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Unpacking the Toolbox of Two-dimensional Nanostructures Derived from Nanosphere Templates

Yujie Ke,^{1,5} Shunsheng Ye,^{2,5} Peng Hu,^{1,3} Hui Jiang,¹ Shancheng Wang,¹ Bai Yang,² Junhu Zhang,^{2,*} Yi Long.^{1,4,*}

1. School of Materials Science and Engineering, Nanyang Technological University, Singapore, 50 Nanyang Avenue, 639798, Singapore.

2. State Key Lab of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, 130012, P. R. China.

3. School of Physics, Northwest University, Xi'an, 710069, P. R. China.

4. Singapore-HUJ Alliance for Research and Enterprise (SHARE), Nanomaterials for Energy and Energy-Water Nexus (NEW), Campus for Research Excellence and Technological Enterprise (CREATE), 1 Create Way, 138602, Singapore.

5. These authors contribute equally.

*Corresponding author: Junhu Zhang (zjh@jlu.edu.cn) and Yi Long (longyi@ntu.edu.sg)

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Abstract

The controlled fabrication of micro-/nanostructures has been a long-standing research focus. The surface patterning technique via templates consisted of monolayer nanospheres is well recognized as an efficient, reliable, and inexpensive method to fabricate two-dimensional (2D) structural arrays. Recent developments of 2D patterned nanostructures via this method grow rapidly and bring out diverse configurations, intriguing structure-induced properties, as well as novel functionalities in a broad range of applications. This review systematically summarizes the recent progress in the 2D nanostructures from fabrications to applications. Particular emphasis is put on the rational design of structure-related functionality for different applications. The diverse configurations derived from monolayer colloidal crystal templates are firstly introduced. Then, we classify the applications by discussing how the properties are benefited from the well-controlled nanostructures. We conclude the review by elaborating the promising functionalities in specific applications including sensors, solar cells, light-emitting diodes, field-effect transistors, photocatalysis, surface-enhanced Raman scattering, biological manipulation techniques, smart windows, photodetectors, transparent

electronic devices, triboelectric nanogenerators, and so on, followed by perspectives on potential challenges and the future development.

1. Introduction

Rational design and fabrication of micro-/nanostructures are fundamental to the modern technologies and crucial for commercial applications due to the strong structure-property correlation.^{1, 2} As an important building block unit, two-dimensionally (2D) ordered arrays, including 2D ordered nanostructural arrays, surface-patterned nanostructures, and free-standing 2D patterned films have been paid considerable attention because of the promising application in extensive areas.³ It is interesting that the properties of these 2D ordered arrays are strongly dependent on their feature structures, allowing the great possibilities of tuning the properties via the controllable growth and fabrication methods. Some reported fabrication methods have been focused on the surface patterns in micro-/nanoscale, such as the dip-pen lithography,^{4, 5} the electron beam lithography,⁶⁻⁸ the nano/microcontact printing,⁹⁻¹¹ the photolithography,^{12, 13} and so on.¹⁴⁻¹⁶ Though many of them can fabricate the high-quality morphological arrays, they are limited by some weak points such as the low throughput, high cost, tedious procedure, and so on. For example, the electron beam lithography and the dip-pen lithography require expensive precision operating systems, such as the focus electron beam system or the atomic force microscope, limiting its application universality for extensive fields. In contrast, the surface patterning technique using colloidal template is recognized as an efficient, inexpensive, fast, and facile method to make large area 2D microstructural arrays.¹⁷⁻²⁰ This method is characterized by the masks consisting of arrayed monolayer nanospheres which are commonly made of silica or polymers and are assembled into periodic arrays through interfacial and convective self-assembly methods.²¹ It is also called “natural lithography”, “nanosphere lithography”, or “colloidal lithography” due to its assembly feature.²²⁻²⁵

So far, diverse 2D micro-/nanostructures made of various materials have been successfully produced via nanosphere templates. A variety of materials, including metals, semiconductors, and organic molecules, were explored on some certain substrates, such as silica-, silicon-, polymer-based surfaces. The library of nanostructural morphologies has been significantly enriched in the past decades. A variety of morphologies were successfully developed, including simple geometries of nanotips, nanonets and so on.²⁶⁻³³ as well as the complex binary and ternary arrays.^{21, 34-40} Similar to other patterning methods, the produced nanostructures or patterns inherit the geometric features of lattice structures and periodicity from the masks. Commonly, nanospheres ranging from 200 nm to several microns were used, resulting in the same periods and a precise geometric feature control that can be scaled down to sub-100 nm. The technique of oxygen plasma etching can be used to shape the polymer-based templates further.^{31, 41-44} In addition, the colloidal templates are easily removed. For example, the hexagonal-patterned polystyrene spheres monolayer is one of the most used colloidal masks as it can be easily removed by the solvent washing, peeling off, or the high-

temperature annealing.^{45, 46} Here, we would like to refer to several comprehensive review works that focus on the preparation of 2D nanostructures via nanosphere templates.^{18-20, 47, 48}

The 2D nanostructures with controllable geometric constructions exhibit attractive structure-dependent properties and arouse extensive explorations in a broad range of applications. These 2D nanostructures experienced a rapid development in the last decade. One of the most investigated field is the optical properties and related applications. For example, the sub-wavelength nanostructure arrays can promote the transmittance of the electromagnetic waves (antireflection) by generating an index gradient between two media. It has been widely applied in the fields of light-emitting diodes (LEDs), solar cells, smart windows, and so on. Besides, surface plasmon resonance (SPR) and structure-induced photonic bandgaps (PBGs) are also extensively studied in these arrayed nanostructures and widely applied in sensors, surface enhanced Raman scattering (SERS), solar cells, smart windows, and so on. In addition, the 2D array offers a larger surface area than the planar one, allowing a series of properties, including the promotion of wettability, the increased active reaction sites, as well as the enhanced roughness-induced friction. These properties contribute to the applications of photocatalysis, smart windows, triboelectric nanogenerators, sensors, and so on.

In this review, we systematically summarize the recent progress in the nanosphere-templated materials from fabrication to applications with particular emphasis on the recent progress of their applications (Fig. 1). Particular emphasis is put on the rational design of structure-correlated functionality for each application (Fig. 1). We start with the briefing of the diverse configurations derived from monolayer colloidal crystal templates. Then, we classify the properties by discussing how the various properties benefit from the well-controlled nanostructures and elaborating the promising functionalities in specific applications including sensors, solar cells, LEDs, field effect transistors (FETs), photocatalysis, SERS, biological manipulation techniques, smart windows, photodetectors, transparent electron devices, triboelectric nanogenerators and so on (Fig. 1). Finally, we provide a perspective on the future development in this area.

2. Template preparation and emerging structures.

The controllable synthesis of 2D nanosphere templates (also called “colloidal crystals” or “colloidal templates”) and various kinds of intriguing structures emerging from 2D colloidal crystals have been reviewed by several previous review articles.^{18-20, 47, 49-59} Therefore, in this section, we will only give a brief summary about the template preparation and covering some of the most recent advances in this field. A typical 2D colloidal crystal template comprises an array of monodisperse colloidal spheres with the diameter ranging from hundreds of nanometers to several micrometers. The colloidal spheres are commonly made of silica and polymers, e.g., polystyrene (PS) and poly (methyl methacrylate) (PMMA). Additionally,

microgel, and hybrid microgel spheres have drawn much attention in recent years and have also been employed as building blocks of 2D colloidal crystals for further applications.⁶⁰⁻⁷³

The library of template structures has been significantly enriched in the last decade. Generally, the commonly used template structures can be concluded as a) closed-packed, b) non-closed-packed, and c) the bilayer nanosphere templates, as well as d) the bilayer template that is the template composed of two kinds of nanospheres with different sizes (Fig. 2a). Moreover, the diversity can be further enriched by, for example, a) preparing on the surface with pre-patterned structures, b) preparing on the curved surfaces, and c) even directly patterning the templates on substrates for hierarchical designs (Fig. 2a). Much more complex templates may also be achieved by integrated two or several methods mentioned above, which are not able to enumerate here and can be referred to several reviews that put significantly more focus on the preparation of nanosphere templates.^{18-20, 47, 49-59}

Thus far, a number of assembly strategies have been developed, of which generally three mechanisms can be concluded. Assembly of nanospheres based on solvent evaporation is one of the most common mechanism. More specifically, the solution with well-dispersed nanospheres is pre-prepared and coated on substrates with carefully control of the solvent evaporation process. Thus, the nanospheres are driven to be assembled on air-liquid interface where the evaporation happens most. In this process, the evaporation speed has to be carefully controlled to eliminate the formation of multilayers and non-continuous film. Base on the mechanism, strategies have been developed, such as the commonly used planar convective assembly, dip-coating, spin-coating, and so on (Fig. 2b). Assembly on interfaces is another common mechanism. In the mechanism, nanospheres are confined on the interface to easily form a monolayer. Air-liquid interfaces are widely applied due to it is simple and reliable, such as the water-air interface was demonstrated to be very efficient for the assembly of monolayer PS nanospheres (Figure 2b). Comparing to air-liquid interface, liquid-liquid interfaces are also efficient while are relatively less used, which may due to the involved complex processes and sophisticated equipment. The third mechanism can be concluded to be the assembly in electric or magnetic field. In these cases, the nanospheres are driven by either electric or magnetic fields unidirectionally to finally assemble on the target substrates. The utilization of electrophoretic deposition is a typical example (Fig. 2b). Strategies based on this mechanism may require certain equipment and significant efforts are needed to avoid the formation of multilayers.

Toward bringing the 2D colloidal crystal-templated materials into real-world applications, the priority is to prepare large-area, high-quality 2D colloidal crystals at low cost and high efficiency. Nevertheless, the scaling-up of highly ordered 2D colloidal crystals, single crystals, in particular, is still of great challenge to meet the needs of industrial-scale mass production. Only a handful of previous researches claimed the capability of synthesizing high-quality 2D colloidal crystals in large areas. Here we give three representative examples. Jiang and co-workers firstly reported the fast fabrication of non-close-packed (NCP) monolayer silica colloidal crystals with high crystalline qualities and wafer-scale sizes using a simple spin-

coating technique (Fig. 3a and b).^{74, 75} A viscous mixture of silica colloids, monomer and photoinitiator were used for the spin-coating process. The ordered arrangement can be assembled by the shear force and subsequent photopolymerization leads to NCP colloidal crystals embedded in a polymer matrix which can be selectively removed by oxygen plasma etching for following templating procedures. This scalable process is compatible with standard semiconductor microfabrication. Recently, Park *et al.* introduced a quick, simple, inexpensive route to assemble spherical spheres into single-crystal monolayers by unidirectionally rubbing the dry powder of colloidal spheres between two rubbery substrates (Fig. 3c-f).⁷⁶ By optimizing the adhesion energy of the substrates, the rubbing speed, and the normal pressure, single-crystal monolayers can be routinely prepared over large areas on both flat and curved surfaces. More recently, Ye and co-workers demonstrated a low-cost micropropulsive injection (MPI) method based on the self-assembly of colloidal nanospheres at the water-air interface and the subsequent transfer process.⁷⁷ They claimed that well-organized 2D colloidal crystals with large areas, even beyond the size of a few square meters, can be fabricated through carefully control of several key parameters, including contact states between the injectors and the water surface, injection speeds, injector numbers, nanosphere concentration, and so forth. Besides, this process presents a mass-production throughput of 250-3000 wafers/h, which is compatible with the high-volume photovoltaic manufacturing (Fig. 3g and h).

