Review

Controlled self-assembly of plasmon-based photonic nanocrystals for high performance photonic technologies

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Abstract

The self-assembled plasmonic nano-enabled photonic crystals (PCs) have been studied as promising platforms to develop next-generation photonic and opto-electronic devices. In this review, we attempt to describe the fundamentals of self-assembled colloidal plasmonic nanostructures and various applications of such devices. Different important aspects, such as interaction between metal NPs (MNPs) and non-metal 3-D crystals, effect of NPs on the spectral properties of materials, the mechanism of plasmonic based PCs, and related challenges and their possible solutions have been demonstrated crucially. The advancements in the self-assembled based plasmonic PCs and their applications are discussed carefully. We believe that nano-enabled self-assembled plasmonic crystals are better candidates of nanostructures to advance photonic technologies with reduced form factor and high performance.

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### Introduction

Photonics, where matter meets with light, is described as the science of light with astonishing breakthroughs and applications [1,2]. Even after a decade, the field is still alive to develop next-generation and more efficient optical technologies through exquisite control of light-matter interactions [1–4] at wavelength and sub-wavelength regimes. A large number of revolutionary advancements have been achieved, such as, the invention of optical fiber and solid-state lightening, with the help of more rigorous light manipulation in the scale much smaller than the incident electromagnetic wave [5–10]. In this direction, nanophotonic structures and devices have been extensively studied to overcome bandwidth and energy dissipation related problems in electronic integrated circuit technology. As an initial concept towards dense optical integrated circuits [11,12], photonic crystals (PCs), also known as high-refractive-index materials based on periodically arranged structures, were proposed [13,14]. Following, due to limited field confinement capability of PCs, where the maximum field localization can be achieved using transparent materials, novel strategies have been emerged. Among them, plasmonics [15–18] appeared being a promising counterpart of nanophotonics by exploiting the unique abilities of noble metals (e.g. large negative dielectric constants) and has been extensively utilized in optical magnetism, switching, nonlinear optics, imaging, biochemical sensing, and photodetection, owing to the unprecedented light concentration level of nanometallic platforms [19–34].

Thus far, the research in the field of PCs and plasmonics has been focused on developing the state-of-the-art photonic technologies with low cost and higher performance [35–37]. To date, researchers primarily pay attention to the refractive indices and crystal symmetry of the constituent materials (e.g. semiconductors and polymers), to form three-dimensional PCs with high-quality (Q) factors. Nevertheless, due to inherent deficiencies of PCs, such as low index contrast, large lattice mismatches, poor crystal quality, researchers tend to find alternative ways to solve these challenges towards achieving superior photonic properties. To this end, a hybrid plasmonic-PC device has been reported, which combines the plasmonic system’s high field localization and PCs’ mode coupling capability and long decay length [38]. Beyond that, researchers have shown that plasmonic nanoparticle-based superlattices can be another valid option to PCs, owing to the adjustable spacing of the metallic nanoparticles and the high refractive index of the lattices [36].

In this article, we review the recent highlights in the field of self-assembled colloidal plasmonic PCs, their fundamentals, and numerous applications of such devices. A brief introduction to PCs, the state-of-the-art plasmonic-based PC concepts, current modalities used in fabrication, advanced applications of hybrid PCs, related challenges, and efforts to improve the device performance are rigorously discussed, and an outlook for the perspectives of this research field is provided.

### Photonic crystals (PCs)

PCs are artificial structures with periodically modified refractive index (or dielectric constant $\varepsilon = n^2$), in which the optical modulation of light propagation is realized by diffraction and refractive index contrast in one, two, or three spatial dimensions respectively [14,36]. As the periodicity approaches to the wavelength of incident light, or the effective wavelength of light meets the Bragg condition, a photonic bandgap appears (similar to the energy bandgap in semiconductors), and the light propagation at a certain frequency in specific directions within the structure become precluded, apart from the localized regions formed by line or point defects in the geometry that can guide and localize light [136].

With the help of exquisite band structure engineering, one can overcome this problem by having an active control on light dispersion and decide which signals of different wavelengths propagate. Researchers have explored these features in a broad range of applications, including but not limited to optical integrated circuits, optical fibers, optical switches, optical memories, and light-emitting diodes [39–41], mostly slowing and confining light in optical nanocavities. Fig. 1 shows schematic illustrations of one-, two-, and three-dimensional PCs. In general, PCs are created using semiconductors and polymers via either bottom-up [42,43] or top-down fabrication modalities [44,45].

Based on the practicality and scalability, bottom-up fabrication processes are mostly utilized to develop PCs [46]. However, these processes have limited control over the lattice parameter and crystal symmetry of the structure [47]. Particularly, for the illustrated PC geometries in Fig. 1, the fabrication methods include: (a) One-dimensional (1-D) PCs: made by alternating dielectric layers deposited on a substrate or adhered together. One can fabricate this type of PC using, for instance, deposition techniques (e.g. electron-beam evaporation or sputtering), epitaxial growth, and lithography. (b) Two-dimensional (2-D) PCs: consist of periodicity in two pre-selected dimensions, in which the PC stays homogeneous in the third dimension. This structure can be realized by using lithographic techniques, for example, by fabricating a lattice of dielectric columns or drilling a lattice of pores into a dielectric material. (c) Three-dimensional (3-D) PCs: consist of a periodic variation of the refractive indices in all three dimensions. These types of structures are difficult to fabricate, and top-down approaches and lithographic techniques are not suitable. To this end, so far, researchers have utilized colloidal self-assembly as a promising approach, where small dielectric spheres suspended in a fluid automatically arrange themselves into close-packed face-centered cubic (FCC) crystals through surface forces [48].

