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COMMUNICATION

A naturally crosslinked chitosan based ionic actuator with cathode deflection phenomenon

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Abstract In this communication, we introduce a chitosan polymer gel ionic actuator with dilute acid as electrolyte solution replacing ionic liquid. Interestingly, the switch not only produces obvious improvements in actuation performance, but the actuator bends towards the opposite direction. It presents a cathode deflection phenomenon instead of the usual anode deflection. Moreover, ion channels inside the electrolyte layer are obtained through a natural crosslinking treatment, so it allows an effective ions transportation inside the electrolyte layer.

Keywords Ionic actuator · Chitosan · Cathode deflection · Crosslinking

Introduction

Ionic actuator, a type of Electroactive Polymer (EAPs), has been intensively studied for their large deformation, light-weight, flexibility, low voltage actuation, etc. They have attracted great attention for their potential applications in intelligent robotics, biomedical devices, and micro electro-mechanical systems (Bar-Cohen and Zhang 2008; Kim et al. 2007; Baughman 2005; Roundy and Wright 2004). Chitosan (Cs), containing amino and hydroxyl groups, is a sustainable resource with potentials of energy transformation. It is lightweight, low cost, and also offers beneficial special characteristics, such as biocompatibility, biodegradability, and anti-bacterial properties (dos Santos et al. 2003; Kim et al. 2007; Cai and Kim 2008). Therefore, it presents great potential in the area of manufacturing biocompatible ionic actuators (Li et al. 2011; He et al. 2015).

The initial report (Lu and Chen 2010; Lu et al. 2013) of Cs based ionic actuator can be tracked back to Lu et al. It mainly comprised of Multi-walled CNTs (MWCNTs) as the conductive electrode and Ionic Liquid (IL) with Cs and MWCNTs as electrolyte. Under applied voltages, the anions and cations migrate to the anode and the cathode respectively in an attempt to balance the electric field. Finally, owing to the steric effects, Cs based ionic actuator bends towards the anode. However, our recent research has observed a Cs based ionic actuator exhibiting a cathode deflection phenomenon, which is completely different from the anode deflection in Lu et al. report. Also, this kind of phenomenon is accompanied by a tremor behavior, similar to that of human muscles. Therefore, the

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cathode deflection phenomenon is deemed worthy for further study.

In addition, modification of chitosan through the cross-linking method is suitable and effective in improving the mechanical properties for practical applications (Di Martino et al. 2005; Neto et al. 2005). Water molecules inside the electrolyte membrane can be preserved through the effective crosslinking and the additive glycerin solvent. As a result, ions efficient movement inside the electrolyte membrane is maintained, and the flexible electrolyte membrane is also retained. To meet the standers for medical treatment and biological sensors, a natural cross-linking agent Genipin is examined in this study. Genipin can react spontaneously with amino acids or proteins to form dark blue pigments (Moura et al. 2007; Chen et al. 2004; Pujana et al. 2013). Coupled with observations previously mentioned, this method of the networking electrolyte to maintain moisture provides a significant motivation and inspiration to fabricate an actuator with high-performance and biocompatibility, specifically using the biological crosslinking method.

As shown in Fig. 1, Cs based polymer (C-polymer) actuator has a layered structure with the electrolyte layer clamped by two electrode layers. Chitosan (deacetylation degree 85.66%, viscosity 450 mPa s, Cs powder) and Genipin (purity >98%, Japan Wako) are applied as the polymer and natural crosslinking agent. The electrolyte layer consists of a mixed solution of Cs/dilute acid solution solution/glycerin/MWCNTs. Dilute acid solution contains Nitric Acid solution (HNO_3), Lactic Acid solution (HL), Acetic Acid solution (HAc). Then it is addressed in Genipin solution to form a network structure. The electrode layers consist of Cs/MWCNTs, formed by water evaporation. Among the electrolyte film, 0.6 g/20 mL chitosan based aqueous solution is crosslinked by concentration of 6 mg/mL of genipin aqueous solution. 1.0, 1.25, 2, 3.3, 6.67 mL genipin aqueous solutions are added to represent different crosslinking ratio as 1:1000, 1:800, 1:500, 1:250, 1:150. The final C-polymer actuator film is fabricated by hot-pressing the two electrode layers and the electrolyte layer under applied load 20 N at 50 °C for 6 h. Due to the solvent evaporation from the hot-pressing technique, the typical thickness of the C-polymer film is 200–250 μm. It is thinner than the sum of the original individual electrode layer and the electrolyte layer. The microscopic structures of C-polymer ionic actuator and MWCNTs electrode surface are illustrated in Fig. 2a, b, respectively.

