Polymerization-Induced Growth of Microprotuberance on the Photocuring Coating

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Supporting Information

ABSTRACT: Surface pattern on the nano- and microscale is of great interest due to its special optical effect, which might find potential application in optical devices such as LCD display, packaging of LED chip, and thin-film solar cell. We here developed a facile bottom-up approach to fabricate microprotuberance (MP) on surface by using curable resin via sequential photocuring at room temperature and thermal polymerization at high temperature. The curable resin is composed of random fluorinated polystyrene (PSF) as binder and trimethylolpropane trimethacrylate (TMPTA) as cross-linker. The polymerization of TMPTA during the annealing process at high temperature induces phase separation between the PSF and TMPTA cross-linked network, resulting in the extrusion of PSF and the formation of protuberance on the surface. The formation mechanism of MP was studied in detail by investigating the effect of annealing time, temperature, thickness of film, and PSF on the size and morphology. MPs with size from one to tens of micrometers were fabricated through this one-pot strategy. Moreover, encapsulation of integrated GaN/InGaN-based LED chip by the cross-linked coating with MP can enhance the light extraction efficiency and light diffusion obviously.

INTRODUCTION

Microprotuberances (MPs) are widely found in the compound eyes of insects1-3 and echinoderms.4,5 Artificial protuberances such as microlens have various applications in photovoltaic devices,6-8 antireflective coatings,9 diffusers,10 and artificial compound eyes.3,11,12 In general, there are two common methods to fabricate structured surface patterns: top-down and bottom-up methods.3,14 Numerous artificial top-down strategies have been used to fabricate micropatterned surface, such as laser ablation,15 ion-beam milling,16 thermal reflow,17 imprinting method,18 droplet method,19 controlled dewetting of polymer films20,21 and confining wrinkling.22 All of these techniques demonstrate the ability to fabricate well-defined nano- and micropatterns with the desired functions, but they involve multiple complex fabricating steps.

In contrast, a bottom-up strategy in biological systems has been adopted to hierarchically structure molecules to meter-scale biological organisms.14 Inspired from the biological systems, over the past decade, the concepts of self-assembling and self-organization of artificially designed molecules provide an alternative method to make a structured surface over large areas through bottom-up approaches.23-26 The bottom-up strategy involves fewer fabricating steps than does the top-down strategy, which is usually time-saving, low cost, and convenient and thus more compatible to the operation process. However, there are few reports on using the bottom-up strategy to fabricate the structured surface with MP. Zhang et al. fabricated microlens by generating highly ordered arrays of microdroplets on a prepatterned substrate through a nucleation and growth process.25 Through the established protocol of the solvent exchange, they also fabricated the polymeric nanolenses by the photocuring of nanodroplets.26

To obtain the MP through a simple and robust way, we here developed a complete bottom-up approach to fabricate MP by using curable resin via sequential photono- and thermal polymerization (Figure 1). The UV irradiation quickly makes the film pre-cross-linked at room temperature, and the following annealing at the high temperature makes the polymerization and self-organization, which might affect of the resulting MP. To the best of our knowledge, this is the first bottom-up approach to fabricate MP by polymerization and self-organization, which might find potential application in optical devices. Finally, LED chip was packaged by this cross-linked coating with MP, and its light extraction efficiency (LEE) and light diffusion can be enhanced obviously.

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The curable resin is composed of commercial trimethylolpropane trimethacrylate (TMPTA) as cross-linker and random fluorinated copolymer (PSF) as PREP. Because of its three acrylate groups and low molecular weight, polymerization of TMPTA can lead to the high cross-linking density of the resulting network. Polystyrene (PS) was chosen as polymer backbone because of its ability of phase separation in the network of cross-linked TMPTA and the relative low surface energy. The introduction of fluorocarbon chains to PS can further lead to the lower surface energy. The thickness of PSF/TMPTA film is 7 μm.

