THOUGHTS ON CURRENT TRENDS IN APPLIED POLYMER/BIOPOLYMER MATERIALS FOR MODERN FUNCTIONAL APPLICATIONS

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Abstract

We discuss current trends in developing novel synthetic polymers, biopolymers, and corresponding soft and functional hybrid nanocomposites for advanced current and future applications with an emphasis on active functional devices and functions. Among a wide variety of polymeric materials and relevant applications, we select the fields, which are close to the authors' research interests. This selection includes strong but lightweight biopolymer composites, gel-like and porous materials for chemical and energy transport control, fast-actuating responsive materials and structures, and thin film electronic materials for chemical, physical, and biological sensing applications compatible with human and robotic interfaces.

Key words: polymer composites; structural polymers; functional and actuating materials; bio-enable composites; metamaterials

Introduction.

In this brief overview, we discuss the authors' viewpoint of current trends in developing novel synthetic polymers, biopolymers, and corresponding hybrid nanocomposites for advanced current and future applications with the focus on current and future active and functional materials, structures, and devices. Among a variety of modern polymeric and biopolymer materials and relevant applications reported to date, we choose several material classes and applied research areas, which are closely relevant to the authors' research interests, preferences, and activities as briefly summarized below with selected examples of recent literature and own results presented in the following section.

1. Structural materials and structure-focused applications.

Research efforts in traditional structure-oriented applications of polymeric and corresponding composites without many functionalities are still critically important for many mature developments and brand new fields in robotics or extreme environments with a high priority on enhanced mechanical strength, high strain, dynamic response control, long-range durability, and overall toughness. For the structure-focused applications of structural materials, significant development efforts have been mostly made *via* exploring novel polymer blends and reinforced nanostructured polymers with the tailored interfaces and hierarchical nanostructured organization; novel highly crosslinked materials, both thermosets and thermoplastics; multiphase block-copolymers and their nanocomposites with nanoparticles. Finally, extreme performance of fiber-reinforced polymer and biopolymer materials and potentially dis-assembled, self-healing, and recyclable materials bring broad attention [1].

2. Functional composites and processing for broader materials and applications.

Furthermore, the highest research activity is observed happens in the field of novel function-oriented polymer/biopolymer-based materials for potential applications that require non-traditional conductive, optical, magnetic, biological, and responsive properties. For instance, large efforts have been made in the development of shape memory polymers, fast actuating materials, biomedically compatible polymers, self-healing behavior and reversibly assembled phenomena, light emitting and photonic properties, and polymers with bio-active and bio-degradable abilities.

Besides, special attention is paid to the development and utilization of novel advanced manufacturing techniques instead of traditional extrusion, casting, or rolling, which rely heavily on bottom-up methods such as additive manufacturing, printing, electrospinning [2,3,4]. Most popular additive manufacturing such as 3D and 4D printing refers to the process of the fabrication of an object by adding multiple materials layers with relatively high spatial resolution in contrast to traditional subtractive manufacturing that removes or cuts away material parts. Common additive manufacturing techniques, such as melt spinning, direct ink writing, inkjet printing, and 3D photo-polymerization provide the fascinating advantage for rational design and fabrication of complex, multiscale architectures that enable unprecedented mechanical properties, physical properties, and added functionality [5,6].

3. Dynamic materials and structures: far from equilibrium materials and structures.

Vast majority of current polymer-based materials are fabricated and explored under close-to-equilibrium conditions and well-annealed to assure their long-term stability and durability. However, the open world around us evolves under far from equilibrium conditions to reach multiple changing states with unique properties and new qualities in temporarily organized non-equilibrium structures in contrast to traditionally designed engineering materials [7,8]. Overall, these transformations can be triggered *via* molecular-based initiation and propagation of locally organized instabilities in metastabale multiphase material elements interconnected into large-scale meta structures and mismatched unstable phase boundaries for extreme materials adaptivity. These materials may demonstrate multi-length scale dynamic behavior with ultra-fast propagation of phase state to deploy initial material configurations into complex pre-programmed large-scale architecture as triggered by minuscues energy disturbances. However, a fundamental understanding of the complex far-from-equilibrium state of multiphase soft materials under dynamic external and internal conditions as prospective self-transforming metamaterials across multi-length scales is lacking.

4. Biologically-enabled and human-centered functional materials.

Finally, current research approaches are increasingly moving beyond traditional biomimetic approaches in order to fabricate "living" materials with their abilities to actuate, self-heal, grow and re-grow, directional and dynamic mechanical response, self-powered locomotion, and biocompatibility and degradable ability. To this end, natural, naturally derived materials, and

corresponding hybrid materials are synthesized, fused, nanofabricated, printed, and designed as natural organs, human sensors, human skins, and brains for enhancement of human and machine functions, performance, communication, and cognition [9, 10].

Examples of polymer-based materials for modern applications.

Below, we briefly discuss several examples of recent composite achievements from literature as well as the authors' research.

