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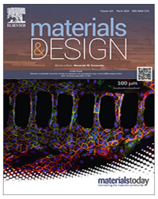


High-performance ionic polymer actuators with Triple-layered multifunctional electrodes

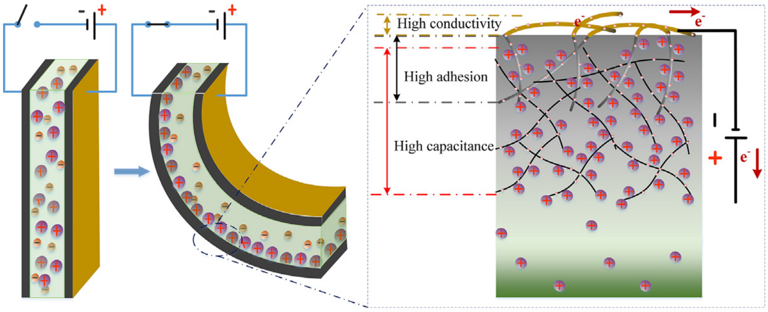
Chun Zhao[a,1], Gangqiang Tang[a,1], Yujun Ji[a], Xin Zhao[a], Dong Mei[a], Lijie Li[b], Yanjie Wang[a,*]

[a] *Jiangsu Provincial Key Laboratory of Special Robot Technology, Hohai University, Changzhou campus, Changzhou 213022, China*
[b] *College of Engineering, Swansea University, Swansea SA1 8EN, UK*

HIGHLIGHTS

- An efficient method to prepare triple-layered multifunctional electrodes for ionic polymer actuators is proposed inspired by zoysia grass.
- Three functional layers are integrated in one electrode using the spraying and electrodepositing Au method.
- Actuators based on multifunctional electrodes are capable of high conductivity (∼3.4 Ω/□), high adhesion (∼328 KPa) and good electrochemical performance.
- The technical challenge that ionic actuators have low performance due to low electrochemical performance and electrode/matrix mismatch was solved.

GRAPHICAL ABSTRACT



Ionic polymer actuator

Triple-layered Multifunctional electrodes

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ABSTRACT

Ionic polymer actuators have attracted attention in recent years due to their remarkably large strain under low-voltage stimulation. However, a key challenge for fabricating high-performance ionic polymer actuators is to develop a firm electrode with high electrical conductivity and electrochemical performance. Herein, inspired by the structure of zoysia grass, we proposed an efficient method to prepare the triple-layered multifunctional electrodes capable of low surface resistance (∼3.4 Ω/□), high adhesion (∼328 KPa) and good electrochemical performance for ionic polymer actuators. Through the spraying and impregnation-electroplating (IEP), three functional layers of multifunctional electrodes are obtained, including MWCNTs/Nafion interfacial layer, Ag NWs fixed layer and Ag NWs@Au layer, which respectively contribute to the charge storage in the electrode, high strength and the uniform and fast charge distribution. The synergic effect of these three functional layers maintains a high stability of multifunctional electrodes after being immersed in DI water for 7 days or 1500 bending cycles, and greatly enhances the actuation performance of ionic polymer actuators, resulting in an extreme bending deformation (increasing by 460%). This work represents an important step towards ionic polymer actuators where the synergic effect in electrodes plays an important role in promoting electrochemical actuation performance.

Abbreviations: MWCNTs, Multi-walled carbon nanotubes.

[*] Corresponding author.

E-mail address: yj.wang1985@gmail.com (Y. Wang).

[1] These authors contributed equally: Chun Zhao, Gangqiang Tang.

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1. Introduction

Over the past decades, bio-inspired artificial muscles have raised considerable interest in bionics. Among them, ionic polymer actuators, which are typically consisted of an ionomer membrane and flexible electrodes on both sides of the membrane, have become a research hotspot due to their low driving voltage (generally less than 5 V), light weight, large deformation, high expansibility and fast response [1–4]. Since the electromechanical strain originated from the ion migration between the two electrodes under the electric field, excellent features of electrodes become crucial to actuators, such as low surface resistance, high stability and good charge storage. Classic electrodes of ionic polymer actuators are typically prepared by forming noble metal electrodes on both surfaces of an ionomer membrane using the impregnation – reduction (IR). These classic electrodes have an interface layer to improve the actuation performance of ionic polymer actuators [5–7]. However, since the complicated process of IR cannot meet the high throughput production of ionic polymer actuators, a simple and efficient process is urgently needed to replace IR [8–11]. Lee et al used single-walled carbon nanotubes (SWCNTs) and Ag NWs to prepare hybrid electrodes for a dielectric elastomer actuator (DEA) with a good actuation performance [12]. Adding a very small amount of SWCNTs to the Ag NWs network resulted in a significant reduction of surface resistance by three orders, which increased maximum strain up to 183%. Rassoul et al used nitrogen-doped crumpled graphene and hollow tubular graphene meshes to prepare a hybrid electrode, which effectively improved the actuation performance of ionic polymer actuators [13].

Although a number of electrodes with good stability and flexibility have been developed through high-performance nanomaterials, there are still some challenges that hinder the application of these electrodes in ionic polymer actuators. Firstly, the electrodes and matrix membrane are stacked layer by layer without introducing interlayer bonding, which easily leads to separation or delamination of the layers in the ionic polymer actuator when subjected to shear stress or in-plane compressive stress. To improve the adhesion of electrodes and matrix membrane, Luo et al used a SWCNT/Nafion mixture to form a firm electrode for ionic polymer actuators [14]. However, the nanomaterial were coated by the insulating Nafion polymer, which greatly increased the surface resistance of electrodes. Therefore, it is often necessary to paste a thin gold foil on the surface of electrodes to improve the electrical resistance [4,15], but pasting a thin gold foil increases the difficulty of preparation process. Second, the surface resistance of the elec-

