrane and cicada wings have been employed as the templates of stencil lithography to design arrays of nanopillars, nano-tubes and nano-holes.^{15–18} Another low-cost method, namely nano-sphere lithography, uses single layer or multiple layers of self-assembled polystyrene nano-spheres as a mask to produce both size- and shape-tunable nano-particle arrays out of a large variety of materials.^{1,19} Furthermore, surface-wrinkling-based patterning technique induced by mechanical instability in a pre-stretched elastic thin film provides a simple approach for periodic one-dimensional (1D) and 2D surface pattern.^{20,21} These micro/nano-structures can find wide applications such as surface-enhanced Raman

scattering (SERS) sensing,² localized surface plasmonic resonant (LSPR) sensing,¹ optical superlenses,²² wearable photonic²³ and nano-electronic devices.⁵

In nature, diverse natural surface patterns exist in different length scales, such as the mud cracks in dry riverbeds, the skin patterns in living creatures like crocodiles and turtles, and the crack patterns on tree bark. Understanding the mechanism behind the formation and growth of these patterns can generate new concepts of surface patterning. For instance, the forming process and mechanism of mud cracks have been well studied and inspired to develop nano-sized channel patterns on both rigid and elastic substrates for nano-fluidics in a controlled manner.^{24,25} Strain-induced cracking is also a common phenomenon that can be found in the natural world and the thin films systems in the field of nanotechnology. Utilizing this phenomenon, researchers have managed to harness cracking patterns and micro/nano channels on elastic substrates that could work as tunable optical components,^{26,27} extracellular matrices,²⁸ and tunable nano-fluidic channels.²⁹ Such strain induced cracking method can also work as a powerful tool to snip complex fibers into micro/nano particles.³⁰

Here we report a controllable lithography-free method to achieve large-scale nano-patterned photonic surfaces on flexible thermoplastic substrates through a polymer cold-drawing process. Polymer cold-drawing is a process in which tensile stress reduces the thicknesses of plastic films or fibers, and has long been used in industrial applications.^{31–33} Here, to be specific, this polymer cold drawing method is realized simply by bi-axially mechanical stretching the polycarbonate (PC) film substrates in a sequential manner, which can break the surface gold nanofilms into nano-structures with good controllability and tunability over the morphology and size. The fabricated gold nano-patterns show high performance in SERS applications. More importantly, this simple micro/nano-patterning method can be easily applied to ultra-thin polymer films with sub-micron thicknesses to produce ultra-flexible and conformal photonic films, which can be transferred to a curved surface of arbitrary geometry and topology to work as flexible conformal sensors or photonic surface devices. This highly versatile nanofabrication method can be further enriched by simply tuning the material properties of the surface layer or the substrate, which may find applications in a wide range of

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fields from flexible photonics, nano-electronics, energy harvesting, to biomechanical science.

2. Results and discussion

2.1. Fabrication process

Fig. 1a sketches the basic process of this micro/nano patterning method. First, we deposit a layer of gold nano-film on a 125- μm -thick PC substrate (See Methods for detailed parameters). Secondly, we stretch the gold/PC film in x -direction (The experimental setup and the mechanical stretching process are illustrated in Fig. S1). The PC film goes through a necking process and imposes stress on the gold film through surface adhesive forces. The gold film breaks into stripes once the stress exceeds the mechanical fracture strength. As the necks in the PC film propagate along the film length, homogeneous gold stripes are formed over the entire film. Thirdly, we re-stretch the as-fabricated film in y -direction to produce 2D micro/nano surface patterns. The PC film goes through a homogeneous elongation and the gold nano-strips further fragment into small pieces under strain induced inner stress. The length of the gold nano-patterns is dependent on the elongation extent of 2D stretching. This simple strain-mediated fragmentation method can be applied to a large area nano-patterning, for example, Fig. 1b shows a centimeter-scale PC film fully covered with gold nano-patterns fabricated by this method. From a production point of view, we can use stretching setups with larger clamps and stretching forces to produce even larger gold nano-patterned PC films. Also, we can adopt a roll-to-roll fabrication strategy³⁴ to further improve the production efficiency.

