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Carbon-Based Janus Films toward Flexible Sensors, Soft Actuators, and Beyond

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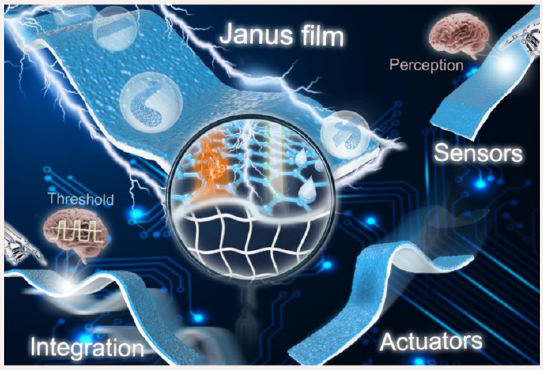

CONSPECTUS: Janus films have attracted widespread interest due to their asymmetric structure and unique physical and/or chemical properties, demonstrating broad and blooming potentials in mechanical sensing, soft actuation, energy management, advanced separation, energy conversion and storage, etc. Among them, based on the unique features of carbon nanomaterials, extensive efforts have been dedicated to exploiting carbon-based Janus films for high-performance electronic skins, soft actuators, and their integration for smart robotics. Drawing inspiration from nature, biological skins can actively perceive external physical/chemical stimuli and further perform specific motion behaviors. However, there still remain challenges of guided structural design principles, an alternative combination of multifunctions, and advanced synergetic applications. Specifically, their intrinsic properties and related device performances are strongly determined by the functional components' coupling, surface wettability, and controllability of the interface structures. The asymmetric combination of carbon nanomaterials and functional polymers in controllable manners can facilitate the design of high-performance sensing, actuation, and integrated devices, enabling the development of smart soft robotics. Therefore, it is highly desired to summarize this research area of carbon-based Janus functional films for sensing, actuating, and integration as well as to have a deep understanding of the relationship between interfacial structures and their performance for directing future development.

In this Account, we will summarize the significant advances in carbon-based Janus films mainly conducted by our group and also discuss the relevant important reported works. We start by introducing the basic properties of commonly used carbon nanomaterials and then discuss the general fabrication strategies for high-performance carbon-based Janus films, including solid-supported physical/chemical approaches and interfacial strategies based on liquid support. Among them, we carefully present the typical combination of two functional components for advanced and synergetic properties. Based on the combined designable functionality, the bioinspired artificial skins that target sensors, actuators, self-sensing actuators, and beyond will be discussed in detail. Finally, challenges and the prospect of structural design, structural interfaces, and integrated functionality will be proposed. We expect that this Account would provide a better understanding of the design, fabrication, applications, and challenges of carbon-based Janus functional films and their significant potential for the development of smart robotics.

1. INTRODUCTION

Janus films are typically characteristic of unique and controllable physical and/or chemical properties as well as synergetic multifunctions, demonstrating diverse applications in sensors, actuators, energy management devices, advanced separation systems, etc.[1−4] Among them, bioinspired soft skins have attracted extensive interest due to their capabilities of active perception, actuation, and functional synergy. The biomimetic soft skins are expected to mimic the unique functions of biological skins with integrated perception and deformation properties enabled by the effective synergy of hierarchical structures, multilevel tissue, and diverse receptors in an elaborate configuration. To achieve these specific properties, it is crucial to alternatively introduce active components and further integrate them into asymmetric structures and perform synergetic functions. As important functional components, carbon nanomaterials (e.g., graphite, carbon spheres, carbon nanotubes (CNTs), graphene, and their derivatives) are expected to be promising alternatives due to their unique electrical conductivity, intrinsic mechanical flexibility, high chemical and thermal stability, and ease of macroscopic assembly.[1] The achievement of carbon-based Janus films can

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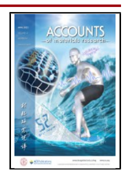

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provide an actively conductive and photo/electrothermal or moisture response platform for facilitating the development of mechanical sensing and actuating.[1,2] Also, the controllable coupling of the functional components and their regulated interfacial structures account for the synergy of multiple functions and structural stability. Therefore, the exploration of effectively integrated methods, the combination principles of functional components, and frontier applications are highly desired.

For years, although Janus films have gained widespread attention and blooming development based on diverse physical, chemical, and interfacial strategies,[3,4] there is still no systematic summary of carbon-based Janus films about their design, properties and potential applications in biomimetic soft sensors and actuators. Moreover, well-defined relationships between structure and performance are lacking. Therefore, a comprehensive summary of the design principles of Janus films and an in-depth discussion of the relationships between surface/interface structures and properties are urgently needed to guide their applications in flexible smart devices.

Here, we summarize the research progress mainly conducted by our group and also some recent important advances on various construction strategies of carbon-based Janus films and their potentials in flexible sensors, soft actuators, and integrated devices (Figure 1). First of all, we discuss the general properties of a series of carbon nanomaterials and then introduce typical fabrication strategies, including physical and chemical methods for solid support and interfacial strategies for liquid support. More importantly, the interfacial and surface structure are carefully discussed to guide the controllable design of high-performance devices. Carbon-based Janus films with multifunctionalities are also demonstrated, which are of tremendous advantage for flexible sensors, soft actuators, self-sensing actuators, and beyond. In the last part, we give a brief discussion of the future challenges and prospects regarding the controllable interfacial structure design and efficient multi-function integration of carbon-based Janus films.

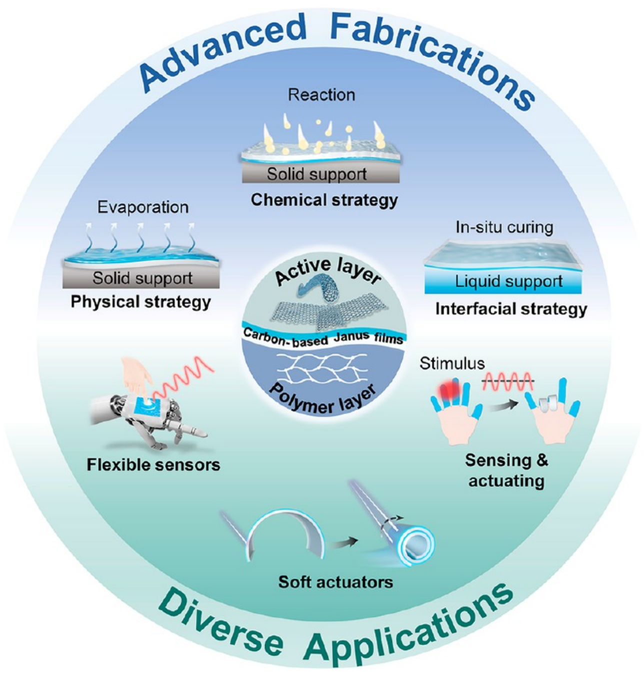

Figure 1. Overview of the advanced fabrication strategies and diverse applications of carbon-based Janus films.

2. INTRODUCTION OF CARBON NANOMATERIALS

Based on the differences in bonding behaviors of carbon atoms, carbon nanomaterials are classified into (i) an entire sp^2 hybrid bonding system (e.g., carbon nanotubes, graphene, and their derivatives and graphite), (ii) an sp^2 and sp^3 hybrid bonding system (e.g., amorphous carbon), (iii) a pure sp^3 bonding system (e.g., diamond), and (iv) a solo sp hybrid bonding system (e.g., carbon chain).[2] Here, we will briefly introduce several carbon nanomaterials with an sp^2 lattice most used in flexible sensing and actuating devices, including their intrinsic structures, physical/chemical properties, advantages and disadvantages of certain species, and potential applications.