Among various kinds of micro-/nano-fabrication methods, the 2D colloidal crystal templating distinguishes itself with its exceptional compatibility with a variety of preparation technologies, including dry/wet etching, physical/chemical vapor deposition, solution growth, self-assembly, electrochemical/electroless deposition, solution/sol dipping deposition, polymerization, soft lithography, photolithography, and so forth.^{18-20, 50, 52, 58} It is worth mentioning that not only the 2D colloidal crystals themselves but their derivative architectures can serve as templates or masks for patterning materials. As a result, numerous structures with diverse morphologies have been successfully prepared, from discrete particles of different shapes (*e.g.*, dots, triangles, disks, rings, crescents, and so on), to one-dimensional structures (*e.g.*, wires, pillars, tubes, rods, *etc.*), to patterned two-dimensional surfaces and films (*e.g.*, holes, pores, cones, bowls, wells, *etc.*), to three-dimensional porous networks and hierarchical architectures. The geometric parameters of these structures, such as periodicity, diameter, height, and so on, can be readily adjusted through the control of sphere diameter and other fabrication conditions, which makes it easy to study their size-dependent properties. In addition to various morphologies, the materials of these 2D colloidal crystal-templated structures also cover a wide spectrum, including metals, metal oxides, semiconductors, (bio)macromolecules, carbon materials, ceramics, and so on.^{18-20, 49, 50, 52-54, 56, 58, 78} The abundance in morphology and constitutive material have given birth to a lot of fascinating properties, functions, and applications, which are the main points in the following parts.

3. Properties

3.1 Antireflection

Antireflective surfaces with 2D nanostructure arrays have aroused great interests and were extensively studied due to the enhancement of light transmission, capturing more incident light to promote the performances of optical and electro-optical devices in practical. The nanostructure-induced antireflection is typically observed in insect compound eyes those are consist of periodic nipple arrays with sub-wavelength nanostructure (Fig. 4a).⁷⁹ Generally, these arrays can eliminate the abrupt refractive index gap on the interface by providing a continuous refractive index gradient (Fig. 4b).⁸⁰

In the regard of antireflective surface fabrication, lithography based on monolayer colloidal template is demonstrated as a powerful technique for various materials.^{83, 84} For instance, antireflective surfaces based on silicon and silica were produced by applying monolayer colloidal crystals as etching masks.⁸⁵ The silicon nanopillar arrays displayed broadband antireflection, a reflection as low as 2.5% over visible to near-infrared (NIR) spectrum. Compared with nanowire (Fig. 4c), silicon nanocone arrays with a more gradual change of refractive index shown better reflection suppression, which suggested the necessity of a gradual reduction of refractive index on the interface for antireflective surface (Fig. 4d,e).^{81, 86} On the other hand, Yang and co-workers developed a simple and time-efficient way to prepare silica cone arrays on fused silica via colloidal sphere lithography and demonstrated the sample with double-sided nanocone surfaces display a better antireflection performance than the planar and the single-sided ones (Fig. 4f,g).⁸² Beyond widely studied silicon and silica, composite-based antireflective surfaces attracted significant research interests more recently. Si₃N₄-coated SiC nanodome arrays were successfully prepared by reactive ion etching (RIE) process with a monolayer nanosphere mask followed by a thin film deposition process.⁸⁷ The coated array presented a reduced reflectance as low as 0.99% in visible range (390-785 nm), while was 20.5% in the plain sample. As a result, a fluorescence enhancement of 138% was observed on SiC. Considerable photoluminescence enhancement was achieved on Al/CdS/SiO₂ composite.⁸⁸ An interesting hierarchical structure consisted of perforating domed Ag/polystyrene was produced by applying RIE with a monolayer colloidal template twice.⁸⁹ This plasmonic antireflection surface presented a broadband omnidirectional antireflection that is a reflection of 0.6% over the spectrum of 400-1000 nm under normal view and a lower reflection of 0.05% under an oblique incidence angle. Electric field simulation confirmed both the plasmonic absorption and diffractive losses contributed to the low reflection property. Omnidirectional antireflection was achieved by Yang and co-workers.⁹⁰ Inspired by the leafhoppers, they produced intricate brochosome-like architectures through bilayer colloidal template, and demonstrated such coating displayed the low reflectance for a wide incident angle varying from 8 to 45°. They further produced the silica-based hierarchic nanocaps arrays using the templates with two different sizes of nanospheres,⁹¹ which also exhibited the omnidirectional antireflection with a <2.5% reflectance on the incident angle of 60°.

Among numerous preparation methods toward antireflective surfaces, the method using colloidal templates demonstrates highly reproducible, facile, and efficient traits. We keep the discussion short by outreaching to several reviews that presented more insightful and comprehensive views on the antireflection.^{80, 92} With the fast development in this field, low-cost, high-performance, and multifunctional antireflective surfaces based on colloidal templates are expected.

3.2 Photonic band gap

The photonic crystal (PC) is a significant class of chromotropic materials consisted of periodic dielectrics, which induce PBGs to forbid propagation of certain wavelengths of light. By adjusting the periodicity, dielectric constant, configuration *et al.*, PBGs can be tuned to selectively forbid propagation of specific wavelength to produce distinct structural colors. Among the numerous fabrication methods, the template-assisted method based on self-assembly of colloidal crystals is intensively studied. The synthesis-structure-property relationship of colloidal-lithography-based photonic crystals (PCs) with periodicity down to the sub-micron range are well developed.

PBG identified as the reflection peak in an optical spectrum (so-called “stop band”) usually can be characterized as the transmittance valley on an optical spectrum. In 2D PCs, its position is mainly depended on three parameters: the medium refractive index, the lattice parameter, and the filling factor.⁹⁶ For example, in 2D ZnO hollow half-shell arrays, a transmittance valley red-shift from 500 to 540 nm was observed with increasing the shell thickness of ZnO from 110 to 260 nm.⁹⁷ Under fixed shell thickness, increasing the colloidal sphere size also caused the stop band shifted to a longer wavelength. Similar phenomena were found on Ni(OH)₂ hollow sphere arrays, where the size of hollow spheres and the shell thickness could fine tune the forbidden band positions, respectively.⁹⁸ Qi and co-workers investigated the PBG of Ag₂S nanonets (Fig. 5a) and concluded a linear relationship between the lattice parameter and the stop band position on Ag₂S nanonets (Fig. 5b).⁹³ In addition, the structure-induced PBGs were also demonstrated on hexagonally patterned composing carbon nanotubes (CNTs) (Fig. 5c), which displays an iridescent color while shows a dark appearance in bulk (Fig. 5d).⁹⁴ Moreover, the single CNT could also be vertically aligned as 2D PCs through the predeposited periodic catalyst of Ni nanodots.⁹⁹ Recently, responsive 2D PCs attracted increasing interests. A promising way is to construct 2D periodic nanostructures using phase transition materials. The vanadium dioxide (VO₂) exhibits thermo-induced metal-insulator transition, accompanied with a large change of the infrared transmittance. This material was coated on 2D hexagonally-closed-packed silica nanospheres (Fig. 5e) to fabricate 2D SiO₂/VO₂ PCs, which generated the stop band in visible range while was dynamically responsive to surrounding temperature in near-infrared range (Fig. 5f).⁹⁵ The method separated the optical controls in the visible and the near-infrared ranges by the structure and the temperature, respectively. Another way is by applying an electrochemical process. The TiO₂ changes to Li_xTiO₂ in a reversible way during the intercalation/deintercalation of lithium ions (Li⁺) process. Yahia Djaoued *et al.* utilized this process to fabricate electrochromic devices by constructing a

sandwiched structure composing the indium tin oxide (ITO)/ Li⁺ conducting layer/ TiO₂ inverse opal/ITO configuration.¹⁰⁰ The absorption edge shift was observed from 337 to 422 nm upon the coloration at 3.5 V. This study might provide an inspiration for dynamically tuning the stop band on 2D PCs derived from colloidal templates.

In regard to 2D patterned nanostructures based on colloidal templates, the synthesis was intensively studied across various materials from metals to semiconductors. This facile and reliable method is expected to be a promising technique in the future study of PCs.

3.3 Surface plasmon resonance

As a fundamental excitation of condensed matters, surface plasmons (SPs) have aroused in-depth investigations on the fundamental properties for both localized plasmons and propagation plasmon polaritons, rising up insight for the novel electro-optical device design and application.¹⁰¹ Localized surface plasmon resonances (LSPRs) can be excited in isolated or discrete metal nanostructures.¹⁰² In contrast, surface plasmon polaritons (SPPs) that the propagating electro-magnetic waves along continuous metal-dielectric interfaces can be excited on nanoscale metallic gratings.¹⁰³ The plasmon energy and its dispersion characteristics relative to the configuration in nanoscale are critical for the plasmonic investigation. As a versatile nanofabrication technique, the lithography based on colloidal templates offer an efficient platform to study the SPRs.

The LSPR is a signature optical property of the noble metal nanoparticles. It occurs when the light with a certain wavelength strikes a metallic nanoparticle, causing the collective oscillation of conduction electrons.¹⁰⁴ The noble metal nanocrystals with a size range from 20 to a few hundred nanometers exhibit distinct extinction enhancements, presenting as extinction peaks in the visible or IR regions of the spectrum. Van Duyne's group pioneered the study of LSPR on the colloidal-templated Ag nanoparticles.^{24, 25} They reported the precise change of extinction peak positions from visible to NIR ranges by changing a number of parameters including the size, shape, interparticle spacing, nanoparticle-substrate interaction, and the surrounding medium. Crescent-shaped Au nanohole antennas were produced and observed with a local field enhancement on its sub-10-nm tip.¹⁰⁵ Moreover, Yang *et al.* developed binary and ternary patterns using colloidal templates by controlling the plasma etching and thermal treatment processes.¹⁰⁶ Due to the complex patterning, multiple LSPR peaks were detected on one sample and their positions were individually shifted according to the excitation angle.

The SPP is a transverse magnetic polarized optical surface wave (typically a visible or infrared wavelength) that propagates, for example, along with a flat metal-dielectric interface.¹⁰⁷ Structures supporting SPPs include plain films and stripes, holes, corrugations, curved surfaces on nanocrystals and so on. Thus, the physical property of interfaces is a significant parameter for SPPs. In regard to this, Wang *et al.* achieved the tuning of the SPP property on patterned Au films deposited on the top of hexagonal-close-packed polystyrene sphere

monolayer.¹⁰⁸ They observed a clear transition from the localized to extended SPP mode when increasing the deposition thickness of Au films. The delocalized SPs were also observed by introducing Au films with elastomeric substrates such as PDMS.¹⁰⁹ In addition, the SPP mode was demonstrated that it could coexist with the waveguided mode induced by the 2D photonic structures suggested by Li and co-workers.¹¹² They clearly depicted the multiple optical resonance modes on a hybrid plasmonic-photonic structure composed of inverse opal silica monolayers coated on plain Au films.

Based on the colloidal template method, diverse plasmonic nanostructures were developed and displayed a series of potential applications. The group of Zhang successfully produced a series of Ag-based nanostructures via colloidal templates, including arrays of nanoholes,^{113, 114} nanowells,¹¹⁰ nanocrescents,¹¹⁵ nanorings,¹¹⁶ and graded structures.¹¹⁷ These plasmonic Ag structures were demonstrated applications in plasmonic sensors and color generation.^{110, 113, 114} For example, they prepared the controlled fabrication of Ag nanowell arrays via colloidal templates (Fig. 6a) and investigated the electric field distributions (Fig. 6b). They demonstrated the coupling between Bragg wave SPP and Raleigh anomalies occurs and significantly contributes to the narrowing of the linewidth. They further demonstrated the position of reflectance dip is responsive to the surface reflective index change (Fig. 6c), which can be applied as plasmonic sensor, for example, to detect the capture of the antibody.

Beyond the conventional noble metals, emerging plasmonic nanomaterials including semiconductors and metal oxides have attracted increasing interests.^{118, 119} SPRs on these nanocrystals were also demonstrated to strongly correlate with the size, shape, surrounding medium and so on.¹²⁰ In this regard, Yang *et al.* explored the SPR on 2D patterned Al nanostructures by a bottom-up colloidal-template-assisted method.¹²¹ They developed various structures including dome-rings, disks, and rings that displayed the plasmonic colors from green, blue, to pink. These colors were demonstrated to come from the reflection induced by the complex resonant modes among the structures. Moreover, the SPRs on semiconductors and metal oxides presented distinct behaviors that were not revealed on noble metals. An interesting example is reported on VO₂, being well-known for its metal-insulator transition (MIT) at critical temperature (~68 °C). Recently, the LSPR was observed on its metal phase (above 68 °C) while quenched on the insulator phase (below 68 °C).^{122, 123} The group of Long detailed the LSPR during the MIT on 2D periodic VO₂ nanoparticle arrays (Fig. 6d).¹¹¹ On the thermo-hysteresis, both the LSPR intensity and position were observed to be tuned reversibly. On heating procedure, its intensity increased gradually accompanying with a red-shift of the peak position (Fig. 6e), of which the temperature range typically matched the range of transition from the insulating to the metallic states. Similar to other plasmonic structures, these particle arrays also exhibited a size- and reflective index-dependent LSPR shift (Fig. 6f).

