Chapter 11

Design, Assembly, and Fabrication of Two-Dimensional Nanomaterials into Functional Biomimetic Device Systems

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Additional information is available at the end of the chapter

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Abstract

Diverse functioning biosystems in nature have inspired us and offered unique opportunities in developing novel concepts as well as new class of materials and devices. The design of bioinspired functional materials with tailored properties for actuation, sensing, electronics, and communication has enabled synthetic devices to mimic natural behavior. Among which, artificial muscle and electronic skin that enable to sense and respond to various environmental stimuli in a human-like way have been widely recognized as a significant step toward robotics applications. Polymer materials have previously been dominant in fabricating such functional biomimetic devices owing to their soft nature. However, lacking multifunctionality, handling difficulty, and other setbacks have limited their practical applications. Recently, versatile and high-performance two-dimensional (2D) materials such as graphene and its derivatives have been studied and proven as promising alternatives in this area. In this chapter, we highlight the recent efforts on fabrication and assembly of 2D nanomaterials into functional biomimetic systems. We discuss the structure-function relationships for the development of 2D materials–based biomimetic devices, their tailoring property features, and their variety of applications. We start with a brief introduction of artificial functional biomimetic materials and devices, then summarize some key 2D materials–based systems, including their fabrication, properties, advantages and demonstrations, and finally present concluding remarks and outlook.

Keywords: 2D nanomaterials, biomimetics, smart device systems, graphene, functional design and fabrication

1. Introduction: functional biomimetic materials and devices

Elegant and sophisticated structures and functionalities of nanoscale biological systems in nature have offered unique inspirations in the development of new concepts, diverse classes of nanomaterials, and various functional devices. The design and synthesis of bio-inspired materials with tailored properties for actuation, sensing, smart electronics, and highly efficient energy harvesting have enabled artificial devices to be endowed with bio-mimicking features, among which artificial muscle and electronic skin that can sense and respond to environmental changes by mimicking human ways have been widely considered as crucially important for new-generation biomimetic devices. In this regard, newly emerged versatile and high-performance two-dimensional (2D) nanomaterials such as graphene and its derivatives have been explored and proven as promising candidates. In this chapter, we aim at highlighting the latest efforts toward design, synthesis, and applications of 2D nanomaterial-based functional biomimetic systems.

1.1. Key concepts of biomimetics

The term "biomimetics" was *first* coined during the 1950s to describe a biological approach to the needs of engineering science. Lepora et al. have recently attempted to make a connectedness of current popular terms in biomimetics (**Figure 1**) [1]. With such a connectedness, biomimetics now encompasses various disciplines of biomaterials that retain their strong connections to biomimetic. Biomimetic materials, or biomaterials, traditionally defined as materials used in medical devices, have been used since antiquity, but recently their degree of

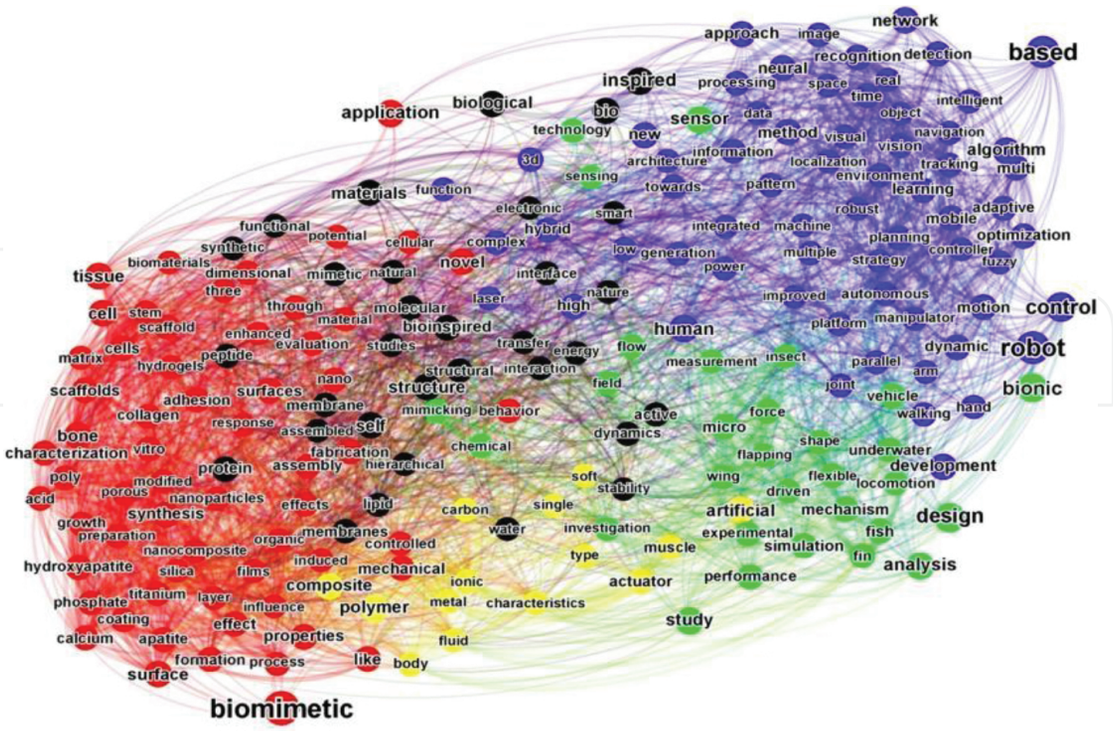

Figure 1. Connectedness of popular terms in biomimetics [1].

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sophistication has been enhanced significantly. Biomimetic materials made today are routinely information rich and incorporate biologically active components derived from nature, and have found use in a wide variety of nonmedical applications [2]. Advancements in materials science, manufacturing process, and continual miniaturization of components have enabled biomimetic materials to have the ability of sensing, actuation, communication, and even computation [3]. Engineers have employed such intelligent materials to fabricate precise, predictable robotic devices and systems, which learned from studying biological systems are now culminating in the definition of a new class of machines that researches refer to as soft robots [4], which connects strongly with biomimetics (**Figure 1**).

Similar to humans, such robots will, in addition to hard components such as bones, have soft bodies made of soft materials, and will be capable of soft movements and soft interactions with people (**Figure 2**). A recent trend in soft robotics is to simplify the typically computationally intensive, neutrally inspired control through smart morphological design and use of functional materials [5–7]. There is no doubt that soft biomimetic materials enable most of the automation of tasks beyond the capacities of current robotic technology. The full integration of biomimetic materials and devices into complete robotic systems is of significant interest in science and technologies, but is full of complex challenges.

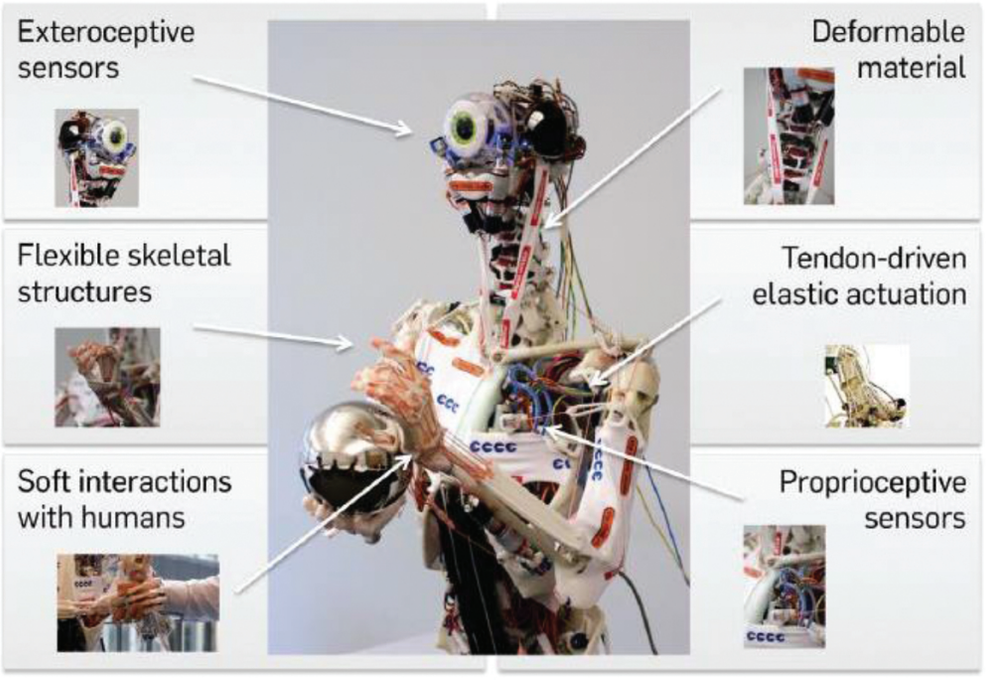

Figure 2. An anthropomimetic humanoid robot ECCE (Embodied Cognition in a Compliantly Engineered Robot) [8].

1.2. Design and synthesis of 2D materials

In a biomimetic material, biomimetic behaviors refer to changing the material properties of the underlying base material to actuating, sensing, and communicating. Some possible mechanisms involve changes of stiffness, volume and shape, electronic properties, or color

(**Figure 3**). For example, inorganic nanowires such as single-walled carbon nanotube (SWCNT), ZnO, Cu, In_2O_3, and etc. offer new material basis and opportunities for flexible electronics that enables many biomimetic applications, including sensors, display devices, and logic gates [9]. All-dielectric meta-materials that can respond to both the electric and magnetic fields of light, support large optical chirality and anisotropy, have promising potential to be used in fabrication of biomimetic meta-surfaces [10]. Ionic polymer-metal composites show large deformation in the presence of low applied voltage and therefore have been widely used as highly active actuators and sensors [11]. Shape-memory polymers are an important class of stimuli-responsive soft materials for which shape-shifting behavior can be programmed, enabling the application as artificial muscles [12]. Overall, from inorganic to organic, from nanoscale to macroscale, various range of materials can be fabricated into designable biomimetic devices including electronic skins [13, 14], artificial muscles [15, 16], etc.

