Color from hierarchy: Diverse optical properties of micron-sized spherical colloidal assemblies

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Materials in nature are characterized by structural order over multiple length scales have evolved for maximum performance and multifunctionality, and are often produced by self-assembly processes. A striking example of this design principle is structural coloration, where interference, diffraction, and absorption effects result in vivid colors. Mimicking this emergence of complex effects from simple building blocks is a key challenge for man-made materials. Here, we show that a simple confined self-assembly process leads to a complex hierarchical geometry that displays a variety of optical effects. Colloidal crystallization in an emulsion droplet creates micron-sized superstructures, termed photonic balls. The curvature imposed by the emulsion droplet leads to frustrated crystallization. We observe spherical colloidal crystals with ordered, crystalline layers and a disordered core. This geometry produces multiple optical effects. The ordered layers give rise to structural color from Bragg diffraction with limited angular dependence and unusual transmission due to the curved nature of the individual crystals. The disordered core contributes nonresonant scattering that induces a macroscopically whittish appearance, which we mitigate by incorporating absorbing gold nanoparticles that suppress scattering and macroscopically purify the color. With increasing size of the constituent colloidal particles, grating diffraction effects dominate, which result from order along the crystal's curved surface and induce a vivid polychromatic appearance. The control of multiple optical effects induced by the hierarchical morphology in photonic balls paves the way to use them as building blocks for complex optical assemblies—potentially as more efficient mimics of structural color as it occurs in nature.

Significance

Controlling the internal structure over multiple length scales can produce materials with superior properties. This hierarchical design is ubiquitous in nature where materials have evolved to show maximum functionality from a limited choice of available building blocks. Mimicking the emergence of functionality from simple building blocks is a key challenge for man-made materials. Here, we show how a simple confined self-assembly of colloidal particles leads to a complex geometry that displays a surprising variety of optical effects. These effects are a result of the intricate interaction of light with the structural features at different length scales, and the geometry of the self-assembled structure. The results underline the importance of controlling assembly processes over multiple length scales to tailor properties and maximize performance.


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interesting confinement for the crystallization process is an emulsion droplet that creates colloidal assemblies known as photonic balls (16–19). Curvature imposed by the spherical confinement is a unique structural element of photonic balls. It is known that curvature induces different types of defect structures in 2D (20, 21) and 3D assemblies (22), which can affect the resulting optical properties. Photonic balls have recently gained attention in various optical applications, including pigments (23–26), sensors (27), magnetically switchable colorants (25, 28), and color-coded substrates for biomaterials evaluation (29, 30).

Here, we provide a detailed physical understanding of the different optical phenomena occurring in photonic balls and trace the origin of these properties to structural details, especially curvature. We use focused ion beam-assisted cross-sectioning to visualize the effect of confinement on the internal morphology and find ordered, layered crystal planes near the interface and a more disordered region toward the center. Tailoring the degree of confinement allows us to control the crystallinity and thus, the resulting color arising from Bragg diffraction. Disorder and defects, caused by frustrated crystallization in the curved confinement, contributes to unwanted broadband scattering of light, which compromises the macroscopic color. We introduce gold nanoparticles as subwavelength, spectrally selective absorbers into the photonic balls to suppress light scattering in spectrally unwanted regions. This synergistic combination of plasmonic absorption with Bragg diffraction leads to a macroscopically purer coloration, if the photonic crystal stop band and gold nanoparticle absorption are appropriately adjusted. Finally, we observe more complex optical signatures in the reflection of light from photonic balls assembled from larger colloidal particles \(d > 400 \mu m\) that result from grating diffraction caused by a regular arrangement of colloids at the surface of the photonic balls.

Our theoretical experimental examination of the influence of curvature and confinement on the different optical phenomena enables us to create a complete picture of the rich optical properties of these simple, hierarchical self-assembled structures.