In the mechanical stretching process, the strain-stress behavior and stretchability of the plastic substrate play important roles in the fragmentation of gold nano-film. The curve in Fig. 1c illustrates the strain-stress behavior of the gold/PC film during 1D stretching (See Methods for details of tensile testing). The middle part of the strain-stress curve represents the necking process where the stress remains constant, and the strain distribution in this necking-assisted fragmentation is localized. This strong localized strain acts as a tool to fragment the gold nano-film. Optical images of the necking region (Fig. S2a-c) clearly show that the quasi-strips are produced in the necking process. This localized fragmentation process can be well described by a modified shear lag model (See Supplementary Information for details).

During 2D stretching, the strain-stress curve (Fig. 1d) behaves like that of elastic polymers: the inner stress in the PC film keeps raising as strain increases and no necking region can be observed, indicating that the film stretches homogeneously across the whole length. Thus the fragmentation of thin film on elastic substrates can be well described by the standard a shear lag model³⁵ (See Supplementary Information for details). When we stretch the PC film in y -direction, the gold nano-strips first break at the center or at defect points. Then the

fragmentation repeats as the stress increases and finally, a minimum size of the fractured segments is reached. More importantly, the PC film goes through plastic deformation in the 2D stretching process, which means the PC film keeps stable when the stretching force is released at any stage of 2D stretching. Thus, by adjusting the elongation in 2D stretching, the length of the nano-patterns can be precisely controlled. SEM images in Fig. 1e presents the gold nano-strips after 1D stretching and the gold nano-patterns at different stages of 2D stretching (thickness of the gold film, 30 nm), which demonstrate the capability of this mechanical strain-mediated nano-patterning method.

2.2. Characterization of gold nano-patterned films

To investigate the controllability and tunability of this method over different morphologies and dimensions of the surface nano-patterns, we characterize the dimensions of the surface patterns fabricated with gold nano-films with different thicknesses after 1D stretching and at different stages of 2D stretching. As a result, Fig. 1f shows that the average width of the nano-strips fabricated by 1D stretching increases from 160 nm to 820 nm linearly as the thickness increase from 10 nm to 50 nm. This linear relationship between average width and film thickness agrees well with the shear-lag model (See Supplementary Information for details) given that the fracture strength of the thin film is a constant or varies slightly with thickness. The plots in Fig. 1g show that the length of the nano-patterns decreases rapidly when elongation increases from 38% to 152%, and Fig. S4 shows SEM images of the gold patterns with the thickness of 10 nm, 20 nm, and 50 nm under different elongation. When strain further increases above 152%, the length of the nano-patterns reaches a minimum size, indicating that the inner stress provided by the PC substrate can no longer break the nano-patterns. At this stage, spatial re-arrangements take place, in which the gaps between nano-patterns widen in y -direction and narrow in x -direction, respectively. Thus, we choose the elongation value of 152% for characterization and application demonstration in our following studies. SEM images (Fig. 1h) of the gold nano-patterns with different thicknesses under the elongation of 152% show that the morphologies of the nano-patterns are similar although their sizes vary with film thicknesses. It should be noted that the elongation of the PC film in the 1D stretching process is a constant, which may constrain the tunability of the width of the nano-patterns. This limitation can be overcome by either conducting the stretching process at different temperatures based on the temperature control on the stretchability of thermoplastic polymers or utilizing other thermoplastic substrates with different stretchabilities. Furthermore, this generic nano-patterning method can be easily applied to other materials and even multi-layered thin films. Fig. S5 shows nano-patterned surfaces fabricated from copper and platinum nano-films.

Apart from the dynamically controllable and tunable sizes, these gold nano-patterns also possess some unique features. As shown in Fig. 1h, these gold nano-patterns are featured

with zigzag boundaries, which not only form massive sharp tips and notches that are favorable for plasmonic enhancement, but also greatly extend the boundary-interactive lengths. Compared with even and smooth boundaries produced by conventional nanofabrication technologies, these zigzag boundaries provide much more binding sites for biochemical molecules. Another feature is the nano-gaps formed by two adjacent nano-patterns. Nano-gaps especially the sub-10-nm gaps between plasmonic metallic nano-structures can confine electromagnetic field in sub-wavelength scale with strong field enhancement. In our case, the fabricated gold nano-patterns are rich of sub-wavelength nano-gaps for all the four thicknesses, and the average size of the nano-gaps decreases globally as the thickness of gold film decreases. All these features indicate that the gold nano-patterns fabricated by this method have strong field enhancement and would be a promising candidate for SERS sensing.^{36–38}