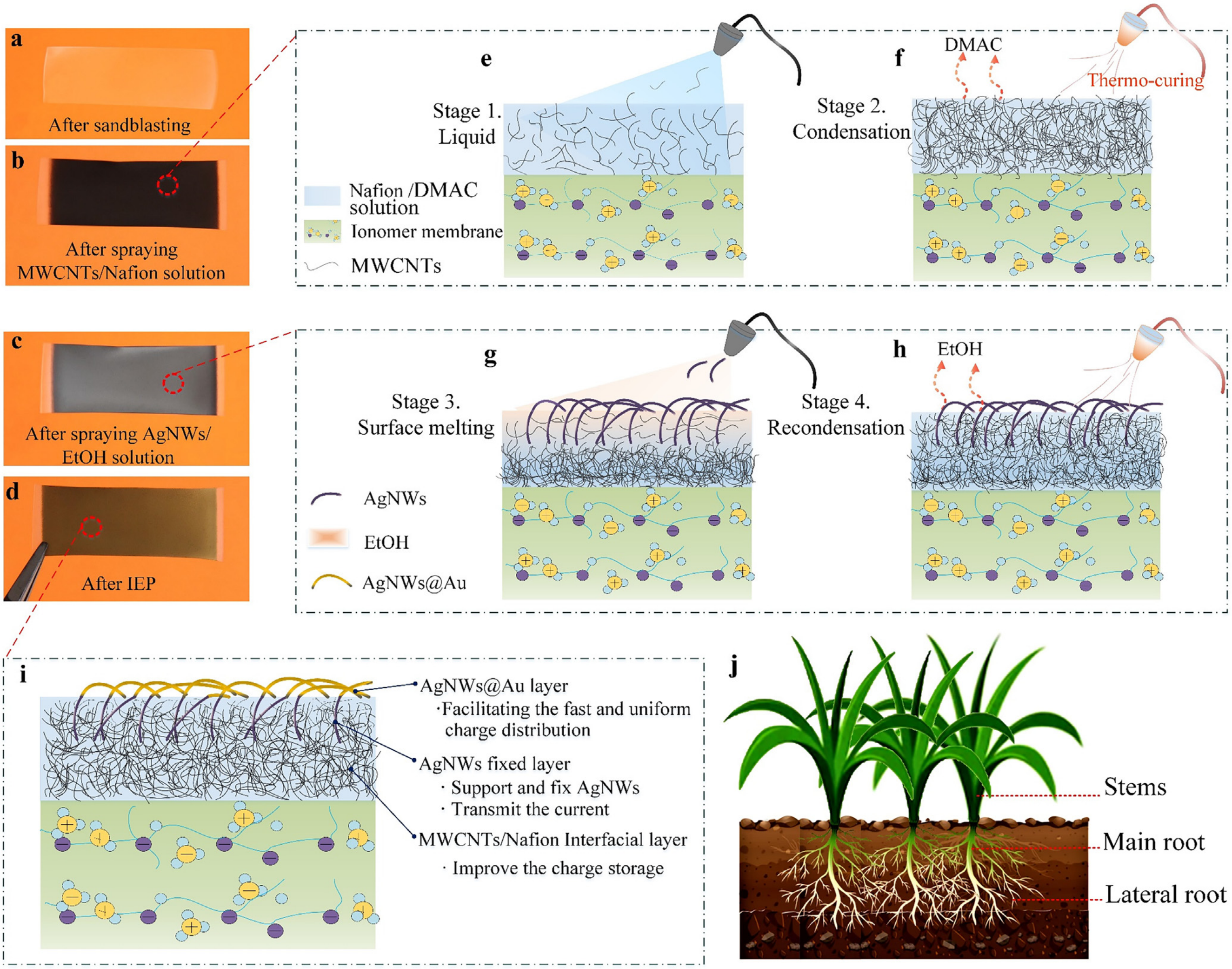

Fig. 1. The preparation of multifunctional electrodes. (a-d) Macromorphology evolution of ionic polymer actuators based on multifunctional electrodes. (e) MWCNTs/Nafion interfacial layer before DMAC evaporating. (f) MWCNTs/Nafion interfacial layer curing. (g) Ag NWs partly rush in the molting layer of interfacial. (h) Ag NWs are fixed in the MWCNTs/Nafion interfacial layer after curing. (i) Corresponding schematic of multifunctional electrodes. (j) Structure of zoysia grass.

trode is affected by the point contact of nanomaterials at nanowire-nanowire junctions [10,13,14,16,17]. To improve the point contact at the junctions between nanomaterials, NWs@noble metal core–shell structure formed by electrodepositing provides NWs with high stability [18–21]. However, this method can only improve the stability and conductivity of the electrode, and cannot effectively improve the adhesion. In addition, many electrodes prepared by nanomaterials can't enhance the actuation performance of ionic polymer actuators due to the lack of an interfacial layer with a high specific surface area [22–25]. Therefore, there is an urgent demand to develop an efficient method to prepare a kind of electrode capable of low surface resistance, good strength and high charge storage for ionic polymer actuators [26,27]. However, it appears difficult to mutually achieve all these features in one electrode design. To date, many works can only achieve a single requirement, as shown in Figure S1, for example Ag NWs electrode has low surface resistance but low stability. The polymer/AgNW or polymer/CNT electrodes have a good adhesion but high surface resistance, which result in poor performance of ionic polymer actuator.

As shown in Fig. 1j, the structure of zoysia grass is mainly composed of three functional layers macroscopically, including stems, main root and lateral root. The stem is exposed to the outside of the soil to facilitate sufficient sunlight for photosynthesis. The main root is deeply embedded in the soil to absorb water and mineral salts, and enhance adhesion of the plant for surviving during complex mechanical force. When the main root is strong enough, some branches will appear, called lateral roots. The lateral roots have the characteristics of large number, long length and wide distribution, which can absorb fertilizer and water from a long distance. Here, the ionic polymer can be assumed to be soil. Similar to the stem exposed to the outside of the soil, if one end of the nanowire is exposed on the surface of the electrode and is not wrapped by the insulating polymer, the electrode will obtain ideal low surface resistance. Similar to the main root embedded in the soil, if the other end of the nanowire is embedded in the polymer, the nanowire will be fixed. Similar to the lateral root, if a large number of conductive nanowires are distributed in the ionomer file to form the interfacial layer with high specific surface area, the charge storage of the electrode will be effectively enhanced [5,13]. Therefore, in this work, inspired by zoysia grass, we proposed a method to achieve three requirements in a single electrode for ionic polymer actuators. Through the spraying and IEP, MWCNTs/Nafion interface layer, Ag NWs fixed layer, and Ag NWs@Au layer are successively present in multifunctional electrodes, which are respectively similar to the lateral root, the main root and the stems of zoysia grass for obtaining the good electrochemical performance, high adhesion and low surface resistance. The synergistic effects of these three functional layers significantly improve the electrochemical performance of the electrodes and the electromechanical of ionic polymer actuators. The performance of the fabricated actuator is better than most of the reported ionic polymer actuators based on Nafion membrane, which indicates that multifunctional electrodes has considerable application prospects in flexible electronic devices.

