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Self-Assembly of Colloidal Particles into Amorphous Photonic Crystals

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Abstract: Colloidal photonic crystals (PCs) have been extensively investigated since they can be prepared in an efficient and low-cost way. Different from the conventional PCs with highly ordered structures, amorphous photonic crystals (APCs) with isotropic photonic bandgap and non-iridescent structural colors have attracted growing interests especially in pigments, angle-independent displays, and optical coatings. This review focuses on the various strategies for the fabrication of the APCs by spraying, infiltration, layer-by-layer deposition, electrolyte-induced assembly, electrophoretic deposition, phase separation, assembly of bi-disperse-suspension, particle with rough surface, soft particles, and low-charged particles. Their potential applications are also summarized, like angle-independent displays, sensors, paintings, anti-counterfeiting labels, information storage, and so on. Finally, we present our perspectives together with the challenges of APCs.
1. Introduction

Photonic crystals (PCs) can be considered as periodic arrangements of regularly shaped materials (often a multiplicity of layers or spheres in a host polymer) with different dielectric constants.\textsuperscript{1, 2} The visible light can be selectively reflected by the microstructures of PCs, which can be explained by Bragg’s law, resulting in iridescent or noniridescent structural colors. According to their structures, PCs can be divided into highly ordered and amorphous photonic crystals (OPCs and APCs). The OPCs with angle-dependent structural colors have been reviewed by some nice works.\textsuperscript{3-9} APCs are comprised of the short-range-ordered colloidal crystals (Fig. 1a), photonic band structure does not exist and only has a nonzero photonic density of states photonic pseudogap.\textsuperscript{10}

As shown in Fig. 1b, the radial distribution function in the APCs with randomly close-packed colloidal particles is almost constant over a large distance range and only has distinct peaks at small distances, which indicates the short-range ordered structure of the APCs. In addition, the ring pattern of the 2D Fourier transform demonstrates the isotropic and short-range ordered structure. The photonic pseudogaps in APCs are independent of the direction, so they scatter light uniformly in all directions.\textsuperscript{11} The coherent scattering of light by an isotropic photonic pseudogap creates non-iridescent structural colors.\textsuperscript{12-15} According to their unique structure, APCs show great potential of various applications in sensors,\textsuperscript{16-32} printings,\textsuperscript{33-39} displays,\textsuperscript{17, 30, 40-50} and anti-counterfeiting.\textsuperscript{45, 51-57}

![Fig. 1](image_url) (a) Schematic of an amorphous colloidal array under white light, and the structural colour from the amorphous array remains nearly unchanged depending on the viewing angle. (b) Histogram of two-dimensional RDF of the APCs structure, and inset is the 2D Fourier transform. (Reproduced with permission.\textsuperscript{36} Copyright 2018, American Chemical Society.)
Diverse fabrication methods of APCs by self-assembly of colloidal nanoparticles have been widely developed in the past decade. Among them, most of the bottom-up strategies are simple and cost-effective. In general, the monodispersed colloidal building blocks have a strong tendency to crystallize,\textsuperscript{58, 59} and the commonly used self-assembling methods for conventional colloidal crystals are difficult to prepare APCs. The key strategy to obtain amorphous colloidal crystals is to inhibit the crystallization of colloidal particles in large scale or to disturb the self-assembling process of colloidal particles into partially ordered arrangement. For example, APCs are prepared by the assembly of colloidal particles in multiple sizes.\textsuperscript{48, 49, 60-66} The monodispersed colloidal particles are assembled into amorphous photonic crystals by the following methods, including surface modification, concentration of building blocks,\textsuperscript{67-69} solvent evaporation,\textsuperscript{44, 45, 70-74} addition of electrolyte\textsuperscript{75-77}, and electrophoretic deposition.\textsuperscript{33, 34, 78-80} In order to reduce the strong incoherent light scattering in the APCs structure, light-absorbing materials are induced into the amorphous colloidal crystal array to enhance the saturation of their structure color, such as carbon black (CB),\textsuperscript{44, 81-83} graphene,\textsuperscript{21, 32, 84} polydopamine (PDA),\textsuperscript{26, 85-87} \(\text{Fe}_3\text{O}_4\),\textsuperscript{17, 19, 41} and the other commonly used light-absorbing materials.\textsuperscript{49, 65} In addition, by combining the non-iridescent structural colors of APCs arrays with the responsive materials, APC devices with different functions can be achieved. However, it remains a challenge to commercialize the APCs.

Herein, we summarize the constructing strategies for the APCs, the light-absorbing materials for improving structure color and their applications. First, a brief overview of the preparation strategies for APCs by self-assembly of colloidal particles are presented, including spraying, infiltration-induced colloidal assembly, layer-by-layer, phase separation, electrophoretic deposition (EPD), space confinement, microfluidic assembly, electrolyte induced assembly, assembly of bi-disperse-suspension, assembly of rough-surface particles, assembly of soft particles, assembly of low-charged particles and polymer-grafted particle assembly. Second, the light-absorbing materials applied for eliminating the incoherent light scattering from colloidal amorphous arrays are summarized. Third, the applications of APCs for sensors, printing, display, and anti-counterfeiting are discussed. Finally, the perspectives and challenges regarding APCs are proposed. This review provides critical insights for the preparation of novel APCs and the extension of their applications.
2. Constructing strategies for APCs

2.1 Spraying of colloidal solutions

Spraying of colloidal solutions is an efficient and productive strategy for the rapid assembly of colloidal particles into the APCs by volatilizing the solvents. When the colloidal suspension passes through the nozzle, the building blocks in the droplets rapidly assemble into APCs due to the concentration of the particles by volatilization of the solvent and the wetting of the substrate.

Takeoka et al. prepared APCs with non-iridescent structural colors by spraying the suspension on glass plates using spherical silica particles as the building blocks and methanol as the dispersion medium (Fig. 2d). When the nozzle was too close to the substrate or a non-volatile solvent was used, the colloidal particles will be assembled in long-range order with iridescent structural colors. Due to the strong incoherent scattering in the APCs array, the entire visible light is scattered rendering the APCs white. The black material can absorb the whole visible light to suppress incoherent scattering, and a small amount of black material can be added to the array of APCs in order to obtain a uniform color saturation with high structural color. Takeoka et al. added CB to the silica suspension for preparing the APCs, which led to the decreasing of baseline of its reflectance spectra. However, its peak intensity remained almost constant, and the color saturation gradually increased with higher proportion of CB. Once this APCs film is wetted, the structural color disappears due to the match of refractive index between the particles and the gap. Therefore, Yang et al. prepared non-iridescent structural color membranes with superhydrophobicity (static water contact angle of ~155° and roll-off angle of ~2°) by spraying monodispersed fluorosilane-functionalized silica particles (Fig. 2a and b). In addition, Yang and co-workers demonstrated that low surface tension of particles and the solvents in moderate volatility were two critical factors in the formation of amorphous arrays in the spraying method, which was acquired by studying the coffee-ring effect on the assembly of colloidal particles. Besides using hydrophobic colloidal particles as building blocks, spraying a hydrophobic solution on an array of APCs is also a commonly used strategy to prepare the hydrophobic APCs. Different from above, Wang et al. developed a method to assemble underwater superoleophobic APCs films with the rough-surface PS@TiO₂ nanoparticles (Fig. 2c). To improve the adhesion of APCs to the substrate and their mechanical properties, highly viscous polymers can be introduced into the suspension, or the assembled APCs arrays can be cross-linked or immobilized on the substrate for good mechanical properties.
properties. Song et al. prepared high-brightness noniridescent structural colors by adding graphene nanosheets containing a small amount of graphene quantum dots to a sprayed colloidal suspension. Graphene can uniformly absorb the visible light enabling APCs the high color saturation. Besides that, the matching of the photoluminescent (PL) wavelength of GQDs with the pseudo photonic bandgap of APCs achieves PL enhancement, which increases the intensity of the reflection peaks by 2.3 times by doping GQDs. Zhao et al. reported a multishell graphene oxide encapsulated colloidal nanoparticles, and brightly colored APCs were prepared by spraying method, where the presence of graphene oxide resulted in high color saturation of the patterns. APCs were prepared briefly and rapidly by spraying the colloidal solution, but unsuitable pressure and distance of the spraying machine may lead to the formation of PCs. In addition, the volatility, viscosity, and surface tension of the solvent have significant effects on the uniformity and arrangement of the colloidal crystal array, for example, when the surface tension of the solvent is too high to spread on the substrate surface causes inhomogeneous APCs.

