Decimating Spatial Frequency Components in Periodically Modulated Nanoscale Surface Structures for Sensing of Ambient Refractive Index Changes

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ABSTRACT: In our previous study, we developed an array of unique porous structures (an array of barnacle-like porous structures) to apply to biosensing chips. The porous structure was formed by an internal swelling phenomenon of a polystyrene colloidal particle monolayer, which was surrounded by a poly(vinyl alcohol) layer, for the duration of the monolayer’s immersion in a toluene bath. Barnacle-like porous structures were formed when polystyrene particles that had rapidly swelled broke the outer layer around the top of the particles. However, after the surface was coated with a thin Ag layer, the porous structure showed a relatively broad extinction spectrum that was undesirable for sensing chips based on both surface plasmon extinction and grating coupling. In this paper, we propose an approach to obtain relatively sharp extinction spectra based on the decimation of the spatial frequencies of the porous structures. This study also investigates formation properties in more detail to control the structural features of the resultant porous structures. A relatively sharp peak in the extinction spectrum was ultimately obtained.

INTRODUCTION

Nowadays, polymer materials are widely used in industrial production because their plasticity makes them easy to manufacture. This merit can be utilized in the development of nano- and microstructures in research fields related to sensing devices, microfluidic devices, etc.1−5 Because fabrication processes must be developed to realize the functionalities of these devices, various techniques have been proposed to achieve this aim. These strategies can be broadly classified into two opposing categories.2,6 The first comprises top-down approaches that are based on targeted functions originating from relatively established processing, while the other encompasses bottom-up approaches that are initiated by unique processing. In the latter, the functionality is designed to enable production associated with unique processing. Both approaches have been successfully addressed and are extremely important to the progress of the related technologies. As a result, many types of available processes and the resultant functional structures using various polymer materials were reported, as described below.

Various lithographical techniques have been employed for the patterning of functional structures, which aim to advance electronic devices, biosensing chips, and microfluidic chips.3,4,7 For example, colloidal lithography is a unique process that uses polymer colloidal particles. Colloidal particle monolayers are typically used as the template in this lithographic process and can be combined with various elements such as capillary forces, chemical reactions, etchings, surface and/or interface interactions, external fields, and physicochemical phenomena.4,9 As a result, various unique structures can be applied to hydrophobic surfaces, bioapplication of a cell culture, sensing chips, electronic devices, etc. Imprint- or molding-based techniques can also be used for the development of polymeric functional structures.10,11 The resultant products have homogeneous structures all over the surfaces, based on the accuracy of prepared molds. Direct laser writing is another specific process that forms artificial structures on polymer surfaces.12 Accurate structuring can be achieved through the optimization of polymer materials, irradiation energy, scanning speed, and step width. The use of laser treatment to induce periodic surface structures is also an effective technique that forms fine ripple structures on polymer surfaces.13−15 Rippled polymer films are adequate for several applications such as cell culture substrates and surface-enhanced Raman scattering sensors.

As mentioned above, advances in the structuring technology of polymer materials mirror the development of novel and high-performance devices. However, the development of
puckered or pinched porous structures such as barnacles or volcanoes has not considerably progressed. In nature, various pinched porous structures can be found such as shells of barnacles, volcanoes, nests of woodpeckers or potter wasps, and nasal cavities of humans. As humans, we also use many similar structures such as bottles, flasks, socks, and balloons. Each porous structure is associated with its functionality to realize its specific objective. Specifically, these pinched porous structures are used to sustain the objects housed inside them apart from the outside of pores. In this way, they are different from the functionality of waistless hole structures. This is highlighted by the difference between a beaker and a flask. Objects can be introduced into the inside of the beaker, and objects can be removed from the inside. Conversely, accessibility to objects inside a flask is significantly reduced, while preservability is increased. This advantage can be similarly utilized in the development of polymeric functional structures, which has led to some effective structures being reported. Lee et al., for instance, have fabricated a pinched structure that can protect the inside from shearing forces, which allows the structure to be used as a container to stably dock cells.16 Yue et al., meanwhile, presented a flask-like porous structure that is deep-set in a silicone rubber substrate for use in cell culture.17 Zhang et al. outlined an approach to form a volcano-like structure in nanoscale.18 In their study, a photosis layer was irradiated by UV light that was scattered by silica beads with a diameter of 50 nm. This resulted in the formation of highly structured and volcano-like structures in nanoscale. The puckered structure cannot be formed using typical photolithographic approaches that are based on proximity irradiation with photomasks. Akerboom et al. have achieved overhang structures in submicrometer scale.19 The void that is surrounded by an overhanging wall was fabricated using interfacial polymerization of polypyrrole at the surface of the colloidal particle monolayer. The surface of the resultant structure generated a hydrophobic effect despite the fact that it was made from a hydrophilic material.