In summary, the colloidal-template patterning with high efficiency and flexibility presents a promising platform to explore the structure-property relationship as well as the practical application of SPRs. In the future, diverse nanostructures and materials derived from the colloidal-template method are expected to give rise to more new physical phenomena.

3.4 Wettability

Wettability, a centuries-old concept, is significant to numerous fields from biological processes to engineering and industrial technologies. This concept has been rediscovered in past decades, largely attributed to a new understanding of the mechanisms inspired by the wetting phenomena in nature.¹²⁶ Generally, the wettability of a surface depends on two parameters: (a) the configuration of nanostructures and (b) the physical and chemical property of materials. It was revealed that micro-/nano- hierarchical structures play an important role in determining the wettability properties. Also, the arrangement and orientation of these structures may control the wetting state. According to Wenzel model, surface roughness can largely change the wettability that is to make the hydrophilicity to superhydrophilicity and hydrophobicity to superhydrophobicity. The superhydrophilic and superhydrophobic properties of a liquid on a roughness-enhanced surface are determined by the intrinsic wetting threshold of the liquid, also being known as the intrinsic contact angle on an ideal surface.

In this regard, the colloidal-template method is a promising candidate for the fabrication of surfaces with superwettability. Because the solid surfaces fabricated via colloidal template display the high controllability of structures over micro- to nano-range as well as the relatively low requirement for the intrinsic physical and chemical properties of target materials, which make diverse structures and materials applicable. So far, a great number of superwettability surfaces was explored.¹²⁷ For example, inspired by the superhydrophobicity of the compound eyes of mosquito, Jiang's group developed a hierarchical structure made of closed packed silica nanospheres on HCP PDMS micro-hemispheres.¹²⁸ This artificial compound-eye analog presents a decent superhydrophobicity as well as a self-cleaning behavior in humid habitat. Monolayer colloidal nanospheres with surface modifications by the Ag nanoparticles (NPs) or CNTs were also demonstrated with the superhydrophobicity.^{129, 130} The Ag NPs/PS-coated glass tube displayed remarkable supporting force on the water surface that remain floating when sustained 4.3 times the weight of itself. Beyond the direct usage of monolayer colloidal nanospheres for structures targeting wettability, colloidal templates were also successfully applied to a number of materials including Si,⁸⁵ Co₃O₄,¹³¹ ZnO,¹³² poly-4-vinyl pyridine (P4VP),¹³³ and so on. For example, Li and co-workers found the colloidal-templated Co₃O₄ hierarchical nanorod arrays via a colloidal-template-assisted pulsed laser deposition (PLD) process exhibited stable superhydrophilicity lasting for half a year without ultraviolet (UV) irradiation.¹³¹ Moreover, they achieved the tuning of wettability by surface modification with fluoroalkylsilane from superhydrophobic to superhydrophilic accompanying with a water contact angle change from 5° to 154°.¹³⁴ By applying a two-step micro/nanosphere lithography, Park *et al.* developed an interesting SiO₂ hierarchical structure composed of nanorod arrays on the top of microrod arrays, presenting an optimizing contact angle of 160°.¹³⁵ Ordered scallion-like ZnO arrays were prepared by Xu *et al.* through a hydrothermal growth of the ZnO on colloidal patterned ZnO seeds.¹³² The superhydrophobic property (water contact angle was larger than 150 °) was demonstrated on the ZnO array after the

hydrophobic surface coating. Recently, the group of Zhang developed anisotropic wetting based on the asymmetric nanostructures made of Janus silicon cylinder arrays.¹³⁶ The two sides of cylinders are modified by molecules with distinct surface energies (Fig. 7a), which could be applied as microfluidics to control the flow direction in microchannels (Fig. 7b).¹²⁴ These arrays can also control the wetting behavior of water or oil liquid under a series of media, including oil, water, and air.¹³⁷ Combining the colloidal templates with the inclined reactive ion etching, geometric gradients of graded silicon cones are produced on a slide (Fig. 7c), which can serve as a wettability “library” study the anisotropic wetting surfaces (Fig. 7d).¹²⁵

In this field, most conventional studies of colloidal-template focus on optimizing the superwettability. However, exploration of its applications is still on the early stage considering the emerging applications of superwettability surfaces extend to anti-icing, anti-fogging, liquid-liquid separation, sensors, printing and so on.¹²⁶ Thus, the explorations of the 2D-colloidal-template method on wettability targeting extensive applications are expected.

4. Applications.

4.1 Chemical and Biological sensors.

The topic of chemical and biological sensors is one of the most studied applications of colloidal-templated 2D nanostructures. An ideal chemical or biological sensor possesses two fundamental characteristics: (a) high selectivity and (b) appropriate sensitivity to the analyte concentrations of interest. Meanwhile, additional characteristics also have attracted growing interests such as the rapid response, the portable design, low cost, the easy sample preparation process, the signal visualization, good durability, and so on. The design and utilization of 2D nanostructures arrays for sensors mainly rely on the structure-induced optical properties from PBG to plasmonics (SPR/SPP). Emerging efforts were also put to non-optical-based sensors. This part summarizes recent progress on the field by classifying from the different mechanisms.

SPR on certain nanomaterial is responsive to the reflective index change induced by the surrounding medium near its surface. Based on such response, chemicals that closed to the plasmonic materials can be detected as the SPR shifting signal in a spectrum. A typical example is the hybrid plasmonic-PCs composing of 2D PS nanospheres on the flat Au surface reported by Braun and co-workers.¹³⁸ On the hybrid nanostructure, both the photonic and plasmonic propagating resonance modes were demonstrated to be of high quality with factors exceeding 100. Sensors based on such nanostructures presented atomic layer sensitivity to detect the ethanol in gas phase via its physisorption on the sensor surface. Another example is the surface-modified 2D ordered porous Ag film.¹³⁹ The Ag film with surface modified by biotin was proved to efficiently detect the captured avidin, presenting a remarkable trough shift on the reflectance spectrum. SPP is also very sensitive to the surrounding reflective index. Using colloidal templates, the group of Ren successfully

narrowed down the resonance linewidth to 3nm to reduce the radiative loss, achieving an extreme high value of figure of merit.¹⁴⁰

Sensors based on the PBG change commonly relied on the local reflective index change and more importantly the pitch size change of the periodic nanostructures. Based on the sensitivity of PBG to the local reflective index, the group of Qi further demonstrated a biological sensor to detect the avidin-based on such local reflective index change.¹⁴³ Another more efficient design is to integrate 2D PCs with stimuli-responsive substrates that can swell or shrink in response to a specific analyte in a very low concentration. The group of Asher has developed a series of sensors based on this method.^{141, 144-148} Produced sensors consisted of embedded 2D PCs embedded on the surfaces of responsive hydrogels (Fig. 8a).^{141, 148} These sensors consisted of different hydrogels can detect a variety of analytes, including pH,^{141, 149} metal ions,¹⁴¹ glucose,^{141, 150} the serum albumin ligand binding,¹⁴⁴ the candida albicans,¹⁴⁶ avidin,¹⁴⁷ lectin concanavalin A,¹⁴⁵ and so on. One significant advantage of them is the visual determination of the analyte. For example, the sensor targeting the glucose detection displays different colors in response to different glucose concentrations (Fig. 8b). To improve the output signals, the group of Li developed enhancement methods, such as coating the 2D PCs on both sides of hydrogels,¹⁵¹ or replacing the colloidal crystals by Au nanosphere arrays.¹⁵² Using the Au arrays, the diffraction intensity of the sensor was demonstrated to be increased 88 times compared to the one based on PS spheres.¹⁵²

Non-optical sensors commonly rely on the increase of surface areas as well as the reaction active sites to enhance the sensitivity. For example, Wang *et al.* developed 2D porous electrodes by the sacrificial colloidal templates (Fig. 8c). The sensor based on these porous electrodes display enhanced sensitivity for NO₂ detection.¹⁴² Dai *et al.* also developed a sensor for NO₂ detection through the self-assembly of monodispersed Nb₂O₅ microspheres.¹⁵³ Detection of the formaldehyde was achieved by Rao *et al.* through the 2D SnO₂ hollow sphere arrays.¹⁵⁴ Besides the increasing surface area, the fabrication strategy of SnO₂ via sacrificial templates is relative mild, which ensures the sensing materials on the active heated area, leading to high sensitivity, fast response and recover times. Besides these, colloidal templates were also applied for the fabrication of sensors for the detection of hydrogen, hydrogen peroxide and heavy metals.¹⁵⁵⁻¹⁵⁷ For example, Sabri and co-workers explored the detection of low-concentration Hg vapor by sensors constructed of Au- or Ag-coated PS sphere monolayers on quartz crystal microbalance transducers.¹⁵⁶ In addition to the sensitivity enhancement, the sensors display the high repeatability, accuracy, and stability.

4.2 Surface-enhanced Raman scattering

With superb sensitivity, SERS has been developed to be a powerful spectroscopic technique in the last decades and widely applied to extensive areas, from chemical, materials, to life science. Compared with normal Raman spectroscopy, SERS integrated the plasmonic substrates composed of noble metal nanostructures that were described by Schlucker in a

simple way as the “equation”: SERS = high molecular specificity of Raman spectroscopy + metal nanostructures supported LSPR + high sensitivity.¹⁶¹ Highly spatial localized regions, the so-called “Hotspot”, are preferred in the design of SERS substrates. These regions commonly observed on tiny structures such as shape tips, narrow gaps and so on.¹⁶² Moreover, the increase density of hot spots is preferred because the possibility is quite low that a target molecule on a hot spot.

A typical material for SERS is Au.¹⁶³ The group of Li fabricated the Au-based SERS substrates by applying a chemical and physical deposition to sacrificial colloidal monolayer templates.¹⁶⁴⁻¹⁶⁶ Through this technique, a number of nanostructures with the Au coating were produced including semi-hollow, inverse opal, honeycomb, regular network, nanoparticle, and hierarchically micro/nanostructured arrays. They observed the following physical deposition process could strengthen the stability of SERS performance. The electromagnetic coupling in produced 10-nm gaps enhanced the sensitivity, which successfully achieved a detection limit of 10^{-12} M R6G. As demonstrated by Hong *et al.*,¹⁵⁸ trapping Au NPs near the center of nanosphere-lithography-derived nanobowtie arrays was also a way to enhance the SERS performance (Fig. 9a). They found the increasing numbers of trapped Au NPs near the tip area could enhance the Raman shift intensity (Fig. 9b). Repeatable and facile fabrication method for SERS substrate is a challenge. Yang *et al.* developed a binary “island” shaped arrays with high-density hot spots, which enabled more installation of Au PNs, resulting an enhanced performance than the Au NPs on planar substrates.¹⁶⁷ Wang and co-workers provided an alternative for repeatable SERS substrates by peeling off the deposited Au film from templated silicon wafers,¹⁶⁸ which were fabricated by anisotropic etching on selected crystal phases with the masks of monolayer nanosphere templates. The free-standing Au film with dense tips and gaps displayed a maximum enhancement factor of 10^7 .

Another typical material is Ag. Instead of processing on solid surfaces, The group of Qi applied the nanosphere lithography on the solution surface where reaction occurred of the two reagents, the N_2H_4/NH_3 in the vapor phase and the $AgNO_3$ in solution.¹³⁹ When used as SERS substrates, the free-standing Ag macroporous films presented an enhancement order of 10^7 for the 4-aminothiophenol (4-ATP). Inverse Ag nanocup arrays were developed by Zhang *et al.* by transferring the nanocup arrays upside down onto a glass substrate,¹⁶⁹ which was demonstrated with a frustum-like and void-like plasmon mode, leading to the improvement of SERS sensitivity. Cavity arrays composing annular Ag were successfully fabricated by the assist of colloidal templates (Fig. 9c,d), presenting the propagating surface plasmons along the cylindrical metal/dielectric interfaces, a potential candidate for SERS (Fig. 9e).¹⁵⁹ A high enhancement with a factor of 10^8 was observed by the group of Oh on periodic Ag nanoring cavities with 10-nm gaps (Fig. 9f).¹⁶⁰ The enhancement was attributed to the excitation of plasmon resonances alongside the ring shape cavities, promoting the enhancement factor of an order of magnitude. The fabrication process was subtle that integrated 2D colloidal templates with the atomic layer deposition (ALD) and ion milling, which produced highly

uniform arrays (Fig. 9f,g). The produced film could reach up to several centimeter scales (Fig. 9h).

