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## Efficient voltage actuators based on rapid heat and electric dual-response poly(aryl ether ketone) shape memory composites reinforced with radially aligned CNTs

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### Abstract

In this paper, we synthesized a shape memory poly(aryl ether ketone) (PAEK) and fabricated the radially oriented CNTs enhanced PAEK composite voltage actuators. The introduction of highly aligned CNTs endowed PAEK matrix great thermal stability, good mechanical properties, and the excellent shape memory effect. The formation of CNTs conductive path in PAEK matrix was instrumental in improving thermal and electrical conductivity, promoting efficient heat/electric dual triggered shape memory effect with high recovery ratio, rapid triggered shape recovery and low triggering voltage. In addition, we utilized aligned CNTs/PAEK composites with 15 wt% CNTs as voltage actuators, and designed the two kinds of voltage actuators (angle-mode and time-mode) to achieve the different actuating actions via the applied voltage (range from 8V to 50V). These efficient composite voltage actuators exhibited the excellent stability and durability in continuous voltage actuating, which were expected to open door for smart actuators and electronic devices.

**Keywords:** A. Carbon nanotubes and nanofibers; A. Polymer-matrix composites (PMCs); B. Directional orientation; A. Smart materials

## Introduction

The developments and advancements in research of smart and rapid responsive actuating materials strive to meet the requirements of smart actuators, which could be widely utilized in electronic devices, biomedical devices, and aerospace applications, etc [1,2]. Shape memory polymers (SMPs), as a kind of responsive smart materials, could be programmed to temporary shape via the external conditions (temperature and force), and recover to permanent shape under certain stimulus, such as heat [3], electric [4], light [5], magnetism [6], solvent [7], humidity [8], and pH [9] etc. Due to the unique deformation-recovery capability, SMPs have various advantages of programming rigidity and low cost, which are used in myriad fields: tissue engineering, artificial muscle, smart actuators, and aerospace components, etc [10-12]. Generally, shape memory effect (SME) originates from the internal net points and switching segment. Crystalline phase and physically or covalently cross-linked regions act as net points, which could memorize the permanent shape and recover to it. The stability is necessary for the fixed net points, ensuring the stable shape upon the high temperature. Flexible segments and amorphous regions act as the switching segment, which could deform undergoing the high temperature and applied external forces. Besides, they could retain the deformed shape while keeping force and decreasing temperature. Then, when the temperature reached above transition temperature, the switching segments are actuated and begin to move. Macroscopically, the SMPs recover to the permanent shape [13,14].

Nevertheless, SMPs exhibit several disadvantages such as poor mechanical properties, low respond speed, and weak strength [15], which largely limit their diverse applications. Commonly, the mechanical performances of SMPs could be improved mainly by two methods [16,17]: Combining shape memory polymers with strengthened and elastic materials, such as silicon elastomer [18]; in addition to dope reinforcing fillers such as carbon nanotubes (CNTs) [19], carbon fibers [20], and  $\text{Fe}_3\text{O}_4$  particles [21], etc. Due to the easy processing and enhanced performances, the integration of reinforcing fillers is more commonly used for the preparation of enhanced shape memory composites. In addition, reinforcing fillers commonly possess the certain functionality which could endow SMPs with unique performances

and diverse stimulated modes. Conventional SMPs almost belong to heat-driven SMPs, which triggered by heating. Magnetocaloric effect of  $\text{Fe}_3\text{O}_4$  particles endows SMPs with magnetic-actuated shape recovery behaviors [22]. The incorporation of CNTs into SMPs matrix could render electric- and light-triggered SME due to the electrothermal and photothermal effect of CNTs [23]. Among the various triggering modes, electric actuation has attracted much attentions due to the convenient manipulation and low cost [24,25]. To fulfill the electric-actuated SME, constructing a conductive path in SMPs matrix is necessary, in addition that CNTs are most usually employed as the conductive fillers to construct the whole path [26]. Due to the axial tubular characteristic of CNTs, the reinforced mechanical properties and conductivity are closely related to the distribution and orientation of CNTs in SMPs matrix. With the simple fabrication techniques (physical blending or filling), reinforcing CNTs are difficult to evenly distribute or radially distribute in SMPs matrix [27]. The dispersion and orientation of fillers in matrix is also a major subject in the preparation of fillers enhanced composites.