Carbon nanotubes (CNTs) are one-dimensional tubular carbon-based structures formed by the convolution of two-dimensional graphene primitives, which possess excellent conductivity [$(0.17-2.0) \times 10^7$ S m^{-1}], high thermal conductivity (up to 6000 W m^{-1} K^{-1}), strong mechanical strength (~1 TPa), and a wide light adsorption spectrum (visible and near-infrared ranges).[1,2] The different curl angles classify single-walled carbon nanotubes (SWCNTs) into the armchair, zigzag, and chiral forms. Generally, the chirality enables both metal- and semiconductor-type conductive properties and even confers wavelength selectivity to SWCNTs, which makes them available for function-specific light-responsive actuators distinct from other carbon nanomaterials. Moreover, predictable deformation behavior (e.g., phototropic and apheliotropic bending and even helical twisting) can be achieved by controlling the orientation of the CNTs in the Janus films.[2] However, the synthesis of such specific chiral CNTs is challenging, making it difficult to apply individual SWCNTs for large-scale applications. In addition, CNTs have ultralong aspect ratios that confer excellent mechanical flexibility along the axial direction, endowing them with typical advantages for highly stretchable strain sensors. Nevertheless, their large aspect ratios also lead to a low sensitivity to temperature response.[1]

Graphene, a class of 2D materials with a honeycomb lattice arrangement, has received tremendous interest in wide range of industries since its discovery in 2014. Compared to carbon nanotubes, graphene exhibits unique optical transparency (97% light transmission) due to the single-atomic thickness that absorbs only 2.3% of white light, and the transparency decreases with the increase of atomic layer thickness.[5] Owing to the strong atomic bonding in the plane, graphene demonstrates superb mechanical properties with a Young's modulus of ca. 1 TPa and a fracture strength of about 130 GPa, while maintaining a fracture strain of ca. 25%.[5] Another distinctive feature of graphene is its zero band gap, which allows it to present high carrier mobility (up to ~20 000 cm^2 V^{-1} s^{-1}) and conductivity (~10^8 S m^{-1}). However, the zero band gap hinders its use in the semiconductor industry. Therefore, extensive efforts have been made to open the band gap of graphene without degrading its electrical conductivity via covalent modification or chemical doping.[6] Specifically, the high transparency of graphene shows significant potential in flexible and transparent touch panels. Besides, graphene maintains a high thermal conductivity [$(5.30 \pm 0.48) \times 10^3$ W mK^{-1}] and light absorption capability (covering the ultraviolet to far-infrared range) as well as excellent photothermal conversion capability for high-performance photo-

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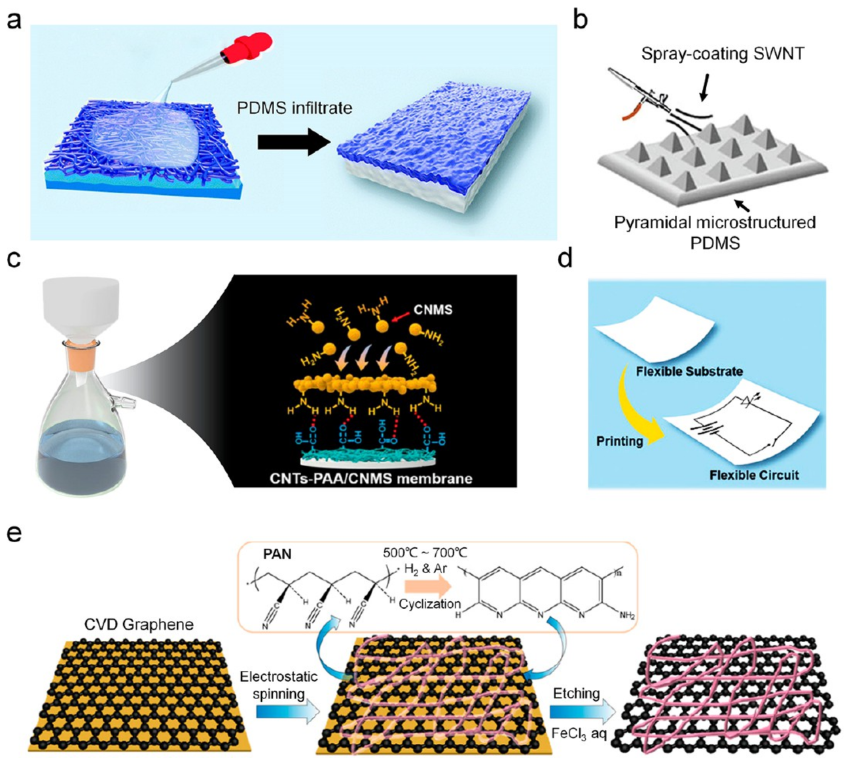

Figure 2. Physical strategies based on a solid support for carbon-based Janus films. (a) Diagram of preparation for a carbon-based Janus film with cracked structure by a drop-casting approach. Reproduced with permission from ref 8. Copyright 2018 Royal Society of Chemistry. (b) Schematic of spraying SWNTs on microstructured PDMS. Reproduced with permission from ref 11. Copyright 2015 Springer Nature. (c) Schematic of the preparation of hydrogen-bonded reinforced bilayers based on vacuum filtration. Reproduced with permission from ref 12. Copyright 2021 John Wiley and Sons. (d) Fabrication of the carbon-based circuit on flexible substrates with various printing techniques. Reproduced with permission from ref 16. Copyright 2020 John Wiley and Sons. (e) Electrostatic spinning-assisted transfer-medium-free strategy for a high-mechanical-strength CVD graphene-based Janus film. Reproduced with permission from ref 17. Copyright 2019 American Chemical Society.

thermal soft actuators.[2,5] However, graphene presents unfavorable bad dispersion in most solvents due to its hydrophobicity. Chemical modification is considered to be a practical and effective solution. However, the electrical, thermal, mechanical, and optical properties of the pristine graphene can be severely reduced due to the damage to its sp^2 hybrid structure.

Graphene oxide (GO) and reduced graphene oxide (rGO) are the two most typical graphene derivatives with the same layer-like structure as graphene. Due to the presence of abundant oxygen-containing functional groups, they exhibit high sensitivity to temperature, humidity, and chemical substances. However, it is the strong interaction with the detection substance that causes them to recover less quickly than pristine graphene when used for gas sensors.[5] Compared to rGO, the abundance of carboxyl, hydroxyl, and epoxy groups on GO gives it excellent hydrophilicity and the ability to form strong hydrogen bonds with water molecules.[1] The layered nanostructure leads to the formation of quantum-confined superfluidic channels inside GO.[7] Therefore, GO nanosheets show significant potentials of building high-performance humidity actuators. However, the surface functional modification leads to the disruption of the conjugated structure, and GO exhibits almost insulating properties and cannot be used as an electrode layer for flexible electronics. rGO is the reduced derivative of GO, which has undergone thermal, chemical, or photo reduction to achieve partial recovery of the aromatic conjugated structure.[2] As a result, rGO possesses electrical, thermal, and optical properties not inferior to those of pristine graphene. Also, it can be employed as an active material for humidity sensing and can even be combined with the photothermal operation to achieve moisture actuating.[2] Remarkably, the chemical or physical properties of GO and rGO can also be effectively controlled by regulating the number and distribution of oxygen-containing functional groups on their surface.

In addition, other carbon materials, such as graphite, carbon black, and amorphous carbon, can be also applied as active layers to construct Janus films for flexible sensors and actuators due to their low-cost fabrication, easy processing, and excellent stability.[2]

3. ADVANCED FABRICATION STRATEGIES FOR CARBON-BASED JANUS FILMS

3.1. Solid-Supported Physical Strategies

The excellent solution processability enables carbon nanomaterials easily to form assembled films via the wet process. Typical strategies include drop casting, spray coating, vacuum filtration, printing, etc. In the conventional drop coating process, the weak van der Waals interactions between the carbon-based functional layers and the polymer substrates result in bilayered Janus structures with weak interfacial strength. To address this issue, we changed the fabrication sequence by adding poly(dimethylsiloxane) (PDMS) solution dropwise to the surface of multilayer CNT films. The porous structure of the CNTs network enabled the PDMS solution to penetrate into the conductive network and wrap part of the