Beyond the Au and Ag, large research efforts were also put on other plasmonic metals as well as composites. For example, an Au-Ag composite prepared by the group of Fan with a periodic particle-in-bowl Ag-in-Au nanostructure by treating the 2D colloidal templates with the atomic layer deposition (ALD) and a post-annealing process.¹⁷⁰ The composite was demonstrated an optimizing SERS enhancement factor of 10^7 . A study by Jeong *et al.* reported a SERS enhancement benefiting from the nanofluidic channels on the HCP monolayer silica nanospheres with Ag-coated on the top-half.¹⁷¹ Materials other than Au and Ag can introduce additional properties. For instance, multilayered Ag and Si coatings on closed-packed monolayer polystyrene nanospheres were proved to significantly promote the electromagnetic fields at the air-dielectric interface,¹⁷² benefitting to the Raman enhancement. Abdelsalam and the co-workers reported stable SERS substrates based on the honeycomb-like Pd and Pt nanostructures, prepared through the colloidal-templated electrodeposition.¹⁷³ Pd and Pt with widely-known catalysis provided the SERS with the advantages to study reactive intermediates and species. Kang and co-workers produced close-packed ZnO hollow nanospheres with Ag nanoparticles hanging inside.¹⁷⁴ SERS substrate based on ZnO with such nanostructures displayed the self-cleaning property. Studies of graphene in this field proved it could contribute to the additional chemical enhancement of SERS sensitivity by stabilizing, for example, the R6G via π - π interaction.¹⁷⁵ The enhancement was demonstrated to coexist with electromagnetic enhancement of materials on SERS substrates made by graphene-Cu and -Au composites.^{175, 176}

4.3 Solar cell

Solar cells, or photovoltaics (PVs), which convert the unlimited solar radiation into clean electrical power, could be one of the emerging solutions to the issue of fossil-fuel energy exhaustion that the whole world is going to face in the future.¹⁷⁷ At present, crystalline Si (c-Si) solar cells with thicknesses of hundreds of micrometers and efficiency up to 22% have dominated the solar-cell market although the price is high due to their substantial silicon material consumption and costly processing. Thin-film solar cells, which have thicknesses within several micrometers and can be deposited on cheap module-sized substrates (e.g. glass, plastic, and so on) have emerged as a feasible way towards the goal of reducing materials usage and manufacturing cost. However, a significant drawback of most thin-film cells is their relatively low energy-conversion efficiency owing to the small light absorbance, especially near the bandgap. Therefore, one ultimate goal of the research and development in the PV community is the realization of ultrathin, low-cost solar cells that do not compromise on energy-conversion efficiency. A viable strategy to trap more light inside the thin devices is to build nanostructures for effective photo management.¹⁸²⁻¹⁸⁸ The nanostructures could play different roles in the solar cells, which depends on their morphologies, materials, and locations. For example, they can be antireflection coatings that reduce reflection losses,^{81, 189,}

¹⁹⁰ resonators that prolong optical pathways,^{181, 191} or antennas that guide more light into the active layers.¹⁸⁵

Among a variety of nanofabrication techniques, 2D colloidal crystals templating fits quite well for nanostructuring thin-film solar cells thanks to its low cost, scalability, and ease of optimizing geometric parameters.^{192, 193} 2D colloidal crystals themselves and their derivative nanostructures can be located at different positions. Firstly, these structures can be placed on the front of thin cell devices.^{178, 194-196} For example, Wang and co-workers deposited a PS 2D colloidal crystal of 800 nm in diameter atop the c-Si thin-film solar cell (Fig. 10a).¹⁷⁸ Their experiments and simulations demonstrated that power-conversion efficiency was improved by 26.5% and the external quantum efficiency (EQE) was almost doubled at several wavelengths. The PS nanospheres here can couple light into strong whispering gallery modes and thus substantially increase light absorption in the c-Si thin cell. Another prominent benefit of this light harvesting scheme is its spherical geometry that naturally accepts light from large angles of incidence, which was previously proven in a numerical simulation work by Grandidier and co-workers.¹⁹⁴ Secondly, nanostructuring at the back surface of a cell may afford a high-performance back reflector.^{179, 193} Ding *et al.* incorporated plasmonic silver nanodomes in solid-state dye-sensitized solar cells (ss-DSCs) as the back contact (Fig. 10b and c).¹⁷⁹ The silver nanodome arrays were fabricated through a direct nanoimprint lithography (NIL) patterning of mesoporous TiO₂ and subsequent thermal evaporation. The quartz master template was fabricated by reactive ion-etching using a silica 2D colloidal crystal as a mask. As a result, the metallic nanodome back reflector that greatly enhanced the light absorption through light scattering and coupling into surface plasmon polaritons led to increased EQE, particularly in the long wavelength region of the dye's absorption band. Lastly, the active layer can be nanostructured as well.^{81, 180, 181, 197-200} For example, instead of using nanocones for antireflection, Zhu *et al.* created nanodome solar cells by conformally depositing the active material on nanocone-structured substrates (Fig. 10d).¹⁸⁰ Based on this geometry, a 280 nm thick hydrogenated amorphous silicon (a-Si:H) layer can absorb 94% of the light in the 400-800 nm range, much higher than the 65% absorption of flat film devices. Such excellent performance could be attributed to the strong antireflection effect in the short-wavelength regime and the efficient in-plane guided mode in the long-wavelength regime. Yao and co-workers used low-quality factor (low-Q) whispering gallery modes in spherical nanoshells to dramatically enhance broadband absorption (Fig. 10e).¹⁸¹ They took nanocrystalline silicon (NC-Si) nanoshells templated by silica nanospheres as a model system. Consequently, a nanoshell absorber of 50 nm in thickness exhibited absorbance equivalent to a 1- μ m-thick planar NC-Si film. Such a remarkable light-trapping efficiency was enabled by the low-Q whispering gallery modes which coupled light in the nanoshells and circulated it in the active material with a considerably long pathway. Notably, the low-Q not only facilitated the coupling of light into resonant modes but also broadened the resonant band and made the absorption enhancement region wider.

4.4 Photocatalysis

Heterogeneous photocatalysis such as photocatalytic degradation and photoelectrochemical (PEC) catalysis offers great potential to decompose organic contaminants and convert solar energy into chemical energy, which promises a possible solution to the global environmental and energy issues.²⁰¹⁻²⁰⁵ Taking the most widely investigated TiO_2 as an example, a general mechanism for heterogeneous photocatalysis is demonstrated in Fig. 11a. The mechanism mainly covers four processes, *i.e.*, charge-carrier generation, charge-carrier trapping, charge-carrier recombination, and interfacial charge transfer.^{206, 207} Specifically, when a photon with an energy matches or exceeds the band gap energy of the semiconductor, an electron in the valence band (VB) is excited into the conduction band (CB), leaving a positive hole in VB. The photoinduced electron-hole pairs can recombine and dissipate the input energy as heat, become trapped in metastable surface states, or react with electron donors and electron acceptor on the semiconductor surfaces or interfaces. Apparently, increasing the rate of the last step is the key to improve the photocatalytic efficiency.

2D colloidal crystals have been employed to prepare high-performance photocatalysts based on nanostructured semiconductors for photocatalytic degradation of organic pollutants.^{208, 211-215} Most of these nanostructured photocatalysts are typically based on 1D nanocolumn arrays and hemispherical nanobowl/shell arrays, which exhibit high specific surface area, superior light harvesting capability, and extended light absorption edge. For example, Li *et al.* fabricated hexagonal-close-packed, hierarchical amorphous TiO_2 nanocolumn arrays by pulsed laser deposition (PLD) using 2D PS colloidal crystals as templates (Fig. 11b).²⁰⁸ Nanobranches in each nanocolumn grew in a radiation-like manner, emanating from a center point on the PS sphere (Fig. 11c). Compared with the amorphous TiO_2 film and anatase nanocolumn arrays, the amorphous TiO_2 column arrays exhibit superior degradation performance for stearic acid (Fig. 11d), which, respectively, can be attributed to the higher specific area of the hierarchical amorphous nanocolumn arrays and enhanced light harvesting due to photonic crystal structures and multiply light scattering within nanobranches. A similar hierarchical architecture was also adopted in a hematite system to improve its photocatalytic performance.²¹³ Wang *et al.* extended the transmission edge of ZnO into the visible region by constructing ZnO nanoshell arrays on 2D PS colloidal crystal templates.²¹⁵ Thus they realized photocatalysis under monochromatic visible light by utilizing the two-photon induced electron-hole pairs in ZnO. In addition to nanostructures with only one kind of material, 2D colloidal crystals were also used to fabricate heterogeneous nanostructures with coupled semiconductors. Zhang *et al.* prepared a coupled photocatalyst comprising a wide-band-gap TiO_2 film covered by a narrow-band-gap Cu_2O microgrid.²¹² Due to the efficient charge transfer between the two phases and the similar opportunity each has to be exposed to irradiation and adsorbates, the coupled photocatalyst showed higher photocatalytic activity for degrading methylene blue (MB) under irradiation of UV-vis, visible, and UV light than pure Cu_2O and TiO_2 films, respectively.

Semiconductors textured by 2D colloidal crystal templates have also proven to act as promising high-performance photoanodes for PEC water splitting.^{209, 210, 216-219} For example, Cheng *et al.* reported the hierarchical urchin-like TiO₂ nanostructure arrays with improved PEC water splitting performance due to the benefits of omnidirectional anti-reflection properties and enhanced charge collection efficiency (Fig. 11e and f).^{209, 216} In recent years, Qi's group have reported a series of work on developing 2D colloidal crystal-templated photoanodes to boost the efficiency of PEC water splitting.^{210, 218, 219} They achieved the facile fabrication of Ag₂S-Ag heterostructured nanobowl arrays consisting of Ag₂S nanonets lying on Ag nanobowl arrays *via* two-step nanosphere lithography at the gas-liquid interface.²¹⁸ This heterostructured nanobowl array showed a much higher photocurrent density than that of a pure Ag₂S nanonet under both visible light irradiation and simulated AM 1.5G solar light, which promises advantages for PEC water splitting. This remarkably enhanced current density could be related to the enhanced charge separation and light harvesting enabled by the Ag nanobowl array under the Ag₂S nanonet. More recently, the same group demonstrated two kinds of hierarchical, heterostructured nanorod@nanobowl (NR@NB) arrays, namely rutile TiO₂ NR@anatase TiO₂ NB arrays²¹⁰ and CdS NR@SnO₂ NB arrays.²¹⁹ Such a structure consisted of NR grown the inner surfaces of NB arrays through interfacial nanosphere lithography followed by hydrothermal growth (Fig. 11g). Both NR@NB arrays were used as the photoanodes for PEC water splitting. The TiO₂ NR@NB arrays and the CdS NR@SnO₂ NB arrays produced photocurrent densities 2 and 2.5 times as high as that of the TiO₂ NR arrays and the CdS NR arrays, respectively (Fig. 11h). Therefore, the heterostructured NR@NB arrays hold great promise for PEC water splitting owing to the increased active surface area for contact with the electrolyte, multiple light scattering arising from the hierarchical structure for improving light harvesting capability, and the band alignment between two kinds of materials for efficient charge separation and transfer processes. Since CdS has stronger visible light absorption and SnO₂ has higher carrier mobility than TiO₂, the CdS NR@SnO₂ NB arrays exhibited an even superior PEC performance for hydrogen generation than the TiO₂ NR@NB arrays.