Fig. 2 (a) Schematic illustration of the spray method. (b) Water droplets (~10 μL) sprayed on the colorful APC films which are constructed by spray. (Reproduced with permission. Copyright 2014, The Royal Society of Chemistry.) (c) Schematic illustration of the fabrication of PS@TiO₂ NPs/CB amorphous structures (Reproduced with permission. Copyright 2019, American Chemical Society.) and (d) the corresponding optical photographs of membranes composed of silica particles with the diameters of 230 nm, 280 nm, and 360 nm, along with 1.7 wt% CB. (Reproduced with permission. Copyright 2013, Wiley-VCH.)
2.2 Infiltration-induced colloidal assembly

Infiltration-induced assembly of colloidal particles enables fast and large-scale printing of non-iridescent structural color. The APCs are assembled with disordered accumulation of colloidal particles on permeable substrates by rapid penetration of solvent during the filtration process.99, 100 Anodic aluminum oxide (AAO) films with uniform and size-controlled columnar channels can be applied for quantitative analysis of solvent infiltration. Duan et al. assembled colloidal particle on AAO membranes with infiltration-induced process, which was taken as a model to show the assembling process due to a strong downward infiltration flow in the porous channel of AAO. The colloidal particles were adsorbed on the substrate with disordered arrangement for lack of a crystallization drive (Fig. 3a).74 After completely infiltrating the solvent, the colloidal particles eventually arranged in order. Finally, non-iridescent structural color printing was achieved on the paper by inkjet printer with the colloidal suspension as an ink. Duan and co-workers fabricated the thin-film APCs which were assembled by spherical/polyhedral metal-organic framework (MOF) colloidal particles.101, 102 Similarly, Chen et al. reported a crack-free, arbitrarily bendable film of APCs with bright structural color prepared by vacuum filtration of colloidal suspension through an reduced graphene oxide-sulfopropyl methacrylate potassium salt (rGO-SPM) substrate (Fig. 3b and c).16 Graphene oxide composites effectively reduced the reflected light from the substrate. The strategy of infiltration-induced assembly for the preparation of APCs enables the rapid construction of short-range ordered structures, which can be conveniently printed on solvent-absorbing paper with APCs patterns by inkjet printers. However, according to its assembly principle, it needs to be assembled on substrates with high infiltration and its use is limited.
Fig. 3 (a) Illustration of the formation of ACAs due to a strong downward infiltration flow. (Reproduced with permission.\textsuperscript{74} Copyright 2018, Wiley-VCH.) (b) Schematic illustration of the fabrication of rGO-SPM and assembly of the rGO-SPM/poly(St-MMA-AA) membranes via membrane separation-assisted assembly (MSAA) method, and Schematic illustration of MSAA method. The method is facile of achieving uniform structural colors. (c) Photographs of three different colloidal films observed at angles from 90° to approximately 30°. (Reproduced with permission.\textsuperscript{16} Copyright 2019, American Chemical Society.)

2.3 Layer-by-layer deposition

Layer-by-layer method (LBL method) is a prevalent assembly method for precisely controlling the thickness of the thin films by electrostatic interaction in most cases.\textsuperscript{103-107} For investigating the thickness of the APCs array and the effect of the black material on their optical properties, Takeoka et al. prepared large-area and uniform films by the charged colloidal particles together with the oppositely charged polyelectrolytes in an alternate LBL deposition process (Fig. 4a).\textsuperscript{108} The polyelectrolytes with opposite charges on the surface of the substrate are randomly distributed, and therefore the APCs are formed with the disordered packing of colloidal particles under electrostatic force. They demonstrated that the saturation of the structural color can be improved by controlling the thickness of APCs and using a black substrate, and the blackness of the substrate can be controlled by rotating the orientation of the polarizer. The saturation of non-iridescent structural colors are tunable by controlling the thickness of APCs films in the LBL process.\textsuperscript{108} The LBL
method can precisely control the thickness of APCs films by the number of depositions and thus adjust the saturation of non-iridescent structural colors. However, the LBL method has not been widely used for the preparation of APCs because each deposition requires immersion in an oppositely charged solution and harsh assembly conditions.

![Preparation method of the colloidal amorphous array](image1)

**Fig. 4** (a) Preparation method of the colloidal amorphous array composed of silica particles and PDDA on a piece of clear glass plate or a black quartz plate using the LBL method. Optical picture of the colloidal amorphous arrays assembled with differentiated silica particles of 190, 250, and 300 nm and PDDA on a clear glass plate or black quartz plate. (Reproduced with permission. Copyright 2017, Wiley-VCH.) (b) SEM image of the colloidal amorphous array composed primarily of fine spherical silica particles together with a small amount of titanium oxide particles. The insets are a two-dimensional fast Fourier power spectrum obtained from the SEM image. The optical images of the colloidal amorphous array under directional white light in different specular directions. (Reproduced with permission. Copyright 2014, The Royal Society of Chemistry.) (c) A saturated matte SA composed of 310 nm SiO$_2$ colloidal particles (30 wt% in the aqueous fluid) and magnetite colloidal particles (1 wt% in the aqueous fluid) in air. A SEM image of a matte SA composed of 250 nm SiO$_2$ colloidal particles. The inset presents the corresponding 2D FFT image. (Reproduced with permission. Copyright 2015, The Royal Society of Chemistry.)
2.4 Electrolyte-induced assembly

Electrolyte-induced assembly is a method based on the stability theory of charged colloidal suspensions. The electrostatic repulsion between colloidal particles in the suspension system is sensitive to the ions. An electrolyte concentration of $10^{-2}$ M is sufficient to break the stability of the system, resulting in a disordered arrangement of colloidal particles. Takeoka et al. reported a secondary particle in APCs prepared by adding NaCl as the electrolyte (Fig. 4b). When NaCl is added to the suspension, it leads to a decreased thickness of the electric double layer of silica particles and a diminished repulsive force between the particles. Therefore, the amorphous array of closely packed silica particles is formed during solvent evaporation. The addition of CB to the colloidal suspension results in a brighter secondary particle structure color. Subsequently, Takeoka et al. prepared monodispersed spherical assemblies with micro-flow-focusing devices and controlled the assembly of silica colloidal particles in the spherical assemblies by the presence or absence of electrolytes, which enabled the spherical assemblies to display iridescent or non-iridescent structural colors (Fig. 4c). In addition, Takeoka and co-workers also reported a method to prepare thin films of APCs by co-assembling a tiny amount of titanium dioxide and silver nitrate with the colloidal suspension of silica. The silver nitrate served as an electrolyte to interrupt the well-ordered assemblies of silica. Electrolyte-induced assembly provides a shortcut for the preparation of APCs as a facile approach. Electrolyte-induced assembly is a simple and facile strategy for the formation of short-range ordered arrangements of colloidal particles by destabilizing the colloids by adding electrolytes to the colloidal suspension. However, the lack of sufficient electrostatic repulsion between colloidal particles and their easy precipitation may lead to the formation of APCs with uneven structural color.