In our previous study, we outlined a unique approach to forming barnacle-like porous structures that focused on a target-collective sensing chip.20,21 The porous structure formation is illustrated in Figure S1. This approach uses a polystyrene colloidal particle monolayer as a template, and the monolayer is then coated with a thin poly(vinyl alcohol) (PVA) layer. When the monolayer is immersed in a toluene bath, the toluene penetrates the polystyrene (PS) part, through the outer PVA layer, which causes the PS to rapidly swell. As a result, this “internal swelling effect” creates internal pressure toward the outside, which breaks the outer PVA layer and creates barnacle-like porous structures. The shell structure of the barnacle is thus formed by a thin and puckered PVA layer, as shown in Figure S2. When the surface of the porous structure array was coated with a thin Au layer (≈100 nm), the array exhibited a relatively broad extinction spectrum, and its characteristics are not suitable for optical sensing chips that detect chemical or biological targets. This is despite a relatively large extinction peak shift dependent on the ambient refractive index (≈480 nm/RIU), as shown in Figure S2. The broad extinction spectrum is attributable to the shape of the barnacle-like structure, which is a hemispherical envelope, and is also based on the initial template of the colloidal particle monolayer.

The present study proposes an approach to modify the spatial frequencies of the resultant fine porous structures for use as sensing chips. This requires an improved fabrication process and a detailed investigation into formation characteristics to control the structural features of the pores. The relationship between the structural features and the exhibited extinction spectra will then be discussed to identify the specific extinction spectra that result in highly sensitive sensing chips for the detection of ambient refractive index changes.

### RESULTS AND DISCUSSION

The improved fabrication process presented in this study was developed based on the sequential process described in the Experimental Section. The first consideration was how to transfer the PS pillars onto a substrate. The PS pillars should be transferred to a substrate without the remaining layer, as this induces the formation of a porous structure that is based on the internal swelling effect, after the PVA coating. (The remaining layer in the fields of imprint processes is illustrated in Figure S3.) If the PS template has a remaining layer the outer PVA layer will not be anchored to the bottom substrate at any point and will be removed in the toluene bath when the internal swelling of the PS pillars occurs. A hemispherical poly(dimethylsiloxane) (PDMS) mold was prepared to optimize the transfer process of the PS template, as shown in Figure 1a. Figure 1b–e presents the transferred PS hemispheres with M₆s of 3250, 9550, 18 000, and 48 000, respectively. The conditions involving 400 rpm for 2 s and 4000 rpm for 50 s were applied to the spin-coating as the first slow spreading and second quick coating, respectively. The

![Figure 1](https://dx.doi.org/10.1021/acsomega.9b03811)

**Figure 1.** (a) PS transfer process. (b–e) PS hemispherical structures using PSts with M₆s of 3250, 9550, 18 000, and 48 000, respectively. (f) Height and (g) diameters of hemispheres depending on the bottom substrate temperature.
heights and diameters of the PS hemispheres, as functions of the temperature of the bottom substrate, were measured and are plotted in Figure 1f,g. The dashed lines plotted in both figures indicate the identical height and diameter of PS hemispheres, based on the structural specifications of the mold, as illustrated in Figure 1a. The larger $M_c$ of PS and the lower temperature of heating both were found to more successfully transfer the PS structures without the remaining layers. This is considered a reasonable result, since the $T_e$ of PS was directly related to the $M_c$. (Their ideal relationship is illustrated in Figure S4.) When the heating temperature was relatively low, most of the PS that filled the mold could be transferred without evaporating. In addition, the viscosity of the melted PS with the higher $M_c$ simultaneously increases. A large portion of the PS could be transferred from the mold to the substrate without breaking the filled PS. Moreover, a significant decrease of the $T_e$ of the polymer surface is reported by many researchers. It is considered that the decrease affects the melting and evaporation of PS under substrate heating. (Simultaneously, there are possibilities of shrinking and remaining of PS portions in the PDMS mold.) As a result, a $M_c$ of 48 000 and a heating temperature of 50 °C were selected as the optimal conditions for this study.