Poly(aryl ether ketone) (PAEK), as a universal engineering thermoplastic, possesses excellent mechanical properties, thermal stability, and chemistry resistance, which expanding to the diverse application fields in aerospace, engineering industry, and energy storage [28-30]. In addition, the rigid structures and flexible chains could be adjusted through the variation of monomers and the integration of other side chains or groups, for the fulfillment of shape memory effect. Herein, we proposed a synthesis route of PAEK to achieve the excellent SME. To obtain the reinforced mechanical properties and excellent electric-actuated SME, CNTs were integrated into PAEK matrix to fabricate heat/electric dual triggered shape memory composite actuators. It was worth noting that the oriented distribution of CNTs in PAEK matrix was achieved through an electro-mixed fusion preparation method. Radially aligned CNTs endowed composites with the more enhanced strength and great conductivity, promoting the efficient heat/electric dual triggered shape recovery. In addition, we employed aligned CNTs/PAEK composites as the voltage actuators, and designed two kinds of voltage actuating modes (angle-mode and time-mode) to achieve diverse actuating actions of applied voltage (range from 8V to 50V). These

efficient composite voltage actuators exhibited the excellent stability and durability in continuous voltage actuating tests, which exhibited the great utilization potential in smart actuators.

## Experimental

### Materials

4,4'-(hexafluoroisopropylidene) diphenol, 4,4'-difluorobenzophenone, potassium carbonate ( $K_2CO_3$ ), and tetramethylene sulfone (TMSF) were bought from Aladdin Industrial. Toluene and N-methyl kelopyrrolidide (NMP) were all supplied by Tianjin Guangfu Chemical Reagent Factory. Multiwall CNTs were bought from Chinese Academy of Sciences, Chengdu Organic Chemistry Co., Ltd.

### Synthesis of PAEK

PAEK was synthesized by nucleophilic substitution using the following polymerization procedure, as depicted in Scheme 1. A certain proportion of 4,4'-(hexafluoroisopropylidene) diphenol, 4,4'-difluorobenzophenone, and  $K_2CO_3$  were carefully added into the TMSF/toluene mixed solvent, in addition that Dean-Stark trap and nitrogen atmosphere were equipped. The mixture was thoroughly stirred, and the temperature was increased to 140 °C for 2 h to remove water. During the reaction process, toluene was used as the azeotropic solvent. Afterwards, the temperature was increased to 170 °C for 3 h to distill the toluene and carry out the polymerization. After polymerization, the viscous product was slowly poured into a beaker containing isopropanol and distilled water. Finally, the precipitate was filtered and washed with distilled water for several times to remove solvents, unreacted monomers, and oligomers. The synthesized PAEK was dried at 40 °C under vacuum for 24 h and the yield was 91%.

Scheme 1 [about here]

### Preparation of oriented CNTs enhanced PAEK composites

Oriented CNTs enhanced PAEK composites were fabricated through an electro-mixed fusion process.<sup>27</sup> PAEK was dissolved into NMP and stirred to obtain the homogeneous solution. Certain amounts of CNTs were added into PAEK solution, and further stirred until the formation of PAEK/CNTs homogeneous mixed dispersion. Subsequently, the PAEK/CNTs mixed dispersion was poured into a homemade mould, equipped with conductive foils in the two sides, which connected with applied external voltage. Then, certain voltage was applied for 2 min to orientate CNTs. Afterwards, the mixture was dried at 80 °C for 48 h. Finally, prepared PAEK/CNTs composites were peeled off from the mould and stored carefully for testing. The fabrication process is illustrated in Figure 1, and different content of CNTs and applied voltages for CNTs orientation were performed to fabricate PAEK/CNTs composites, recorded in Table 1.