2. Experimental section

2.1. Materials.

Nafion® 117 membrane (183 um in thickness) and Nafion solution (20% Nafion dispersion solution) was purchased from Dupont™ (Shanghai, China). The MWCNTs (10–20 nm in diameter and 10–30 um in length) and Ag NWs (20 mg mL^{-1}, 100 nm in diameter and 100–200 um in length) were purchased from XFNANO Tech Co., Ltd (Nanjing, China). N, N-dimethylacetamide (DMAC, 99%) and anhydrous ethanol (EtOH, 99.5%) were purchased from Aladdin (Shanghai, China). Auxiliary reagents such as NaOH (96%) and HCl (37%) were also purchased from Aladdin (Shanghai, China). The above materials were all used as received.

2.2. Fabrication of the solutions.

(1) Nafion solution: MWCNTs: DMAC solution weight ratios of 250: 1: 2500 was used. It was prepared using the following method. First, 10 g of Nafion solution and 0.04 g of MWCNTs were dispersed in 100 g of DMAC solution. Secondly, the mixture was stirred by magnetic stirring at room temperature for 2 h. Then, the mixture was stirred at room temperature for 3 h by sonication to fully disperse MWCNTs into Nafion/DMAC solution. (2) Ag NWs: EtOH volume ratios of 1: 50 was used. It was prepared using the following method. 2 mL of Ag NWs was fully dispersed in 100 mL of EtOH solution by ultrasonicating the mixture for more than 40 min.

2.3. Pretreatment of Nafion membrane.

The pretreatment of Nafion membrane mainly includes the roughening, cleaning and cation (Na^+) exchange. The first step is to use sandblasting machine (sand-size: 120#, pressure: 0.5 MPa) to polish Nafion membrane for 45 s (3.5 cm × 3.5 cm). The second step is cleaning. First, Nafion membrane after roughening was put into DI water for cleaning by sonication at room temperature for 40 min. Secondly, Nafion membrane was put into HCl solution (0.2 mol/L, 100 mL) for acid boiling at 100 °C for 1 h. Then, Nafion membrane was put into DI water (200 mL) for water boiling at 100 °C for 1 h. Step 3, Nafion membrane was immersed in NaOH solution (0.6 mol/L, 100 mL) for 2 h to conduct Na^+ exchange. Finally, Nafion membrane was put into DI water for standby use.

2.4. Preparation of ionic polymer actuator based on multifunctional electrodes.

(a) Preparation of MWCNTs/Nafion interfacial layer on the surface of Nafion membrane. It was prepared using the following method. First, a Nafion membrane (Size of 3.5 cm × 1.5 cm) with pretreatment was fixed on the heating platform. Then, a spray gun with 0.5 mm caliber was used to spray 2 mL of MWCNTs/Nafion/DMAC solution on the surface of the Nafion membrane. DMAC and other solvents were then completely removed by heating Nafion membrane at 130 °C. The thicknesses of the thus-obtained MWCNTs/Nafion interfacial layer on the surface of Nafion membrane were 15–20 um. Because MWCNTs/Nafion solution dispersed on the surface of Nafion membrane cannot be solidified for a short time, resulting in the aggregation of the solution, which prevented the formation of MWCNTs/Nafion interfacial layer. Therefore, when there is liquid on the surface of Nafion membrane, it is necessary to wait for its thermal curing before continuing spraying. (b) Preparation of Ag NWs fixed layer on the surface of MWCNTs/Nafion interfacial layer. A spray gun with 0.3 mm caliber was used to spray 2.5 mL of Ag NWs/EtOH solution on the surface of MWCNTs/Nafion interfacial layer. EtOH were then completely removed by heating Nafion membrane at 90 °C, and Ag NWs fixed layer was obtained. Next, steps (a) and (b) were repeated to form the electrode layer on the other side of Nafion membrane. (c) Preparation of Ag NWs@Au layer on the surface of Ag NWs fixed layer. An electroplating device consisting of a gold electroplating solution (1.2 g/L), a cathode, a DC power supply (3.5 V) and a titanium anode was built. Impregnation-electroplating Au was carried out under 3.5 V for around 50–60 s on each side to form Ag NWs@Au layers. Then, an ionic polymer actuator was obtained.

2.5. Characterization.

A ZEISS Sigma 500 field emission SEM was used to characterize the microstructure of multifunctional electrodes. A VICTOR 86E multimeter (Yisheng Victor Tech Co., Ltd.) and a M3 four-probe meter (Jingge Electronics Co., Ltd.) were used to measure the resistance of electrodes. A self-made machine was used to test the actuation performance of actuator. As shown in Figure S3, the signal generator (APS3003S-3D) and power amplifier (RIGOL PA1011) generate the drive signal, which excites the ionic actuator to produce a bending motion. The Laser sensor (IL-065) measures the peak displacement curve of the ionic actuator. The record module (NI USB-6001 and PC) is responsible for transferring and recording data. All experiments were carried at 25 °C and 57% (humidity). The strain difference (ε, %) can be calculated using Equation (1).

$$\varepsilon = 2ai/(L^2 + i^2) \ (1).$$

Where L, i, and a are the free length, maximum bending displacement, and the thickness of the actuator, respectively [14]. Cyclic voltammetry (CV) test was performed by using CHI800D electrochemical analyzer of ChenHua Instrument Co., Ltd (Shanghai, China). In CV test, the electrochemical material is ionic polymer actuators. Ionic polymer actuator is a composite material, including two triple-layered hybrid electrodes and an electrolyte layer consisting of Nafion membrane and Na^+. Specific capacitance can be calculated by Equation (2).

$$C = A/2mv\Delta V \ (2).$$

Where, A is the area of the cyclic voltammetry (CV) curve, m is the mass of ionic polymer actuator on the working electrode, v is the scanning rate, and ΔV is the electrochemical window.

