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The new material science towards sustainable robotics

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The new material science towards sustainable robotics

Wusha Miao and Hedan Bai*

Sustainable robotics is an emerging field of research that aims to develop robotic automation solutions to address the United Nations' Sustainable Development Goals. The material-centric approach to sustainable robotics focuses on designing robots with novel sustainable materials starting from natural or recycled raw materials, demonstrating self-healing reusability, and eventually recycled, upcycled, or biodegraded with minimal environmental impact. The ultimate goal is to realize a physical robotic embodiment with a circular life-cycle. This perspective highlights recent advances in material science, ranging from self-healing materials to biodegradable and recyclable materials, which serve as the foundation for this emerging class of robots. We then showcase examples of functional material integration in sustainable robotic components and discuss challenges and opportunities towards an entirely sustainable robotic system.

1. Introduction

As humanity is nowadays faced with the ever-pressing challenge of climate change, robotic automation plays an increasingly important role in achieving the United Nations' Sustainable Development Goals. The new material science of sustainable robotics emerges at a time when the society's needs for

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automation and sustainability become ever more demanding and intertwined. For example, while the wide adoption of industrial robotic automation has greatly improved efficiency and promoted green transformation of enterprises in the manufacturing sector,[1] the entire life-cycle of each robot should also be taken into account when considering the circular economy of the society as a whole to validate further prevalence.[2] On the other hand, robotic automation explicitly towards environmental ends (*e.g.*, pest control, pollution cleanup, pollination, *etc.*) provides opportunities to address

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climate change and biodiversity loss in much more efficient and advanced manners.[2] Such a scheme, however, would require a large-scale deployment of robots to sample, monitor, or influence the environment that sustainability of the robots themselves become a major concern. At multiple fronts underpinning the request for simultaneous automation and sustainability is a new framework that creates robots entirely from sustainable materials (*i.e.*, natural/recycled raw material, self-healable and reusable, and biodegradable/recyclable) with advanced robotic functions to serve sustainable causes.

Conventional robots assemble mechatronic components composed of rigid materials (*i.e.*, metals, plastics) into sophisticated functional modules for robotic actuation, sensing, and control. The sustainability challenge, therefore, is comparable, if not more pronounced due to the complex construction, to electronic wastes. Alternatively, soft robotics is a maturing field that adopts a bottom-up approach to drive robotic advances with material innovations. Emulating the material composition of living organisms where soft materials occupy a majority of the body mass, soft robotics uses soft materials (*i.e.*, hydrogel, silicone, polyurethane elastomers, *etc.*) to create novel actuation, sensing, and control mechanisms for a goal of advanced robotic physical intelligence. From the sustainability perspective, the new material science of sustainable robotics naturally echoes with the approach of soft robotics, as (i) soft materials have seen rapid progress in the expanding material and mechanism library that addresses sustainability (*e.g.*, self-healing, recyclable, biodegradable); (ii) design paradigm for functional actuation, sensing, and control mechanisms in soft robotics could be smoothly translated to sustainable robotics.

An ideal circular life cycle of a sustainable soft robot (Fig. 1) would entail (i) starting with a raw material that is either natural or recycled; (ii) self-heals once damaged to enable reuse; (iii) biodegrades or can be recycled/upcycled at the end-of-life. As the exciting sustainable organic material library burgeoning in recent years, functional sustainable materials start to spur the growth of green electronics and spark the development of sustainable robotics.[3] Even in its nascent stage, soft robotic components have already addressed certain aspects of a sustainable cycle (Fig. 1). In this perspective, we will discuss sustainable materials and mechanisms to achieve a circular robotic life-cycle and show examples of soft robotic devices tackling different parts of this cycle. At last, it is worth noting that as we start to build robots with sustainable soft materials, not only could we address sustainability challenges, but also bring opportunities to advance robotic intelligence to become closer to living organisms. In essence, we can use sustainable materials to improve robots' ability to survive, reconfigure, and adapt without supervision.

2. Use and reuse by self-healing

Inspired by living organisms which can heal and recover from injury, self-healable robots would reuse and refunction after damage with expanded lifetime. Self-healing function in robots

Fig. 1 The life cycle assessment of sustainable soft robots. Three main phases are classified from cradle to grave. Raw materials that are natural or recycled and manufacturing encode the original sustainable character at the start-of-life. Self-healing enables to reuse and refunction from damage at the middle-of-life. Degradable and recyclable allows degradation and recycle into a new life at the end-of-life instead of being discarded directly. Reproduced from ref. 4; Copyright 2023, Springer Nature. Reproduced from ref. 5; Copyright 2020, Springer Nature. Reproduced from ref. 6; Copyright 2022, the American Association for the Advancement of Science. Reproduced from ref. 7; Copyright 2023, Springer Nature. Reproduced from ref. 8; Copyright 2023, the American Association for the Advancement of Science. Reproduced from ref. 9; Copyright 2017, the American Association for the Advancement of Science.

brings two exciting opportunities to address challenges in autonomy and sustainability. First, autonomy against damage could greatly expand robust robotic operation from well-defined environments (*e.g.*, assembly line) to dangerous and remote locations (*e.g.*, space, deep sea). Robots' ability to self-heal without human intervention is invaluable especially during hazardous operations, involving for example, radiation, explosion, falling objects and toxic contamination, or remote explorations, such as space and deep sea, where human access costs great expenses.[10] Second, resilience to damage could allow waste reduction, bearing substantial significance for sustainability of industrial robots vastly deployed across different industries at an increasing speed. At its infant stage, the development of self-healing robots emerged from self-healing materials, is now advancing into functional materials and robotic devices, and will one day enable self-healable, autonomous robotic system. In this section, we will discuss the underlying self-healing materials and mechanisms and recent progress in self-healing robots with the bottom-up materials innovation.

2.1 Self-healing materials and mechanisms

Beginning with novel materials, self-healing polymers[11] are good choices for soft robotic design towards reusability from damage. Three approaches for self-healing are developed and demonstrated in Fig. 2a.[12,13] Encapsulation and cardiovascular network can be grouped into extrinsic self-healing.[14] Damage could trigger the rupture and release of the pre-embedded