Figure 1 [about here]

Table 1 [about here]

## Characterization

<sup>1</sup>H-nuclear magnetic resonance (<sup>1</sup>H NMR) spectra was obtained from an ADVANCE III 400 MHZ 010601 spectrometer (Bruker). CDCl<sub>3</sub> was used as the solvent and tetramethylsilane (TMS) was used as the internal reference. Fourier transform infrared (FTIR) spectroscopy was recorded over the frequency range of 4000 cm<sup>-1</sup>-400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> by a Spectrum Two (PerkinElmer). Wide-angle X-ray diffraction (WAXD) patterns were performed on an X'pert XRD analyzer (Panalytical B.V.). The range of 2θ was 5°-55°, and a step size was 10°/min. Differential scanning calorimetric (DSC) curves were obtained from a DSC 1 STAR System (Mettler-Toledo) over a temperature range of 25 °C-300 °C. Thermal gravimetric analysis (TGA) was analyzed on a TGA/DSC 1 STAR System (Mettler-Toledo) with a temperature range of 25 °C-800 °C and a heating rate of 10 °C/min. Section morphology of PAEK/CNTs composites on parallel and vertical current directions was observed using a scanning electron microscope (S-4300, Hitachi). Before testing, the samples were brittle fractured by liquid

nitrogen and sputtered gold. Mechanical properties of PAEK/CNTs composites on parallel and vertical current directions were measured from a universal mechanical testing machine (SBA-10, Hake Keji). The samples were cut into the size of 30 mm × 10 mm. The gauge length was 20 mm and the loading rate of 4 mm/min. The testing results were averaged from 5 samples.

### Shape memory test

The heat-triggered shape memory behaviors of PAEK/CNTs composites on parallel and vertical current directions were investigated through the “U” shape samples. The samples with the size of 10 mm × 30 mm were fixed into a “U” shape by the mould above the temperature of  $T_g$ . Then, they were cooled down quickly to room temperature for shape fixity. The samples were detached from the mould, and the angle was recorded ( $\theta_0$ ). Afterwards, the temperature was increased to  $T_g + 10\text{ }^\circ\text{C}$ , and the shape recovery could be observed. The whole recovery process was recorded by a digital video camera. The recovery ratio ( $R_r$ ) and fixity ratio ( $R_f$ ) were calculated from the following formulas:

$$R_r = \frac{\theta(t) - \theta_0}{180 - \theta_0} \times 100$$

$$R_f = \frac{180 - \theta_0}{180} \times 100$$

Where  $\theta_0$  is the deformation angle at time of 0s, and  $\theta(t)$  is at time of t s.

The electric-actuated shape memory behaviors of PAEK/CNTs composites on parallel and vertical current directions were investigated through the similar steps mentioned above. The fixity of temporary shape was the same, whereas the shape recovery was triggered by electric. The samples with fixed temporary shape were imposed with different triggering voltages for shape recovery. The whole process was recorded, and  $R_r$ ,  $R_f$  could be calculated. In addition, the conductivity of PAEK/CNTs composites was measured by a RT-70 V/RG-7C four-point probe (Napson Corp).

### Results and discussion

## Characterization

The chemical structures of synthesized PAEK could be characterized by  $^1\text{H}$  NMR analysis, shown in Figure 2a. The chemical shifts at 7.09 ppm, 7.26 ppm, and 7.80 ppm, were corresponded to the protons of 1, 2, and 3 [31]. FTIR spectra is showed in Figure 2b. For pure PAEK, the peak at  $1656\text{ cm}^{-1}$  was attributed to the stretching vibration of aryl carbonyl groups, and the peak at  $1239\text{ cm}^{-1}$  was concerned with the characteristic peak of aryl ether groups. Meanwhile, there was not any differences of peaks position after the addition of CNTs, indicating the physical blends between PAEK and CNTs. In addition, after incorporating CNTs, the transmittance of composites decreased, due to intrinsic dark-color feature of CNTs.

Figure 2 [about here]

WAXD curves are showed in Figure S1. Pure PAEK showed characteristic diffraction peak, which became broader after the addition of CNTs, indicating that the integration of CNTs destructed the crystalline structure of PAEK. Nevertheless, while the CNTs content reached up to 15 wt%, the diffraction peak got sharp, which could be attributed to the aggregation of CNTs in PAEK matrix. Comparing with the relative homogeneous dispersion of CNTs in PAEK matrix, the aggregation of CNTs didn't cause the destruction of crystalline of PAEK.