To fabricate puckered or pinched porous structures, a pillar array mold with the same height and diameter of 1 μm was also prepared. Then, the PS pillars were transferred, coated with PVA, and immersed in toluene according to the process illustrated in the Experimental Section. The resultant structures were observed by scanning electron microscopy (SEM), as shown in Figure 2a–c. PS pillars without the remaining layers and PVA-coated pillars with a PVA layer attached to the bottom substrate were both obtained, as indicated by the red and blue arrows. Puckered porous structures subsequently opened, which resembled volcanoes or hollow stumps, as a result of the internal swelling effect. Thus, the toluene infiltrated the outer thin PVA layer, as expected. Openings in the upper side of the pillars would not have been obtained if there was insufficient anchoring of the PVA layer attached to the substrate. (The anchored skirts are indicated by the yellow arrow.) To understand this formation in more detail, the fabrication process was performed under various conditions in terms of both the PVA concentration of the aqueous solution and the plasma treatment time before immersion in toluene. These results are summarized as a phase diagram in Figure 3. Use of PVA solutions with relatively low concentrations (< 2 wt%) to coat the PS pillars results in porous structures with low profiles, which is an unfavorable formation. Conversely, properly adjusted PVA solution concentrations (~ 3 wt%) obtained more favorable and expected porous structures. The opening could not be generated when excessive PVA concentrations (> 4 wt%) were applied, which resulted in another unfavorable formation. Thus, favorable and unfavorable formations are closely associated with the thickness of the PVA layer that surrounds the PS pillars, meaning that the PVA must be of a concentration that can be broken by the internal swelling effect. Simultaneously, it must also be of a concentration that can be sustained as a self-standing structure. Plasma treatment time is another controlling factor that affects the thickness of the PVA layer, since, even in situations where the PVA concentration was exceeded, a favorable formation can be obtained through a relatively long plasma treatment. This outcome is attributable to plasma treatment’s etching effect on the outer PVA layer. Therefore, the formation can be controlled by both conditions. The phase diagram indicates the other point with respect to the internal swelling effect. The border between phases (B) and (C) can be defined...
approximately and, therefore, suggests that there is a threshold value of internal force in terms of what is needed to break the PVA layer, especially around the top of the structure. This force corresponds to the pressure exhibited by the PS when it swells effectively. If the PVA layer is excessively thick, the internal outward force expands in all directions within the PVA layer. This results in overly expanded structures that lack an opening, as depicted in the upper SEM image of phase (C) in Figure 3. (Besides, the deformation indicates that toluene can penetrate through the relatively thicker PVA layers.) Consequently, this experiment clearly revealed the relationship between the thickness of the surrounding PVA layer and the resultant structures. In addition, the formation of the porous structure can be explained by a mechanical action resulting from the PS swelling, which puts pressure on the outer thin PVA layer. Our next step was to focus on structural variations that influence a favorable formation in the region of phase (B).

The heights of the porous structure ($H$) and its thin wall (or shell) structure ($\Delta H$) were measured using SEM observations for all of the porous structures that had been fabricated under various conditions within the region of phase (B), as shown in Figure 4a,b. $H$ increased as the PVA concentration increased relatively high concentrations. The reason for the initial increase is similar to the explanation for $H$. However, the mechanism for the decrease at relatively high concentrations is unclear even taking into account the differences in the plasma treatment time. (If $\Delta H$ was saturated to the increasing of PVA concentration, the $\Delta H$ would be limited at a certain height, based on the mechanical properties of PVA.) Possibly, the increase of $H$ has affected the decrease of $\Delta H$. When $H$ is relatively low, the anchoring force of the substrate works on the upper PVA layer. Conversely, when $H$ is relatively high, the effect of the anchoring force decreases rapidly. As a result, $\Delta H$ decreases when the PVA concentration increases. These results suggest that the structural features ($H$ and $\Delta H$) can be controlled by both PVA concentration and plasma treatment time.

This experiment revealed the formation mechanism of a unique porous structure and the factors that control its structural features, as the previous discussion emphasizes. To achieve the initial objective of attaining highly sensitive sensing chips with sharp extinction peaks, we investigated the optical characteristics of sensing chips that are based on this porous structure. The diameter of the initial PS pillar array was modified to 500 nm to obtain the extinction peak in a visible region.

