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2018

Chen, G., Cui, Y., & Chen, X. (2019). Proactively modulating mechanical behaviors of materials at multiscale for mechano-adaptable devices. *Chemical Society Reviews*, 48(6), 1434-1447. doi:10.1039/C8CS00801A

<https://hdl.handle.net/10356/138144>

<https://doi.org/10.1039/C8CS00801A>

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Journal Name

TUTORIAL REVIEW

Proactively modulating mechanical behaviours of materials at multiscale for mechano-adaptable devices

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

How materials behave when subjected to mechanical stresses was studied by *mechanics of materials*. However, the application of flexible and stretchable devices exposes materials under dynamic mechanical environment. Therefore, mechano-adaptable materials and devices that can respond as pre-designed have been explored. There are two main ways to proactively modulate mechanical behaviors for materials, which are concluded into molecular design and structural design. Molecular design has effectively integrated mechanically sensitive groups into synthetic materials for anticipated mechanoresponse. Structural design has broadened the boundary of conventional materials, generating mechanical metamaterials at multiscale with unique mechanical properties. Furthermore, molecular, structural plus systematic design for the application of mechano-adaptable devices have realized better electrical performance, human-interaction, long-term sustainability, and even higher efficiency. Various devices based on design ideas have been summarized and future challenge on proactively modulating mechanical behaviours of mechano-adaptable devices was discussed.

Key learning points:

- (1) Molecular design can achieve proactive modulation of materials with desired mechano-response by integrating mechanically sensitive groups- mechanophores.
- (2) Structural design at multiscale enables mechanical metamaterials with unconventional mechanical properties including negative Poisson's ratio, programmability, and so on.
- (3) Proactive modulation for mechano-adaptable devices have realized smart and desired functions for the application of flexible and wearable devices.

1. Introduction

Materials would suffer from deformations and even breaking down upon being applied mechanical stresses.¹ Much research efforts have been paid to understand and predict the mechanics of materials. Recently, the emergence of the field of flexible and stretchable devices has raised up new research focus into the investigation between dynamic mechanics and materials.^{2, 3} Flexible and stretchable devices targets to interface with complex geometry and dynamic movement of human, which can engage bio-information in internet of things (IoT). The features of long-term functioning and lightweight, conformability and good user-interaction are directly beneficial to improving signals fidelity and reducing discomfort of wearing. However, under this scene, the materials and devices inevitably would be exposed to mechanical stresses. Therefore, the capability of materials/devices under mechanical

deformations to maintain performance is a prerequisite for this application.

Mechano-adaptable devices refer to devices which can tolerate mechanical deformation and even realize mechanoresponsive functions. Targeting at upcoming mechanical environment, proactive design can prevent or provide solutions to expected problems through strategical methods. For materials to construct mechano-adaptable devices, molecular design and structural design are regarded as two routes to realize proactive modulation. Moreover, smart mechano-response and mechano-adaption of biological creatures (e.g. cephalopods and chameleon) greatly inspire us to proactively build devices with intelligent functions to handle intricate surroundings.⁴

Molecular design means you can select proper chemical constituents for your desired products. Early study on mechanoresponsive materials have revealed that certain chemical groups are sensitive to mechanical stimuli. They are recognized as mechanophores. Effective employment of mechanophores have generated plenty of synthetic materials with fascinating mechanoresponsive characteristics. These mechano-responses are devoted by the energy transformation from mechanical energy into optical, electrical and mechanical

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Fig. 1 (a) A scheme showing the proactive modulation of materials by molecular design and structural design. Reprinted from ref. 6 with permission from Nature Publishing Group, copyright 2017 and ref. 9 with permission from Nature Publishing Group, copyright 2007. (b) Examples of proactive-modulated mechano-adaptable devices which are enabled through structural design, molecular design and systematic design. Reprinted from ref. 29 with permission from Nature Publishing Group, copyright 2016, ref. 46 with permission from Wiley-VCH, copyright 2014, ref. 35 with permission from Wiley-VCH, copyright 2018, ref. 41 with permission from Nature Publishing Group, copyright 2018 and ref. 49 with permission from Nature Publishing Group, copyright 2015.

energy and so on.⁵ Therefore, the appropriate models at molecular level was realizable to engender anticipated mechanoresponsive materials.

The other path is structural design. It has long been regarded as the method to resist applied loads without failure. Surprisingly, a class of materials called mechanical metamaterials, has been used to achieve unconventional mechanical properties independent of its constituents.⁶ By constructing various structures from microscale to macroscale, various unique properties have been realized. For example, kirigami structures can introduce stretchability to non-stretchable materials. Therefore, structural design has flourished mechano-adaptable materials since the structural deformations can be designed in advance.⁷ Furthermore, the implementation of additive manufacturing has lowered the barrier to fabricate complicated structures.

Both newly synthesized materials and well-designed structural materials are serving to promote the applications for mechano-adaptable devices. These materials with proactive design can be directly employed as the functional layers for mechanochromic devices, mechano-electrical sensors, mechano-healing devices and so on. Furthermore, a more

effective solution to achieve mechano-adaption is systematic design to strategically assemble assorted functional components. This means we only need to minimally modify or innovate materials, while achieving interlinked utility at device level.

In this tutorial review, how to modulate mechanical behaviours of materials by molecular or structural design would be summarized (Fig. 1a). The subsequent performance of mechanochromic, mechano-electrical, self-reinforcing would be discussed from the view of mechanism. Structural design induced unconventional mechanical properties would be explicated, which inspires device-level structural design as well. The next part would be how molecular, structural, and systematic design empower the field of mechano-adaptable devices from five kinds of mechanoresponsive devices. Mechanochromic device, highly sensitive sensors, mechanoactuated devices, self-healing and smart deployable devices were included (Fig. 1b). These design-based emergent materials and devices have undoubtedly shed a light on next-generation mechano-adaptable devices for better interactive functions and intelligence.