2.5 Electrophoretic deposition

The structure of APCs and PCs can be constructed by applying an electric field between the colloidal suspension and the substrate. Kang et al. prepared liquid APCs with tunable structural color by applying different bias voltages on Fe$_3$O$_4$@SiO$_2$/propylene carbonate suspensions. Fe$_3$O$_4$@SiO$_2$ shows high electrophoretic mobility and high refractive index contrast, allowing liquid APCs to be sensitive to voltage response and high color saturation. Zhang et al.
reported a multicolor conductive fiber with APCs structure prepared by depositing polystyrene colloidal particles of different sizes on the surface of conductive carbon fibers \textit{via} EPD.\textsuperscript{78} In order to solve the problem that structural color fibers cannot be fabricated on a large scale, Zhang \textit{et al.} developed a electrosprinning method (Fig. 5a and b).\textsuperscript{33} The homogeneity of the electric field during the EPD process directly affects the assembly of colloidal particles. For example, Kang \textit{et al.} reported a method of assembling the dielectric particles in eccentric core-shell microcapsules controlled by dielectrophoresis (DEP) (Fig. 5c), in which the dielectric particles subjected to an inhomogeneous electric field move to the high- or low-field region depending on the dielectric environment.\textsuperscript{79} In addition, Takeoka \textit{et al.} successfully constructed structural-color coatings of APCs with silica colloidal particles as the building blocks on the conductive substrates by EPD. Co-deposition of CB can reduce the effect of incoherent scattered light on the scattering spectrum and improve the visibility of structural colors. The deposited particles in different sizes produced a variety of brilliant coatings (Fig. 5d), and the evolution of the coating structure from long-range-ordered arrangement to amorphous packing could be controlled by increasing the deposition voltage.\textsuperscript{34} EPD prepared APCs allow precise tuning of structural color and uniform deposition of colloidal particles by adjusting the bias voltage or changing the size of colloidal particles. In particular, the liquid APCs reported by Kang \textit{et al.} achieve rapid response to voltage and structural color tuning, which provides a new idea for the design of dynamic photonic pixels.\textsuperscript{41} However, EPD cannot prepare APCs on nonconductive substrates and power consumption is also a problem.

![Fig. 5](https://example.com/fig5.png)

\textbf{Fig. 5} (a) Schematic illustration of the process of colloidal electrospinning and fabrication of
2.6 Phase separation

The structural-color principle of the barbs on bird feathers in nature inspired the phase separation assembly of APCs. According to Dufresne and Prum et al., the amorphous nanostructures in barbs are self-assembled by phase separation of β-keratin from the cellular cytoplasm. Polymerization of B-keratin drives phase separation within the cell, and entanglement or cross-linking of β-keratin fibers immobilizes the phase separation structure. Inspired by this assumption, Takeoka et al. developed a phase-separated porous polymer membrane with non-iridescent structural color with solvent- and temperature-responsive properties. Song et al. designed a layered photonic material with APCs structure and deformation-insensitive based on cascade-microphase-separation (CMPS) (Fig. 6a). The lipophilic alkyl-functionalized silica nanoparticles, carbon black, silicone oil and siloxane-based organogels were co-assembled in chloroform. The organogels were crosslinked and gelated by supramolecular hydrogen bonding during solvent evaporation which resulted in microphase separation. The separated silicone oil microdroplets and silica aggregates were immobilized by the gelation and entanglement of supramolecular chains. The silica aggregates were randomly distributed in the composite film, the interior of which consists of short-range-ordered arrangements of silica particles. Phase separation methods can be used to acquire the structural color bright membrane materials, to impart the ability of APCs to respond to membrane stimuli by introducing stimuli-sensitive polymer systems, or to prepare deformation-independent APCs composites by using the colloidal particle aggregates formed by phase separation to composite with elastic organogels. However, the phase separation process is time-consuming and complicated and is not suitable for large-scale preparation of APCs.
2.7 Space confinement and microfluidic assembly

A series of functionalized photonic microspheres were prepared by Yang and co-workers based on microfluidic technology. Such photonic spheres show angle-independent structural colors because of the spherical symmetry and their internal structure by long-range ordered packing of colloidal particles. APCs structures can be generated by controlling the volume fraction of the colloids particles within the photonic microspheres. For example, Kim et al. demonstrated an
elastic photonic capsule whose optical properties could be controlled by osmotic pressure. The crystallization of the colloidal particles was inhibited by transferring the photonic capsule to a high concentration of aqueous NaCl solution due to a large osmotic pressure difference.121, 135 Accordingly, Manoharan et al. fabricated photonic capsules with non-iridescent structural colors by microfluidic techniques with soft-shelled colloidal particles encapsulated in ethoxylated trimethylolpropane triacrylate (ETPTA) and concentrating the suspension with an osmotic pressure gradient (Fig. 6b).122 Photonic capsules in APC structure possess a more uniform structural color compared to the colloidal crystal microspheres. In contrast to the above, Song et al. utilized a novel "controlled micellization" self-assemble mechanism to achieve non-iridescent structural color microspheres with short-range ordered porous structures (Fig. 6c and d).123, 136-138 Using amphiphilic bottlebrush block copolymers (BBCPs) as surfactants, the controlled swelling of the reverse BBCPs micelles was induced by the confinement of toluene-water microdroplets to make the self-assembled droplets comparable in size to the visible light wavelength. With the evaporation of toluene, short-range ordered porous structures with self-assembled water droplets as templates were formed. Microparticles with non-iridescent structural colors produced by the space confinement and microfluidics techniques show the potential to replace pigments and dyes.83, 139, 140 Microparticles with non-iridescent structural colors prepared by space confinement and microfluidics techniques can display vivid structural colors even at lower concentrations, and such assembled APCs particles can be used as an alternative to dyes and pigments. However, this strategy generally involves a complex preparation process by microfluidics, and the preparation efficiency remains a challenge.

2.8 Assembly of bi-disperse-suspension

The assembly of bi-disperse-suspension is a common method for preparing the APCs, and the assembly of the mixed colloidal particles in two sizes ensures the formation of the APCs structure.51, 61, 141-146 Takeoka et al. obtained APCs with non-iridescent structural colors by self-assembly of monodisperse silica colloidal particles of two different sizes.62 Recently, a simple method to systematically control the degree of structural ordering of colloidal photonic crystals and APCs based on adjusting the size contrast of binary particles was proposed by Kim and co-workers (Fig. 7a).147 At a two particle size contrast of 0.13, the long-range ordered bi-disperse array exhibited high reflectivity and narrow reflection peaks. A short-range ordered structure was established when
the size contrast was increased to 0.23 (Fig. 7b). In addition, by discussing the bi-disperse colloidal particles assembled with reverse emulsion and the evaporative assembled membranes, Xiao and co-workers demonstrated that small-sized colloidal particles tended to stay on the surface of microspheres while the synthetic melanin particles preferred the microsphere surface over silica particles. That work offered a new pathway to the assembly of colloidal particles with different particle sizes and different particle chemistries. The structure of APCs can be created by controlling the coefficient of variation (CV) of colloidal particle diameters. For example, Kohri et al. prepared APCs with bright non-iridescent structural colors by assembling the polydopamine (PDA) particles in CV around 4.4-7.8% and (Fig. 7c).

