Photonic Crystals with Tunable Lattice Structures Based on Anisotropic Metal–Organic Framework Particles and Their Application in Anticounterfeiting

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1. Introduction

Photonic crystals (PCs) have shown various applications in the fields of color display,[2] printing,[3] pigment,[4] sensing,[5] biology,[6] and anticounterfeiting[7] thanks to their unique photonic characteristics originated from the periodic nano-/microstructures. Due to the entropically favored packing of isotropic particles, conventional PCs based on spherical colloids usually possess the face-centered cubic (FCC) or hexagonal closely packed (HCP) lattices. In contrast, PCs assembled from the anisotropic particles with different lattice structures have demonstrated new optical properties and applications.[8] For example, only a pseudophotonic bandgap exists in the spherical particles-based PCs due to a symmetry-induced degeneracy at the W- or U-point of the band structure, which can be broken using shape-anisotropic colloidal particles as building blocks.[9]

Up to now, limited strategies have been successful in fabricating PCs with brilliant structural colors based on direct self-assembly of anisotropic particles into lattice structures other than FCC and HCP.[10–12] Ellipsoidal Fe₂O₃@SiO₂[10] and Fe@SiO₂[11] core@shell particles with tunable aspect ratio can assemble into PCs with face-centered orthorhombic (FCO) lattice in the presence of a magnetic field. The structural color determined by the orientation of the magnetic-responsive particles in these PCs can be well controlled through manipulating the orientation of particles using magnetic field.[10] In addition, PCs with rhombohedral lattice and Minkowski lattice can also be fabricated through self-assembling of anisotropic ZIF-8 and UiO-66 particles, respectively.[12] Although many
anisotropic particles with diverse geometries have been fabricated,\[13\] it is necessary to establish a relationship between the geometry of the colloidal particles and the lattice structures of their assembled long-range ordered structures. In fact, theoretical calculation has predicted that the optimal packing of super-balls in 3D changes with the shape parameter $m$ of the super-balls. The $m$ value of a particle indicates to what extent the particle shape has deformed from that of a perfect sphere ($m = 2$) and that of a perfect cube ($m = \infty$),\[14\] which is the key to control the crystal form of the PC. However, there is little experimental result to show the changes in lattice structure with variation in $m$ values in PCs.\[15\]–\[17\] Moreover, the structural color of conventional spherical-particle-based PCs is mainly originated from the first-order diffraction.\[18\] Although weak high-order diffraction peaks have been observed in reflection spectra, the bright structural color due to the second-order diffraction of PCs has not been realized to our best knowledge.\[19\]

Here, we report the synthesis of monodispersed anisotropic ZIF-8 particles with diverse shape parameters ($m$) and new PCs with tunable lattice structures and photonic characteristics (Figure 1) assembled by these particles. Ordered structures with simple-cubic, rhombohedral, and FCC lattice are generated using anisotropic ZIF-8 particles with $m$ value of 9.7, 4.7, and 2.5, respectively. Compared with the conventional spherical-particle-based PCs, the anisotropic ZIF-8 particle-based PCs show not only intense reflectance at the reflection peaks of the first-order diffraction, but also strong second-order diffraction as well, both of which can result in bright structural color. Consequently, brilliant color can be generated by the first- or second-order diffraction of the PCs, which can be controlled by altering the size of ZIF-8 particles. Inspired by this feature, a new information encryption technology was developed by combining the first-order diffraction of rhombohedral PCs with first- and second-order diffraction of simple cubic PCs. The information can be well encrypted into the background and cannot be recognized by naked eyes due to their similar colors originated from similar reflection peak positions in the visible range. Only under the probe mode, the information can be decrypted by merging the reflection signals of at visible and near-infrared (NIR) ranges. The wide tunability of lattice structures, photonic bandgaps, and structural colors of PCs based on the anisotropic porous ZIF-8 particles enlightens new applications of PCs, especially in the regions of anticounterfeiting, precise sensing, and displays.

