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Assembly of nanoparticles on patterned surfaces by noncovalent interactions

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Abstract

This article reviews the recent developments in the assembly of nanoparticles into patterned arrays. An introduction is given on nanoparticles assembly and its applications. This is followed by a discussion on recent papers, seen from the perspective of the interaction between particle and substrate: (i) absence of interactions, (ii) presence of electrostatic interactions, and (iii) presence of supramolecular interactions. The techniques used to create the patterns and to assemble the nanoparticles are discussed as well.

Keywords: Nanoparticles; Self-assembly; Interface chemistry; Electrostatic interactions; Supramolecular interactions; Surface patterning

1. Introduction

Being able to place nano-objects at the desired position is of highest interest for the possible integration of these building blocks into devices [1]. Among these nano-objects, nanoparticles (NPs) are one of the most widespread. Integration of NPs with high accuracy inside circuits is a promising route for the development of photonic devices, high-density patterned media, and catalysis [2]. When the surface of the referred nanoparticles is functionalized, they have a potential as chemical and biological sensors [3].

There are several ways to confine nanoparticles into patterns. In the first approach, a topographical template for the assembly of NPs is created, using a top-down lithography method. A second approach consists of producing a chemically patterned substrate, generally using a bottom-up methodology, which will direct the nanoparticle assembly.

Here, we will review various methods to direct NP deposition, using nonspecific interactions and, subsequently, using chemical, such as electrostatic and supramolecular, interactions. We will discuss the confinement of nanoparticles within physical and chemical patterns and the resolution of the obtained features.

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2. Nanoparticle assembly in the absence of specific interactions

Interesting effects can be observed when creating nanoparticle (NP) patterns depending on the relation between particle size and the pattern feature size, shape of the confining features and type of confinement. Nanoparticles can be confined on any type of pattern. When using topographical templates, capillary forces play an important role in the ordering process especially with respect to pattern design and the continuity of the features.

In a striking example, Xia et al. used templates made of Si (photolithography and RIE) to confine particles inside the patterns by means of the meniscus method [4•,5]. In the meniscus method, capillary forces push the particles inside the pattern. Xia et al. studied the different configurations obtained with particles confined in holes of various shapes such as circles, squares, rectangles (lines), triangles, and rings. Expressions for the geometrical requirements in order to obtain a given cluster configuration taking into account the diameter of the particle d, and the dimensions of the pattern features, such as hole diameter D or linewidth w, were deduced which explained the observed results. Moreover, zigzag confinement in helical shapes was shown by using V grooves [4•].

Kumacheva et al. studied nanoparticles confined within micrometer grooves in which, by tuning the width of the grooves, perfect ordering or defect zones were seen, showing

the importance of the d/W ratio on ordering [6,7]. Two states of particle arrays could be distinguished: highly ordered hexagonal packing and random dense packing corresponding to the configuration where NPs have too much free space inside the pattern. It was predicted that hexagonal packing of NPs could be obtained when the width of the grooves (D_c) and the radius of the NPs (R) followed the expression: $D_c = 2R[(n-1)\cos 30° + 1]$.

Following these examples, intense research efforts were devoted to confine NPs in nanopatterns on SiO_2 using different patterning techniques such as FIB [8•] and EBL [9], and on other types of substrate [10–12]. Ozin and Yang made use of microfluidics to pattern particles inside V grooves closed by a flat piece of PDMS [13]. Colloids were patterned in diverse, nonregular and nonrectilinear, patterns [9]. Kim et al. showed one-dimensional groove patterns with single particle attachment in the shape of a necklace [14].

After using a topographical pattern for confining particles, the physical barrier can sometimes be removed after the NP assembly. Geissler and Xia demonstrated confinement on the sub-200-nm scale by spin-coating NPs into polymer grooves made by laser interference lithography (LIL) [15]. The polymer pattern was removed afterwards. Capillary forces pushed NPs inside the grooves, but confining particles in closed patterns such as holes was not so efficient. The NP arrays could be annealed in order to improve their attachment to the substrate prior to polymer removal.