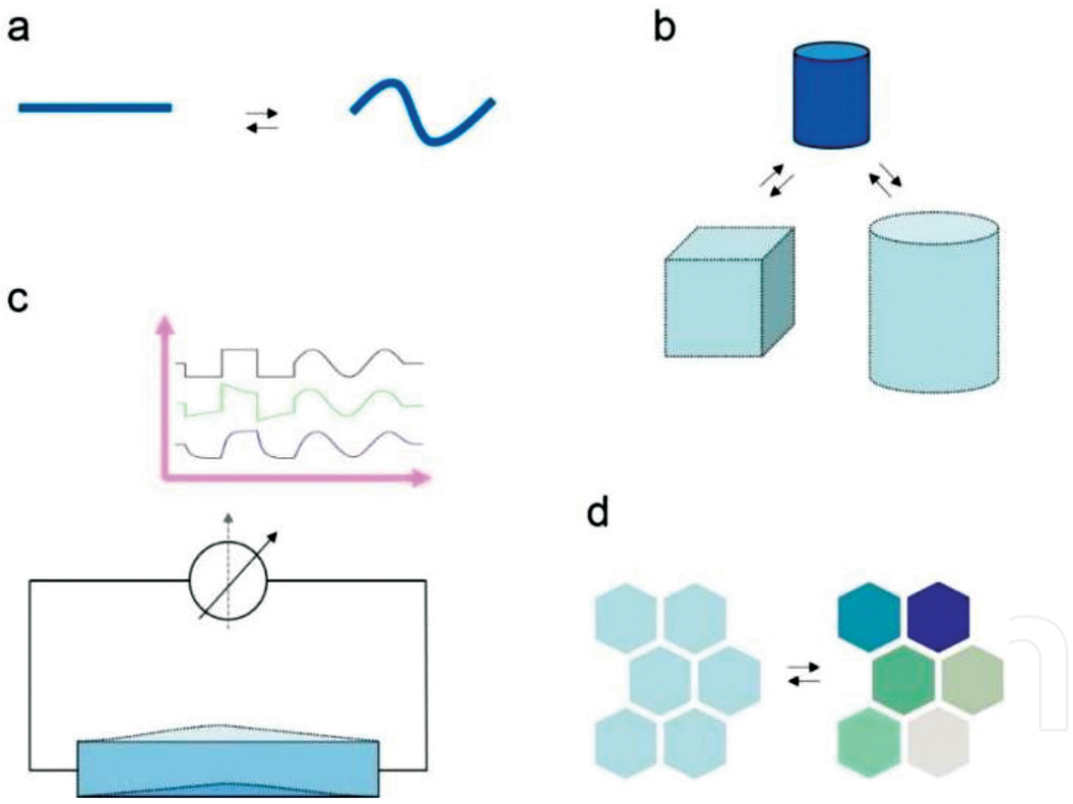

Figure 3. Examples of a biomimetic material working toward changing the crucial properties of the base material. Changes in (a) stiffness and (b) shape/volume could enable shape-changing actuation materials. Robotic skins could utilize changes in (c) electronic responses and (d) appearance to sense and communicate.

Particularly, due to their inherent flexibility and novel properties, 2D-layered nanomaterials as the *in situ* unit of biomimetic materials hold great promise in flexible and versatile biomimetic devices. Here we summarized the reported alternative 2D materials, and the description has been organized in an order according to their synthesis methods.

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In addition to graphene, micromechanical exfoliation has been extended to prepare other 2D inorganic materials. In fact, following this approach, individual crystal sheets from a variety of layered materials have been isolated. Monolayers of BN, MoS_2, $NbSe_2$, and $Bi_2Sr_2CaCu_2O_x$ have been prepared by rubbing a layered crystal against a substrate and leaving random flakes on it [17]. Among the resulting flakes, single layers were always found. This method leads to high crystal quality and macroscopic continuity, and is considered as one of the easiest and the fastest ways, as in the case of well-known graphene. However, a serious drawback is noticed: monolayers obtained by micromechanical exfoliation are in a great minority among accompanying thicker flakes. Despite allowing the first example of characterization of one-atom-thick monolayers, this is not a feasible procedure for large-scale production of 2D materials for technological applications. Therefore, in the last few years, new methods have been developed to approach scalable synthesis of 2D inorganic materials.

Vapor deposition techniques have been most extensively explored due to their potential for high scalability and morphological control. By balancing the production cost and the above prerequisites, chemical vapor deposition (CVD) is the most promising route to produce large-area device-grade graphene. Normally, the procedure involves two steps: *first*, pyrolysis of a precursor to form carbon and disassociation of carbon atoms, and then the formation of the graphene. The pyrolysis to disassociate carbon atoms must be carried out on selected substrates to prevent the precipitation of carbon clusters during the gas phase. This leads to a problem and metal catalysts must be used to reduce the reaction temperature required for pyrolytic decomposition of precursors. During the reaction, the metal substrate not only works as a catalyst to lower the energy barrier of the reaction, but also determines the graphene deposition mechanism, which ultimately affects the quality of graphene [18]. Graphene growth has been demonstrated on a variety of transition metals such Ni, Pd, Ru, Ir, or Cu, and is also achievable on insulating SiC [19]. In a similar process, metal containing precursors [e.g., MoO_3, WO_3, or $(NH_4)_2MoS_4$] are vaporized and reacted with chalcogen elements through vapor-solid reactions, leading to the growth of 2D materials beyond graphene on a substrate downstream [20]. Alternatively, 2D material bulk powders can also be used as the precursor directly [21]. For example, Feng et al. [22] employed a tree-zone furnace to synthesize large-area 2D $MoS_{2(1-x)}Se_2x$ semiconductor alloys.

Liquid-phase exfoliation is Low-cost and scalable method which has been widely used for preparing individual sheets of 2D materials. Typically, this method requires homogeneous dispersion of 2D materials in diverse solvents or aqueous solutions. With the assistance of sonication, the weak van der Waals bonds between the layers are broken and individual layers are obtained. Shen et al. [23] have reported an effective strategy to exfoliate 2D materials in a high yield. In addition to the total surface tension, efficient solvents for liquid-phase exfoliation were found to be those which have a similar ratio of polar components to dispersive components of surface tension to the 2D materials. Mono- to few-layer graphene, WS_2, MoS_2 h-BN, $MoSe_2$, Bi_2Se_3, TaS_2, and SnS_2 were prepared with low-toxic and low-boiling point solvents, such as 1:1 IPA/water for graphene, WS_2, h-BN, and $MoSe_2$; 1:4 IPA/water for Bi_2Se_3, and SnS_2; 7:3 IPA/water for MoS_2, acetonitrile for TaS_2.

2. 2D materials enable sensing, actuation, and communication

Smart advanced materials that are flexible, adaptable, multifunctional, and meanwhile "green" are essential for biomimetic approaches. Since it was *first* isolated in 2004 [24], graphene has attracted tremendous attention because of its extraordinary electrical, thermal, and mechanical properties [25–27]. It is not surprising that graphene leads to 2D material research and has developed *rapidly* to several important applications such as energy technologies [28, 29], electronics [30, 31], and biomedicine [32, 33]. Among these applications, graphene-based intelligent devices that can spontaneously detect and respond to external stimuli are of broad practical interest and importance. Inspired by the great success achieved through the research of graphene-based materials, the similar ideas and methodologies have also been extended to study other layered materials. This is well indicated by the number of new 2D inorganic nanomaterials blossomed in the past few years. In this section, we offer a brief overview of the successes reported on the biomimetic performance of 2D materials.

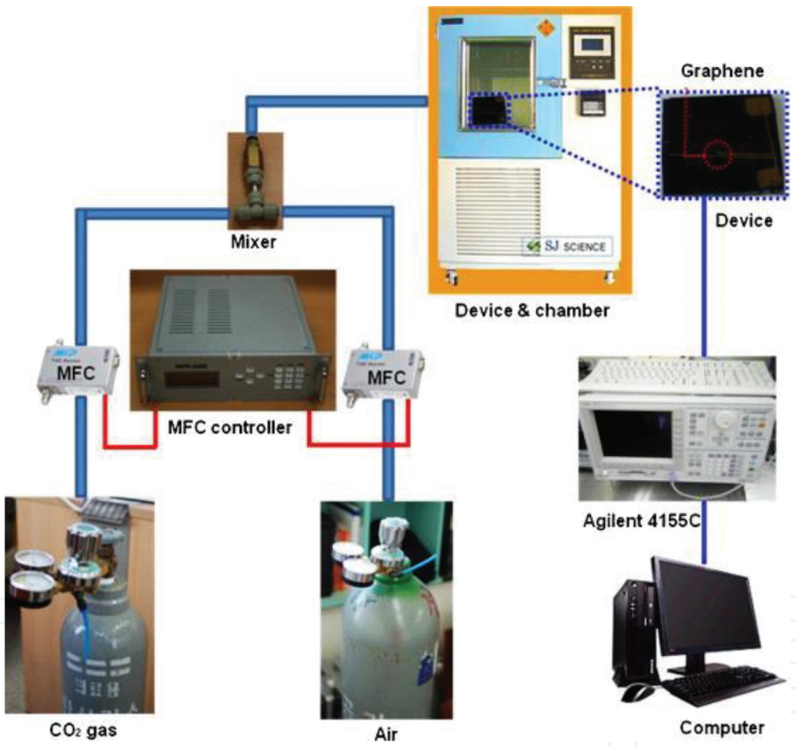

Figure 4. Experimental setup for measurements performed using the graphene CO_2 gas sensor [35].