2. Results and Discussion

2.1. Synthesis of Anisotropic ZIF-8 Particles

Anisotropic ZIF-8 particles are prepared by injection of 2-methylimidazole (2-MiM) and cetyltrimethylammonium bromide (CTAB) mixed solution into the aqueous solution containing Zn²⁺.\[12\] The shape of the anisotropic ZIF-8 particles can be controlled by altering the injection speed of 2-MiM. As shown in the field-emission scanning electron microscopy (FE-SEM) images and schematic illustrations (Figure 2A–I), anisotropic ZIF-8 particles with different truncated rhombic dodecahedral morphologies are synthesized when the injection speed of 2-MiM and CTAB mixed solution was increased from 0.7 to 1.7 mL min⁻¹ (samples in Figure 2(A–C), (D–F), and (G–I) are named as sample 1, 2, and 3, respectively). The size of sample 1, 2 and 3 is measured to be 358, 314, and 291 nm, respectively. It was found that all these anisotropic ZIF-8 particles possess six square facets and 12 {110} hexagonal facets but with different surface area ratios. The surface ratio of {100}/{110} facets of sample 1, 2, and 3 is 5.4, 1.66, and 0.64, respectively, indicating the significant effects on the morphology of ZIF-8 particles of the injection rate. In addition, the shape of these ZIF-8 particles is likely to be fixed.
at the early stage of the synthesis process according to the SEM images obtained during the growing process (Figure S2, Supporting Information). As shown, the shape of the ZIF-8 particles is almost unchanged while the size gradually increases. The diverse shapes of these anisotropic ZIF-8 particles may be likely due to the different growth speed of the {100} and {110} facets controlled by CTA\(^+\) adsorption on the surfaces of ZIF-8 seeds. In the absence of CTAB, the as-prepared ZIF-8 particles have a typical rhombic dodecahedron shape with 12 {110} faces exposed (Figure S1, Supporting Information). This result indicates that the {100} facets of ZIF-8 seed have higher surface energy and faster growth speed than that of {110}, which leads to the disappear of {100} facets in the end. In the presence of CTAB, the CTA\(^+\) prefer to absorbing on the {100} facets of the ZIF-8 seeds, which slows down the growth of {100} facets. At a slow injection speed of 2-MiM and CTAB mixed solution, the instant concentration of 2-MiM is low, which leads to slow growth of ZIF-8 particles. In comparison, the relative adsorption speed of CTA\(^+\) on the {100} facets compared with the growth of ZIF-8 particles is fast, leading to the slow growth of {100} facets and thus the nearly cubic particles (sample 1) with high percentage of {100} facets. When the injection speed increases, the relative adsorption speed of CTA\(^+\) on the {100} facets decreases and the growth of {100} facets is accelerated, resulting in cubes with beveled edges (samples 2 and 3). Here, the \(m\) is used to quantitatively describe the shape of ZIF-8 particles, which can be calculated by Equation (1).\(^{[14]}\)

\[
m = \frac{2}{1 - 2 \log_2 \left( \frac{R}{L} \right)}
\]  

where \(R\) is the diagonal of the surface and \(L\) is the edge length of anisotropic particles, respectively. The \(m\) indicates extent of deformation from a sphere (\(m = 2\)) to a cube (\(m \rightarrow \infty\)).\(^{[14]}\) In this work, particles with high ratio of {100} facets will have a large \(m\) value. The \(m\) values of samples 1–3 are calculated to be 9.7, 4.7, and 2.5, respectively.

In contrast to the diverse shapes, these ZIF-8 particles show similar physical and chemical properties. For example, the powder X-ray diffraction (PXRD, Figure 2I) patterns of these ZIF-8 particles are similar to the simulated one, demonstrating they are crystallized ZIF-8. In addition, due to the adsorption of CTA\(^+\), the surfaces of these ZIF-8 particles are positively charged with \(\zeta\)-potential values ranged from 26 to 32 mV (Figure 2K).