The structure of APCs can be acquired by introducing an additive into the monodisperse suspension. Zi et al. proposed a strategy to prepare APCs by mixing monodisperse polystyrene particles and ink particles of cuttlefish for self-assembly, cuttlefish ink particles are introduced into colloidal suspensions for assembly for absorbing incoherent scattering and disrupting the long-range ordered structure of the colloidal particles. Kim et al. reported a strategy for preparing the mechanochromic photonic films by co-assembly of silica particles, poly(ethylene glycol) phenyl ether acrylate and polydopamine particles (Fig. 7d). In this system, the repulsive force between the neighboring silica particles caused by the solvation layer results in the formation of colloidal crystal arrays. As the concentration of polydopamine particles increases, the interaction of polydopamine on the surrounding colloidal particles inhibits the crystallization of silica particles and therefore a short-range-ordered arrangement structure is gradually formed. APCs were prepared easily and rapidly by bi-disperse-suspension assembly, and the transformation from PCs to APCs structure could be achieved by adjusting the size contrast of binary particles. However, it is necessary to alter the size of binary particles and the ratio of each component when adjusting the structural color, which is a tedious process.
Fig. 7 (a) Schematic illustrations showing the arrangement of the colloidal particles in two different diameters. (b) Optical microscope (OM) images and optical images of photonic films prepared with various volume fractions of large particles. Cross-sectional SEM images of the films at different volume fractions. (Reproduced with permission.\textsuperscript{147} Copyright 2019, Wiley-VCH.) (c) Photographs of photonic films constructed by black PDA particles. (Reproduced with permission.\textsuperscript{48} Copyright 2015, The Royal Society of Chemistry.) (d) Polydopamine nanoparticle-loaded non-close-packed colloidal arrays in the elastic matrix. (Reproduced with permission.\textsuperscript{153} Copyright 2019, American Chemical Society.)

2.9 Assembly of particle with rough surface

The rough-surface colloidal particles assist in the assembly of the APCs structures. Yang \textit{et al.} grafted polypyrrole (PPy) particles onto the surface of polystyrene nanoparticles by \textit{in situ} polymerization, which led to the formation of amorphous arrays due to the bumpy surface of the core-shell nanoparticles (Fig. 8a and b). The black PPy shells provided strong contrast in the APCs by suppression of incoherent scattering and multiple light scattering.\textsuperscript{154} In addition, Yang \textit{et al.} reported the colloidal particles consisting of PPy shell and silica core, which can be directly written to prepare APCs by dispersion in a solvent. The surface grafted polypyrrole effectively suppressed the coffee-ring effect during drying of the colloidal suspension.\textsuperscript{155} Similarly, Kohri \textit{et al.} used polydopamine (PDA)-coated polystyrene (PS) as the building blocks and created a highly visible structural color with APCs structure by controlling the thickness of the PDA shell which decides the surface roughness of the colloidal particle of PS@PDA (Fig. 8c).\textsuperscript{156} Sheng \textit{et al.} co-assembled PS@PDA nanoparticles with 3-aminopropyltriethoxysilane (APTES) and managed to counteract
the tensile stress caused by the shrinkage of the colloidal suspension during drying due to the generation of covalent bonds between PDA and APTES, addressing the cracking problem during the preparation of APCs (Fig. 8d). The utilization of surface roughness of the assembled particle can simplify the preparation process to obtain APCs in high quality. High-quality APCs can be prepared with surface rough particles, which are not constrained by substrates and solvents, and the rough black viscous shell improves the light absorption efficiency and adhesion properties of the particles to the substrate. However, the modification of a certain thickness of rough shell on smooth colloidal particles is not easily controlled, which limits their large-scale synthesis.

Fig. 8 (a) Schematic illustration of modification of PS NP with PVP. (b) Photographs of films assembled with PS and PPy@PS NPs observed from different angles. (Reproduced with permission. Copyright 2016, American Chemical Society.) (c) Structural color pellets of PST(X)@PDA(Y) core-shell particles. (Reproduced with permission. Copyright 2014, Springer Nature.) (d) Photographs of crack-free PS@PDA/APTES hybrid PC films observed from different viewing angles. Relations between peak wavelengths from the reflection spectra and the incident angle. (Reproduced with permission. Copyright 2017, The Royal Society of Chemistry.)

2.10 Assembly of soft particles
The high viscosity of the particles during the assembly of soft particles leads to interparticle adhesion and a significant decrease of the assembling efficiency, which results in the formation of APCs structures. By assembling the N-isopropylaerylamide-derivative nanoparticles into hydrogel opal, Hu et al. demonstrated that the nanoparticles self-assembled into a short-range-
ordered glass phase when the concentration is more than 5% wt. Subsequently, Hu and Gao discussed the assembly of N-isopropylacrylamide (NIPA) gel particles in water and revealed that the NIPA gel particles endured a phase transition from liquid to glassy state through crystal at room temperature as the NIPA concentration increased. Takeoka et al. reported that the structural color by amorphous assembly of charged spherical particles is angle-independent and responds rapidly to temperature changes (Fig. 9b). The liquid APCs system is promising as the display material with non-iridescent and permanently non-fading features.

![Fig. 9](image)

**Fig. 9** (a) Schematic illustration of the osmosis-driven condensation process. The optical image and optical microscope image of the photonic pigment in water after UV-curing of the ETPTA shell. SEM image of the particles. (Reproduced with permission. Copyright 2014, Wiley-VCH.) (b) Optical images of gel suspensions with different polymer contents. (Reproduced with permission. Copyright 2009, American Chemical Society.) (c) Appearance of PMMA- and PBnMA-grafted silica colloidal suspensions. (Reproduced with permission. Copyright 2010, American Chemical Society.) (d) Photograph of soft glassy colloidal arrays in an IL at different particle concentrations. (Reproduced with permission. Copyright 2009, The Royal Society of Chemistry.) (e) Digital photos of APCs and OPCs which were assembled from aminated silica particles under different pH values. (Reproduced with permission. Copyright 2020, American Chemical Society.)

Amorphous arrays can also be realized by constructing the colloidal particles with hard-core and soft-shell as the assembly blocks. Takeoka et al. prepared poly(N-isopropylacrylamide) (PNIPA) coated silica particles in core-shell structure whose diameter is variable with water temperature. The soft PNIPA shell is bonded and retains thermal response, so that the optical properties of APCs...
assembled from core-shell particles reversibly depend on temperature. Manoharan et al. synthesized the colloidal particles consisted of polystyrene core and poly(N-isopropylacrylamide-co-acrylic-acid) shell in a similar way and assembled them as the APCs membranes (Fig. 9a). The non-iridescent photonic pigments in the visible range were prepared by Manoharan et al. The pigments can weaken multiple scattering by using microfluidic techniques to encapsulate the colloidal particles in spherical capsules. The APCs assembled by colloidal particles coated with soft polymer shells exhibit weak incoherent scattering and bright structural colors. And the assembly of particles with temperature-sensitive polymer shells can be used to obtain APCs with temperature response.