1. Structural composite materials and corresponding bio-based materials.

To summarize state-of-the-art developments in strong and lightweight structural composite materials, Nepal and co-workers compared the mechanical properties of the enormous range of structural composite materials from traditional engineering to bioinspired composites with multifunctional attributes in the same parametric space in two corresponding Ashby plots with different aspects of mechanical performance (Figs. 1, 2) [1]. The data collected from recent studies are organized in color code presenting the same groups: 1) hierarchical biological materials, 2) hierarchical nacre-mimetic materials, 3) hierarchical Bouligand structured materials, 4) hierarchical fiber-inspired materials, 5) ordered, layered structured materials, 6) disordered, bio-based structures that can be used in common hierarchical materials, and, finally, 7) engineering materials [1] (Figs. 1, 2).

Analysis of available strong and elastic materials data in terms of their mechanical strength and elasticity (ultimate strength *vs.* ultimate strain), which are vital for practical materials with high resilience, tailored strain, and non-brittle failure, shows that the known bio-inspired composites occupy practically the same parametric space as traditional composite inorganic and metal/ceramic reinforced materials (Fig. 1). The majority of known bioinspired composites with soft components, such as CNT-silk and PVA-montmorillonite clay (MTM)-fibrillated cellulose composites, are comparable in the ultimate strength to common engineered ceramics, polymers, and metals (~0.1 - 1 GPa). The strength of existing biological and bioinspired composites can also match advanced synthetic fiber-based composites, such as when silks, keratins, and aramid nanofibers combined with inorganic nanoparticles and carbon nanotubes [1].

The softer components, reconfigurable interfaces, and gradient organization in the composites facilitate higher deformability than in traditional synthetic composites, including high maximum strains of 10% and their ability to reconfigure from planar to highly curved or wrinkled for dynamic morphing.
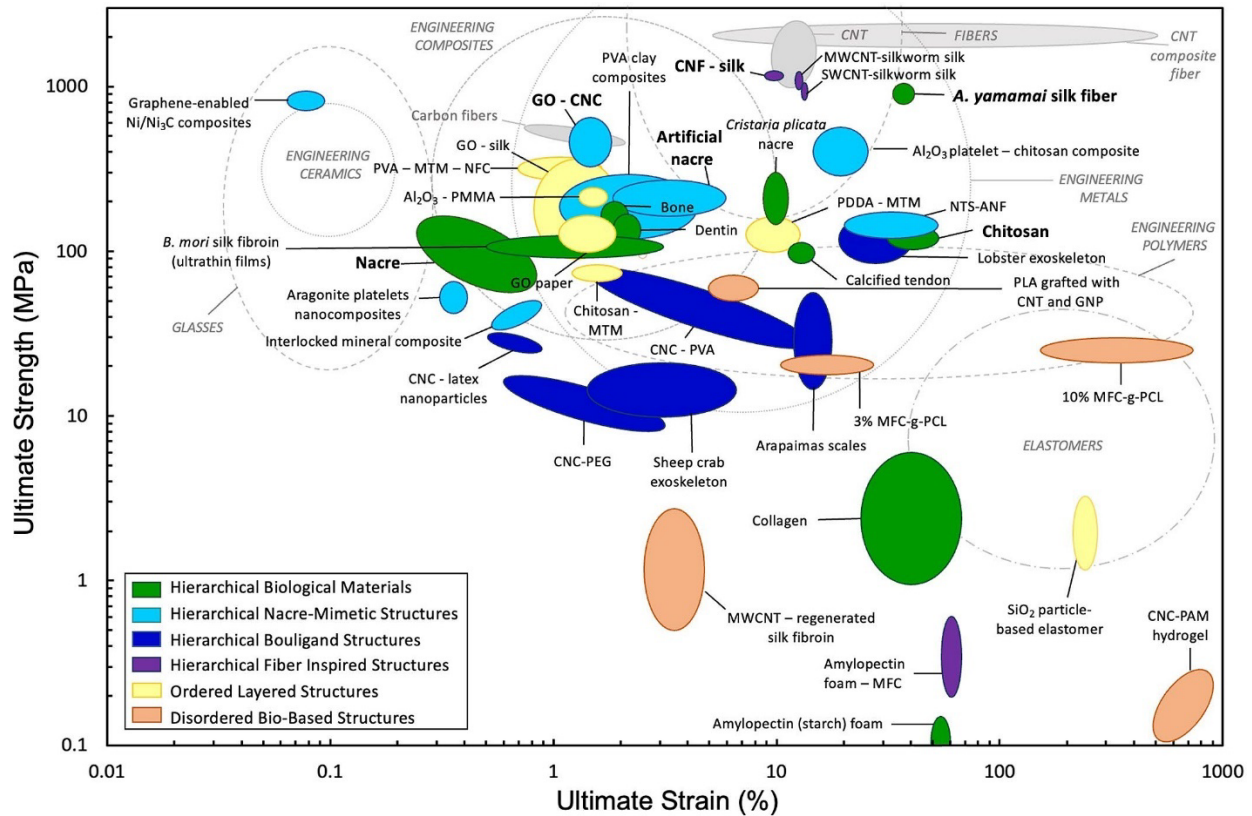