2. Proactive-modulation of materials mechanics by molecular design and structural design

2.1 Molecular design enabled mechanoresponsive materials

Molecular design, or molecular engineering, is a field of study to assemble materials, or systems for specific function based on design of molecular properties. Those carefully designed new materials based on molecular physics, relate to emergent functions including optical, electronic, and other functional properties. This happens especially for newly synthetic polymers.

For most of bulk polymer materials, they would experience failure or breaking down upon mechanical stress out of the breaking of weak covalent bond. The earliest mechanochemical synthesis was enabled by grinding which provides activation energy to break those covalent bonds of polymers including polyethylene, polypropylene, polyacetylene, polystyrene, polyisobutene, poly(methyl methacrylate) (PMMA) and so on, and to generate active radicals for chemical reactions. Typical examples include C-C covalent bond breaking down upon mechanical force, which is so called the homolytic cleavage. Afterwards, researchers have explored and concluded mechanically sensitive groups- mechanophores, which can selectively break and re-form covalent bonds. With the introduction of mechanophores into molecular structures of polymers, the application of mechanical stress can be targeted at a specific site. Generalized examples of moieties which are capable of efficiently transform the mechanical stress into bond activations are summarized (Fig. 2a).⁸ Homolytic cleavage and dative bond scission were used for specific mechano-chemical reactions and force-activated catalysts. It's worthwhile that those mechanophores based on cycloreversion and electrocyclic ring opening have contributed enormous breakthrough in mechano-oriented reactions, mechanochromic

Fig. 2 (a) As summarized mechanophores which contain force-activated bonds (as highlighted in red) for effective mechanochemical reactions. R = site of polymer attachment; X = F, Cl. Reprinted from ref. 8 with permission from American Chemical Society, copyright 2013. (b) Synthetic mechanochromic materials which was prepared from 80 kDa PMA and mechanophores of spiropyrans. Upon force, the colourless spiropyran would transfer into coloured merocyanine forms of the mechanophores. Reprinted from ref. 10 with permission from Nature Publishing Group, copyright 2009. (c) A mechanoluminescent polymer which incorporates 1,2-dioxetane unit to emit light upon opening of the four-membered dioxetane ring. Reprinted from ref. 11 with permission from Nature Publishing Group, copyright 2012.

and self-healing or self-reinforcing materials. For example, cycloreversion includes opening of strained three- and four-membered rings like cyclobutenes, and formal retrocycloaddition. One case of electrocyclic ring opening is spiropyran chromophores which at the same time change colours under tensile stress. Benzocyclobutene and dichlorocyclopropane are also the cases which would have electrocyclic ring openings upon mechanical forces. Hickenboth et al. have discussed on the difference influences of light, heat and stress on the rearrangement of benzocyclobutene, which suggested the specific outcome of chemical reaction can only

Fig. 3 (a) Reaction scheme of mechanochemical transformation of insulating polyaddereene into PA-containing block copolymer under mechanical sonication. Reprinted from ref. 13 with permission from The American Association for the Advancement of Science, copyright 2017. (b) The mechanochemical self-reinforcing materials which contains a gDBC mechanophore to have a ring-opening reaction under scission force. The activated mechanophore (black triangle to red dot) would react with the crosslinker to form another active bond for self-reinforcement. Reprinted from ref. 14 with permission from Nature Publishing Group, copyright 2013. (c) The self-healing materials which incorporate $[\text{Fe}(\text{Hpdca})_2]^+$ moiety to reverse rupture after mechanical damages. Reprinted from ref. 16 with permission from Nature Publishing Group, copyright 2016.

be activated though mechanical stimuli due to the conrotatory variation.⁹

Synthetic polymeric materials by incorporating force-activated spiropyran into elastomeric poly (methyl acrylate) (PMA) and glassy poly(methyl methacrylate) (PMMA) were demonstrated by Davis et al.,¹⁰ which can locally visualize the electrocyclic ring-opening reaction under tensile stress by colour change. (Fig. 2b) Here, the used mechanophore would reversibly transform from a closed, colourless spiropyran form into a highly coloured, planar merocyanine structure upon mechanical stress to break the spiro carbon-oxygen (C-O) bond. With higher plastic deformation, the synthetic PMA-mechanophores materials with spiro-junction showed a changing colour while control samples without spiro-junctions didn't. When reaching a strain over 1,000%, the active PMA-mechanophores failed and behaved an intense red colour. It is shown that proper design of mechanophores and efficient chemical response pathways can enable a responsive material which can show smart mechano-responsiveness. This advanced characteristic can be used as force sensors with visual interaction and the predictor for materials failure which is important in architectures.

Besides mechano-responsive colour change to indicate experienced mechanical stress, mechano-luminescence for polymers incorporating 1,2-dioxetane unit has been report by Chen et al. (Fig. 2c).¹¹ The four-membered 1,2-dioxetane ring

here was adopted as mechanophores connected with PMA which would emit a light on opening of the dioxetane ring. Furthermore, the emission peaks can be tuned by varying the acceptors into 510 nm and 650 nm, which correspond to green and red colour. This real time monitoring of light emission from materials under deformation can also be used to indicate the failure of polymeric materials.

