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Perspective

Perspective on smart materials for empowering small-scale manipulation

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At the macroscopic world, we often take the manipulation of objects in our environment for granted. However, at the micro/nanoscale, the precise and controlled alteration, handling, or actuation (i.e., manipulation) of materials and structures are highly challenging and different due to the scaling effects and increased complexity of dominant interaction forces at these length scales [1], requiring new materials and methods. On the other hand, smart materials, also known as intelligent or stimuli-responsive materials, have transformed various multidisciplinary fields [2], offering new possibilities for redefining our interaction with the small-scale world. They possess unique ability to respond to various external stimuli, including thermal, electrical, mechanical, optical, magnetic, and acoustic signals, and adjust their intrinsic properties accordingly [3] (Fig. 1). This responsiveness enables them to self-deform, self-sense, self-adapt, self-heal, and even self-diagnose, which collectively endows them with the potential to create various smart devices [4].

Among various types of smart soft materials, deformation behaviors in response to a diverse range of stimuli stand out as a crucial aspect of their functionality [5]. Such deformations can be initiated by various means, including field-induced forces, such as magnetic [6] and acoustic [7] forces, or intrinsic property alterations, such as the hydrophilic/hydrophobic transition of hydrogels [8] and the nematic-to-isotropic transition of liquid crystal elastomers (LCE) [9]. To achieve the desired deformations, functional additives, such as magnetic and conductive particles, are often incorporated into a polymer matrix [10]. In particular, the introduction of anisotropic properties is commonly employed to boost the resultant deformation. For instance, LCEs are meticulously programmed with specific molecular alignments [9], and the axially-aligned LCEs exhibit contraction along the molecular alignment (director) and expansion perpendicular to the director. Furthermore, in the case of a nanocomposite made of graphene/alginate [11], bending deformation occurs in response to stimuli as a result of the locally distinct alignment of graphene. These deformations exhibited by smart materials serve as a potent catalyst for the manipulation of objects at the micro/nanoscale. Their unique attributes, including wireless or contactless actuation, make them particularly well-suited in achieving small-scale manipulation and their applications in enclosed spaces, such as inside the human body or microfluidic chips.

Typical strategies for the manipulation of structures at small length scales include direct manipulation using micro/nanofabricated smart materials and indirect manipulation of passive micro/nanostructures actuated by smart materials (Fig. 1). Direct manipulation involves making the micro/nanostructures themselves from the smart materials [3,6,12,13]. These materials can respond to external fields, allowing precise control over their deformation or movements [14,15]. In contrast, in the indirect manipulation strategy, passive micro/nanostructures are manipulated through the actions of nearby smart materials [9]. The smart materials generate forces or induce changes in the passive structures to achieve the desired outcome [8].

Building upon their macroscopic stimuli-responsive properties, micro/nanofabrication of smart materials stands as the most direct and effective means to control, actuate, and manipulate these micro/nanostructured materials. Thus, micro/nanofabrication of smart materials becomes a crucial prerequisite for realizing these objectives [3]. In the realm of micro-electromechanical systems (MEMS), lithography-based fabrication has played a pivotal role in the creation of these minute structures [16]. The fabrication of smart materials through lithography-based methods can be a complex endeavor, primarily because most smart materials are not inherently photo-patternable and cannot directly apply to photopatterning. Such methods involve integrating passive photoresists for patterning, followed by subsequent processes like coating, sputtering, vapor deposition, and atomic deposition of smart materials. Finally, micro/nanostructured smart materials are obtained after removing the passive photoresists. While this lithography-based fabrication method facilitates large-scale production of structured smart materials, creating complex three-dimensional (3D) architectures remains a challenging endeavor.