2.3. Modeling and simulation of near-field enhancement

We carry out 3D FDTD simulations to assess and understand the near-field enhancement. The geometries and dimensions of gold nano-patterns are extracted from SEM images (See Methods for details of simulation). A typical plot of the normalized electrical field distribution and the source SEM image are shown in Fig. 2a. By analyzing the field distribution, a local field enhancement of about two orders can be achieved, which is mainly contributed by hotspots located at sharp tips and notches on the boundaries, holes in the nano-patterns, as well as nano-gaps between adjacent nano-patterns, especially sub-10-nm gaps. Fig. S6 presents the simulation results of the gold-patterns with different thicknesses, and similar electric field enhancements are observed. Moreover, the nano-patterns with a thickness of 20 nm show both the highest local field enhancement and the highest surface density of hotspots, indicating its excellent performance in SERS sensing.

2.4. SERS performance on planar PC substrates

To experimentally demonstrate the strong electromagnetic field enhancement in our gold nano-patterns, we conduct SERS measurements using a Raman active molecule, 2-naphthalenethiol (NT) as the analyte (See Methods for detailed information on substrate preparation and Raman measurements).

First, we investigate the SERS performance of the four samples with different thicknesses. From the Raman spectra in Fig. 2b, we can clearly observe several Raman peaks at around 1065 cm^{-1} , 1379 cm^{-1} , 1449 cm^{-1} and 1618 cm^{-1} for all the four substrates, which are consistent with the reported results.^{39,40} To verify the enhancement of the substrates, we also test gold nano-films without strain-mediated fragmentation. The Raman spectra presented in Fig. S7 show that only low fluorescent background signals are recorded for gold nano-films with thicknesses of 20 nm, 30 nm, and 50 nm. While, for the 10 nm-thick gold nano-films, relatively low-intensity Raman peaks of

NT are observed, which may be caused by the rough surface of the 10 nm-thick gold film. Therefore, the high-intensity Raman peaks reveal that the gold nano-patterns fabricated by this method provide significant SERS enhancement. Moreover, 20 nm-thick gold films offer the strongest SERS enhancement (Fig. 2c), which is in a good agreement with the simulated results. Sensitivity and reproducibility are primary parameters for SERS substrates towards practical applications. Thus, we evaluate the sensitivity and reproducibility using gold nano-patterns with the optimal thickness of 20 nm. Fig. 2d shows the Raman spectra of NT with concentrations ranging from 1 pM to 100 nM, and a limit of detection (LOD) of 1 pM for NT is achieved by tracking the Raman peak at 1379 cm^{-1} . Furthermore, the SERS signals at 20 random positions across the entire film are measured, as shown in Fig. 2e, 2f, and 2g. The corresponding relative standard deviation (RSD) values at peak 1379 cm^{-1} and 1449 cm^{-1} are 5.34% and 8.74%, respectively, indicating a good reproducibility of our SERS substrate. It should be noted that the reproducibility is dependent on the accuracy of the thickness of the gold film. In order to achieve low deviations, the thickness of the gold film should be precisely controlled.

2.5. Ultra-thin and ultra-flexible gold nano-patterned films

Although the demonstrated gold nano-patterned film on a 125- μm -thick PC substrate is flexible to some extent, it can only be used as a planar SERS substrate. Here we further extend this method to produce nano-patterns on ultra-thin polymer films with sub-micron thickness by simply introducing a water-soluble thin PVA layer onto the PC substrate and an ultra-thin PC hosting layer on top of the gold film. Fig. 3a schematically illustrates the fabrication steps (See Method for the detailed process), and an ultra-thin photonic film floating on the surface of water. Then, the fabricated ultra-thin photonic film is attached on a flat silicon chip and characterized by SEM and atomic force microscopy (AFM). The SEM image in Fig. 3b illustrates the gold nano-patterns with the average size below 500 nm. The line profile measured along the red line in the AFM image (Fig. 3c) shows that the thickness of the gold film is around 20 nm and the overall thickness of such a gold nano-patterned film is only about 40 nm. This nano-scale thickness not only equips the film with excellent flexibility and conformability to be seamlessly attached to a curved surface of arbitrary geometry and topology, but also minimizes the impact of attached thin nano-patterned film on the existing platform, for example, low integration-induced losses including both absorption loss of the PC substrate and scattering loss of the interface. Fig. 3d shows optical micrographs of the ultra-flexible nano-patterned films that are coated on the curved side faces of optical fibers with different diameters.