3. Results and discussion

3.1. Design of ionic polymer actuator based on multifunctional electrodes

Ionic polymer actuators are typically made of an ionomer membrane sandwiched by two flexible electrodes. Currently, studies have shown that the actuation performance of ionic polymer actuator is directly related to low surface resistance (because the driving voltage of the ionic polymer actuator is less than 5 V, a high resistance will hinder the fast and uniform charge distribution), good stability and interfacial layer with high specific surface area [13]. However, it is still a technical challenge to realize these three requirements in a single electrode. Inspired by the structure of zoysia grass, an efficient method were proposed to prepare triple-layered multifunctional electrodes for achieving three requirements in a single electrode. Through taking use of the spraying and impregnation-electroplating method, the prepared multifunctional electrodes have triple-layered composite structures, including Ag NWs@Au layer, Ag NWs fixed layer, and MWCNTs/Nafion interfacial layer (Fig. 1i). Ag NWs@Au layer is similar to the stems of zoysia grass and distributed on the surface of the interfacial layer, which has an extremely low surface resistance for facilitating the fast and uniform charge distribution. Ag NWs fixed layer is similar to the main root of zoysia grass and embedded in the interfacial layer firmly, which can fix the Ag NWs and pass current to MWCNTs in the interfacial layer. MWCNTs distributed in the interfacial layer have the characteristics of large number, long length and wide distribution, which is similar to the lateral root of zoysia grass and contributes to the charge storage of the electrode. Compared with other electrodes, multifunctional electrodes have extremely low surface resistance, good stability and interfacial layer with a high specific surface area.

Fig. 1a ~ d shows the macromorphology of ionic polymer actuator based on multifunctional electrodes after different steps. Fig. 1a shows the Nafion membrane after surface roughening. Rough surface can enhance adhesion between the interfacial layer and membrane. Additionally, in order to prevent the degradation of actuation performance, Nafion membrane after sandblasting must be ultrasonically cleaned to remove the quartz sand remaining on the surface. Meanwhile, acid boiling and DI water boiling must be sequentially used to remove impurity ions [5]. Fig. 1e ~ i show the preparation process of multifunctional electrodes. The first step is to form an interfacial layer with a high specific surface area by spraying the MWCNTs/Nafion solution (Fig. 1e). Since the Nafion membrane can absorb a large amount of DMAC solvent, MWCNTs/Nafion dispersed in DMAC solution will further penetrate the membrane to enhance the adhesion. After thermos-curing, MWCNTs/Nafion interfacial layer changes from liquid to solid (Fig. 1f), and a tight connection between interfacial layer and Nafion membrane is formed (Fig. 2b). Since MWCNTs are uniformly distributed in the interfacial layer, which can improve the charge storage in the electrode for enhancing the electromechanical performance of ionic polymer actuators [13]. However, the conductivity of interfacial layer is poor due to the insulating properties of Nafion polymer, it is necessary to deposit a conductive layer with good stability and low surface resistance on the surface of interfacial layer for facilitating the fast and uniform charge distribution. In the second step, an Ag NWs fixed layer is formed on the interfacial layer by spraying Ag NWs/EtOH solution. For the reason that EtOH will make the surface of solidified interfacial layer melt for forming a thin molting layer, so Ag NWs can partly rush in the melting layer with the help of gravity and speed to form an Ag NWs fixed layer. Additionally, other parts of the Ag NWs were embedded in the interfacial layer incompletely, and distributed on the surface, which can help to improve conductivity of the electrodes (Fig. 1g). After thermos-curing, the molting layer of interfacial layer will become solid again, which results in the Ag NWs to be fixed (Fig. 1h). The third step is electrodepositing Au onto the Ag NWs distributed on the surface of interfacial layer through IEP process. Additionally, Au atoms fill the gaps among the Ag NWs and weld them together after IEP (Fig. 1i), greatly reducing surface resistance of electrodes.

3.2. Characterization of multifunctional electrodes

As shown in Fig. 2a, after spraying MWCNTs/Nafion solution, the surface resistance of the interfacial layer is ~ 614 Ω/□, the reason is that the MWCNTs are wrapped by nonconductive Nafion polymer (Fig. 2c), which increases the surface resistance. After electrodepositing Au^+, the surface resistance of multifunctional electrodes is reduced from 199 Ω/□ (Fig. 2d) to 3.4 Ω/□ due to the welding connection among Ag NWs. Remarkably, before IEP, ionic polymer actuator has no actuation performance because the high surface resistance restricts the fast and uniform charge distribution. Additionally, Fig. 2e shows the enlarged micromorphology of multifunctional electrodes. The black and transparent part is the interfacial layer, and it can be found that after electrodepositing Au^+, the edges of each Ag NWs disappear at nanowire-nanowire junction, and large weld beadings were formed, which indicates that Au atoms fill the gaps among the Ag NWs and weld them together to form conductive path. In addition, because Ag NWs distributed on the surface can be electroplated Au, while Ag NWs fixed layer cannot be electroplated Au due to embedding in Nafion polymer, the diameter of former is significantly larger than the latter after IEP. Based on the above analysis, it can be found that the slim end of Ag NWs are buried in the interfacial layer to fix the Ag NWs@Au layer and connect the interfacial layer. In addition, the other thick end of Ag NWs and large weld beadings are exposed