As an advanced additive manufacturing technique, two-photon polymerization (2PP) stands at the forefront of high-resolution 3D printing at the micro/nanoscale [12]. Unlike conventional UV-3D printing methods, two-photon polymerization harnesses the unique properties of femtosecond (fs) laser to create intricate

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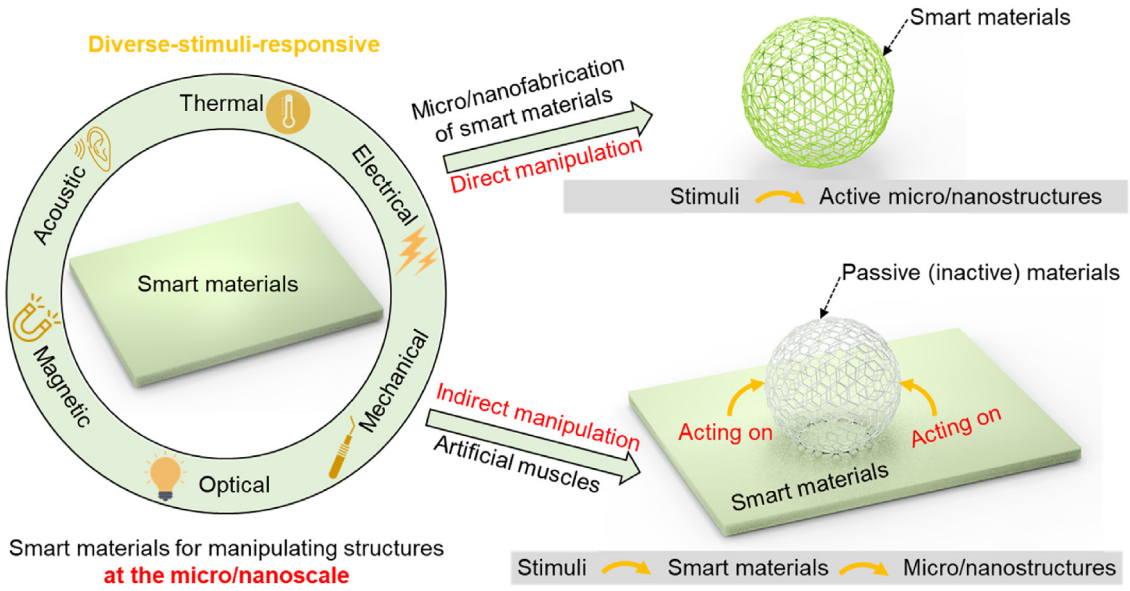


Fig. 1. (Color online) Schematic illustration of two typical strategies for utilizing smart materials in micro/nanostructure manipulation: Direct manipulation of micro/nanofabricated smart materials and indirect manipulation of passive micro/nanostructures through actuating smart materials.

and finely-detailed 3D structures with exceptional precision and resolution (up to 100 nm). This technology relies on a nonlinear optical phenomenon known as two-photon absorption, where two photons are simultaneously absorbed by a photosensitive material, triggering a polymerization reaction at a microscopic scale. This results in the precise layer-by-layer construction of objects, enabling the fabrication of complex and minuscule structures that were once considered unattainable.

To achieve actuation and manipulation, these fabrication methods often involve linking active components or directly printing smart materials. For example, magnetically responsive Janus microparticles can be directly linked with soft or rigid polymer structures through the 2PP process [6] (Fig. 2a). The micromachines fabricated in this manner, exhibit remarkable 2D and 3D shape transformations and complex surface locomotion when subjected to programmable magnetic fields. Moreover, micro/nanostructured smart materials can be created by directly printing their precursor photoresists, thereby granting us control over these active 3D objects. One such example is the responsive hydrogel known as poly N-isopropylacrylamide (PNIPAM), which can be directly printed via the 2PP process of its monomer [14]. As the temperature crosses the low critical solution temperature (LCST), the hydrogel undergoes isotropic shrinkage due to a transition from hydrophilic to hydrophobic properties. By incorporating functional particles (such as magnetic particles) or monomers (pH-sensitive monomers) within the isopropylacrylamide monomer, the fabricated structures exhibit multi-stimuli responses. For instance, 2PP-processed hydrogel micro-balls exhibit response to temperature, magnetic fields, pH values, and ion concentration [14] (Fig. 2b). This broad range of responses has immense potential for performing complex tasks under various and challenging conditions, which is essential for achieving complex functionalities, such as triggered and controlled drug delivery. For example, printed microswimmers with magnetically steerability can controllably release loaded drugs under the illumination of light [15] (Fig. 2c).