Fig. 2 shows 1-D and 3-D PCs with their dispersion relation of light propagation. As clearly seen from the photonic band plots, as a tool to investigate the relation between energy and propagation vector of light within the structure, each system has frequencies where no light propagation occurs along the direction of periodicity (known as photonic bandgaps). For the 1-D case (Fig. 2a), the
dielectric function is only modified in $z$-axis. Therefore, light propagation can only be prohibited along this direction. On the contrary, the 1-D PC acts as a homogenous medium for light propagation in $x$- and $y$-axes. For the FCC-like 3-D colloidal PC (Fig. 2b), the light propagation can be hindered in all axes, which can provide useful features, such as the ability to tailor the photonic density of states (DOS). Moreover, to perceive the physical mechanism behind this concept, one can make a comparison between the behavior of photons in a PC and that of electrons in a crystal lattice. In this configuration, the crystal lattice can be considered as a periodic ensemble of atoms or molecules that can scatter light. As a direct outcome of the periodically arranged electronic potential, the energy levels are restrained as allowed energy bands, which are split by energy gaps.

**Combination of plasmonic nanoparticles with PCs**

In the past decade, we witnessed an extensive amount of investigation and development of multifunctional plasmonic metal nanoparticles (MNPs) of various size, shape, structure, and tunable plasmon resonances from visible to near infrared regime, by using novel fabrication and optical characterization methods [49,50]. The
recent reports of such systems have been focusing on the synthesis, characterization, theoretical analysis, and surface functionalization of plasmonic NPs with bio-specific molecular probes, especially in the field of nanomedicine and nanobiotechnology [51–54]. In spite of classical colloidal PCs, as indicated in Fig. 3, where the synthesis of hybrid AgNPs-polystyrene (PS) colloidal PC films are conducted through thermal-assisted self-assembly process [55], with the advent of novel methods, researchers have developed next-generation nanocomplexes combining metallic NPs (e.g. AuNPs) and polymer-based PCs [56,57], to compensate deficiencies of PCs mentioned in Introduction section using the promise of plasmonics. Since semiconductor electronics is limited [58] due to delay-time issues and photonics is inadequate owing to diffraction [59], the advancements in plasmonics emerge as a crucial concept to complement the gap between conventional photonics and electronics towards future technologies [60].

The assembly of hybrid metal-dielectric systems with various photonic entities, including but not limited to nanocrystals, semiconductor quantum dots, and MNPs, can yield a step forward in nanoscale analysis of chemical, biological, and physical entities and bring functionalities that exceed those of the individual sub units [61–64]. With this strategy, one can modify the optical properties of PCs using light scattering within the metal section of the system (by changing the permittivity of the PC), where different diffraction resonances can be achieved depending on the topology of the whole system. Besides, the collective electron excitations can be back scattered into the light before they are being spread out in the metal. Fundamentally, the idea of introducing metals in PCs was originated from reaching a high refractive index contrast air and metal. To this end, most of the effective studies were accomplished using 1-D and 2-D PCs, since they can possess a high degree of crystal ordering via standard fabrication methods [65]. Nevertheless, to be able to have much precise control on the light flow, one should use 3-D PCs. For the first time, the omnidirectional photonic band gap was predicted for 3-D metal-dielectric PCs by using highly reflective nanospheres [66,67], nevertheless, the fabrication of identical metal spheres is extremely hard. As an alternative way, metal nanoshells synthesized on dielectric cores were proposed as a 3-D opal-like PC [68,69], where a complex reflectance spectra was achieved due to the interplay between diffraction and localized plasmon resonances. However, independent from various core-shell synthesis techniques [70,71], unexpected results have been observed (e.g. strong absorption) owing to the defects of metal coatings on the surface of nanospheres [72,73]. On the other hand, colloidal self-and force-assembly [74,75] offers a practical framework for developing various methods to modify the structure of 3-D metal-dielectric PCs. In spite of their successful story, these homogeneously distributed colloidal crystals suffer from distinct problems. For instance, the optical response of the whole system will occur at the metal surface, because of the high metal reflectivity, and from the interaction of metal coatings on the surface of nanospheres, absorption results and increases with the increment of the quantity of plasmonic-photonic layers [65].

In order to realize low-dissipation along the system, one would directly put a metal film on the PC surface rather than dispersing the metal over the PC regime for the following reasons: (i) the absorption of the metal section will be restricted, comparison to its volume fraction [76], and(ii) the light penetration into the PC become possible through surface plasmon polaritons [15,77–79]. Besides, cavity and guided modes of PC will be prominent due to robust light localization.

Defects in PCs

Well-defined defects play a crucial role in controlling optical properties and light manipulation capability of PCs to actualize functional tools [80–82]. One can compose structural defects using ordinary fabrication techniques, such as top-down nanolithography (which time consuming due to step-by-step patterning process [82]) and bottom-up colloidal self-assembly. Even though the formation of a multilayer crystal can be easily achieved in a single step using bottom-up colloidal self-assembly, having controlled defects within the PCs require more sophisticatedmodalities [42,83]. To this end, Rinne et al. [84] proposed a two-photon polymerization (TPP) method to successfully introduce defects in self-assembled 3-D PCs towards the realization of all-optical integrated circuits. As mentioned in Combination of plasmonic nanoparticles with PCs section, once the PC has sufficiently high refractive index contrast or a propagating wave destructively interferes with a scattered wave from the crystal lattice, a photonic bandgap is formed [13,14]. Once a complete photonic bandgap is created, one can conduct defect engineering to have further optical functionalities within the same geometry. In Fig. 4a, a point defect (as a micro-cavity) in a 3-D PC is illustrated to localize incident electromagnetic wave for low-threshold lasing. Following, in Fig. 4b, a line defect is presented, which behaves as an optical path for light. Lastly, a planar defect, as a planar waveguide, is demonstrated in Fig. 4c. Furthermore, as an emerging strategy, researchers have focused on combining the top-down and bottom-up methods to utilize the characteristic features of each approach towards the realization of practical optical devices. In this scheme, defects can be engineered through standard nano-fabrication on a self-assembled colloidal multilayer, which is overlaid with a second 3-D crystal afterwards. Even though one can create point, line, and planar defects, the intentionally introduced
defect would eventually affect the crystalline quality of the additional crystal, in which the regions close to the defect regime. As a well-known fact that the photonic bandgap is extremely susceptible to the unintended defects, which can eventually perturb the bandgap. Thus, the geometrical characteristics of the introduced imperfection should be comparable with the crystal lattice of the bottom crystal to provide a much better single-crystalline coating. As indicated in Fig. 4d, one can create defects inside a self-assembled colloidal crystal using the TPP. Firstly, the planar colloidal silica crystal is established via vertical deposition, and then diffused with a photosensitive material. After a highly precise polymerization of the photosensitive material using focused laser beam, 3-D defects are attained after dissolving unexposed portions of the material (Fig. 4e) [84]. Subsequently, the interstitial areas among silica colloids are filled with amorphous silicon by chemical vapor deposition to ensure the high-refractive index contrast (Fig. 4f). Finally, the formed silica template and polymer defects can be etched to produce inverse opals (Fig. 4g) [85].