2.1. Sensing

2D materials are usually good candidates for gas sensors due to their large surface-to-volume ratio and the associated charge transfer between gas molecules and the substrates [34]. Graphene has very high electron mobility at room temperature, and hence, its gas sensitivity

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is very high. Yoon et al. [35] fabricated a graphene-based CO_2 gas sensor by mechanical cleavage and micromachining. The graphene sensor shows significant conductance changes when exposed to various concentrations of CO_2 in air. The response time of the sensor is less than 10 s. The overall system is illustrated in **Figure 4**. They have shown the principle idea, but the sensing systems might need to be upgraded to wearable devices in order to meet the fashion applications. Late et al. [36] reported a comprehensive suite of sensing behavior of atomically thin-layered MoS_2 structures in a transistor-like configuration. MoS_2-based field emission transistor (FET) showed outstanding sensitive response to NH_3, NO_2, as well as water vapor at room temperature and atmospheric pressure. 2D material-based FET showed improved mobility and wearable capability, due to its nanoscale size and facile and precise testing systems. Kou et al. [34] reported first-principles calculations that examine the adsorption of several typical molecules, CO, CO_2, NH_3, NO, and NO_2 on phosphorene. They determined their preferential binding positions and the corresponding binding energy. Their results show that the strength of binding is highly dependent on the extent of charge transfer between the adsorbed molecules and the phosphorene layer, which is similar to that observed in graphene and MoS_2. However, the adsorption of gas molecules on phosphorene is notably stronger resulting in a more pronounced effect on the sensitivity.

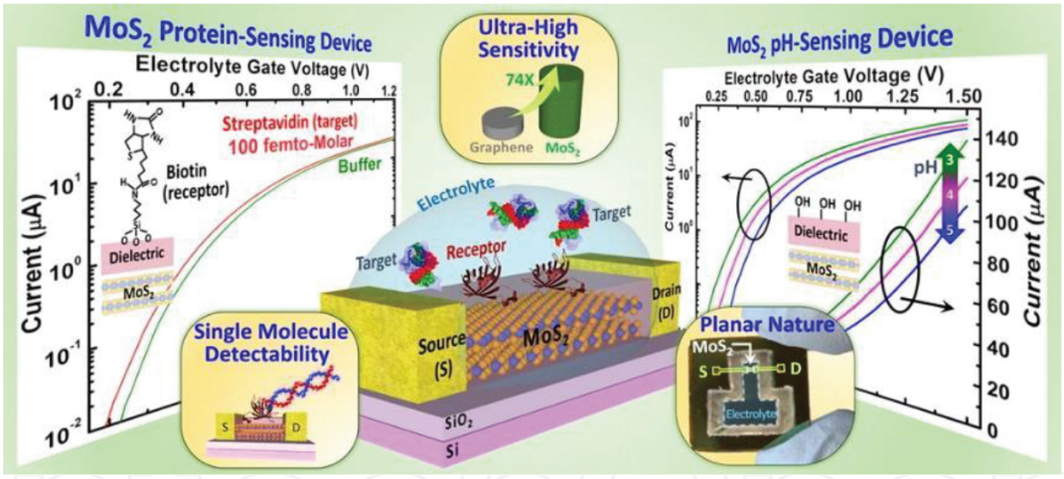

Figure 5. MoS_2-based FET biosensors, which provides high sensitivity and at the same time offers possibility for facile patterning and device fabrication [38].

Biosensors based on 2D material FETs have also attracted much attention, as they offer rapid, inexpensive, and label-free detection of biologically related signals. Development of 2D material FETs may bridge the technological gap between signal transduction, conditioning, processing, and wireless transmission in a wearable biosensing device, by merging plastic-based sensors that interface the skin with silicon-integrated circuits on a flexible circuit board for complex signal processing [37]. Sarkar et al. [38] demonstrated a FET biosensor based on MoS_2. This sensor shows ultrahigh sensitivity (713 for a pH change of 1 unit) and wide operation range (pH of 3–9) (**Figure 5**). It also demonstrates specific detection of protein as well as an extremely high sensitivity of 196 even at 100 femtomolar concentration.

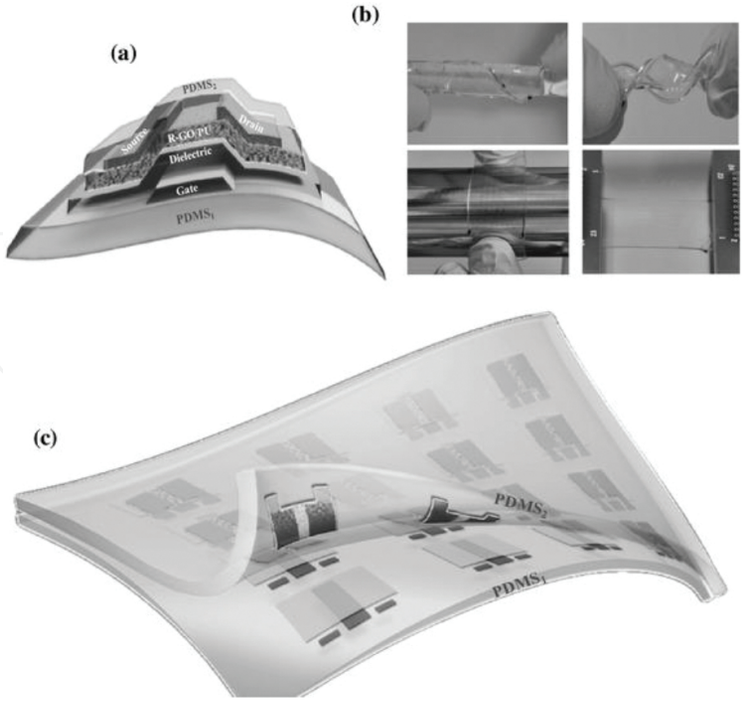

Figure 6. Schematic of device structure and fundamental characteristics of the all-elastomeric transparent stretchable gated sensor [42].

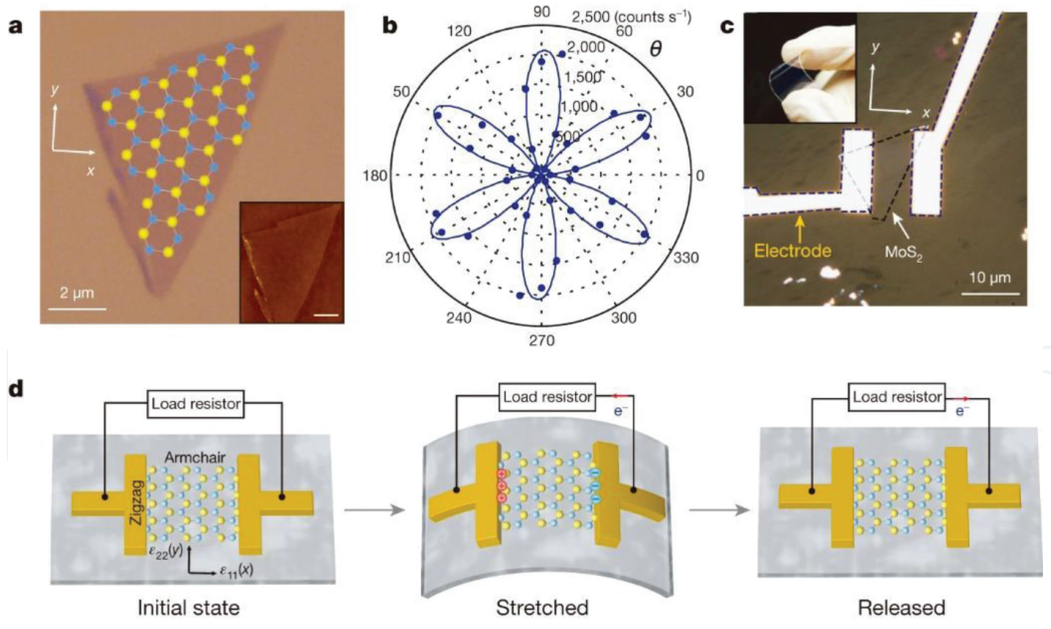

Figure 7. (a) Optical image of the single-atomic layer MoS_2 flake. Blue and yellow spheres represent Mo and S atoms, respectively.(b) Polar plot of the second harmonic intensity from single-layer MoS_2 as a function of the crystal's azimuthal angle θ.(c) A typical flexible device with single-layer MoS_2 flake and electrodes at its zigzag edges.(d) Operation scheme of the single-layer MoS_2 piezoelectric device [43].

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In addition to the examples described above, sensing platforms equipped or integrated with temperature, strain, and humidity sensors have attracted more and more attention due to their natural skin-like biomimetic sensing behavior [39–41]. Trung et al. [42] developed a very simple fabrication process to realize the all-elastomeric temperature sensor array. They integrated a strain sensor on a platform which can be attached as a patch to objects or human skin (**Figure 6**). Reduced graphene oxide (rGO) nanosheets embedded in a elastomeric polyurethane matrix were used as the temperature sensing layer. Notably, most function layers of the device are intrinsically transparent and stretchable.

Wu et al. [43] reported an experimental observation of piezoelectricity in single-atomic-layer 2D MoS_2 and explored its application in mechanical energy harvesting and piezotronic sensing (**Figure 7**). Cyclic stretching and releasing of odd-layer MoS_2 flakes produced oscillating electrical outputs, which could convert mechanical energy into electricity. The strain-induced polarization charges in single-layer MoS_2 can also modulate charge carrier transport at the MoS_2–metal barrier and enables enhanced strain sensing. This study has demonstrated the potential of 2D nanomaterials for powering nanodevices, adaptive bioprobes, and tunable/stretchable electronics/optoelectronics.

In short, these sensors have shown great potential for their adaptability to wearable skin electronics for recognition of human activity and environmental changes.