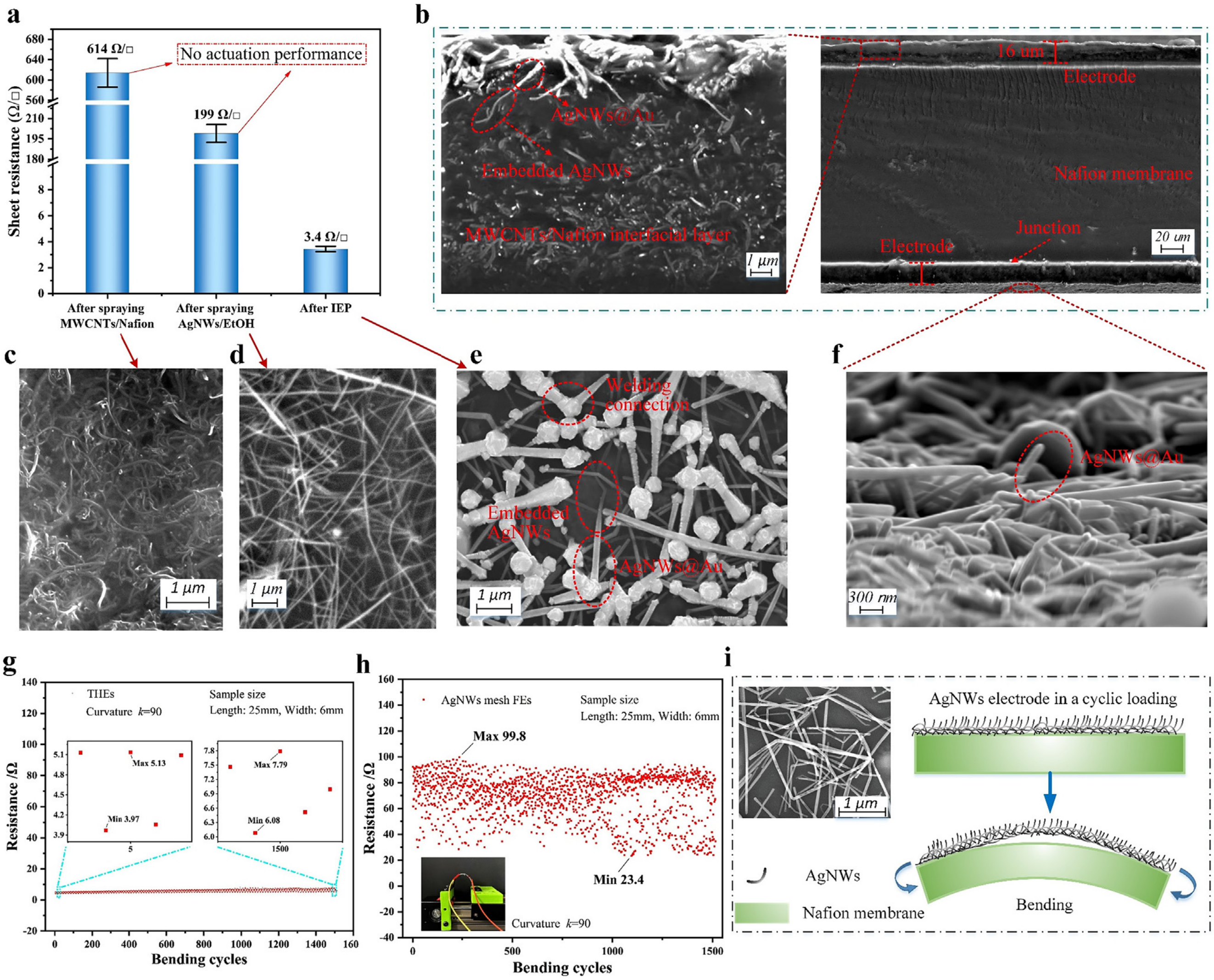

Fig. 2. The characterization of multifunctional electrodes. (a) Surface resistance of multifunctional electrodes. (b) Cross-section of multifunctional electrodes. (c) Micromorphology of multifunctional electrodes after spraying MWCNTs/Nafion. (d) Micromorphology of multifunctional electrodes after spraying Ag NWs/EtOH. (e) Micromorphology of multifunctional electrodes after IEP (front view). (f) Micromorphology of multifunctional electrodes (oblique view). (g) Resistance of multifunctional electrodes in a long cyclic loading. (h) Resistance of Ag NWs electrode in a cyclic deformation. (i) Corresponding schematic of Ag NWs electrode in a cyclic loading.

on the surface of interfacial layer (Fig. 2f), which can facilitate the fast and uniform charge distribution. Compared with the traditional Ag NWs electrodes, this structure effectively improves the strength and surface resistance of electrodes. In the Fig. 2b, MWCNTs are evenly distributed in the interfacial layer, having the characteristics of large number, long length and wide distribution, which is similar to the lateral roots of zoysia grass, enhancing the charge storage in the electrode.

Another important factor improving the performance of ionic polymer actuators is the adhesion between matrix membrane and electrodes. Weak adhesion will lead to the delamination of electrode layer and significantly reduces the lifetime of actuators. Fig. 2b shows the cross-section of actuator with multifunctional electrodes. The highlight part is the junction between the electrodes and the membrane. It can be clearly observed that there are no gaps between Nafion membrane and electrodes, which indicates that the electrode is well bonded to Nafion membrane. In order to further confirm bonding strength, the electrical conductivity of multifunctional electrodes were characterized in flexural mode (Fig. S2). As shown in Fig. 2g, the maximum variation of electrical resistance for multifunctional electrodes was less than 1.71 Ω under mechanical deformation, which exhibited much lower variation of resistance than Ag NWs electrodes. Meanwhile, multifunctional electrodes also showed high stability in long cyclic deformation. After 1500 bending cycles, the resistance of multifunctional electrodes was increased by only 2.66 Ω. The high stability of multifunctional electrodes is mainly because of Ag NWs fixed layer and the seamless connection between the membrane and electrodes. However, the Ag NWs electrode had an unstable behavior under long cyclic loads, as shown in Fig. 2h. The reason is that Ag NWs electrodes are easy to delamination or shedding during complex mechanical force due to lack of adhesive. Besides, Ag NWs will move relative to each other easily owing to the weak contacts among Ag NWs, resulting in deteriorated conductivity [28], as can be seen in Fig. 2i.