As another strategy to add a planar defect within a PC, Griffette and co-workers [86] demonstrated a stepwise combination of Langmuir Blodgett and PC template methods to build a novel and universal approach to enhance the response time and sensing ability of hydrogel-based inverse opal PCs. As a proof of concept, in Fig. 4h, poly(methacrylic acid) (PMAA) containing 3-D PC is illustrated. Here, the planar defect included-colloidal crystal was composed using Langmuir Blodgett technique [87,88], in which the defect layer is based on a 2-D layer of silica particles different in diameter. Then, the inverse opals were built by infiltrating the gaps along the crystal with PMAA and then removing the silica spheres to obtain a 3-D macroporous geometry. The corresponding scanning electron microscope (SEM) images of the developed colloidal-crystal pattern and resulting polymer hydrogel platform are shown in Fig. 4i and j, respectively. As clearly indicated, the close-packed face-centered cubic (FCC) 3-DPC is transformed into hexagonally arranged, hydrogel covered air spheres.

**Fig. 4.** Various types of defects in self-assembled 3-D colloidal PCs: (a) a point defect, (b) a line defect, and (c) a planar defect. Fabrication steps to create random defects in self-assembled PCs: (d) An ordered 3-D silica opal is located on a silicon substrate. (e) Judiciously selected polymer defects are tailored using a tightly focused laser beam through the platform, which is immersed in a photosensitive monomer. (f) The gaps between the silica particles are filled up with amorphous silicon via low-temperature chemical-vapor-deposition procedure. (g) The silica-sphere templates and polymer defects are removed by wet etching and calcination. (h) A diagram for the defect-containing direct opal and inverse opal hydrogel (IOH) films. Scanning electron microscope (SEM) images of (i) the colloidal-crystal template including planar defect layer of larger macropores. Reflectance spectra of (k) the defect-free and (l) defect-included IOH films in different pH-level solutions (solid line: pH = 2, dashed line: pH = 7, dotted line: pH = 11). In both plots, the insets represent wavelength as a function of pH value (squares and down-triangles associated to pH increase, whilst circles and up-triangles correspond to pH decrease).

(g) Adapted with permission from Ref. [83]. Copyright 2008 Nature Publishing Group. Adapted with permission from Ref. [86]. Copyright 2011 Royal Society of Chemistry.

**Controlled self-assembly of plasmonic-based PCs**

**Controlled self-assembly techniques**

As elucidated in Defects in PCs section, one can use top-down and bottom-up fabrication methodologies to constitute PCs. In the top-down approach, high-precision lithography, embossing, and scanning tip methodologies are mostly preferred [89,90]. Thus, top-down methods are generally expensive and require a longer time duration to fabricate these structures on a large scale, because of the repetitive nature of the approach. In contrast, the bottom-up technique relies on self-driven assembly of basic building blocks in order to get well-arranged periodic structures. This procedure is usually quicker and cheaper than the top-down approach, however, it is lack of precise control to tailor PCs. Nonetheless, the lower cost and ease of fabrication brings the bottom-up approach one step ahead.

The search for next-generation fabrication techniques, particularly at nanoscale, has traditionally been an enormous challenge in the past, and even with the current technology available, it still remains as a challenge to discover a cost-effective, fully-precise, and reproducible method to fabricate PCs and other nanoscale structures. Apart from the discussion on finding the most effective fabrication method, recently, research in nanotechnology has reached the stage where the subjects of advanced studies are the assemblies of NPs, which possess much greater complexity [91–93]. These assembled systems possess enhanced physical and chemical properties (depending on the particle size and spacing), which play a vital role for emerging device applications in the field of photonics, electronics, and biological sensing [94–97]. To make the use of NPs more efficient, surface of NPs can be functionalized through attaching chemical agents to change the interfacial surface of NP assemblies by designing 2-D patterns and 1-D arrays surfaces. Beyond that, among various reported colloidal PC fabrication methods, self-assembly strategy is considered as the most feasible
and frequently utilized one [65,98], because of possessing much more degrees of freedom to modify the PC composition. Being more specific, self-assembly represents the process of structure organization without applying any intervention, and materials developed with this procedure attained extensive attention at the nanoscale [99]. As mentioned above, having precise control during nanofabrication requires more sophisticated and expensive tools. That is why self-arrangement provides more flexibility in terms of obtaining a high quality crystal, improving the optical performance of ordered photonics, and minimizing the residual disorder.