2.2. Actuation

The crumpling of materials is widely observed in various objects as small as biological membranes, in objects as thin as a piece of paper, and in systems as large as the Earth's crust. 2D actuation systems responsive to electrochemical, light, and other external stimuli can convert different energy forms (electric, chemical, photonic, thermal, etc.) to mechanical energy that is potentially profitable for diverse applications ranging from robots, sensors to memory chips [15, 44]. Theoretically, Roger et al. [45] have studied the electrochemical actuation of monolayer graphene upon charge injection and ionic liquid (IL) electrolyte immersion. They have concluded that the electrostatic double layer could induce strains of more than 1% and its contribution to the overall strain was always equal to or higher than that of the quantum-mechanical strain (~0.2%) from charge injection of −0.1 e per C atom. Based on these theoretical predictions, GO is in principle an excellent material for actuators and artificial muscles.

Zhang, et al. [46] performed molecular dynamics simulation to create a nanosized graphene origami box. By warping the top graphene layer downward and the bottom graphene layer upward, the cross-shaped cubic graphene nanocage could encapsulate nano objects such as biomolecules (**Figure 8**). This paradigm opens up a new avenue to control the 3D architecture of 2D-layered materials and provides a feasible way to exploit and fabricate the 2D nanosized actuators.

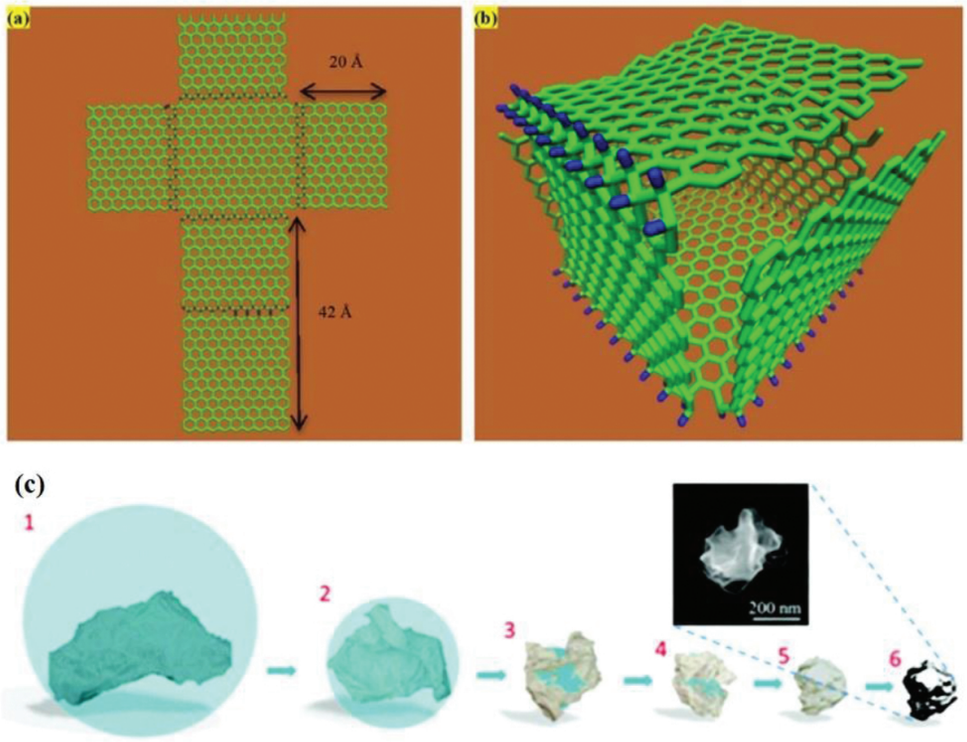

Figure 8. Programmable graphene folding with designed morphology.(a) and (b) represent the initial and final configurations of a graphene nanocage, respectively.(c) Schematic illustrating rapid loss of H_2O in GO and subsequent crumpling of GO nanosheets [46, 47].

Ma et al. [47] experimentally proved that GO in aqueous solution could be aerosolized and dried to produce crumpled nanopaper-like sheets, which are similar to the graphene nanocage. They used online size selection and aerosol mass analysis to determine the fractal dimension (D) of crumpled GO nanosheets. D is able to be tuned by altering solvent conditions. Typically, a 10% acetone mixture increases D to 2.68 ± 0.02 from 2.54 ± 0.04. Calculations of the confinement force indicate that crumpling of GO nanosheets is driven by the capillary force associated with rapid loss of the solvent.

Similarly, a fluidic motion of alcohol molecules which across the interlayer gap in layered double hydroxide (LDH) could enable rapid and reversible tuning of interlayer spacing of the LDH at sub-Å precision, reported by Ishihara et al. [48]. This so-called hydrogen bond–driven "homogeneous intercalation" mechanism could be used in rapid, reversible, and ultraprecise actuation of LDH materials.

Similar approaches could also be applied to magadiite [49] and layered potassium hexaniobate [50]. Novel photoactivated artificial muscle model units could be obtained as they reported. For example, as seen in **Figure 9**, it is clearly observed on a cross-cut section of the layered hybrid film that upon photoirradiation of a layered hexaniobate intercalated with a polyfluoroalkyl azobenzene derivative, a very large magnitude lateral movement (sliding) of the nanosheets was reversibly induced. By applying this strategy, organic/inorganic hybrid nanosheets reversibly and horizontally slide on a macroscale upon on/off photoirradiation, which results in vertically shrinking and expansion of the interlayer spaces in the layered

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hybrid structure. The sliding movement of the structure on such a giant scale is the first example of an artificial muscle model unit having remarkable similarity to that in natural muscle fibrils.

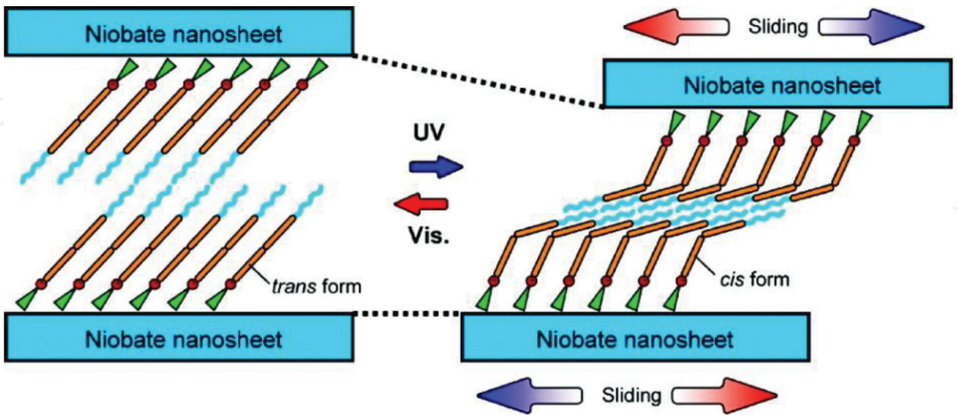

Figure 9. Schematic diagram of the niobate nanosheet sliding movement and interlayer distance change induced by photochemical trans–cis isomerization of the azobenzene molecules [50].

2.3. Communication

Emotional (or feeling) communication skills are natural behavior in biological systems. However, similar communication between humans and autonomous robots is a tremendous challenge to be achieved.

Appearance and texture identification in an artificial skin allows creating and broadcasting emotional cues, which may facilitate the acquisition of the robot's emotional behavior. The fabrication of a network consisting of mechanically flexible sensors is the key to achieve artificial intelligence that comes into direct contact with humans for biomedical applications such as prosthetic skin. To mimic the interaction behavior such as tactile sensing properties of natural skin, large arrays of pixel sensors on a flexible and stretchable substrate are usually required [51]. The integration of 2D materials in FET arrays as the dielectric layer leads to a new type of active sensing devices which not only have high sensitivity but also enable to initiate responsive interactive behavior. In this context, there are several cases reported. For example, Wang et al. [52] integrated various electronic, sensor, and light-emitting components (involving both organic and inorganic materials) on a thin plastic substrate (**Figure 10**). This work demonstrated a possibly practical technology platform serving as a flexible user-interactive system that could not only detect and spatially map external stimuli such as pressure, but also respond with a seamlessly integrated display. The responsive pressure profile is instantaneously visible without the need of sophisticated data acquisition circuits and electronic boards on such systems. Such approach based on integration of 2D functional materials into a flexible thin film device could lead to an emerging and hot research topic, i.e., electronic skin, or e-skin.

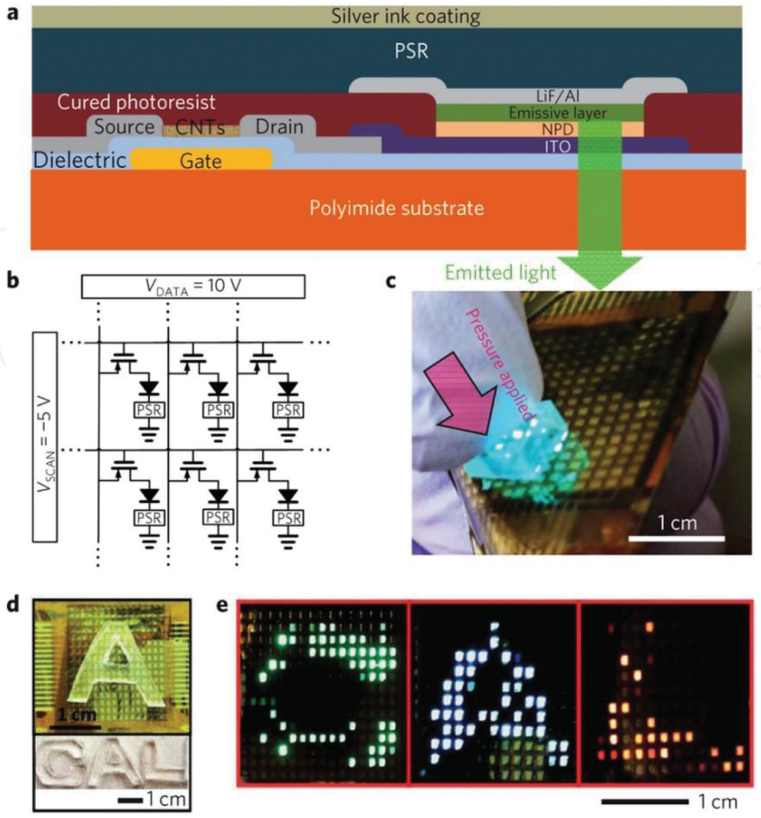

Figure 10. (a) Cross-sectional schematic showing one pixel of the interactive e-skin device, consisting of various components.(b) Schematic of the e-skin circuit matrix.(c) Photograph of an integrated device showing that light is locally emitted when the device surface is touched. (d) PDMS slabs with C, A, and L shapes are prepared and used to apply pressure onto the sensor array.(e) Green, blue, and red color interactive e-skins are used to spatially map and display the pressure [52].