4.5 Triboelectric nanogenerator

The technique of triboelectric nanogenerator has undergone a fast development in the past five years, while the output performance is limited.^{220, 221} One of the significant methods for the performance enhancement is to control the surface morphology of friction layers.²²² The group of Yan successfully applied the colloidal crystal monolayer onto the surface of the friction layers.²²³ They developed a triboelectric nanogenerator constructed by two arch-shaped friction layers and coated the top surface of the bottom layer with polystyrene spheres (Fig. 12a). The nanogenerator works when been pressed and released repeatedly, resulting in an output voltage as high as 220 V per cycle (Fig. 12b). Moreover, the nanogenerator is highly stable and maintains its output voltage after 1000 cycles (Fig. 12c).

4.6 Smart windows

Two-dimensional colloidal crystals is demonstrated as an effective method toward the fabrication of VO₂-based thermochromic films targeting energy-saving smart windows application due to the benefits of (1) the temperature-dependent LSPR,^{111, 224, 225} (2) the colourful PCs,⁹⁵ (3) enhanced transparency,^{226, 227} and (4) the antireflective properties emerged from the structured VO₂.²²⁸

An architectural window can significantly reduce the energy-consumption of air-conditions by smartly regulating the indoor solar irradiation, for example, by making the sunlight through on winter while blocking the infrared part on summer (Fig. 13a).²²⁹⁻²³² VO₂ is one of the dominated materials in this field since its reversible phase transition between the low-temperature monoclinic and the high-temperature rutile phase (inset of Fig. 13b),²³³⁻²³⁵ accompanying with a drastic transmittance change in infrared range (Fig. 13b).^{229, 231} However, several challenges remain on VO₂-based thermochromic glazing including the limited solar modulation, low visible transmittance, undesired yellow-brown appearance and so on.^{231, 233, 236}

Periodic VO₂ films prepared from 2D colloidal templates promise the solutions. For example, periodic VO₂ nanoparticles arrays are produced through high-temperature annealing using the sacrificial 2D PS templates (Fig. 13c).¹¹¹ The periodicity can be controlled down to 160-nm with an average particle size of 67 nm (Fig. 13d). By varying the PS size in templates, the diameter of VO₂ particles can be controlled and presents the size- and temperature-dependent LSPR. It is suggested that tuning the LSPR valley position to the spectrum range with dense solar energy can significantly promote the solar modulation property. Periodic nanonet and nanodome arrays are also achieved by adjusting the physical property of vanadium precursors.^{111, 237} Another example is to address the intrinsic yellow-brown appearance of VO₂ by coating the VO₂ (20 nm) on 2D close-packed SiO₂ PCs (Fig. 13e).⁹⁵ Hexagonally close-packed structure maintains after VO₂ overcoating indicating as the TEM image in Fig. 13f. By changing the size of the silica sphere and the diameter of the individual core-shell structure, final samples display tunable colors covering from red, green to blue. However, the sol-gel method can only produce VO₂ nanoparticles attaching to the SiO₂ spheres instead of uniform VO₂ shells. Integration of antireflection to thermochromic films can promote both the visible transmittance and the solar modulation properties. This is demonstrated on VO₂-films with biomimetic moth-eye structures, composing closed-packed nipple arrays (Fig. 13g). Qian *et al.* produced such structures by coating the ~40 nm of VO₂ on the pre-fabricated SiO₂ nipple arrays with different periodicity from 200 to 1000 nm (inset of Fig. 13h).²²⁸ Fig. 1h represents the SEM image of VO₂/SiO₂ nipple arrays with the periodicity of 400 nm. They found the optimized thermochromic performance achieved on 200-arrays, which is smaller than the visible wavelength and suggested further decreases the periodicity will enhance the thermochromic performance. In addition, they found the 200-nm patterns

provide an increasing contact than the planar one, which leading the potential functionality of self-cleaning for smart windows.

4.7 Light-emitting diode

GaN-based LEDs have been widely used in the area of solid-state lighting, which are gradually replacing conventional light bulbs and change the way we light the world. For general lighting purposes, high brightness, *i.e.*, high light output power (LOP), is definitely required. The LOP is mainly determined by internal quantum efficiency (IQE) and light extraction efficiency (LEE). For GaN-based LEDs, the IQE is always degraded by the high threading dislocation density, resulting from the strain-induced piezoelectric field, the nonradiative recombination, and the large lattice mismatch and thermal expansion between the epitaxial GaN films and sapphire substrates. The LEE is limited by the total internal reflection (TIR) at the interface of the semiconductor and air. The large contrast in the refractive indices between GaN ($n = 2.5$) and air ($n = 1$).²³⁸ prohibits the majority of photons generated in the active layer from escaping the LED beyond critical angle of 23.5° . Thus, the emission is reabsorbed by semiconductors and electrodes and the performance of the LEDs is degraded.

2D colloidal crystals have been demonstrated to effectively improve LEE and IQE.^{57, 58} One of the most feasible strategies to enhance LEE is to incorporate PCs based on 2D ordered nanostructures into the LED structure. Here PCs serve as diffraction gratings that are able to efficiently couple the waveguided light within dielectric layers into the air, therefore boosting the LEE. Besides, PC-assisted LEDs usually exhibit better light focusing effect, compared to those without PCs since radiation through PCs can be redirected to the top escape cone, thus resulting in smaller divergent angles.^{52, 57, 58} Fig. 14a sketches the profile of a conventional InGaN/GaN multiple quantum well (MQW) LED structure. Researchers have demonstrated that 2D PCs emerged from 2D colloidal crystals can be constructed at different positions of the LED devices. PCs on the top surface were most frequently adopted. PCs on LED top surfaces with diverse geometries have been fabricated using 2D colloidal crystal templates, including nanocones,^{243, 244} nanopillars,²⁴⁵ nanoholes,^{239, 246, 247} nanodisks,²³⁹ nanopillars,²⁴⁸ and other complex nanostructures,^{249, 250} all of which were proven to be superior LOP. For example, Wei *et al.* fabricated SiO₂ nanodisk PCs mounted in the *p*-GaN and corresponding air-hole PCs to improve the LEE of GaN-based LEDs.²³⁹ The SiO₂ nanodisk PCs (Fig. 14b) were realized by nanospherical-lens photolithography and selective area growth of *p*-GaN. The corresponding air-hole PCs (Fig. 14c) were obtained by etching away SiO₂ nanodisks. By using PS nanospheres with different diameters, PCs with periods of 900 nm and 700 nm and a similar diameter of 450 nm were investigated. According to the light output power-current-voltage (*L-I-V*) curves shown in Fig. 14d, the LOP of SiO₂ PC-assisted LEDs with periodicities of 900 nm and 700 nm and corresponding air-hole PC-assisted LEDs are enhanced by 71.3%, 83.8%, 49.3%, and 67.7%, respectively, compared to that without PC at 350 mA injection current. Fig. 14e shows the angular emission profiles of the LEDs with and

without PCs operated at 200 mA. For LEDs with PCs, the light is effectively redirected to the top escape-cone of the LED through SiO₂ and air-hole PCs, resulting in smaller divergent angles. PCs can also be embedded in the *n*-GaN layer.^{251, 252} Recently, Wei *et al.* investigated the InGaN/GaN LEDs with bottom PCs of SiO₂ nanodisks embedded in *n*-GaN, top PCs mounted in *p*-GaN, and double PCs in both *n*- and *p*-GaN layers. The authors found that the LED with double PCs exhibited not only the highest LOP, compared with that without PC, but produced the most significant focusing effect, showing a view angle (136.9°) 14.4° smaller than that of the planar LED (151.3°).²⁵² Instead of directly nanostructural semiconductor layers, Kim *et al.*²⁴⁶ and Choi *et al.*²⁵³ demonstrated that PCs of ITO nanopillar arrays fabricated by dry etching using 2D colloidal crystals as etch masks were capable of improving LEE. The introduction of 2D PC coatings of high-index materials was proposed without modifying any parts of the as-grown LEDs.^{240, 254-257} Do *et al.* constructed a 2D SiN_x nanohole PC layer on Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce) yellow ceramic plate phosphor (CPP) in order to enhance the forward emission of YAG:Ce CPP-capped high-power white LEDs (Fig. 14f).²⁴⁰ Fig. 14g shows the electroluminescent spectra of two different white LEDs at an identical current of 350 mA. As a result of introducing 2D PC on top of the CPP, the intensity the yellow emission of the 2D PC-assisted YAG:Ce CPP-capped white LED became higher than that of the flat CPP-capped white LED while the intensity of the transmitted blue light became lower. These phenomena significantly lowered the correlated color temperature with the aid of the 2D PC layer. Besides, the correlated color temperature of the 2D PC-assisted CPP-capped white LED remained almost unchanged at ~5500 K independent of the applied current or the viewing angle. The luminance of the white LED with 2D PCs was also higher than that without 2D PC layer (Fig. 14g). Though the luminous efficacy of the conventional and 2D PC-assisted CPP-capped LEDs decreased with the increased applied current, the enhancement ratio of luminous efficacy by the 2D PC layer was almost constant over all applied current ranges (Fig. 14h). They further demonstrated that a higher efficacy could be realized by replacing the 2D SiN_x nanohole PC layer with the 2D TiO₂ nanobowl PC layer, which benefited from the higher refractive index of TiO₂.^{255, 256} Similar strategy was also employed to the LEE of the polymer LED.²⁵⁸

The IQE can be improved by utilizing the coupling of SPs and InGaN MQWs and patterned sapphire substrates (PSS).^{57, 58} The strong local electromagnetic field around metal nanostructures can increase the radiative efficiency of a nearby radiating dipole.^{259, 260} Therefore, when metal nanostructures that support SPs are located in close proximity to the InGaN MQW, the IQE can be enhanced due to the contribution from radiative recombination rate enhancement. It is noteworthy that the SP-MQW coupling can occur only if the metal nanostructures are adjacent to the MQWs. Generally, the spacing should not be larger than 40-50 nm.²⁶¹ Wei *et al.* reported InGaN/GaN LEDs with Ag nanodisk arrays embedded in the *p*-GaN layer, which was realized through nanospherical-lens photolithography and subsequently selective regrowth.²⁴¹ Fig. 14i shows an SEM image of an Ag nanodisk array formed after being annealed at the *p*-GaN growth temperature. The spacing between Ag nanodisk arrays and InGaN/GaN MQWs was controlled by the time of dry etching of the AlGaN

film. In this work, two spacings of 20 and 35 nm were investigated. As shown in Fig. 14j, compared with LED without Ag nanodisks, the optical output power of the SP-enhanced LEDs with the spacings between Ag nanodisk arrays and MQWs being 20 and 35 nm is increased by 26.7 % and 31.1%, respectively, at an injection current of 350 mA. Additionally, the LED with an Ag nanodisk array exhibits a reduced emission divergence compared to the conventional LED, which might benefit from the PC embedded in the *p*-GaN layer. Apart from nanodisks, Ag nanotriangles fabricated by using 2D colloidal crystals as deposition masks were also presented by Kao *et al.* to enhance the LOP of GaN-based LEDs.²⁶²

PSS can improve IQE and LEE simultaneously. On the one hand, PSS can give rise to high-quality epitaxial GaN films with low dislocation density, resulting in an improved IQE by decreasing nonradiative recombination rate. On the other hand, PSS can serve as PCs that efficiently couple the waveguided light into the air. PSS is featuring hemispheres,²⁶³⁻²⁶⁵ concave triangular nanocones,^{242, 266} periphery-rounded nanoprisms,²⁶⁷ nanovolcanoes,²⁶⁸ *etc.* have been successfully prepared using 2D colloidal crystals and other materials nanostructured by them as masks for dry/wet etching. For instance, Dong *et al.* presented AlGaIn-based deep ultraviolet LEDs (UV-LEDs) grown nano-PSS fabricated *via* the combination of nanospherical-lens photolithography and wet chemical etching.²⁴² The patterns on the nano-PSS surface are concave triangular cones (see the inset in Fig. 14k) as a result of the anisotropic etching of the sapphire crystal in a mixture solution of H₂SO₄ and H₃PO₄. As shown in Fig. 14k, the AlN film grown on the nano-PSS completely coalesces after 3-μm growth, which is much shorter than that of 10 μm for AlN grown on micro-strip substrates. X-ray rocking curves further confirm that the AlN film on the nano-PSS is of high quality. The screw and edge dislocation densities of which were estimated to be $1.6 \times 10^7 \text{ cm}^{-2}$ and $1.2 \times 10^9 \text{ cm}^{-2}$. According to light output power-current-external quantum efficiency (LOP-I-EQE) curves in Fig. 14l, both the LOP and EQE of the nano-PSS-based deep UV-LED are 98% higher than those of the LED with a flat sapphire substrate at an injection current of 20 mA. It is noteworthy that though the IQE enhancement of the NPSS LED was estimated to be 60%, the LEE benefiting from light scattering at the AlN/nano-PSS interface made a great contribution to the large EQE enhancement. Su *et al.* proved the feature size of the PSS is related to the LED performance.^{264, 265} They compared the performance of GaN-based LEDs grown on nano-PSS and micro-PSSs fabricated nanosphere lithography and photolithography, respectively. They found that micro-PSSs with large aspect ratio led to a GaN film with better crystalline quality while NPSS exhibited the better capability of light extraction. Consequently, the nano-PSS-based LED was found to have larger LOP.