CNT layer, endowing the resulting Janus film with excellent mechanical properties to form a stable crack structure without the slip of the CNT layer (Figure 2a).[8] Although the drop-casting method is relatively simple, the coffee ring phenomenon usually exists, which may decrease the performance of devices to a certain extent.[9] The spray coating method has been adopted to construct homogeneous carbon-based Janus films in an efficient and controllable manner, in which the microstructures can be effectively tuned by adjusting the spraying factors (e.g., pressure, time, moving speed, and distance) and solvent evaporation time.[10] The refinement of droplets is conducive to the deposition of carbon-based solution on surfaces with elaborate microstructures. For example, SWCNTs could uniformly cover the PDMS with a pyramidal microstructure, exhibiting excellent conductivity and stability (Figure 2b).[11] In addition, Janus films with adjustable stacking density could be obtained by vacuum filtration techniques. We have recently introduced the hydrogen bond interactions during the sequential filtration process, which endowed the composite film with a robust interface (Figure 2c).[12] Moreover, the pressure gradient change in the filtration process contributed to the film with variable interlayer space.[13] The adjustable viscosity or concentration of the dispersion enabled the carbon-based films to be fabricated by other typical wet processes, such as blade coating[14] or advanced printing techniques, which have potential in the scalable and low-cost mass production of macroscale flexible devices.[15] For example, Zhang et al. demonstrated that the CNT ink stabilized by silk sericin could be used to print different designable patterns on various flexible substrates through diverse printing methods, including inkjet printing, stencil printing, and direct writing (Figure 2d).[16]

The generation of high-performance carbon-based functional layers is critical for devices with enhanced performance. Compared with the wet approaches, chemical vapor deposition (CVD) is also the most popular technique used to obtain high-quality carbon films with fewer defects in a dry environment. However, the electronic and mechanical properties of the deposited films may be degraded because of polymer contamination and mechanical cracks during the transfer process. As shown in Figure 2e, Liu et al. deposited polyacrylonitrile fiber films on one side of CVD graphene by an electrostatic spinning method to achieve reinforced mechanical properties for nondestructive transfer at a large size.[17] Moreover, the CVD-enabled carbon-based films could be transferred onto large flexible pieces of plastic without metal etching and polymer residues via a green roll-to-roll (R2R) strategy for high-performance nanogenerators.[18]

Apart from the above physical strategies for carbon-based Janus films, other methods (e.g., pencil drawing,[19] direct adhesion[20]) have also been employed to construct high-performance flexible devices. Physical modification allows the simple and efficient integration of asymmetric physical/chemical properties into carbon-based thin films, resulting in the achievement of specific electrical performance. For instance, the asymmetrical introduction of noncovalent interactions (e.g., $\pi-\pi$ stacking, hydrogen, and coordination bonds) of small molecules and functional polymers into graphene derivatives can remarkably modulate the band structure.[21] This approach is expected to form charge-transfer complexes to tailor the electronic structure and electrical conductivity for biochemical sensors and field-effect transistors. Another example of building delicate gratings and hierarchical micro-/nanoporous structures further endows the macroassembled carbon-based films with functional features for humidity actuation and waterproof flexible electronics, respectively.[7,10] Alternatively, to improve the mechanical strength of Janus films, the formation of interlocking structures or strong $\pi-\pi$ interaction between the carbon-based active layers and the elastomeric matrix is desirable.[8,17]

3.2. Solid-Supported Chemical Strategies

Covalent small-molecule decoration or polymeric grafting through asymmetric modification of one or both sides of a monolithic film is another broad class of methods used to prepare Janus films. As early as 2013, Liu et al. first realized the fabrication of monolayer Janus graphene through a two-step asymmetric covalent modification strategy. As a result, four types of Janus graphene with cograted halogen and aryl or oxygen functional groups on each side by photochlorination, fluorination, prenylation, diazotization, and oxygenation reactions were fabricated, which endowed the graphene monolayer with asymmetric surface wettability and chemical reactions (Figure 3a).[22] Besides, Dai et al. demonstrated

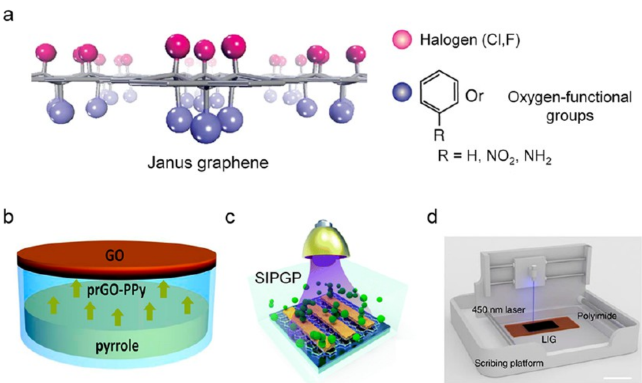

Figure 3. Chemical strategies based on a solid support for carbon-based Janus films. (a) Schematic diagram of forming Janus monolayer graphene with covalent group modification. Reproduced with permission from ref 22. Copyright 2013 Springer Nature. (b) Reactive vapor unilateral modification for the preparation of a Janus GO film with asymmetric layer space. Reproduced with permission from ref 24. Copyright 2016 American Chemical Society. (c) Asymmetric grafting of polymer brushes on a GO film by the SIPGP technique. Reproduced with permission from ref 26. Copyright 2017 Royal Society of Chemistry. (d) Scribing platform for the preparation of LIG on PI. Scale bar, 2.5 cm. Reproduced with permission from ref 27. Copyright 2017 Springer Nature.

asymmetric surface properties of a monolithic graphene film treated with hexane and O_2 plasma for asymmetrical wettability and electrochemical responses.[23] Qu et al. reported the asymmetric reduction of GO through a unidirectional vapor reaction in which the absorbed pyrrole monomers simultaneously experienced *in situ* polymerization and the partial reduction of GO, resulting in the formation of gradient sheet space with a robust binding interface (Figure 3b).[24]

The abundant functional groups on the GO surface are considered to be an active platform for asymmetric modification. A typical route for asymmetrically grafting polymer brushes on a GO surface was achieved by the combination of microcontact printing of initiator molecules and surface-initiated atom-transfer radical polymerization.[25] Subsequently, we improved the reaction process by a self-initiated photografting and photopolymerization (SIPGP)

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Acc. Mater. Res. 2023, 4, 334−347

technique for single-side growth of hydrophobic or hydrophilic brushes with controlled thickness to endow the GO film with adjustable wettability. It is worth noting that the exposed −OH groups are important photoactive sites for the grafting reaction, enabling the SIPGP method to be an efficient and universal route for asymmetric chemical decorations (Figure 3c).[26]

Lasers have been proven to be a flexible approach in creating Janus structures due to their excellent controllability, programmability, and high resolution. Typical examples of the laser-controlled reduction of GO with adjustable gradients and patterns are reported to achieve programmable or local deformation manipulation.[27,28] Moreover, one striking discovery in 2014 demonstrated that the laser was capable of fabricating a highly conductive porous graphene layer directly on a commercial polyimide (PI) film, which was defined as laser-induced graphene (LIG).[30] In this process, the sp^3 carbon atoms were photothermally converted to the sp^2 form with a CO_2 infrared laser. Recently, Ren et al. improved the LIG process through the blue laser writing technique for LIG with larger and more regular pores (Figure 3d).[27] The high thermal conductivity, low heat capacity, and excellent piezoresistive sensitivity endowed the LIG-based Janus film with integrated generation and detection of sound.