3. Functional biomimetic devices based on 2D materials

As described above, the development of integrated intelligent devices is essential to the realization of biomimetic systems. In this section, we discuss the two most promising classes of biomimetic devices: e-skins and artificial muscles based on 2D materials.

3.1. e-Skins

The skin, as the largest organ in the human body, is mechanically self-healing and can provide a variable degree of touch sensitivity. Mimicking the functions of natural skins is therefore widely accepted to be very important in the future for robots used by humans in daily life for numerous applications. Thus, the development of an artificial skin, also known as electronic skin (e-skin) that is flexible and stretchable [51–54], sensitive enough to perceive touch [55–57], and yet able to heal itself following damage [58, 59] is in high demand in robotic applications.

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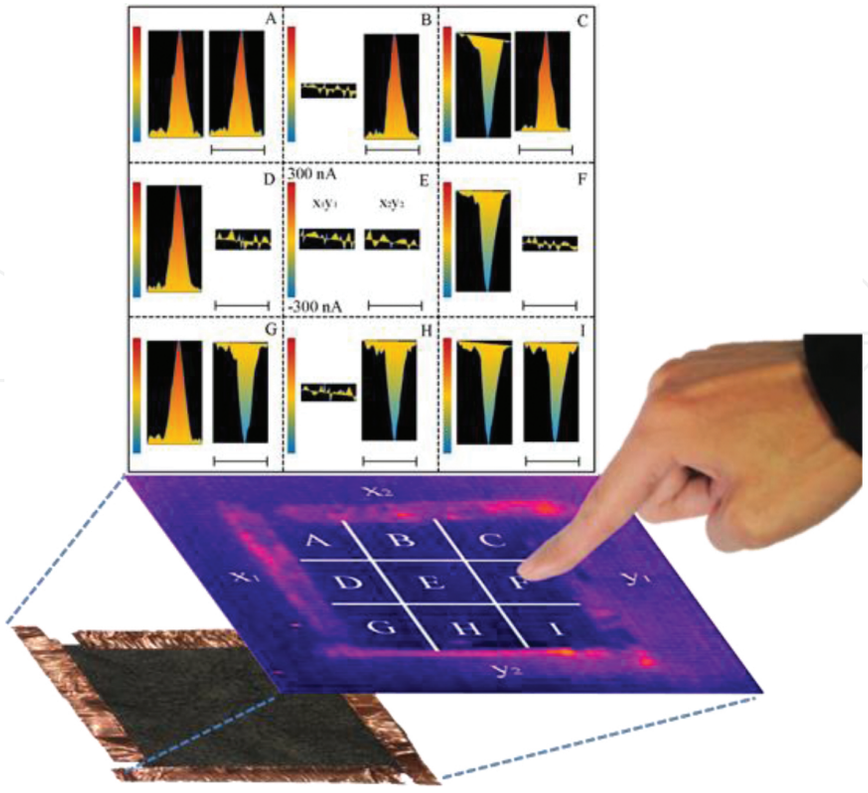

Figure 11. Real-time current curves of the sensor pad during a finger touch/remove cycle on its surface [60].

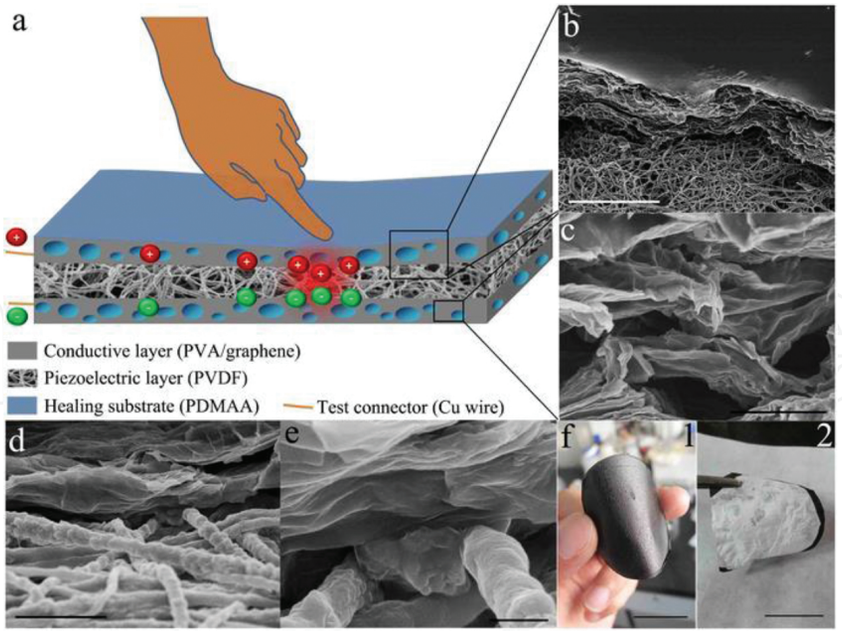

Figure 12. (a) Schematic of the hybrid e-skin and its pressure sensitivity.(b–e) Cross-sectional FESEM images of the hybrid e-skin showing microscopic structures and the boundary between functional layers. Scale bars are 30 μm, 5 μm, 3 μm, and 500 nm, respectively.(f)Photographs of the hybrid e-skin. Scale bar is 2 cm [59].

Hou et al. [60] designed and fabricated a novel reduced graphene oxide foam (rGOF) that is free-standing, flexible, and elastic. As shown in **Figure 11**, the rGOF shows temperature sensitivity based on thermoelectric effects in the graphene with assistance of its good electrical properties. The rGOF can respond rapidly to finger pressure owing to the finger heating effects. As a proof of concept, the authors also produced rGOF pressure sensor pad that can locate finger pressure points and measure the pressure level. Most importantly, all sensing abilities of this device can operate by itself without the need of any additional power supply.

Hou et al. [59] also presented the first self-healing, mechanically strong and stretchable, self-activated pressure-sensing device based on rGO. The device is composed of various functional components including piezoelectric and electrically conductive layers as well as a healing substrate **Figure 12**. Poly(N,N-dimethylacrylamide), poly(vinyl alcohol), rGO, and polyvinylidene difluoride are employed in this hybrid device. It is suggested that preparing flexible and porous hybrid foams with interconnected 3D networks is a practical way to fabricate stretchable and self-healing thin film e-skin.

In order to improve the texture resolution of e-skin, FET technology is usually involved in the design and fabrication of sensors. Mannsfeld et al. [51] reported an organic thin film pressure sensor, which employs a key organic FET structure consisting of a thin, regularly structured rubber. The dielectric capacitance in organic FET devices directly depends on the output current, which enables the sensing of an applied pressure. This device provides high sensitivity in both medium- and low-pressure regimes. Besides, unprecedentedly fast response and relaxation times ($\ll$1 s) are also reported.

Sun et al. [61] reported a piezopotential-powered active matrix strain sensor arrays which combined coplanar gate graphene transistors and piezoelectric nanogenerators. The strain sensor demonstrated excellent performances including a high sensitivity (gauge factor = 389) and a minimum detectable strain as low as 0.008%. Excellent device durability was also observed after 3000 bending-releasing cycles. This transparent and conformal strain sensor could be mounted onto a human hand for continuous monitoring of hand movements.

In addition to graphene, other 2D nanomaterials, such as MoS_2, WS_2, and vanadium disulfide (VS_2), have also been recently explored for effective conversion of environmental stimuli into electric signals.

For example, The VS_2 nanosheets with a quasi-two-dimensional electronic structure are very promising building block material for high moisture responsiveness. Intriguingly, the structural characteristics and calculation results indeed revealed theoretical feasibility to achieve VS_2 material in ultrathin structures with only a few atomic layers. Feng et al. [62] synthesized ultrathin VS_2 nanosheets and assembled them into a highly cooriented structure, which had a maximum resistance response of almost two orders of magnitude toward moisture. Using VS_2 nanosheets as the sole functional material, a new concept, flexible touchless positioning interface based on the spatial mapping of moisture distribution was demonstrated (**Figure 13**). This moisture-based positioning interface provides a new conceptual approach to practical real-time moisture mapping matrix or noncontact control interfaces for advanced man-made interactive systems.

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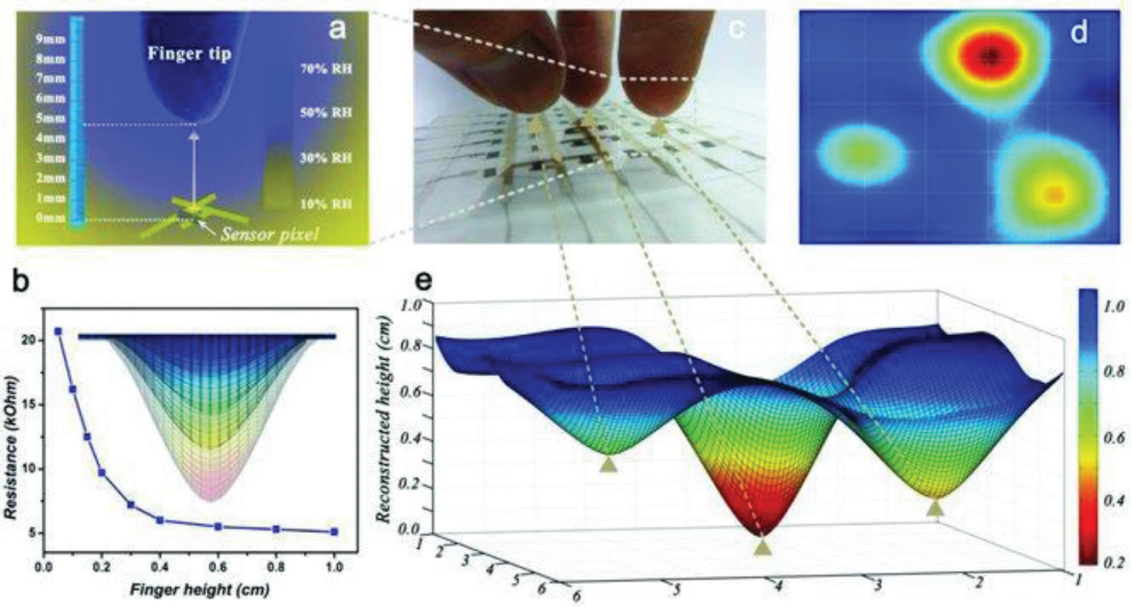

Figure 13. Flexible touchless positioning interface based on the spatial mapping of moisture distribution [62].