Fig. 1. Mechanical properties of various composites in comparison with natural and traditional materials classes. Ashby plot compares the ultimate strength *vs.* ultimate strain for various hierarchical biological materials, nacre-mimetic structural, Bouligand structural, circular hierarchical, fiber-inspired structural, layered ordered composites, and random bionanocomposite materials. The hierarchical materials (biological, nacre-mimetic, Bouligand, and cylindrical fibers) are included in green, light blue, dark blue, and purple, respectively. The ordered layered composites are in yellow and the random, disordered bio-based structures are included in orange. These materials are compared against common materials, which are included in light grey in the background, such as engineering metals (stainless steel, gold, copper, silver, tin, nickel, various alloys, titanium, Al/Si Carbide, zinc), engineering polymers, elastomers, polymer fibers, carbon fiber/carbon nanotubes, engineering ceramics and metals, glasses, and multi-component engineering composites. Fig. 1 reprinted from Ref. [1].

Beyond the elastic regime, yielding and strain hardening can result from local molecular and nanoscale rearrangements such as disentanglement, strain-induced crystallinity, nanostructures reorientation/aggregation and chain slippage. Such processes add significant plasticity might

result in ultimate strains of hundreds of percent. The combination of high ultimate strains with high strength in some wood-keratin composites sometimes surpasses that reported for synthetic fibrous composites (Fig. 1).

Second, if the advanced mechanical performance is considered in terms of toughness *vs.* stiffness (Young's modulus) and excluding ultimate strains, biological and bio-derived composites (*i.e.,* those utilizing some quantity of natural materials) also can compete with traditional composites (Fig. 2) [1]. Bio-inspired composites dramatically extend the parametric space towards extremely compliant materials with uniquely combined high toughness and modulus, comparable to engineering polymers and ceramics.
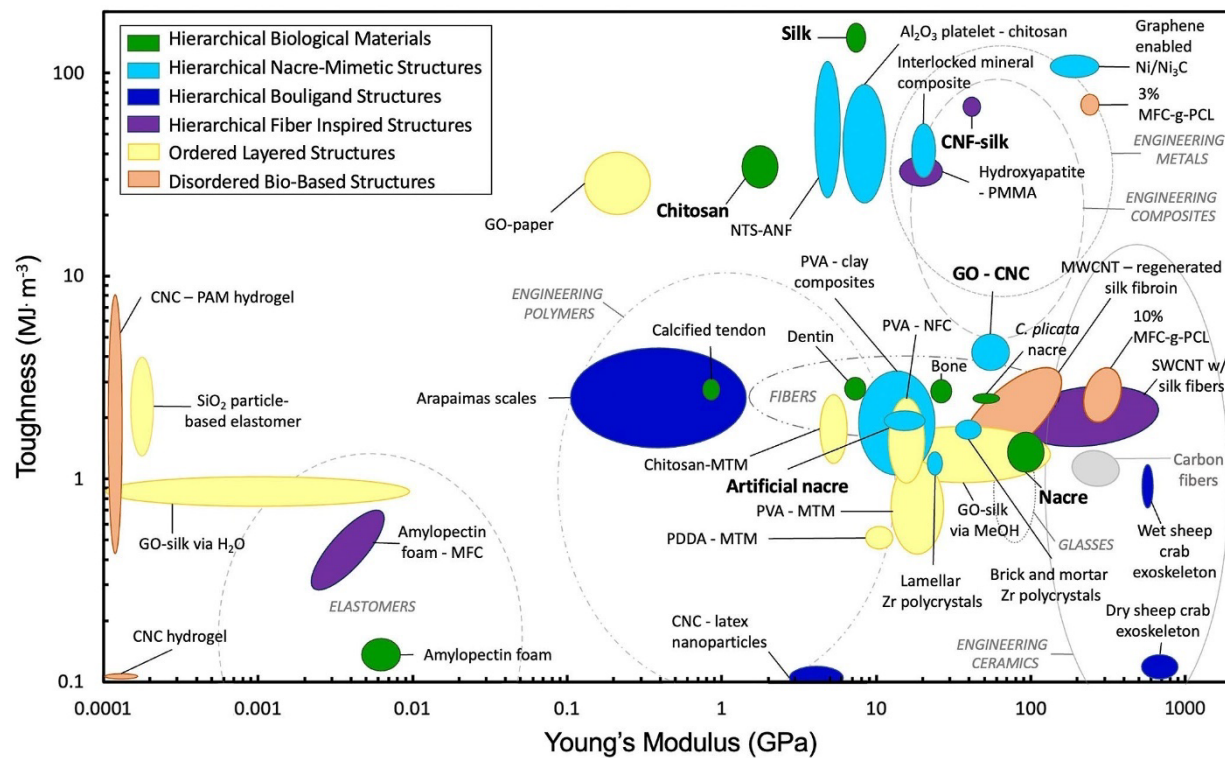

Fig. 2. Mechanical properties of various composites in comparison with natural and traditional materials classes. Ashby plot compares the toughness *vs.* Young's modulus for various hierarchical biological materials, nacre-mimetic structural, Bouligand structural, circular hierarchical, fiber-inspired structural, layered ordered composites, and random bionanocomposites (see Fig. 1 for details). Reprinted from Ref. [1].