The chemical covalent bonds are considered to remarkably enhance the robustness of the obtained carbon-based Janus films compared with the noncovalent interactions. A typical example of asymmetric chemical grafting can effectively modulate the band gap over symmetric structures for two-dimensional graphene sheets. Based on a series of covalent modification strategies (e.g., hydrogenation, halogenation, small molecules, and polymers), it not only controls the graphene band structures for adjusting the electrical properties (electroneutrality, P-type doping, N-type doping, etc.) but also achieves asymmetric wettability modulation.[21] In addition, patterned Janus graphene superlattices coupled with controlled laser treatment have been applied to multifunctional integrated circuits and chemical sensors with specific recognition sites.[31] For macroscale carbon-based films, asymmetric wettability can be achieved by typical plasma reactions or specific polymer decoration, targeting humidity and electrochemical actuators and field-effect transistors.[23,26,32] Moreover, gradient structures through adjustable light or vapor reactions exhibit asymmetric photothermal properties, hydrophilicity, and layer spacing for light or moisture actuators.[24,27,28] There is also a class of LIG-based Janus porous structures that exhibit asymmetric electrical conductivity, photothermal conversion capability, and hydrophobicity suitable for the development of bionic artificial throats and photothermal swimming actuators.[30,33]

3.3. Liquid-Supported Interfacial Strategies

The air−liquid interface[34] or liquid−liquid interface[35] has been considered to be an active functional platform for well-controlled self-assembly and flexible asymmetric physical or chemical reactions of various organic and inorganic materials. Generally, the Langmuir−Blodgett (LB) technique has been proven to be a controllable strategy for achieving 2D assemblies on liquid surfaces. In order to assemble the hydrophilic nanomaterials, Huang et al. improved the deposition process with a novel electrospray approach in which the direct and turbulent mixing with the water subphase could be efficiently avoided owing to the aerosolized spreading droplets on the micrometer scale, thus easily forming a homogeneous GO monolayer (Figure 4a).[36] Moreover, to

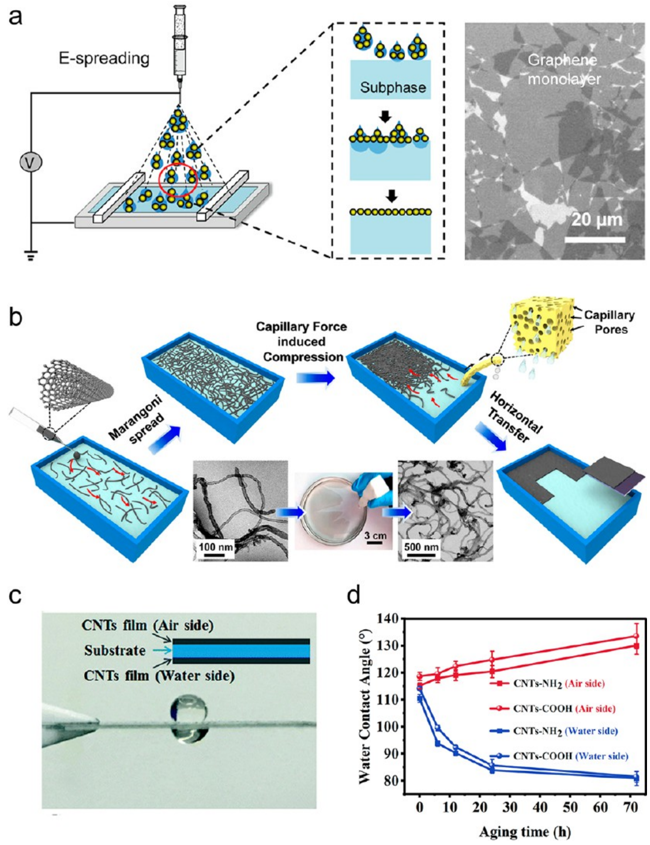

Figure 4. LB assembly of carbon-based films with asymmetric wettability. (a) Electrospray spreading of water-miscible solvents on the water for the assembly of a uniform GO monolayer. Reproduced with permission from ref 36. Copyright 2015 American Chemical Society. (b) Rapid LB assembly of the carbon-based film at the water/air interface assisted by sponge extrusion. Reproduced with permission from ref 32. Copyright 2016 American Chemical Society. (c) Photograph of asymmetric wettability on two sides of the resulting film. (d) Relationship between the water contact angle and the aging time for the assembled CNT film with different hydrophilic groups. Reproduced with permission from ref 40. Copyright 2018 Royal Society of Chemistry.

simplify the LB process, large-area 2D graphene films with excellent conductivity have been previously reported, which was induced by the Marangoni effect-enabled self-assembly process.[9] We have proposed an efficient and simplified method for LB assembly after years of effort, in which the extrusion process is replaced by a porous material-induced siphoning action. The 2D nanofilms formed at the air−liquid interface are capable of further experiencing physical or chemical modification for multifunctional Janus films. In this section, we first briefly introduce the process and modulation strategies for the carbon-based thin films based on our modified LB technique, followed by a discussion of different approaches for Janus films.

3.3.1. Interfacial Strategies for 2D Carbon-Based Assemblies with Asymmetric Wettability. As shown in Figure 4b,[32] the assembly process of the carbon-based films started with the spreading of the dispersion onto the water surface through drop or spray coating. Owing to the strong Marangoni effect, the nanoscaled CNTs were quickly pushed outward from the ethanol-rich regions with low surface tension to water-rich regions with high surface tension. A porous

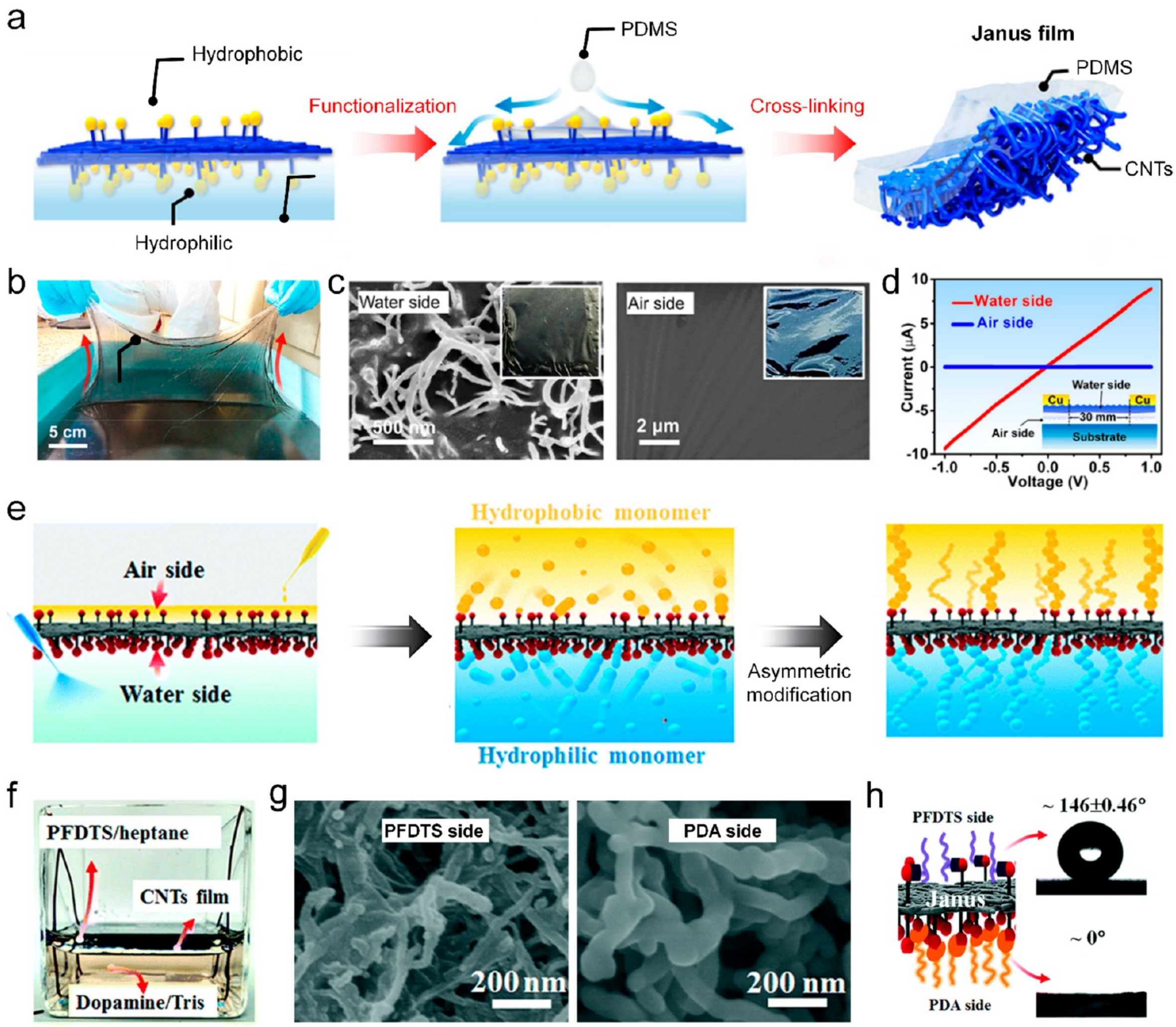

Figure 5. Interfacial asymmetric modification for carbon-based Janus films. (a−d) Physical strategies. Reproduced with permission from ref 42. Copyright 2019 American Chemical Society. (a) Preparation of ultrathin Janus films with embedded interfacial structures by the *in situ* interfacial curing method. (b) Photograph of the resulting ultrathin and elastic Janus film in a large area. (c) Asymmetric surface morphology and (d) electrical conductivity of the carbon-based Janus film. (e−h) Chemical strategies. Reproduced with permission from ref 40. Copyright 2018 Royal Society of Chemistry. (e) Schematic of a free-standing Janus hybrid film prepared by the synchronous interfacial reaction. (f) Asymmetric modification with the addition of hydrophobic and hydrophilic solutions on the air and water sides, respectively. (g) Asymmetric microscopic surface morphology of two sides. (h) Asymmetric wettability of the Janus hybrid.