3.2. Artificial muscles

Artificial muscles or biomimetic actuators are a type of devices that can operate on a certain source of energy, such as electric current, pressure and chemical energy, and transform the energy into motion. To build a self-folding structure, active materials that convert other forms of energy into mechanical work to enable folding and unfolding operations are required. Previous research on active materials has mainly focused on polymers, including gels [63], liquid crystalline polymers [64], shape memory polymers (SMPs) [65], and conjugated polymers [66]. These materials can respond to environmental stimuli including pH, temperature, solvent, humidity, electricity, and light to change their shapes or/and other physical properties.

Although polymer-based actuators have value in certain context, they still face a number of practical challenges. For example, the actuation behavior of shape memory polymers is restricted by the number of temporary shapes that can be memorized in each cycle, and the ability to tune the transition temperature for shape changes. A disadvantage of another example, polymer multilayers, is their poor stability, because the multiple components do not expand/shrink uniformly which can cause interface problems. Some other demos have typically employed a circuit connection, but they are not favored for remote control applications.

In order to address the above-mentioned issues, Mu et al. [67] developed a series of graphene monolayer (GM) papers with a gradient-reduced graphene oxide/graphene oxide structure. In the gradient GM paper, the GO region could readily desorb/adsorb water molecules in response to environment stimuli including changes in humidity, temperature, or light, leading to shrinking/swelling of the GO sheets. On the contrary, the rGO is inert to water molecules.

Considering the excellent photothermal properties of rGO and GO [68], as well as its high flexibility and mechanical robustness, a rGO/GO hybrid paper holds great potential for photothermoresponsive actuator applications. Mu et al. exploited these properties to yield GM paper with reversible, fast (~0.3 s), powerful (7.5×10^5 N/kg force output), and controllable mechanical deformation and recovery, in response to moisture, heat, and light. The response of this water-driven actuator to multiple stimuli allows the artificial muscles and electric generators to be fabricated. Furthermore, it was found that with a programmed dual-gradient (vertical and lateral) structure, a self-folding all-graphene origami was also developed to demonstrate three types of capability: (i) producing predesigned shapes, (ii) walking, and (iii) turning a corner (**Figure 14**) [69].

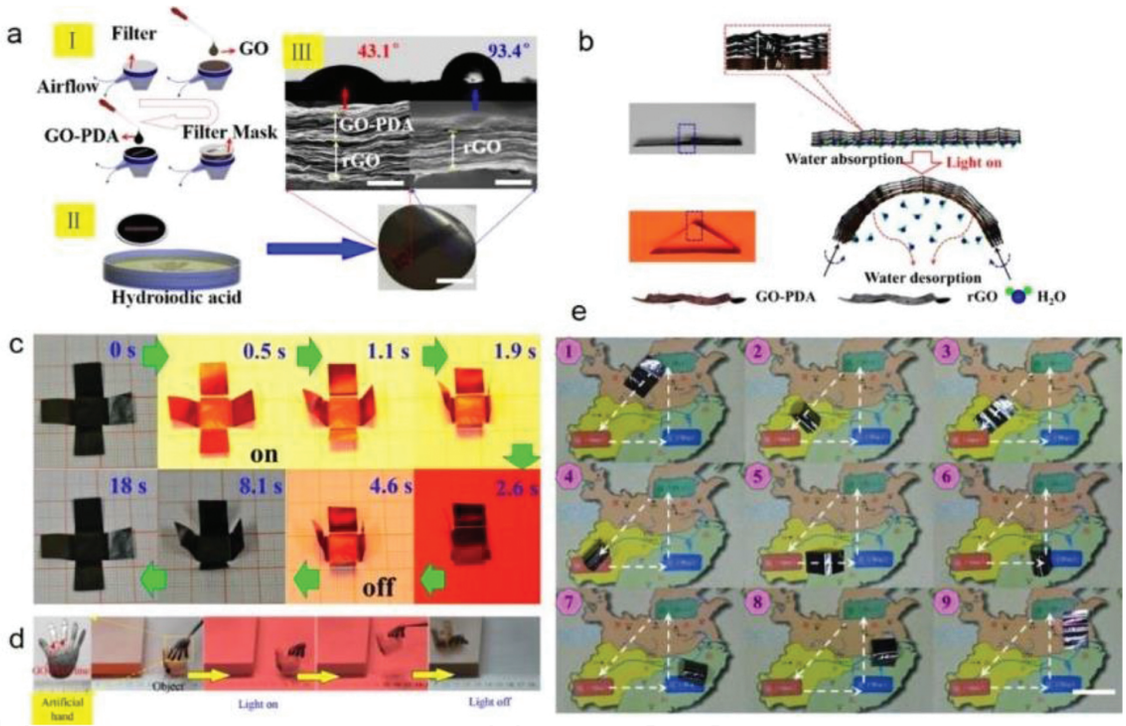

Figure 14. (a) I. Illustration of the mask-assisted filtration process, scale bar is 2 cm; II. Cross-sectional SEM images of different regions of the actuator, scale bar is 1 μm; III. CA measurement of the opposite surfaces of the actuator.(b) Schematic representations of the structures and mechanisms of the actuator paper.(c) Time profiles of self-folding movements of a cross-shaped piece of paper with and without NIR light irradiation.(d) Optical images showing artificial/robotic hand holding an object driven by light irradiation.(e) Optical images showing the "micro robot" walking and turning on a map driven by light irradiation [69].

The hydration-triggered actuation of GO materials opens up a new possibility to synthesize graphene-based actuators responsive to changes in environmental water and/or relative humidity. Cheng et al. [70] designed and fabricated the region-asymmetric graphene/graphene oxide (G/GO) fiber actuators in virtue of the laser positioning reduction of the freshly spun GO fibers. The graphene-based fiber actuators display complex and well-controlled motion and deformation in a predetermined manner in response to moisture changes. This work offers a strategy for producing region-asymmetric G/GO fibers which can be deformed deliberately

http://dx.doi.org/10.5772/64127

and can walk as a single-fiber robot along a channel. The fiber-based actuator with such a unique structure provides a new platform for the development of the wearable devices such as smart textiles.

Differently, the mechanisms based on ionic liquid (IL) electrolyte immersion have also been reported for graphene-based actuators. Lu et al. [71] showed that IL could be inserted to separate the layers of paralleled graphene nanosheets. The rGO–IL with 66.7 wt% of IL displayed a 98% variation in the thickness upon a 2 V electrical voltage stimulation.

Alternatively, graphene can be used as electrodes [73], fillers [74, 75], and conductive substrates [72] for actuators rather than being as the solo functional material. These have been well reviewed elsewhere. We next focus on other 2D materials themselves in biomimetic actuation applications. However, the successful examples are still very few up to date.

Yang et al. [76] tailored magnetic, optical, and electrical properties of $ReSe_2$ nanosheets by local strain engineering through formation of $ReSe_2$ wrinkles on elastomeric substrates. Local strain induced by generation of wrinkles could perform several actions: (1) to modulate the optical gap as evidenced by red-shifted photoluminescence peaks, (2) to enhance light emission, (3) to induce magnetism, and (4) to adjust electrical properties. Their work not only shows how to create materials with vastly different properties at the nanoscale, but also enables a wide range of applications based on 2D materials, including strain sensors, stretchable electrodes, flexible field-effect transistors, artificial-muscle actuators, solar cells, and other spintronic, electromechanical, piezoelectric, photonic devices.

Yang et al. [77] analyzed electromechanical coupling effects in suspended doubly clamped single-layer MoS_2 structures, by which they designed suspended-channel FETs and vibrating-channel nanoelectromechanical resonators. In direct current gating scenario, signal transduction processes (such as deflection, electrostatic actuation, mobility, straining on bandgap, carrier density, and their intricate cross-interactions) have been analyzed with considering the strain-enhanced mobility (by up to 4 times), in order to determine the transfer characteristics.

Yuan et al. [78] reported synthesis of monolayer perovskite-like $KCa_2Nb_3O_{10}$ nanosheets, and therefore they were able to study the size-dependent properties of these nanosheets as monolayer nanosheet seed layers to grow functional thin films for piezo-microelectromechanical systems (piezo-MEMS). Their results implied that larger $Ca_2Nb_3O_{10}$ nanosheets can be useful for constructing scale-up piezo-MEMS devices, such as microactuators.

4. Outlook and perspective

Over the past 5 years, advances in 2D material fabrication, 3D assembly, and biological analysis have accelerated development of soft materials in biomimetic applications. In the future, integration of other sensor components can be predicted using a similar platform to enable more sophisticated human-surface interfacing. Additional circuits, sensors (e.g., strain gauges, thermal flux sensors), and actuators (LEDs, pacing/ablation electrodes) have been designed with these design considerations in order to enable conformal integration with soft and

curvilinear organs (**Figure 15**) [39, 79]. We believe that these 2D material-based biomimetic platforms would find a wide range of applications in automotive control panels, interactive input devices, robotics, and medical and health monitoring devices.