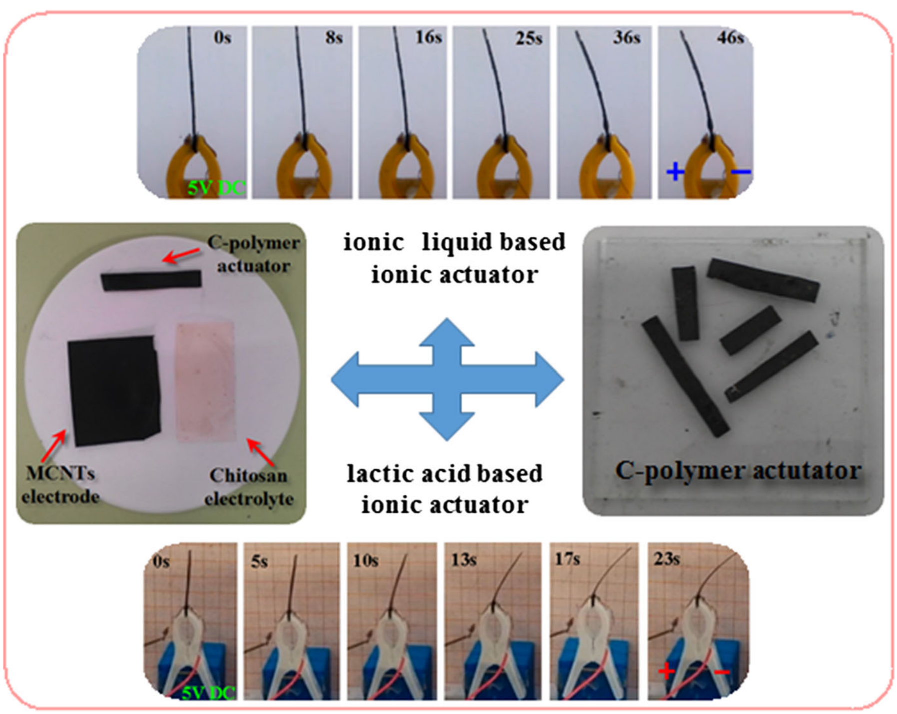

Fig. 1 The cantilever beam model structure of C-polymer actuator

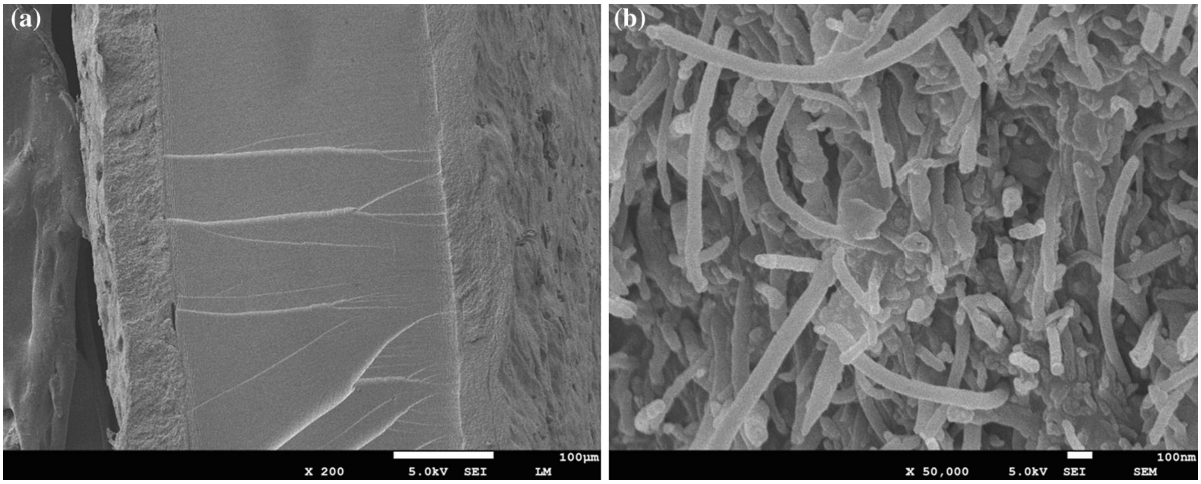

Fig. 2 Microscopic structure: **a** the whole C-polymer actuator, **b** MWCNTs electrode surface

