



Fabrication of Ultrafine Soft-Matter Arrays by Selective Contact Thermochemical Reaction

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Patterning of functional soft matters at different length scales is important for diverse research fields including cell biology, tissue engineering and medicinal science and the development of optics and electronics. Here we have further improved a simple but very efficient method, selective contact thermochemical reaction (SCTR), for patterning soft matters over large area with a sub-100 nm resolution. By selecting contact between different precursors through a topographically patterned PDMS stamp and subsequently any heating way for thermalchemical reaction, thermal-related soft matters can be patterned to form controllable micro or nano structures, even three-dimensional structures. The fine tunability and controllability of as-prepared micro and nano structures demonstrate this versatile approach a far wide range of uses than the merely academic.

Fabrication of well-ordered soft-matter-based micro and nano structures over large area has drawn great interests in recent years due to their increasing applicability in polymer electronics¹, soft machines², flash memory, chemical and biosensors^{3–5}, particularly biological applications such as tissue-engineering⁶, surface modification^{7,8} and microfluidics⁹. Owing to the importance associated with the soft-matter-based micro and nano structures, numerous conventional experimental methods have been developed to date to fabricate the pattern of functional soft-matters, such as photolithography¹⁰, inkjet printing¹¹, direct-laser writing¹², dip-pen and polymer pen lithography^{13–15}. Although these techniques are mature for use in microelectronics and contributed important roles in modern digital life for the high density of integration, less power consumption and good performances, they do have some limitations, such as high operational costs from the high-priced equipment and clean room demanding processes, incompatibility with curved surfaces, poor suitability for three-dimensional (3D) fabrication, little or no control over surface chemistry and exclusive application in the direct patterning of a limited set of functional materials¹⁶. These limitations have created substantial interest in exploring unconventional fabrication approaches, such as those based on certain types of contact printing, molding, embossing, and writing¹⁷. Soft lithography¹⁸, as an umbrella term for a set of known unconventional methods, shows powerful vitality in preparing well-ordered micro and nano structures of soft matter.

Among the emerging in recent years, many outstanding characteristics especially low-cost, easy manipulation and high universality reveal soft lithography a full-blown application future. As the forerunner of soft lithography, microcontact printing (μ CP)¹⁹ provides an attractive route for in-situ fabrication soft-matter patterns based on elastomeric stamps, typically poly(dimethylsiloxane) (PDMS). Generally speaking, μ CP offers an ability to engineer the properties of surfaces²⁰, pattern onto curved or elastomeric substrates²¹ and easy to establish 3D structures²². Following the in-depth study of μ CP, researchers have focused their efforts on modifying this method to match the demands of functional microdevices by changing inks, substrate materials, transfer procedures and further pattern-induced reactions in or after transfer procedure²³. For example, rigid film have been used in modified- μ CP which named nano transfer printing (nTP) and nano transfer edge printing (nTEP) for patterning of zero-dimensional or one-dimensional soft-matters^{24,25}. Meanwhile, different chemical reactions have been introduced in contact process for patterning of functional materials especially polymers such as “double-click” chemistry²⁶, surface-initiated atom-transfer radical polymerization (ATRP)²⁷.



In our previous study, we introduced hydrogel stamps and contact etching into μ CP for fabricating thin, electrically conductive metal films on the sidewalls of relief patterns on PDMS stamps, and subsequently used these PDMS edged stamps to generate conducting polymer nanowires on solid substrates²⁸. We also used metal-coated PDMS stamps as patterned electrodes for fabricating functional polymer micro/nano arrays through a combination of μ CP and electric-field-induced polymerization⁴. Furthermore, we have introduced the concept of heat and energy^{7,29–32} into μ CP to get broad applicable fields for the widespread thermal reactions. Comparing to conventional micro or nanolithographies, these μ CP techniques have the unique advantage of enabling larger area patterning of soft-matters at low cost but easy manipulation. Actually, most of these patterns have been demonstrated great potential in the manufacturing of flexible electronics, optical devices and other microdevices. All these achievements about μ CP are aimed to universality and industrial possibility.