The vertical deposition method (Fig. 5) also involves the evaporation of the liquid phase of a colloidal suspension to induce the convective assembly of a colloidal crystal onto a substrate. However, in this method, unlike drop-casting approach where the substrate lays horizontal, the substrate is held vertically and partially submerged in a colloidal suspension [103–105]. This method requires very good control on deposition conditions and environment. However, a long deposition time, sometime a few days, requires for evaporating solvent (generally water). Any interruptions during the drying process will severely affect the quality of the colloidal crystal obtained. A very high quality of colloidal crystals can be obtained using this methodology. Cai et al. further demonstrated the possibility of fabricating 2D non-close packed colloidal crystals using a combination of polystyrene spheres and tetraethyl-orthosilicate sol [106].

Dip coating involves the controlled withdrawal of a substrate from a colloidal suspension [107–109]. The substrate is vertically held on one end and first submerged into a colloidal suspension. As substrate slowly pulled up from the suspension, and convective assembly takes place at the interface of substrate surface and air/liquid. The thickness of the colloidal crystal deposited can be tuned by adjusting the speed of substrate withdrawal. Shear ordering makes use of a narrow channel between two planes to confine and induce the packing of the particles in a colloidal suspension via shear forces [110]. However, this method is difficult to perform because of the complexity to maintain a uniform shear force throughout.

The Langmuir Blodgett (LB) method is more precise and accurate but different than above discussed methods. The previous methods involved the fabrication of colloidal crystal directly on to the substrates, while the technique is two-step process wherein a 2D colloidal crystal monolayer is firstly formed on a water surface and then it is transferred onto the substrate [111–113]. Zhang et al. reported the flexible control in structure and stopband position of 2D PC superlattices by stacking of colloidal monolayer’s with different diameters of polystyrene [114].

Usually, self-assembly occurs through thermodynamic processes when the system finds its own phase space, and more easily occurs in a colloidal suspension where the particles form Brownian motion. In colloidal assembly, the following force factors are significant to take into account: (a) intrinsic driving forces for monodispersed particles, (b) long range external forces (e.g. centrifugation or gravity), and (c) repulsion forces between particles to hinder possible aggregation due to van der Waals forces [100–102]. The self-assembly of colloidal crystals can be accomplished using several methods, including but not limited to vertical deposition [103–105], spin-coating [106,107], Langmuir Blodgett [108,109], and sedimentation [110]. In Table 1, some of the most common self-assembly techniques are summarized.

In comparison to other techniques, gravity sedimentation is the simplest method of direct assembly onto a substrate, in which the natural opals are formed as a result of this process [112]. In fact, the widespread usage of these methods is particularly depends on the application. For instance, vertical deposition leverages the maximum optical quality, thus it should be utilized when basic optical properties are required. In a similar fashion, spin coating should be taken into account for large-scale composition [74,99,118]. Another relatively straightforward method is drop casting. In this case, a drop of colloidal suspension is dropped onto the substrate surface and allowed to dry by evaporation [111]. As water evaporates, the receding meniscus helps to pull the particles together and they rearrange themselves in the lowest surface energy configuration. Temperature and humidity control, suspension concentration, and the type of the substrate are some of the key factors that can be adjusted to obtain higher quality colloidal crystals.

In centrifugation and spin-coating, the centrifugation forces are utilized in order to squeeze the particles in a colloidal suspension. For the former, a colloidal suspension is placed in a centrifuge and spun at high speeds to bring the particles together, which results in good quality bulk colloidal crystals [119]. In addition to large-scale composition, the latter can also be used to make thin films or monolayer of colloidal crystals on planar substrates [114,115,120,121]. However, due to force differences in suspension along different parts of the substrate, the obtained colloidal crystal films vary according to the position of the rotation axis. On the other hand, in 1999, Jiang and colleagues developed the vertical deposition method for the synthesis of 3-D PCs [104]. In this technique, a piece of glass slide is placed vertically into a beaker which contains the particles suspension. The colloidal suspension wets the substrate

Fig. 5. Schematics to explain (a and b) the vertical deposition through gradual evaporation of the suspension and (c) the vertical lifting of the substrate from the suspension. (a) is adapted from Ref. [48]. Copyright 2011 Ph.D. thesis and (b and c) adapted with permission from Ref. [122]. Copyright 2011 Wiley-VCH.
and a meniscus forms at the line where the substrate, air, and liquid met. As indicated in Fig. 5, the spheres are pushed towards the substrate and attracted to each other due to capillary forces, which tend to order them in a close-packed monolayer, while the solvent flows towards the meniscus region. When water starts to evaporate, particles will deposit onto the glass slide and assemble as a colloidal crystal film through capillary force [122–126]. Here, the crystal film thickness can be controlled with the particle concentration in the suspension and sedimentation is avoided via placing a vial. Beyond that, the vertical deposition method also involves evaporation of the liquid phase of a colloidal suspension to induce the convective assembly of a colloidal crystal onto the substrate through shear forces (see Fig. 5). Unlike the drop casting method where the substrate is located horizontally, the substrate is held vertically and partially submerged in the colloidal suspension [103–105]. Thus, this modality requires a rigorous control on the deposition conditions (e.g.,

<table>
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<th>Method</th>
<th>Remarks</th>
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<tbody>
<tr>
<td>Top-down method</td>
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</tr>
<tr>
<td>Photo lithography</td>
<td>Photo polymerization of monomer in colloidal crystal assembly 2D and 3D patterning possible, different particles and periodicities combination.</td>
</tr>
<tr>
<td>Microimprint Lithography</td>
<td>Interplay of adhesion between particles and particles/substrate important, different particles and periodicities combination.</td>
</tr>
<tr>
<td>Printing/Plotting</td>
<td>Printing of confined structure and controlled drying rounded edges due to drying.</td>
</tr>
<tr>
<td>Bottom-up method</td>
<td></td>
</tr>
<tr>
<td>Surface Functionalization</td>
<td>Wetting contrast between hydrophilic and hydrophobic areas.</td>
</tr>
<tr>
<td>Large topographic pattern</td>
<td>Capillary forces-aided infiltration of trenches.</td>
</tr>
<tr>
<td>Microfluidic channels/Micro-molding</td>
<td>Infiltration and drying in closed channel.</td>
</tr>
<tr>
<td>3D molding</td>
<td>Additional structuring in all three space dimensions.</td>
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Table 1
Comparison study of top-down and bottom-up method.