RESULTS AND DISCUSSION

Fabrication of MP by Polymerization. As to selecting the chemistry and materials to fabricate MP, we took a variety of physical and chemical features into consideration (Figure 1). The curable resin is composed of commercial trimethylolpropane trimethacrylate (TMPTA) as cross-linker and random fluorinated copolymer (fluorinated polystyrene (PSF)) as matrix. Because of its three acrylate groups and low molecular weight, polymerization of TMPTA can lead to the high cross-linking density of the resulting network. Polystyrene (PS) was chosen as polymer backbone because of its ability of phase separation in the network of cross-linked TMPTA and the relative low surface energy. The introduction of fluorocarbon chains to PS can further lead to the lower surface energy. PS containing different content of fluorocarbon chain was synthesized by the random radical polymerization (Figures S1 and S2).

The whole strategy for fabricating MP is illustrated in Figure 1. In a typical experiment, the toluene solution of PSF and TMPTA (the mass ratio of PSF/TMPTA is 1/1), with a trace amount of photoinitiator I907, was spin-coated onto the substrate. After evaporation of the solvent, the curable layer of PSF and TMPTA was irradiated with UV light at room temperature to form the pre-cross-linked film. It should be noted that there is still a considerable amount of unreacted acrylate groups because the UV-curing reaction caused the solidification of the TMPTA phase and the dramatic decrease in TMPTA mobility, which prevented the further reaction of acrylate groups. The resulting UV-cured film was then annealed at 180 °C for 20 min, and its surface morphology was revealed by optical microscopy, scanning electron microscope (SEM), and atomic force microscope (AFM). As shown in Figure 1 and Figure S3, MP with size of ~30 μm and height of 1.1 μm formed on the surface on large scale. In the annealing process at 180 °C, the residual acrylate groups underwent the further polymerization to form a more compact cross-linked network, which induced phase separation between the cross-linked TMPTA network and PSF because of the decrease in the Gibbs free energy of mixing. As a result, PSF was “extruded” onto the surface to form the MP with shape of sphere. The formation of MP leads to the obvious light diffusion. After covered by the film with MP, the observation of objective was dependent on the distance between the film and objective (Figure S3a). In addition, we observed the circular rings across the surface of MP (Figures S3c), which is the typical optical phenomenon of sphere-shaped protuberance: Newton ring. In this phenomenon, an interference pattern is created by the reflection of light between two surfaces: a spherical surface and an adjacent flat surface that arises from the lens shape of the transparent microstructures.27,28 All of these results confirmed the success of our bottom-up approach in the fabrication of MP.

To gain insight into the formation mechanism of MP, we then traced the formation process of MP by AFM and SEM images and studied the effect of a variety of factors on their size and morphology (Figure 2, Figure S4). The UV-cured film was smooth, and no phase separation was observed in AFM image before annealing. After heating to 120 °C for 20 min, MP with ~0.8 μm in diameter and ~25 nm in height appeared on the surface (Figure S4). The characteristic size (D) and contact angle (θ) of MP should be determined by the solid substrate in force balance condition (right). Geometry for the calculation of liquid contact angle (θ) of the solid substrate (left). (c) Characteristic size (D) and contact angle (θ) of MP as a function of annealing time at 120 °C.

Figure 1. Fabrication of microprotuberance (MP) on photocuring coating: (a) Strategy to fabricate MP by curable resin via sequential UV and thermal polymerization. (b) Chemical structure of formulation used in photocuring coating: fluorocarbon chain containing polystyrene (PSF) and multifunctional acrylate (TMPTA). SEM image (c) and 3-D optical microscope image of the resulting MP. The PS-F/TMPTA film was irradiated by 365 nm UV light for 3 min, followed by heating to 180 °C for 20 min. The thickness of PSF/TMPTA film is 7 μm.

Figure 2. AFM images of the UV-cured PSF/TMPTA films annealed at 120 °C for different time: (a) 60, (b) 120, and (c) 300 min. The inset images are the AFM line analysis of the marked lenses with straight lines and diameter distribution of MP. The bar scales in panel a and in panels b and c are 4 and 10 μm, respectively. The average thickness of the films is ∼7 μm. (d) Schematic illustration of liquid drops on the solid substrate in force balance condition (right). Geometry for the calculation of liquid contact angle (θ) on the solid substrate (left). (c) Characteristic size (D) and contact angle (θ) of MP as a function of annealing time at 120 °C.
leads to the higher mobility of PSF and faster polymerization of TMPTA, consequently resulting in faster phase separation. We used real-time FT-IR to trace the thermal polymerization of TMPTA at different annealing temperatures (Figure 3d). Both conversion and polymerization speed of residual acrylate groups were enhanced significantly at the higher temperature of annealing. It is interesting that the growth of MP continued even after the curing reaction was almost complete, which might be ascribed to the polymerization-induced phase separation.