Pattern confinement has been used to control lattice and superlattice symmetry by modeling the periodicity (p) and height (h) of the pattern. This technique is called colloidal epitaxy. Van Blaaderen et al. were the first to demonstrate epitaxial assembly of NPs using topographically patterned square arrays of holes, creating a 2D square microarray [16]. The feature sizes of the directing pattern were smaller than the NPs in order to direct their ordering [7,17–19]. Kim et al. showed that for h/D (D being the diameter of the colloid) > 0.35, multilayer square array patterns were obtained [14]. For $0.28 < h/D < 0.35$, pseudo-{110} structures were obtained and for $h/D < 0.28$ no 3D crystallization was observed, but tetragonal or hexagonal cluster formation.

Manipulation of individual NPs to create patterns has also been demonstrated. Van Blaaderen et al. made use of optical tweezers in order to arrange particles one by one into the desired shape [20••,21,22]. With the use of a nanorobot [23], Lopez et al. constructed a multilayer of particles with a diamond-type structure on a patterned silicon substrate that directed the lattice formation.

3. Nanoparticle assembly in the presence of electrostatic interactions

In order to avoid harsh processes (such as annealing) to bind particles to the substrate, a chemical functionalization can be performed on the noncovered areas of the substrate to anchor NPs with the appropriate complementary functionalization [24•] (Fig. 1). Chemical templates can be used to direct the assembly of particles of various compositions, such as polymeric (PS or PMMA), SiO_2, or magnetic materials [25]. The, generally functionalized, particles are attached selectively to one area of the pattern. One of the advantages of this process is that the substrate is not modified topographically and can be used directly after particle attachment for further processing. The most popular chemical pattern for NP attachment is a hydrophobic/hydrophilic contrast made in SAMs patterned by e.g. photolithography [26,27•] or μCP [28,29]. NP suspensions do not wet the hydrophobic areas and NPs remain on the hydrophilic areas. Various shapes, periodic and nonperiodic, have been made using NPs commensurate to the chemical pattern [30]. Jonas et al. and Koumoto et al. studied the effect of chemical confinement while using the meniscus method [27•,30].

The attachment of the particles was governed by wetting properties and the shape of the meniscus. The discontinuity of the wetting properties at the interface on the chemical pattern made well-defined edges difficult to obtain. Moreover, the shape of the meniscus, that was higher on the center of the pattern than on the edges, led to the formation of a multilayer on the center [31]. Ordered single particle attachment along a continuous line was obtained by Koumoto et al. using a chemical pattern made by a liquid mold and its drying process [30]. The process of attachment on chemical templates is more

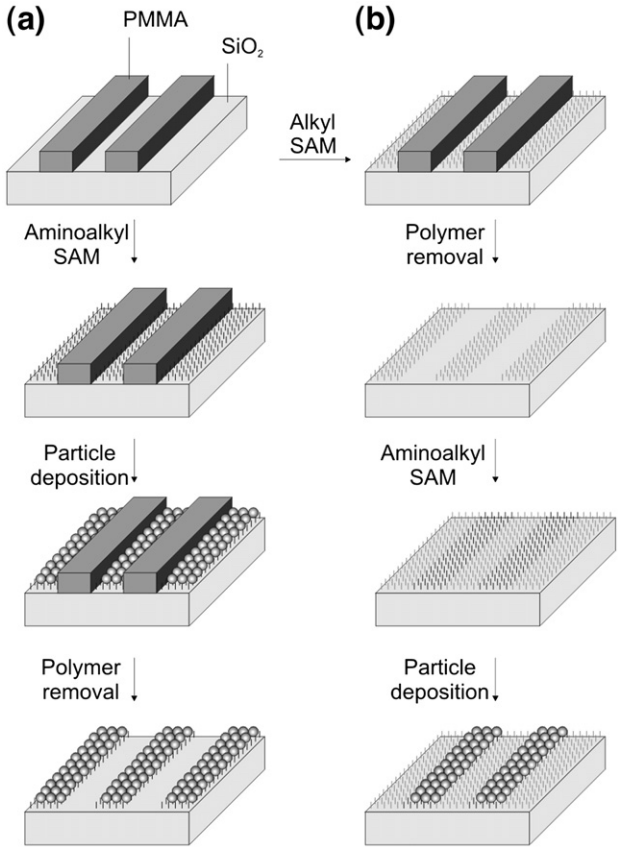

Fig. 1. Schematic representation of the processes to fabricate patterns of nanoparticles using chemical templates in combination with (a) or without topographical barriers (b). The polymer templates were prepared by nanoimprint lithography, SAMs were formed by gas-phase deposition, and nanoparticles were attached using capillary assisted assembly (see also Ref. [24•]).