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healing agent to react and repair. The difference between capsule and vascular network lies on the store of healing agents which are embedded in discrete capsules or interconnected channels, respectively. This correspondingly leads to singular or multiple local repair by the delivery of healing agents *via* channels. Notably, extrinsic self-healing allows a large-scale damage to be repaired by the flow and fill of healing agents at the interface without the need of intimate contact. For the evaluation of self-healing performance, healing rate and efficiency are key characters. In detail, healing rate highly depends on the polymerization rate of healing agents. Healing efficiency quantitatively determines the extent of restore of a particular material properties after healing. Amongst, mechanical properties (strength, elongation, and *etc.*) before and after repair are crucial to define healing efficiency. In terms of practical application, the stability and reliability of healing agents are important aspects to consider, which have stringent requirements for the compatibility of the healing agents and the matrix. Furthermore, extrinsic self-healing materials are generally limited to hard and brittle matrix (average 10° GPa level of elastic modulus and <10% elongation at break) due to the demands for rapid break and rupture of embedded healing agents induced by crack, which could not be ideal material choice for soft robots. These aspects could be compensated by intrinsic self-healing without any external reagents.
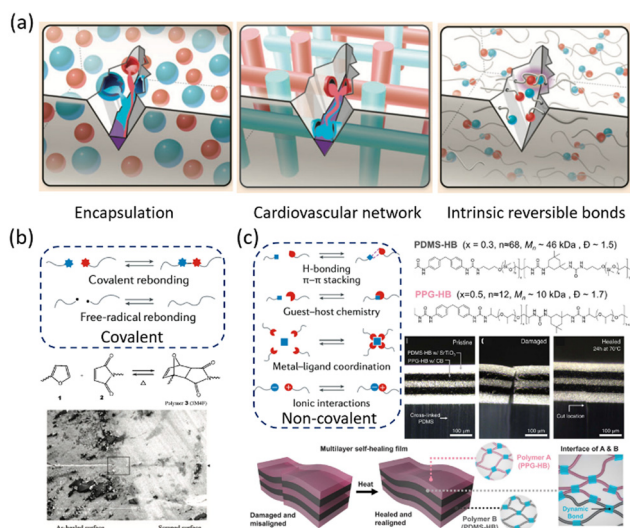

Fig. 2 Self-healing materials and mechanisms. (a) Three approaches for self-healing. From left to right shows the mechanism of encapsulation, cardiovascular network and intrinsic reversible bonds.[12] Reproduced from ref. 12. Copyright 2010, Annual Reviews. (b) Self-healing based on dynamic covalent chemistry. The scraped surface could be self-healed by intrinsic dynamic Diels–Alder exchange reactions at the interface upon heating (120 °C).[11,15] Reproduced from ref. 11; Copyright 2020, Springer Nature; reproduced from ref. 15; Copyright 2002; the American Association for the Advancement of Science. (c) Self-healing based on dynamic non-covalent chemistry, including H-bonding, π–π stacking, guest–host chemistry, metal–ligand coordination and ionic interaction.[11] Multi dynamic layers could be autonomously self-aligned *via* phase separation and healed by association and dissociation of hydrogen bonds.[16] Right: Chemical structures of different layers. Reproduced from ref. 11; Copyright 2020, Springer Nature; reproduced from ref. 16; Copyright 2023, the American Association for the Advancement of Science.

Intrinsic self-healing relies on the breakage and reformation of reversible bonds,[17] which can be generally categorized into two types, covalent and non-covalent, differentiated by the feature of dynamic bonds (Fig. 2b and c).[11,18] For dynamic covalent chemistry, bonds are covalently linked, but can undergo dynamic bond exchange reaction to achieve self-healing. Two types (covalent and free radical rebonding) are illustrated in (Fig. 2b). In comparison, free-radical rebonding could easily suffer from deactivation due to oxygen and moisture in the open environment, that negatively affects healing performance. The more stable process of covalent rebonding allows to achieve self-healing with higher repair efficiency. Fig. 2b shows the first example of intrinsic self-healing achieved by dynamic Diels–Alder (DA) bonds.[15] Triggered by heat, DA adducts (3M4F) would break above 120 °C that activates the mobility of polymer chains at the rubbery state to repair the scraped surface. The significant advantage of dynamic covalent chemistry is that it offers comparable bonding strength with common covalent bonds, which are suitable matrix to design strong and tough healable materials. The mechanical strength could be programmed from 10^5 Pa to 10^8 Pa. Herein, external stimulus (heating) is necessary to trigger the break and reform of DA bonds, which could be termed as non-autonomous self-healing. Instead of heating, other triggers including light, pH and mechanical force are explored by delicate chemistry design.[19,20] In contrast, autonomous self-healing allows the process to proceed without external intervention, which is enabled by spontaneous dynamic bonds. For example, aromatic disulfide bonds can undergo dynamic exchange reactions without any triggers due to the resonance stabilization and steric effect of benzene rings.[21] This would offer unprecedented opportunities to soft robots that can autonomously recover from damage.

Compared with dynamic covalent chemistries, supramolecular (noncovalent) bonds that are linked by electrostatic interaction, van der Waals forces can break and reform more easily, which offer more flexibility in material design (Fig. 2c).[22] For instance, hydrogen bonds based on electrostatic attraction can form between various atoms and functional groups, such as oxygen, nitrogen, and fluorine. Owing to the intrinsic character of non-covalency, the strength of hydrogen bonds is generally weaker than covalent bonds. However, it could bring in high tunability of their strength. Combing multiple types of hydrogen bonds of different strength, strong and stretchable materials can be achieved. In detail, Bao *et al.* demonstrated a supramolecular elastomer with excellent mechanical properties (high stretchability of 1200% and high toughness of 12 000 J m^{-2}) by utilizing multi-strength hydrogen bonds.[23] Two types of hydrogen bonding are formed in the network between aromatic/aliphatic nitrogen and hydrogen groups, which are cooperative (strong) and anti-operative (weak), respectively. At the same time, autonomous self-healing was achieved by the intrinsic hydrogen bond, even under artificial sweater. Furthermore, the geometry and distance of hydrogen bond strongly influence its strength. Distinguished from conventional linear hydrogen-bonding, zigzag-array of dense hydrogen bonds make it possible to synthesize mechanically robust (~1.4 GPa of elastic modulus) yet readily healable polymers.[24] The versatility and flexibility of hydrogen

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bonds offer the benefit of material programmability and therefore, are attractive for use as robotic materials with diverse molecular design possibilities. For example, leveraging hydrogen bonds on two immiscible backbones, multiple dynamic layers could automatically self-align *via* phase separation and self-heal by association and dissociation of hydrogen bonds at the interface[16] (Fig. 2c). In addition, other types of non-covalent chemistry, including host–guest bonding, metal–ligand coordination and ionic interaction also enable readily accessibility and ease programmability. For example, the coordination strengthen of metal–ligand bonds could be programmed by introducing different metal ions and ligands, which results in tuneable dynamic mechanical properties.[25–27] Furthermore, ion dipole interaction between ionic liquids and fluorinated polymers is another type of ionic interaction that have been successfully developed as ionic conductors for soft sensors.[28] The easily broken and reformed dynamic supramolecular bonds could proceed without external intervention, enabling fast and autonomous self-healing. The dynamic nature of both covalent and supramolecular dynamic bonds, however, leads to severe viscoelasticity, which creates undesired effects in robotic actuator and sensor performance, as we will discuss in later sections.