2.11 Assembly of low-charged particles

Colloidal particles with surface-grafted polymer tend to form short-range-ordered arrangements during assembly due to reduced electrostatic repulsive forces. Watanabe et al. prepared the arrays of soft glassy APCs with ionic conductivity by dispersing poly (methyl methacrylate) (PMMA)-grafted monodispersed silica colloidal particles in ionic liquids (Fig. 9d). Then, they detailedly investigated the relationships among colloidal glass transition, ion transport and structural color in this system. They demonstrated that the soft glassy colloidal arrays underwent glass transition in higher volume fraction than the one in the hard sphere systems and the APCs preformed higher ionic conductivity in the high concentration region. Moreover, they also reported the assembly of thermosensitive poly(benzyl methacrylate) (PBnMA)-modified silica particles in ionic liquids, and showed phase separation at lower temperatures over a wider temperature range (Fig. 9c). In the colloidal system assembled by ionic liquid, the presence of ions reduces the electrostatic repulsion between colloidal particles, while the steric forces and solvation effectively stabilize the colloidal particles. Based on that, Watanabe and co-workers prepared colloidal glasses and gels by assembling grafted polymeric silica particles and unstable silica particles in an ionic liquid. Colloidal glass with APC structure shows uniform non-iridescent structural color and fluidic properties that are expected to be used in wide viewing angles for color displays.

When the polymer is incorporated directly into the colloidal suspension, the absorbed polymer on the colloidal particles results in the closely packed short-range ordered structure. Kim et al. prepared APCs in uniform thickness by evaporating the solvent from a colloidal suspension of
polyethylene oxide (PEO)-coated silica on a heated substrate.\textsuperscript{175} The temperature of the substrate allows the generation of Marangoni flow within the droplets of the water-ethanol mixture to inhibit the formation of coffee-rings, and the physical adsorption of PEO on the surface of silica prevents the crystallization of colloidal particles.\textsuperscript{175} Kofinas \textit{et al.} reported an assembly strategy of colloidal particles into gels of APCs by which the protein degradation peptides lead to the adsorption of polymers onto the particle surface.\textsuperscript{27} Sheng \textit{et al.} reported an APC with excellent mechanical properties by co-assembling PS@PDA particles with chitosan which plays the role of enhancing the hydrogen bonding networks between colloidal particles and inducing the assembly of colloidal particles into APCs.\textsuperscript{176}

Our group has developed a series of strategies for preparing colloidal particles by controlling their surface charge in the dispersant. First, we synthesized Fe$_3$O$_4$@SiO$_2$ core-shell particles by \textit{in situ} deposition of Fe$_3$O$_4$ nanoparticles on SiO$_2$ particles. The Fe$_3$O$_4$ shell significantly reduces the potential of silica particles and eventually results in a short-range-ordered arrangement of Fe$_3$O$_4$@SiO$_2$ colloidal particles. The absorption of scattered light by the black Fe$_3$O$_4$ shell is important for the formation of uniform and bright structural colors.\textsuperscript{177} Subsequently, we introduced polyvinylpyrrolidone (PVP) into the silica suspension and prepared APCs by an evaporative self-assembling method.\textsuperscript{111} The decreased $\zeta$-potential value of silica and particle agglomeration is critical to the formation of amorphous arrays due to the adsorption of silica on PVP during self-assembly. In another work, APCs and PCs were fabricated by co-assembling amidated silica particles and carbon black in acidic aqueous solution (Fig. 9e).\textsuperscript{168} The high concentration of H$^+$ ions promotes the protonation of particles to produce large $\zeta$-potential values on the silica particles, which facilitates the crystallization of colloidal particles. Therefore, the ordering of the assembled particles can be precisely controlled by adjusting the pH of the colloidal solution. Moreover, we synthesized YOHCO$_3$ particles with tunable size, compositions and optical properties before self-assembled them into the APCs.\textsuperscript{150} The YOHCO$_3$ colloidal particles were assembled into the amorphous structure by low surface potential, and the APCs patterned by the Eu$^{3+}$-doped YOHCO$_3$ colloidal particles presented red under UV irradiation. In the subsequent work, we obtained Y$_2$O$_3$(:Eu) by a hydrothermal process \textit{via} the high-temperature calcination of YOHCO$_3$(:Eu) particles. The low surface potential of the particles as well as their high polydispersity contributed to the formation of APCs.\textsuperscript{178} The invisible photonic prints with UV irradiation were prepared by assembling Eu-doped
and Eu-undoped $\text{Y}_2\text{O}_3$ particles. In addition, we reported a novel method to prepare APCs with non-iridescent structural colors by assembling colloidal particles in less-polar dispersant.\textsuperscript{179} Based on the sensitivity of the APCs to the refractive index contrast, their structural color disappears once the APCs is wetted. Accordingly, we developed an information storage system for water recognition. Our works have important implications towards the simple and fast large-area preparation of APCs in non-iridescent structural colors and understanding the assembly behavior of colloidal particles in different pH and diverse polar solutions. Generally, there are two ways to obtain low potential colloidal particles, one is by grafting on the surface of the particles and the other is by adding polymers to the colloidal suspension. Both strategies can prepare APCs with uniform structural color, but the former requires further modification of the particles synthetically is time-consuming, while the latter can simply and rapidly prepare APCs by merely introducing polymers to co-assemble with colloidal particles.

### 3. Applications of APCs

The short-range-ordered structure of APCs generates non-iridescent structural colors and stronger incoherent scattering compared with PCs in well-ordered arrangement, which provides a unique advantage for APCs in potential applications. For example, for displays and printings, APCs have tunable structured colors covering the entire visible spectrum. More importantly, their structural colors are angle-independent which effectively avoids color confusion. APCs can be embedded in or constructed by responsive materials with optical signals modulated in response to external stimuli, including mechanical deformation,\textsuperscript{29, 180} temperature,\textsuperscript{30, 166, 170} light,\textsuperscript{24, 75} humidity,\textsuperscript{21, 23} magnetic\textsuperscript{28, 82} and electric fields.\textsuperscript{19, 41} In addition, the combination of non-iridescent properties of APCs and iridescent structural colors of PCs provides new ideas for anti-counterfeit labels.\textsuperscript{51, 178}

#### 3.1 Sensors

APCs offer an effective solution for sensors due to their unique and designable optical properties in response to external stimuli. Zhu \textit{et al.} reported a mechanochromic supramolecular elastomer prepared by immobilizing isotropically arranged $\text{SiO}_2$ in the elastomer of amino-terminated poly(dimethylsiloxane) (Amino-PDMS) which is ligated with cerium trichloride metal...
As the tensile strain increases from 0 to 120%, the reflection peak of the APCs elastomer shifts from 660 nm to 550 nm along with the shift of the structural color from red to green. They concurrently developed a recyclable APCs elastomer prepared by combining short-range-ordered SiO$_2$ arrays with a water-soluble ureidopyrimidinone (UPy) which is cross-linked with poly(ethylene glycol) (PEG) polymeric matrix. The reversible cross-linking and water solubility of PEG-UPy polymers confer excellent recyclability of APCs elastomers. Recently, they proposed a wide-spectrum responsive APCs elastomer assembled with carbon-coated Fe$_3$O$_4$ as building blocks followed by embedding in Amino-PDMS, which exhibits a wavelength difference of $\approx$ 223 nm during reversible stretching (Fig. 10a). Kim et al. prepared mechanically discolored APC elastomers by studying the assembly of bi-dispersed colloidal particles in PEGPEA resin. Some of the APC elastomers with self-healing properties will be fully utilized in colorimetric sensors.