2.6. On-site and in-situ pesticide sensing

Facilitated by the recent development of flexible photonics, on-site and in-situ sensing becomes a powerful tool to greatly simplify the sensing process and reduce detection time.^{41–44} Due to the excellent flexibility and conformability of the

fabricated gold nano-patterned film and the excellent optical clarity and bio-compatibility of PC, this gold nano-patterned film can be easily attached to the complicated surfaces of real bio-samples to realize on-site and *in-situ* SERS sensing, for example, to detect pesticide residues. The fast and accurate detection of pesticide residue on the surface of vegetables and fruits is of great importance in both public health and food industry.⁴⁵ SERS has gained much popularity and tremendous efforts owing to their merits of label-free, fast detection and low cost, compared with the well-established biochemical assay methods including enzyme-linked immunosorbent assay (ELISA), fluorescent detection, and chemiluminescent detection.^{45–47} However, most of demonstrated SERS substrates are on rigid and smooth glass slides or silicon wafers, which have fundamentally limited their usage for on-site analysis on real bio-samples with complex surfaces. On-site and *in-situ* SERS sensing still remains challenging.^{45–47}

Fig. 4a shows the basic procedure for rapid on-site and *in-situ* SERS assay. First, we transfer the nano-patterned photonic films onto the surfaces of real bio-samples (See Method for bio-sample preparations). Then a drop of ethanol is added to sample surface to extract the pesticide residue molecules and concentrate them on the gold nano-patterns. Then the sample is placed under objective lens directly for SERS detection. Fig. 4b shows a basil leaf covered with a piece of gold nano-patterned film shown as the dark yellow color covered region. The film is optically transparent, and the leaf veins can be clearly observed. As shown in the magnified micrograph, the flexible film is completely compliant with the 3D surface microstructures and the stomata below the film can also be clearly observed.

In this study, we take thiram as the analyte molecule. Thiram is a widely used pesticide that can lead to serious skin and eye illnesses, and carbon disulfide released from thiram can cause damage to the liver.⁴⁸ Thus, the detection of thiram on vegetables or fruits is of great practical significance. We first characterize the Raman band of thiram using planar SERS substrates (PC film, 125 μm ; gold film, 20 nm). The Raman spectra in Fig. S8 show several distinct peaks at 550 cm^{-1} , 1140 cm^{-1} , 1376 cm^{-1} and 1501 cm^{-1} , which are consistent with reported Raman peaks for thiram.⁴⁹ For the on-site and *in-situ* SERS measurement on real bio-samples, we only measure the strongest Raman band around 1376 cm^{-1} so as to shorten the detection time. The on-site Raman spectra (background subtracted) from basil leaves are shown in Fig. 4c. It is obvious that the minimum detectable surface concentration of thiram residue is slightly above 48 ng/cm^2 .

Similarly, the nano-patterned film is also transferred onto the surfaces of an apple, as shown in Fig. 4d. Quantitative assay results for thiram residues on apple peel are shown in Fig. 4e, which exhibits a much lower LOD of 0.48 ng/cm^2 . The dissimilar performance of the ultra-flexible photonic film on various bio-samples may arise from the differences in surface structures and tissue compositions.

Compared with other nano-patterning methods that are used for SERS sensing, our proposed method has the advantages of simple, cost-effective, high throughput and can produce ultra-thin photonic films for on-site and *in-situ* sensing. More importantly, this method has the potential of stretch for immediate use, which can avoid the chemical contamination during the traditional nano-fabrication process and the storage.

3. Conclusion

Large-area nano-patterning on flexible thermal plastic films through a simple stretching process is demonstrated. By varying the thickness of thin nano-film and the second mechanical stretching elongation, both size and arrangement of the nano-patterns can be well controlled. These nano-patterned films can enable a large variety of applications ranging from plasmonics to electronics. Taking gold nano-patterned film as an example, we have successfully fabricated plasmonic structures on PC films and adapted them as SERS substrates, owing to their strong SERS enhancement, high sensitivity, and good reproducibility. Furthermore, we demonstrate to extend this controllable lithography-free nanofabrication method for constructing ultra-thin and flexible photonic surfaces, which can be conformally and easily transferred onto various complex structured surfaces to form conformal on-site SERS sensors for the fast and reliable screening of pesticide residues. This simple, generic, and highly efficient nano-patterning method can be applied to various optical/electronic materials and even multi-material nano-films, and would enable a wide spectrum of applications especially in flexible photonics and electronics.