2.2 Self-healing soft actuators and sensors

From the application perspective, the significant challenge for intrinsic self-healing materials is viscoelasticity, which causes drift in actuating/sensing function of soft robotics due to the dynamic character of reversible bonds under various dynamic loading conditions. Healing rate and efficiency are governed by dynamic bonds and mobility of polymer chains. In detail, the rapid breakage and reformation of dynamic bonds and appropriate fluidity of polymer chains enable excellent healing rate and efficiency. However, this leads to severe viscous characteristics such as creep and stress relaxation that could be limitation on robotic application, whose requirements for mechanical properties are demanding and strongly correlated with actuating/sensing. For instance, actuators integrated with sensors undergo various dynamic mechanical deformation to perform functions. Precise and reliable robotic control would demand highly repeatable sensing and actuation performances, demanding the constituent materials to be free of time/loading-variant viscous properties. Therefore, the trade-off between self-healing performance and viscous characteristics should be systematically balanced and optimized. Nevertheless, the advances on self-healing polymers open up a new avenue to soft robots,[29] which endows high sustainability and reliability.

One way to achieve self-healing actuator is through macroscopic integration of self-healing materials with existing soft robotic actuation mechanisms. Fluidic elastomer actuators (FEA) based on mechanical deformation triggered by fluid pressure are widely explored due to ease fabrication. In a self-healing FEA, a biosynthetic protein could recover from micro and macro-level damage within seconds enabled by optimized network morphology (Fig. 3a).[30] Herein, hydrogen-bonded β-sheet nanostructures are served as physical crosslinks to offer adequate mechanical strength. The easily broken and reformed
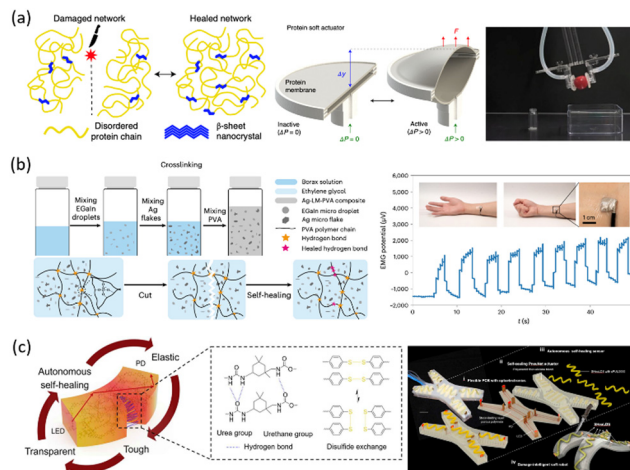

Fig. 3 Self-healing soft actuators and sensors. (a) Pneumatic actuators built from biosynthetic protein with optimized hydrogen-bonded β-sheet nanostructure and network morphology to balance healing efficiency and viscoelasticity for soft grippers.[30] Reproduced from ref. 30; Copyright 2020, Springer Nature. (b) Electrical sensors based on an organogel composite with conductive particles embedded in. Spontaneous mechanical and electrical self-healing can be achieved by hydrogen bonds and reconnection pathways of conductive particles, respectively.[7] Reproduced from ref. 7; Copyright 2023, Springer Nature. (c) A damage intelligent soft-bodied system as the optomechanical sensor fabricated on self-healable, transparent and tough polyurethane in combination of dynamic hydrogen bonds and aromatic disulfides.[6] Reproduced from ref. 6; Copyright 2022, the American Association for the Advancement of Science.

multiple hydrogen bonds enable chain diffusion to achieve fast self-healing. The exquisite material design allows to balance the competition between healing efficiency and mechanical strengthen for soft grippers. The post-healing strength could reach up to 23 MPa after extremely limited healing time (1 s). At the same time, 400% actuation performance and 5 N output force can be achieved for grippers. Beyond, electroactive actuators exploit Maxwell stress to induce expansion/contraction under electrical stimuli. An interesting example is hydraulically amplified self-healing electrostatic (HASEL) actuators, where liquid dielectric substitutes solid elastomer as the dielectric material in electroactive actuators to enable self-healing from electrical breakdown.[31] With different geometry design, HASEL can achieve various actuation modes with muscle-like performance under electrostatic and hydraulic forces. Another method to encode self-healing ability in actuators is *via* microscopic molecular design. Self-healing dynamic bonds are introduced into stimuli responsive networks that generate actuation upon stimulus such as heat, light, electrical, chemical, magnetic and acoustic, allowing remote control of untethered soft robot to operate in remote or inaccessible environments.[32] More recently, dynamic covalent network polymers that exhibit solid-state plasticity to allow shape-morphing are drawing increasing attention.[18,33] Instead of reshaping at fluidic state, permanent shape reconfiguration can be achieved at solid state by dynamic bonds exchange to relax internal stress. The reshaping process proceeds without need of traditional shaping moulds that allows access to more complicated shapes. For

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example, by incorporating dynamic ester bonds, dielectric elastomers with the ability to be manipulated into arbitrary 3D geometry could achieve multimodal motions, rather than planar expansion/contraction, in dielectric elastomeric actuators.[34] It is predicted that dynamic bonds could allow shape-morphing and self-healing at the same time owing to intrinsic dynamic bonds exchange. This would enable promising application on self-healable robots with multimodal motions that can perform complex tasks in complex environments.

Liquid-crystalline based actuators are widely exploited due to ease operation and large deformation. From a molecular level, the underlying actuation mechanism relies on reversible liquid crystalline phase change that results in macroscopic deformation.[35] For instance, triggered by light, azobenzene liquid crystals can undergo reversible *cis–trans* isomerization that offer the advantage of photomechanical motion. An azobenzene-containing liquid crystalline polyurethane was synthesized to exhibit light-driven actuation. At the same time, the intrinsic hydrogen bonding between urethane bonds enables self-healing with muscle-like performance.[36] Besides, actuators based on bilayer structures are also explored due to ease of programmability. The underlying mechanism is that composites have totally different responses (thermal expansion coefficient, solvent absorption, and *etc.*) between bilayers.[37–39] A robust, healable robot with noncovalent assembled gradient nanostructures is designed to exhibit light-triggered locomotion, resulted from the mismatch of volumetric changes between the upper and bottom sides.[37] Multiple hydrogen bonds enable high self-healing efficiency (89%) at room temperature.

