Synthesis of High Refractive Index and Shape Controllable Colloidal Polymer Microspheres for Super-Resolution Imaging

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Supporting Information

ABSTRACT: A conventional optical microscope fails to resolve features with sizes smaller than 200 nm due to the Abbe diffraction limit. Herein, we synthesize two kinds of high refractive index and shape controllable colloidal polymer microspheres, poly(9,9′-bis[4-(2-acryloyloxyethoxy)phenyl]fluorene) (poly(BAEPF)) and poly-(2-phenylphenoxyethyl acrylate) (poly(OPPEA)), used for solid immersion lens. It is the high refractive index and close contact with the surface features that can make the colloidal polymer microspheres-based microlens effectively collect evanescent information on the substrate and form a clear and magnified virtual image at a certain position below the substrate surface. Thus, as small as 60 nm feature size on the substrate can be clearly resolved through the microlens under a visible light optical microscope, which is far beyond the resolution limit of a visible light microscope.

INTRODUCTION

Because of the Abbe diffraction limit, the far-field optical microscope cannot resolve objects with dimensions smaller than λ/2 (λ is the illumination wavelength), namely, <200 nm resolution under white light. In order to break this resolution limit, researchers have explored various methods, such as near-field scanning optical microscopy (NSOM), metamaterial superlenses, and metamaterial superlenses, which achieve super-resolution imaging through near-field evanescent wave illumination or transformation of evanescent waves into propagating waves, respectively. Besides, various fluorescence-based super-resolution imaging techniques can also achieve super-resolution imaging, e.g., stimulated emission depletion (STED) microscopy, structured illumination microscopy (SIM), photoactivation localization microscopy (PALM), and stochastic optical reconstruction microscopy (STROM). Among them, the super-resolution mechanisms of STED and SIM lie in the modulation of point spread function of the systems, while those of PALM and STROM rely on the stochastically switching on and off of single fluorophore in time and space; then an overall image of the sample is reconstructed through a certain location algorithm. Nonetheless, these techniques have some shortcomings which impede their wide applications. For example, the low scanning rate of NSOM makes it not suitable for real-time imaging. Metamaterial superlenses have the problems of complex preparation steps and non-negligible optical losses; Fluorescence-based super-resolution techniques are only applicable to fluorescent-labeled samples and are confronted with the challenge of photobleaching.

Recently, optically transparent dielectric microspheres (SiO₂, BaTiO₃, TiO₂—BaO—ZnO, polystyrene microsphere, etc.) have been combined with a traditional optical microscope to achieve super-resolution imaging. Although the low refractive index SiO₂ microsphere could realize 50 nm resolution of anodic aluminum oxide (AAO) substrate, it relied on the plasma enhancing effect of the gold coating layer on the AAO surface. Besides, the point contact mode between microsphere and the object surface is unfavorable for sufficiently collecting of evanescent waves, which often results in a low image contrast. As for high refractive index microspheres such as BaTiO₃ and TiO₂—BaO—ZnO, they should be totally immersed in a liquid medium for reducing the distance between the imaging plane and the object surface to achieve super-resolution imaging. However, this immersion effect reduces the refractive index contrast between microspheres and their surrounding medium, which results in a low image magnification factor and an achievable resolution not exceeding 75 nm. The solid immersion lens (SIL) technique is another method that achieves super-resolution imaging through a hemispherical or superhemispherical dielectric microlens that is placed on top of the object surface. This technique can easily obtain high contrast super-resolution imaging of the substrate on the condition that the SILs have enough deformability to fully penetrate the underlying substrate. Several methods have been used to fabricate SILs, including self-assembly of small organic molecules, thermal reshaping or reflow, and transferring of prepolymer droplet to the substrate via modulation of

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EXPERIMENTAL SECTION

Materials. 2-Phenylphenoxyethyl acrylate (OPPEA, n = 1.57) and 9,9′-bis[4-(2-acryloyloxyethoxy)phenyl]fluorene (BAEPF, n = 1.62) were purchased from Nantong Manor Chemical Co., Ltd. (China). Lauroyl peroxide (LPO, 98%) and 1-hydroxycyclohexyl phenyl ketone (Photoinitiator-184) were from Aladdin Reagent Co., Ltd. (China). Poly(vinyl alcohol) (PVA1788) and chloroform (CHCl₃) were obtained from Sinopharm Chemical Reagent Corp (China).

The semiconductor chips containing subdiffraction-limited patterns of 104, 75, and 60 nm gaps were cut into small pieces, washed with ethanol, and dried for the super-resolution imaging experiments.