<table>
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<td>Microfluidic channels/Micro-molding</td>
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<td>3D molding</td>
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<tr>
<td>Drop casting [111,112]</td>
<td>Slow and simple process, but it is difficult to maintain exact conditions</td>
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<tr>
<td>Vertical deposition [103–105]</td>
<td>Very slow process, but it provides high-quality PC structures and good control on evaporation techniques</td>
</tr>
<tr>
<td>Centrifugation [113]</td>
<td>Quick and simple process, useful for forming bulky colloidal crystals</td>
</tr>
<tr>
<td>Langmuir Blodgett [108,109]</td>
<td>Sequential process where monolayer of particles (compressed on water surface) is transferred on a substrate to create multilayer structures as desired</td>
</tr>
<tr>
<td>Spin coating [106,107]</td>
<td>Quick and simple process, where monolayer formation is attainable</td>
</tr>
<tr>
<td>Magnetic self-assembly [114,115]</td>
<td>Requires highly charged monodispersed magnetic colloidal particles inside the liquid media</td>
</tr>
<tr>
<td>Dip coating [116,117]</td>
<td>Thickness of the layer can be controlled</td>
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</table>
suspension concentration, type of solvent, temperature, humidity, ground vibrations etc.) and the deposition time, since longer tie duration will eventually evaporate the liquid. Besides, any unwanted circumstance during the drying process will severely affect the quality of the obtained colloidal crystal. Cai et al. [127] further demonstrated the possibility of fabricating 2-D non-close-packed colloidal crystals using a combination of polystyrene spheres and tetraethylorthosilicate solution. In this mechanism, the authors also utilized dip coating for controlled withdrawal of the substrate from the colloidal suspension [116,117,128].

As another self-assembly technique, the Langmuir Blodgett (LB) method is slightly different from the above mentioned ones. The previous methods involved the fabrication of colloidal crystal directly onto the substrates, while the Langmuir Blodgett technique is a two-step process where a 2-D colloidal crystal monolayer is created on the water surface, then it is transferred onto the substrate [108,129,130]. Recently, Zhang et al. [131] reported the flexible control on the structure and the stop band position of 2-D PC superlattices by stacking the colloidal monolayers with different diameters of polystyrene (see Fig. 6).

The use of magnetic self-assembly based on paramagnetic colloidal particles is another feasible way of fabricating the colloidal PCs. The main requirement here is the use of highly charged monodisperse super magnetic colloidal particles. Due to their highly charged nature, the colloidal particles have a tendency to self-assemble into aligned arrangements, which can be manipulated by an external magnetic field. As an example, Asher and co-workers have shown different synthesis procedures to make such colloidal particles and their subsequent self-assembly [114,115,132].

Convective self-assembly

Various fabrication techniques have been developed to produce different structures (e.g. strips, coatings, and patterns) utilizing NPs [133–136]. As an example, in Fig. 7, scanning probe lithography (e.g. dip-pen nanolithography) was employed to create pre-defined patterns with NP ink [137,138] with nanoscale resolution, but it is limited by the inadequate control of ink transport and deposition process [139–141]. Drop-on-demand printing is another widely utilized technique for patterning complicated features using NP-based ink [142,143]. The printing performance of drop-on-demand printing is closely related to the viscosity and surface tension of the carrier ink, and it may suffer from satellite or non-uniform drop issues [144]. To overcome these possible bottlenecks, transfer printing techniques (e.g. roll-to-roll gravure printing, flexographic printing, screen printing) were recently developed to deposit NPs on flexible or non-planar substrates with high yield, rapid, and accurate positioning [145–148]. For the above mentioned techniques, viscosity, polarity, and volatility of the liquid ink are the main considerations, and their molds need to be redesigned whether the printing patterns are changed.

On the other hand, in general, film deposition methods (e.g. spin coating [149], drop casting [150], and Langmuir–Blodgett [151]) were applied to form NP coatings on flat substrates over large areas. They usually show low degree of controllability over the considered structural parameters and need a special treatment of the substrates. In comparison to these deposition modalities, convective self-assembly (CSA) is a low-cost and easy-to-implement technique for NP deposition [152,153], which has the following distinctive advantages: (a) well organized arrangement of NPs can be
achieved, making the assembled structures highly homogeneous [135,153], (b) a wide range of solvents (e.g. aqueous, organic) can be used for dispersing different NPs without modifying the solvent properties [154–156], and (c) the driving force of the assembling process could be tuned by external stimuli (e.g. temperature, pH, magnetic field) [133,157] and directing surfaces (e.g. confined spaces, interfaces) [158]. By considering these characteristics, Prevo et al. [159,160] has developed a controlled CSA technique by constantly dragging NP droplets, which are confined in a moving meniscus between two plates, and multilayered coatings of Au NPs (12 or 16 nm) were deposited from aqueous suspension. Similarly, Farcau et al. [161,162] presented another CSA modality using meniscus-mediated horizontal deposition setups, and Au NPs (18 nm), which are synthesized in aqueous phase, were assembled as conductive wires with firm geometries and spacing on flexible substrates by stick-slip mechanism.