DSC and TGA curves are showed in Figure 3. In Figure 3a, the glass transition temperature ( $T_g$ ) of the composites was  $168.8\text{ }^\circ\text{C}$ ,  $169.9\text{ }^\circ\text{C}$ ,  $171.6\text{ }^\circ\text{C}$ , and  $171.3\text{ }^\circ\text{C}$ , corresponding to the CNTs content of 0 wt%, 5 wt%, 10 wt%, and 15 wt%, respectively. In Figure 3b, the first degradation stage occurred at around  $130\text{ }^\circ\text{C}$ , which was concerned with the removal of nonvolatile solvent and absorbed water. The degradation of PAEK main chains occurred at around  $495\text{ }^\circ\text{C}$ , which postponed slightly after the addition of CNTs. When the temperature reached up to  $800\text{ }^\circ\text{C}$ , as the increasing of CNTs content, the residual mass of composites increased gradually from 31.2%, to 34.9%, 50.1%, and 52.2%, corresponding to the CNTs content of 0 wt%, 5 wt%, 10 wt%, and 15 wt%, respectively.



Figure 3 [about here]

The microstructural characteristics of PAEK/CNTs composites on parallel to current direction with diverse CNTs contents and different applied voltages are showed in Figure 4. It could be observed that as the increasing of CNTs content from 5 wt% to 15 wt%, the CNTs in matrix became dense and aggregated. For the samples with 10 wt% CNTs, as the increasing of applied voltage, the oriented dispersion of CNTs became more obvious and almost all the CNTs were rearranged in the same direction after treatment at applied voltage of 15V.

Figure 4 [about here]

The parallel and vertical morphologies of PAEK/10 wt% CNTs composites treated with different applied voltages are showed in Figure 5. When increasing applied voltage to 15V, the radial alignment of CNTs became mostly significant. In parallel direction, the CNTs in images were almost rearranged to a direction. The sectional images show that, as the increasing of applied voltage, the arrangement of CNTs section became dense in vertical direction, which further reflected the orientation of CNTs.

Figure 5 [about here]

### Mechanical performances

Static tensile test results of PAEK/CNTs composites on parallel and vertical directions are showed in Figure 6 (a-f: the samples on parallel direction were employed for testing). Figure 6a shows the stress-strain patterns of the composites with various CNTs content. Pure PAEK sample exhibited the yield stage during the tensile process, and with the increasing of CNTs content, the yield stage occurred earlier, at the strain of 5.43%, 4.48%, and 4.19% corresponding to the CNTs content of 0 wt%, 5 wt%, and 10 wt%, respectively. When the content of CNTs was 15 wt%, the fracture mode changed to brittle fracture, and there was not the occurrence of yield stage. Figure 6b reflected the effect of CNTs content on tensile strength and elongation at break. As the increasing of CNTs content from 0 wt%, 5 wt%, 10 wt%, and 15

wt%, the corresponding tensile strength increased gradually, from 44.95 MPa to 46.11 MPa, 48.89 MPa, and 52.22 MPa, respectively. Meanwhile, the elongation at break decreased from 6.33% to 5.70%, 5.67%, and 3.54%, respectively. The phenomenon could be attributed to that the enhanced stiffness of CNTs increased the strength, whereas weakened the toughness of composites. As a result, with the increasing of CNTs content, the tensile strength increased, and the elongation at break decreased. The changing trend of Young's modulus is showed in Figure 6c. As the increasing of CNTs content, Young's modulus increased gradually, from 0.83 GPa to 1.04 GPa, 1.13 GPa, and 1.48 GPa, corresponding to CNTs content of 0 wt%, 5 wt%, 10 wt%, and 15 wt%, respectively. It also should be concerned with the introduction of high stiff CNTs, as mentioned above.