**Results and Discussion**

**Synthesis and Internal Morphology of Photonic Balls.** We use droplet-based microfluidics to emulsify an aqueous dispersion of polystyrene colloids in a continuous fluorocarbon oil phase (31). The cross-junction devices are conveniently prepared from poly(dimethylsiloxane) (PDMS) by soft lithography and enable us to create stable emulsions with narrow size distributions in a continuous-flow process as illustrated in Fig. 1A (32). After emulsification, the water is removed from the generated droplets at 45 °C, resulting in shrinkage of the emulsion droplets and self-assembly of the colloids in their spherical confinement. We control the diameter of the produced photonic balls from below 10 \(\mu m\) to above 100 \(\mu m\) by tuning the concentration of colloids in the aqueous dispersion and the size of the emulsion droplet generated in the microfluidic device (Fig. S1). The surface of the balls, visible in Fig. 1 B and C, shows colloids ordered in a polycrystalline, close-packed lattice, previously assigned as the \((111)\) lattice plane of the 3D crystal formed in the spherical confinement (23, 24). However, the curvature in the confinement impedes the formation of a perfectly ordered crystal, resulting in characteristic defects and assembly structures (20, 21). A focused ion beam (FIB) was used to cross-section photonic balls and uncover their internal crystal structure, which we show in Fig. 1D and Fig. S2. The cross-sections reproducibly indicate the presence of a layered morphology of the colloidal crystal toward the interface, consisting of several close-packed \([i.e., \,(111)\)] planes stacked into a curved 3D crystal. Towards the center of the ball, the assembly appears increasingly disordered, presumably as a consequence of increasing frustration. The higher the level of confinement is \(i.e.,\) the smaller the ratio of the diameters of ball and colloid, \(d_{\text{ball}}/d_{\text{col}}\), the fewer ordered layers exist \(\text{Fig. S2}\). It is worth noting that the structures we observe seem less faceted and appear to follow the curvature of the confinement more than would be expected from thermodynamic considerations (22), indicating that kinetic effects may play a significant role in our system.

![Fig. 1. Photonic balls are prepared by self-assembly of colloids in the spherical confinement of emulsion droplets.](https://www.pnas.org/cgi/doi/10.1073/pnas.1506272112)

This curved crystal structure relates to multiple optical properties observed in photonic balls, as schematically illustrated and labeled in Fig. 1E. We estimate the amount of order present in photonic balls of a given size based on the intensity of structural coloration that we observe from Bragg diffraction at the ordered lattice planes \(d_{\text{ball}}\). We show that broadband scattering of light, caused by the photonic ball dimensions and the internal disorder, induces a whitish macroscopic appearance \(d_{\text{ball}}\), which can be mitigated by incorporating gold nanoparticles. Finally, we identify the ordered arrangement of colloids at the surface of the photonic ball as the origin of color from grating diffraction \(d_{\text{ball}}\).

**Coloration Arising from Bragg Diffraction.** We investigate the color of individual photonic balls, using a fiber-optic cable to collect and spectrally analyze reflected light of individual photonic balls through a microscope objective lens. Fig. 2A shows optical images and corresponding measured reflection spectra \(d_{\text{ball}}\) of individual balls \(d_{\text{ball}} = 30 \mu m\) consisting of colloids with sizes of 180 nm, 225 nm, and 250 nm that display blue-green, and red structural color, respectively. This color has been previously assigned to Bragg diffraction, i.e., constructive interference of light reflected at individual lattice planes in the curved colloidal crystal \(23\). The FIB cross sections \(\text{Fig. 1D and Fig. S2}\) confirm the presence of such layers in our system. A consequence of the spherical nature of the photonic balls is the lack of angular dependence under illumination conditions in a microscope as shown in Fig. 2B.

![Fig. S2.](https://www.pnas.org/cgi/doi/10.1073/pnas.1506272112)

We model the photonic balls as a multilayer structure in a 1D transfer matrix simulation with a refractive index profile corresponding to a stacked, close-packed colloidal crystal \(d_{\text{ball}}\) \(23\). The simulated spectra, shown as dotted lines in Fig. 2A, match the experiments, corroborating that multilayer interference at stacked \(d_{\text{ball}}\) can cause the observed color. To match the peak intensity, simulations were performed assuming seven \(180\)-nm colloids and nine \(225\)-nm and \(250\)-nm colloids) perfectly ordered layers of colloidal crystal.