To further confirm the component of the resting MP, we immersed the as-prepared film with MP into the toluene solution for 10 min. The fuzzy film became transparent and much thinner (from 7 to 4 μm), and the MP completely disappeared (Figure S5a–d), suggesting that MP was removed in toluene. We analyzed the polymer dissolved in toluene by 1H NMR and found that its 1H NMR spectrum is the same as that of PSF, which further indicated that MP results from the phase separation of PSF from the cross-linked network of TMPTA (Figure S5e). We also prepared the UV-cured PSF/TMPTA films with different thickness of 1, 3, 6, and 12 μm, which were then annealed at 180 °C for 20 min. SEM images revealed that the size of the resulting MP increased obviously with the increasing thickness of film (Figure S6). This can be explained by the fact that a greater amount of PSF in the UV-cured film resulted in the extrusion of more PSF, consequently leading to the larger MP.

On the basis of these experimental results, we proposed that the growth of the self-organized MP probably involves two types of processes: spilling growth and coalescing. In the spilling growth process, annealing at high temperature induces a continuous conversion of C==C, which leads to the continuous up-migration of PSF and makes the MP grow in size. In the coalescing procedure, the adjacent PSF polymer in viscous state can mix together because of the continuously growing volume and limited interspace. Some bigeminal MP can be found on the surface, which shows the incomplete fusion of two neighboring microlenses (Figure 4). Especially for the sample quickly quenched at a low temperature, we observed many cohesive MPs in the AFM images, indicating that the fusion phenomenon accompanies the spilled process and both processes determine the size and morphology.

**Morphology of MP.** The final morphology of MP might be dominated by the surface tension. The MP can be seen as the spilled PSF droplet in viscous state attached to the cross-linked TMPTA surface. Three coefficients of surface tension must be considered: γLA for the liquid–air interface, γLS for the liquid–solid interface, and γSA for the solid–air interface (Figure 2d). Young’s equation γSA = γLS + γLA cos θ provides the relationship between surface tension and contact angle (θ) of MP.30 We used AFM and laser scanning confocal microscopy (LSCM) measurements to determine contact angle (θ) of MP and found that θ of MP increased with the increasing time of annealing at 120 °C (Figure 2e and Table S1). According to Young’s equation, at constant temperature and air pressure, the contact angle of the micro droplet on a solid surface is determined only by the physical properties of the liquid drops and solid materials. During the heating process of the UV-cured PSF/TMPTA film, the continuous migration of PSF creates a gradient PSF/TMPTA layer between the surface of PSF and
the substrate of TMPTA. The component of PSF in the solid PSF/TMPTA interface decreases with the increasing time of annealing. This leads to the increase in the surface energy of the solid interface, resulting in the increasing $\theta$. The contact angle of the MP formed at the higher temperature (e.g., 160 and 180 °C) showed no obvious changes because the complete migration of PSF creates a homogeneous TMPTA network solid interface.

The fluorinated chains also play an important role in the control of the morphology of the MP. We observed that the patterns of lens change from irregular shapes to a regular spherical shape when the content of the fluorinated chains in PSF increases (Figure S5). As for sample of PS/TMPTA without fluorinated chains, although the annealing treatment can induces the surface patterns, the shape of lens is irregular. When the fluorinated chains were introduced into the backbone of PS, the shape of the lens gradually changed into the regular hemispheres. This might be due to a great difference on surface energy of these two formulas, and this deduction also can be further verified by the change of the $\theta$ value. The $\theta$ values of PS, PSF-2, and PSF-1 decreased with the increasing content of fluorinated chains and were approximately 25, 21, and 18°, respectively. This might be ascribed to the decreasing surface energy of PS caused by the introduction of fluorinated chains. The resulting MP of PSF-1/TMPTA is very stable, and its size and morphology remain unchanged even if at high temperature (e.g., 180 °C) for 24 h and at room temperature for 3 months (Figure S7).