sponge was applied to squeeze the preassembled film for the formation of a dense entanglement network at the water/air interface. Based on the excellent mechanical performance, the obtained film could be transferred intact onto the rigid or soft substrates. Note that this interfacial assembly strategy is suitable for other nanomaterials, such as graphene,[37] carbon spheres,[38] SiO_2,[32] and hybrids.[39] Interestingly, the self-assembled films exhibited hydrophilic and hydrophobic properties on the water and air sides, respectively (Figure 4c). The asymmetric wettability was time-dependent and dominated by the hydrophilic groups (e.g., −OH, −COOH, and $-NH_2$) (Figure 4d).[40] Moreover, the self-assembly of carbon-based films on other aqueous surfaces (e.g., poly(ether imide) (PEI) solution,[38] GO solution[41]) was achieved by the synergistic Marangoni effect and other interactions (e.g., electrostatic effect, $\pi-\pi$ interaction), allowing the whole assembly process to be no longer confined on water surfaces.

3.3.2. Interfacial Asymmetric Modification for Carbon-Based Janus Films. The formation of a Janus film based on the interfacial assembled carbon nanomaterials could be achieved through physical and chemical approaches. In general, physical strategies include interfacial transfer and *in situ* composite. The interfacial transfer method can combine a carbon film at the liquid−air interface with the received polymer substrate based on weak van der Waals interaction.[37] To further improve the interfacial interactions, we developed an *in situ* composite strategy to prepare Janus films in one step.[42] As illustrated in Figure 5a, the PDMS solution was uniformly spread onto the surface of the CNT film by drop-casting or spray-coating approaches, followed by a curing procedure to obtain large-area and ultrathin Janus films featuring superior elasticity and flexibility (Figure 5b). Owing to the immiscibility of the water and PDMS solution, the resulting Janus film exhibited asymmetric microstructures with CNTs partially wrapped by the PDMS (Figure 5c), which ensured favorable interface strength and good conductivity (Figure 5d). The ultrathin characteristic endowed the Janus film with superior adhesion, allowing it to be conformally

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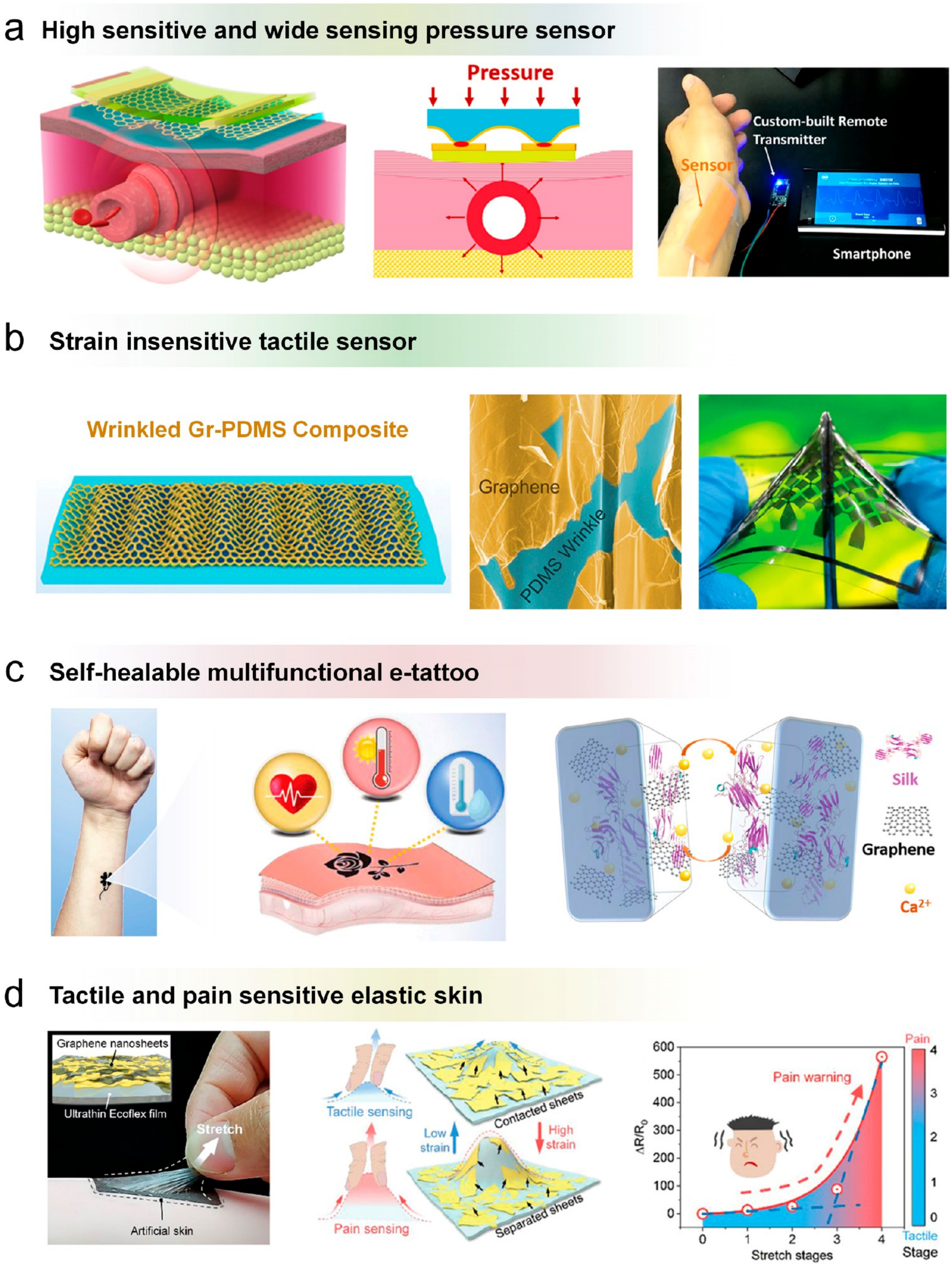

Figure 6. Carbon-based Janus films for high-performance e-skins. (a) Pressure sensor with high sensitivity under a wide linear range based on a micropatterned Gr/PDMS film for a high-accuracy and wearable pulse monitoring system. Reproduced with permission from ref 37. Copyright 2019 Elsevier. (b) Strain-insensitive tactile sensor based on a conformal wrinkled graphene−elastomer composite for a human−machine interface. Reproduced with permission from ref 44. Copyright 2022 John Wiley and Sons. (c) Self-healable e-tattoo based on a graphene/silk fibroin/Ca^{2+} composite for multifunctional sensing. Reproduced with permission from ref 15. Copyright 2019 John Wiley and Sons. (d) Ultrathin graphene-based elastic skin with a pain-sensing function enabled by the SPS effect to mimic the pain perception of natural skin. Reproduced with permission from ref 50. Copyright 2022 John Wiley and Sons.

attached to the surface of the soft skins, curved glass, rough leaf, and even a beaker in a self-supporting form. The specific transfer feature is superior to the conventional construction method based on solid substrates.