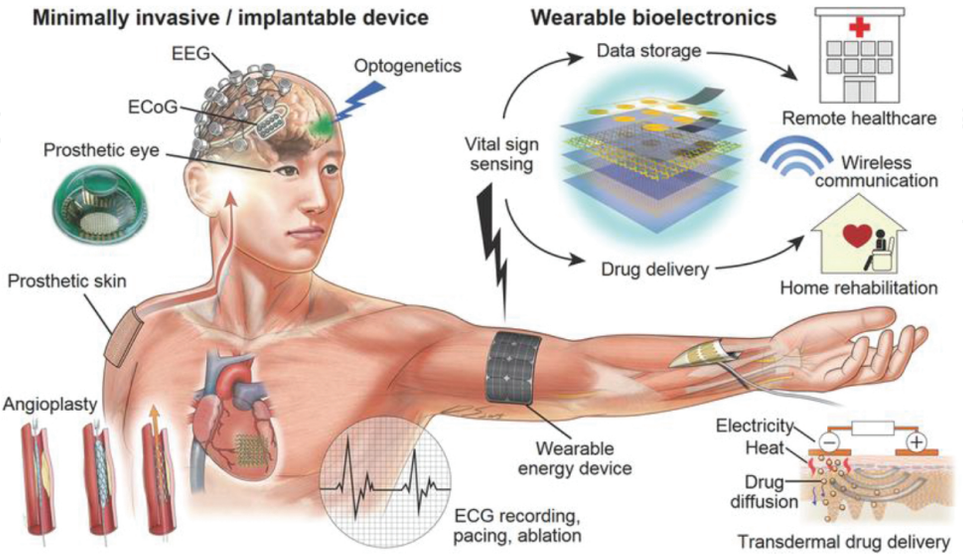

Figure 15. Bio-integrated flexible and stretchable systems: schematic illustration of bio-integrated electronics in development today across a broad range of biomedical applications. Minimally invasive and implantable devices include electrophysiological sensors (ECoG, ECG), angioplasty tools, prosthetic eye/skin, and optoelectronic nerve stimulator, etc. Wearable bioelectronics include physiological sensors (pressure, strain, temperature sensors) integrated with transdermal drug delivery devices and data storage devices. Continuous monitoring and real-time feedback therapy are performed in conjunction with the wireless communication. Energy supply module is an essential component to bioelectronics systems for mobile and personalized healthcare [34, 38, 73, 76, 77].

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References

[1] Lepora NF, Verschure P, Prescott TJ, The state of the art in biomimetics. Bioinspiration & Biomimetics. 2013; 8: 013001. Doi:10.1088/1748-31828/1/013001.

[2] Huebsch N, Mooney DJ, Inspiration and application in the evolution of biomaterials. Nature. 2009; 462: 426–432. Doi:10.1038/nature08601

[3] McEvoy MA, Correll N, Materials that couple sensing, actuation, computation, and communication. Science. 2015; 347: 1261689. DOI: 10.1126/science.1261689.

[4] Rus D, Tolley MT, Design, fabrication and control of soft robots. Nature. 2015; 521: 467–475. DOI: 10.1038/nature14543

[5] Kim S, Laschi C, Trimmer B, Soft robotics: a bioinspired evolution in robotics. Trends in Biotechnology. 2013; 31: 23–30. DOI:10.1016/j.tibtech.2013.03.002

[6] Studart AR, Additive manufacturing of biologically-inspired materials. Chemical Society Reviews. 2016; 45: 359–376. DOI: 10.1039/c5cs00836k

[7] Case JC, White EL, Kramer RK, Soft material characterization for robotic applications. Soft Robotics. 2015; 2: 80–87.DOI: 10.1089/soro.2015.0002.

[8] Pfeifer R, Lungarella M, Iida F, The challenges ahead for bio-inspired 'soft' robotics. Communications of the Acm. 2012; 55: 76–87. DOI:10.1145/2366316.2366335.

[9] Liu Z, Xu J, Chen D, Shen GZ, Flexible electronics based on inorganic nanowires. Chemical Society Reviews. 2015; 44: 161–192. DOI: 10.1039/C4CS00116H.

[10] Jahani S, Jacob Z, All-dielectric metamaterials. Nature Nanotechnology. 2016; 11: 23–36. DOI: 10.1038/NNANO.2015.304

[11] Bhandari B, Lee GY, Ahn SH, A review on IPMC material as actuators and sensors: fabrications, characteristics and applications. International Journal of Precision Engineering and Manufacturing. 2012; 13: 141–163. DOI: 10.1007/s12541-012-0020-8

[12] Zhao Q, Qi HJ, Xie T, Recent progress in shape memory polymer: new behavior, enabling materials, and mechanistic understanding. Progress in Polymer Science. 2015; 50: 79–120. Doi:10.1016/j.progpolymsci.2015.04.001

[13] Bauer S, Simona BG, Graz I, Kaltenbrummer M, Keplinger C, Schwödiauer R, 25th anniversary article: a soft future: from robots and sensor skin to energy harvesters. Advanced Materials. 2014; 26: 149–162. DOI: 10.1002/adma.201303349

[14] Park M, Park J, Jeong U, Design of conductive composite elastomers for stretchable electronics. Nano Today. 2014; 9: 244–260. DOI:10.1016/j.nantod.2014.04.009

[15] Zhao Y, Song L, Zhang ZP, Qu LT, Stimulus-responsive graphene systems towards actuator applications. Energy & Environmental Science. 2013; 6: 3520–3536. DOI: 10.1039/C3EE42812E

[16] Fleischmann EK, Zentel R, Liquid-crystalline ordering as a concept in materials science: from semiconductors to stimuli-responsive devices. Angewandte Chemie-International Edition. 2013; 52: 8810–8827. DOI: 10.1002/anie.201300371

[17] Mas-Balleste R, Gomez-Navarro C, Gomez-Herrero J, Zamora F, 2D materials: to graphene and beyond. Nanoscale. 2011; 3: 20–30. DOI: 10.1039/C0NR00323A

[18] Zhang Y, Zhang LY, Zhou CW, Review of chemical vapor deposition of graphene and related applications. Accounts of Chemical Research. 2013; 46: 2329–2339.DOI: 10.1021/ar300203n

[19] Mattevi C, Kim H, Chhowalla M, A review of chemical vapour deposition of graphene on copper. Journal of Materials Chemistry. 2011; 21: 3324–3334. DOI: 10.1039/c0jm02126a

[20] Bhimanapati GR, et.al., Recent advances in two-dimensional materials beyond graphene. Acs Nano. 2015; 9: 11509–11539. DOI:10.1021/acsnano.5b05556.

[21] Wang F, Wang ZX, Wang QS, Wang FM, Yin L, Xu K, Huang Y, He J, Synthesis, properties and applications of 2D non-graphene materials. Nanotechnology. 2015; 26: 292001. DOI:10.1088/0957-4484/26/29/292001.

[22] Yang L, Wang WH, Huang J, Huang JL, Zhang JY, Xiang B, Large-area synthesis of monolayered MoS2(1-x)Se2x with a tunable band gap and its enhanced electrochemical catalytic activity. Nanoscale. 2015; 7: 10490–10497. DOI: 10.1039/c5nr02652k

[23] Shen JF, He YM, Wu JJ, Gao CT, Keyshar K, Zhang X, Yang YC, Ye MG, Vajtai R, Lou J, Ajayan PM, Liquid phase exfoliation of two-dimensional materials by directly probing and matching surface tension components. Nano Letters. 2015; 15: 5449–5454. DOI: 10.1021/acs.nanolett.5b01842

[24] Novoselov KS, Geom AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA, Electric field effect in atomically thin carbon films. Science. 2004; 306: 666–669. DOI:10.1126/science.1102896

[25] Katsnelson MI, Graphene: carbon in two dimensions. Materials Today. 2007; 10: 20–27. DOi:10.1016/S1369-7021(06)71788-6

[26] Park S, Ruoff RS, Chemical methods for the production of graphenes. Nature Nanotechnology. 2009; 4: 217–224. DOI: 10.1038/NNANO.2009.58

[27] Berger C, et al., Electronic confinement and coherence in patterned epitaxial graphene. Science. 2006; 312: 1191–1196. DOI: 10.1126/science.1125925

[28] El-Kady MF, et al., Laser scribing of high-performance and flexible graphene-based electrochemical capacitors. Science. 2012; 335(6074): 1326–1330.