The most prominent feature of the optical microscope images throughout Fig. 2 is an area with intense, uniform color in the center of the ball surrounded by a pale, almost colorless rim. We attribute this color pattern to the spherical nature of the hierarchical assembly: Only the center of the photonic ball...
reflected light that can be detected in the microscope objective (Fig. S4A). Larger angles of incidence and reflected light—causing a blue shift of color—are not picked up by the microscope objective (Fig. S4A), creating the observed uniform coloration. The colorful area of the ball corresponds to the angular range of back-reflected light, which can be explained by the curved nature of the ball and directly visualized by illumination from the side (D). The reflected light intensity depends on the size of the photonic balls and reaches saturation for balls with a diameter of 50 μm and larger. The intensity correlates with an increase in the number of ordered layers obtained from simulations (solid line) (F). (All scale bars, 10 μm) F, Insets show photonic balls with a diameter of 8 μm (Left) and 100 μm (Right).

Unlike typical thin film photonic crystals, photonic balls exhibit transmission spectra that are not the inverse of the reflection; instead, only light above a critical threshold wavelength is transmitted, whereas light with energies higher than the observed reflection peak seems unable to pass the structure (Fig. 2C). Again, we attribute this unexpected behavior to the curved nature of the crystal, as schematically illustrated in Fig. 2D. Even though only light reflected normal to the ball’s surface is picked up in the reflection spectrum (resulting in a green reflection peak in the illustration), reflections also occur at different angles (although they are not picked up by the microscope as described above). Such reflections will have a larger angle between incident and reflected light, which translates to constructive interference occurring at lower wavelengths (i.e., cyan and blue light in the illustration) (33). Therefore, only light with wavelengths higher than the threshold defined by the constructive interference at normal incidence is transmitted, leading to the transmission characteristics shown in Fig. 2C. This phenomenon can be observed directly, if a photonic ball is illuminated from the (Fig. 2D).

The size of the photonic balls, and thus the confinement of the colloids, can easily be controlled synthetically. Fig. 2E exemplarily shows reflection spectra of photonic balls prepared from 250-nm colloids with a size of 15 μm, 30 μm, and 100 μm (to-scale microscope images are shown in Fig. 2F, Insets). With increasing size of the photonic ball, the intensity of the Bragg reflection peak increases and reaches values close to saturation for balls with a size of 50 μm (Fig. 2F). This indicates an increase in crystallinity as a result of a less severe confinement with increasing ball size. We then compare the measured reflected light intensity for different ball diameters with simulated values of multilayer reflection with increasing numbers of crystalline layers (Fig. 2F). The measured reflectivities closely follow the simulated values, indicating that the amount of order is directly correlated to the degree of confinement. Consequently, we can use optical information to indirectly assess the degree of internal order of individual photonic balls by comparing the measured and simulated intensity of reflected light.

Mitigating Scattering by Incorporation of Spectrally Selective Absorbers

The spherical confinement of the photonic balls inherently induces disorder in the colloidal arrangement, leading to a whitish appearance due to scattering. To create structural color with high chromatic values, the nonresonant scattering needs to be controlled. The addition of broadband absorbers (for example, carbon black) can suppress scattering, increasing the contrast between spectral background and Bragg diffraction peak (34, 35). However, the Bragg peak itself can decrease as well due to the unselective nature of absorption. In contrast, light absorption of noble metal nanoparticles at their plasmon resonance frequency occurs over a rather narrow part of the visible spectrum and can be tuned by changing size and shape of the metal nanoparticle (36). Such nanoparticles can serve as spectrally selective absorbers that absorb scattered light at undesired wavelengths (37). Most importantly, their absorption frequency can be tailored to minimize interference with the Bragg diffraction peak of the photonic crystal. This leads to a purification of the optical spectrum by suppression of the intensity of scattered light from undesired parts of the spectrum with minor effects on the intensity of the Bragg peak.