The asymmetric chemical reaction is mainly based on the wettability difference between the two sides of the self-assembled carbon nanomaterials. As shown in Figure 5e,[40] hydrophilic and hydrophobic monomer solutions were added to the water side and the air side of the assembled carbon film, respectively. The CNT film functionalized with −OH acted as a medium to conduct interfacial reactions for asymmetric polymeric grafting. Typically, two monomers with distinct wettability were introduced into each side of the self-assembled CNT film for polymer grafting reactions (Figure 5f). The resulting Janus film showed completely different surface morphology on both sides (Figure 5g), allowing the water side with enhanced hydrophilicity and the air side with increased hydrophobicity (Figure 5h). In addition, the interfacial self-assembled carbon film could be used as a 2D reaction generator for the *in situ* synthesis of gold nanoparticles (AuNPs), resulting in a macroscopic 2D free-standing Janus CNTs/AuNPs ultrathin film.[43]

Overall, the carbon-based Janus films fabricated on the liquid−liquid or liquid−air interfaces show typical advantages of controllable preparation procedures, easy transferability, and favorable adaptability on diverse targets. The asymmetric wettability of the interfacially assembled carbon-based film can be achieved by aging treatment or asymmetric chemical decorations, facilitating their functional coupling with the polymer matrix.[40] The asymmetric surface micro/nanostructures (e.g., micropatterns, conformal wrinkles) can be imparted to pristine carbon films by an interfacial asymmetric transfer strategy, enabling remarkable performance enhancement in sensing and actuating devices.[37,44] Besides, the semi-embedded structures with the *in situ* composite strategy confer asymmetric conductivity and excellent mechanical properties to the Janus film. Meanwhile, the elastomer side retains superior adhesion and hydrophobicity, demonstrating significant potentials in underwater sensors and actuators in a self-supported form without any encapsulation or superhydrophobic treatment.[45,46] Moreover, the postcuring procedure of the elastomer enables easy transfer onto diverse target substrates in a semicured state for stable flexible electronics with superconformal adhesion.[47]

4. DIVERSE APPLICATIONS OF THE CARBON-BASED JANUS FILMS

4.1. Flexible Sensors

Flexible sensors with asymmetric structures have attracted extensive interest due to the effective functional synergy and designability of the active layers and the flexible ones. Among them, owing to their superior mechanical flexibility and conductivity, carbon-based thin films have demonstrated great potential in the fields of epidermal electronics, biomedical monitoring, human−machine interfaces, etc. In this section, we will focus on the application of carbon-based Janus films based on our proposed interfacial strategies and other advanced techniques for high-performance electronic skins and noncontact sensing devices.

4.1.1. High-Performance Electronic Skins. Currently, inspired by the intrinsic structures and functions of biological skins, electronic skins (e-skins) show great promise for advanced applications in wearable electronic systems and intelligent robots. Toward these applications, flexible sensors are highly dependent on superior sensitivity and stretchability. However, there is a trade-off between high sensitivity and a wide linear sensing range. Recently, we addressed this contradiction by balancing the thickness and conductivity of a micropatterned graphene film.[37] The asymmetric interfacial transfer strategy facilitates the conformal attachment of a nanoscaled graphene film and endows the micropatterned PDMS surface with excellent conductivity. The achieved Janus structure enables a large initial contact area and sufficient deformation space for the achievement of both high sensitivity (1875.53 kPa^{-1}) and a wide sensing range (up to 40 kPa) (Figure 6a). Generally, the performance of the pressure sensor is inevitably weakened by additional strains from daily use. Therefore, diverse design strategies including kirigami structures[48] and mechanically strengthened micropatterns[49] have been developed for stable pressure perception. We recently proposed a strain-insensitive tactile sensor composed of a conformally wrinkled graphene/PDMS film. In this system, the remarkable modulus difference between graphene and elastomer contributes to the formation of dynamic wrinkles, which balances the concentrated stress among the graphene interconnects by unfolding itself to maintain the intact conductive pathway during the stretching process. Furthermore, the asymmetric interfacial transfer coupled with lithography and the shadow mask technique can contribute to high-resolution graphene patterns for designing desirable tactile sensor arrays (Figure 6b).[44]

The human skin interacts with the external environment based on its multi-stimulus responsiveness and excellent self-healing properties. Inspired by these features, Zhang et al. designed a conformal electronic tattoo (e-tattoo) via a screen printing-assisted asymmetric fabrication method for the highly sensitive perception of strain, temperature, and humidity simultaneously (Figure 6c).[15] The unidirectional deposition of conductive ink consisting of graphene/silk fibroin/Ca^{2+} (Gr/SF/Ca^{2+}) provides multi-stimulus responsiveness, and the water-induced adhesiveness enhancement of the SF/Ca^{2+} substrate allows the electronic tattoo to seamlessly adhere to the skin, thus ensuring the fidelity of the output signal. Moreover, the dynamic hydrogen bonds and coordination bonds at the fractured interface enabled a self-healing efficiency of up to 100%. These excellent properties further enhanced the reliability for application in complex environments.

In fact, human skin is capable of sensing pain to protect us from injury. Recently, we demonstrated a concept of strain−perception−strengthening (SPS) induced pain perception. Benefiting from the asymmetric interfacial construction strategy, the nociceptive response threshold could be effectively regulated by rationally tuning the thickness of the self-assembled graphene layers. Moreover, the favorable adhesion and elasticity of the elastomeric side enable the film to form a suspended one for mimicking nociception in a skin-like 3D deformation (Figure 6d).[50]

In short, the innovation of the introduction of novel materials, the design of special structures, and the combination of asymmetric fabrication processes have contributed to the performance improvement for e-skins, resulting in the emergence of a variety of electronic skins integrated with specific properties such as self-powered sensing,[44] breathability,[51] etc. As a result, it is expected to significantly boost the development of electronic skins.

4.1.2. Noncontact Sensing. Compared with the conventional contact perception mode, noncontact sensing systems have the typical advantage of capturing external stimuli signals, such as wind, sound, environmental humidity, etc. in a