3.3. Performance of multifunctional electrodes

To further illustrate the strong adhesion of multifunctional electrodes, we tested the adhesion, as shown in Figure S5. The adhesion of multifunctional electrodes is much higher than that of traditional Ag NWs electrode, up to 327 KPa. In addition, the adding of appropriate MWCNTs will not affect the bonding strength between electrodes and the matrix membrane. Even after long cyclic sticking with tape, the increase in the surface resistance of the electrode is still negligible (Vid. S1). In addition, the ionic polymer actuators need to have good electrical stability for long-term lifetime. Sinusoidal AC voltages of 0.1 Hz with different voltage amplitude were applied to electrodes on both sides of the actuator to test the electrical stability of electrode (Power-on period 30 s). Fig. 3a indicates that multifunctional electrodes show good voltage stability. When the AC voltages increase to ± 4 V, the surface resistance of multifunctional electrodes only varies by 2.5 Ω/□. Even when the AC voltages reach ± 6 V, the surface resistance is still within 10.7 Ω/□. The reason is that the welding connection among Ag NWs and Au protective shell effectively enhance the conductivity and electrical stability of multifunctional electrodes. Moreover, ionic polymer actuators need to be immersed in deionized water before using. In Fig. 3b, after immersing in deionized water for 7 days, then stir for 30 min, the surface resistance of Ag NWs electrode gradually increased from 23.2 Ω/□ to 155.7 Ω/□. On the contrary, the multifunctional electrodes exhibit a low resistance and good stability, even after cyclic washing in deionized water (Vid. S2), the surface resistance still remain unchanged. Fig. 3c shows a cyclic voltammetry (CV) test, aiming at studying the electrochemical performance of actuators. It can be clearly seen that Ag NWs electrode sample shows almost straight line, and specific capacitance can be ignored (~5.6 mF/g). Multifunctional electrodes samples show almost regular curve, indicating normal double layer capacitance. Nevertheless, actuator with MWCNTs/Nafion interfacial layer shows better electrochemical performance than the actuator without interfacial layer (Fig. 3d). The reason is that the charge storage capability of electrode is as important as the electrical conductivity. Although multifunctional electrodes without MWCNTs have low surface resistance, its low charge storage capacity restricts the migration of mobile cations. On the contrary, the charge in multifunctional electrodes can be easily distributed throughout whole electrode through MWCNTs, so mobile cations can be attracted quickly and stored evenly in the MWCNTs/Nafion interfacial layer, which can effectively enhance the electrochemical performance of actuators, as shown in Fig. 3e.

3.4. Actuation performance of ionic polymer actuator based on multifunctional electrodes

Microscopically, Nafion is mainly composed of long fluorocarbon chains, short chains and sulfonic acid groups, in which the long fluorocarbon chains constitute the skeleton structure of Nafion, the short chains are connected with the sulfonic acid groups at the end, and the sulfonic acid groups are agglomerated to form nanochannels. The water molecules accommodated in the nanochannel can dissociate the cation into hydrated cations. Therefore, Nafion has a solid–liquid two-phase structure. The solid phase is served as a framework to support the polymer structure, and the liquid phase is used to accommodate free cations and serve as a way for ion migration. Macroscopically, the prepared ionic actuator is composed of a Nafion film and two electrode layers to form a sandwich structure, as shown in Fig. 4a. The electrodes as conductive material can realize the transmission of current, which can be regarded as a parallel-plate capacitor. When a voltage is applied to the electrodes on the two sides, an electrostatic field is generated between the electrodes. Hydrated cations in Nafion film can directionally migrate accumulatively towards the negative electrode along the nano-channel under the action of the electrostatic field, causing a water molecule concentration difference on both sides of ionic polymer actuator. At this time, the side with higher concentration expands and the other side shrinks, resulting in bending deformation of ionic polymer actuator [2]. In our case, the fabricated ionic polymer actuator exhibits the typical belt shape (4 mm in width, 30 mm in length, and 215 μm in thickness). The

