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Bio-inspired, topologically connected colloidal arrays via wrinkle and plasma processing

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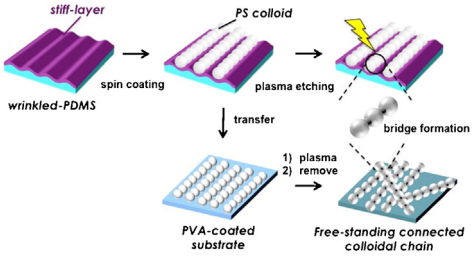
HIGHLIGHTS

- Topologically 1D arrays of colloidal particles were arranged in wrinkle grooves.
- We were able to transfer a large number of free-standing topologically arrays.
- We demonstrated the feasibility of the preparation of anisotropic particles arrays.

GRAPHICAL ABSTRACT



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ABSTRACT

We investigated the fabrication of various topologically patterned 1D arrays of polystyrene colloidal particles, including single, helical, zigzag, triple-line, and random arrays integrated in sinusoidal wrinkle grooves, through simple spin-coating. In an additional processing step, we used the wrinkled substrates as stamps to transfer the formed polystyrene patterns onto planar supports. Subsequent plasma etching of the particle strings yielded anisotropic, topologically connected particles. Interestingly, these colloidal chains can be easily released and dispersed to maintain the topological alignment and long length (>100 μm) with free-standing capability. Depending on the topological structures, these connected particle arrays would enable us to create new bio-inspired materials and devices such as artificial muscles and soft robotics with flexible motion.

1. Introduction

Mother nature provides the ultimate inspiration for various topologically ordered patterns, structures, and flexible motion from one-dimensional (1D) linear structures such as actin filaments and muscle fibers, two-dimensional (2D) arrayed compound eyes of insects, *Morpho* butterfly wings composed of three-dimensional (3D) hierarchical complex structures, etc. With self-assembly and self-organization, which are the driving principles in the formation of these natural structures, a number of biologically inspired artificial materials have been created [1–4].

Similarly, dimensionally controllable arrays of colloidal particles, from 1D to 2D and 3D colloidal crystals, have attracted much attention because of their potential for many applications in fields ranging from optical and electronic devices to biological and chemical sensors [5–10]. In particular, anisotropic linear arrangements have been greatly anticipated for various fields including energy conversion, surface patterning, coatings, etc. [11–13]. For the most part, two types of approach to self-assembly, such as template-free and template-assisted processes, have been proposed for the fabrication of an anisotropic 1D particle array. Using the template-free self-assembling process [14–23], Watanabe and co-workers obtained spontaneous striped patterns of various colloids on flat substrates by vertical-deposition

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convective self-assembly [14–17]. Lin and co-workers reported a simple method to assemble latex nanoparticles into regular striped patterns (i.e., coffee-ring-like deposits) over large areas by allowing a drop of an aqueous solution of polystyrene (PS) nanoparticles to evaporate from a liquid capillary bridge, which was formed when the solution was confined between a cylindrical lens and a Si substrate (i.e., cylinder-on-flat geometry) [18]. Ressier and co-workers fabricated a strain sensor consisting of colloidal nanoparticles assembled in wire arrays on a flexible substrate using stop-and-go convective self-assembly (SG-CSA) [19–22]. Similarly, Mori and co-workers proposed a quick fabrication method for striped films using silica arrays and the convective self-assembly technique based on a horizontal coating [23]. However, these 1D particle arrays were mainly arranged into hexagonal or random colloidal aggregates, whose arrangement did not consist of single particle arrays or topologically controlled complex arrays.

On the other hand, template-assisted colloidal assembly under physical confinement [24–31] offers various types of arrangement of colloidal particles, which are difficult to fabricate using template-free approaches. Sow and co-workers reported an effective method for size-selective positioning of colloidal particles on a topographically pre-patterned photoresist surface. The template was fabricated using a direct-laser-writing technique [24]. Yoon and co-workers discovered that by rubbing dry spherical colloidal particles into patterned nanowell arrays, the spherical colloidal particles were very quickly organized into large and perfect 1D arrays [25]. Meseguer and co-workers analyzed the influence of patterned surfaces on the formation of 1D colloidal crystals using a digital versatile disk (DVD) for template-based surface processing [26]. Xia and co-workers obtained 1D zigzag colloidal aggregates under physical confinement by channels etched in a thin film of photoresist that was spin-coated on the surface of a glass substrate [27–30]. Kumacheva and co-workers used electrodeposition of monodispersed charged colloidal particles onto an indium–tin-oxide (ITO) substrate patterned with an array of electroconductive grooves, whose progressively diminishing width was commensurate or incommensurate with the dimensions of a discrete number of colloidal particles [31]. While these forms of template-assisted self-assembly show impressive control over positional order and provide directions for the design of complex structures, the template structure is usually produced by top-down approaches such as photolithography, extreme-UV interference lithography, e-beam lithography (EBL), focused-ion-beam (FIB) etching, etc. The employed processes are rather expensive, time- and energy-consuming, and multiple steps are required.