4.8 Field effect transistor

Using 2D colloidal crystals using as a template is an effective way to fabricate nanopore or nanorod array structures to improve the performance of electrical and electronic devices, such as FETs, field emitters, and so on.^{269, 270}

The FET has served as a versatile tool for the electrical characterization of the nanostructure performance.²⁷¹ Bottom-gate, bottom-contact configuration in FET is considered as the simplest way to manufacture organic circuits.²⁷² The applications of bottom-contact devices are limited by the small injection area and the disadvantageous injection path limit.²⁷³ Fuchs *et al.* reported that nanopore-structured electrodes could tremendously improve the grain structure of the semiconductor. Such nanopore-structure semiconductor reduces the contact resistance and accordingly enhances charge carrier injection, which results in the improved mobility of charge carriers.²⁶⁹ Polystyrene nanospheres are used as templates to form porous on the electrodes, as shown in Fig. 15a. A 30 nm pentacene active layer is employed to investigate the FET properties. Fig. 15b shows the typical transfer curves of the transistor based on source/drain electrodes with and without nanopores. The device without nanopore structure shows mobility of about $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, while the higher performance is observed from the device with nanopore structures with a mobility of $0.22 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The mobility of charge carriers in the FET with nanopore structures is about 20 times higher than it in those without nanopore structures. The porous electrode facilitates the forming of nanopore structure active layers with small grain boundaries at the electrode interface. Subsequently, it not only reduced the contact resistance but also affected the growth of the semiconductor, thus further improving the performance of the device.

Golberg *et al.* prepared a series of hexagonal NCP, periodic anatase TiO_2 nanorod arrays through a PLD process by using PS monolayer as templates (Fig. 15c).²⁷⁰ The SEM images indicate that TiO_2 process an ordered and well-structured array with a HCP arrangement (Fig. 15d). This method is much cheaper compared to optical lithography, X-ray lithography, electron beam lithography, and soft lithography.^{274, 275} They found the periodicity of a nanorod array can easily be controlled by using PS templates with different sphere sizes. The results show that the prepared nanorod array with an HNPC arrangement exhibited enhanced field effect properties compared to particle films. Furthermore, the field-enhancement factor decreased and the turn-on field increased with the increasing periodicity of the hexagonal NCP array.

4.9 Photodetector

Photodetectors utilizing semiconducting materials to convert incident light into photocurrent signals have shown promising applications in optical communication, medical diagnostic, environmental detection and other imaging areas.²⁷⁶⁻²⁷⁸ There are several figures of merit that are routinely used to characterize the performance of photodetectors, such as responsivity, dark current, response speed, quantum efficiency (QE), EQE, stability, *etc.*²⁷⁶ 2D colloidal crystals are distinguished as an effective tool for templating semiconductor nanostructures. Such nanostructures can greatly contribute to photodetectors' performance, which may benefit from (1) enhanced light harvesting capability favored by specific geometries, (2) improved material quality, and (3) large surface-to-volume ratio. Lin and co-

workers fabricated Au nanocrystal array/Si nanoantennas comprising hexagonally arranged single crystalline Au nanocrystal arrays inlaid in Si substrates through the combination of 2D colloidal crystal templating and metal-assisted chemical etching (MACE) (Fig. 16a and b).²⁷⁹ The Au nanocrystal array inlaid Si nanoantennas exhibited wavelength-selective photocurrent enhancement by tuning the depth of immersion of Au nanocrystals in Si via a MACE process. Such a feature was enabled by the dielectric environment sensitive LSPR of the Au nanocrystal arrays. When the device was illuminated by the light close to the LSPR band in wavelength, the incident electromagnetic waves could be confined to the Au nanocrystals and greatly enhanced local electric field, leading to increased light absorption in Si and photocurrent as well. In contrast, without the wavelength matching between detected light and LSPR band, the local electric field amplification and strong light absorption did not occur. In this circumstance, the shielding effects of Au nanocrystal arrays gave rise to a negative enhancement of photocurrent. Wang and co-workers reported the facile fabrication of organometal halide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) nanonets using 2D colloidal crystal arrays as templates (Fig. 16c).²⁸⁰ Compared to the conventional compact films $\text{CH}_3\text{NH}_3\text{PbI}_3$ photodetectors, the nanonet-based photodetector has a high responsivity of 10.33 A W^{-1} (under 700 nm light illumination), six times higher than that for the compact film counterpart (Fig. 16d), faster response speed, and better stability. The excellent photodetection performance can be ascribed to three key characteristics of the device. Firstly, the nanonet geometry can strongly scatter the incident light, thereby considerably enhancing light harvesting and increasing photocurrent. Secondly, the nanonets with thin walls afford direct carrier transport pathways which favors the diffusion and collection of photogenerated charge carriers. Thirdly, the 2D colloidal crystal templates offer a suitable environment for the perovskite crystallization process, resulting in large grain sizes with superior crystallinity. The high-quality materials ensure the efficient and fast charge carrier transportation across the perovskite nanonets and good stability in ambient conditions. The authors further demonstrated that this strategy could be applied to fabricating flexible photodetectors with excellent bending durability. Notably, similar porous geometry was previously adopted by Wu's group to nanostructure SnO_2 and Mg^{2+} doped NiO achieved via a one-step oil-water interface self-assembly process.^{281, 282} Both photodetector devices based on these two nanostructures exhibited impressively high enhancements of photocurrent. The enhanced light harvesting ability was also found in the photodetectors based on hollow spherical nanoshell arrays of MoSe_2 and MoS_2 fabricated via 2D colloidal crystal templating and chemical vapor deposition.²⁸³ It is worth mentioning the exceptional "SP-SP" junction barriers conducting mechanism resulting from the close packing of nanoshells significantly contributed to carriers tunnelling and transport processes and therefore increasing the response and recovery speed.

4.10 Transparent conductor

Transparent conductors with good optical transmittance and high electrical conductivity act as essential top electrodes of various optoelectronic devices, such as solar cells, touch screens, flat panel displays, organic light-emitting diodes (OLEDs), smart windows, bioimaging and sensing devices, *etc.*²⁸⁴⁻²⁸⁹ For decades, ITO, one of the transparent conductive oxides, has always been the primary choice of transparent electrodes for current optoelectronic devices, due to its outstanding transparency in the visible and near-UV window and good electrical conductivity.²⁹⁰ But the scarcity of indium (In) and sophisticated fabrication conditions undoubtedly increase manufacturing costs.²⁹¹ Besides, the brittleness of ITO hinders its applications in emerging flexible devices, such as wearable electronics, implantable sensors, foldable displays, flexible photovoltaic devices, *etc.*²⁸⁷ Substitutes that can be fabricated in a low-cost, scalable way are therefore highly desired. Both the scientific and industrial communities have made efforts to seek alternative solutions, among which 2D mesh-based structures of conductive materials (*e.g.*, metals, carbon materials) are most frequently adopted.^{292, 293} The voids in a mesh allow light to pass through while the continuous network affords pathways for charge carriers, enabling the combination of sufficient transparency and conductivity.

2D colloidal crystals have already proven to be inherently ideal templates for mesh-like micro-/nanostructures owing to uniform, ordered arrangements.^{18, 19} A typical route to 2D nanomeshes with circular apertures comprises etching of colloidal spheres, vertical materials deposition, and removal of colloidal crystal templates. Based on this process, several transparent conductors were successfully fabricated.²⁹⁴⁻²⁹⁹ Zhu *et al.* incorporated a gold nanomesh electrode into a poly(3-hexylthiophene) and [6,6]-phenyl-C61 butyric acid methyl ester (P3HT:PCBM) organic solar cell, resulting in a high fill factor of 61% and a considerable PCE of 3.12% for that time.²⁹⁴ Gao *et al.* demonstrated the fabrication of Cu nanomeshes using 2D colloidal crystals and comprehensive simulation and experimental studies on their optical and electronic properties (Fig. 17a).²⁹⁶ The Cu nanomeshes showed 80% diffuse transmission at $17 \Omega/\text{sq}^{-1}$, which is comparable to ITO (80-90% transmittance, $8\text{-}15 \Omega/\text{sq}^{-1}$). Notably, using Cu, a cheaper metal compared to Au, Ag, and In, favors the reduction of costs. Moreover, the Cu nanomeshes showed application prospect in flexible devices since they can be prepared on flexible PET substrates and can endure repeated bending and abrasion, and long-time heating. Seo *et al.* investigated the electrochemical impedance properties and electrode sensing performances of Au nanomeshes on flexible parylene substrates.²⁹⁷ The Au nanomeshes showed better properties in terms of electrical impedance, transparency, cell viability, and flexibility than ITO and graphene electrodes, making them a potential candidate for high-performance electrophysiology electrodes. According to the findings of previous works, it can be concluded that transparency and conductivity are two contradictions that show opposite dependence on geometric parameters, including thickness, void diameter, and periodicity. Normally, it is easier to obtain both high transmission and conductivity for nanomeshes with large periodicities. That is the reason why most of these highly conductive and transparent metallic meshes employed colloidal crystal templates with diameters larger than $1 \mu\text{m}$.^{296, 297, 303} Kwon *et al.* even employed a $10\text{-}\mu\text{m}$ -diameter colloidal crystal to

achieved 83% transmittance and $20 \text{ } \Omega/\text{sq}^{-1}$ square resistance in an Ag honeycomb mesh.³⁰³ Alternatively, meshes with novel shapes produced by modifying the deposition process may also lead to high-performance transparent conductors.^{300, 301, 304} Lee *et al.* took advantage of large cast shadows during oblique deposition to fabricate Ni/Au (20 nm/100 nm) meshes with metal occupying merely 10% of the substrate surfaces (Fig. 17b).³⁰⁰ When the thin metal film electrode was replaced by such a mesh electrode, the photoresponsivity, quantum efficiency, UV-visible rejection ratio, and detectivity are elevated from 0.135 A/W, 50.75%, $1663 \text{ cmHz}^{0.5}\text{W}^{-1}$, and $2480 \text{ cmHz}^{0.5}\text{W}^{-1}$ to 0.248 A/W, 93.23%, $1.78 \times 10^{10} \text{ cmHz}^{0.5}\text{W}^{-1}$, and $2.43 \times 10^{10} \text{ cmHz}^{0.5}\text{W}^{-1}$, respectively. Qiu *et al.* demonstrated a novel Cu crosswire grid comprising two overlapping wire patterns fabricated through stepwise angle-resolved nanosphere lithography (Fig. 17c).³⁰¹ The authors claimed that an average optical transmittance of 80% at a sheet resistance of $100 \text{ } \Omega/\text{sq}^{-1}$ could be achieved using PS nanospheres with a relatively small diameter of 750 nm. In addition to metals, other conductive materials like CNTs also might be good choices for transparent conductors. Kim *et al.* reported the fabrication of CNT network-based transparent electrodes by concurrently assembling silica nanospheres and CNTs into complex 2D colloidal crystals and then etching the sacrificial silica nanospheres away (Fig. 17d).³⁰² Though their square resistances were over $1.5 \text{ k}\Omega/\text{sq}^{-1}$, the transmittance could exceed 90%. Interestingly, the authors found that the conductivity can be significantly enhanced by increasing the thicknesses of the CNT bundles of the networks and doping the CNT films with HAuCl_4 . More recently, Qiang *et al.* extended the application of colloidal-templated electrodes to the field of neuroscience.³⁰⁵ They prepared a composite nanomesh microelectrode through the colloidal templates and demonstrated its capability to simultaneously record the electrophysiology and two-photo imaging in the brain of an awake mice.