The other examples involve sparse incorporation of a reported mechanophore into a mechanochemically inert polymer. Highlighting for this work is a macromolecular scaffold that rearranges dramatically under force, converting a series of strained σ bonds to π bonds, thus transforming an insulating nonconjugated structure to a semiconducting structure with continuous extended conjugation (Fig. 3a).¹² This work has demonstrated that by carefully designing the ladderane monomers with mechanophores, the ring-opening metathesis polymerization can be driven by the release of mechanical strain. As a result, the generated polyacetylene copolymers has realized a conductivity of 2.6×10^{-7} S/cm, which further supports the mechanochemical reaction enabled electrical properties change from insulators to semiconductors. This example indicates that mechano-responsive materials can convert mechanical stimuli into not only coloration, luminescence but also electrical conductivity, which open more opportunities for smart materials with expected mechanoresponse.

Apart from color change, luminescence, fluorescence and electrical properties, materials with toughening mechanical properties^{13–15} also have great potential to meet with applications on wearable, stretchable devices since they can withstand multiple mechanical manipulations and wearing. A successful design on mechanophores could lead to effective self-reinforcing materials or even self-healing materials, where after chemical bonds are broken, new chemical bonds are formed to restore the original properties by repeated mechanical scission and recombination of dynamic covalent bonds. Ramirez et al. have chosen *gem*-dibromocyclopropanes as the mechanophores of which the ring opening can be mechanically triggered, generating a 2,3-dibromoalkene product (Fig. 3b).¹⁴ The carefully designed mechanophores-embedded poly(butadiene) (PB) materials can have a reinforcing mechanical property (orders-of-magnitude) upon destructive shear forces than those unactivated polymers. Besides, self-healing polymers were realized based on combining dynamic metal-ligand interaction and weak binding sites. Fe(III)-2, 6-pyridinedicarboxamide (pdca) coordination complex was introduced into a poly(dimethylsiloxane) (PDMS) backbone (Fig. 3c).¹⁶ Weak binding sites in 2,6-pyridinedicarboxamide can easily break and re-form, while the strong metal-ligand interaction maintained the ligands close to re-form, cooperatively contributing to the healing property. The synthetic recyclable and sustainable polymers demonstrated that the desired strengthening and healing properties can be achieved through molecular design.¹⁵ The self-strengthening and self-healing properties upon destructive forces have undoubtedly equipped emergent functions to materials society with smart features.

Through all these examples of careful design on synthetic polymers with mechano-responsive properties upon physical environments, it's convincing that researchers are at the age of creating 'new' materials from molecular scale based on specific mechanics and mechanophores. Besides mechanophores, enormous materials generation in soft active hydrogels and synthetic polymers through molecular designs, have greatly made the realm of proactive-modulated materials thrived.¹⁷ Although current molecular design are mostly chasing mechano-responsiveness, we believe that a plethora of novel materials will further flourish for function-driven purpose with the establishment of the general concept of molecular design. Section 3 includes some examples of how these synthesized materials can be utilized for flexible and wearable devices, and more space in this field is pending for exploration.

2.2 Structural design enabled mechanoresponsive materials

Besides molecular designs, the structural designs also enabled much advancement in obtaining new materials with unexpected mechano-behaviors. The typical examples are mechanical metamaterials which exhibit mechanical properties and functionalities that cannot be realized in conventional materials and only depends on structures but not constituent materials. Until now, the rational design has realized effectively stronger, tougher, lighter materials and controllable three-dimensional transformations through kirigami and origami strategy. This section would briefly conclude the new mechanical metamaterials based on their emergent functions.

Firstly, the ultra-stiff and ultralight mechanical metamaterials were reported by Zheng et al. by designing a network of nearly isotropic microscale unit cells with high structural connectivity and nanoscale characteristics (Fig. 4a).¹⁸ Combining projection microstereolithography with nanoscale coating methods, arbitrary, microscale, three-dimensional structures (stretch-dominated lattice) were fabricated with a resolution of ~ 5 μm , which enables the ultralow density. Furthermore, various constituent materials including solid polymers 1,6-hexanediol diacrylate (HDDA), metallic nickel-phosphorous (Ni-P), ceramics (alumina) were demonstrated to have high mechanical efficiencies without degradation. Unlike other Ni-P lattice, the stretch-dominated metallic lattice is much stiffer in the same density range. Furthermore, its specific stiffness keeps nearly unchanged, measured as 1.8×10^6 m^2/s^2 and 2.1×10^6 m^2/s^2 at densities of 14 mg/cm^3 and 40 mg/cm^3 , respectively. Later, they further demonstrated macroscale, metallic, mechanical metamaterials which have realized high strength, ultralow density, as well as high compressive and superelastic tensile performance with hierarchical structures from nanoscale to bulk scale (Fig. 4b).¹⁹ The hybrid and multiscale design can further extend materials with more unconventional combinations of properties, which broaden the view of proactive-modulated materials by structural design.

Another example related to auxetic metamaterials with negative Poisson's ratios which would have a lateral expansion rather than contraction under stretch.^{20, 21} It's found that for natural auxetic materials including cancellous bone, living cow skin and zeolites, their negative Poisson's ratios originate from

Fig. 4 (a) Ultrastiff, ultralight mechanical metamaterials which contain a stretch-dominated octet-truss unit cell and be packed into a cubic microlattice. The ultrahigh strength with low relative density was realized in 1,6-hexanediol diacrylate (HDDA), metallic nickel-phosphorous (Ni-P) and ceramics (alumina). Reprinted from ref. 18 with permission from The American Association for the Advancement of Science, copyright 2014. (b) Multiscale metamaterials of octet-truss units and critical features at seven orders of magnitude of length scale made of nickel alloy. Reprinted from ref. 19 with permission from Nature Publishing Group, copyright 2016.