Synthesis of Polymer Microspheres and Their SILs. Suspension polymerization was used to synthesize poly(OPPEA) and poly(BAEPF) colloidal microspheres. Typically, 0.07 g of PVA was added into 120 g of deionized water, heated to 65 °C for 10 min to obtain a 0.058 wt % PVA aqueous solution, and cooled down to room temperature. Then a homogeneous oil phase composed of 0.35 g of OPPEA (or BAEPF), 0.5 g of CHCl₃, 0.005 g of LPO, and 0.006 g of photoinitiator-184 was poured into the above PVA aqueous solution. After being emulsified with a homogenizer at 6000 rpm for 3 min, CHCl₃ was removed from the mixture by a rotary evaporator at 150 rpm and 40 °C for 40 min. Subsequently, the dispersion was poured into a 250 mL four-neck round-bottom flask equipped with a mechanical stirrer, a thermocouple, a reflux condenser, and a nitrogen gas inlet. The system was degassed by nitrogen for 30 min and then heated to 75 °C for polymerization at 250 rpm for 7 h to obtain polymer colloidal microspheres. Because of high viscous monomers, the monomer conversion was only around 60% monomer conversion. We refer to it as “incomplete” suspension polymerization.

After a certain polymerization time (3–7 h), a drop of the microsphere suspension was taken from the reaction flask and spread onto the semiconductor chips. Thus, some microspheres rolled to the right position that above the patterns need to be imaged. Although these microspheres were stable enough on the surfaces of the target objects after dried under room temperature for 5 min, the residual monomer molecules would influence the imaging behavior. Therefore, these microspheres were subsequently further solidified via UV exposure in a sealed chamber under a nitrogen atmosphere for 25 min, and microsphere SILs were obtained.

Super-Resolution Imaging of Polymer Microsphere SILs. Super-resolution imaging behavior of the polymer microsphere-based
SIL was characterized by an Olympus optical microscope (BX63) fitted with an objective lens of 100× and numerical aperture NA of 0.8 in the reflection mode. A halogen light source (λ peak ∼ 550 nm) was used for white light illumination, and a blue (λ peak ∼ 470 nm) light was obtained by using a blue filter. These SILs can be removed from the surfaces after imaging without destroying the surfaces of the objects.

**Characterization.** The morphologies of the SILs and surface microstructures of the chip were observed by a Philips XL30 scanning electron microscope (SEM).

## RESULTS AND DISCUSSION

**Synthesis of Polymer Microspheres for SILs.** Two kinds of high refractive index monomers OPPEA and BAEPF were used to prepare polymer microsphere SILs, whose structures are shown in Figure 1. The fabrication of SILs can be divided into two steps: one is partially solidified poly(OPPEA) and poly(BAEPF) microspheres synthesized through suspension polymerization, and another is further solidification process via UV exposure when they are transferred to the chips. Before further solidification, the partially solidified polymer microspheres would undergo a gravity-induced deformation which makes SILs intimately contact with the surface patterns of the objects.

**Super-Resolution Imaging of Polymer Microsphere SILs.** In order to study the super-resolution imaging of these polymer microsphere-based SILs, semiconductor chips were used as the target objects, whose surfaces have subdiffraction patterns of 104, 75, and 60 nm gaps between specific stripes of

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**Figure 3.** Super-resolution imaging of the chip shown in Figure 2a through poly(BAEPF) SILs with h/d ratios of 0.35 (a1, a2), 0.40 (b1, b2), 0.55 (c1, c2), 0.87 (d1, d2), 0.89 (e1, e2), and 0.92 (f1, f2) under white light (a1–f1) and blue light (a2–f2). Insets: the side SEM images of the poly(BAEPF) SILs with h/d ratios of 0.35, 0.40, 0.55, 0.87, 0.89, and 0.92, but the same diameter of ∼13 μm, which were obtained at polymerization time of 2.92, 3.25, 3.50, 4.17, 4.58, and 5.25 h, respectively, and then cured by UV exposure. All the inserted SEM images have the same scale bars as that of (a1), which are 5 μm.
All the inserted SEM images have the same scale bars as that of (a1), which are 5 μm (Figure 3a1).

However, at too large h/d ratios, as shown in Figure 4a1, when h/d increases from 0.40 to 0.89, these features cannot be discerned under white and blue lights, respectively, which is obviously unresolvable, unless the SILs of h/d ratios of 0.61−0.84. All the inserted SEM images have the same scale bars as that of (a1), which are 5 μm.

Figure 4. Super-resolution imaging of the chips under white light (a1−d1) and blue light (a2−d2) through poly(BAEPF) SILs (d ~ 14 μm) with various h/d ratios of 0.61 (a1, a2), 0.75 (b1, b2), 0.79 (c1, c2), and 0.84 (d1, d2). The white arrows indicate 75 nm gaps, while the red arrow indicates the 60 nm gaps that can be resolved by the SIL. Insets: the side SEM images of the poly(BAEPF) SILs (d ~ 14 μm) with h/d ratios of 0.61−0.84.