4. Experimental Section

4.1. Gold nano-film deposition.

Gold nano-films with different thicknesses are deposited on PC films (McMaster-Carr, 125 μm thick with smooth and glossy surfaces on both sides) using an E-beam evaporator (Cello Ohmiker-80) with a deposition rate of 0.5 $\text{\AA}/\text{s}$. The temperature in the vacuum chamber during the coating process are kept below 60° C to prevent the PC film from possible thermal expansion or deformation induced by build-in stress, which would result in defects or wrinkles in the gold film.

4.2. Tensile testing.

For the tensile test of 1D stretching, gold/PC film is cut into 1-cm wide stripes and tested using a house-made tensile testing setup (gold film, 50 nm; stretching speed, 0.02mm/s). To prepare the sample for 2D stretching, we first conduct 1D stretching using a piece of gold/PC film (width, 3 cm; gold film, 50 nm; stretching speed, 0.02mm/s). Then we cut the film

along y-direction into 1 cm-wide stripes to conduct 2D stretching and the tensile test.

4.3. 3D FDTD simulation.

3D models of the gold nano-patterns are extracted from SEM images. The grid of the mesh is set to be 2 nm. Unpolarised excitation laser with a wavelength of 785 nm is launched from z-direction. The modeling is carried out using a commercial software FDTD Solutions (Lumerical).

4.4. SERS detection of NT on planar substrates.

For SERS enhancement measurements, four kinds of SERS substrates with different thicknesses as well as the intact gold films which are used for control experiments are immersed into 50 μ M NT (Sigma) in ethanol solution (Sigma) for 30 mins, and then rinsed thoroughly with ethanol before SERS measurements. The Raman spectra are acquired using Renishaw equipment (wavelength of excitation laser, 785 nm; power level, 450 μ W; integration time, 10s; objective lens, 50 $\times$). To test the LOD and reproducibility, the excitation power is increased to 900 μ W, while other parameters keep the same.

4.5. Fabrication of ultra-flexible photonic films.

As shown in Fig. 3a, the fabrication process begins with spin-coating a poly(vinyl alcohol) (PVA) layer onto a 125 μ m-thick PC film substrate (PVA, Sigma, 8% aqueous solution; speed of spin-coating, 2000 r/min), followed by depositing a 20 nm-thick gold nano-film using E-beam evaporation. Sequentially, another PC nano-film is deposited on top of the gold film by spin-coating (8% PC solution in dimethylamide; speed of spin-coating, 2000 r/min). Then the multi-layered film is mounted on a stretching setup and goes through the 2D stretching procedure. The gold nano-film sandwiched between the PVA layer and the PC layer breaks into 2D nano-patterns. The multi-layered film is placed on the surface of the water with the ultra-thin PC film facing up. The PVA film gradually dissolves into water and eventually, the thick PC base detaches and the ultra-thin photonic film floats on the water surface. Then, the nano-scale ultra-flexible photonic film can be transferred to any surfaces by simply pressing against the thin film into water and the film adheres to the surface tightly and conformally.

4.6. SERS detection of thiram on planar substrates.

The substrates are immersed in thiram solution in ethanol with different concentrations ranging from 1 nM to 100 μ M for half an hour and rinsed thoroughly with ethanol. The Raman spectra are acquired using Renishaw equipment (wavelength of excitation laser, 785 nm; power level 900 μ W; integration time, 10s; objective lens, 50 $\times$).

4.7. Sample preparation for on-site SERS sensing.

For the sample preparation, basil and green apples purchased from a local supermarket are washed with DI water thoroughly. To simulate the pesticide contamination, we spray

5 μ L thiram (Sigma) in ethanol solution onto each piece of the basil leaves and apple peels and let them dry at room temperature. The prepared samples are incubated in a humid environment for 1 day to let the pesticides fully absorbed by the surface. Then the flexible SERS film is transferred onto the real bio-samples by pressing the peel against the thin film. And finally, the film is conformally and tightly attached to the complex peel surface with the gold nano-patterns facing outside. Before the on-site SERS detection, 10 μ L of ethanol is added to the flexible film covered sample to extract the pesticide residues from the surface^{50,51} and let it dry naturally to concentrate the pesticide residues onto the ultra-flexible photonic film. The concentration process is illustrated in Fig. 4a. The Raman spectra are acquired using Renishaw equipment (wavelength of excitation laser, 785 nm; power level 900 μ W; integration time, 10s; objective lens, 50 $\times$).