Takeoka et al. prepared APCs by assembling soft particles with temperature-sensitive shell which caused reversible changes of reflection peaks with temperature. To develop a temperature-responsive chromatic sensor, they constructed the porous PNIPA hydrogels in APCs structure by dipping PNIPA into SiO$_2$ amorphous array templates and removing the templates by etching. Owing to the large proportion of PNIPA in this system, the porous PNIPA hydrogels exhibited rapid volume and structural color changes when the temperature varied. Xia et al. reported a hydrogel membrane consisted of the amorphous arrangement of microgels with a dual responses in temperature and pH value. The volume phase change temperature of the Poly(N-isopropylacrylamide) (pNIPAAm) polymer in water provides thermochromic properties in the hydrogel membrane, while the methacrylic acid provides pH-response to the hydrogel membrane (Fig. 10d).

Xiao et al. reported a colorimetric humidity sensor assembled by melanin nanoparticles that produced continuous structural color changes when the relative humidity changed from 10% to 90%. The sensor exhibited excellent cycling performance and high sensitivity at a given humidity level. Song et al. infiltrated amide monomers into the templates of APCs to obtain the humidity sensor by UV curing. Its structural color showed a reversible change from blue to red when the relative humidity varied between 45% and 100%. The sensor exhibited structural color changes in different humidity ranges with colloidal particles in different sizes (Fig. 10b). Takeoka et al. utilized the
photoelectrochemical reaction of Ag/Ag⁺ to modulate the intensity of noncoherent scattered light and the variation of saturation in the APCs array by light (Fig. 10e).²⁵ Xia et al. developed an APCs hydrogel with near-infrared light modulation of color change, which was prepared by packing dry thermosensitive microgels in pNIPAAm and introducing multi-walled carbon nanotubes (MWCNTs).²⁴ MWCNTs can not only absorb near-infrared light but also convert luminous energy into thermal energy to produce structural color changes in hydrogels.²⁴ Zhao et al. prepared infrared-light-responsive APCs hydrogels by infiltrating n-isopropylacrylamide gels into the APCs templated by multi-shell particles.³² The graphene oxide shell converts the energy of infrared light radiation into heat, which results in volume contraction and self-healing of the APCs hydrogel (Fig. 10c).³² Magnetically responsive APCs sensors are usually prepared by Janus particles as the building blocks. For example, Takeoka et al. prepared Janus particles composed of SiO₂ colloidal particles and Fe₃O₄ nanoparticles by the microemulsion method. Their orientations could be changed by a magnetic field, and the structural color changed accordingly.²⁸ To construct the electrically responsive APCs sensor,⁴¹ Chung et al. reported the APCs self-assembled by Fe₃O₄@SiO₂, whose structural color changed from mahogany to dark blue under the voltage ranging from 1.0 to 4.0 V.¹⁹ Recently, Ge et al. reported for the first time that a thin layer chromatography (TLC) based on mesoporous silica particle was assembled with high separation efficiency and convenient recognition (Fig. 10f and g).¹⁸² In contrast to the conventional TLC, the large number of micron-sized pores in the APCs greatly enhances the capillary forces and accelerates solvent diffusion. The mesoporous silica APC membranes show uniform non-iridescent structural colors, and the color changes with good distinction during the separation of the analyzed chemical compounds
Fig. 10 (a) Photographs of red Fe₃O₄@C/PDMS PE40 by stretching (upper) and releasing (lower) at various strains ranging from 0% to 114%. (Reproduced with permission. Copyright 2020, Wiley-VCH.) (b) Photograph and reflectance spectra of the brilliant structural color sensor at reversible RH variations. (Reproduced with permission. Copyright 2018, Wiley-VCH.) (c) Scheme of the photothermal response of the inverse opaline hydrogel of NIPAM and side views of shrinking process. Controllable movement of the human-shaped NIPAM hydrogel. (Reproduced with permission. Copyright 2019, Elsevier.) (d) Optical photographs of PM0 in water at a certain temperature with different observing angles. (Reproduced with permission. Copyright 2021, American Chemical Society.) (e) The reflection spectra and the optical images of the amorphous colloidal array with an aqueous solution of silver nitrate under 313 nm UV light passed through a bandpass filter and optical images of the colloidal amorphous array that was irradiated with visible light (λ > 420 nm) for 12 h under the conditions as shown in the left. (Reproduced with permission. Copyright 2014, The Royal Society of Chemistry.) (f) Digital photos of m-SiO₂ APC films prepared by 236 nm, 276 nm, and 309 nm particles and blue APC films at different viewing angles. (g) Direct recognition of seven chemical compounds on (up) m-SiO₂ APC film and their recognition on traditional fluorescent SiO₂ gel plate (middle) under UV light or (bottom) after dyeing. (Reproduced with permission. Copyright 2020, The Royal Society of Chemistry.)

3.2 Painting

Full color painting and printing of APC patterns in large area can be achieved by spray or infiltration-induced assembly. The patterns painted or printed with the inks of APCs are environmentally friendly with low energy consumption and are operational with wide viewing
angles. Takeoka et al. successfully drew Mt. Fuji by spraying a colloidal suspension of carbon black-doped silica (Fig. 11a). Duan et al. developed a large-scale full-spectrum structural color printing technique by infiltration-induced colloidal assembly. The patterns were printed by the colloidal inks with strong solvent absorption capacity. The structural color can be easily tuned with a CMYK mode of a domestic inkjet printer (Fig. 11b). The strong permeability of the paper to solvents ensures the colloidal particles to form APCs on the paper. Gu et al. painted robust non-iridescent structural colors of Peking Opera character faces by spraying SiO$_2$@PDA on different substrates (Fig. 11e). Zhang et al. painted the patterns of APCs by spraying a mixed emulsion of thiodiphenol-formaldehyde particles and carbon black on a thermoplastic polymeric film followed by sandwiching the structure to obtain an integrated composite film by hot pressing (Fig. 11d). The APCs composite film fully compensates for the lack of mechanical properties of the printed APCs.

Zhang et al. proposed a new method to prepare homogeneous APCs on a variety of substrates by atomized deposition of the colloidal suspensions of silica with poly (vinyl alcohol) (PVA) (Fig10. f). Patterns can be painted on the fabric, and the introduction of PVA improves the adhesion between the APCs and the fabric, maintaining almost the same structural color after stretching, rubbing and washing tests. Shen et al. used a mixture of chitosan (CS) and PS@PDA particles for dyeing cotton fabrics, which resulted in a robust coating of PS@PDA/CS on the substrate due to the enhanced bonding of APCs by CS and the bonding of colloidal particles to the cotton fibers. Tang et al. added the synthetic aqueous polyureas (WPU) to the APCs assembled with polysulfide colloidal particles to obtain the non-iridescent structural color coatings. The products show high color contrast, favorable mechanical properties and self-healing properties. With WPU as the efficient binder to the gap-locking structure of the amorphous array, this method can be applied for fabric dyeing (Fig.10c). Zhang et al. printed non-iridescent structural colors and structurally stable patterns of APCs on fabric with a rapid screen printing technique. In addition, our group printed structural color patterns of APCs with multicolor vivid non-iridescent colors by hand-painting and spraying methods (Fig.10g).
Fig. 11 (a) A picture of Mount Fuji drawn by spraying the suspensions of silica particles and CB. (Reproduced with permission.\textsuperscript{44}Copyright 2013, Wiley-VCH.) (b) A multicolored painting of a landscape with high resolution, scale bar: 1 cm. (Reproduced with permission.\textsuperscript{74}Copyright 2018, Wiley-VCH.) (c) A complex pattern sprayed with PSFs and WPU in four different diameters on silk. (Reproduced with permission.\textsuperscript{38}Copyright 2019, American Chemical Society.) (d) Schematic diagram of the preparation of TPU composite phone shell with non-iridescent structure color. (Reproduced with permission.\textsuperscript{39}Copyright 2019, The Royal Society of Chemistry.) (e) The multi-color patterns of PDA@SiO\textsubscript{2}-AM arrays on glass, PMMA, Al foil and paper. (Reproduced with permission.\textsuperscript{89}Copyright 2018, The Royal Society of Chemistry.) (f) Cyan-color dyed toy of angel using 212 nm diameter of silica NPs together with 4 wt % PVA (inset, pristine angel toy) and enlarged view. (Reproduced with permission.\textsuperscript{36}Copyright 2018, American Chemical Society.) (g) Colorful patterns with blue, green, yellow, and red structural colors obtained by hand painting or writing on paper. (Reproduced with permission.\textsuperscript{150}Copyright 2019, American Chemical Society.)

