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Two-dimensional nanofabrication and supramolecular functionality controlled by mechanical stimuli

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ABSTRACT

Thin film environments can be used to combine several dimension-dependent properties since the axis of thickness can be nanometric while lateral dimensions can be at macroscopically visible length scales. Coupling between a mechanical stimulus in the lateral direction and molecular motion parallel with the axis of thickness may result in connection of macroscopic mechanical stimuli with molecular-scale and nanometer scale functions. In this short review, we focus on recent developments in the challenging and unexplored science and technology of mechanical control of nanoscale properties of thin films. Research described here has been classified according to: (i) nanofabrication based on mechanical processes, (ii) mechanical control of soft matter functionality, (iii) mechanochromics, (iv) mechanical control of nanosystems, and (v) hand-operated nanotechnology for control at the nanoscale using macroscale manipulation. Several examples, including formation of two-dimensional molecular and microscopic patterns, self-healing properties, molecular release stimulated by mechanical stretching and enzyme reactions, mechanochromic functions, manipulation of small objects including molecules and clusters, investigation of electrical and mechanical properties in self-assembled monolayers, and mechanical control of molecular machines, are described.

1. Introduction

The recent rapid development of nanomaterials has made a significant contribution to advanced nanotechnology where materials with well-designed nanostructures lead to various functions [1,2]. For example, mesoporous materials with well-defined pore structures [3,4] can be used to effectively control molecular encapsulation and are therefore anticipated to be of use for various applications such as materials' separations [5,6], molecular sensing [7–10], and drug delivery [11,12]. However, nanomaterials themselves do not always result in any practically useful functions since, in many cases, they require formation into appropriate morphologies. In particular, formation of functional nanomaterials into thin films [13] is an important fabrication step for integration of nanostructure functions into various device structures such as electrodes and transistors [14,15]. Thin film fabrication by various methods including dip-coating [16,17], spin-coating [18,19], and layer-by-layer (LbL) assembly [20–22] has now become an important method to prepare devices.

Apart from thin films on solid rigid surfaces, soft and flexible thin films have become attractive media in which to investigate functions [23]. Many sophisticated functions in biological systems are expressed at flexible thin films such as cell membranes so that we can expect that many unexpected functions could be similarly developed using synthetic thin films. A simple but important factor for controlling soft thin films is a mechanical stimulus. In fact, soft thin films can accept external mechanical stimuli such as stretching and bending and provide controlled functions. So far most outputs from thin films upon application of mechanical forces are considered macroscopic. Moreover, mechanical control of nanomaterials and nanosystems [24] has been reported but surprisingly not been well explored except for a few pioneering examples in thin films [25].
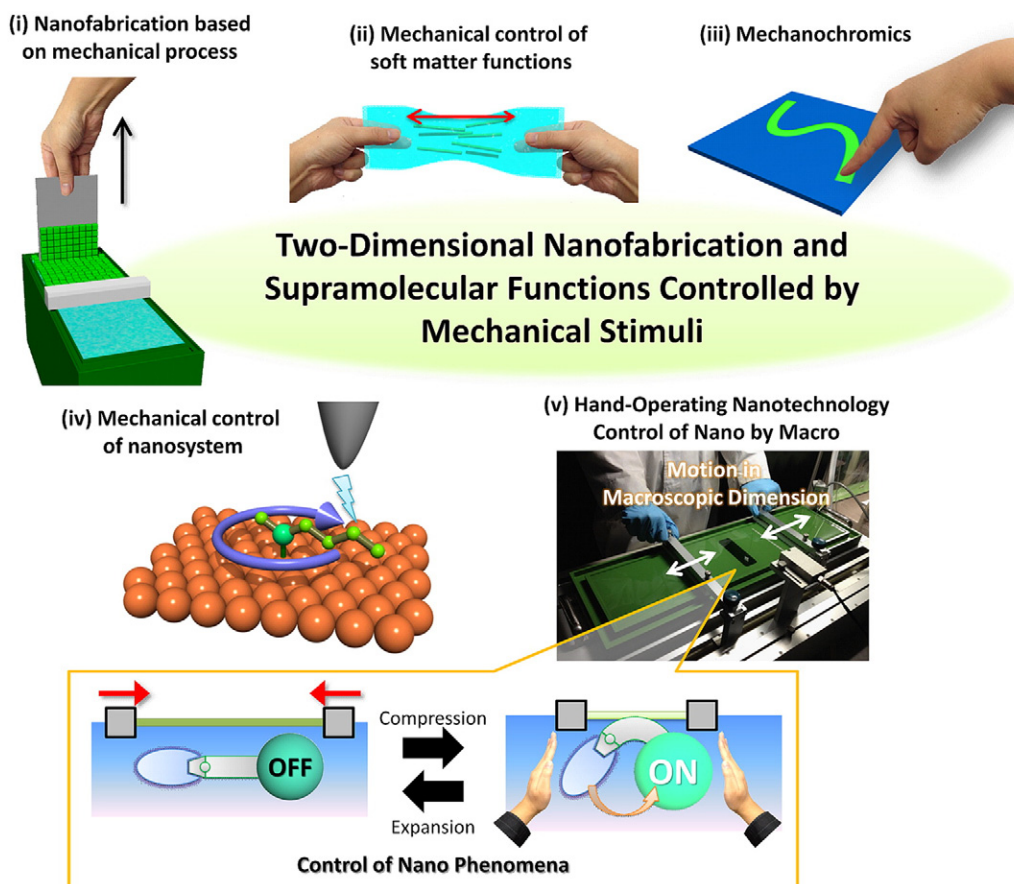
In this short review, we focus on recent developments in the challenging and unexplored science and technology of mechanically controlling the nano-properties of thin films. Selected examples are briefly described according to the classification: (i) nanofabrication based on a mechanical process, (ii) mechanical control of soft matter functions, (iii) mechanochromics, (iv) mechanical control of nanosystems, and (v) hand-operated nanotechnology for control at the nano-level from the macroscale (Scheme 1).