Figure 6d shows the effect of applied voltage on stress-strain behaviors of the composites. It could be observed that, without applied voltage, the sample was brittle fracture because of randomly dispersed CNTs in PAEK matrix. When applying the voltage (5V and 10V), CNTs were rearranged to become obediently dispersed in matrix, promoting the roughness of composites. As a result, yield stage occurred during the tensile process. When the applied voltage was 15V, the orientation of CNTs was adequate, which tightly placed in matrix (observed in SEM images). Due to the intrinsic stiffness, composites exhibited decreased toughness, and the fracture mode became brittle fracture. The effect of applied voltage on tensile strength and elongation at break is showed in Figure 6e. With the increasing of applied voltage, tensile strength increased gradually, from 30.63 MPa to 35.55 MPa, 49.23 MPa, and 55.39 MPa, corresponding to the voltage of 0V, 5V, 10V, and 15V, respectively. While applied voltage was 0V and 5V, elongation at break had almost no change, of 4.31% and 4.34%, respectively. When the applied voltage was 10V, the toughness of composites was significantly reinforced, and the elongation at break was 6.58%, which could be concerned with the oriented and obedient dispersion of CNTs in PAEK matrix. Nevertheless, when applied voltage increased to 15V, tight placement of CNTs in matrix was detrimental to the toughness, and as a result, elongation at break was 4.08%. Figure 6f shows the effect of applied voltage on Young's modulus. With the increasing of applied voltage, oriented dispersion of

CNTs in matrix reinforced Young's modulus, from 0.71 GPa to 0.88 GPa, 1.05 GPa, and 1.36 GPa, corresponding to the voltage of 0V, 5V, 10V, and 15V, respectively.

Difference value (D-value), in this paper, was defined as the value of which on parallel direction subtracted the value on vertical direction. D-value of mechanical properties of the composites upon the voltage of 10V are showed in Figure 6g. As the increasing of CNTs content, D-value of tensile strength was almost increased, of 6.07 MPa, 5.90 MPa, and 6.54 MPa, corresponding to the CNTs content of 5 wt%, 10 wt%, and 15 wt%, respectively. As for elongation at break, D-value was 1.17%, -1.17%, and -0.36%, corresponding to the CNTs content of 5 wt%, 10 wt%, and 15 wt%, respectively. The toughness of composites on vertical direction was in general better than composites on parallel direction, which might be concerned with the pull out effect [32,33] of CNTs in PAEK matrix during the stretching process, depicted in Figure S2. As the increasing of CNTs, D-value of Young's modulus increased gradually, from 0.21 GPa to 0.28 GPa, and 0.30 GPa, corresponding to CNTs content of 5 wt%, 10 wt%, and 15 wt%, respectively. The increasing of CNTs content quantitatively improved the orientation extend of CNTs, reinforcing the Young's modulus. D-value of mechanical properties of the composites with CNTs content of 10 wt% are showed in Figure 6h. With the increasing of applied voltage, D-value of tensile strength increased gradually from 3.62 MPa, 5.90 MPa, and 7.16 MPa corresponding to the voltage of 5V, 10V, and 15V, respectively. Increasing the applied voltage, the orientation extent of CNTs improved, conducive to the tensile strength. D-value of elongation at break was 1.02%, -1.17%, and -0.37%, corresponding to the voltage of 5V, 10V, and 15V, respectively. As for Young's modulus, D-value increased gradually as the increasing of applied voltage, from 0.13 GPa to 0.28 GPa, and 0.32 GPa, corresponding to the voltage of 5V, 10V, and 15V, respectively.

Figure 6 [about here]