the geometry and microstructures. With the further exploration, typical mechanical auxetic structures were explored including re-entrant bow-tie,²¹ arrowhead, Lozenge grid and square grid, 3-STAR, 4-STAR, 6-STAR systems and 3D re-entrant bow-tie structures to have increasing volumetric compression ratios (Fig. 5a,b).²² For example, in re-entrant honeycomb structures, the deformation is dominated by the realignment of the ribs inside the cell which originally have a negative angle. Upon stretch, the hinging of the ribs would cause vertical expansion, which results in negative Poisson's ratio. Various classes of materials including metals, metal dichalcogenides, ceramics, polymers and proteins have been

proved to have auxetic forms and the scale can be hierarchical. It's convincing that the proper design in auxetic structures for advanced materials would have broad applications in devices, which would be discussed in next section, since they are able to harness high indentation resistance, energy absorption, hardness, fracture toughness, etc. Their application in energy devices, stretchable and flexible devices are attracting more attention and the utilization of 3D additive manufacturing has enabled complex and elegant structures.

Origami and kirigami, are two ancient art for aesthetics. Nowadays, they are recognized as the framework of mechanical metamaterials design which enables programmable, foldable,

Fig. 5 (a) Typical re-entrant bow-tie structure in rest and under tensile loading. Reprinted from ref. 20 with permission from The Royal Society of Chemistry, copyright 2017. (b) A 3D re-entrant hexagonal structure. Reprinted from ref. 22 with permission from Wiley-VCH, copyright 2012. (c) Paper in-plane kirigami springs. Reprinted from ref. 23 with permission from Nature Publishing Group, copyright 2015. (d) A Miura-ori with complex defects structures to alter the crease patterns. Reprinted from ref. 24 with permission from The American Association for the Advancement of Science, copyright 2014.

reconfigurable functionalities. From the understanding of the words, kirigami refers to cutting papers and origami refers to paper folding. Through combining kirigami and origami, two-dimensional starting materials with strategically configured arrays can transform into three-dimensional structures by buckling and folding processes. Graphene kirigami was demonstrated by Blees et al. to be customized into resilient and movable parts at microscale dimensions (Fig. 5c).²³ Another example is utilizing origami design principles to realize programmable mechanical metamaterials that eight configurations were programmed into a single sheet with 13 consecutive reprogramming with programmed modulus (Fig. 5d).²⁴ This design principles of programmable metamaterial would be significant for self-folding robotics and engineering devices which can alter the mechanical properties as desired. The assembly principles based on kirigami and origami have been carefully demonstrated on mono-crystalline silicon to metal and plastic into 3D structures,²⁵ which corresponds well with theoretical studies. This mechanically driven 3D assembly would further advance the construction of 3D micro/nanosystems technology, which is discussed later in details.

Mechanical metamaterials has greatly expand our vision beyond traditional mechanical properties. The strategic assembly methods involve more creativity on extending materials dimensions. The emergent functionalities and space would harness a lot of applications in functional devices, especially in the field of stretchable and deployable devices. However, current related techniques such as 3D printing and two-photon lithography are still under development and available base materials are limited. Broadening suitable base materials can definitely increase the complexity of mechanical metamaterials and give rise to hybrid materials with various classes of functionalities. Further, models and rational design of periodic structures for targeted functions need to be further discovered.

3. Proactive-modulated mechano-adaptable devices

Beside materials which can respond to mechanical stimuli as-predefined, functional devices is of great importance to have adaptable response to mechanical stimuli. Proactive-modulated devices with desired mechanical properties (e.g. mechanical compliance, flexural rigidity and stretchability) and performance have been realized from last decades by thoughtfully choosing the constituent components. Furthermore, the abovementioned modulated materials also have been utilized into functional devices including mechanochromic display, mechanoresponsive energy devices, deployable three-dimensional devices, etc. This section would have some discussions on how above-discussed materials can be assembled into functional devices. More importantly, the rationale to design smart devices is considered, which arouse more enthusiasm into future mechano-adaptable devices in proactive-modulated manner.

3.1 Mechanochromic devices, mechanoluminescent devices, mechanofluorescent devices

Mechanochromic devices refers to those devices which would have color change upon mechanical stimuli. It can be categorized into two kinds of devices: 1) directly utilizing mechanochromic materials as the display which have a color change upon mechanical stimuli; 2) integrated system with components design which don not have a mechano-induced chromic material.

Firstly, the mechanochromic devices which directly utilized mechanochromic materials was achieved. Metal complexes have been applied in mechanochromism for a while. Sun et al. has reported ionic iridium (III) complexes which has $-NH_2$ moiety that are sensitive to grinding, solvent vapor and electrical field and lateral demonstration as a data-recording device (Fig. 6a).²⁶ Specifically, $[ppy_2IrNH]^+PF_6^-$ was selected to investigate mechanochromic properties of these Ir(III) complexes. This complex exhibited a green colour phosphorescence at 543 nm and after grinding, a red-shift of emission to 585 nm as a yellow-emitting powder occurred. Therefore, the grinded complex was coated on a quartz plate as the 'paper'. Interestingly, the vapor of CH_2Cl_2 , $CHCl_3$ or THF can revert the emission colour back to green due to the recrystallization induced by vapour. As a result, the special pen made with CH_2Cl_2 vapour as the ink can write a word 'IAM' with green colour on the yellow 'paper', which composed a rewritable data recording device. After using, the word can be easily erased by grinding which may be important for data security protection.