2. Nanofabrication based on mechanical processes

As has been experimentally proven [26,27] and is theoretically supported [28,29], the air–water interface provides a medium for efficient molecular interactions between thin films (Langmuir monolayers) and aqueous species. Such molecular-level interactions often induce

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(i) Nanofabrication based on mechanical process

(ii) Mechanical control of soft matter functions

(iii) Mechanochromics

Two-Dimensional Nanofabrication and Supramolecular Functions Controlled by Mechanical Stimuli

(iv) Mechanical control of nanosystem

(v) Hand-Operating Nanotechnology Control of Nano by Macro

Motion in Macroscopic Dimension

Compression — OFF

ON

Expansion

Control of Nano Phenomena

Scheme 1. Mechanical control of nanomaterials and nanosystems in thin films.

formation of regular ultrathin film structures with molecular-level precision leading to so-called two-dimensional molecular patterns [30,31]. Aqueous template molecules specifically bind to amphiphiles at the air–water interface and the complexes are two-dimensionally crystallized to provide a regular array of amphiphiles. For example, an aqueous dicarboxylate template can bind to two dialkylguanidinium molecules with the spacer between the two carboxylates of the template affecting the crystalline behavior of the guanidinium amphiphiles [32]. Monolayers interacting with aqueous oxalate (containing no methylene spacer) have a crystalline structure. Use of malonate [(CH_2) spacer] or succinate [$(CH_2)_2$ spacer] as a template maintains the monolayer in a crystalline state but a further increase in the spacer length [glutarate with $(CH_2)_3$ spacer and adipate with $(CH_2)_4$ spacer] induces formation of an amorphous phase of the monolayer. However, this is not limited to an isolated binding motif and alternate binding between amphiphiles and templates provides a linear extension of the molecular complex at the air–water interface. For example, complementary hydrogen bonding chains involving alkylmelamine and aqueous barbituric acid results in a molecular ribbon with an oblique array of methyl terminals [33]. Template molecules with different binding sites for various types of amphiphile molecules can provide more sophisticated complexes and patterns. A flavine adenine dinucleotide (FAD) molecule can potentially bind two guanidinium molecules at phosphate groups, one orotate molecule at adenine sites, and diaminotriazine at the isoalloxazine ring [34]. Repeated height differences in the Ångstrom range were observed as a resulting molecular pattern in guanidinium/orotate mixed monolayers interacting with FAD [35]. Fixing of the polar heads of the monolayer components to the aqueous template leads to differences in the positions of terminal methyl groups of the amphiphiles resulting in regular patterns at Ångstrom-level precision.

Because Langmuir monolayers on a water surface has a highly dynamic nature, processes such as mechanical compression/expansion and transfer from liquid surface to solid surface yield possibilities for formation of regular patterns based on materials flow and transport. Kitagawa and coworkers reported formation of Langmuir monolayers of porous coordination polymers (or metal organic frameworks) [36]. They found that adsorption of porous polymer structures could be regulated during the monolayer transfer process depending on the crystalline lattice (Fig. 1). Orientation on the substrates of the crystalline blocks was determined by morphology of the building blocks. Deposition on various substrates resulted in uniform structures with controllable density of the crystals over several square centimeters. In addition, closely packed films could be fabricated as freestanding sheets.

In another example, it was reported that appropriate motion of a solid substrate through a lipid monolayer induces formation of regularly striped patterns with submicron-level intervals [37–39]. Recently, Köpf and coworkers reported temperature control of stripe patterns of dipalmitoylphosphatidylcholine on planar mica substrates that were produced by a simple Langmuir–Blodgett (LB) transfer process [40]. The width of the stripes and the overall spatial period of the patterns increased with increasing subphase temperature. Such stripe patterns are ascribed to alternating monolayer domains in the liquid-expanded and liquid-condensed phases. Phase behavior could be minutely regulated by varying subphase temperature, resulting in controlled patterns using a simple mechanical process.

Recently, Mori et al. proposed a simple method for fabrication of organic quantum-disk-size objects with uniform height and tunable diameter at the nanometer scale through mechanical contact of a solid substrate onto a Langmuir monolayer at the air–water interface (Fig. 2) [41,42]. This method is based on two concepts, (i) relatively weak intermolecular interactions within an interfacial medium and (ii) two-dimensional quick dewetting, using an amphiphilic triimide, tri-n-dodecylmellitic triimide and a water-soluble