Although these μ CP techniques show valuable characteristics for the patterning of soft matter or other functional materials, one common flaw still prevents them from broader application: the using materials suffer some restrict in the relevant techniques for further industrialized production. Even the simple hot- μ CP process²⁹, we have further improved for patterning soft matter, would be used only relevant to rapid thermal chemical reaction. Herein, we propose a novel and simple idea, selective contact thermochemical reaction (SCTR), for soft-matter patterning. By selecting contact between different reaction mixtures through a topological PDMS stamp and subsequently heating up, thermal-related soft-matters can be patterned to form controllable micro or nano structures.

Results

Figure 1 illustrates the general procedure to fabricate the micro or nano patterns by SCTR. Firstly, we have prepared a PDMS stamp with topography preliminarily determined by photolithography.

PDMS stamp was plasma-treated and subsequently dip-coated a precursor film on the surface, until a thickness of approximately 100 nm is reached. Meanwhile, another precursor thin film (~ 100 nm) was spin-coated onto a plasma-treated silicon substrate. Secondly, the PDMS stamp is placed on top of the second precursor thin film that is supported by the silicon wafer, and this system was then heated to a certain temperature. Upon imposing an appropriate temperature and time, the area of these two films that are in direct contact between PDMS and silicon wafer are thermochemically crosslinked, while the rest of the thin films without contact are left in a non-crosslinked state. After peeling and developing the film with an appropriate solvent, the crosslinked part of the film is left on the silicon wafer, and produces an expected pattern. Otherwise, utilizing the tunable size-reduction effect, we got thermochemical patterning through wrinkled PDMS stamps, as shown in Figure 1d–f. In this procedure, thin gold films are rapidly deposited onto a heated PDMS stamps by means of magnetic sputtering for fabricating wrinkles on the surface of PDMS stamp⁷.

There are several factors to determine the shape and size of as-prepared ultrafine soft-matter arrays. As shown in figure 1a–c, the microscopic shapes of the ultrafine structures are incontestably determined by PDMS stamp, the same as typical nTP and other soft lithography process, successor to the oft-photolithography original. Whereas, the structures are not just determined by PDMS stamp when introducing the concept of wrinkle as shown in figure 1d–f. The morphology of wrinkles on the PDMS surface controls the contact areas for thermal reactions. The contact time and developing time also affect the defect rates of patterns. Finally, when the features of PDMS stamp are small enough (less than or close to the size of wrinkles), together with the wrinkles generates between them, is also the influence factor towards the final nanostructures.

Figure 2 shows a set of scanning electron microscopy (SEM) images of as-prepared ultrafine structures with polymer as soft matter. Figure 2a shows a complex array realizing from our design,