Bioinspired composites can perform much better than regular elastomers/gels, showing high toughness values of up to 10 MJ/m^3. Amazingly, some of these bio-inspired materials occupy valuable, non-traditional parametric space with extreme toughness, up to 100 MJ/m^3 for silk, chitosan, and wood-based composites, as well as high elastic moduli up to tens of GPa [1].

Overall, as a result of continuous, recent and current research efforts hierarchically structured polymer and biopolymer composites achieve the highest combinations of strength and strain, as well as toughness and stiffness. The reinforced composites containing biological fibrous components are among the best-performing materials. Hierarchical microstructures imbue unique property combinations *via* multiple and complementary weak interactions and strong interfaces and interphases. These reinforcing mechanisms might improve the performance of soft composites making them better than common engineering materials.

2. Tailored flow of materials and energy with polymer and hybrid composites

Traditional membrane materials. Porous materials, such as zeolites, have a limited range of pore sizes and suffer from nonuniform pore distribution, limiting their applications in energy storage and advanced separations. Popular synthetic membranes are made of polytetrafluoroethylene (Teflon), polystyrene, polycarbonate, polysulfones, poly(vinylidene fluoride), reinforced crosslinked gels, and polyamides [11,12,13,14]. Accordingly, significant efforts have been made to develop novel materials for more efficient membrane processes. For instance, *N*-Aryl–linked spirocyclic polymers were used for membrane separations of complex hydrocarbon mixtures [15]. The developed membrane materials are composed of aromatic rings and flexible *N*-Aryl linkages for preventing swelling, plasticization, and ultimately maintaining selectivity during operations. Among other organized materials, polystyrene latexes and block copolymers with ordered channels have demonstrated prospective high flux membranes [16,17].

The most commonly exploited natural and bioderived materials for separation membranes include cellulose and other fibrous components due to their good mechanical properties, high porosity, simple processing, and thermal stability (*e.g.*, common filtration papers). Particularly, interest in cellulose-type materials for filtration and separation is ascribed to their natural abundance, high natural porosity, low solubility in water, and solubility in many common organic solvents along with good chemical resistance [18].

2D organized transport-mediating materials. An interesting avenue for molecular transport control includes the use of two-dimensional (2D) materials like graphene, transition metal dichalcogenides, and hexagonal boron nitrides [19,20,21,22,23,24,25,26], which is originated

from their high mechanical stability, electrical conductivity, interlayer spacing control, and rich surface chemistries [2,27].

Particularly, $Ti_3C_2T_x$ MXenes, the most studied MXene materials, have been found to work well as molecular sieving membranes due to the large lateral size of their nanosheets and molecular gaps with surface functional groups (T_x) of either -OH, =O, -Cl or –F allowing dispersion in aqueous media (Fig. 3a) [28,29,30]. Thin films of MXene (80 nm thickness) show selective rejection rates ranging from 40% to 95% for

Fig. 3. (a) Scheme for silk-MXene composites and chemical structure of $Ti_3C_2T_x$ MXene (T_x=O, OH, F). (b) Scheme for porous MXene membranes and (c) Permeance *vs*. rejection rate for diverse membranes. Panels a, b, and c reprinted from refs. [35], [33], and [33], respectively, with permission.

various dyes [31]. With the addition of graphene oxide, the thin MXene-graphene oxide membranes were able to reject higher percentages of dyes including 100% for brilliant blue [31].

Another approach showed that MXene membranes could be tuned to have fouling-resistant and ultrahigh-flux properties by incorporating silver or iron hydroxide nanoparticles (Figs. 3b, c) [32,33]. Similarly, MXene membranes ($Ti_3C_2T_x$) combined with alumina (Al_2O_3) nanoparticles to enlarge interlayer spacing and high separation performance [34]. We demonstrated that membranes from silk-modified MXene can show highly selective filtration performance (Fig. 3a) [35]. Natural materials such as proteins and polysaccharides have been explored to modify graphene oxide-based membranes for molecular transport control [36,37].