Five samples of the porous structure, with different structural features, were prepared. Their properties are summarized in Table 1 and depicted as a phase diagram in Figure S5, which is similar to that in Figure 3. The influence of the modified diameter is evident in the shift of phase (B) toward a region of a lower PVA concentration. The SEM images and extinction spectra of these samples are presented in Figure 5. Each sample was coated with thin Ag layers, with an approximate thickness of 80 nm, and the extinction spectra were measured using an optical setup, which is illustrated in the Experimental Section. Each extinction spectrum in Figure 5 has a different shape, depending on their structural features. Differences are particularly evident in the two distinct peaks (the first and second peaks) at around 460 and 550 nm. The extinction ratios for these two peaks (ratios of the extinction values of the second peak to the first peak) were calculated to characterize these differences. These were then plotted as functions of $H$ and $\Delta H$ in Figure 6a,b, respectively. These characteristics indicate a wealth of important information in terms of designing sensing chips based on the detection of spectral peak shifts. First, either peak can be enhanced by selectively adjusting $H$, as shown in Figure 6a. In addition, the equivalent extinction of both peaks can also be realized using a sample with a relatively high $H$, of around 500 nm. Moreover, the second peak can be enhanced by controlling $\Delta H$, which results in a relatively sharp single peak, as shown in Figure 6b. (This design guideline for the second peak enhancement is

![Figure 4](image_url)

**Figure 4.** (a) and (b) show the heights of the porous structure ($H$) and the thin wall structure ($\Delta H$), respectively. (c), (d), and (e) show typical examples of a porous structure with $H$ of 240, 390, and 560 nm, respectively.

| Sample | PVA concentration (wt %) | Plasma treatment time (s) | $H$ (nm) | $\Delta H$ (nm) |
|--------|--------------------------|---------------------------|--------|-------------|
| A      | 2.0                      | 10                        | 170    | 70          |
| B      | 3.0                      | 40                        | 220    | 120         |
| C      | 4.0                      | 60                        | 300    | 230         |
| D      | 6.0                      | 90                        | 380    | 220         |
| E      | 8.0                      | 110                       | 480    | 150         |

**Table 1. Sample Properties in the Fabrication Process and Structural Features**
adjustment of $H$ and $\Delta H$ provides numerous possibilities for designing in terms of both functionality and sensitivity. As expected, this could result in improved sensing chips with respect to the sharpness of the extinction peak. To understand these optical characteristics, we evaluated the extinction spectra taking the structural features of fine surfaces into account. In Figure 7a, the extinction spectrum of sample C is replotted and the extinction spectrum of the PVA-coated pillars before the immersion in toluene is plotted simultaneously. The profile of the PVA-coated pillars is relatively close to a sinusoidal shape, compared to the original pillars, as shown in the inset SEM images in Figure 7. Both the spectra were synthesized directly, and the resultant spectrum is plotted in Figure 7b to compare with the extinction spectrum of Ag-coated original pillars. Both the spectra are noticeably similar. This compositional analysis led to an interesting conclusion, namely, that a sharp extinction spectrum can be obtained by removing the sinusoidal component that corresponds to the fundamental spatial frequency of the periodic structure of the original pillar structures. This exactly matches the formation of the porous structure through the proposed process, which uses the internal swelling effect. As a result of this effective decimation of spatial frequencies, the sharpness of the extinction peak can be substantially improved, compared with that of our previous sensing chips, which are illustrated in Figure S2. This approach is supported by a theoretical treatment of surface plasmon resonance in periodic metallic structures.\textsuperscript{26–29} When an optical wave is incident to such a periodic metallic substance, the wavenumber vector of the coupled wave is described as $k_i \sin \theta + mK$, where $k_i$ and $\theta$ are the wavenumber vector and the incident angle of the incident wave, respectively, and $mK$ corresponds to the $m$th-order spatial frequency of the periodic structure. A surface plasmon wave with a wavenumber vector $k_{SP}$ is then elicited from the incident optical wave in the metallic portion. When both wavenumbers are consistent with each other, as represented by

\begin{equation}
  k_{SP} = k_i \sin \theta \pm mK
\end{equation}

strong surface plasmon resonance is generated. In eq 1, the $\pm m$th order of the coupled waves is defined practically. The resonance can be observed experimentally, as sharp extinction spectra at specific wavelengths, when the incident optical wave has a continuous spectrum. Strong and sharp extinction spectra are observable when the shape of the metallic structure is properly designed, which include certain spatial frequencies with the fewest possible $m$ numbers. This effect could be utilized to improve sensing chips that are based on the proposed fabrication process.