Elastic photonic crystals have a structural colour originated from Bragg diffraction of periodic microstructures to light and would have a colour change upon mechanical deformation. The ease of fabrication by moulding, high sensitivity upon mechanical stresses, and good tunability of colours make elastic photonic crystals a good candidate for mechanochromic devices. Inspired by tropical fish, a full-colour switching by photonic hydrogels (Fig. 6b) was reported by Yue et al.²⁷ The

Fig. 6 Mechanochromic devices based on mechanochromic materials and structural materials. (a) Mechanochromic behaviours of [ppy2IrNH]⁺PF₆⁻ to realize rewritable data recording devices. Reprinted from ref. 26 with permission from Nature Publishing Group, copyright 2014. (b) A bio-inspired mechanochromic display based on ultrafast colour switching of the photonic hydrogel which contains hydrolysed (h)-PAAm and rigid polymerized-DGI bilayer domains. Reprinted from ref. 27 with permission from Nature Publishing Group, copyright 2014. (c) Mechanochromic devices based on systematic integration of deformation-controlled cracks and folds, reflector layer, fluorescent layer and luminescent layers. Reprinted from ref. 29 with permission from Nature Publishing Group, copyright 2016.

photonic hydrogels were consisting of a uniaxially aligned poly(dodecyl glyceryl itaconate) (PDGI) bilayers and a polyacrylamide (PAAM) hydrogel network. This nanostructured hydrogel behaves colour switching over all visible wavelength and can be used into a pressure-actuated displays, which can be switched by a very minor compressive stress in the orders of kilo Pascals. Various photonic gels were also demonstrated as the deformation-based display panels and sensors applications.²⁸ Dyes incorporated systems and liquid crystals were also investigated for mechanochromic crystals but we would have a detailed discussion.

For the mechanochromic devices without mechano-induced chromic materials, the mechanochromic response were carefully designed methodically. Being inspired by cephalopods which can display various colours selectively for camouflage and communication, mechanochromic devices based on design strategy of all components have been reported by Zeng et al.²⁹ Three types of mechanochromic devices were realized including transparency changing upon stretch and mechanofluorescent and mechanochromic devices (Fig. 6c). Pre-stretch induced wrinkles and cracks was utilized to realize transparency change. Furthermore, a series of design strategy for following mechanofluorescence and mechanochromism were exploited.

The luminescence mechanochromism devices incorporated a rigid ultraviolet-shielding film and a soft PDMS substrate containing a fluorophore layer and a reflector layer. Under stretch situation, the crack development in the ultraviolet-shielding layer increased the exposure area of the underneath fluorophore. As following, for the colour alteration mechanochromism, one more thin film of laponite/fluorescein with green fluorescence was coated on top of the rigid UV-shielding film. At the same time, a soft layer with europium-doped yttrium oxide (Y₂O₃: Eu³⁺), emitting orange fluorescence is underneath. The device exhibited green fluorescence without strain and changed into yellow and to orange with increasing strain due to the cracked-exposed Y₂O₃: Eu³⁺ layer. This work has proved that a strategic design of each component in devices can realize a series of mechanochromic behaviours with anticipated smartness.

In practical, mechanochromic devices have to consider the working scenarios and ease of manipulation. For examples, full-colour switch and distinguishable colour changes are important in touch-visual interaction for naked eyes. But for data security issue, mechanofluorescent devices manipulating in invisible wavelength is better. And for the mechanochromic devices without mechano-chromic materials, sensible design with higher efficiency need to be carefully schemed. Therefore, mechanochromic, mechanoluminescent or mechanofluorescent devices have included broader research efforts also more inspirations compared with mechanochromic materials. The design strategy can enhance the complexity of mechanochromic devices for multifunctional visual interaction.

3.2 Mechano-sensors with high sensitivity

When talking about response on mechanical stimuli, mechano-sensors is highly demanded as it can detect the mechanical deformation. Especially, structural design is believed to be a very helpful way to render mechano-sensors with high sensitivity. Recent years we have seen the explosion of highly sensitive mechano-sensors including pressure sensors, strain sensors, etc. In this part, we would mainly discuss how structure designs benefit high sensitivity and other properties as well.

Inspired by nature, highly sensitive pressure sensors based on pyramidal structures (Fig. 7a) was reported by Mannsfeld et al.³⁰ By moulding the elastomers (PDMS) into pyramidal structures, this structured material can be incorporated into field effect transistors as the dielectrics which can detect the tiny pressure of a flyer stopping. It is recognized that the microstructures induced contact area and dielectric constant change under pressure is the contributing factor to the high sensitivity. Later, multiple pressure sensors were reported based on moulding the structures of interlocking structures of beetles, nanohair, rose petals, mimosa leaf, lotus leaf, spongia, etc. Through combining the active materials such as CNT-based active materials, graphene-based materials, nanowires based materials as well as organic and polymer-based materials with the microstructures, the mechanical stimuli were transformed into readable electrical signals through the way of piezoresistivity, piezoelectricity and capacitance transduction.

Fig. 7 Highly sensitive mechano-sensors with structural designs. (a) Highly sensitive pressure sensors based on pyramidal microstructures. Reprinted from ref. 30 with permission from Nature Publishing Group, copyright 2014. (b) Spider inspired highly sensitive strain sensors. Reprinted from ref. 31 with permission from Nature Publishing Group, copyright 2014. (c) Fiber-shaped strain sensors based on beads-on-fiber structures. Reprinted from ref. 32 with permission from Wiley-VCH, copyright 2018. (d) 3D structured strain sensors for out-of-plane force detection. Reprinted from ref. 33 with permission from Wiley-VCH, copyright 2018. (e) Auxetic structures-based strain sensors with high sensitivity. Reprinted from ref. 35 with permission from Wiley-VCH, copyright 2018.