In additional to shapes, the size of the anisotropic ZIF-8 particles can be tailored by adjusting the concentration of CTAB. For example, ZIF-8 particles (Figure S3, Supporting Information) with size of 188, 210, and 239 nm with corresponding \(m\) value of 3.7, 3.5, and 4.9 were synthesized with CTAB concentrations of 1.36, 1.18, and 1.10 mM are used, respectively. Higher concentration of CTAB could induce a slower growth of the ZIF-8 seeds and thus smaller ZIF-8 particles. Taking advantages of the precise control of their shape and size, the highly uniform anisotropic ZIF-8 particles can work as ideal building blocks for constructing colloidal PCs with different lattice structures.

Figure 2. A,B,D,E,G,H) SEM images, C,F,I) schematic illustration, J) XRD patterns, and K) potential value of sample A–C) 1, D–F) 2, and G–I) 3. The injection time for sample 1, 2, and 3 is 7 min, 5 min, and 3 min, respectively. The injection liquid volume is 5 mL, and the concentration of CTAB is 0.92 mM for all three samples.
2.2. PCs with Tunable Lattice Structures by Self-Assembling Anisotropic ZIF-8 Particles

Dense hard-particle packings are fundamental issues as useful models of heterogeneous materials and granular media, which are intimately related to the structure of low-temperature phases of matter.\(^{[16]}\) Computational constructions for nonspherical-shaped superball packings have revealed a correlation between the shape parameter \(m\) of the particles and the lattice structure of the assembled super structures.\(^{[15,16]}\) Here in this work, ordered super structures with various lattice structures can be obtained by tuning the \(m\) values of the uniform ZIF-8 particles. Typically, the aqueous colloidal solution of sample 1–3 are casted on PDMS substrates separately. After evaporation of the solvents, long-range ordered structures with different brilliant structural colors, lattice structures, and optical properties are prepared (Figure 3). As shown in Figure 3A–C, when cubic like ZIF-8 particles (sample 1, \(m = 9.7\)) are self-assembled into long-range ordered structures, the particles are closely packed into PC with simple-cubic lattice (PC-SCL), with a packing fraction of 97.4%. The PC has two reflection wavelengths (Figure 3D) located at 1053 and 531 nm, which can be ascribed to the first and second diffraction of light by the ordered structures, respectively. The reflection peak positions of the PC can be calculated by Equation (2–4).

\[
\lambda_1 = 2d(n_{\text{eff}}^2 - \sin^2(90 - \theta))^{1/2} \\
\lambda_2 = nd(n_{\text{eff}}^2 - \sin^2(90 - \theta))^{1/2} \\
n_{\text{eff}} = n_f^2 + n_s^2
\]

where \(\lambda_1\) and \(\lambda_2\) are the first- and second-order diffraction of light, respectively. \(\theta\) is the angle between the incident/reflective light and the horizon line. \(n_{\text{eff}}, n_f,\) and \(n_s\) are the effective refractive index of PC, ZIF-8 particle, and air, respectively. \(f_i\) and \(f_s\) are the volume fraction of PC-SCL and air, respectively. \(d\) is the lattice constant of the simple-cubic lattice, which equals to the size of ZIF-8 particles. Using Equation (2–4), the \(\lambda_1\) and \(\lambda_2\) are calculated to be 1045 and 523 nm, respectively, in good agreement with the measured values, 1053 and 531 nm, respectively. The intense reflectance of the reflection signals strongly supports that the highly ordered structures of PC-SCL are obtained. This comparable intensity of the first- and second-order diffraction of the anisotropic ZIF-8 particles-based PC provides a new approach to achieve bright structural colors and enrich their applications.