In contrast to actuators that undergo mechanical deformation upon stimulus, sensors can detect physical and chemical signals as soft electronics. The sensing function is principally attributed to the change of resistive and capacitive under triggers, which are determined by intrinsic conductive polymers (*e.g.*, polypyrrole PPy, poly(3,4-ethylenedioxythiophene) PEDOT, and polyaniline PANI) or embedded conducting fillers (*e.g.*, metallic particles, ionic liquid, carbon nanotubes and graphene). Herein, the requirement for material substrate is demanding that it should have robust elasticity, high healing efficiency and good compatibility with conducive particles, which determines the reliability and stability of sensing signals. Dynamic bonds enable self-healing efficiency that the function of sensing should keep unchanged before and after damage, however, unavoidably leads to unwanted viscoelasticity that causes drift and hysteresis to impedes the accuracy of signals. And autonomous self-healing is preferable, where external stimulus (high temperature) to trigger dynamic bonds reaction could adversely affect electrical percolate network. Therefore, the design of dynamic chemistry should be carefully considered. To achieve the goal, an organogel composite with electrically conductive silver microflakes and liquid metal microdroplets embedded was synthesized to enable high conductivity (7×10^4 S m^{-1}) and stretchability ($>400\%$) with potential application in soft circuits and reconfigurable bioelectrodes (Fig. 3b).[7] Herein, mechanical healing was enabled by reformation of dynamic hydrogen bonds with healing efficiency up to 96.4%. And electrical healing was achieved *via*

reattach and reconnection between neighbouring electrical particles to restore conductive pathway with 95% healing efficiency. Beyond inorganic metallic particles, ionic liquids are a type of ion conducive monomers that also could be suitable candidates for electrical sensors.[40,41] An ion conductor with ion-mediated-cluster exhibits fast self-healing efficiency 90% within 1 min *via* quick formation of ion clusters between ionic liquids and charged units in polymers.[41]

Parallel to soft electrical sensors, soft optical sensors present an emerging sensing platform that leverages the broad bandwidth of light and its interaction with soft materials to achieve robust, multimodal robotic/tactile sensing performance.[42] Optical waveguide presents a simple embodiment of such sensor, which consists of an elastomeric dielectric core with higher refractive index surrounded by an elastomeric cladding with lower refractive index (which can also be air). Soft optical sensors are intrinsically compatible with self-healing functions since (1) the simple construction does not require conductive materials and thus circumvents the stringent requirement of realignment of conductive pathway; and (2) light can overcome small gaps and continue propagation in a waveguide and therefore allows more robust self-healable sensing signal. For self-healing soft optical sensor, the material requirement is much simpler to enable self-healable signal-dielectric soft material with high transparency. To simultaneously achieve good sensing performance, on the other hand, requires much more elaborate design, as in the case with soft electrical sensors. Fig. 3c demonstrates a self-healable soft optical sensor composed of self-healing polyurethane–urea (sPUU) that is not easily broken (high toughness, ~ 60 MJ m^{-3}), autonomously self-heals rapidly, and measures dynamic motions reliably (no drift, non-hysteric).[6] The combination is achieved through both multi-strength dynamic bond molecular design and structural engineering. To achieve a fast and strong self-healing material, hydrogen bonding for fast self-healing and aromatic disulfide bond for autonomous and strong self-healing are combined in the system. To address hysteresis and drift problems under cyclic loading caused by the viscoelasticity of dynamic bonds, sPUU adopts a wavy shape to leverage structural compliance to realize entirely elastic response, enabling reliable dynamic sensing performance for robotic motion feedback. The optical sensor could detect damage, as well as recover signal from severe damages, such as multiple cuts or material removal (punctures). Demonstrated on a soft quadruped, the self-healing optical sensor enables robotic intelligence towards damage, where it senses injury, self-heals, and adapts to the adverse environment. Up to date, efforts are progressively devoted to self-healing robots with material innovation that can recover and reuse even under harsh environments.[43,44]

3. Biodegradation and recyclability at the start/end-of-life

For a life cycle assessment of robots, raw material at the start-of-life determines its lifetime sustainability, as the original and intrinsic character of resource encodes biodegradation and

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recyclability at the end-of life. Biodegradability and recyclability are of particular interest to robotic applications in two aspects: reduced lifecycle carbon emission of industrial robots, and robotic automation in environmental health monitoring and intervention. Similar to self-healing function in industrial robots that prolongs operational lifetime, recyclability of the expansively deployed industrial robots (*e.g.*, robotic assembly lines) boosts sustainability by allowing reuse of waste materials at the end-of-life. Building industrial robots with raw materials that come from renewable or recycled sources could further reduce carbon footprint. For environmental health monitoring, robotic automation could greatly improve efficiency by mapping information to allow targeted intervention. This, however, would require large-scale deployment of robots, which, in turn, would create sustainable challenges itself. Biodegradability of robots, for this application, becomes substantial. In this section, we will discuss the development of biodegradable and recyclable robots enabled by intrinsic properties of materials.

3.1 Biodegradable and recyclable materials and mechanisms

Biodegradable materials decompose in natural environments through enzymatic or hydrolytic processes without imposing ecological harm during the process (Fig. 4a).[45] Functional devices, and one day, robots, built with such materials bring the opportunity to deploy intelligent machines at large scale for various operations, which then eventually biodegrades in nature at the end-of-life without creating waste. The material library for biodegradable functional devices has been rapidly growing in the past decade. One field that has spurred this development is bioresorbable implants for transient clinical applications,[46-48] where bio-absorption (*i.e.*, metabolization within an organ) follows biodegradation.[49] We refer the readers to ref. 46-52 for detailed review in this topic, and only highlight a few material examples of interest here. In general, biodegradable materials consist of natural or synthetic polymers, as well as hydrolyzable inorganic materials that can serve as insulator, semiconductor and conductor. Biobased (*e.g.*, cellulose, gelatin, alginate and polyhydroxybutyrate PHB) and synthetic polymers (*e.g.*, poly(lactic-*co*-glycolic acid) PLGA, polyvinyl alcohol PVA, polycaprolactone PCL and polyethylene glycol PEG) are typical insulators for transient electronics. Bioresorption mechanism can be mainly divided into physical dissolution interacted with water and chemical depolymerization that involves enzymatic, hydrolytic and oxidative reaction to break and cleave chemical bonds in the polymer chain. For example, naturally derived silk can full degrade *via* dissolved into water in 4 weeks in phosphate-buffered saline (PBS) at 37 °C.[50] Synthetic polymers usually undergo chemical depolymerization with degradation rate from several days to years that depends on chemical composition, network morphology (crystallinity) and level of hydrophobicity. In addition, metal oxides and nitrides (SiO$_2$, Si$_3$N$_4$, MgO) can serve as inorganic insulators that degrade *via* hydrolysis from 10^{-1} to 10^1 nm day^{-1} under physiological conditions. Regarding conductors, metals and alloys (*i.e.*, Mg, W, Mg-based alloy) are well exploited as electrodes that can degrade vis electrochemical oxidation. An attractive alternative is conducting polymers (CPs)
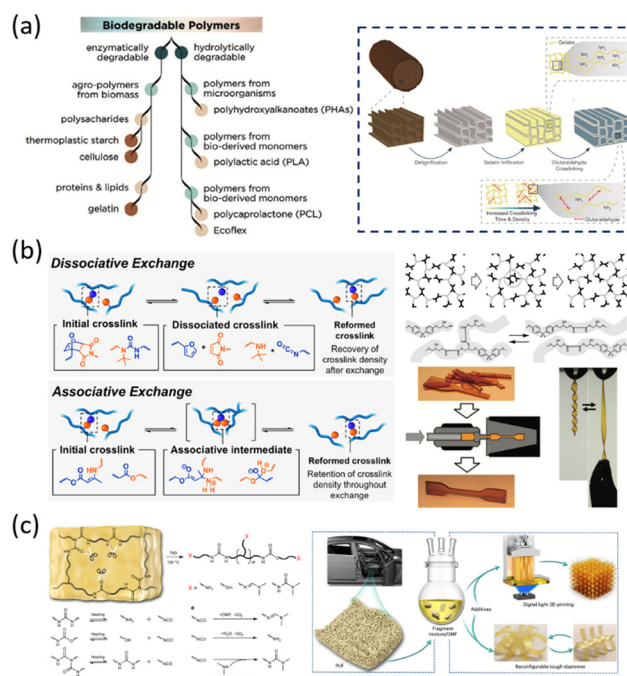