An effective approach, based on removing fundamental spatial frequencies, has been employed in some cases that have applicable only in the region of phase B in Figure S5.) Thus,
yielded significant benefits. A well-known example is stimulated emission depletion (STED) microscopy.\textsuperscript{30} Traditional fluorescent microscopy with a high resolution uses a highly focused excitation beam to obtain a smaller emission spot, resulting in high-resolution fluorescent imaging. However, the reduction of the focused beam diameter is limited by the diffraction barrier. This issue has been addressed using doughnut-like STED beams that deplete the peripheral fluorescent emission. The skirts of the gradually distributed optical intensity of the STED spot effectively generate a narrow remaining emission spot. This approach can also be used in photopatterning to realize fine structuring.\textsuperscript{31–33} Therefore, hollow distributions of structure or energy could significantly benefit many research fields.

The sensing ability for detecting refractive index changes was evaluated from several samples. Figure 8a depicts the peak shift of the extinction spectra of sample E, which exhibits similar extinctions in its first and second peaks as functions of $\Delta H$. 

![Figure 8](https://dx.doi.org/10.1021/acsomega.9b03811)

Figure 8. (a) and (b) show extinction spectra depending on ambient refractive index changes for samples E and D, respectively. (c) Peak shifts of the first and second peaks as functions of $\Delta H$.

of the extinction spectra of sample E, which exhibits similar extinctions in its first and second peaks. According to changes in the ambient refractive index, the peaks shifted toward longer-wavelength regions. Their shifts can be characterized as linear functions of the ambient refractive index, as shown in Figure S6a. This means that the porous structures, with a $\Delta H$ of 150 nm, enable two-channel sensing. A functional sensing chip with high reliability is thus proposed, which uses either of the peaks as the subchannel for a parity check, to inhibit operational error. Figure 8b depicts the peak shift of the extinction spectra of sample D, which exhibits the enhanced second peak and suppressed first peak. Here, the peaks similarly shifted toward longer-wavelength regions, depending on the ambient refractive index changes. Their shifts were also characterized as linear functions, as shown in Figure S6b. The sensing ability of sample D was evaluated using proportional constants in the linear fittings of the peak shift characteristics, including that of the other samples that are listed in Table 1. The results are plotted in Figure 8c as a function of $\Delta H$. The spectral peak shift has a unit of nm/RIU (i.e., wavelength shift per unit refractive index), which corresponds to the sensing ability that was used as a figure of merit for the optical sensing chips. Sensitivity increased as $\Delta H$ increased. Second peaks yielded relatively large peak shifts, and the value exceeded that of our previous sensing chip, depicted in Figure S2. Since $\Delta H$ can be controlled by the PVA concentration, even within a relatively narrow range, the resultant sensitivity can be determined by the conditions of the fabrication process. The sensitivity of sample D, which had a relatively high $\Delta H$ of 220 nm, exhibited a higher sensing ability of around 530 nm/RIU, as well as an enhanced second extinction peak, which is shown in Figures 5 and 8b.

It can thus be concluded that the structural features of the porous structure are closely related to the characteristics of both the shapes and peak shifts of its extinction spectra. Structural features ($H$ and $\Delta H$) were also determined by both PVA concentration and plasma treatment time. Therefore, the realization of usable sensing chips requires effective strategic processes that engage with a range of factors. In addition, it may be necessary to include both top-down and bottom-up approaches in the practical development stage. Simultaneously, some interesting phenomena can be identified from a material science perspective. For example, in terms of the physical property of the pore lips, the thin PVA layer that forms the lips was elongated and fractured under the internal swelling effect of PS pillars, resulting in the volcano-like shape being stably sustained. Although Figure 2c illustrates that the wall thickness is less than 100 nm, the lips actually resemble a beaker that has been melted down during the manufacturing process. Therefore, the macromolecular property of the PVA may differ significantly among the lips, walls, and flat sections on a substrate.\textsuperscript{34} The deposition of Ag atoms during sputtering would subsequently also be affected by these differences.\textsuperscript{35,36}

In addition, the internal swelling effect is itself an attractive phenomenon. In the present study, this was utilized to produce a porous structure using an internal physical action, namely, the pressure of the PS swelling toward the outside of the PVA layer. When the internal pressure exceeds the net external force of the toluene fluidic pressure and the reaction force of the PVA layer, the PVA layer fractures and the opening begins to form. This outcome could be employed to perform a quantitative analysis of the internal pressure of polymer materials through swelling using conditions on the border between phases (B) and (C), which are illustrated in Figure 3. These advanced conclusions will be useful in further investigations into both unique and functional structures composed of polymer materials.