Although micro/nanostructured smart materials indeed demonstrate efficient actuation, a significant limitation lies in the scarcity of active photoresists suitable for use with the 2PP process. This constraint substantially hinders the full realization of their potential for complex manipulation. Most smart materials, once intricately fabricated, are typically no longer compatible with the 2PP process. Consequently, the micro/nanofabrication of these smart materials remains notably challenging. In lieu of solely utilizing active photoresists for 2PP in the creation of micro/nanostructures, exploring alternate dosage domains of fs lasers offers a spectrum of engaging photon-material interactions. These interactions, mainly governed by the fs laser's dosage domain, encompass processes like ablation in high dosage domains and photobleaching in low dosage domains [13]. This versatility in photon-material interactions presents a unique opportunity to fabricate micro/nanostructures directly onto pre-existing smart materials, elevating the adaptability in developing micro/nanostructures within versatile smart materials. A pertinent example of this technique is the use of variable dosage domains of the fs laser to engineer as-fabricated PNIPAM hydrogels [13]. These hydrogels can be intricately designed with micro/nanostructures that contain complex, multi-channel information. Such a design allows the PNIPAM hydrogel to exhibit information that dynamically alters in response to thermal stimuli.

Rather than fabricating micro/nanostructures within smart materials for their direct manipulation, an alternative approach involves utilizing the smart materials themselves to interact with passive micro/nanostructures [8,9]. This strategy offers an indirect strategy for the manipulation and control of micro/nanostructured passive elements. These passive structures are readily fabricated from commercial photoresists either through lithography-based methods [16] or 2PP process [12]. The forces or any changes generated by these triggered smart materials pave the way for acting on these passive structures; therefore, offering a means to circumvent the challenges associated with directly micro/nanofabricating smart materials. This allows a diverse range of smart materials for selection, and their customized outputs can be designed and programmed to meet specific conditions and requirements.

For instance, uniaxially aligned LCEs can serve as a synthetic skin with large anisotropic deformation. When subjected to heating, these LCE materials exhibit anisotropic deformation, generating strain that drives attached passive kirigami micro-metastructures on the LCE's surface to transform into different configurations (Fig. 2d). Upon cooling, the LCE restores its original patterns, resulting in a fascinating reconfigurability [9]. Furthermore, in another