Here, we use 12-nm gold nanoparticles (details in SI Materials and Methods) to mitigate the whitish appearance caused by the presence of disorder, producing a more crisp red coloration as demonstrated in Fig. 3. Due to their small size, the gold nanoparticles do not interfere with the assembly of the colloidal particles, enabling the creation of hybrid photonic–plasmonic balls (38). Fig. 3 A–C shows single-particle spectra of three different types of such hybrid balls. A disordered ball containing gold nanoparticles, prepared by mixing two populations of colloidal particles with diameters of 200 nm and 250 nm chosen to induce disorder by lattice mismatch, does not show a Bragg reflection peak (Fig. 3A). The plasmon resonance of the gold nanoparticles leads to a dip in the reflection spectrum at 520 nm, indicated by an arrow in Fig. 3A, resulting in a dull, reddish appearance. An ordered photonic ball, consisting of 250-nm colloids without gold nanoparticles, is shown in Fig. 3B, with a red color stemming from the Bragg diffraction peak at 600 nm. Figure 3B shows a photonic ball without gold nanoparticles that shows a Bragg diffraction peak at 620 nm. The addition of gold nanoparticles to an ordered photonic ball (Fig. 3C) combines the two spectral features: A dip in reflection, caused by the plasmon resonance, lowers the reflected light intensity in the lower-wavelength (blue/green) part of the spectrum but does not affect the higher-wavelength (red) region with the Bragg peak. Theoretical investigations reveal that the position of the gold
Color purification by incorporation of spectrally selective absorbers. The absorption of the Au NPs lowers the reflection of light in the blue/green part of the spectrum (arrow), giving the ball a dull, red appearance. An ordered photonic ball with gold nanoparticles shows lowered reflection at the blue/green part of the spectrum without affecting the Bragg reflection peak. Control of scattering properties by addition of Au NPs in ensembles of photonic balls. Microscopic images (D and E, taken with identical exposure times) and macroscopic images (F) reveal an increased contrast.

Coloration Arising from Grating Diffraction. Photonic balls assembled from colloids with a diameter above 400 nm show color patterns that differ substantially from their analogs with smaller colloid sizes. Bright, multichromatic color patches appear at the outer regions of the photonic ball, showing color travel from blue to red with increasing distance from the center. This contrasts with the uniform coloration with colorless rims observed for photonic balls from colloids with sizes smaller than 400 nm.

Previously, such color patterns in larger colloid assemblies were attributed to Bragg diffraction from different crystal planes (38) and grating diffraction effects (39). Here, we present further evidence that Bragg diffraction from different crystal planes is an unlikely origin of color patterns and that diffraction-grating effects, arising from periodic arrangements of colloids at the surface of our micron-scale photonic balls, are responsible for the optical effect. A representative SEM image (ball diameter 15 μm), highlighting the ordered, close-packed arrangement of 400-nm colloids at the surface of the spherical superstructure, is shown in Fig. 4A. A microscope image of a larger photonic ball (d = 100 μm) from similar-sized colloids, shown in Fig. 4B, shows strong rainbow colors extending toward the rim. The lateral distribution of colors is not affected by the ball size (38) and can be seen in all samples with photonic ball diameters between 15 μm and 100 μm (Fig. S7). Clearly, the coloration is characterized by a gradual change from blue to red. Such a color travel is characteristic of grating diffraction, as described by the grating equation, \( m \lambda = d(\sin \theta_i + \sin \theta_r) \) (39). For each diffraction order \( m \), the wavelength of constructive interference (\( \lambda \)) changes with increasing angles of incident light (\( \theta_i \)) and reflected light (\( \theta_r \)) and with the distance (\( d \)) between the individual scatterers.

In contrast, were the colors to arise from Bragg diffraction at different crystal planes, few distinctive colors would be observed.