5. Conclusions and perspectives

The controlled fabrication of structures in nanoscale has been a long-standing research focus. The development of two-dimensional patterned nanostructure via nanosphere lithography grows rapidly, bringing out diverse configurations, intriguing structure-induced properties, as well as decent functionality in a broad range of applications. Here, we systematically summarize recent advances in the colloidal-templated 2D nanostructures. We start with a briefing on the progress of the preparation method. The technology is of high flexibility and is suitable for a variety of materials as well as numerous substrates, such as silica-, silicon- and polymer-based surfaces. Colloidal templates are successfully prepared on arbitrary surfaces and the scale up to several square meters is producible. The library of nanostructure morphology has been significantly enriched, including simple repetitive arrays as well as binary and ternary complex arrays. Particular emphasis is put on outlining the rational design of structure-induced functionality for each application. We discussed the structure-dependent properties, covering the PBG, antireflection, SPR, and wettability, which have aroused extensive explorations in a broad range of applications. We further demonstrate the

applications and focus on the structure-dependent properties benefits in certain applications. This field has experienced rapid development in the last decade with significant concentrations on optical properties and related applications. For example, devices such as the LED, solar cells, smart windows *et al.* are benefited from the antireflection property, enhanced by the sub-wavelength nanostructure arrays that promote the transmittance of the magnetic wave by generating a gradual index gradient. The other optical properties of the SPR and the PBG are also extensively studied in these arrayed nanostructures and widely applied in sensors, the SERS, solar cells, smart windows, and so on. Besides the investigation of optical properties, the increase of surface areas of 2D arrays comparing to the planar one leads to the promotion of wettability, active reaction sites, as well as roughness-induced frictions. These contributed to the performance enhancement in technologies of photocatalysis, smart windows, triboelectric nanogenerators, sensors, and so on.

Though the surface patterning technique based on colloidal templates is considered as a facile, time-saving, reliable, and inexpensive method, its shortages remain and are worthy to be improved. Defects of grain boundaries are commonly observed on the colloidal templates especially in large-scale samples. So far, it is challenging to prepare single crystalline colloidal templates alone centimeter scales and these defects inevitably forms during the self-assembly process. These defects significantly limit the patterning method in some applications and usually lead to deviations between the produced and the expected results in most applications. Improvements are expected for developing large-area and defect-free colloidal templates. In addition, the applicable templates offer limited configurations that are most of the studies rely on the colloidal templates with the hexagonal packed configuration. The hexagonal pack is widely observed as the most thermodynamic stable one in the self-assembly process. To break the packing way, additional techniques are necessary to control the self-assembly process, while they commonly sophisticate the preparation process, leading to the reduction of reliability as well as the cost increase. It is expected to develop a simple and reliable ways to provide colloidal templates with configurations beyond the hexagonal pack. Moreover, the methods to remove the colloidal templates after lithography are limited, narrowing the capable materials and applications. Take an example of the polystyrene (PS) sphere template, common methods for removal are based on the high-temperature annealing or wet-chemistry method using solvents with high polarity. These methods are suitable to some inorganic materials, while not applicable to most organic materials. Broadening the methods for templates removal also promise to be meaningful. Lastly, it is worth to mention that the production of structures with their feature size less than 100 nm is still challenging by this method, which is due to the difficulty to prepare the high-quality templates using sub-100-nm nanospheres.

Compared to the fruitful achievements in the preparation, we believe the exploration of the application of colloidal-templated nanostructures is still in the early stage. Considering the extensive fields of applications and their rapid development as well as the increasing concentration in nano/microscale in future, we envision a plentiful contribution to the applications of the colloidal-based surface patterning in a broader range of devices and

applications. A better understanding of the properties of colloidal templates is critical to their application. Though the optical properties including the SPR, PBG, and antireflection are well-established, there remains many uncertainties and unrevealed properties. For example, the mechanical properties of colloidal templates are relative rarely investigated. The group of Yan turns their attention to the field recently using an atomic force microscope (AFM) with a peak-force quantitative nanoscale mechanical (QNM) mode.³⁰⁶⁻³⁰⁸ The nano/micromechanical plays a significant role in flexible and stretchable devices, such as the triboelectric nanogenerator.²²³ Moreover, integration of the colloidal-based surface patterning with other lithography/patterning methods may be widely applied.³⁰⁹ Thus, the rational design of the integration method for specific materials, nanostructures, or devices is important. With great advances achieved, it is expected to further apply the colloidal-based surface patterning in extensive fields with the aid of improved template quality, preparation methods, and the emerging properties.

Abbreviations

4-aminothiophenol	4-ATP
Amorphous silicon	a-Si:H
Atomic layer deposition	ALD
Carbon nanotube	CNT
Ceramic plate phosphor	CPP
Conduction band	CB
Colloidal crystal monolayer	CCM
Crystalline Si	c-Si
External quantum efficiency	EQE
Field effect transistor	FET
Hexagonal closed-packed	HCP
Indium tin oxide	ITO
Infrared	IR
Internal quantum efficiency	IQE
Light-emitting diode	LED
Light extraction efficiency	LEE
Light output power	LOP
Localized surface plasmon resonance	LSPR
Low-quality factor	Low-Q
Metal-assisted chemical etching	MACE
Metal-insulator-transition	MIT
Methylene blue	MB
Micropropulsive injection	MPI
Multiply quantum well	MQW
Nanobowl	NB

Nanocrystalline silicon	nc-Si
Nanoimprint lithography	NIL
Nanoparticle	NP
Nanorod	NR
Near-infrared	NIR
Non-close-packed	NCP
Organic light-emitting diode	OLED
Patterned sapphire substrates	PSS
Photoelectrochemical	PEC
Photonic bandgap	PBG
Photonic crystal	PC
Poly(dimethylsiloxane)	PDMS
Photovoltaic	PV
Poly-4-vinylpyridine	P4VP
Poly (methyl methacrylate)	PMMA
Polystyrene	PS
Pulsed laser deposition	PLD
Quantum efficiency	QE
Reactive ion etching	RIE
Scanning electron microscope	SEM
Solid-state dye-sensitized solar cell	ss-DSC
Surface-enhanced Raman scattering	SERS
Surface plasmon	SP
Surface plasmon polariton	SPP
Total internal reflection	TIR
Transmission electron microscopy	TEM
Two-dimensional	2D
Ultraviolet	UV
Valence band	VB

Conflicts of interest

The authors declare no conflicts of interest.

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Fig. 1 Schematic of the diverse properties and applications derived from the toolbox of 2D nanostructures derived from nanosphere templates. The property and application are distinguished by the red and blue hexagons, respectively.

Fig. 2 (a) Illustration of the commonly used methods for the preparation of the nanosphere templates, including the planar convective assembly, dip-coating, spin-coating, electrophoretic deposition, and interfacial-assembly. (b) Illustration of the diverse templates, which can be classified as closed-packed, non-closed-packed, binary, and bilayer templates, as well as the templates on patterned surface, on curved surface, and in patterned array.

Fig. 3 (a) Wafer-scale NCP silica 2D colloidal crystals made by spin-coating. Reproduced with permission from ref. 74. Copyright 2006, AIP Publishing LLC. (b) Typical scanning electron microscope (SEM) image of NCP silica 2D colloidal crystals prepared by spin-coating. The upper inset showing a higher-magnification image and the bottom inset showing a Fourier transform of a $40\ \mu\text{m} \times 40\ \mu\text{m}$ region. Reproduced with permission from ref. 75. Copyright 2005, American Chemical Society. (c) Schematic illustration showing the rubbing process. (d) Photography of the resulting monolayer assembly of PS beads ($1\ \mu\text{m}$ in diameter) on the entire surface ($20\ \text{cm} \times 20\ \text{cm}$) of the poly(dimethylsiloxane) (PDMS) rubber substrate. (e) Monolayer particle assembly processed by rubbing on a glass bottle and a 100 mL flask. The glassware had been coated with PDMS before the particles were rubbed. (f) Wafer-scale single-crystal monolayer of closely packed particles formed by repeated unidirectional rubbing and micropatterning of the colloidal monolayer. Inset: Diffraction pattern obtained by projecting a commercial laser pointer through the monolayer. Reproduced with permission from ref. 76. Copyright 2014, Wiley-VCH. (g-h) Photographs of PS 2D colloidal crystals prepared by the micropropulsive injection method on (g) 36 wafers and (h) a 1-m^2 glass substrate. Reproduced with permission from ref. 77. Copyright 2015, American Chemical Society.

Fig. 4 (a) The high-magnification photograph of compound eyes of *Calliphora* and the SEM image of its ommatidium surface. Reproduced with permission from ref. 79. Copyright 2003, Nature Publishing Group. (b) Schematics of (1) the light propagation through the nanostructure array and (2) its refractive index gradient. Reproduced with permission from ref. 80. Copyright 2015, The Royal Society of Chemistry. (c) SEM images of the silicon (1) nanocone and (2) nanowires arrays. (d) The photograph of samples of the silicon thin film, nanowires, and nanocones. (e) Absorption spectra of these three samples at a normal incident angle. Reproduced with permission from ref. 81. Copyright 2009, American Chemical Society. (f) The photograph of (left) the planar silica substrate and (right) the substrate with double-sided nanocone arrays. (g) Transmittance spectra of the planar, single-sided, and double-sided silicon samples. Insets are the illustrations of these three samples. Reproduced with permission from ref. 82. Copyright 2009, Wiley-VCH.

Fig. 5 (a) Transmittance spectra of the Ag₂S nanonet arrays with different pitch size from 500-1000 nm, determined by the colloidal crystal monolayer (CCM) particle diameter. (b) The PBG position (λ) versus the CCM particle diameter. Reproduced with permission from ref. 93. Copyright 2010, American Chemical Society. (c) SEM images of the patterned CNT arrays. (d) The photograph of the CNTs with and without patterning on a polycarbonate substrate. The patterned CNT arrays on the top display colorful appearance due to coherent diffraction. Reproduced with permission from ref. 94. Copyright 2010, American Chemical Society. (e) Photographs of the samples with monolayered silica nanospheres arrays on quartz substrates. Diameters of the silica nanospheres are 400, 600, and 700 nm from Figures on the top to the bottom. (f) Calculated transmittance spectra of the monolayered SiO₂-VO₂ core-shell nanosphere arrays with nanosphere diameters of 400-700 nm. Reproduced with permission from ref. 95. Copyright 2016, American Chemical Society.

Fig. 6 (a) Schematic of the fabrication process of Ag nanowell arrays and the cross-section of the nanowells (x - z plane). (b) The time-averaged electric field distribution on the x - z plane of the Ag nanowells on an incident light of $\lambda = 512$ nm. (c) Normalized reflectance spectra of the nanowells in a series of solutions with different reflective index. Reproduced with permission from ref. 110. Copyright 2014, Wiley-VCH. (d) Schematic of the fabrication process of VO₂ nanoparticle arrays. (e) Temperature-dependent extinction spectra of the VO₂ nanoparticle array, which displays an LSPR switch-on property at elevated temperatures. (f) Effects of the particle diameter of VO₂ and the medium reflective to the LSPR position. Insets are the SEM images of the VO₂ nanoparticle arrays with diameters of 67, 125, 287 nm, respectively. Reproduced with permission from ref. 111. Copyright 2014, American Chemical Society.