Self-assembly of 3D plasmonic colloidal nanostructures

As a well-known fact that, the ideal self-assembly method should be easily integrated into current fabrication schemes (e.g. roll-to roll processing). Such techniques typically involve specific design criteria, such as solvent flow, liquid interfaces, and wetting properties (see Fig. 8). For micro-scale devices, self-assembly of 3-D electrical networks and large device arrays have been demonstrated using capillary forces driven by hydrophobic interactions or liquid menisci for the aggregation of nanoscale building blocks [163,164]. Moreover, researchers have focused on spontaneous assembly of colloidal solutions. Early examples including the fabrication of opals (composed of silica spheres) and super lattices of colloidal semiconductor quantum dots [115], magnetic NPs [104], and metal nanocrystals [165–167] have been demonstrated using sedimentation, solvent or water slow evaporation [205]. Beyond these fabrication methodologies, what the researchers achieved is the spontaneous crystallization of these structures through adjusting the interparticle forces by optimizing solvent composition, evaporation rate, particle concentration, and particle surface chemistry. To this end, mostly, micro fluidic channels and convective flow cells have been utilized for direct solvent flow during the assembly process [168–170].

On the contrary, large-scale patterning of nanostructures with the mentioned methods would be problematic. Besides, the lattice crystallization can be sensitive to sample quality and often requires nanostructures exhibiting high monodispersity and near-spherical shapes. As mentioned in Combination of plasmonic nanoparticles with PCs section, plasmonic nanomaterials emerged as an alternative method to the conventional PCs and they have been extensively exploited for light manipulation in numerous applications [171–173]. As a well-known fact that plasmonic nanostructures have been exploited to build functional devices with their ability to localize the incident light into a sub-wavelength regime [174–177], which are characterized by localized surface plasmon polaritons (LSPR). Among plasmonic-photonic systems reported so far, a flat metallic surface coated with a self-assembled monolayer array of latex spheres is the most studied one due to low cost and facile fabrication and tunability of the resulting optical response by simply tailoring the geometric parameters [178–180]. Next, we described some of the nanoparticle-assisted technique where one can address the difficulties related to fabrication and patterning.

Self-assembly and patterning

In early 2000, a new method to realize low-dimensional arrangement of NPs has been proposed [181–183]. In this modality, particle wires and a pattern of the close-packed particle monolayer
were fabricated in a solution at room temperature. Self-assembled monolayers (SAMs) were formed on Si substrates and modified to be useful as precise templates. To this end, particles were set to the desired positions through well-controlled electrostatic interactions and chemical bond formation between particles and substrates (see Fig. 9). In the subsequent sections, the significant parameters that are affecting the self-assembly formation of PCs are discussed.

**Temperature**

As a well-known fact that keeping the evaporation rate at an optimal value is crucial to form high-quality PCs. For example, high or low speed solvent evaporation can induce stacking faults and macroscopic cracks inside the colloidal crystals. During the evaporation process, temperature is considered to be the key factor for solvent evaporation, which also directly affects the self-assembly of colloidal particles [184]. It has been shown that high temperature...
will cause an increase in the kinetic energy of the colloidal particles, which results a poorly ordered array, whereas low temperature will increment the process time. Fig. 10 demonstrates how an applied temperature gradient allows convective flow to help the growth of proper assembly of silica NPs [42,185] (Fig. 11).

**Air pressure**

Besides temperature, other growth parameters, such as air pressure, solvent type, and humidity are also critical for keeping the evaporation rate steady to obtain the optimal growing condition for PCs. To determine the evaporation rate of the solvent based on the relation between pressure and boiling point of the solvent, the optimal heating temperature can also be significantly altered by changing the pressure. Zheng et al. [186] employed a controlled negative pressure during isothermal heating in vertical deposition, and found the optimal condition for making high-quality colloidal crystals by varying the pressure in a wide range. With the help of low pressure and low temperature, the materials of building blocks could be largely extended, especially the organic and biological active materials [94].

**Solvent type**

When PCs are deposited onto solid substrates, contraction leads to macroscopic cracks during solvent evaporation. The contraction is caused by shrinkage of the colloids and reduction of the separation between the micro-spheres. Therefore, one can say that solvent type plays an important role in the self-assembly of PCs, and Li and Marlow [187] investigated the effects of solvent deposition on PCs from colloidal suspensions of polystyrene microspheres. The authors found that both the surface morphology (e.g. crack distribution and film thickness) and the ordering of spheres were influenced by the solvent significantly. Besides, they concluded that most of the self-assembly processes prefer ethanol or water as the solvent, where a mixture of water and ethanol in different ratios is also considered to tune the properties of the solvent (e.g. surface tension, viscosity, and volatility). Consequently, the outcomes have verified that the effects of the solvent type not only offer opportunities to control the morphology and improve the quality of the PCs, but also provide more information to understand the working principle of different PC fabrication techniques.

**Humidity**

As discussed in a detailed way in Chung et al. [188] high-quality PCs can be obtained in a regulated humidity system, in which the capillary forces between particles are enhanced. The authors also mentioned in a detailed way. They compared the morphology of PCs obtained at 70 °C, 60 °C, and 45 °C with constant high humidity (90%). High-quality colloidal crystals were obtained at 45 °C in 24 h, while poorly-ordered structures were attained for the remaining temperatures. When the temperature is 45 °C and the humidity is 40% or 60%, the PC loses its structural quality, which means that humidity is a major factor to define the characteristic features of PCs. Moreover, the effect of the humidity level on the capillary force is also demonstrated, where the capillary force can effectively change the relative position of the neighboring colloids, and decrease the number of defects towards the formation of perfect PCs [189].