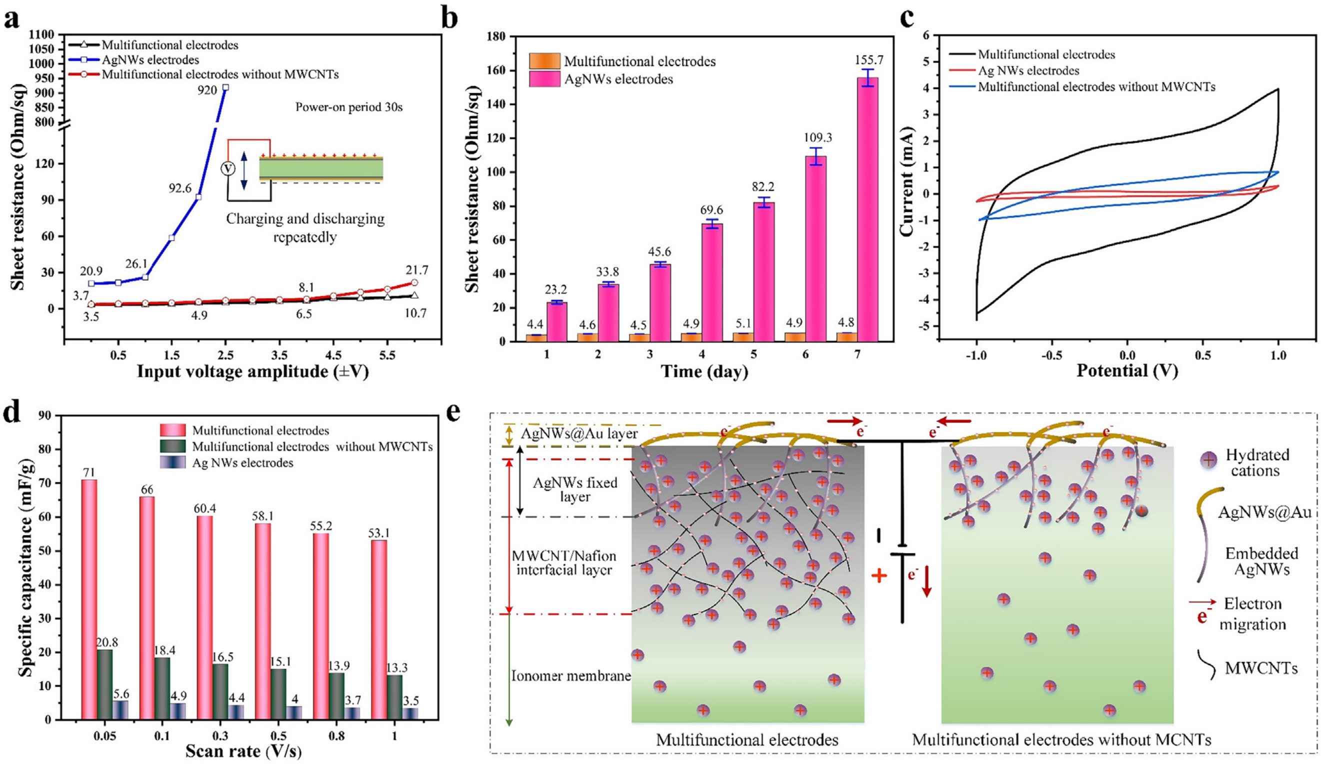

Fig. 3. The performance of multifunctional electrodes. (a) Surface resistance of multifunctional electrodes under sinusoidal AC voltages with different voltage amplitude. (b) Surface resistance of multifunctional electrodes after immersion in DI water. (c) Cyclic voltammetry test for actuators at sweep rate of 0.3 V s^{-1}. (d) Specific capacitances of actuators. (e) Actuation mechanism of electrodes.

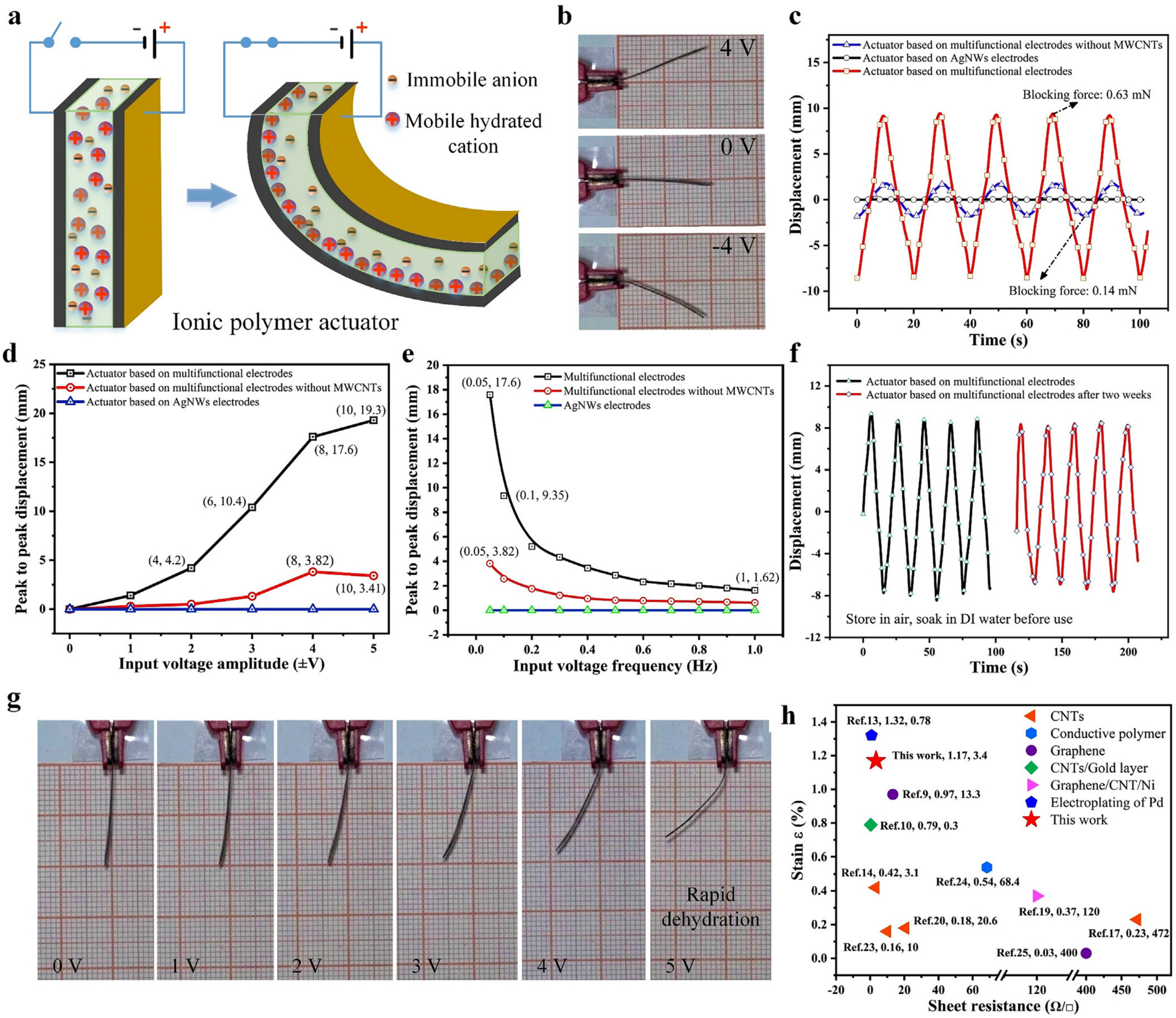

Fig. 4. Actuation performance of ionic polymer actuator based on multifunctional electrodes. (a) An ionic polymer actuator based on multifunctional electrodes. (b, c) Tip displacement of actuators under a sine wave with ± 4 V and 0.05 Hz. (d) Maximum displacement of actuators under sine voltages with various amplitudes and 0.05 Hz. (e) Maximum displacement of actuators under sine voltages with various frequencies and ± 4 V. (f) Actuation performance after two weeks. (g) Maximum displacement of actuators under sine voltages with various frequencies and ± 4 V. (h) Bending strain-surface resistance curve in comparison with Nafion-based ionic polymer actuators reported with different electrodes.