Fig. 4 Biodegradable and recyclable materials and mechanisms. (a) Classi-fication of biodegradable polymers.[45] Right: The synthetic process of a bio-composite with delignified wood and gelatin hydrogel to exhibit a wide range of mechanical strength (1.2–18.3 MPa) and stiffness (170–1455 MPa) that can be suitable matrix for soft machines.[54] Reproduced from ref. 45; Copyright 2021, John Wiley & Sons; reproduced from ref. 54; Copyright 2023, Elsevier. (b) Recycling enabled by dynamic covalent bonds. Left: Two distinct exchange (dissociative & associative) pathways.[55] Right: Malleable thermoset epoxy network due to transesterification triggered by heating and catalyst.[56] Reproduced from ref. 55; Copyright 2019, American Chemical Society. Reproduced from ref. 56; Copyright 2011, the American Association for the Advancement of Science. (c) Chemical upcycle of polyurethane foams into reconfigurable elastomers and 3D printable resins with the addition of various network reforming monomers during upcycle process.[4] Reproduced from ref. 4; Copyright 2023, Springer Nature.

including PPy, PEDOT and PANI. We note that CPs with con-jugated backbones are chemically reliable and stable that cannot degrade under physiological environments. To address the issue, three methods have been explored to achieve different level of biodegradation through conjugated network design and fabrica-tion. (I) Physical blends and coating of CPs into insulating bioresorbable hosts (above polymer insulators). Herein, degrada-tion rates rely on the bioresorbable matrices. (II) Chemically modifying or integrating CPs with biodegradable materials. For example, cleavable ester groups are chemically introduced into pyrrole monomers to synthesize PPy that can reach 27% weight loss after 80 days (PH 7.2, 37 °C).[51] (III) Copolymerization between conducting prepolymers (*e.g.*, aniline and pyrrole oligomers) and degradable segments with cleavable bonds such as ester, urethane and acid groups. A bioresorbable and conducive copolymers with aniline trimers as electroactive elements and PCL as degradable segments can undergo enzymatically degradation with 24% weight loss over 14 days in a physiological condition.[52] For semiconductors, the wide-applied silicon is biodegradable *via* hydrolysis at nanoscale, which establishes significant foundation

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for transient electronics. Up to date, various silicon nanostructures (nanofilms, nanowires, nanorods and *etc.*) are exploited, whose degradation rates strongly depends on geometry, type and amounts of doping into silicon and surface chemical features. Monocrystalline silicon nanofilms degrade at ~ 2–5 nm day^{-1} in a physiological condition.[53] Progress on above bioresorbable materials including natural-derived & synthetic polymers and inorganic matrices provides unprecedented opportunities for transient electronic.

In regards of degradable soft actuators and sensors, biodegradable elastomers are ideal material substrates with programmable degradation performance and mechanical properties.[57] Naturally derived polymers like gelatin, alginate and cellulose offer the advantage of renewable sources and cytobiocompatibility with lower carbon footprints. Fig. 4a demonstrates that an anisotropic bio-composite with combination of different bio-based matrix (delignified wood and gelatine hydrogel) was synthesized across a broad strength and stiffness range (1.2–18.3 MPa and 170–1455 MPa, respectively),[54] which would be a capable material for building biodegradable soft machines. Beyond, synthetic elastomers that have cleavable bonds such as ester, amide and anhydrides in the backbones can undergo enzymatic or hydrolytic degradation. Among them, thermoplastic elastomers are physically cross-linked that polymer chains have enough mobility to flow above glass transition temperature (T_g) or melting temperature (T_m), which offers good (re)processability, yet unreliable mechanical performance with time and temperature. In comparison, thermoset elastomers with chemically cross-linked network enables reliable and stable functions, which in turn loss processability once cured. It is worthwhile to note that synthetic elastomers with biodegradability provide highly programmability of mechanical, optical and dielectric properties for robotic applications from the bottom-up micromolecular synthesis.

In contrast to degradation, recycling allows materials to be cycled and reused at the end-of-life. Physical recycle involves mechanical process (*e.g.*, grinding, shredding, compressing). The process is generally limited to thermoplastic resins and undergoes through high shear force, high temperature and high pressure, which unavoidably leads to polymer chain breakage with significantly decreased qualities and properties compared to the virgin material.[58] By contrast, chemical recycling allows thermoset to become malleable by incorporating dynamic covalent bonds without markedly degradation.[59] Regarding the exchange mechanism, two types (dissociation and association) of dynamic bonds are illustrated, where the distinction is characterized by crosslinking density during exchange[55] (Fig. 4b). For dissociative bonds such as Diels–Alder adducts and hindered ureas, crosslinking density decreases as a result of the sequential bond breakage and reformation process in the exchange reaction; associative exchange (transesterification, olefin metathesis and dioxaborolane) maintains constant crosslinking density through the formation of intermediate. Pioneered by Leibler's team, thermoset epoxy can be reprocessed *via* dynamic ester bonds exchange.[56] The epoxy materials with mechanical strength 55 MPa are insoluble and robust at room temperature, however reshaped and reprocessed at high temperature ($>200\ ^\circ$C) enabled

by transesterification under catalysts. The key feature of the malleable material is that it exhibits Arrhenius-like gradual viscosity variations like vitreous silica. Therefore, "Vitrimer" is defined to distinguish these materials from common polymers whose viscosity varies abruptly near the glass transition.[60] This offers significant advantages that reshape programming can be proceeded in a local region to achieve sophisticated shapes, which unleashes limits from conventional shaping moulds. The intrinsic reshape and recycle characters of vitrimers initiate unexplored opportunities to sustainable robots.

Beyond recycling, upcycling that transforms unwanted waste into materials with higher quality or value have attracted continuous attention.[61,62] It allows upcycled materials to exhibit superior properties that could be endowed with new functionalities. For example, commodity polyurethane foams have been demonstrated to chemically upcycle into reconfigurable tough elastomers and high-performance 3D photo-printable resins[4] (Fig. 4c). In this process, polyurethane waste was chemically fragmented into a dissolvable mixture triggered by heating (120 $^\circ$C) and catalyst, which can be transformed into high value products with the addition of various network reforming additives. Upcycled polyurethane elastomers exhibit a mechanical strength of 22 MPa and a toughness of 67 MJ m^{-3}, the remarkable improvement to the directly compression-moulded films with <5 MPa mechanical strength and <2 MJ m^{-3} toughness. Notably, the underlying upcycle mechanism that depolymerize urethane, urea and biuret bonds into functional alcohol and amine groups could be versatile to other polyurethane polymers. With various additives, upcycled materials could be programmed with new functionalities, showing promise as raw materials for next-generation upcycled robots.