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgments

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References

- 1 T. R. Jensen, M. D. Malinsky, C. L. Haynes and R. P. Van Duyne, *J. Phys. Chem. B*, 2000, **104**, 10549–10556.
- 2 Z. Liu, *Nat. Commun.*, 2017, **8**, 14910.
- 3 K. Li, T. Zhang, G. Liu, N. Zhang, M. Zhang and L. Wei, *Appl. Phys. Lett.*, DOI:10.1063/1.4961981.
- 4 N. Zhang, G. Humbert, T. Gong, P. P. Shum, K. Li, J. L. Auguste, Z. Wu, D. J. J. Hu, F. Luan, Q. X. Dinh, M. Olivo and L. Wei, *Sensors Actuators, B Chem.*, 2016, **223**, 195–201.
- 5 Y. Sun, W. M. Choi, H. Jiang, Y. Y. Huang and J. A. Rogers, *Nat. Nanotechnol.*, 2006, **1**, 201–207.
- 6 A. Zhang and C. M. Lieber, *Chem. Rev.*, 2016, **116**, 215–257.
- 7 A. M. Stolyarov, L. Wei, F. Sorin, G. Lestoquoy, J. D. Joannopoulos and Y. Fink, *Appl. Phys. Lett.*, DOI:10.1063/1.4733319.
- 8 L. Wei, T. T. Alkeskjold and A. Bjarklev, *Appl. Phys. Lett.*, DOI:10.1063/1.3455105.
- 9 L. Wei, W. Xue, Y. Chen, T. T. Alkeskjold and A. Bjarklev, *Opt Lett*, 2009, **34**, 2757–2759.
- 10 J. Weirich, J. Laegsgaard, L. Scolari, L. Wei, T. T. Alkeskjold and A. Bjarklev, *Opt. Express*, 2009, **17**, 4442–4453.
- 11 S. Donthu, Z. Pan, B. Myers, G. Shekhawat, N. Wu and V. David, *Nano Lett.*, 2005, **5**, 1710–1715.