Ionic and coordinated open-pore materials for ion and energy transport. Ionic liquids are pure molten salts capable of being new potential electrolyte materials [38]. They have gained considerable attention due to their unique properties—high ionic conductivity, high chemical and thermal stability, a large electrochemical window, and low vapor pressure—which can be tuned by choosing different combinations of cations and anions for high-performance electrolytes for
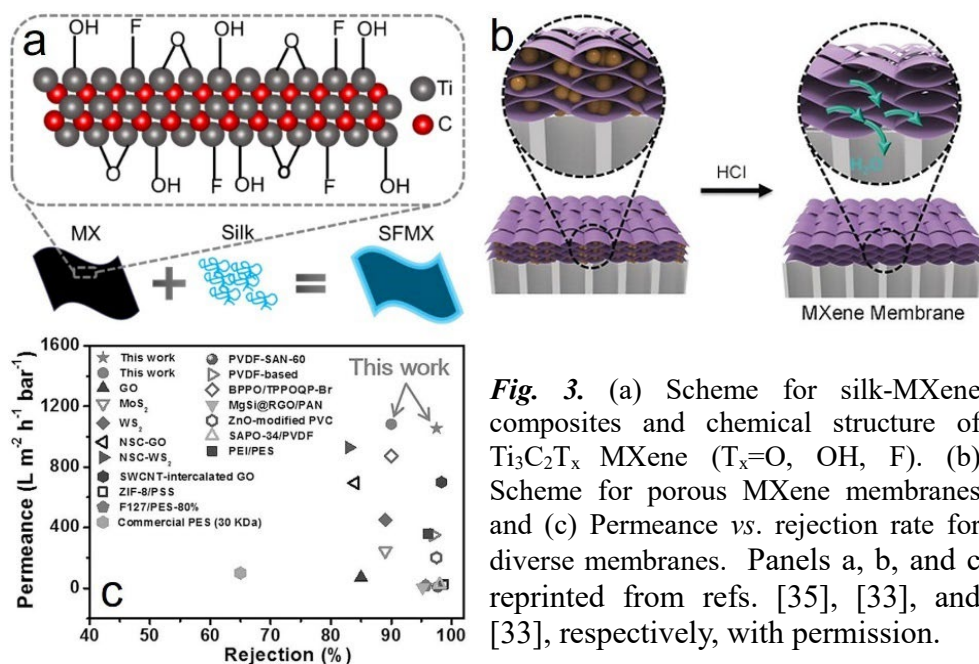
electrochemical applications in devices such as batteries, capacitors, and solar cells [39]. However, their viscous fluidic nature impedes their ability to sustain a self-supporting, free-standing shape; instead, they require solid confinement, which compromises their portability and leads to the issues of leakage [40]. One common strategy for ionic liquid immobilization in handleable materials without a significant sacrifice in their transport properties is *via* the formation of ionogels in which ionic liquids are encapsulated within inorganic or polymeric matrices [41].

Mechanically strong and highly conductive ionogels can be used as mechanically reinforced and robust network matrices for ion transports [42,43,44]. For example, the ionogels composed of zwitterionic copolymers displayed high room-temperature ionic conductivities above 1 mS cm^{-1} and compressive elastic moduli in the range of several MPa [44]. Examples of biopolymers used for robust ionogels include cellulose [45], gelatin [46], and chitosan [47]. Ionic liquids can be entrapped into the readily formed network of nanocellulose, resulting in materials with enhanced mechanical stability and/or ionic liquid loading without the dissolving/regeneration of cellulose components.

3D organized transport-mediating materials. Recently introduced organized porous materials from metal-organic frameworks (MOFs) demonstrate enhanced ion as well as chemical transport/loading capabilities due to their unique open porous and ordered microstructures and controlled chemistries [48]. Their well-defined porosity metrics allow for selective ion-conduction through dimensional confinement. Their tunable and controllable surface functionalities also enable favorable interfacial interactions with different electrolytes. The ion conduction capabilities of MOFs highly depend upon their porosity, unit organization and alignment, the ionic surrounding, and electrolyte interactions.

The tunable and precisely defined MOF porosity can also be advantageous for small-molecules and biomolecules separations through ***size-sieving*** depending on the MOF pore sizes [49]. Some designed MOFs were able to reversibly switch between distinct ordered and disordered states [50]. Biomolecules are promising building blocks for MOFs due to their ability to coordinate with metal ions and their potential for selective interactions with biomolecules [51]. In contrast to traditional units, MOFs possessing biomolecules as critical structural elements are defined as "bio-MOFs" (Fig. 4) [51]. The biomolecules in open frameworks include peptides and proteins as "structural" components (Fig. 4) [51,52,53,54,55].
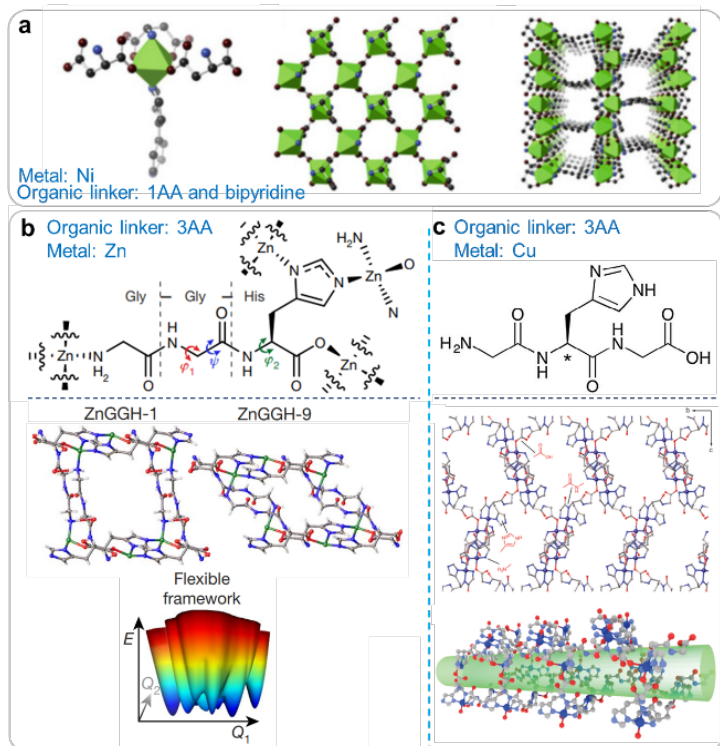
Fig. 4. Examples of peptide MOFs: (a) amino acid-MOFs, (b) oligopeptide (Gly-Gly-His)-MOFs, (c) oligopeptide (Gly-His-Gly)-MOFs. Figs. 4a, 4b, and 4c adapted from refs. [51], [54], and [55] with permission.