3.2 Biodegradable and recyclable soft actuators and sensors

Continuous progress has been achieved for sustainable robots with advances in above biodegradable and recyclable materials. Apparently, the mechanical requirement for actuators towards biodegrade and recycle is the same as self-healable actuators, which adequate strength, toughness and elasticity should be basically fulfilled to undergo repeated and controllable shape deformation under triggers. Natural-derived materials are ideal candidates due to the intrinsic feature of biodegradation. Among them, gelatin is widely explored because of versatility in the fabrication. A gelatin-based biogel combines outstanding elastic properties ($\sim 10^{-1}$ MPa of mechanical strength and $\sim 200\%$ of stretchability) and fully degradation *via* enzymatical process at dispose (<10 days in wastewater).[5] To overcome dehydration in the open-air condition, large amounts of water were replaced with non-volatile glycerol that shows stability and prolongs the use time. The s-shaped pneumatic actuators were built as a gripper with tuneable movement (Fig. 5a). We note that a significant challenge for biobased materials lies in poor resistance to washing and aging owing to a large number of intrinsic hydroxyl, carboxyl and other oxygen-containing groups, which affects the stability and reliability of robotics. To address the issue, this gelatin-based gel uses hydrophobic biodegradable coating (shellac resins) strategies. Coated biogel

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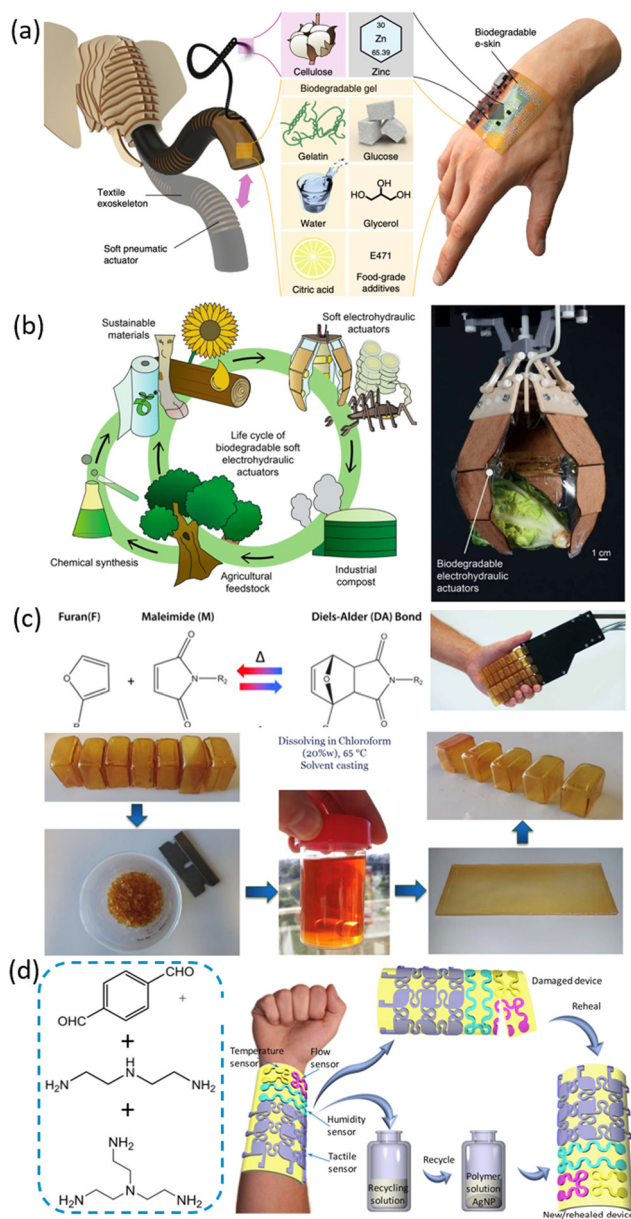*J. Mater. Chem. C*, 2024, **12**, 12721–12733 | **12727**

Fig. 5 Biodegradable and recyclable actuators and sensors. (a) Gelatin-based biogels with outstanding elasticity ($\sim 10^{-1}$ MPa of mechanical strength and $\sim 200\%$ of stretchability) and fully degradation (<10 days in wastewater) for soft actuators and electronics.[5] Reproduced from ref. 5; Copyright 2020, Springer Nature. (b) Electrohydraulic actuators systemically built from various biodegradable materials that involves NaCl-infused gelatin as electrodes, vegetable oils as liquid dielectrics and polylactic acid PLA & bio-polyester as insulating layer exhibit good endurance more than 100 000 cycles and comparable actuation performance to nonbiodegradable counterparts.[8] Reproduced from ref. 8; Copyright 2023, the American Association for the Advancement of Science. (c) Recyclable actuators based on dynamic Diels–Alder bonds. The recycle process proceeds via solvent casting upon heating (65 °C).[9] Reproduced from ref. 9; Copyright 2017, the American Association for the Advancement of Science. (d) Recyclable electronics based on transamination and the recycle mechanism can go back into monomers that allows full restore of sensing function before and after recycle.[66] Reproduced from ref. 66; Copyright 2018, the American Association for the Advancement of Science.

shows no signs of degradation after 48 h in water or 24 h in acidic solution. The dissolution of coating layer is only triggered in basic solutions (pH 8.1), then followed by the complete degradation of the biogel. Beyond physical coating, chemical modification is well explored to stabilize biobased materials. For example, carbon–carbon double bonds are introduced to permanently crosslink the network. By utilizing photo-crosslinkable ability of these double bonds, bio-materials could be 3D printable that offers shape freedom with a high-level complexity towards multimodal actuation.[63,64] For instance, biocompatible and degradable micro-swimmers triggered by magnet was built from photocrosslinkable gelatin hydrogel with ~ 15 μm s^{-1} actuation speed.[64] With the systematic integration of various degradable materials that involves NaCl-infused gelatin as electrodes, vegetable oils as liquid dielectrics and polylactic acid PLA & bio-polyester as insulating layer, a biodegradable electrohydraulic actuator was fabricated to enable actuation performance comparable to nonbiodegradable counterparts and good endurance with more than 100 000 cycles (Fig. 5b). Reliable operation under high electric field of 200 V μm^{-1} was achieved, at the same time, biodegradable polymers can disintegrate over 50 days through hydrolytic and enzymatic process in an industrial composting environment.[8] Beyond biodegradability, photodegradable chemistry was exploited to design on-demand lifetime-configurable soft actuator.[65] Triggered by UV light to release catalyst of fluoride species, the PDMS matrix of actuators can undergo depolymerization via Si–O bond cleavage at 120 °C for 30 min.