These microstructured pressure sensors based on soft elastomers have high sensitivity and fast response time. In addition, the ease of being fabricated into thin film based multipixel sensor arrays has flourished the electronic skin field with a large-area and sensitive tactile perception. The applications for health monitoring include pulse detection, gesture recognition and respiration motions, etc.

For strain sensors, microcracks-based strain sensors have attracted much attention due to the ease of tuning sensitivity. A strain sensor based on microcracks (Fig. 7b) was reported by Choi et al.³¹ The microcrack network was realized by depositing a stiff, 20 nm-thick platinum layer on top of polyurethane acrylate (PUA). This viscoelastic polymer would generate controllable cracks on the platinum layer under mechanical strain while the electrical conductance can be measured. The gauge factor (GF) is larger than 2,000 at strains of 1–2%, which is a case of controlled crack formation realizing ultrasensitive mechanosensor. Later, structural design such as gradient structures,³² beads-on-fibers structures (Fig. 7c),³³ 3D whiskers structures (Fig. 7d)³⁴ were reported to give rise of highly sensitive strain sensors. Beads-on-fiber structures have achieved a surface strain redistribution so that certain region would have accumulated strain (Fig. 7c). By depositing the active layer of resistive strain sensors at that region, the gauge factors can be effectively enlarged. This fiber-shaped highly

sensitive strain sensor is significant for smart textiles which can detect physiological signals of human beings. Further, effective 3D structural designs, which is a whisker on strain sensors, can render them the capability to detect out-of-plane force (Fig. 7d). Being assisted by a capillary force enabled 3D self-pinning effect, carbon nanotubes (CNT) was chose as the active layer by dropping the solution at the root of the whiskers. The CNTs would not only form a network at the root of the hair, but also form multiple rings on the sensor body. In this case, with the 3D structures, the strain sensor is able to detect tensile, compression, bending and distinguish strain directions. These studies have demonstrated that a strain redistribution can be efficiently tuned through either microstructures or macrostructures to have a higher strain gauge factor and 3D sensing capability.

Especially, an auxetic mechanical metamaterials based stretchable strain sensor (Fig 7e) with enhanced sensitivity was reported to have a higher sensitivity compared to non-auxetic structures.³⁵ The auxetic structures result in vertical expansion under lateral stretch, which further enhance the cracks propagation of the CNTs active layer. Therefore, a higher sensitivity (gauge factor) of ~800 was realized compared with flat films. What's more, the auxetic structures also induce a larger linear strain sensing range up to 15%, which is important for practical sensing of strain for calibration. We have discussed the meaning of mechanical metamaterials in last section to introduce unconventional mechanical properties like negative Poisson's ratio. This work has further promoted the real application of auxetic mechanical metamaterials for higher sensitivity and inspired more transformation from study and design on metamaterials into obtaining excellent devices performance. The highly sensitive strain sensors benefit the integration of soft robotics for joint motion detection, which is also bringing intelligence to devices.

Based on the cases we discussed, it is reasonable the structures of materials integrated with devices can further enhance the sensitivity, which is on demand for especially the field of flexible and stretchable electronics. However, mechanosensors with 3D-structured design to some extent are not compatible with the fabrication of multipixel arrays. For example, traditional strain gauge using single crystal silicon nanomembrane is fabricated for strain sensor arrays based on thin-film technology. Thus, future efforts on improving the scalability and resolution of 3D multipixel sensor arrays are indispensable. Development of related technique such as high-resolution 3D additive manufacturing may be helpful to address this issue.

3.3 Mechano-actuated devices based on buckling mechanism

As discussed in section 2.2, kirigami and origami combined buckling method enables the generation of 3D structures as designed.³⁶ Rogers' group has proved buckling driven 3D assemblies of single-layer materials including metals, silicones and polymers by combining prestrain methods and lithographically patterned bonding points.³⁷ However, for the real devices application, various classes of functional materials should be integrated in multiple layers with higher complexity with various feature size and patterns. Therefore, 40 3D

Fig. 8 Mechanoactuated devices based on kirigami, origami and structural design strategy. (a) A 3D NFC device with enhanced Q factor compared to 2D coils. Reprinted from ref. 38 with permission from The American Association for the Advancement of Science, copyright 2016 (b) Freestanding three-dimensional mesostructures for electronic scaffolds for formation of dorsal root ganglion (DRG) neural networks. Reprinted from ref. 40 with permission from National Academy of Sciences, copyright 2017. (c) Three-dimensional microswimmers based on kirigami structures with controlled motion modes and trajectories. Reprinted from ref. 40 with permission from National Academy of Sciences, copyright 2017. (d) Morphable 3D mesostructures for integrated circuits with silicon transistors with unchanged current-voltage (I - V) characteristics based on buckling mechanics. Reprinted from ref. 41 with permission from Nature Publishing Group, copyright 2018.

structures formed utilizing silicon, polymer, metal, and their heterogeneous combinations were studied by experiments and theoretical studies to have structural stability and topological complexity. An application on 3D antenna (Fig. 8a) made from multi-layered 2D precursors for near-field communication (NFC) technologies was demonstrated to obtain higher quality factor and improved performance compared with its 2D components.³⁸

The reason of applying 3D structures into bioelectronics is resulted from the three-dimensional topology of biological tissues.³⁹ An example involves in fabricating 3D electrodes for stimulating and recording of dorsal root ganglion (DRG) cells (Fig. 8b) to study the electrophysiological behaviours of DRG cells.⁴⁰ The 3D framework can also be used to guide the growth of DRG cells that the cells were organized into networks following the 3D scaffolds with ribbons connected. The transferring of 3D electrodes into biological tissues and cells for growth and electrophysiological behaviours study has extended the possible application of this 3D electrodes which may be integrated with chemical, thermal electrical or optical stimuli to facilitate the fundamental research on cells and tissues study. Besides, self-propelled micro-robots with geometrically controlled dynamics and motion trajectory (Fig. 8c) was shown by strategic designs of active materials and 3D kirigami

structures. Being immersed into hydrogen peroxide (H_2O_2 , 30% by weight), the strategically patterned films of platinum (Pt) can catalyse the production of water and oxygen (O_2) at room temperature. The generated O_2 bubbles drive the movements of the 3D structures in a controlled manner into either linear or curvilinear motions through patterning the location of Pt thin films. This example has broadened the range of engineered actuators and motors by simply structural designs to have desired functions.