Overall, bio-MOFs have attracted significant attention in recent research due to their exact compositional match with biological materials, mild processing conditions, environmental compatibility and nontoxicity, and thus, have been employed for biomolecular highly selective porous membranes or potential selective drug loading and release in bio-medical applications [56,57,58].

3. Far-from equilibrium and active meta-materials.

Significant recent progress in stimuli-responsive materials has allowed the rapid development of active and complex 3D architecture metamaterials that can transform their geometry from 2D to 3D space under different stimuli (Fig. 5) [7,8,59,60,61,62].

These structures can be produced by combining functionally responsive materials and fabricated reconfigurable kirigami frame structures, allowing far-from-equilibrium states with built-in mechanical instability of engineered inter-phase connectors for a fast dynamic local response along pre-programmed pathways in response to various remote different triggers (Fig. 5). Such kirigami metamaterials will enable not only achievement of ultrafast shape self-transformation but also answering the grand challenge scientific questions: how localized materials transformations can be amplified by a meta-stable and confined organization of interconnected elements in multi-phase kirigami frame for triggering global 3D shape transformations.

The elements of reconfigurable structures can be composed of various functional materials with tunable phase volumes, which are embedded into engineered boundaries with far-from-equilibrium state caused by local stress at phase boundaries and incommensurate geometries and mismatched properties (Fig. 5).
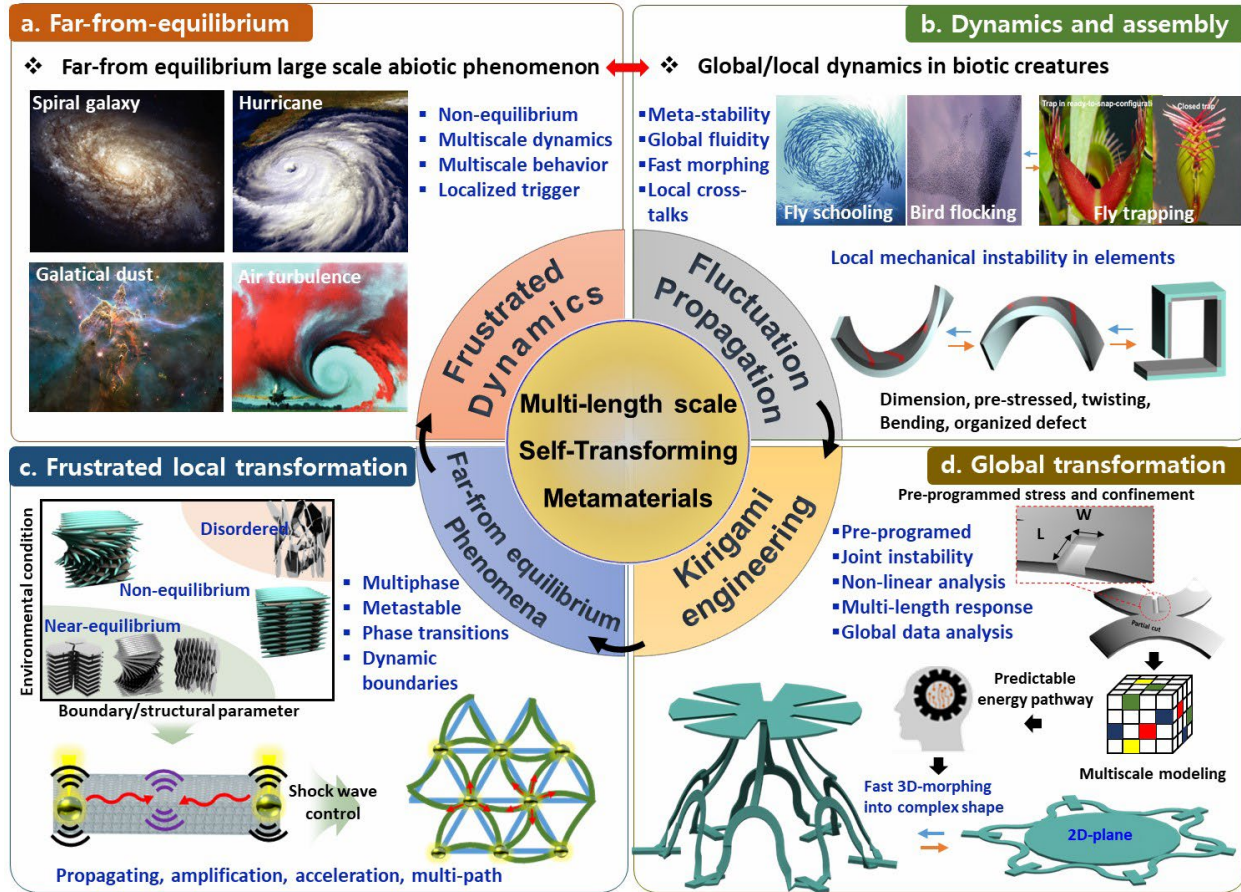
Fig. 5. Reconfigurable kirigami metamaterials with far from equilibrium transformation embedded into metastable frames for fast actuation. (a) Natural far-from-equilibrium phenomena such as spiral galaxies of stars with various shapes, hurricanes generated by the thermal energy of the ocean that behaves as the dissipative structure with vortex shape, galactical dust, composed of different matters (gas in ionic, atomic, and molecular forms as well as dust) between star systems, and air turbulences, generated by pressure and flow vortices in propelled aircraft. (b) Global swarm dynamics in living creatures such as fish schooling and bird flocking where the local energy input of individual constituents gives rise to complex organized collective motion; the dynamic of Venus flytrap's biological structure with rapid leaf closure for the leaves for fly trapping is based on a snap-buckling instability. (c) Phase diagrams of frustrated material transformations and shock wave propagation for far-from-equilibrium phenomena: Multiphase materials-structure in non-equilibrium by combining metastable environment instability will produce a local response with a shock wave that amplifies, accelerate, and propagate along the built-in phase boundaries for an ultrafast global response. (d) Microfabricated designs and multiscale modeling of the chaotic energy propagation along metastable boundaries and the predictive models will give a powerful approach for controlled chaos with complex global shape transformation and fast morphing from 1D to 2D and to 3D/4D structure. Figs. 5a and 5b images reprinted from (ref. [7] and Space Telescope Science Institute) for Fig. 5a images and (ref. [7], University of Canterbury Research Repository, and ref. [61]) for Fig. 5b images with permission from (arXiv and Space Telescope Science Institute) and (arXiv, University of Canterbury Research Repository, and United States National Academy of Sciences), respectively.