[29] Yang XW, Cheng C, Wang YF, Qiu L, Li D, Liquid-mediated dense integration of graphene materials for compact capacitive energy storage. Science. 2013; 341: 534–537. DOI: 10.1126/science.1239089

[30] Dean CR, et al., Boron nitride substrates for high-quality graphene electronics. Nature Nanotechnology. 2010; 5: 722–726. DOI:10.1038/NNANO.2010.172

[31] Wei ZQ, et al., Nanoscale tunable reduction of graphene oxide for graphene electronics. Science. 2010; 328: 1373–1376. DOI:10.1126/science.1188119

[32] Yang K, Feng LZ, Shi XZ, Liu Z, Nano-graphene in biomedicine: theranostic applications. Chemical Society Reviews. 2013; 42: 530–547. DOI: 10.1039/c2cs35342c

[33] Byun J, Emerging frontiers of graphene in biomedicine. Journal of Microbiology and Biotechnology. 2015; 25: 145–151. DOI: 10.4014/jmb.1412.12045

[34] Kou LZ, Frauenheim T, Chen CF, Phosphorene as a superior gas sensor: selective adsorption and distinct I-V response. Journal of Physical Chemistry Letters. 2014; 5: 2675–2681. DOI:10.1021/jz501188k

[35] Yoon HJ, Jun DH, Yang JH, Zhou ZX, Yang SS, Cheng MMM, Carbon dioxide gas sensor using a graphene sheet. Sensors and Actuators B-Chemical. 2011; 157: 310–313.DOI: 10.1016/j.snb.2011.03.035

[36] Late DJ, et al., Sensing behavior of atomically thin-layered MoS_2 transistors. ACS Nano. 2013; 7: 4879–4891. DOI: 10.1021/nn400026u

[37] Gao W, et al. Fully integrated wearable sensor arrays for multiplexed in situ perspiration analysis. Nature. 2016; 529: 509–514. DOI:10.1038/nature16521

[38] Sarkar D, Liu W, Xiun XJ, Anselmo AC, Mitragotri S, Banerjee K, MoS_2 field-effect transistor for next-generation label-free biosensors. ACS Nano. 2014; 8: 3992–4003. DOI: 10.1021/nn5009148

[39] Kim J, et al., Stretchable silicon nanoribbon electronics for skin prosthesis. Nature Communications. 2014; 5. DOI: 10.1038/Ncomms6747

[40] Hattori Y, et al., Multifunctional skin-like electronics for quantitative, clinical monitoring of cutaneous wound healing. Advanced Healthcare Materials. 2014; 3: 1597–1607. DOI: 10.1002/adhm.201400073

[41] Yeo WH, et al., Multifunctional epidermal electronics printed directly onto the skin. Advanced Materials. 2013; 25: 2773–2778. DOI: 10.1002/adma.201204426

[42] Trung TQ, Ramasundaram S, Hwang BU, Lee NE, An all elastomeric transparent and stretchable temperature sensor for body attachable wearable electronics. Advanced Materials. 2016; 28: 394–394. DOI: 10.1002/adma.201504441

[43] Wu WZ, et al., Piezoelectricity of single-atomic-layer MoS_2 for energy conversion and piezotronics. Nature. 2014; 514: 470–477. DOI:10.1038/nature13792

[44] Stuart MAC, et al., Emerging applications of stimuli-responsive polymer materials. Nature Materials. 2010; 9: 101–113. DOI: 10.1038/NMAT2614

[45] Rogers GW, Liu JZ, Graphene actuators: quantum-mechanical and electrostatic double-layer effects. Journal of the American Chemical Society. 2011; 133: 10858–10863. DOI: 10.1021/ja201887r

[46] Zhang LY, Zeng XW, Wang XQ, Programmable hydrogenation of graphene for novel nanocages. Scientific Reports. 2013; 3. DOI:10.1038/Srep03162

[47] Ma XF, Zachariah MR, Zangmeister CD, Crumpled nanopaper from graphene oxide. Nano Letters. 2012; 12: 486–489. DOI: 10.1021/nl203964z

[48] Ishihara S, et al., Hydrogen-bond-driven 'homogeneous intercalation' for rapid, reversible, and ultra-precise actuation of layered clay nanosheets. Chemical Communications. 2013; 49: 3631–3633. DOI:10.1039/c3cc40398j

[49] Ogawa M, Ishii T, Miyamoto N, Kuroda K, Photocontrol of the basal spacing of azobenzene-magadiite intercalation compound. Advanced Materials. 2001; 13: 1107–1110. DOI:10.1002/1521-4095(200107)

[50] Nabetani Y., et al., A photoactivated artificial muscle model unit: reversible, photoinduced sliding of nanosheets. Journal of the American Chemical Society. 2011; 133: 17130–17133. DOI: 10.1021/ja207278t

[51] Mannsfeld SCB, et al., Highly sensitive flexible pressure sensors with microstructured rubber dielectric layers. Nature Materials. 2010; 9: 859–864. DOI: 10.1038/NMAT2834

[52] Wang C, et al., User-interactive electronic skin for instantaneous pressure visualization. Nature Materials. 2013; 12: 899–904. DOI: 10.1038/NMAT3711

[53] Someya T, Sekitani T, Kato Y, Kawaguchi H, Sakurai T, A large-area, flexible pressure sensor matrix with organic field-effect transistors for artificial skin applications. Proceedings of the National Academy of Sciences of the United States of America. 2004; 101: 9966–9970. DOI: 10.1073/pnas.0401918101

[54] Liu X, Long YZ, Duan XF, Fan ZY, Large-scale integration of semiconductor nanowires for high-performance flexible electronics. ACS Nano. 2012; 6: 1888–1900. DOI: 10.1021/nn204848r

[55] Takei K, et al., Nanowire active-matrix circuitry for low-voltage macroscale artificial skin. Nature Materials. 2010; 9: 821–826. DOI: 10.1038/NMAT2835

[56] Maheshwari V, Saraf RF, Tactile devices to sense touch on a par with a human finger. Angewandte Chemie-International Edition. 2008; 47: 7808–7826. DOI:10.1002/anie.200703693

[57] Maheshwari V, Saraf RF, High-resolution thin-film device to sense texture by touch. Science. 2006; 312: 1501–1504. DOI: 10.1126/science.1126216

[58] Toohey KS, Sottos N, Lewis JA, Moorw JS, White SR, Self-healing materials with microvascular networks. Nature Materials. 2007; 6: 581–585. DOI:10.1038/nmat1934

[59] Hou CY, Huang T, Wang HZ, Yu H, Zhang QH,Li YG, A strong and stretchable self-healing film with self-activated pressure sensitivity for potential artificial skin applications. Scientific Reports. 2013; 3. DOI:10.1038/Srep03138

[60] Hou CY, Wang HZ, Zhang QH, Li YG, Zhu FM, Highly conductive, flexible, and compressible all-graphene passive electronic skin for sensing human touch. Advanced Materials. 2014; 26: 5018–5024. DOI: 10.1002/adma.201401367

[61] Sun Q, Seung W, Kim BJ, Seo S, Kim SW, Cho JH, Active matrix electronic skin strain sensor based on piezopotential-powered graphene transistors. Advanced Materials. 2015; 27: 3411–3417. DOI: 10.1002/adma.201500582

[62] Feng J, et al., Giant moisture responsiveness of VS_2 ultrathin nanosheets for novel touchless positioning interface. Advanced Materials. 2012; 24: 1969–1974. DOI: 10.1002/adma.201104681

[63] Sidorenko A, Krupenkin T, Taylor A, Fratzl P, Aizenberg J, Reversible switching of hydrogel-actuated nanostructures into complex micropatterns. Science. 2007; 315: 487–490. DOI: 10.1126/science.1135516

[64] Lu W, et al., Use of ionic liquids for pi-conjugated polymer electrochemical devices. Science. 2002; 297: 983–987. DOI:10.1126/science.1072651

[65] Lendlein A, Kelch S, Shape-memory polymers. Angewandte Chemie-International Edition. 2002; 41: 2034–2057. Doi 10.1002/1521-3773(20020617)

[66] Smela E, Conjugated polymer actuators for biomedical applications. Advanced Materials. 2003; 15: 481–494. DOI:10.1002/adma.200390113

[67] Mu JK, et al., A multi-responsive water-driven actuator with instant and powerful performance for versatile applications. Scientific Reports. 2015; 5. DOI:10.1038/Srep09503

[68] Balandin AA, Thermal properties of graphene and nanostructured carbon materials. Nature Materials. 2011; 10: 569–581. DOI: 10.1038/NMAT3064

[69] Mu JK, Hou CY, Wang HZ, Li YG, Zhang QH, Zhu FM, Origami-inspired active graphene-based paper for programmable instant self-folding walking devices. Science Advance. 2016; 1: e1500533. DOI: 10.1126/sciadv.1500533

[70] Cheng HH, et al., Graphene fibers with predetermined deformation as moisture-triggered actuators and robots. Angewandte Chemie-International Edition. 2013; 52: 10482–10486. DOI: 10.1002/anie.201304358

[71] Lu LH, Liu JH, Hu Y, Chen W, Large volume variation of an anisotropic graphene nanosheet electrochemical–mechanical actuator under low voltage stimulation. Chemical Communucation. 2012; 48: 3978–3980. DOI: 10.1039/C2CC18165G

[72] Jang H, Park YJ, Chen X, Das T, Kim MS, Ahn Jh, Graphene-based flexible and stretchable electronics. Advanced Materials. 2016; 28: 4184–4202. DOI:10.1002/adma.201504245

[73] Liang JJ, et al., Electromechanical actuators based on graphene and graphene/Fe_3O_4 hybrid paper. Advanced Functional Materials. 2011; 21: 3778–3784. DOI: 10.1002/anie.201304358

[74] Lian YF, Liu YX, Jiang T, Shu J, Lian HQ, Cao MH, Enhanced electromechanical performance of graphite oxide-nafion nanocomposite actuator. Journal of Physical Chemistry C. 2010; 114(21): 9659–9663. DOI: 10.1021/jp101337h

[75] Bakhtiarpour P, Parvizi A, Müller M, Shahinpoor M, Marti O, Amirkhani M, An external disturbance sensor for ionic polymer metal composite actuators. Smart Materials and Structures. 2016; 25. DOI:10.1088/0964-1726/25/1/015008

[76] Yang S, Kang J, Yue Q, COey JMD, Jiang CB, Defect-modulated transistors and gas-enhanced photodetectors on ReS_2 Nanosheets. Advanced Materials Interfaces. 2016; 1500707. DOI: 10.1002/admi.201500707

[77] Yang R, Islam A, Feng PXL, Electromechanical coupling and design considerations in single-layer MoS2 suspended-channel transistors and resonators. Nanoscale. 2015; 7: 19921–19929. DOI:10.1039/c5nr06118k

[78] Yuan HY, Nguyen M, Hammer T, Koster G, Rijnders Elshof JE, Synthesis of KCa2Nb3O10 crystals with varying grain sizes and their nanosheet mono layer films as seed layers for piezoMEMS applications. ACS Applied Materials & Interfaces. 2015; 7: 27473–27478. DOI: 10.1021/acsami.5b09456

[79] Ko HC, et al., A hemispherical electronic eye camera based on compressible silicon optoelectronics. Nature. 2008; 454: 748–753. DOI:10.1038/nature07113