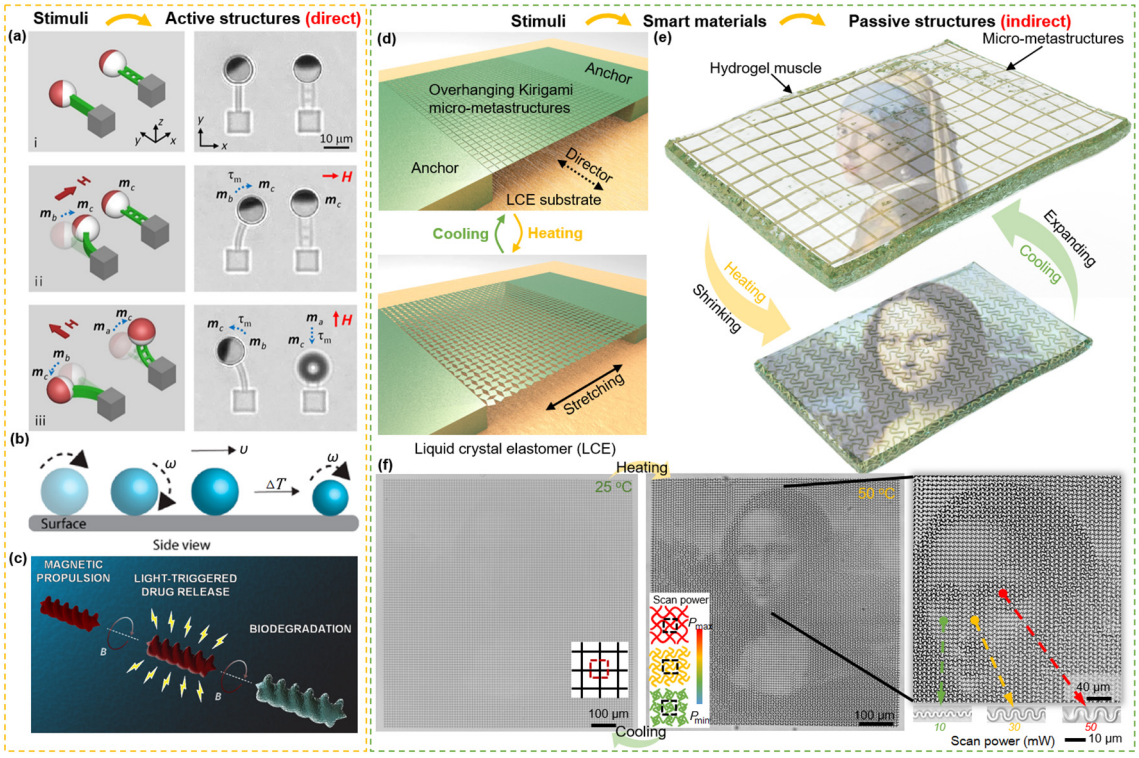


Fig. 2. (Color online) Examples of direct and indirect strategies using smart materials for the micro-manipulation. (a) Schematics and optical images showing the motion of magnetically responsive soft micromachines [6]. (b) Schematics of two-photon polymerized (2PP) micro-balls capable of magnetic and thermal actuation [14]. (c) Schematically showing 2PP helical structures actuated by light and magnetic field [15]. (d) Schematics depicting liquid crystal elastomer (LCE)-actuated kirigami micro-metastructures [9]. (e) Schematics showing the reconfigurable micro-metastructures with encrypted complex information powered by hydrogel muscle [8]. (f) Optical images showing the micro-metastructures displaying a complex image (*Mona Lisa*) achieved through the shrinkage of hydrogel muscles [8].

case of grid micro-metastructures, the basic building blocks can buckle when subjecting to isotropic static pressure generated by a transparent and uniformly-deforming hydrogel [8]. The configurability is achieved by embedding 2PP-processed micro-metastructures within hydrogel artificial muscles in a bone-in-flesh fasion, where these basic building blocks transform into wave-like structures when the hydrogel muscles are heated. Intricate reconfigurations can be achieved, including complex 2D and even 3D architectures (Fig. 2e). By varying printing parameters such as scanning power or speed, these building blocks can convert into various morphologies, allowing for the encoding and encryption of complex images into these micro-metastructures. As the hydrogel shrinks, locally-variant patterns emerge from the grid micro-metastructures, thus revealing the encoded complex image (Fig. 2f). This unique attribute, enabled by smart materials like LCEs and hydrogels, opens up exciting possibilities for revolutionizing the design of dynamic and reconfigurable miniature devices with applications across various domains.

In summary, the integration of smart materials into the micro- and nanoscale manipulation landscape has proven highly efficient and promising. The continuous progresses in achieving remarkable capabilities of smart materials, coupled with the advancement of various manufacturing techniques, empowers us to exert precise control and manipulation over the micro- and even nanoscale world. As we continue to push the boundaries of micro- and nano-manipulation, the future of smart materials beckons a multi-dimensional approach. A key focus lies in synthesizing and characterizing novel smart materials to exploit their unique or enhanced stimuli-responsive properties. Concurrently, the integration of these materials with cutting-edge functional elements, such as microelectronics and sensors, is important for achieving more autonomous, adaptive, and intelligent manipulation systems. Scaling up manufacturing processes for these advanced materials, while ensuring their environmental sustainability and biocompatibility, especially for biomedical applications, is another critical avenue. Moreover, the development of comprehensive computational models to accurately predict material behavior and structural functionalities will significantly streamline the design and optimization of the micro/nanoscale manipulation. As we further explore, tailor, and harness the high-performance of the smart materials, it becomes evident that the future of technology and innovation will be significantly influenced by their capabilities. This not only paves the way for a wide array of applications in fields such as MEMS, nanotechnology, biomedical engineering, miniature robotics, and photonics but also offers boundless opportunities for cutting-edge advancements and fundamental discoveries.

Conflict of interest

The authors declare that they have no conflict of interest.

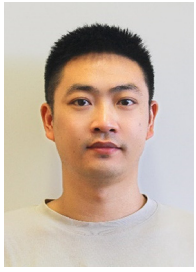
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