Photo-/electro- chemical/magnetic-induced transitions within active elements can result in global shape changes with fast actuation *via* induced internal stresses that cause fast transformation of transient local elements [63].

4. Functional materials for wearable and integrated sensors for human interfaces.

In the materials-oriented research efforts for wearable and integrated sensors, it has been considered that the design, synthesis, and fabrication of hierarchical biomaterial patches with a thickness of several microns and patterned conductive circuitry. These adhesive flexible thin materials patches with embedded flexible electronic circuity can be exploited without the need for thick elastomeric supports, sealing templates, and metal electrodes (Fig. 6) [36,64,65,66,67,68,69]. Our group has demonstrated examples of robust, flexible, and patterned conductive multilayered hybrid materials composed of graphene oxide monolayers firmly glued together by silk fibroins (Fig. 6 a, b) [65,66].

These materials show superior mechanical stability with the broad range of elastic modulus within the 100 MPa – 10 GPa range, high flexibility, and resilience to bending, compatibility with metal electrodes, high sensitivity to chemical environment, and good conductivity of electrochemically reduced electrodes (10^5 Om/cm) (Fig. 6 c, d) [66,67]. It has been also shown that wafer-size material patches can be fabricated by scaling up the assembling process (Fig. 6 e) [67]. Furthermore, conductive grids can be printed with electrochemical contact or ink-jet printing (Fig. 6 f) [68]. Adjustments of elastic modulus for enhanced stretchability with preservation of high conductivity under severe deformations such as twisting can be conducted with materials possesing kirigami patterning fabricated *via* screen-printing (Fig. 6 g, h) [60].

Further modification of the interfacial properties, adherence, and compatibility (biological, mechanical, electrical, thermal) with supporting surfaces (*e.g.*, skin or skull) can be conducted by chemical modification of graphene oxide nanosheets and their multilayered morphology by, for example, using cellulose nanofiber nets to wrap individual nanosheets before assembly (Fig. 6 i) [36].

Recently, we demonstrated that the integration of adhesive synthetic materials with photonic material gives rise to switchable photonic bio-adhesive materials that can change adhesive and shear strength at variable humidity and simultaneously can monitor them through the visible color change of the adhesive materials (Fig. 6j) [70]. Resulting humidity-responsive and colorimetric