3.3 Displays

The non-iridescent structural colors make APCs a promising next-generation display device with wide-viewing angles. In the work of Kang \textit{et al.}, they prepared the angle-independent photonic pixels that can vary with voltage.\textsuperscript{41} When the bias voltage increased from 1.0 V to 4.0 V, the reflection peak of the photonic pixel reversibly shifted from 655 nm to 490 nm and the structural color changed from red to blue covering the entire visible region (Fig. 12b).\textsuperscript{41} In addition, the photonic pixels have high sensitivity and excellent operating stability. Yang \textit{et al.} reported a smart display window prepared from an array of silica particles compositied with poly (dimethylsiloxane)
(PDMS) elastomer (Fig. 12a). The elastic film is initially highly transparent due to the matched refractive index of silica particles and the PDMS. When it is stretched and the strain is greater than 40%, the micro-wrinkles and voids are generated and therefore the transmittance is reduced to 30% and the film shows non-iridescent structural colors. Kim et al. dispersed silica colloidal particles in a light-curing resin to form an amorphous arrangement and fixed it by irradiation. After that, silica particles were removed to obtain an inverse glassy structures. The inverse glasses are an isotropic arrangement of cavities with low refractive index, thus producing a distinct non-iridescent structural color (Fig. 12c). Zhou et al. prepared organogel nanocomposites with non-iridescent structural color, rapid self-healing properties and self-cleaning ability by co-assembling the monodispersed octadecyl-grafted silica particles and carbon black together with the self-healing gels (Fig. 12d). Yu et al. synthesized a photonic gel with non-iridescent structural color, high processability and self-healing ability (Fig. 12e). By adjusting the mechanics of the photonic gel and the size of the internal short-range ordered silica particles, the photonic gel can be processed into bright multicolor patterns.

Fig. 12 (a) Optical images of reversible revealing and hiding process of the letters patterned by the silica nanoparticle/PDMS film under stretching and releasing test. (Reproduced with permission. Copyright 2015, Wiley-VCH.) (b) Photographs taken at 1.0 V, 2.5 V and 4.0 V of bias voltages. The pixel size is 5 cm × 5 cm. (Reproduced with permission. Copyright 2010, Wiley-VCH.) (c) Series of optical images of the films containing micropatterns of inverse glasses under diffusive light illumination taken at three different angles, as denoted in each panel. (Reproduced with
3.4 Anti-counterfeiting labels

Anti-counterfeiting technologies attract a considerable amount of attention due to the widespread use in banknotes, ID cards, checks and passports. APCs can be prepared easily and rapidly by the colloidal suspensions with non-iridescent structural colors. It is easy to process and miniaturize, and has shown great potential for applications in anti-counterfeiting and information encryption when combined with PCs or fluorescent materials. Specifically, the APC patterns revealed or disappear by changing the effective refractive index strength of the assembled structure and their incoherent scattering. Therefore, APCs offer new approaches to the development of anti-counterfeiting and encryption devices.

Because of the incoherent scattering of the amorphous silica arrays, the thick amorphous arrays always appear white color regardless of the particle size. Based on that, Takeoka et al. sprayed patterns on APCs composed of silica particles in the diameters of 277 nm and 211 nm, where the patterns could not be identified by the naked eye due to strong incoherent scattering. Subsequently, they deposited carbon uniformly on the APCs film by pressure-pulsed chemical vapor deposition, and therefore the structural color of APCs gradually showed up as most of the incoherent scattering was absorbed by carbon. Takeoka et al. prepared multicolored APCs patterns by spraying a silica suspension containing tannic acid (TA) on a piece of white paper. The whole paper was white and the multicolor patterns could not be identified (Fig. 13a). When spraying the solution of iron chloride on the patterns, they appeared immediately with visible color since iron ions react with TA to form black complexes which absorb incoherent scattering. Kim et al. prepared polydopamine particle-doped APC elastomers and took the stretching tests. The structural color turned from blue to brown as the background by stretching because the polydopamine particles were flooded (Fig. 13d). An anti-counterfeiting label based on APCs was prepared by Song and
co-workers. In the dry state, the APCs presents white color consistent with the middle layer due to incoherent scattering; in the wet state, the middle layer turns to transparent and the APCs pattern appears due to the absorption of incoherent scattering by the black background which improves the color saturation (Fig. 13e). Tang et al. reported a filament film with a single-layer of inverse quasi-amorphous structure. The laminated inverse quasi-amorphous structure based on a silk fibroin film (SFLIS) builds up the water-responsive anti-counterfeiting devices where SFLIS hide the pattern in air and reveal it in wet (Fig. 13f).

By combining APCs with PCs, anti-counterfeiting labels with unique optical properties can be achieved. Wu et al. used monodispersed CdS particles in different diameters as inks to print a waterproof photo paper with vibrant structural colors by an inkjet printer (Fig. 13b). The crystalline arrays of CdS in different diameters were printed on the amorphous arrays of CdS, and invisible anti-counterfeiting patterns can be achieved by a simple rotation angle. Tang et al. reported a polyvinylidene fluoride structural color film consisting of the inverse opal structure with ordered array layers and amorphous array layers (Fig. 13c). At the specular reflection angle, the structural color of the amorphous array layer is suppressed by Bragg diffraction and the film displays iridescent color. Therefore, the patterns on the film are switched between hiding and displaying by changing the observing angles. Zhang et al. reported a long-range ordered and short-range ordered PS nanoarrays in PDMS elastomer. When the elastomer was stretched, cracking and surface wrinkling of the PS array reduced the light transmission, thus allowing programmable patterns to be hidden and shown. Duan et al. reported a complex anti-counterfeiting encoded composite structure of APCs that combined coherent scattering with the thin film interference (Fig. 13g). Non-iridescent structural colors displays in natural light, with bright mixed colors and special reflection under specular lighting.
**Fig. 13** (a) Left: Whitish sheet obtained by the suspensions composed of silica fine particles in various particle diameters (220, 250, and 300 nm) and TA and dried. Right: Colored diagram obtained by spraying FeCl$_3$ aqueous solution (10 mg/mL) onto the whitish sheet via a mask and drying. (Reproduced with permission. Copyright 2019, American Chemical Society.) (b) Digital photographs of an anti-counterfeiting pattern. The pattern is invisible at the viewing angle of 70° but clearly visible at the viewing angle of 10°. (Reproduced with permission. Copyright 2017, American Chemical Society.) (c) Diagram of the specular reflection mode and the corresponding digital photo of the BLIHS film in red at the incident angles $\theta$ of 5°, and diagram of diffuse reflection mode and the corresponding digital photo in blue with the placement angles $\beta$ of 5°. (Reproduced with permission. Copyright 2018, American Chemical Society.) (d) A zebra-like pattern at the relaxed state (left panel) and a hidden pattern at the stretched state (right panel). The bottom OM images correspond to the pattern region (#1) and surroundings (#2). (Reproduced with permission. Copyright 2019, American Chemical Society.) (e) Time-lapsed photographs of the anti-counterfeiting label and the intermediate layer being immersed in water. The structural color emerged within 3 s, which was accompanied by the transition into transparency of the intermediate layer. (Reproduced with permission. Copyright 2019, The Royal Society of Chemistry.) (f) Digital photos of QR code encryption and decryption. (Reproduced with permission. Copyright 2020, American Chemical Society.) (g) The optical images of an anti-counterfeiting label captured under natural light and specular reflection illumination at different viewing angles, scale bar: 0.5 cm. (Reproduced with permission. Copyright 2020, Wiley-VCH.)