Encapsulation of LED Chip. Motivated by the facile and robust approach of one-pot fabrication, we used the cross-linked coating with MP to encapsulate the integrated LED chips and studied the enhancements of LEE and diffusion properties (Figure 6). Usually, LEE of LED chips is reduced severely by total internal reflection (TIR) because of the trapped light inside a high-refractive-index semiconductor.29,30 LED chips are encapsulated by transparent polymer coating with sphere shape, which can increase the light-escape cone.31,52 Moreover, the micropattern might cause the light diffusion, which will be very useful in the light source of LED, especially for illumination or display. This is indeed true that after passing through PSF/TMPTA film with MP a point light from collimated red laser changed into the bigger circle spot. The radiation patterns of the MP diffuser are shown in Figure 6a. Compared with the blank laser source radiation angle, the MP diffuser shows a larger radiation angle of $\sim$120° and a special three-peak radiation pattern (Figure 6a, Figure S8).

Figure 6b,c presents the scheme and picture of encapsulation of integrated GaN/InGaN-based LED chip with MP. A luminance meter was used to determine the luminance of different areas in the integrated LED device. As shown in Figure 6d and Table S2, the average luminance of the area for nine pieces of LED chips encapsulated by the flat coating without MP is $\sim$1340 cd/m², and that of the MP-coating encapsulated device is $\sim$950 cd/m². The average luminance values of the area among the chips without and with MP encapsulated devices are 25 and 69.5 cd/m², respectively. As for device encapsulated with MP, the luminance of the chip emitting area decreases, while the luminance in the blank areas increases, which should be ascribed to the light diffusion function of the MP. We compared the electroluminescence spectra generated from the flat encapsulated LED chips and the MP encapsulation under a DC current injection of 100 mA.

Figure 5. AFM images of MP fabricated with PS containing different amount of fluorinated carbon chains/TMPTA: (a) PS/TMPTA, (b) PSF-2/TMPTA, and PSF-1/TMPTA. The films were annealed at 180 °C for 10 min, and the thickness of films is 7 μm. Scale bar is 20 μm.

Figure 6. (a) Measured luminance of the laser spot light source before and after coated with PSF/TMPTA film with MP as a function of the angle. The inset is the diffusion spot of the laser spot passing through PSF/TMPTA film with MP. (b) Scheme for encapsulation of LED chip with MP to enhance light extraction efficiency (LEE) and light diffusion. (c) Photo of the integrated GaN/InGaN-based LED device and schematic illustration of the luminance measurement areas. (d) Measured luminance according to the schematic illustration area on the device; black and red denote the encapsulation with and without MP, respectively. (e) Electroluminescence spectra of the integrated LED device encapsulated by coating with or without MP. The integrated LED device was coated with PSF/TMPTA film, followed by irradiation of UV light and annealing at 180 °C for 10 min.
shown in Figure 6e and Table S3, the light output power of the LED chip increases after the encapsulation with MP. The average LEE values of the flat and MP encapsulated LED chips are 131.4 and 148.4 lm/W, respectively. The LEE of the integrated LED chips is enhanced by ~9.5% with the encapsulation of MP. This might be explained by the fact that the curved encapsulant/air interface of MP can decrease the Fresnel reflection, resulting in the extraction of more light from LED chips.

**CONCLUSIONS**

We demonstrated a facile and robust bottom-up approach to fabricate MP on the surface of photocuring coating though polymerization-induced phase separation. By using curable resin composed of random PSF as blinder and TMPTA as cross-linker, MP was generated after sequential photocuring at room temperature and thermo-polymerization at high temperature. The size and morphology of the MP can be controlled by annealing temperature, time, and thickness of the film and fluorinated copolymers. The prepared MP can enhance the LEE and light diffusion, which may be used to encapsulate LED back-light systems in the displays. It is believed that this novel strategy will open a new way to fabricate micropatterns on various surfaces.