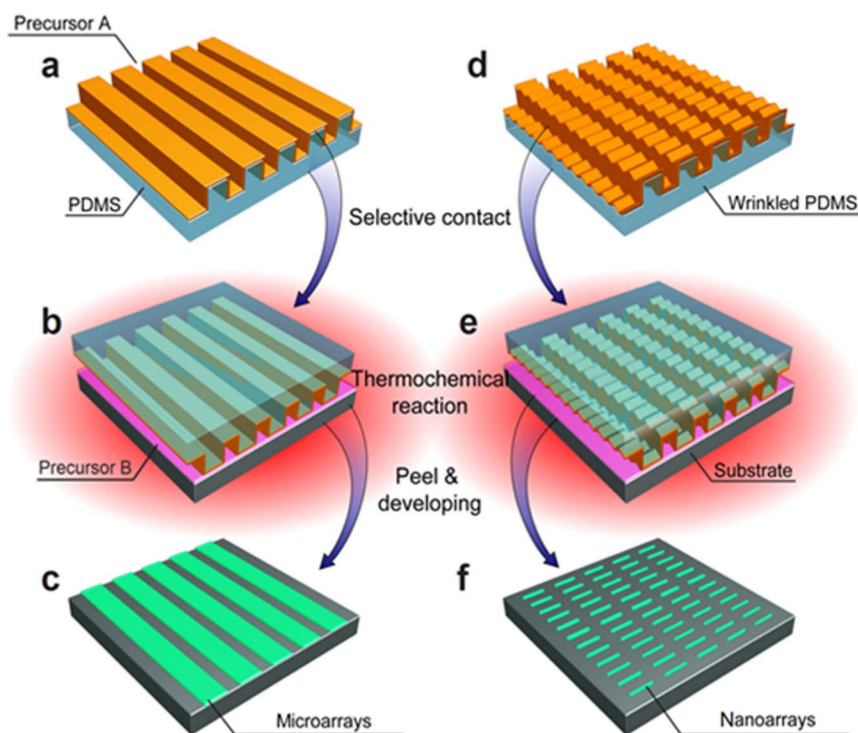


Figure 1 | Schematic illustration of the patterning of soft-matter thin films using SCTR. (a) Dip-coating of a precursor film on the plasma-treated PDMS stamp. (b) Placing the PDMS stamp on top of the second precursor thin film (spin-coated on the plasma-treated silicon wafer). (c) Developing the non-crosslinked part of the polymer thin film on the Si wafer to generate the final pattern. (d) Dip-coating of a precursor film on the plasma-treated wrinkled PDMS stamp. (e) Contacting two substrates for SCTR. (f) Developing the non-crosslinked part of the thin film for fabricating nanoarrays.

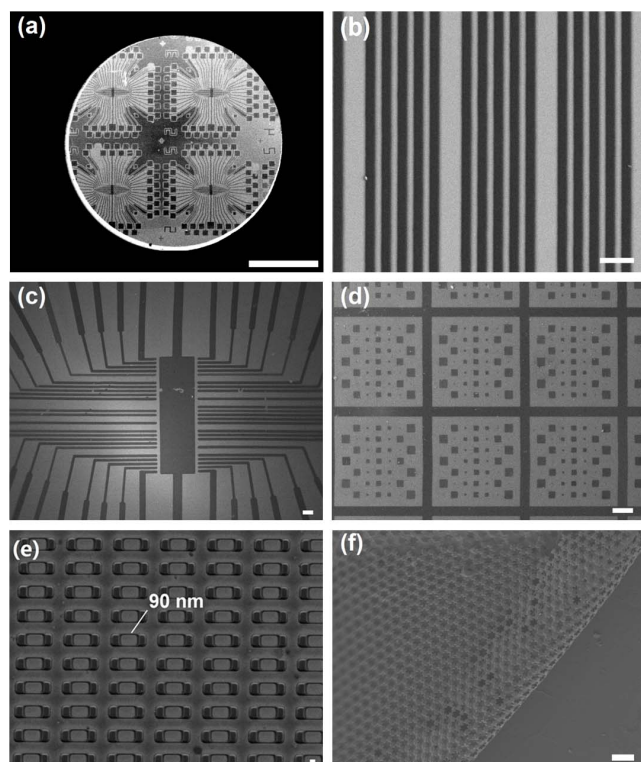


Figure 2 | SEM images of as-prepared polymer microstructures after SCTR. (a) Large-area polymer microstructures. (b–d) SEM images of polymer arrays exhibiting a range of geometries on the silicon substrates. Dark and bright areas correspond to the polymer film and the bare silicon wafer, respectively. (e) SEM images of polymer nanoarrays. (f) Free-standing polymer thin film with ultrafine structures. Scale bars: (a) 1 mm, (b–d) 10 μm , (e) 500 nm, (f) 10 μm .

which demonstrates the ability of this method for large-area fabrication. Meanwhile, various geometries of polymer microstructures were obtained by using a range of PDMS stamps with different features. In these results, the shape and spacing of the metal nanostructures are determined by the PDMS stamp, no matter the array scale is uniform or not. Figure 2a–e show a series of microarrays composed of different microstructures ranging from 100 μm to sub-100 nanometers (as shown in Figure 2e). Furthermore, a plasma-treated silicon wafer with 3–5 nm SiO_2 was used to replace the silicon wafer and finally etched the SiO_2 thin film after the SCTR to generate free-standing polymer micro/nano structures, as shown in Figure 2f.

Figure 3 shows the results of the wrinkled PDMS stamps and the fabricated polymer patterns via introducing these wrinkled stamps in SCTR. For fabricating wrinkles, the PDMS stamp (with its flat face adhered to glass) is heated in the vacuum chamber of a sputtering instrument, and subsequently sputter 2 nm thick titanium film and 50 nm gold film on the surface. The heat expands the PDMS surface during sputter processing, and after cooling to room temperature highly regular structures with good periodicity are spontaneously generated on top of the PDMS stamp, as shown in Figure 3a. The wrinkles are of good periodicity (around 1 μm), with a depth of approximately 400 nm. Figure 3b show the corresponding periodic polymer nanoarrays fabricated by SCTR using wrinkled PDMS stamps. The thermochemical reaction just occurs in the contact area, the crest of each wrinkle. Figure 3c shows the result of SCTR through the using of PDMS stamp with small enough features (close to the size of wrinkles) and wrinkles on the surface at the same time. Obviously, when the scale of the structures goes down to the wrinkle scale (around 1 μm or sub-micrometer), wrinkles only formed in the