**Moving speed of the contact line**

During the evaporation step of the self-assembly process, highest solvent evaporation rates appear at the edge of the colloidal suspension film. Based on the reported studies so far, the self-assembly of colloids starts at the contact line between the substrate/air and the suspension. As the contact line moves with the liquid surface by solvent evaporation, colloidal crystals form on the substrate. The motion of the contact line can be manipulated by lifting the substrate out of the suspension at a constant speed. In Ref. [190], the authors investigated the correlation between the morphology of colloidal crystals and the lift-up speed. As plotted in Fig. 12, the colloidal structure can be tuned through the lift-up speed at a fixed concentration. To be able to obtain monolayer colloidal crystals over a large area, one needs to find the optimal lift-up speed. Without having the appropriate lift-up speed, multilayer colloidal crystals will be acquired, owing to the non-uniform colloidal particle aggregation on the contact line. For instance, at a higher lift-up speed, structures with low coverage were obtained, since the colloidal particles have insufficient time to move up along the contact line. In the case of multilayered colloidal crystals, the

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**Fig. 11.** (a) Photographs and (b) reflection spectra of seven different colloidal crystal suspensions prepared using various concentration of silica nanoparticles. The concentrations are as following (from right to left): 0.1, 0.13, 0.16, 0.2, 0.23, 0.27, and 0.3 g/mL. (c) Photographs and (d) reflection spectra of the PC films during the fabrication process. Adapted with permission from Ref. [189]. Copyright 2016 American Chemical Society.
The thickness of the film can be controlled by changing the lift-up speed. In the upcoming part, we will present some of the potential applications of plasmonic based PCs along the hybrid materials-based research. Table 2.

Advanced applications of plasmonic-based PCs

Optoelectronic platforms

In 2013, Li and colleagues [191] demonstrated a light-emitting diode (LED) platform with embedded PCs. In this work, the authors used nanosphere lithography (NSL) technique to create a close-packed array of nanopillars which is embedded into an InGaN/GaN LED structure. The proposed nanopillar structure can provide light extraction and suppress the piezoelectric field through strain relaxation of the InGaN/GaN quantum wells at the same time. They reported that the LEDs with the embedded PCs can exhibit 20% more light than the considered reference LED. On the other hand, dye synthesized solar cell (DSSC) concept is another way of producing photovoltaic devices, alternative to the conventional solid state semiconductor ones mainly due to their low cost of fabrication. Zhang et al. [192] conducted theoretical

Fig. 12. (a) The change in the shape of the meniscus as the lift-up rate increases: (b) 20 µm/s, (c) 45 µm/s, and (d) 75 µm/s. SEM surface images of the colloidal crystals with the lift-up rate of (e) 20 µm/s and (f) the side view of the obtained trilayer. SEM surface images of the colloidal crystals with the lift-up rate of (g) 45 µm/s and 75 µm/s and (h) SEM surface image 5 µm/s.

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investigations on the effect of the presence of a PC on the optical absorption of DSSCs (see Fig. 13). To this end, a wavelength selective PC concentrator DSSC has been developed. By overlapping the stop-band of the colloidal crystal films with the maximum fluorescence wavelength of the dye in the defect layer, highly efficient laser-feedback is obtained because of the photonic bandgap effect of the colloidal crystal films. The low threshold lasing was realized through the confinement of radiated photons from the light-emitting layer in the laser-cavity structure. Besides, it showed the promise of the colloidal crystals as effective and selective reflection mirrors for lasers. These achievements are some of the major steps towards low-threshold, ultra-lightweight, low-cost, and flexible light generation devices for opto-electronic applications.

Surface-enhanced Raman scattering

Surface-enhanced Raman scattering (SERS) has still been receiving substantial attention of since its discovery in 1970s [195]. As a well-known fact that, it is a powerful spectroscopic technique to provide sensitive and selective identification an analyte or analyte mixture up to single-molecule level [196,197]. On the other hand, coupled NPs with close spacing and sharp curvatures can demonstrate substantially concentrated electromagnetic (EM) fields associated with strong localized surface plasmon resonance (LSPR) [198,199], which would contribute to substantial Raman enhancement. Therefore, control of the orientation, shape, and self-assembly of NPs has provided important features in most of the SERS-based studies [200–203]. It has been realized that increasing the volume fraction of the "hot-spot" region in the entire system is the key factor to get reliable and reproducible of Raman signals [204,205]. The reproducibility of SERS signals can also be enhanced by patterning the surface of periodic noble metal nanostructures. Nevertheless, more precise control on the particle size, density, and dielectric properties of the surrounding medium are still needed to optimize the field characteristics on the surface.

Zhao et al. [206] reached an ultrasensitive molecular detection (pico-molar) by using metallo-dielectric PC (MDPC)-enhanced SERS signal. The authors demonstrated that Si-PCs, when embedded in multiple MD units, can remarkably increase the field enhancement at the air-dielectric interface. Fig. 14 shows the schematic illustrations and corresponding SEM images of the fabrication procedures.
of MDPCs. During the fabrication process, the PS self-assembled monolayer (PS SAM) was obtained through modified self-assembly. As indicated, the PS SAM has ordered hexagonal arrangement where the diameter of the PS spheres is 978 nm. This modality is applicable to wide-range permutations of insulating and conducting flat surfaces, regardless of hydrophilic or hydrophobic surface of the supporting substrates. To enhance the mechanical strength of PS SAM and Si-filling, it was thermal treatment was applied. After this step, the diameter of PS spheres was about 800 nm, yielding an average shrinkage of ~18% as observed in Fig. 14c. It is noteworthy to mention that the thermal-treated PS SAM exhibited a similar arrangement with the PS SAM, with very few dislocations and cracks. Next, a thin layer of a-Si was sputtered onto the thermal treated PS SAM to form a-Si PCs, as presented in Fig. 14f. The SEM image in Fig. 14g verified the hexagonal alignment and the monolayer integrity of the obtained a-Si PCs. Lastly, silver and a-Si are sequentially sputtered onto the a-Si PCs to form MDPCs with the desired MD configuration simply by adjusting the sputtering time. Fig. 14d schematically summarizes the structural formation of a section plane of the a-Si PCs containing four MD units. For a better view, the SEM image of a-Si PCs integrated with MD units is given in Fig. 14h.