In addition to the simple-cubic lattice, PCs with rhombohedral lattice (PC-RL) are assembled using ZIF-8 particles with smaller \(m\). As shown in Figure 3E–G, ZIF-8 particles with \(m\) value of 4.7 self-assembled into long-range ordered structures with 3D rhombohedral lattice, which behaves as a PC with vivid color. Similar to the PC-SCL scenario, two intense reflection peak positions located at 888 and 450 nm are observed due to the first- and second-order diffraction of PC-RL, respectively (Figure 3H). The bright blue color is arisen from the second-order reflection of light at 450 nm. Noticeably, the second-order diffraction of the PC-RL with simple-cubic like self-assembled from the ZIF-8 particles is so strong that brilliant blue color can be observed, which is difficult for the spherical-particles-based PC. The origin of the intense reflection of the second-order diffraction of these PCs will be studied in a future work.

Unlike to the highly ordered structures packed by the ZIF-8 particles with high \(m\) value (9.7 and 4.7), two phases are existed in the structure self-assembled from ZIF-8 particles with low \(m\) value (2.5), confirmed by the SEM image (Figure 3I–K). One is a crystal phase with face-centered-cubic lattice closely packed by ZIF-8 superball particles. The other one is an amorphous phase with short-range ordered structures of random packed particles. This discrepancy in packing randomness between high \(m\) and low \(m\) ZIF-8 particles is reasonable since high \(m\) particles dominated with \{100\} facets and sharp corners tends to assemble into long-range ordered structure. Specifically, these high \(m\) particles prefer packing into face-to-face structures by their \{100\} facets rather than face-to-corner structures to minimize the entropy for the whole colloidal system. In striking contrast, for the low \(m\) ZIF-8 particles, the face-to-face packing can be accomplished by \{100\}-to-[100], [110]-to-[110], or [100]-to-[110] fashion. Increase in defects during the assembly process due to these various packing ways would lead to amorphous phases, and thus cause the strong scattering of noncoherent light and pale structural color (Figure 3L).

2.3. Tunable Photonic Stop Bands and Corresponding Structural Colors

The optical properties of PCs including photonic stop band and corresponding structural colors can be well controlled through adjusting the size of ZIF-8 particles.\(^{[18]}\) For example, PC-RL with similar rhombohedral lattice (Figure 4A–C) but different reflection wavelength and structural colors (Figure 4D–F) are fabricated by altering the size of the ZIF-8 particles used for self-assembly while keeping the \(m\) values similar. PC-RL with reflection peak positions located at 438, 528, and 620 nm and corresponding to blue, green, and red colors can be obtained using ZIF-8 particles with size (\(m\) value) of 188 nm (3.7), 210 nm (3.5), and 239 nm (4.9), respectively. Different from the PC-SCL (Figure 3D) and PC-RL built from larger particles whose color from the second-order diffraction, the brilliant structural colors of these PCs are arisen from the first-order diffraction of the visible light. In addition, the reflection wavelengths of these PCs blue shift as the incident light and viewing angles simultaneously altered from 0° to 60°. According to Bragg’s law (Equation (2)), the decrease in \(\theta\) will lead to the decrease in \(\sin \theta\) and blue shift of the reflection peak position (Figure 4G–H). The corresponding reflection spectra are shown in Figure S4, Supporting Information. The variation of the reflection signal under different viewing angles further proves the ordered structures of these PC-RL.

Similar to the PC-RL, the reflection wavelength and the structural color of PC-SCL can also be tuned by tailoring the size of particles. Briefly, PC-SCL with reflection peak positions located at (412, 801, Figure 5A) and (590, 1154, Figure 5B) nm, and corresponding deep blue and red colors can be obtained when cubic like ZIF-8 particles with size of 318 and 515 nm are used, respectively. The brilliant colors of these PC-SCL come from the second-order diffraction of light by the ordered there structures rather than the first-order diffraction commonly in spherical PCs.
In addition, these PC-SCL also possesses simple-cubic-like lattice (Figure 5C–D) due to their high $m$ values (9.2–9.5). Therefore, one can alter the stop bands and corresponding structural colors of PCs by simply adjusting the size of particles.