To resolve the origin of the coloration, we model the surface of a photonic ball as a regularly spaced arrangement of spheres on a hemispherical substrate, as shown in Fig. 4C. We assume that the colloids serve as a curved diffraction grating and calculate the angular distributions of constructively interfering waves for different colors from the grating equation for different positions along the surface. Although the illumination is fixed from the top (normal to the substrate plane), the angle that the incoming light beam forms with the ball’s surface differs at different positions as a result of the curved nature of the photonic ball. It is necessary to keep in mind that only light reflected in a small range of angles given by the numerical aperture around the surface normal (with respect to the substrate plane, not the ball surface) is collected by the microscope objective lens (indicated by dotted cones in Fig. 4C). Colors that are visible in the microscope image must therefore be reflected at angles within this cone. Because the angle of incident light with the curved surface changes with increasing distance from the center, so does the wavelength of light constructively interfering at angles that can be picked up by the objective lens. As we move the beam away from the center (Fig. 4 A, C), grating diffraction predicts the shortest wavelength (blue light, modeled at 400 nm) to be picked up by the microscope first (Fig. 4 C, 2). With increasing distance from the center, the light arriving in the microscope changes gradually along the visible spectrum via green (550 nm, Fig. 4 C, 3) toward red (750 nm), which the model predicts to reach the objective lens only by reflection close to the rim (Fig. 4 C, 4).

To facilitate comparison between model and experimentally observed coloration, we present the results of the model in a top-view representation in Fig. 4D. Light of a given wavelength that is collected by the microscope objective at a given distance from the center is represented by a colored dot. We choose to illustrate the
data obtained by the 1D model on the surface of a disk, representing the photonic ball as seen in a microscope, and assign a sixfold symmetry for the color map to depict the symmetry of a colloidal crystal. Image analysis, performed by measuring the distance of different color patches from the center of the photonic ball, reveals quantitative agreement on the color position between model and experiment (Table S2).

From the grating diffraction model, we expect a shift of the diffracted colors toward lower angles with larger periodicities. For the photonic ball, this translates into a shift of the rainbow-colored patches toward the center of the ball if the size of the constituent colloids is increased (38). The theory also predicts the appearance of higher-diffraction orders at larger angles (39), which should be observed at locations farther from the center of the ball. Indeed, both features are visible in the optical micrographs shown in Fig. 5. Photonic balls assembled from 610-nm colloids illuminated from the top and side are shown in Fig. 5 B and C, with a second grating order visible toward the rim of the structure. The position of the individual colors again coincides with the model quantitatively (Table 1 and Fig. S8). More remarkably, in photonic balls from 1,060-nm colloids (Fig. 5 F and G), three diffraction orders are visible and can be correlated with the model (Fig. 5, Table S2, and Fig. S8). The color patches assigned to the individual diffraction orders in the model (Fig. 5 D and H) are offset for better visibility.

To unambiguously assign the observed color to grating diffraction and not Bragg diffraction (24, 38), we coat large, 50-μm polystyrene microbeads with a monolayer of 610-nm colloids—the same particles used to assemble the photonic balls in Fig. 4 A–C—following a protocol from the literature (40). This monolayer-on-microbead architecture, shown in Fig. 5I, mimics the surface of a photonic ball but not its crystalline interior. Therefore, it cannot show Bragg diffraction. However, in the optical microscope image shown in Fig. 5I, we observe similar color patterns to those for the 3D photonic ball, with matching lateral position of the colors (Table 1). Therefore, we conclude that we indeed observe diffraction-grating effects on individual microscale photonic balls.

### Conclusion

We explore how hierarchical order influences the properties of a self-assembled structure by studying individual microscale spherical colloidal crystals, known as photonic balls. Curvature, imposed on the colloidal crystal through the spherical confinement of an emulsion droplet, is the key element that alters the properties of the assembly. We provide a complete physical understanding of all optical effects observable in the prepared photonic balls and connect them to their structural origins.