Last but not least, the buckling induced 3D assembly was demonstrated to be compatible with modern planar technologies and related microelectromechanical system (MEMS) for a 3D reconfigurable metal-oxide-semiconductor field effect transistors (MOSFET) applications (Fig. 8d).⁴¹ The device was first fabricated in a planar configuration using conventional photolithography to pattern various layers including transistor layer, electrodes, encapsulation layer and bonding points with elastomeric substrates. Two intermediate states of the integrated circuits can be obtained by tuning the stretch and release sequence, which is reversible, easy to obtain and stable. And the transistor performance would not degrade under two states compared with 2D structures. The good compatibility with traditional MEMS related techniques makes this strategy particularly reliable to program other kinds of planar devices into 3D frameworks. Besides transistors, optoelectronic device and radiofrequency electronic device were also demonstrated to achieve morphable 3D structures.

Based on all the above-mentioned cases, kirigami/origami combined buckling method to introduce 3D devices with reconfigurable, reprogrammable performance and controllability is a reliable way for devices integrations to achieve mechano-actuation. Better actuating efficiency and multiple materials choices would be good for the realization of programmable complex devices systems. Mechanoactuated devices which enable motions upon mechanical stimuli undoubtedly benefit the next generation of soft robotics with reprogrammability.

3.4 Self-healing devices

Self-healing materials discussed in last section is more about the recovery of dynamic coordinate bonding. When self-healing property emerged with electronic skin, the self-healing or self-repairing capability of the functional devices is highly desired.⁴² Inspired by skin's self-heal ability, it is exciting and environment-friendly if the devices can recover back to functional states even under destructive situation. Therefore, many research efforts have been contributed in this area to explore self-healing devices such as self-healing wires, lithium ion batteries, solar cells, supercapacitors, sensors, transistors, etc.^{42, 43} Unlike self-healing materials, self-healing devices need to recover functioning with higher recovery efficiency and long-term mechanical robustness. Therefore, attentions have been not only focused on self-healing substrates but also on molecular-level design and device-level optimization of functional materials. And the recovery of devices is based on the self-healing properties of polymer matrix and physical contact of active materials upon various stimuli.

Fig. 9 Self-healing electronic devices. (a) An electrically and mechanically self-healing composite composed of micro-nickel particles and self-healing polymers. The pressure- and flexion-sensitive properties electronic skin applications with self-healing functions. Reprinted from ref. 44 with permission from Nature Publishing Group, copyright 2012. (b) A mechanically and electrically self-healing supercapacitor which contains self-healing composite made by hierarchical flower-like TiO_2 nanostructures and supramolecular network. Reprinted from ref. 46 with permission from Wiley-VCH, copyright 2014. (c) Intrinsically stretchable and self-healable semiconducting polymers for transistor applications. Reprinted from ref. 47 with permission from Nature Publishing Group, copyright 2016. (d) An integrated electronic skin system with self-healing capability based on hydrogen-bond-driven assembly with self-healable interconnects, EMG/strain sensors and LEC array. Reprinted from ref. 48 with permission from Nature Publishing Group, copyright 2018.

Self-healing conductors by blending the self-healing polymers with conductive materials including graphite, metal particles and thin films, ionic liquids, liquid metals were reported. On rupture, these self-healing conductors can recover their electrical conductivity and mechanical properties after healing process. A self-healable conductor (Fig. 9a) was reported to be both flexion- and pressure-sensitive composites with nickel microparticles dispersed in the supramolecular hydrogen bonding network.⁴⁴ Here, the used self-healing supramolecular polymers has a glass transition temperature below room temperature, which makes the polymer chains to rearrange and diffuse, followed with the 'broken' hydrogen bonds dynamically healing at room temperature. A conductivity of 40 S cm^{-1} has been realized for self-healing conductors. After being cut, by bring the edges into contact and applying a gentle pressure of 15 s, the conductor can recover the conductivity. Even more, by reducing the μNi particles, self-healing piezoresistive sensors was achieved due to the closer μNi under compression for tactile applications.

Besides the conductors, a self-healable chemical sensor was reported by Huynh et al. by assembly of self-healing substrate (disulphide-cross-linked polyurethane (sh-crl-PU)), electrodes, and molecularly functionalized gold nanoparticles.⁴⁵ A self-healing supercapacitor (Fig. 9b) which can restore its specific

capacitance up to 85.7% of its original value after 5th cutting was reported by Wang et al.⁴⁶ Self-healing sensors and energy harvesting system were realized to retain its performance even upon a mechanical destruction, which greatly improve the devices life time for long-term applications.