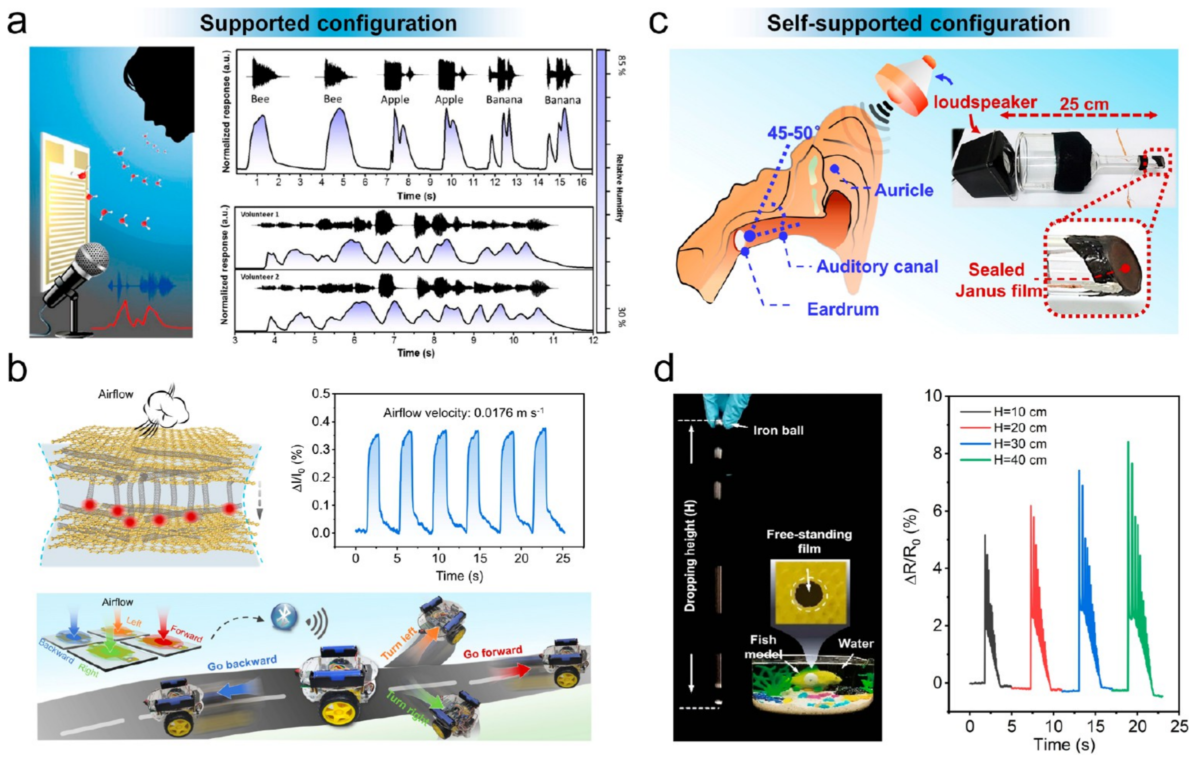

Figure 7. Carbon-based Janus films for noncontact sensing application. (a, b) Janus films with supported configuration. (a) Graphene-PDA heterojunction-based humidity sensor for high-precision voice recognition. Reproduced with permission from ref 52. Copyright 2018 American Chemical Society. (b) Microspring effect-mediated airflow sensor with an ultralow detection limit of 0.0176 m s^{-1} for noncontact manipulation. Reproduced with permission from ref 39. Copyright 2021 John Wiley and Sons. (c, d) Janus films with self-supported configuration. (c) CNT/PDMS hybrid film used as an artificial ear for the detection of acoustic vibration. Reproduced with permission from ref 42. Copyright 2019 American Chemical Society. (d) Biomimetic lateral line sensor based on the free-standing graphene film for highly efficient vibration perception. Reproduced with permission from ref 45. Copyright 2022 Springer Nature.

noncontact way. Generally, there are two configurations for achieving noncontact sensing, including supported and self-supported forms. For the supported one, the as-prepared sensor is attached to the substrate and responds to the applied stimulus through the change of resistance or capacitance. For instance, we designed a humidity sensor composed of a graphene-polydopamine (PDA) heterogeneous sensing junction, in which the dynamic hydrogen bonding induced the rapid adsorption and desorption of water molecules, resulting in the current increase mediated by the proton-hopping mechanism. The rapid response behaviors of the humidity sensor present the potential for voice recognition (Figure 7a).[52] In addition to humidity, we demonstrated that a Janus film based on graphene and a CNT hybrid sensing layer was featured with a microspring effect, enabling the capability of ultrasensitive airflow perception with an ultralow detection limit of 0.0176 m s^{-1}. Moreover, the highly sensitive airflow sensor can be integrated into a sensor array to remotely control the motion of a wireless vehicle by distinguishing the strength and direction of the applied airflow (Figure 7b).[39]

Specifically, for the self-supported configuration, Janus films can function in the form of direct interaction with specific media (e.g., air, water) and undergo mechanical deformation and further change their contact resistance. A typical example of a bioinspired ear composed of an ultrathin self-supported Janus CNTs/PDMS film was demonstrated to sensitively detect acoustic signals (Figure 7c).[42] Owing to the ultrathin characteristic, the self-supporting Janus film was capable of capturing the weak acoustic vibration, allowing the real-time perception of a loudspeaker with different amplitudes and frequencies even away from 25 cm. Also, the Janus structure of the self-supported sensor enables the hydrophobic elastomer side to directly contact with water without decreasing the conductivity of the sensing layer. For example, inspired by the lateral line sensing function of natural fish, we recently developed a novel underwater flexible sensor system based on a Janus film composed of graphene/Ecoflex, which was capable of remotely sensing stimuli from the surrounding environment, including the fall of a nearby steel ball, the walk of a human, and so on (Figure 7d).[45]

In addition, Janus films based on these two configurations enable noncontact sensing through magnetic[53] and capacitive[54] principles, which greatly promotes its development in the fields of noncontact human−machine communication and remote intelligent control.

4.2. Soft Actuators

Janus structures have manifested significant advantages in the construction of soft actuators for the full utilization of the unique properties and asymmetric responsiveness of both sides. Owing to the excellent mechanical flexibility and multi-stimulus response (e.g., heat, light, electric, and humidity) of carbon nanomaterials, flexible actuators based on carbon-based thin films are widely used in diverse actuating applications. Compared to other stimuli, light is promising energy for manipulating carbon-based actuators due to its flexible controllability and remote operation capability. Owing to the superior photothermal effect of carbon nanomaterials, the resulting asymmetric thermal expansion behaviors of the two

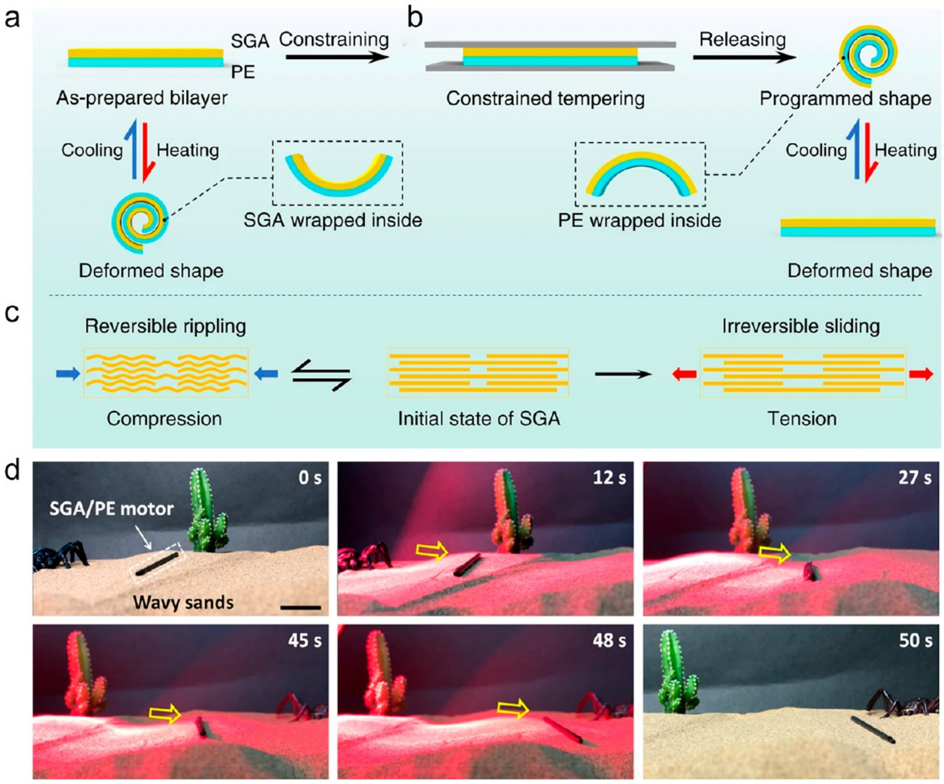

Figure 8. Carbon-based Janus films for light-driven wrap robots. Schematic of the different deformation behaviors for (a) the as-prepared SGA/PE bilayer and (b) a constrained tempered one. (c) Mechanism for the unusual deformation characteristic of the constrained tempered bilayer. (d) Photographs of the SGA/PE motor moving on wavy sands with applied light. Scar bar, 2 cm. Reproduced with permission from ref 55. Copyright 2020 Springer Nature.