### Heat-actuated shape memory behaviors

Heat-actuated shape memory behaviors of PAEK/CNTs composites were investigated and showed in Figure 7 (a-c: the samples on parallel direction were employed for testing). The whole shape recovery process of the composites with CNTs content of 10 wt% upon the applied voltage of 10V at 181 °C ( $T_g + 10$  °C) is showed in Figure 7a. The whole shape recovery process could finish within 12s as the sample recovered approximately to the permanent shape of “bar” shape from the temporary shape of “U” shape (The whole shape recovery process was recorded in Video S1). Figure 7b reflected the effect of CNTs content on recovery ratio of the composites. Synthesized PAEK sample exhibited the excellent recovery behaviors, whose recovery ratio of 96.5%. As the addition of CNTs, the recovery ratio of the composites decreased, of 93.7% and 94.9%, corresponding to CNTs content of 5 wt% and 10 wt%, respectively. It could be attributed to that the integration of tubular and stiff CNTs in PAEK matrix was detrimental to the movement of molecular chains above triggering temperature, which decreased the recovery ratio. When the CNTs content increased to 15 wt%, recovery ratio decreased to 78.2%, which could be concerned with the dense dispersion of CNTs in matrix seriously hindered the movement of molecular chains of PAEK. Figure 7c reflected the effect of applied voltage on recovery ratio of the composites. The recovery ratio of the composites with CNTs content of 10 wt% without applied voltage was 93.2%. As the increasing of applied voltage, the recovery ratio of increased gradually, of 94.2%, 94.9%, and 98.7%, corresponding to the voltage of 5V, 10V, and 15V, respectively. The orientation of CNTs in matrix occurred by applied voltage, and the orientation extent became higher as the increasing of the voltage. Due to the intrinsic thermal conductivity of CNTs [34], the radially aligned CNTs array formed efficient thermal conduction path in PAEK matrix, conducive to the heat transmission in the composites. Besides, comparing with random dispersion of CNTs in matrix, obediently oriented CNTs were not so detrimental to the movement of molecular chains along with the macroscopic movement direction. Figure 7d shows the recovery ratio of the composites with CNTs content of 10 wt% upon different applied voltage (5V, 10V, and 15V) on parallel and vertical directions. While the CNTs content was 10 wt%, the recovery ratio of obtained samples were above 93%, whatever the composites on parallel direction or vertical direction, indicating to the good shape recovery capability. It could be observed that

the recovery ratio of the composites on parallel direction was slightly higher than it on vertical direction, and the D-value became larger with the increasing of applied voltage (of 0.4%, 1.3%, and 3.2%, corresponding to the voltage of 5V, 10V, and 15V, respectively). It might be concerned with the fabrication and enhancement of thermal conduction path. Figure 7e shows the fixity ratio of the composites with diverse content of CNTs, upon different voltage, on parallel and vertical directions. It could be observed that the fixity ratio of all the samples were over 98%, indicating the excellent shape fixity capability. With increasing of the CNTs contents and the applied voltage, the fixity ratio increased. The oriented and dense dispersion of CNTs in PAEK matrix expanded the rigid segments in the composites, promoting the shape fixity. Besides, the fixity ratio of the composites on parallel direction always slightly higher than the corresponding sample on vertical direction.

Figure 7 [about here]

### **Electric-actuated shape memory behaviors**

The electric-actuated shape memory behaviors of PAEK/CNTs composites were investigated and illustrated in Figure 8 (a-d: the samples on parallel direction were employed for testing, and the imposed triggering voltage was 40V). Figure 8a shows the whole shape recovery process of the composites with CNTs content of 10 wt% upon applied voltage of 10V. The original shape could be recovered within 10s, which exhibited the electric-actuated rapid recovery capability. Thermal infrared images were captured for the monitoring of the temperature variation caused by the electrothermal effect of CNTs, depicted in Figure 8b. Along with constant triggering voltage, the temperature increased rapidly, which finally reached up to 107.1 °C as the achievement of the recovery process. Figure 8c shows the recovery ratio of composites with diverse content of CNTs. As the increasing of CNTs content, the recovery ratio increased gradually, from 82.2 % to 93.2%, and 94.2%, corresponding to the CNTs content of 5 wt%, 10 wt%, and 15 wt%, respectively. In these tests, the samples on parallel direction were employed, and the recovery ratio of samples on vertical direction was lower than the corresponding samples on parallel

direction, shown in Figure 8e. Meanwhile, the composites with CNTs content of 5 wt% on vertical direction could not achieve the shape recovery upon the triggering voltage of 40V, which indicated the significance of the orientation of CNTs in PAEK matrix by applied voltage. The recovery ratio of composites with diverse applied voltage is showed in Figure 8d. As the increasing of applied voltage, the recovery ratio of the composites with CNTs content of 10 wt% increased gradually, from 82.4%, to 85.7%, 93.2%, and 94.2%, corresponding to the voltage of 0V, 5V, 10V, and 15V, respectively. With the increasing of applied voltage, the orientation extent of CNTs improved, which conducive to the current path and promoting to the shape recovery. Figure 8e shows the recovery ratio of the composites upon different applied voltage on parallel and vertical directions. The recovery ratio of the composites on parallel direction was slightly higher than that of the samples on vertical direction, which could be closely related to the enhancement of conductive path. Due to the shape fixity of the composites triggered by electric was the same with them triggered by heat, it was not repeatedly illustrated. Figure 8f shows the conductivity of the composites with diverse CNTs contents on parallel and vertical directions. Significantly, the conductivity of the composites on parallel direction was always slightly higher than the corresponding sample on vertical direction. All the samples except for the sample with 5 wt% content of CNTs on vertical direction could realize the shape recovery. The electrothermal effect of 5 wt% CNTs with the lowest conductivity of 0.219 S/cm could not provide the sufficient thermal power to trigger the shape recovery. When the content of CNTs was 15 wt%, the conductivity increased significantly, and the triggering voltage decreased from 40V to 30V. The orientation of CNTs was instrumental in the construction and enhancement of current path, and as a result, the conductivity increased.