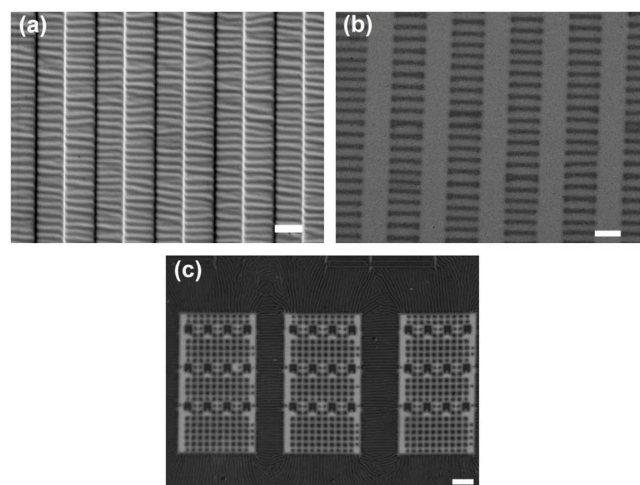


Figure 3 | SEM images of the wrinkled PDMS stamps and the polymer patterns via introducing these wrinkled stamps into SCTR. (a) Metal-coated PDMS stamp with wrinkle patterns. (b) The corresponding polymer nanostructures produced using the PDMS stamp with periodic wrinkles on the surface shown in Figure 3a. (c) The polymer nanostructures after SCTR through the using of PDMS stamp with small enough features and wrinkles on the surface at the same time. Scale bar: 5 μm .

interspace, not on the surface of structures. The responding results exhibited as Figure 3c shows the potential adjustment of nano or sub-micrometer polymer structures through the control of wrinkle's formation.

Discussion

The highly regular polymer structures with good periodicity that are shown in the figures are of interest for potential applications in microelectronics, optical sensors, diffraction gratings, surface modification and building blocks for three-dimensional (3D) patterning. Herein, we demonstrate a simple further study on the fabrication of 3D polymer microstructures which play important roles in surface modification, tissue engineering, and cell research. This step doesn't need any other equipment, further design or sophisticated control. Just through the repeat of precursor-coating, contact reaction, and subsequently developing, the 3D polymer microstructures can easily

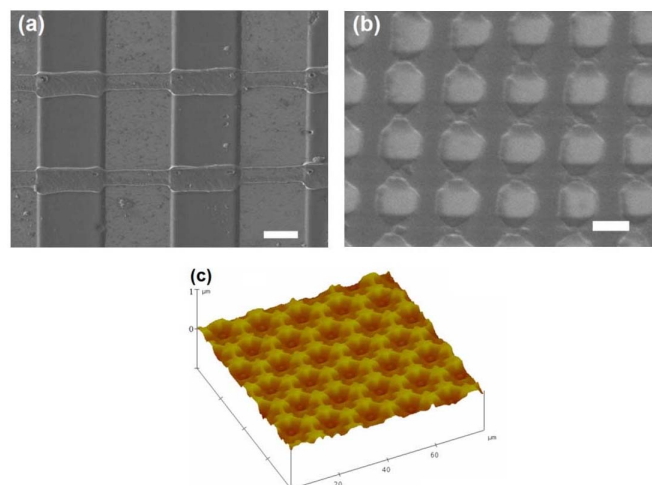


Figure 4 | (a,b) SEM images show the as-prepared 3D polymer microstructures. Scale bar: 5 μm . (c) AFM image shows the as-prepared 3D polymer microstructures.



realized. Figure 4 a–c show the multilayer polymer microstructures with different morphology of each layer, respectively. Meanwhile, we developed this method for fabricating of ultrafine arrays with nanoparticles or quantum dots as soft-matters. Through dissolving of 0.5 mM AgNO_3 in the precursor, reducing and calcining at 400°C after SCTR procedure, silver nanoparticle microarrays can be carried out as shown in Figure 5a–c, with shapes in keeping with the original PDMS stamp. Figure 5 d–f show the quantum-dot/polymer composite microarrays on silicon substrates through dispersing quantum dots (1 mM) in the precursor at the beginning.