In another approach, colloidal patterning methods in static solution systems [32] or dry processes [33,34], without using template molds or grooves, have been developed to prepare particle wires and strings. However, since most of the aforementioned colloidal structures are formed on rigid substrates such as Si or glass, the methods have limited use in practical applications. Therefore, there is a demand for straightforward fabrication of flexible templates with design features that can be easily varied from nanoscale to microscale.

Surface wrinkling is an inventive and unconventional technique that is also fast and inexpensive for various types of surface patterning involving sinusoids (ripples), herringbones, labyrinthine designs, etc. It is especially suited for large-area surfaces of poly(dimethylsiloxane) (PDMS) elastomers based on mechanical (buckling) instability [35–37]. This self-organization buckling phenomenon is widely observed in natural systems such as human skin, brain cortex, fruits, and plants [38,39]. Owing to the periodic structure and dynamically tunable wrinkles, it has been used in many applications including diffraction gratings [40], stretchable electronics [41,42], antifouling [43], microcontact printing [44], and switching of surface wettability [45,46]. In addition to spherical and inorganic particles [47–54], various materials such as tobacco mosaic viruses (TMV) [55,56], liquid crystals [57,58], and human embryonic stem cell (hESC)-derived cardiomyocytes [59] have been organized (or aligned) into wrinkle grooves (or on surfaces) through dip-coating, spin-coating, and blade processing. In particular, Fery's group demonstrated outstanding results of aligned, 1D gold nanoparticles and poly-N-isopropylacrylamide (pNIPAM)-coated nanostars prepared from their organization into wrinkle grooves, which showed effective surface-enhanced Raman scattering (SERS) platform those. [60,61].

Herein, we describe the fabrication of various topological 1D colloidal arrays, including single, helical, zigzag, triple-line, and random arrays integrated in sinusoidal wrinkle grooves, through simple spin-coating. Moreover, the particles in these arrays can be connected using plasma etching, forming beaded, robust, and long (>100 μm) colloidal chains. Interestingly, these colloidal chains can be easily released and dispersed to maintain the topological alignment and length in a free-standing state. Depending on the topological structures, these connected particle arrays would enable us to create new bioinspired materials and devices such as artificial muscles and soft robotics with flexible motion.

2. Experimental

2.1. Materials

Styrene (Kanto Chemicals, Japan) was purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent-grade potassium persulfate (KPS) was used as an initiator without further purification. PDMS was obtained in a Sylgard 184 elastomer kit from Toray Dow Corning, Japan, which consisted of Sylgard 184 monomer and Sylgard 184 base. Polyvinyl alcohol (PVA; $M_w \approx 2000$) was purchased from TCI, Japan.

2.2. Synthesis of polystyrene particles

Monodispersed PS particles with a mean diameter of 560 nm were synthesized by emulsifier-free polymerization with KPS as the initiator in water [62,63]. Styrene monomer (15 g) and water (180 mL) were added to a 300-mL glass reactor, and the temperature was raised to 75 °C under vigorous stirring. An aqueous solution (20 mL) of KPS (0.35 g) was added to the reactor.

2.3. Preparation of wrinkles

PDMS was prepared by mixing the monomer with a base in a weight ratio of 10:1. The mixture was poured into a clean planar petri dish, and the 1-mm-thick film was cured for 2 h at 65 °C after degassing overnight under ambient conditions. The crosslinked PDMS was used as the substrate and cut into rectangular pieces with dimensions of 1 cm × 2 cm. To form the surface pattern, the substrate was clamped in a custom-made stretching apparatus and uniaxially stretched until it was 15% longer than its original length. The PDMS was subsequently oxidized in this pre-strained state using a PIB-20 Plasma Ion Bombarder (Vacuum Device, Japan) at a controllable power level (discharge current) for an adjustable exposure period, and periodic wrinkles were formed perpendicular to the stretching direction once the strain was released. In this study, we prepared four types of wrinkle substrates: (A) approximate wavelength of 1.3 μm and amplitude of 220 nm (7 mA, 5 min); (B) approximate wavelength of 2.3 μm and amplitude of 400 nm (7 mA, 25 min); (C) approximate wavelength of 3.8 μm and amplitude of 660 nm (40 mA, 10 min); (D) approximate wavelength of 5.0 μm and amplitude of 800 nm (40 mA, 10 min).