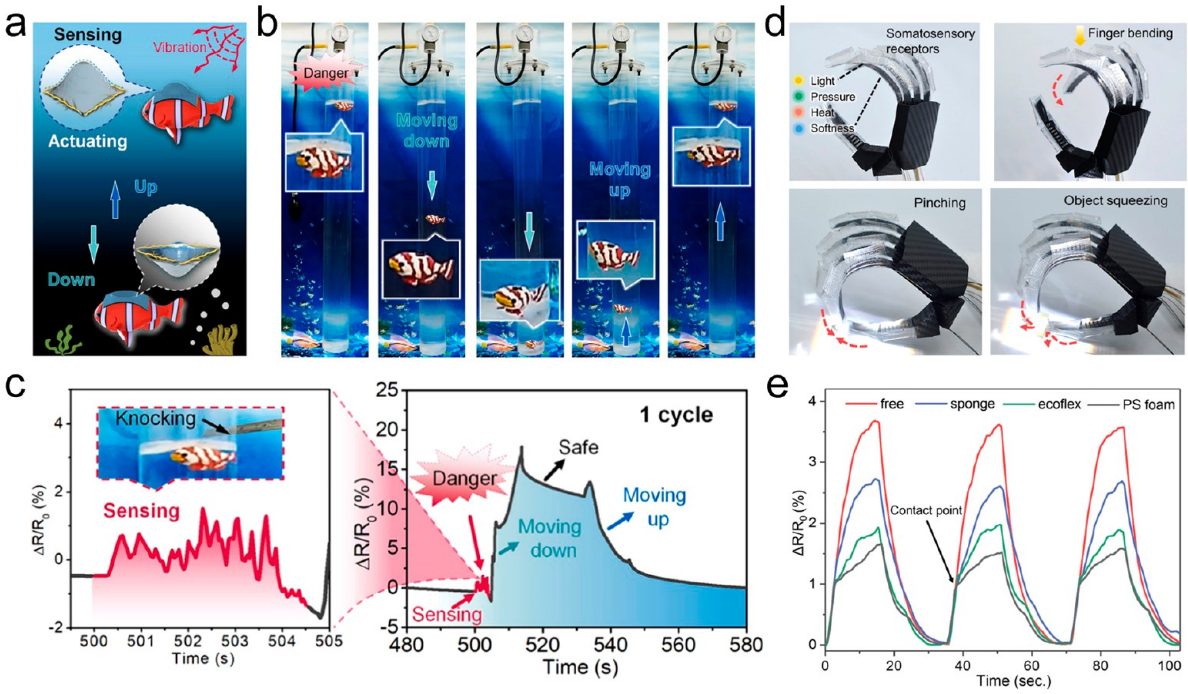

Figure 9. Carbon-based Janus films for the self-sensing soft actuating system. (a−c) Biomimetic swim bladder. Reproduced with permission from ref 46. Copyright 2021 Elsevier. (a) Schematic illustration of the artificial swim bladder pneumatic actuator with self-perceptive ability. (b) Photographs of the diving and surfacing process when the actuator senses external danger. (c) Dangerous signals sensed by the bionic swim bladder and the real-time signals during the subsequent movement. (d, e) Artificial somatosensory and light-actuated hand. Reproduced with permission from ref 60. Copyright 2020 John Wiley and Sons. (d) Photographs of the somatosensory hand and light-driven bending for picking up objects. (e) Real-time resistance response in the pinching motion.

sides of a Janus film enable the activation of asymmetric deformation for high-performance actuation behavior. Based on this mechanism, an ultralight wrap robot based on stacked graphene assembly/polyethylene (SGA/PE) film was rationally designed in which a photothermal graphene layer heated the polymer layer with a high coefficient of thermal expansion for controllable bending and curling behaviors (Figure 8a).[55] More interestingly, when the constrained tempering treatment technique was introduced into this system, the resulting Janus film experienced a transition of a balanced state from the original stripe shape to the curled one (Figure 8b). The interesting phenomenon may originate from the asymmetric elastoplasticity of the graphene layer (Figure 8c). Contributing to the good photothermal conversion capability of the graphene layer, the tempered Janus film could be manipulated to roll under infrared light, enabling an untethered light-driven motor for soft robots (Figure 8d). Moreover, photothermal stimuli also allows us to locally operate the bending of bionic joints[28] or to achieve phototropic self-locomotion based on the self-oscillatory mode.[56] Furthermore, a controllable actuation behavior on liquid surfaces can even be realized based on the photothermal Marangoni effect.[33]

In addition to photothermal conversion, the humidity variation can also be exploited for actuation. Specifically, GO as a typical humidity-responsive material is widely employed to create diverse actuating structures, including building material gradients based on the photoreduction approach,[29] constructing structural gradients with soft lithography,[7] or directly exploiting humidity gradients for driving.[57] Notably, the gradient structure demonstrates significant advantages of improving the durability of the actuators. Endowing carbon-based actuators with multi-stimulus responsiveness allows them to perform more complex and multi-dimensional movements. For instance, Sun et al. prepared GO-based drivers coupled with the gradient distribution of Fe_3O_4 nanoparticles for multifield-coupling remote manipulation, including magnetism, light, moisture, and an ultrasonic wave.[58] This synergistic multifield stimulus response performance empowers carbon-based actuators to explore more complex environments in the future, demonstrating the huge potential for developing advanced robotic systems.

4.3. Self-Sensing Actuators

Flexible actuators with integrated sensing capabilities are of great significance for the development of the next generation of soft robots. Since the equipped sensing function can monitor and provide feedback on the actuating process in real time, it significantly enhances the adaptability and multitask processing ability of the robots in complex environments.[59] Recently, we proposed a self-sensing biomimetic swim bladder consisting of a self-supported CNTs/PDMS Janus film (Figure 9a), which could be pneumatically actuated to swim up and down through the switching behaviors of the inflation and deflation of the elastic Janus film (Figure 9b).[46] The reverse stretching of the CNTs network under mechanical deformation enables the artificial swim bladder to sensitively perceive the real-time actuation process and external vibration (Figure 9c). Generally, external stimuli factors can also result in resistance change, which will severely weaken the accuracy of the feedback signal. To address this issue, Sitti et al. eliminated the thermoresistivity resulting from the photothermal actuation process through the hybridization strategy of metallic graphite and semiconductive CNTs with suitable ratios.[14] Also, Ho et al. constructed the somatosensory light-driven hand through the combination of conductive graphite−carbon nanotube composites, ferroelectric poly(vinylidene difluoride), and photothermal polydopamine reduced graphene oxide. The achieved smart hand demonstrated the synchronous and noninterfering perception of strain, pressure, and temperature during the photothermal actuation (Figure 9d).[60] Moreover, the light-induced finger bending allowed the achievement of object grasping and closed-loop feedback (Figure 9e). The novel smart robots integrated with multiple sensing functions offer a new opportunity for friendly human−robot interaction, complex environment adaptation, and the implementation of closed-loop control in actuation and sensation systems.

5. CONCLUSIONS AND OUTLOOK

We have summarized the recent progress of bioinspired carbon-based Janus films toward frontier fields of flexible sensors, soft actuators, and their integrated devices. In this Account, we first discussed the general properties of various carbon nanomaterials and then introduced typical strategies for the preparation of carbon-based Janus films enabled by solid-supported physical and chemical approaches, and further highlighted the newly developed interfacial engineering techniques based on liquid support for large-area, ultrathin, and homogeneous films. Also, the relationship between the preparation process and the intrinsic properties of the Janus films was discussed in detail. Then, advanced applications of biomimetic electronics skins, soft actuation, and self-sensing actuating systems were also demonstrated. Specifically, we mainly focused on the Janus films based on the air/water interface strategy for high-performance epidermal electronics, noncontact sensing, light-controlled actuators, and self-sensing bionic fish bladders.

Although significant effort has been devoted, some challenges still remain. First, there is still no conclusive answer to the biological toxicity of carbon nanomaterials. To reduce the risk of toxicity, compounding by biocompatible materials and encapsulating the devices are expected to be alternative strategies. Typically, a robust two-phase structural interface is required to ensure stable actuation behaviors and highly reliable and accurate sensing feedback signals. Alternative approaches include the construction of effective interlocking interfaces, the formation of covalent interactions, and the combination of physical and chemical strategies. Moreover, when exposed to harsh environments, carbon-based Janus films should be actively endowed with specific functions such as self-healing, abrasion resistance, high-temperature resistance, and frost resistance. Also, endowing carbon-based Janus films with multifunctionality is highly significant for the achievement of complicated and intelligent soft robotic systems. Besides, some rational engineering strategies are highly preferred to ensure effective functional synergy and the capability of executing actions without functional interference in an error-free manner under changeable environments. Meanwhile, pursuing well-controlled patterns on Janus films for high-performance devices (e.g., high-precision, location-identification sensors, and programmable multistage actuators) in an accessible and efficient way is highly desired. Finally, the in-depth development of interfacial strategies combined with advanced *in situ* printing and roll-to-roll technologies is expected to be a promising pathway for achieving new sensing and/or actuating functions and related soft robotics.

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Notes

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