Furthermore, we demonstrate another two applications of as-fabricated polymer microstructures: direct using in grating preparation and modification of the wetting behavior of a surface. Figure 6a and b show the morphology and magnified view of a polymer grating with sub-micro resolution, which shows up yellow under CCD camera. Figure 6d and e show the shape of a water droplet on a smooth film and a film exhibiting periodic polymer structures (as shown in Figure 3b). The contact angles were measured to be 33.5° and 24.2° , respectively. This result suggests the tunability about wettability of surfaces via controlling the surface morphology, which is full agreement with previous experimental observations and theoretical predictions^{7,33}. The result also indicates the possibility of superhydrophilicity through chemical modification of as-fabricated micro-/nanostructured surfaces.

In summary, this communication demonstrates a universal method for fabricating ultrafine arrays of soft-matters such as polymer, nanoparticle and quantum dot through selective contact controlled thermochemical reaction. Such functional polymer structures can be achieved by means of selecting contact of different precursors through a topological PDMS stamp, followed by heating up in any form to induce the thermochemical reaction, and developing in the last to finish the patterning step. Through the design of appropriate wrinkled PDMS stamps, it also can fabricate soft-matter structures with periodic patterns or complex nanoscaled features with tunable size-reduction effect. Besides inheriting the advantages of soft lithography such as low-cost, inexpensive, simple, large area fabricating and accessible for general users, this strategy has the following exceeding advantages: (i) It can form polymer structures with sizes down to 100 nanometers which are difficult by using other techniques. (ii) It is possible to fabricate the nanostructures onto a soft substrate (especially PDMS), as shown in Figure 6a and b. (iii) By designing appropriate precursors, it is possible to fabricate nanostructures not limited to PAA-PVA, PVPH-MMF, PF-HMMM (detailed in the part of Methods) and other thermal-crosslinking

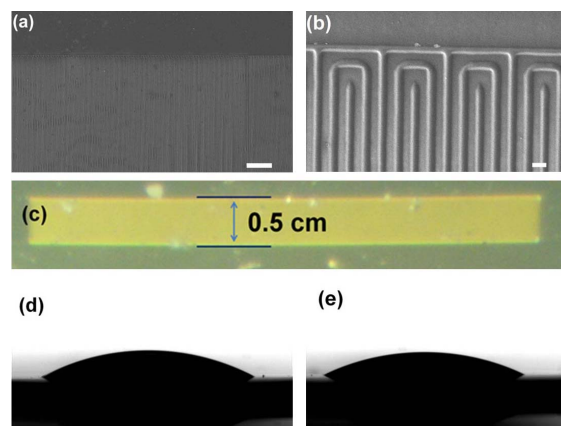


Figure 6 | (a,b) SEM images of the polymer grating on PDMS substrates. Scale bars: (a) 20 μm , (b) 1 μm . (c) The output of this polymer grating with a CCD camera. (d,e) Shape of a water droplet on the surface of a smooth polymer film (d) and a film exhibiting periodic polymer structures (as shown in Figure 3b). Their contact angles were measured to be 33.5° and 24.2° respectively.

polymer, thermo-degradation polymer, thermal decomposition polymer or other thermo-related polymers are also suitable for our methods. (iv) The method is cost-effective since the polymer pattern is readily made with a PDMS mold without any requirements of expensive infrastructure. These advantages make this versatile approach, as a new step of the industrialization for soft lithography, very useful in manufacturing next-generation soft-matter-based microdevices ranging from photonics, chemical and biosensors, biotechnology and microelectronics.

Methods

Fabrication of wrinkled PDMS stamps. PDMS was purchased from Dow Corning. Soft lithography and rapid prototyping were used to fabricate features in SU-8 (Micro-Chem Corp.), which were subsequently replica-molded using a PDMS prepolymer to fabricate the flexible stamps. The stamps obtained were coated with 2 nm-thick layer of Ti and 20–100 nm-thick layer of Au. Au-film deposition by means of magnetic sputtering at 180°C and 2 nm s^{-1} achieved a wrinkled PDMS stamp.