**CONCLUSIONS**

This study evaluated a strategy for attaining highly sensitive sensing chips for the detection of ambient refractive index changes. This approach focuses on the structural features of the unique porous structure that can be obtained using an improved fabrication process that utilizes an internal swelling
effect. This strategy yielded highly sensitive sensing chips that are suitable for detecting targeted substances, materials, and biomolecules. In addition, this study identified many benefits with respect to the formation mechanism of the porous structure, the factors controlling the structural features, the relationships between structural features and extinction spectra, and design factors that influence highly sensitive and/or functional sensing abilities. These results confirm the effectiveness of the proposed approach. However, the metallic layer may contain another element that relates to plasmonic excitation, which holds the possibility of further improving the sensing ability. Future developments should subsequently focus on the complete strategy and include numerical electromagnetic analysis to realize the practical usability of sensing chips.

**EXPERIMENTAL SECTION**

**Materials.** To improve the porous structure fabrication process, which is based on the internal swelling effect, PS pillar templates were prepared. Various PSs with different molecular weights ($M_w$) of 3250, 9550, 18,000, and 48,000 (Sigma-Aldrich Co. CLL.) were tested for the fabrication of PS pillar arrays because the proposed approach includes a thermal treatment for transferring PS pillars from molds to substrates. Poly(dimethylsiloxane) (PDMS, SIM-360, Shin-Etsu Chemical Co.) was used for the fabrication of the molds of a pillar array. Soft imprint that uses PDMS molds was preformed to transfer PS structures without the remaining films. A modified PVA with silanol moieties in the side chains (R2105, Kuraray Co.) was used to coat the PS templates, and the degrees of polymerization and hydrolysis were 500 and 97.0–99.0, respectively. The chemical structure is shown in Figure 9a. This PVA is suitable for puckered or pinched porous structures, as the thin outer shell of the pores can be sustained by the inter- and intramolecular cross-linking of silanol moieties. In addition, this PVA is durable in terms of swelling, which is also preferable for a fabrication process that involves an internal swelling effect.

**Methods.** The fabrication process is schematically illustrated in Figure 9b. First, a PDMS mold was prepared, with an array pattern of pillars. The pillar mold was filled with PS by means of the spin-coating method, which used a toluene solution of PS with a concentration of 3 wt %. The filled PS was transferred onto a glass substrate without the remaining layer. This transfer process focused on optimizing the conditions of PS molecular weight and the temperature of the substrate, as well as the pressure applied to the PDMS mold. In this study, a pressure of 5 N/cm$^2$ was applied, based on a preliminary investigation. Plasma treatment was performed using a plasma cleaner (YHS-R, SAKIGAKE Semiconductor Co.) to obtain the proper wettability of PS and the bottom substrate. The duration was determined as 30 s from a preliminary investigation. Then, the PS pillars on the substrate were coated with PVA by means of the spin-coating method, which uses various aqueous solutions of PVA with different concentrations. The concentration of the solution is directly associated with the thickness of the wall (or the shell) in the resultant pores. The PVA-coated PS pillars on the substrate were dried in a vacuum oven and then plasma-treated again. Finally, the substrate was immersed in a toluene bath. During the immersion process, the internal PS pillars became swollen because the toluene infiltrated the outer PVA layer. Puckered or pinched porous structures were formed as a result.

The formed porous structures were revealed using scanning electron microscopy (SEM, JSM-5910LV, JEOL). Their surfaces were coated with thin Ag layers, with an approximate thickness of 80 nm, to evaluate the sensing ability. Extinction spectra were measured using an optical microscope system, with both a digital camera and a spectrometer, as shown in Figure 9c. The reflected light from the Ag surface was adjusted to an almost normal reflection arrangement using an object lens with a relatively low NA of 1.3. To measure sensitivity in terms of ambient refractive index changes, a spectral measurement was performed on porous structures that were surrounded by different media (air, ethanol, isopropyl alcohol, and decane) with refractive indexes of 1.000, 1.363, 1.375, and 1.411, respectively.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03811.

Schematic illustration of porous structure formation; barnacle-like porous structures; illustration of the remaining layer; Fox–Flory relationship; phase diagram of porous structure formation; characterized spectral peak shifts (PDF)
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Notes
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