- 12 M. J. Cryan, M. Hill, D. C. Sanz, P. S. Ivanov, P. J. Heard, L. Tian, S. Yu and J. M. Rorison, *IEEE J. Sel. Top. Quantum Electron.*, 2005, **11**, 1266–1276.
- 13 C. M. Sotomayor Torres, S. Zankovych, J. Seekamp, a. P. Kam, C. Clavijo Cedeño, T. Hoffmann, J. Ahopelto, F. Reuther, K. Pfeiffer, G. Bleidiessel, G. Gruetzner, M. V. Maximov and B. Heidari, *Mater. Sci. Eng. C*, 2003, **23**, 23–31.
- 14 B. J. Wiley, D. Qin and Y. Xia, *ACS Nano*, 2010, **4**, 3554–3559.
- 15 W. Lee, R. Ji, U. Gösele and K. Nielsch, *Nat. Mater.*, 2006, **5**, 741–747.
- 16 H. Masuda and K. Fukuda, *Science (80-.)*, 1995, **268**, 1466–1468.
- 17 C. Mu, Y. Yu, R. Wang, K. Wu, D. Xu and G. Guo, *Adv. Mater.*, 2004, **16**, 1550–1553.
- 18 S. Zhao, H. Roberge, A. Yelon and T. Veres, *J. Am. Chem. Soc.*, 2006, **128**, 12352–12353.
- 19 J. C. Hulteen and R. P. Van Duyne, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.*, 1995, **13**, 1553–1558.
- 20 K. Efimenko, M. Rackaitis, E. Manias, A. Vaziri, L. Mahadevan and J. Genzer, *Nat. Mater.*, 2005, **4**, 293–297.
- 21 S. Lin, E. K. Lee, N. Nguyen and M. Khine, *Lab Chip*, 2014, **14**, 3475–3488.
- 22 E. P. Chan and A. J. Crosby, *Adv. Mater.*, 2006, **18**, 3238–3242.
- 23 P. Kim, Y. Hu, J. Alvarenga, M. Kolle, Z. Suo and J. Aizenberg, *Adv. Opt. Mater.*, 2013, **1**, 381–388.
- 24 K. H. Nam, I. H. Park and S. H. Ko, *Nature*, 2012, **485**, 221–224.
- 25 M. Kim, D. Ha and T. Kim, *Nat. Commun.*, 2015, **6**, 6247.
- 26 J. Parra-Barranco, M. Oliva-Ramirez, L. Gonzalez-Garcia, M. Alcaire, M. Macias-Montero, A. Borrás, F. Frutos, A. R. Gonzalez-Elipé and A. Barranco, *ACS Appl. Mater. Interfaces*, 2014, **6**, 11924–11931.
- 27 Z. Li, Y. Zhai, Y. Wang, G. M. Wendland, X. Yin and J. Xiao, *Adv. Opt. Mater.*, DOI:10.1002/adom.201700425.
- 28 X. Zhu, K. L. Mills, P. R. Peters, J. H. Bahng, E. H. Liu, J. Shim, K. Naruse, M. E. Csete, M. D. Thouless and S. Takayama, *Nat. Mater.*, 2005, **4**, 403–406.
- 29 D. Huh, K. L. Mills, X. Zhu, M. A. Burns, M. D. Thouless and S. Takayama, *Nat. Mater.*, 2007, **6**, 424–428.
- 30 S. Shabahang, G. Tao, J. J. Kaufman, Y. Qiao, L. Wei, T. Bouchenot, A. P. Gordon, Y. Fink, Y. Bai, R. S. Hoy and A. F. Abouraddy, *Nature*, 2016, **534**, 529–533.
- 31 Z. Zheng and D. Feldman, *Prog. Polym. Sci.*, 1995, **20**, 185–210.
- 32 B. D. Coleman, *Comput. Math. with Appl.*, 1985, **11**, 35–65.
- 33 P. I. Vincent, *Polymer (Guildf.)*, 1960, **1**, 7–19.
- 34 N. Kooy, K. Mohamed, L. T. Pin and O. S. Guan, *Nanoscale Res. Lett.*, 2014, **9**, 1–13.
- 35 Y. Wang, P. Kanjanaboos, E. Barry, S. McBride, X. M. Lin and H. M. Jaeger, *Nano Lett.*, 2014, **14**, 826–830.
- 36 P. H. C. Camargo, M. Rycenga, L. Au and Y. Xia, *Angew. Chemie - Int. Ed.*, 2009, **48**, 2180–2184.
- 37 M. Rycenga, M. R. Langille, M. L. Personick, T. Ozel and C. A. Mirkin, *Nano Lett.*, 2012, **12**, 6218–6222.
- 38 W. Zhu and K. B. Crozier, *Nat. Commun.*, 2014, **5**, 5228.
- 39 A. N. Severyukhina, B. V. Parakhonskiy, E. S. Prikhozhdenko, D. A. Gorin, G. B. Sukhorukov, H. Möhwald and A. M. Yashchenok, *ACS Appl. Mater. Interfaces*, 2015, **7**, 15466–15473.
- 40 T. Jiang, X. Wang, S. Tang, J. Zhou, C. Gu and J. Tang, *Sci. Rep.*, 2017, **7**, 9795.
- 41 X. Shen, T. J. Cui, D. Martin-Cano and F. J. Garcia-Vidal, *Proc. Natl. Acad. Sci.*, 2013, **110**, 40–45.
- 42 T. Yokota, P. Zalar, M. Kaltenbrunner, H. Jinno, N. Matsuhisa, H. Kitanosako, Y. Tachibana, W. Yukita, M. Koizumi and T. Someya, *Sci. Adv.*, 2016, **2**, e1501856–e1501856.
- 43 S. Aksu, M. Huang, A. Artar, A. A. Yanik, S. Selvarasah, M. R. Dokmeci and H. Altug, *Adv. Mater.*, 2011, **23**, 4422–4430.
- 44 L. Li, H. Lin, S. Qiao, Y. Zou, S. Danto, K. Richardson, J. D. Musgraves, N. Lu and J. Hu, *Nat. Photonics*, 2014, **8**, 643–649.
- 45 A. P. Craig, A. S. Franca and J. Irudayaraj, *Annu. Rev. Food Sci. Technol.*, 2013, **4**, 369–380.
- 46 P. Kumar, K.-H. Kim and A. Deep, *Biosens. Bioelectron.*, 2015, **70**, 469–481.
- 47 S. Pang, T. Yang and L. He, *TrAC - Trends Anal. Chem.*, 2016, **85**, 73–82.
- 48 Q. Wang, D. Wu and Z. Chen, *RSC Adv.*, 2015, **5**, 70553–70557.
- 49 Y. Zhang, Z. Wang, L. Wu, Y. Pei, P. Chen and Y. Cui, *Analyst*, 2014, **139**, 5148–5154.
- 50 Y. Zhang, Z. Wang, L. Wu, Y. Pei, P. Chen and Y. Cui, *Analyst*, 2014, **139**, 5148–5154.
- 51 H. B. Wan, M. K. Wong, P. Y. Lim and C. Y. Mok, *J. Chromatogr. A*, 1994, **662**, 147–152.