**EXPERIMENTAL SECTION**

Preparation of MP. For a typical experiment, PSF, cross-linker TMPTA, and photoinitiator I097 were dissolved in toluene solution, the mass ratio of PSF, TMPTA, and toluene was fixed at 1:1:1, and the content of I097 was fixed at 1 wt % of TMPTA. The mixture was coated on a piece of solid substrate such as glass slide by a spin-coating procedure to form film of PSF/TMPTA. After cured by 365 nm UV light with the intensity of 10 mW/cm² for the fixed 5 min, the film was then annealed at the desired temperature for the desired time. The morphology of MP on the film was observed by AFM and SEM. The thickness of PSF/TMPTA film was controlled by the spin-coating speed. Except for the special statement, fluorinated polystyrene used in the formulation is PSF-1.

Measurements. The AFM images were obtained using a scanning probe microscope (Nanoscope III, Digital Instruments) that was operated in tapping mode with silicon cantilevers (with a force constant of 40 N/m). Surface line profiles were analyzed from the acquired AFM images using a digitized Nanonavi II (Seiko) offline software, and the values of amplitude and distance between two peaks of each image were statistically calculated from 20 typical MPs. SEM was performed using a Sirion-200 electron microscope (FEI Company) at 5 kV. The contact-angle measurements were recorded using a spinning drop interface tensiometer (SL200C, USA KINO Industry). LSCM was conducted on a Keyence VK-X110 apparatus. The photopolymerization kinetics were traced using real-time FT-IR, Spectrum 100 Fourier transformation infrared absorption spectrometer (Perkin-Elmer). The AFM images were obtained using a scanning probe microscope (Nanoscope III, Digital Instruments) that was operated in tapping mode with silicon cantilevers (with a force constant of 40 N/m). Surface line profiles were analyzed from the acquired AFM images using a digitized Nanonavi II (Seiko) offline software, and the values of amplitude and distance between two peaks of each image were statistically calculated from 20 typical MPs. SEM was performed using a Sirion-200 electron microscope (FEI Company) at 5 kV. The contact-angle measurements were recorded using a spinning drop interface tensiometer (SL200C, USA KINO Industry). LSCM was conducted on a Keyence VK-X110 apparatus. The photopolymerization kinetics were traced using real-time FT-IR, Spectrum 100 Fourier transformation infrared absorption spectrometer (Perkin-Elmer). The photopolymerization kinetics were traced using real-time FT-IR, Spectrum 100 Fourier transformation infrared absorption spectrometer (Perkin-Elmer). The photopolymerization kinetics were traced using real-time FT-IR, Spectrum 100 Fourier transformation infrared absorption spectrometer (Perkin-Elmer). The photopolymerization kinetics were traced using real-time FT-IR, Spectrum 100 Fourier transformation infrared absorption spectrometer (Perkin-Elmer). The photopolymerization kinetics were traced using real-time FT-IR, Spectrum 100 Fourier transformation infrared absorption spectrometer (Perkin-Elmer).

**ASSOCIATED CONTENT**

Supporting Information

Experimental section. Results. Table S1. Size and contact angle of the MPs obtained under different conditions. Table S2. Measured luminance according to the schematic illustration area on the device. Table S3. Luminous flux of different integrated LED chips before and after encapsulation. Figure S1. Synthesis process and molecular parameters of PSF. Figure S2. 1H NMR spectra of PSF-1 in CDCl₃ solution. Figure S3. Photo of UV-cured PSF/TMPTA attached on and away from the substrate paper before and after annealing at 180 °C for 20 min. 3D AFM image and planar optical microscope image of PSF/TMPTA film. Figure S4. AFM images of surface morphology of PSF/TMPTA film annealed at 120 °C for different time. Figure S5. SEM and AFM images of PSF/TMPTA film before and after washed by toluene solvent. 1H NMR spectra of PSF and the polymer washed off by toluene solvent. Figure S6 SEM images of PSF/TMPTA films annealed at 180 °C for 20 min. Figure S7. SEM images of the PSF/TMPTA films annealed at 180 °C for 24 h and stayed at room temperature for 3 months. Figure S8. Schematic illustration of the measurement setup for the radiation patterns of the PSF/TMPTA film with MPs as diffuser. (PDF)

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Notes

The authors declare no competing financial interest.

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**REFERENCES**


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