Fabrication of soft-matter microstructures on Si wafer. Polyacrylic acid (PVA, $M_w \sim 10,000$), polyacrylic acid (PAA, $M_w \sim 2,000$) Poly(vinylphenol) (PVPh) and methylated poly(melamine-co-formaldehyde) (MMF) were purchased from Aldrich. Phenol-formaldehyde resin (PF) and hexamethoxy methyl melamine (HMMM) were

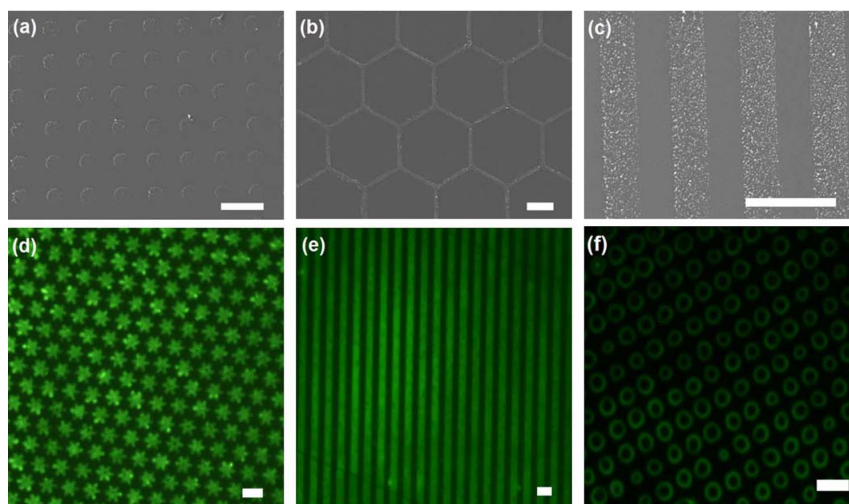


Figure 5 | (a–c) SEM images of the silver nanoparticle microarrays from SCTR. Scale bar: 5 μm . (d–f) Optical images of the quantum dot/polymer microstructures. Scale bar: 10 μm .



purchased from Sinopharm Chemical Reagent Beijing Corporation. Silicon wafers were treated with 30% H₂O₂ + 70% H₂SO₄ and washed with deionized water. PVA powder (1.0 g) was added into deionized water (100 mL) and then heated steadily to ≈85°C with vigorous stirring until the solution became clear. The resulting solution was then spin-coated at 2000 rpm to form a thin film on a fresh treated silicon wafer. PAA solution (5 mg mL⁻¹) was dip-coated onto a plasma-treated PDMS stamp. As the parallel experiments, 10 mg mL⁻¹ PVPh ethanol solution was spin-coated at 2500 rpm on a fresh treated silicon wafer; 5 mg mL⁻¹ MMF ethanol solution was dip-coated onto a plasma-treated PDMS stamp; 12 mg mL⁻¹ PF in N,N-dimethylformamide (DMF) and ethanol (Volume ratio, 5:1) solution was spin-coated at 3000 rpm on a fresh treated silicon wafer; mixture of 3 mg mL⁻¹ HMMM and 0.03 mg mL⁻¹ diphenyliodonium hexafluorophosphate was dip-coated onto a plasma-treated PDMS stamp. And then both silicon wafer and PDMS stamp were semi-dried at 40°C. After cooling, these two parts were brought into conformal contact and put into a vacuum oven containing 5 mL water. After heating under vacuum at 50°C for 6 h, the whole system was then warmed to 100°C and maintained for 2 h (at a heating rate of 5°C min⁻¹, also 120°C/2 h, 180°C/2 h and 250°C/2 h as parallel experiments). The vacuum oven was degassed again and cooled down to room temperature. Finally, the silicon wafer was separated from PDMS stamp and washed to achieve the polymer microstructures. Crosshatched polymer microarrays were obtained by sequential repeat these processes.

Measurement of water contact angles. Contact angles were measured using a Dataphysics OCA20 contact-angle system at room temperature. Water droplets (2 mL) were placed onto smooth polymer surfaces or polymer patterns in order to conduct measurements of the wetting behavior.

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Author contributions

M.Q.X. initiated the project, conceived and supervised the experiments, analyzed the data and wrote the paper. X.C., M.Q.X. prepared the samples, carried out the SEM measurements. Y.W., X.W.W., J.H.J., J.H., F.P. provided assistance with the SEM, AFM and optical measurement. J.T.C. initiated the project, conceived the experiments.

Additional information

Competing financial interests: The authors declare no competing financial interests.

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