Dynamic covalent bonds were well studied for recyclability. It is not surprising that self-healing can be achieved simultaneously, due to the same underlying mechanism for the breakage and reformation of dynamic bonds. We note that the requirement of recyclability is more demanding than self-healing, as fully flowability of bulk materials is essential and therefore high pressure ($>10^\circ$ GPa)/plenty of solvents is sometimes necessary to accelerate the mobility of polymer chain. In comparison, self-healing proceeds in a local area (crack or scrape surface) where chain mobility in the bulk solid is sufficient to allow chain interfusion across the damages surface. In a self-healing and recyclable soft pneumatic actuator, Diels–Alder bonds dissolved in solvents enabled material recyclability by shifting the equilibrium towards reactants upon heating[9] (Fig. 5c). However, the recycled material had a slight drop in modulus due to undesired maleimide homopolymerization during the recycling solvent-cast process with heating. The decrease in mechanical properties is not rare, resulted from unwanted side-reaction during recycle process within high temperature and pressure.[67] To address the issue, closed-loop recycle without loss of properties was achieved that can convert synthetic material into raw monomers.[68,69] Anastasaki et al. demonstrated reversible addition–fragmentation chain-transfer (RAFT) polymerization that allows RAFT polymethacrylates to depolymerize back to monomers. Herein, RAFT polymers can generate chain-end radicals to trigger unzipping depolymerization polymers at 120 °C.[68] The novel approach provides intriguing aspects towards close-loop recyclable robotic materials.

Besides biodegradable and recyclable actuators, electronics that can sense multiple signals (*e.g.*, strain, temperature and humidity) are directly built from a biodegradable gel[5] to decompose at the-end-of life. Biogels with different elasticity (1.4, 0.4 and 0.2 MPa) were assembled into graded-modulus bio-matrix that accommodates patterned electrical sensors. Since material viscoelasticity determines sensor performance and material modulus & stretchability determines compatibility with soft actuators or biological tissues, elasticity and adequate stretchability are important parameters in designing material matrix with biodegradable polymers. Fig. 5d demonstrates a fully recyclable electronic device fabricated from dynamic polyimine.[66] The intrinsic transamination allows polyimine to depolymerize into monomers with the addition of primary amines. The recycled solution can be reused to fabricate new electronics by proportionally added monomers and silver nanoparticles. This recycling mechanism that depolymerizes the polymer back to only monomers enables full restore of sensing function before and after recycle.[70] However, the polyimine matrix has a high modulus ($\sim 10^0$ GPa) and low stretchability ($< 5\%$) that could easily fail under large movements when used as electronic skin. Increasing efforts are dedicated to dynamic chemistry that should be readily accessible for robotic materials and avoid obvious performance reduction before and after recycling. Rather than seeking full restore of performance during recycle, upcycle represents a novel approach that materials can be reprocessed into value-added products with superior function. Distinguished from conventional recycling, upcycling makes it possible to refunction commodity plastics with higher value. Future work needs extensive studies on developing more mild and economic methods for upcycle.[71] Undoubtedly, this advance would accelerate soft robots towards further sustainability with the bottom-up material innovation.

4. Renewable energy source and living materials towards integrated sustainable robots

Energy source presents perhaps the biggest challenge in realizing an entirely sustainable soft robotic embodiment, where the whole system is built from materials that are renewable/recycled at the start of life, self-healable during operation, and biodegradable/recyclable at the end of life. Approaches towards sustainable energy source for soft robots could be categorized as (1) system integration of existing sustainable energy solutions, such as biodegradable/recyclable batteries and solar cells and (2) material innovation for sustainable embodied energy. Progress in recycling commonly used lithium-ion batteries, as well as development of biodegradable batteries and super capacitors with an expanding biodegradable material library (*e.g.*, conductor: Mg, Zn, Mo, W; metal oxide: TiO_2, WO_3, MoO_3; electrolytes: phosphate-buffered saline, and various ionic liquids) show promise for use as sustainable energy sources in robotic systems,[72] but their performance (*i.e.*, full recyclability, energy density, capacity) would need improvement for practical sustainable robotic applications.

In addition, advances in photovoltaic cells that convert the largest renewable resource: solar energy into electricity push the boundaries of fully sustainable soft robots further. Biobased polymers substrates (cellulose, chitosan and polysaccharides) as electrolytes, conjugated polymers (*e.g.*, PEDOT and PPy) as electrodes and green fabrication process without use of toxic solvents form the basis of organic solar cells towards degradability, recyclability and eco-friendliness.[73] More extensive studies are devoted to improving photovoltaic efficiency and fully green fabrication.

Alternatively, sustainable energy harvesting and storage possibilities in the form of embodied energy may present exciting opportunities. The term ''Robotic Embodied Energy'', coined by Shepherd *et al.*, describes the design philosophy that the energy storage module, instead of being a stand-alone module, merges with another functional/structural module and distributedly powers local functions.[74] While the original purpose for this design principle is to optimize robotic endurance and operation time, interesting potentials arise for sustainable energy source—if energy harvesting and storage schemes could be embedded in the sustainable material construct of a soft robot, then we would be one big step closer to an entirely sustainable robotic system.