The development of self-healable semiconducting polymers has further demonstrated the molecular design strategy and possibility to achieve all polymers based integrated circuits. An intrinsically stretchable and self-healing semiconducting polymer (Fig. 9c) was realized in conjugated polymers via dynamic bonding for organic thin-film field-effect transistor (OTFT) usage.⁴⁷ Oh et al. has chosen 3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (DPP) based semiconductors and 2,6-pyridine dicarboxamide (PDCA) to introduce hydrogen bonding for the self-healing semiconducting polymers. Mobilities were measured to be large than $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ while healing of transistor was achieved by a solvent and thermal healing process without almost no degradation of mobility. The molecular design in this semiconducting polymer has both benefited the self-healing property and stretchability, which proves the molecular design strategy for devices level integration is a reliable method for introducing desired mechanics for wearable and stretchable devices.

All of these functional devices prove that self-healing property for wearable devices is one of the exciting 'smartness' for sustainable applications. Besides individual functional device, systematic integration of multifunctional devices has also been developed. Recently, Bao's group has integrated a self-healing electronic skin system with multifunctionalities containing self-healing interconnects, electrocardiogram (ECG)/strain sensors and a light-emitting capacitor (LEC) based on a nanowire conductive network supported by self-healing polymer matrix (Fig. 9d).⁴⁸ The supramolecular design has enabled self-healing properties as well as high stretchability and systematic devices based on polymers for electronic skin application. What's more, the continuous monitoring with robustness and self-repairing capacity render wearable electronics with long-term sustainability and human-like characteristics. All of these development on self-healing materials and devices do advance the future usages into cutting-edge robotics and prosthetic electronics for unbreakable devices.

3.5 System-level proactive structural design for smart deployable devices

To recap the definition of proactive-modulated materials and devices, a key factor is to obtain smart functions based on mechanical designs on materials and devices. Sometimes, without much materials innovation, structural design alone at system level is able to obtain higher efficiency, higher stretchability and other desired functions. For example, the kirigami dynamic structures based solar tracking system (Fig. 10a) has obtained higher efficiencies for optical tracking.⁴⁹ Traditional photovoltaic devices, such as solar cells would suffer from optical coupling losses originating from the misalignment of the devices and sun. The coupling efficiency decreases with

Fig. 10 Systematic integration for deployable devices. (a) A novel kirigami optical tracker for higher optical coupling efficiency which can change the angle of the element by lifting or lowering one end of the sheet. Reprinted from ref. 49 with permission from Nature Publishing Group, copyright 2015. (b) A stretchable supercapacitor with customizable stretchability enabled by kirigami design, which shows a cyclability up to 1000 cycles of 400% strain. Reprinted from ref. 50 with permission from Wiley-VCH, copyright 2018.

the increase of source angle between sun and solar cells. By mounting the crystalline gallium arsenide (GaAs) photovoltaic cells with the kirigami tracking structures, this dynamic trackers can tilt the solar panels with a precise control within $\pm 1^\circ$ enabled by the linked bars under strain. Therefore, an increased efficiency of 20~40% was realized by tilting the solar panels into an angle at normal incidence with larger effective area. The installation is quite easy to achieve without cumbersome support system. This case demonstrates that proper mechanical design can provide creative and effective solutions. Specifically, the increased coupling efficiency by integrating structural design is the key parameters to evaluate the smart photovoltaic system. Besides this solar system, mechanical metamaterials were reported to tune the optical beam steering and diffraction gratings.

The other case which kirigami strategy plays an important role to obtain desired function is the editable supercapacitor (Fig. 10b) with programmability. With the development of stretchable electronics, the demand to realize stretchable energy devices is important to fit with other stretchable components like stretchable sensors and electrodes. A stretchable supercapacitor was reported to be edited into

honeycomb-like structures, pyramid pop-up structure, living-hinge structure, and so on for stretchability in an arbitrary direction.⁵⁰ The electrodes of this supercapacitor compose of CNTs and ultralong MnO_2 nanowires sandwiched by nanocellulose fibers, which render the electrodes high robustness, high energy density and editability. The capacitor has a specific capacitance of 227.2 mF cm^{-2} and a stretchability up to 500% without degradation of electrochemical performance. This is the highest value of stretchability of the state-of-art stretchable supercapacitors. The capacitance can be maintained after 10,000 cycles of stretch of 400% and release. Same approach through structural design to obtain stretchability of other energy harvesting devices, which further supports the versatility of this method.

The abovementioned cases prove that the mechanical designs can play an important role to acquire new functions. The proactive design concept inspires more innovation and value-added functions for future intelligent devices.

4. Conclusions

To summarize, the proactive modulation concept from materials to devices, should be those new materials composite, integrated devices with desired mechanics that we create based on the known theories including mechanics of materials, molecular structures and physical structures. Either from materials aspect or devices level, the realization of expected functions such as mechano-responsiveness, unconventional mechanical behaviours, higher efficiency and mechanical stretchability are explosive when we grasped the laws. The arrival of the age of artificial intelligence can be augmented by material science from the perspective of materials strategy and device system. From materials and devices point of view, we are generating of new ideas, materials and devices with unconventional functions. Challenges for proactive modulation lie on building up more common rules and models and designing more intelligent devices for broader applications. At the same time, how to realize multiscale fabrication for tangible application especially multipixel arrays needs to be considered and is limited by the development of related techniques. The mutual promotion between materials and mechanics has become a synergy to further progress in fundamental theories as well as materials/devices innovation. The upcoming field of mechanomaterials undoubtedly is to be flourished by the efforts to further explore the interaction between materials and mechanics, which is an unpredictable future in a predictable manner.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank the financial support from the National Research Foundation, Prime Minister's office, Singapore, under its NRF Investigatorship (NRF-NRFI2017-07) and Singapore Ministry of Education (MOE2017-T2-2-107).

Conflicts of interest

There are no conflicts to declare.

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