thickness of multifunctional electrodes is 15–17 μm. Because the bending stiffness of actuators can be affected by the uniformity and thickness of electrodes, asymmetrical spraying of materials may lead to asymmetrical actuation in both directions [13]. Fig. 4b and Vid. S3 show the tip displacement with respect to sine wave voltage with an amplitude of ±4 V and excitation frequency of 0.05 Hz. It is obvious that ionic polymer actuator based on multifunctional electrodes has good symmetrical actuation performance, which is mainly attributed to the consistency of thickness and uniformity of electrodes distributed on both sides of Nafion membrane. In addition to good symmetry, multifunctional electrodes also enhance the actuation performance of the actuator. As is known, the ionic polymer actuator is driven by low voltage (less than 5V). The poor adhesion and high surface resistance of the electrode restrict the rapid and uniform distribution of charges. In addition, since the ionic polymer actuator works as a capacitor, good charge storage of the electrodes is also very important. Multifunctional electrodes have three functional layers, in which the Ag NWs@Au layer has extremely low surface resistance, the Ag NWs fixed layer enhances the adhesion of the electrode, and the MWCNTs/Nafion interfacial layer with a high specific surface area improves charge storage and provides more space for movable hydrated cations (Fig. 3e). Fig. 4c indicates that the dynamic output response of tip displacement with respect to sine wave with a voltage amplitude of ± 4 V (0.05 Hz). An appealing fact about the presented results is superior actuation performance of ionic polymer actuator based on multifunctional electrodes. It is evident that addition of MWCNTs to the multifunctional electrodes increases the maximum displacement of actuators by about 460% (17.6 mm). Meanwhile, the MWCNTs/Nafion interfacial layer also improves the blocking force of ionic polymer actuator, which is about 0.63 mN. In contrast, it is worth noting that the ionic polymer actuator with Ag NWs electrode does not have any actuation performance, which is mainly due to the poor stability and the absence of the interfacial layer.

In order to examine the influence of amplitudes and frequencies of the applied voltage on the performance of prepared actuators, some actuation tests were carried out. Fig. 4d and Fig. 4g compare the displacements of three actuators, among them, ionic polymer actuator based on multifunctional electrodes outperformed the other two and showed the highest peak-to-peak displacements in all applied voltages, as expected from the earlier characterizations. When the driving voltage is less than ± 4 V, the peak-to-peak displacement of the prepared actuator increases with the increase of voltage, and the growth rate shows a gradually increasing trend. When the driving voltage is ± 5 V, the peak-to-peak displacement reaches a maximum (19.3 mm), but the growth rate shows a downward trend. This is because high voltage will rapidly electrolyze water molecules in the actuator, thereby reducing the performance of ionic polymer actuators [29]. Furthermore, peak-to-peak displacements of three actuators were measured at various excitation frequencies from 0.05 to 1 Hz under the voltage of ± 4 V. Displacement of all actuators decrease with increasing frequency (Fig. 4e). The reason mainly lies on that the time duration for ion migration into electrode is insufficient at higher frequencies [2]. Fig. 4h shows that ionic polymer actuator based on multifunctional electrodes not only outperforms other two ionic polymer actuators in this study, but also being comparable or even superior to most of the reported ionic polymer actuators based on Nafion membrane, including CNTs, conductive polymers, graphene, and CNTs/gold layer. In addition, the actuation performance of ionic polymer actuator based on multifunctional electrodes is second only to conventional Nafion®–IPMC made via the electroless plating of Pd, and the generated $\varepsilon\%$ differs by only 0.15. Undoubtedly, the excellent stability, low surface resistance and superior energy storage capacity would make some breakthroughs for the ionic polymer actuator based on multifunctional electrodes. In order to further explore the durability of actuator. We exposed the actuator to the air for 2 weeks, then test its peak-to-peak displacement under the same conditions. As shown in Fig. 4f, after two weeks, the actuation performance change of the prepared actuator can be ignored. In addition, Figure S6a shows the durability of ionic polymer actuator. It can be found that the actuation performance is stable first, and then gradually attenuate. However, when we spray water on the surface of the actuator again, the actuation performance of the actuator is restored to its original state again, which shows that the prepared ionic polymer actuator can be reused, as shown in Figure S6b.

4. Conclusion

In this work, we proposed an efficient method to prepare multifunctional electrodes for ionic polymer actuators with unique simplicity and fastness. Through taking use of the spraying and IEP method, three functional layers of multifunctional electrodes are formed, similar to the structure of zoysia grass, including Ag NWs@Au layer, Ag NWs fixed layer, and MWCNTs/Nafion interfacial layer, which provide respectively low surface resistance, good stability and interfacial layer with a high specific surface area for ionic polymer actuators. Compared to other flexible electrodes, multifunctional electrodes have excellent adhesion up to 328 KPa and low surface resistance. After immersing in deionized water for 7 days or 1500 bending cycles, the relative change in surface resistance is negligible. In addition, the maximum displacement of the prepared ionic polymer actuator based on multifunctional electrodes showed 460% improvement, which is comparable or even superior to most of the reported ionic polymer actuators based on Nafion membrane, including CNTs, conductive polymers, graphene, and CNTs/gold layer, and be second only to conventional Nafion®–actuators made via the electroless plating of Pd. This outstanding enhancement mainly resulted from the synergic effect of three functional layers. MWCNTs/Nafion interfacial layer with high specific surface area contributes to the charge storage of the electrode. Ag NWs fixed layer is firmly embedded in the interfacial layer, which is used to fix the Ag NWs@Au layer and connect the interfacial layer. Ag NWs@Au layer provides an extremely low surface resistance for facilitating the fast and uniform charge distribution. The satisfactory performance of ionic polymer actuator based on multifunctional electrodes indicate that multifunctional electrodes has considerable application prospects in smart flexible electronic devices.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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