Material innovations would drive this direction of research, and examples of triboelectric nanogenerators and living materials could already show early signs for this vision. Triboelectric nanogenerator (TENG) harvests mechanical energy (touching, rotation, twisting and *etc.*) into electricity by coupling triboelectric effect and electrostatic induction[75] (Fig. 6a). Here, electricity with a peak output power density of ~ 10.4 mW cm^{-3} is generated through PET & Kapton as triboelectric layers and Au alloy as electrodes. Under mechanical compression such as bending, PET is positively charged and Kapton is equally negative-charged due to electrostatic effect, leading to the formation of triboelectric potential interface that drives the flow of charges to generate electricity. Numerous endeavors have been dedicated to increase the output power of TENG, where mainly two approaches including modification of triboelectric materials and optimization of effective contact surface are studied to achieve several tens of mW cm^{-2} for output energy.[76] It is worth noting that synthetic polymers such as PDMS, PTFE, Nylon and PET are commonly used as triboelectric materials to fabricate flexible TENG, which provides highly promise to accommodate and harvest mechanical motions into energy for use as self-powered soft robotic systems. Furthermore, sustainable TENG based on recycled materials such as PET recycled from waste bottles, as well as biobased polymers including cellulose, silk and lignin are explored to achieve recyclability and biodegradability.[77] An interesting example is that dynamic bonds are introduced into TENG to endow self-healing ability,[78,79] which shows highly sustainable prospect for robotic application. For instance, vitrimer based TENG was achieved by incorporating dynamic disulfide bonds to exhibit self-healing and shape adaptability as self-powered electronics[79] (Fig. 6b). In regards of robotic application, the electricity output of TENG should be sufficient and reliable to power the actuating/sensing function of robots. Ongoing
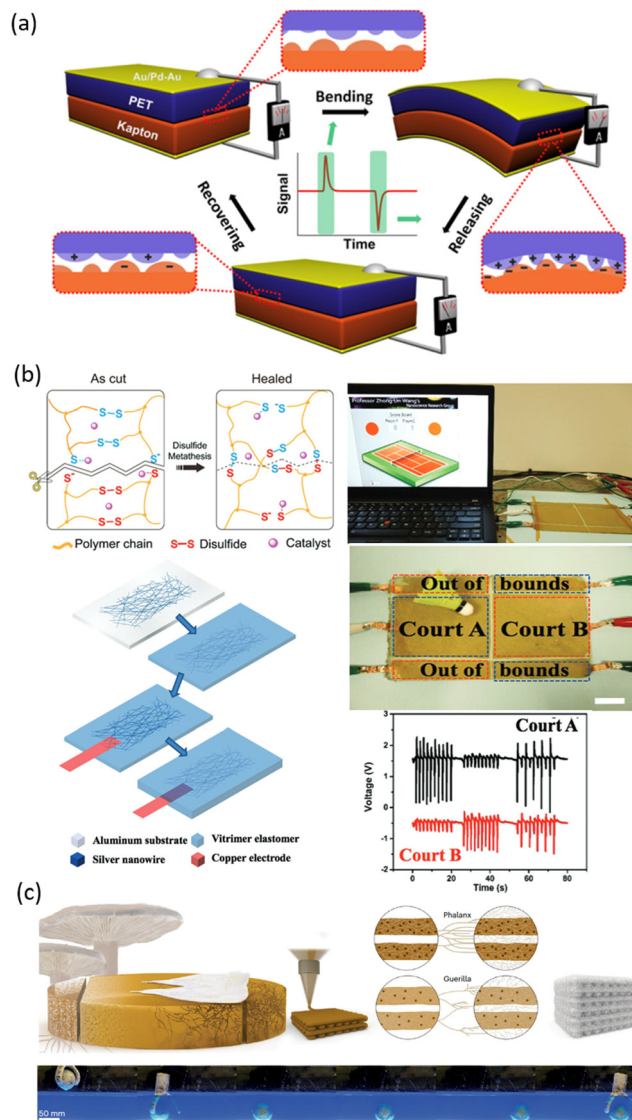
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Fig. 6 Renewable energy source and living materials for soft robots towards fully sustainability. (a) Schematic process of triboelectric nano-generator by converting mechanical energy (bending) into electricity with a peak output power density of ~10.4 mW cm^{-3}.[75] Reproduced from ref. 75; Copyright 2012, Elsevier. (b) A vitrimer based triboelectric nanogen-erator (VTENG). Left: The mechanism for self-healing based on dynamic disulphide bonds exchange (upper), the schematic process of VTENG fabrication (bottom). Right: Self-powered tactile sensor built from VTENG to give real-time feedback where badminton falls.[79] Reproduced from ref. 79; Copyright 2018, John Wiley & Sons. (c) 3D printable hydrogel with living microorganisms embedded in as living materials towards engineer-ing application. Upper: Scheme shows the printed structure can grow and regenerate by harvesting nutrients from environments. Bottom: Living hydrogels as robotic materials for soft gripper and untethered rolling robot.[80] Reproduced from ref. 80; Copyright 2022, Springer Nature.

research are devoted to developing and integrating TENG with high efficiency and reliability towards practical applications.

Radically different from renewable energy source, living materials that harvest nutrients directly from environment[81] to support operation could unleash new possibility of robotics towards further sustainability. The key feature is to bring life

into materials that can grow, regenerate and adapt to complex environment. Engineered living materials are a flourishing field of smart materials that leverage the unique properties (*e.g.*, growth, metabolism, sensing, regeneration) of the biolo-gical processes in living organisms to realize responsive or active functions.[82] A variety of microorganisms, ranging from bacteria, fungi, algae to animal cells have been integrated into scaffold/matrix materials such as silk, hydrogels, polymers, and concrete, while the active/responsive material properties could be regulated by nutrient supply. These features offer interesting possibilities for their use as sustainable robotic materials, as soft robots built with living materials could scavenge nutrients from the environment as energy sources to support its opera-tion. While the rapidly expanding field of biohybrid robotic actuators have demonstrated a plurality of mechanisms to exploit living cells and tissues for actuation,[83] the emphasize has been on improving soft actuator performances (*e.g.*, force, stroke, efficiency, *etc.*) and the sustainability aspect has been rarely discussed. A recent example of 3D printed mycelium-hydrogel complex material shed light on living soft robot for sustainability considerations. Exploring nutrient regulation in 3D hydrogel scaffold to control exploratory and exploitation strategies in fungal mycelia, Studart *et al.* achieved emerging adaptive behavior of self-repair, regenerate, and adapt to fulfill an engineering function in the living material (Fig. 6c).[80] Demonstrated as the robotic skin of a gripper and a rolling robot, mycelium-hydrogel exhibits mechanical robustness, soft-ness, self-healing and waterproof functions of interest to robotic applications. It is worthwhile to note that from the sustainability aspect, the mycelium living material enables self-healing, and the bio-based material could be potentially adapted to allow biodegradability. The ability to 3D print such living material presents a first step to create complex structures with adaptive properties for advanced robotic materials. To realize the embodied sustainable energy for biohybrid robots, substantial future research would need to look into how such adaptive structures could scavenge nutrients from the environ-ment, and how the living material's growth/response, regulated by the nutrients, could be translated into meaningful robotic actuation.

5. Conclusions

The new material science of sustainable robotics explores possibilities to achieve functional robots composed entirely of sustainable materials. Rooted deeply in basic science, this approach allows innovation in robotics with profound impacts to both automation and sustainability. Sustainable robot design based on novel materials, however, is still in its infancy. Works in the field so far have only demonstrated proof-of-concept robotic components highlighting certain aspect of sustainability;[84,85] a robotic system composed entirely of sus-tainable materials and embodied energy source, demonstrates a circular life-cycle has yet to be achieved. One reason is that sustainable materials bring properties (*e.g.*, severe viscous

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characteristics from the dynamic bonds in self-healing/recyclable polymers) challenging to overcome for good robotic performance (*e.g.*, high repeatability, precision, endurance, *etc.*). Furthermore, complexity of tight integration and convolution of various robotic functions encompasses material and device design challenges with hybrid functional sustainable materials. And finally, sustainable energy source/storage satisfying the energy and sustainability requirements for circular life-cycle robots has yet to be developed. These challenges transcend disciplines and future development requires close collaboration of material scientists, roboticists, chemists, and biologists. Moreover, in parallel to addressing the scientific challenges, it is essential to communicate with environmental policy makers and industries to identify sustainable robotic applications that would bring the most impact both in the near future and in the long term. Such exchange could provide valuable insights that steer the direction of fundamental scientific research for the applied purpose. The participation of excellent researchers across these transdisciplinary fields will lead to a paradigm shift in the field of robotic towards a sustainable future.

Author contributions

CRediT: Hedan Ban conceived the concept. Wusha Miao drafted figures. Wusha Miao and Hedan bai wrote original-draft and editing.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts to declare.

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