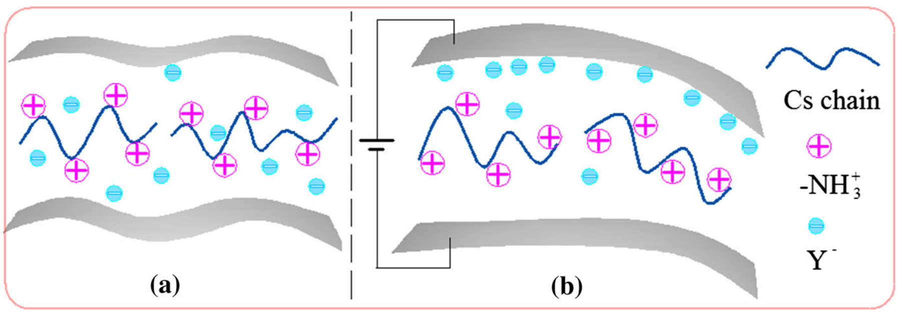

Fig. 3 Motion mechanism of C-polymer actuator: **a** without electricity, **b** the cathode deflection after electricity

Figure 1 presents results of the cycle deflection experiment of an IL based C-polymer actuator and a HL based C-polymer actuator against 5 v DC. It shows that under electric excitation, IL based C-polymer actuator produces an anode deflection, whereas HL based C-polymer actuator produces a cathode deflection. Response times of IL based C-polymer actuator and HL based C-polymer actuator are 46 and 23 s, respectively. The results demonstrate that the response time of the latter HL based actuator is reduced by half. Therefore, it behaved a significant improvement in its actuation speed.

The main chain of the Cs structure contains a large number of aminos ($-NH_2$), which could be hydrolyzed in a dilute acid aqueous solution. During hydrolysis, numerous free amino groups from the molecular chain combines with the hydrogen ions H^+ in aqueous solution to form the positively charged polyelectrolyte ($-NH_3{}^+$). The reaction leaves free anion from the dilute acid root ($-Y^-$) in a scattered state. Commonly used dilute acid roots ($-Y^-$) are acetic acid root (Ac^-), lactic acid (L^-) and hydrochloric acid root (Cl^-).

From the above, the electrically induced movement of cathode deflection phenomenon can be interpreted as follows. Under the electric excitation, the charges at the cathode and anode generate an electric double layer. While the positively charged cations ($-NH_3{}^+$) are kept stationary, which are restricted by the main chain of Cs structure. Through the action of Van der Waals force, the anions ($-Y^-$) move towards the anode surface and increase the concentration over time. The apparent concentration gradient between both electrodes induces the electrode surface strain, which produces the deflection of the C-polymer actuator towards the cathode, as shown in Fig. 3.

Figure 4 is the curve of the bending force under various electrolyte solutions. It shows the tip bending forces of IL, Nitric Acid solution (HNO_3), Lactic Acid solution (HL), Acetic Acid solution (HAc) are 1.875,