Sensors based on plasmonic PCs

The field of plasmonic PCs-based sensing has received a copious interest in the last decade to develop next-generation photonic applications, since the sensors based on optical measurements generally provide safer, faster, and easier implementation in comparison to their counterparts [207]. In general, PCs-based sensors exploit the sensitivity of PC dispersion bands to the modification of their refractive index and periodicity. In its simplest form, optical sensing can be realized through monitoring PC’s reflectivity or transmissivity, due to the infiltration of PC voids by various materials [208–210].

In Ref. [209], Kuo and colleagues developed an optical sensor for the detection of ethanol concentration through attaching PS and inverse TiO$_2$opal films on glass substrate using self-assembly colloidal crystal template method (see Fig. 15). In addition, in Fig. 15, Fenzl et al. [210] presented a novel way of acetylcholine (ACh) sensing by combining an enzyme hydrogel with a PC hydrogel layer, to be responsive to ionic changes. Indeed, this concept would be useful for measuring the ACh concentrations in human fluids for diagnosis and treatment purposes to prevent certain diseases (e.g. Alzheimer).

Ultra-sensitive biosensing in 3-D plasmonic crystal metamaterials

Due to their versatile and specific characteristics, plasmonic biosensor platforms form the core of current biomedical research [211,212]. In general, the transduction is relied on the refractive index monitoring of the binding event and the difference between biological molecules and the surrounding. Rather than using conventional methods, one can improve the sensitivity of the plasmonic transduction by considering novel mechanisms, such as 3-D plasmonic crystal structure. In this regard, Aristov et al. [213] developed a metal based woodpile crystal nanostructure as an advancement in the field of plasmonic biosensing technology (Fig. 16). They showed that this nano architecture excites a novel plasmon mode, which brings high sensitivity values (>2600 nm/RIU (spectral) and > 3E4 degree of phase/RIU (phase)). Besides, it offers a high surface-to-volume ratio for bio immobilization towards promising sensing functionalities.

Conclusions and future perspective

In summary, we presented the recent progress in plasmon-based PCs in terms of fundamental study and applications. In this Review, our main focus was on nanostructure self-assembly mechanisms and physical properties of the plasmon-based PCs. A
wide-range of strategies for fabricating self-assembled materials were also discussed. The various applications of hybrid photonic materials for engineering, energy and environmental science, nano-devices, and biosensors were introduced and discussed in details. Various experimental processes/methods to obtain the self-assembly of nanostructured plasmonic materials were highlighted, and the noticeable challenges related with methods and device development have crucially been discussed. Based on a careful literature review and our own understating, we believe that the fabrication of large scale plasmonic-based PCs without structural deformation, which is important for having high quality optical devices, is still a major issue. Numerous applications of plasmonic...
photonic crystals, such as in Raman spectroscopy, PCs based biosensors, improved emission of fluorophores containing PPCs and so on, have been presented.

Looking to the future, there are some important points related to next-generation technology in the field of plasmonic PCs. For instance, more research must be conducted on the synthesis techniques to enhance the properties according to device requirement. Plasmonic-based PCs show many promising applications for materials science and nano-electronics. Currently, the controllable formation of 3-D structures is challenging and very difficult to predict, due to a lack of fundamental knowledge. Nevertheless, there are still many challenges for the current self-assembly approaches and practical applications of PCs, and this work convincingly demonstrates that plasmonic NPs should go into the lattice structures. They could revolutionize the fields, such as bio-photons, lasing, and integrated photonics devices, thereby tremendously widening the scope of applications of these materials. Even though the preparation of hybrid composites is still in its infancy, once the major challenges in fabrication are addressed, the following outcomes can be attainable: (a) Attachment of plasmonic PCs with dye molecule scan absorb the incident light (at certain wavelengths corresponding to electronic transitions) and emit fluorescence. A wide wavelength of emission from ultraviolet (UV) to the near-infrared (NIR) can be accessible with different laser dyes. They can offer a broad gain bandwidth and wavelength tunability, as well as the potential for ultra-short pulse generation with passive mode locking. Thus, plasmon-based PCs would be unique materials for such devices and one can use that kind of structures for the dye lasers to further improve efficiency and decrease the pulse width. (b) Laser interaction with 3-D plasmonic PCs at high power would be useful for lasing devices, and low-threshold and high performance photonic chips.

Overall, we explained the salient features of controlled self-assembly of plasmonic PCs along with the related applications and future prospects. This review will serve as a guideline for the researchers to understand the subject in order to conduct/plan future research towards designing and developing functional and efficient plasmonic-based PCs for future technologies.

Fig. 15. (a) An illustration for the preparation of the PS opal and titanium dioxide (TiO$_2$) inverse opal sensor. The proposed sensor consisting of analytic permeable membranes built on a SiO$_2$ slide. (b) As a result of the enzymatic reaction (in the presence of the analytic molecules), the PC shrinks owing to the electrostatic environment alteration of the system. (c) The change in the reflected wave is monitored through a fiber optic spectrometer. (a) Adapted with permission from Ref. [209]. Copyright 2016 MDPI. Adapted with permission from Ref. [210]. Copyright 2015 Royal Society of Chemistry.
Fig. 16. (a) Schematic illustration of the proposed metamaterial for biosensing. (b) An illustration of a Woodpile crystal, in which the unit cell is highlighted. (c) SEM image of the proposed metamaterial fabricated by multiphoton laser polymerization and Ag-based metallization. Theoretical (dashed line) and experimental (solid line) spectra for ellipsometric reflection (ω) and phase (Δ), when the system is in (d) air and (e) water environments. It is worth mentioning that the plots are provided for an angle of incidence of 60° and 47°, respectively. Polarization of incident light dependence of the metamaterial in (f) air and (g) water conditions.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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