2.4. Encryption of Information through Combinations of PCs

Compared with the conventional spherical-particles-based PCs, the wide-range and precise tunability of the photonic stop bands, structural colors, and especially the lattice structures of PCs, together with the anisotropic and porous ZIF-8 particles will facilitate the application of PCs in color displays, precise detection, optical device, and anticounterfeiting. In this work, we have developed a new information encryption technology based on the specific optical characteristics of PC-RL and PC-SCL, which broadens the PCs-based anticounterfeiting applications.

As discussed earlier, the structural color of the anisotropic ZIF-8 particle-based PC can be generated from their first-order or second-order diffraction using small or large size of particles, respectively. For example (Figure 6A), the green color can be
generated from 1) the first-order diffraction of PC-RL, particle size of 210 nm and m value of 3.5, and 2) the second-order diffraction of PC-SCL, particle size of 358 nm, and m value of 9.7. The visible reflection wavelengths of PC-RL and PC-SCL are comparable at 528 and 531 nm, respectively, implying that they can show very similar colors (as confirmed by the inset in Figure 3D and Figure 4E). Compared with the PC-RL, PC-SCL have an additional reflection peak located at near-infrared (NIR) region. These unique characteristics inspire us to develop a new technology to encrypt information through combination of PC-RL and PC-SCL with similar peak position at visible range but different reflection behavior at the NIR range. The encryption of information is realized by the self-assembly of anisotropic ZIF-8 particles with different m values. 3D-ordered superstructures with simple-cubic, rhombohedral, and face-centered-cubic lattices are obtained when m values of the particles are 9.7, 4.7, and 2.5, respectively. Different from the conventionally spherical-particle-based PC, the anisotropic ZIF-8 particle-based PCs have intense reflectance at the second-order diffraction. Brilliant structural colors can be generated by their first- or second-order diffraction of the PCs, which can be well controlled through altering...

3. Conclusions

In summary, PCs with tunable lattice structures, photonic bandgaps, and structural colors are fabricated through the synthesis and self-assembly of the anisotropic ZIF-8 particles with different m values. 3D-ordered superstructures with simple-cubic, rhombohedral, and face-centered-cubic lattices are obtained when m values of the particles are 9.7, 4.7, and 2.5, respectively. Different from the conventionally spherical-particle-based PC, the anisotropic ZIF-8 particle-based PCs have intense reflectance at the second-order diffraction. Brilliant structural colors can be generated by their first- or second-order diffraction of the PCs, which can be well controlled through altering...
the lattice structures and size of the anisotropic ZIF-8 particles. A new information encryption technology is developed by the combinations of PC-SCL with two reflection signals (531 and 1053 nm) and PC-RL with one reflection peak (528 nm). At normal conditions, the information is hidden and cannot be recognized by naked eyes due to the similar reflection wavelength of these PCs at visible regions. In contrast, the information can be decrypted by merging the reflection signals of visible and NIR range of the PC-RL and PC-SCL. This work opens up a new way to fabricate nonspherical-particle-based PCs with

Figure 5. A,B) Reflection spectra, digital photos, C,D) SEM images and schematic illustration of PC with simple-cubic lattice with anisotropic ZIF-8 particles of different sizes, A,C) 300 nm and B,D) 407 nm. The inset images in (A), and (B) are the photographs of the PCs corresponding to the reflection spectra with scale bars to show the size of these PCs.

Figure 6. A) Reflection spectra of PCs with rhombohedral and simple-cubic structures self-assembled from anisotropic ZIF-8 particles with different sizes and m value (up inset, size: 210 nm, m: 3.5; bottom inset, size: 358 nm, m: 9.7). B) Digital photo and C) reflection signal distribution of the PCs-based encryption of information system. D) Decryption of the information by merging the reflection signal at visible and NIR regions by the eye mode and spectra mode.
tunable lattice structures and specific photonic characteristics, and will promote the applications of PCs in the field of anticounterfeiting, optical sensing, and display.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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