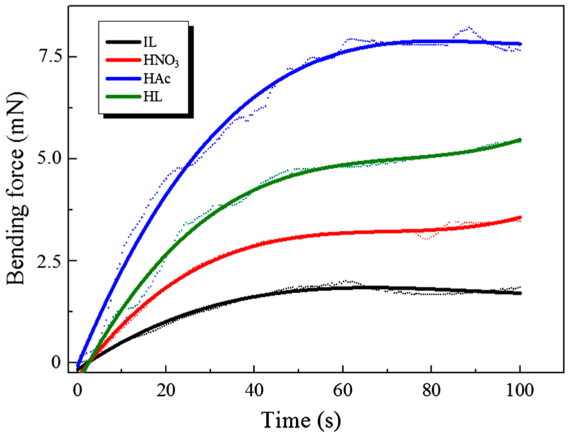

Fig. 4 Bending force under various electrolyte solutions

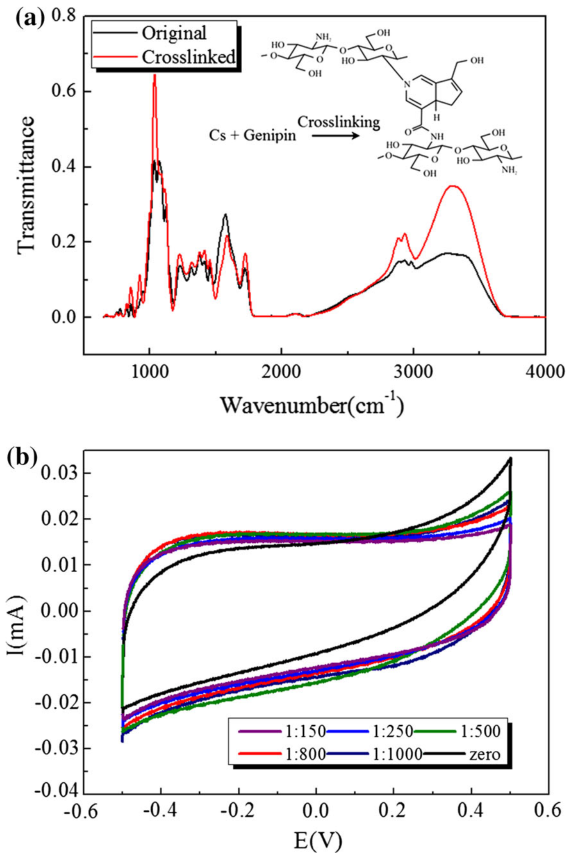

Fig. 5 **a** FT-IR curves of chitosan and genipin, **b** CV curves of various crosslinking ratios

3.475, 7.725, 5.435 mN, respectively. The output force and the response speed of dilute acid solution based C-polymer actuators are significantly better than IL based C-polymer actuator counterpart. From the results, the actuation force of the HL based C-polymer actuator is greatest 4.12 times higher than that produced by IL based C-polymer actuator; the weakest in the set. This demonstrates that C-polymer actuator with the cathode deflection phenomenon presented significant advantages in terms of overall actuation performance.

The crosslinking reaction occurs on the amino-primary amine of Cs molecular chain, and its crosslinking mechanism is to convert the primary amine into amide or tertiary amine. In order to confirm the biological crosslinking reaction, Genipin crosslinking electrolyte is tested by Fourier Transform Infrared Spectroscopy (FT-IR), as shown in Fig. 5a. The vibration effect causes by the covalent bond N–H of Cs molecular chain, it creates some apparent absorption visible in 1570 cm^{-1}. A series of vibration absorption peaks appear in 800–1300 cm^{-1}, which are caused mainly by the absorption of the sugar ring vibration. There is an obvious absorption of the covalent bond N–H of tertiary amine at 1260 cm^{-1} that existed in the electrolyte after crosslinked. The results verify that the crosslinking reaction between Cs molecular chain and Genipin molecule is successful.

Figure 5b are CV curves of various crosslinking agent contents and a normal without crosslinking treatment (zero) at a scanning speed of 100 mv/s. The crosslinking ratios between Genipin and Cs are 1:150, 1:250, 1:500, 1:800, 1:1000, zero. The capacitances of the crosslinked agents are 6.9, 7.2, 7.9, 7.7, 7.9, 6.7 mF/g, respectively. The lack of significant variances in capacitances proves that the crosslinking network can change the efficiency of ion movement inside the electrolyte layer, but has no effect on the conductivity of the electrolyte layer.

Conclusion

In this communication, we have developed a Cs polymer gel ionic actuator with dilute acid as ion electrolyte solution replacing ionic liquid. The bending direction is towards the cathode deflection instead of anode deflection, which is caused by an apparent concentration gradient between both electrodes to induce the electrode surface strain. Moreover, effective ions transportation is gained by a natural crosslinking electrolyte layer. In addition, these changes have produced obvious improvements in actuation performance.

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