FIB-assisted cross-sectioning indicates a layered morphology in the photonic balls that consists of radially ordered layers stacked from the interface toward the interior and a more disordered assembly towards the center. The layered structure gives rise to structural coloration by Bragg diffraction. When observed in a microscope, the presence of curvature creates uniform, angle-independent colors with a distinct colored ball area that reflects the numerical aperture of the objective. In contrast to flat opal films, the transmission spectra of a photonic ball are not the inversion of the reflection spectra but resemble a long-pass filter—again caused by reflection of light from the curved crystal. We control the degree of crystallinity via the size of the photonic balls and correlate the internal structure with the observed color intensity. Furthermore, we show that gold nanoparticles can be used as spectrally selective absorbers to suppress scattering, leading to a macroscopically brighter color. We present evidence that photonic balls assembled from colloids with a diameter of 400 nm or larger show diffraction-grating coloration arising from the periodic arrangement of colloids at the surface of the particles.

We anticipate these results will lead to several research directions. First, additional insight into crystallization in spherical confinements, especially with respect to the crystallization mechanism and its kinetics, is needed to understand and control the assembly of colloids into spherical superstructures. Second, if the quality of the photonic balls can be reproducibly provided, they may serve as interesting materials for potential use as miniaturized photonic elements, for example as long-pass filters, diffraction gratings, or colorimetric sensors; in (optical) laboratory-on-a-chip applications; or as dispersible structural color pigments. Finally,

### Table 1. Lateral positions of selected colors observed experimentally (r_{meas}) and calculated from the diffraction-grating equation (r_{calc}) for 3D photonic balls and monolayer-on-microsphere architecture (both from 610-nm colloids)

<table>
<thead>
<tr>
<th>D.O.</th>
<th>λ, nm</th>
<th>r_{calc}/r_{ball}</th>
<th>r_{meas}/r_{ball}</th>
<th>Discrepancy, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photonic balls (d_{ball} = 610 nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>400</td>
<td>0.33</td>
<td>0.30 ± 0.03</td>
<td>9.7</td>
</tr>
<tr>
<td>550</td>
<td>0.45</td>
<td>0.46 ± 0.04</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>0.61</td>
<td>0.69 ± 0.05</td>
<td>13.7</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>400</td>
<td>0.66</td>
<td>0.62 ± 0.04</td>
<td>5.0</td>
</tr>
<tr>
<td>550</td>
<td>0.90</td>
<td>0.81 ± 0.05</td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td>Monolayer-on-microbead architecture (d_{micro} = 610 nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>400</td>
<td>0.33</td>
<td>0.27 ± 0.01</td>
<td>16.3</td>
</tr>
<tr>
<td>550</td>
<td>0.45</td>
<td>0.45 ± 0.04</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>0.61</td>
<td>0.73 ± 0.03</td>
<td>19.3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>400</td>
<td>0.66</td>
<td>0.65 ± 0.02</td>
<td>1.4</td>
</tr>
<tr>
<td>550</td>
<td>0.90</td>
<td>0.81 ± 0.05</td>
<td>10.8</td>
<td></td>
</tr>
</tbody>
</table>

Data are presented as fractions of the ball radius r_{ball} for the different diffraction orders (D.O.).
the use of photonic balls as building blocks to create higher levels of hierarchy by self-assembly into more complex superstructures is a promising approach to further refine and exploit their rich optical properties.

Materials and Methods

Colloidal particles were synthesized by surfactant-free emulsion polymerization with acrylic acid as comonomer (41). PEG-modified gold nanoparticles with a size of 12 nm were synthesized by reduction of sodium tetrachloroaurate (Fig. 59) as described in the literature (42). Microluidic devices were prepared by soft lithography from masters prepared by photolithography (31). Simulation of the optical properties was performed as a 1D transfer matrix method implemented in Matlab and effects of gold nanoparticles were included by adjusting the refractive index profile (43). Optical spectra of individual photonic balls were measured through a microscope objective lens. All procedures are described in detail in SI Materials and Methods.

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