Fig 1. Fabrication and characterization of gold nano-patterns. (a) Schematic illustration showing the fabrication process of metallic micro/nano-patterns on flexible substrates through two-step mechanical stretching. (b) Photograph of a centimeter-scale flexible photonic surface fully covered with gold nano-patterns fabricated by 2D stretching. (c) and (d) Stress-strain curves for the gold/PC film composite in 1D and 2D stretching processes, respectively. (e) SEM images of the gold patterns at different stages of 2D stretching (thickness of gold film, 30 nm). (f) Average width of the gold stripes fabricated by 1D stretching as a function of gold film thickness. (g) Average length of the gold patterns at different stages of 2D stretching. (h) SEM images of the 2D gold patterns with different thicknesses (strain, 152%). Scale bars: (e) 2 μm ; (h) 1 μm ; inset picture, 100 nm.

Fig. 2 Surface-enhanced Raman scattering performance. (a) Simulated electromagnetic near field distribution of the gold nano-patterns showing strong E-field enhancement (thickness of gold film, 20 nm; wavelength, 785 nm; scale bar, 100 nm). (b) SERS spectra of NT for gold nano-patterns with different thicknesses. (c) Raman intensities of Raman peaks at 1065 cm^{-1} , 1379 cm^{-1} and 1618 cm^{-1} for gold nano-patterns with different thicknesses. (d) Peak intensity at 1379 cm^{-1} and 1618 cm^{-1} as a function of NT concentration (thickness of gold film, 20 nm). Inset: SERS spectra of NT at concentrations ranging from 1 pM to 100 nM. (e) SERS spectra of NT (100 pM) acquired from 20 random sites on a 20 nm-thick SERS substrate. (f and g) The corresponding bar charts for the peak intensity at 1379 cm^{-1} and 1449 cm^{-1} from the 20 random sites.

Fig. 3 Fabrication of ultra-flexible photonic films and coating the ultra-flexible photonic film onto curved surfaces. (a) Schematic illustration of the fabrication of ultra-flexible photonic film and the transfer process onto a leaf. (b) SEM image of the ultra-flexible photonic film which is transferred onto a flat silicon chip. (c) AFM image with line profile of the ultra-flexible photonic film which is transferred onto a flat silicon chip. (d) Optical micrographs of optical fibers with different diameters that are coated with ultra-flexible nano-patterned film. Scale bars: (b) 1 μm; (c) 1 μm; (d) upper micrograph: 100 μm, bottom micrograph: 200 μm.

Fig. 4 Ultra-flexible and conformal gold nano-patterned film for on-site SERS sensing. (a) Schematic illustration showing the process of on-site SERS sensing. (b) Photography of a basil leaf coated with an ultra-flexible gold nano-patterned film and micrograph of the surface morphology. (c) On-site SERS spectra acquired using ultra-flexible gold nano-patterned films from basil leaves with different concentrations of thiram residue (background subtracted). (d) Photography of an apple covered with an ultra-flexible gold nano-patterned film and micrograph of the surface morphology. (e) On-site SERS spectra acquired using ultra-flexible gold nano-patterned films from apple peels with different concentrations of thiram residue. Scale bar: (b) 50 μm ; (d) 100 μm .