Considering the super-resolution imaging of poly(BAEPF) microsphere-based SILs is quitely clear for 104 nm microstructure which is considerably far beyond our expectation, we further used them to observe these finner feature on the chips as shown in Figure 2d. As shown in Figure 4, under white light, the 75 nm gaps (indicated by white arrow) of the chip cannot be resolved unless the SILs of h/d ≥ 0.75 are used. With the increase of h/d ratio from 0.61 to 0.84, both focus depth Z and image magnification factors M increase, and the image resolution increases first and then decreases (Figure 4a1−d1).

Also, blue light can make these SILs obtain much clear images (Figure 4a2−d2) and even resolve 60 nm gaps indicated by red arrow at h/d = 0.79 (Figure 4c2).

We also used another high refractive index monomer, 2-phenylphenoxyethyl acrylate, to prepare poly(OPPEA) microsphere-based SILs using the same procedure as above. Compared to BAEPF, OPPEA has only one C==C bond and needs longer polymerization time before its partially modified microspheres are transferred onto the chips to form poly(OPPEA) SILs with similar h/d ratios to those of poly(BAEPF) SILs. The side SEM images of the as-prepared poly(OPPEA) SILs shown in the insets of Figure 5 present a slightly shrinking surface topography, which probably resulted from the linear oligomers in the poly(OPPEA) microspheres, which are prone to shrink under vacuum. As shown in Figures 5a1−d1 and 5a2−d2, the poly(OPPEA) microsphere-based SILs have similar super-resolution imaging behaviors to poly(BAEPF) ones: The increase in h/d ratio from 0.65 to 0.89 increases both focus depth Z and image magnification factors M. When poly(OPPEA) SILs with h/d ≥ 0.74 are used, 75 nm features on the chips can be resolved under white light, while under blue light the super-resolution imaging images are more clearly.

The influence of diameter of the SILs on their super-resolution imaging behaviors has also been investigated using poly(OPPEA) SILs with the same h/d of 0.79. As shown in Figure 6, all these superhemispherical SILs can clearly resolve the 75 nm gaps on the chip under white light and 60 nm gaps.
under blue light. When the diameter increases from 7.9 to 12.8 μm, both the field of view and focus depth Z increase while the image magnification factor reveals little change.

Super-Resolution Imaging Mechanism. This super-resolution imaging of poly(BAEPF) and poly(OPPEA) SILs cannot be explained by classical solid immersion mechanism. Based on $\lambda/(2n_{SIL})$ under an optical microscope with $\lambda$= 550 nm white light and 470 nm blue light illumination, the highest resolutions of the SIL made of poly(BAEPF) are 170 and 145 nm, while those of poly(OPPEA) are 175 and 150 nm, respectively, which are significantly lower than our 75 and 60 nm resolutions obtained here. Their working mechanism is not very clear at present. Based on our previous study, $^{23,24}$ there may exist a light interaction with densely packed metamaterial media formed by three-dimensional stacking of high-index TiO$_2$ and ZrO$_2$ nanoparticles. However, there is no inorganic component in the polymer microsphere-based SILs here. We guess there may exist crystalline domains in these polymer microspheres, which have been later confirmed by XRD (see Figure S2). Thus, this possible light interaction with crystals could help to collect the microstructure information on objects to increase resolution of the SIL.

**CONCLUSION**

We have demonstrated the synthesis of two kinds of high refractive index and shape controllable colloidal polymer microspheres using incomplete suspension polymerization combined with postcuring by UV light. The incompletely polymerized microspheres can form SILs with tunable $h/d$ ratios when...
transferred onto the target substrates. This deformable morphology combined with high refractive index can guarantee the SILs closely contact with the surface features to effectively collect evanescent information on the substrate and form a clear and magnified virtual image, and the parameters such as h/d ratios and diameters of these SILs have important influences on their super-resolution imaging behaviors. At optimum parameters, as small as 75 and 60 nm features on semiconductor chips can be clearly resolved by the pure polymer colloidal microsphere-based solid immersion lens with an optical microscope under white light and blue light illumination, respectively, which vastly excels the 200 nm resolution limit for visible light optical microscopes and also exhibits considerably enhanced resolution compared to the previously reported pure polymer spheres as SILs (130 nm resolution). The polymer microsphere-based SILs can not only be used for super-resolution imaging but may also find applications in the fields of optical memory storage, spectral signal enhancement, near-field lithography, and so on.

ASSOCIATED CONTENT

Supporting Information
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Figures S1 and S2 (PDF)

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