photonic adhesive material demonstrated its ability to monitor the wound healing process and contamination of the target surface by liquid *via* color changing property.
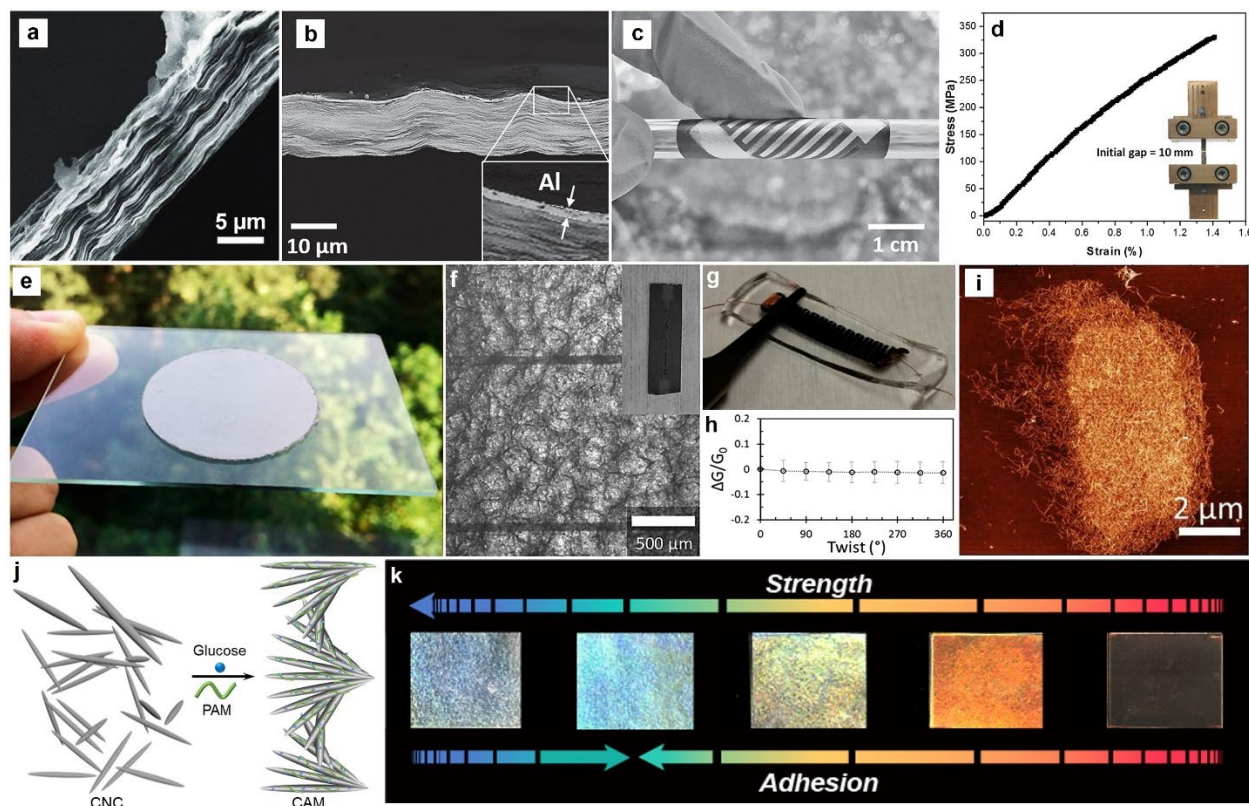

Fig. 6. Flexible bio-hybrid multilayered films from graphene oxides and silk fibroins. SEM images of the cross-section of graphene-silk composites (a) and those integrated with the metal electrode (b); flexibility of metal-graphene-silk grids (c); mechanical performance with an ultimate strength of 0.35 GPa (d); wafer-size uniform conductive film (e); electrochemically patterned electronic grid (f); kirigami stretchable films with a self-powered ability (g); resilience of resistivity (<1% variability) for full film twisting (up to 360º) (h); and AFM image of individual graphene oxide nanosheet wrapped with cellulose nanofibers for mechanical performance enhancement and control (i); schematic of self-assembly of the chameleon adhesive material from synthetic components and cellulose nanocrystals (j); correlated iridescence-adhesion-strength change of photonic adhesive films at relative humidity from 0% to 97% (from left to right) (k). Figs. 6a, 6b, 6c, 6d, 6e, 6f, 6g, 6h, 6i, 6j, 6k reprinted from refs. [65], [66], [66], [67], [67], [60], [60], [36], [70], and [70], respectively.

Furthermore, post-chemical surface modification can be used to induce strong adhesion to various substrates with complex topography of wearable conformal stickers, prints, and even tattoos (*e.g.*, high roughness and porosity, presence of hairs) to directly adhere to human clothes, gadgets, and skin.

Conclusions.

In conclusion, we suggest that the continuous research focus in the broad field of advanced polymer and biopolymer composite materials is continuously shifting from traditional structurally oriented materials with enhanced mechanical performance to complex functional materials and structures with added, non-traditional properties such as enhanced conductivity, highly tailored materials with nanoscale control for directional materials and energy transport, resilient photonic materials with active optical appearance, and flexible/bendable meta-materials with fast multi-stimuli response and actuating behavior.

On the other hand, bio-derived/enabled "living" intelligent soft materials have gained significant attention in the past decade and current research focus in this materials class includes biologically-inspired properties and added functions such as ability to growth and regrown, self-propellant locomotion ability, self-healing behavior, and the ability for full integration and synchronized functions into the cellular environment, human body, skin, and brain for self-transforming structures, hyper-sensitive sensors, sight-off communication, adaptive traps/channels for acoustic and light waves, or autonomous adaptive human-friendly materials for enhanced survivability, adaptivity, and sustainability for biomedical applications health monitoring, human performance enhancement, extreme environments, and defense applications.

Acknowledgements.

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