Fig. 7 (a) Schematic of the anisotropic wetting surface for liquid direction in microfluidics. The surface consists of chemistry-asymmetric “Janus” silicon cylinder arrays with hydrophobic (-R) and hydrophilic (-OH) coating on each side. (b) Photographs of the liquid behavior in the T shape microchannel. The up and below outlets are along the hydrophilic and hydrophobic directions. The arrows indicate the liquid flow directions. Surface tension of the injected liquid are illustrated below the images. The scale bar is 1 mm. Reproduced with permission from ref. 124. Copyright 2017, American Chemical Society. (c) Schematic of the wettability “library” consisted of gradient silicon cone arrays and the contact measurements of sessile droplets on a different position of the “library”. Reproduced with permission from ref. 125. Copyright 2017, Wiley-VCH.

Fig. 8 (a) Schematic of the sensor constructed by 2D colloidal crystals onto stimuli-responsive hydrogel surfaces. The hydrogel containing recognition groups can react with the analytes and swell, resulting in the reflective color change. (b) Photographs of a glucose sensor based on such design that display different colors at different glucose concentrations. Reproduced with permission from ref. 141. Copyright 2015, American Chemical Society. (c) Schematic of the non-optical NO_2 sensor based on 2D porous electrodes. The NO_2 reduction reaction happens on the cathode. Reproduced with permission from ref. 142. Copyright 2016, American Chemical Society.

Fig. 9 (a) Pseudocolored SEM image of the Au NPs trapping near the tips. Au NPs and nanobowties are indicated as yellow and red, respectively. (b) Schematic of the enhanced Raman spectroscopy and the Au NPs trapping process near the tips. Corresponding measured Raman spectra are illustrated below for the detection of 10 μm R6G solutions. The figures display an increasing number of trapped Au NPs from left to right. Reproduced with permission from ref. 158. Copyright 2016, American Chemical Society. (c) Schematic of an annular cavity with geometric dimensions indicated. The compositions are indicated using different colors. (d) Cross-section SEM image of the produced annular cavity. (e) Simulated electric field enhancement distributions of an annular cavity from the cross-section (Figure on the left) and top views (Figure on the right) at $\lambda = 1416$ nm. Reproduced with permission from ref. 159. Copyright 2015, American Chemical Society. (f,g) SEM images of the plasmonic nanorings cavity arrays in low and high magnifications. Inset of (f) if the illustration of the Ag nanoring cavity with a 10-nm gap. (h) Photograph of the produced plasmonic nanorings cavity arrays in a circular area with a diameter of 2 cm. Reproduced with permission from ref. 160. Copyright 2013, Wiley-VCH.

Fig. 10 (a) Schematic of the dielectric nanosphere solar cell. The ultrathin film crystalline silicon (c-Si) has ITO as the front contact and Ti/Ag as the back contact. A hexagonal close-packed (HCP) monolayer of PS 2D colloidal crystal lies on the top of the solar cell device. Reproduced with permission from ref. 178. Copyright 2015, Elsevier. (b) Schematic illustration and (c) the cross-sectional SEM image of the configuration of the plasmonic ss-DSC with a 2D array of silver nanodomains in the back contact. Reproduced with permission from ref. 179. Copyright 2010, Wiley-VCH. (d) Schematic showing the cross-sectional structure of nanodome solar cells. Reproduced with permission from ref. 180. Copyright 2010, American Chemical Society. (e) SEM cross-sectional image of a monolayer of spherical Si nanoshells on a quartz substrate. Reproduced with permission from ref. 181. Copyright 2012, Springer Nature.

Fig. 11 (a) Schematic illustration of the photoexcitation of a semiconductor (*e.g.*, TiO_2) and the subsequent generation of an electron and a hole, which are trapped by an oxidant (Ox) and a reductant (Red), respectively. For TiO_2 photocatalysis, the “Ox” is surface-adsorbed oxygen molecule, and the “Red” is a surface-bound hydroxyl group. Reproduced with permission from ref. 206. Copyright 2010, American Chemical Society. (b) Side-view SEM image of the TiO_2 nanocolumn array obtained by PLD using a PS colloidal monolayer as the substrate. (c) TEM image of a single TiO_2 nanocolumn from the side. The inset is the corresponding electron diffraction pattern. (d) Photocatalytic activity evaluation of different substrates based on the absorbance ratio A/A_0 as a function of UV irradiation time. A and A_0 are the absorbance after UV irradiation and that from the initial surface, respectively. Reproduced with permission from ref. 208. Copyright 2008, American Chemical Society. (e) SEM image of the urchin-like TiO_2 array. (f) Linear sweep voltammetry measurements of the urchin-like TiO_2 and TiO_2 microsphere electrodes, collected both in dark and 100 mW cm^{-2} simulated sunlight illumination. Reproduced with permission from ref. 209. Copyright 2014, The Royal Society of Chemistry. (g) Tilted-view SEM image of a TiO_2 NR@NB array obtained after 5 h of hydrothermal growth. (h) Linear sweep voltammograms of TiO_2 NB, NR, and NR@NB array electrodes recorded in a 1 M NaOH solution under simulated one sun illumination (AM 1.5G, 100 mW cm^{-2}). Reproduced with permission from ref. 210. Copyright 2016, Wiley-VCH.

Fig. 12 (a) Schematic of the triboelectric nanogenerator consisting of two arch-shaped friction layers. (b) The measured output voltage of the nanogenerator under five times of finger tapping. (c) The durability test of the nanogenerator under a continuous tapping of 1000 cycles at a frequency of 3 Hz. Reproduced with permission from ref. 223. Copyright 2015, The Royal Society of Chemistry.

Fig. 13 (a) Schematic of the thermochromic smart window toward architectural energy-conservation by selectively blocking infrared (IR) light at high temperature. Reproduced with permission from ref. 229. Copyright 2017, Wiley-VCH. (b) A typical example of temperature-dependent transmittance spectra of a VO_2 -based thermochromic film. The spectra are from 160-nm VO_2 nanodome arrays. Inset is the corresponding crystallographic diagrams of the monoclinic and rutile phases VO_2 at low (20 °C) and high (95 °C) temperature, respectively. (c) Illustration of the VO_2 nanoparticle arrays derived from PS sphere templates. The VO_2 particles crystalize and PS template sacrifices under high-temperature annealing. (d) The SEM image of 160-nm patterned VO_2 nanoparticle arrays. The hexagonal patterns with ~ 160 nm in periodicity are indicated as the yellow hexagons. Reproduced with permission from ref. 111. Copyright 2017, American Chemical Society. (e) Illustration of the 2D core-shell SiO_2 - VO_2 PCs characterized by a VO_2 shell thickness of 20 nm. (f) TEM image of the 2D core-shell SiO_2 - VO_2 PCs and an amplifying image as the inset. Reproduced with permission from ref. 95. Copyright 2016, American Chemical Society. (g) Illustration of the antireflective moth-eye structures. (h) SEM image of the biomimetic moth-eye nanostructure consisting of VO_2 -overcoated SiO_2 nipple arrays with a periodicity of ~ 400 nm. The inserted TEM image of (h) presents the uniform VO_2 coating of ~ 40 nm on the structured SiO_2 substrates with ~ 200 -nm periodicity. Reproduced with permission from ref. 228. Copyright 2014, American Chemical Society.

Fig. 14 (a) Schematic illustration of a conventional InGaN/GaN MQW LED structure. (b) Tilted SEM image of a SiO₂ PC structure with a periodicity of 700 nm and a diameter of 450 nm regrown on *p*-GaIn. (c) Corresponding air-hole PC after removing SiO₂ disks in (b). (d) Forward voltages and light output power of LEDs with and without PC structures as the functions of injection current. (e) Far-field emission patterns of the LEDs with and without PCs. Reproduced with permission from ref. 239. Copyright 2012, AIP Publishing. (f) Schematic diagram of a YAG:Ce CPP-capped LED with a 2D Si_xN_y PC coating. (g) The blue-conversion-white electroluminescent spectra and (h) luminous efficacy of a conventional YAG:Ce CPP-capped LED and a 2D Si_xN_y PC-assisted YAG:Ce CPP-capped LED. Reproduced with permission from ref. 240. Copyright 2011, Optical Society of America. (i) Ag nanodisk array formed after the temperature reaches the *p*-GaIn growth temperature. The inset sketches the configuration of the SP-enhanced blue LED with Ag nanodisks embedded in the *p*-GaIn layer. Reproduced with permission from ref. 241. Copyright 2014, AIP Publishing. (j) The optical output power of Ag nanodisk array-enhanced LEDs as a function of injection current. (k) Cross-sectional SEM image of AlN grown on nano-PSS. The inset is the SEM image of nano-PSS obtained via wet etching. (l) LOP-I-EQE curves of the deep UV LEDs grown on the nano-PSS and the flat sapphire substrate. Reproduced with permission from ref. 242. Copyright 2013, AIP Publishing.

Fig. 15 (a) The structure of FET with (I) and without (II) nanopore-structured electrodes. (b) Typical transfer characteristics of the transistor based on source/drain electrodes with and without nanopore structure. Reproduced with permission from ref. 269. Copyright 2015, Wiley-VCH. (c) Schematic of the nanorod array fabrication. PS: Polystyrene. (d) SEM images of a nanorod array by PLD using a colloidal template monolayer with 350 nm PS spheres in O₂ at a pressure of 6.7 Pa for 60 min and subsequent annealing in air. Reproduced with permission from ref. 270. Copyright 2009, Wiley-VCH.

Fig. 16 Enhancement of photocurrent of (a) the Au nanocrystal array on Si substrate and (b) semi-inlaid Au nanocrystal array in Si under 532 and 655 nm laser illumination at 10, 100, and 200 mV. Insets show tilted SEM images of corresponding samples. The enhancement of photocurrent is defined as the difference between the photocurrent increment of Au nanocrystal array/Si nanoantennas and bare Si divided by that of bare Si. Reproduced with permission from ref. 279. Copyright 2013, American Chemical Society. (c) SEM image of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanonet formed on Si substrate. The periodicity of the nanonet is 1 μm . (d) Photocurrent-time (I - t) curves of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ photodetectors based on nanonet and compact film illuminated under monochromatic light at 700 nm. Reproduced with permission from ref. 280. Copyright 2017, Wiley-VCH.

Fig. 17 SEM images of 2D network-based transparent conductors with various geometries and materials. (a) Cu nanomesh with a periodicity of 1300 nm, a width of 150 nm, and a thickness of 40 nm on a quartz substrate. Reproduced with permission from ref. 296. Copyright 2014, American Chemical Society. (b) Nanomesh electrode fabricated through oblique deposition using a 1500-nm-diameter PS nanosphere array as a mask. Reproduced with permission from ref. 300. Copyright 2015, Springer Nature. (c) Cu crosswire grid comprising two overlapping nanowire arrays via stepwise angle-resolved nanosphere lithography. Reproduced with permission from ref. 301. Copyright 2016, Wiley-VCH. (d) Network-structured CNT film using a 900-nm-diameter silica colloidal crystal as a template. Reproduced with permission from ref. 302. Copyright 2008, Wiley-VCH.

TOC (5*4 cm)

This review summarizes the advance in the 2D nanostructures derived from nanosphere templates, from applications, properties, to fabrication.

Author biographies

Yujie Ke obtained his B.Eng and Master degrees from Wuhan Institute of Technology, China in 2013 and University at Buffalo, the State University of New York (SUNY-Buffalo), US in 2015, respectively. Currently, he is a Ph.D. candidate in Nanyang Technological University (NTU), Singapore. His research interest includes the micro-/nanoscale fabrication and the related applications.

Shunsheng Ye is currently a postdoctor in the Department of Macromolecular Science, Fudan University. He received his Ph.D. degree in chemistry from Jilin University under the supervision of Prof. Junhu Zhang and Prof. Bai Yang in 2017. His recent research interests include directed assembly and interfacial self-assembly of plasmonic nanoparticles and their applications in diverse fields.

Junhu Zhang is currently a professor in state key laboratory of supramolecular structure and materials. He received his Ph.D. degree in chemistry from Jilin University under the supervision of Prof. Bai Yang. His recent research interests focus on biomimetic and functional microstructures on surface and interface, and the application on functional surface and devices.

Yi Long is a Senior Lecturer in the School of Materials Science and Engineering at NTU. She obtained her Ph.D. degree from the University of Cambridge, UK. She has successfully implemented technology transfer from lab to industry for hard-disk Company and car grooming Company. Her recent research is to develop thin-film coatings and micro/nanostructures for functional devices.