Our group has developed various strategies for anti-counterfeiting and information storage based...
on APCs. In the APCs prepared by self-assembly of Y$_2$O$_3$ particles, both Y$_2$O$_3$ particles and Y$_2$O$_3$:Eu particles are easy to assemble into APCs with non-iridescent structural colors due to their instability and high polydispersity. Thus, patterns assembled with these two particles in the same diameter present the same structural color observed by naked eyes.$^{178}$ Here, we handwrote the patterning letters with Y$_2$O$_3$:Eu particles and the rest letters with the Y$_2$O$_3$ particles in the same diameter as background. Irradiated by natural light, these letters show a consistent structural color, while they immediately present red fluorescence under UV illumination. Thus, we successfully constructed a fully reversible hiding-showing patterns by UV irradiation. (Fig. 14a and b). This invisible printing method has the following advantages: (1) the invisible photonic printing is realized based on high contrast of luminous intensity between the pattern and the background other than the structural color and (2) multicolor display can increase the difficulty of identification. In the work on modulating the assembly behavior of colloidal particles by pH value, we developed a new method construct two photonic microstructures by assembly of one type of silica particles.$^{168}$ More importantly, a coding/decoding system based on the two photonic crystals with different optical properties has been developed by combining APCs with PCs. APCs and PCs with the same stop band were prepared by the solution of aminated silica particles with different pH values. The two films present the same structure color with the same reflective wavelength but different reflection intensity at the viewing angle of 0°. Therefore, by shifting the reflected wavelength to the near infrared region, the color contrast is nearly the same because the human eye is insensitive to near infrared light. As proof-of-concept, we construct a 3 × 3 circular grid with the combination of APCs and PCs at the wavelength of 668 nm. At a viewing angle of 0°, APCs and PCs cannot be identified because of their similar structural colors and low contrast. At other viewing angles, the structural color of APCs remains constant while the structural color of PCs changes, and therefore the APCs are identified (Fig. 14c and d). The coding/decoding system is superior in easily hiding the signal of structural color and combining multiple codes. In our work on assembling the APCs by less polar solvents, a novel system for information storage and identification was developed based on the wetting character of APCs. Their structural colors disappear by wetting due to the reduction of the internal refractive index contrast.$^{179}$ A 6-circular-grids system was constructed with APCs whose displaying region were hydrophobic after treated with fluoroalkylsilane and the background remained hydrophilic. The APCs in the hydrophilic background are easily wetted water and along
with disappearance of their structural color, while the structural color of the displaying region remains unchanged (Fig. 14e and f). The displaying region recovered to be invisible after drying and the storage-recognition process showed good reversibility. Similarly, multiple information storage systems can be constructed by APCs in multicolor can construct. Our group has developed a series of anti-counterfeiting and information storage systems by fully utilizing the unique properties of APCs, such as the non-iridescence and high sensitivity to refractive index contrast. We also combine the APCs with fluorescent composites to enhance their practical value as anti-counterfeiting devices.

Fig. 14 (a) Invisible photonic printing of “ABABBAABBA” pattern observed under ambient light and UV light. (b) Invisible photonic printing of a multicolor “Chemistry” pattern under ambient light and UV light. (Reproduced with permission. Copyright 2019, The Royal Society of Chemistry.) (c) Scheme and photos of single color-based coding/decoding systems observed at varied angles. (d) Scheme and photos of multicolor coding and decoding systems observed at varied viewing angles. (Reproduced with permission. Copyright 2020, American Chemical Society.) (e) Digital photos of single-color based coding/decoding system. (f) Digital photos of the multicolor based information storage and recognition system at dry and wetted state, respectively. (Reproduced with permission. Copyright 2020, Wiley-VCH.)

4. Summary and Outlook

We summarize the recent research progress in the preparation strategies, light-absorbing materials and applications of APCs combining the perspective of self-assembly of colloidal particles into APCs in this review. The preparation methods of APCs are flexible and can be broadly classified into two categories. One is to disturb the equilibrium assembly of colloidal particles to form an
amorphous arrangement by external technical means. The assembly methods include spraying, infiltration-induced colloidal assembly, layer-by-layer deposition and electrophoretic deposition. The other is to weaken the surface potential of the building blocks or change their surface roughness by surface modification or shell coating. For example, assembly of rough-surface particles, assembly of soft particles and assembly of polymer-grafted particles. Subsequently, we detailly listed several methods to eliminate the strong incoherent scattering of APCs. The first approach is taking the colloidal particles with high light absorption capacity and high refractive index as building blocks, including PDA, polysulfide, CdS and Fe$_3$O$_4$. The second method is to dope the amorphous array with ferrous materials, e.g., CB, graphene, PDA, Fe$_3$O$_4$, etc. In addition, the incoherent scattering of APCs can be absorbed with black substrates. Finally, various applications of APCs are described, including applications in sensors based on external stimulus response, structural color printings, wide-view displays, and anti-counterfeit labels.

Although great progress has been made in the preparation of APCs, much efforts still required for the application of APCs. First, the broad peaks and faint structural colors of APCs limit their application in sensors. For example, the APCs-based mechanochromic sensors show blurry change of structural color during the deformation of APCs elastomers. In contrast, PCs sensors have vivid and sensitive change in structural color. Second, the applications of APCs in display and printing usually require consideration of durability, compatibility and cost, but most APCs have poor mechanical properties and are out of use after recycles. Third, anti-counterfeiting labels based on APCs have excellent mechanical properties and stability, and can simply identify the security pattern by stretching or rotating a certain angle. The solutions to the present challenges of APCs will boost their development and lead to the ideal optical devices with unique features and wide applications.

It should be noted that noniridescent structural colors also can be obtained by particle aggregations that originates from the electromagnetic resonances of the silica particles rather than the scattering of light by the amorphous structures. Recently, our group reported that brilliant non-iridescent structural colors can be fabricated by the random aggregation of large silica particles (300-500 nm). Unlike the conventional non-iridescent structural colors, the new structural color can be attributed to the significant enhancement of electromagnetic resonances by particle aggregation. This work paves a new strategy for the fabrication of unconventional structural
colors and will advance their applications in green printings, displays, optical coatings, and wearable devices.

**Conflicts of interest**

The authors declare no conflict of interest.

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