Figure 8 [about here]

#### **Rapid heat- and electric-response**

Upon the applied voltage, CNTs were significantly oriented in PAEK matrix consistent with the current direction. With the increasing of CNTs content, continuous radially aligned CNTs constructed an efficient conductive path, conducive to the thermal conductivity and electric conductivity, as depicted in Figure 9a. Thereby, heat- and electric-triggered shape memory behaviors could be strengthened through the construction of conductive path. Figure 9b shows the heat-actuated shape recovery behaviors of the PAEK/CNTs composites with the same CNTs content and applied voltage, except for the current direction. The composite on parallel direction exhibited the more rapid shape recovery pace (within 12s) than it on vertical direction (within 18s), which were due to the internal constructed conductive path. In Figure 9c, when the CNTs content was 5 wt%, the composite on parallel direction could recover to its original shape actuated by electric, but on vertical direction it could not be actuated by electric power. In Figure 9d, the composite on parallel direction exhibited more efficient shape recovery than it on vertical direction. These radially aligned CNTs/PAEK composite actuators containing efficient heat/electric dual triggered shape memory effect exhibited exciting application prospects.

Figure 9 [about here]

### **Voltage actuators**

Based on the investigations above, we employed aligned CNTs/PAEK composites with 15 wt% CNTs as the voltage actuators, due to the excellent mechanical performances and durability. Besides, comparing with the PAEK/CNTs on vertical direction, aligned CNTs/PAEK composites exhibited rapid electric-response speed and extended applied voltage ranges, which imparted the voltage actuators the enhanced sensitivity and large actuating range. Initially, we investigated the recovered angles of the composite actuators at the different voltage, shown in Figure 10. The range of applied voltage was from 8V to 50V, which was attributed to that the voltage below 8V could not triggered the shape recovery of actuators, in addition that the recovery angle and speed did not exhibit difference while the voltage over 50V. It could be obtained that the recovered angles increased gradually when the voltage was lower than

20V. In this stage, the treated time was 300s, in order to obtain the completed recovered angles. While the voltage was from 20V to 25V, the actuators almost finished the shape recovery within 110s, and the recovered angles increased up to around 155°. Subsequently, continually increased the voltage, the recovered angles almost kept stability and the recovered time decreased.

Figure 10 [about here]

According to the diverse recovered angles and time, shown in Figure 10, we designed the two kinds of voltage actuators catering to different voltages. In Figure 10a, we utilized the recovered angles of voltage actuators to measure the actuating actions. Different applied voltage could trigger the actuator to deform to the different angles, and as the increasing of voltage, the recovered angles increased. It was visual to obtain the actuating actions through the recovered angles of the actuators. In addition, in this mode, the applied range of actuators was from 8V to 19V. While the applied voltage was over 20V, we could utilize the recovered time of voltage actuators to measure the actuating actions, shown in Figure 10b. When the testing voltage was 20V-22V, the recovered time was almost 110s, and when it increased to 25V, the recovered time was decreased to 35s. Afterwards, the gradual decreasing of recovered time reflected the increasing of testing voltage. We could obtain the testing voltage value in accordance with the recovered time of the sensors. In this time-mode, the testing range of sensors was from 20V-50V. The angle and time mode of voltage sensors was employ to visually measure the testing voltage, which impart the wide utilization potential in fields of electronic devices.

Figure 11 [about here]

The durability and stability were significant for sensors, and we conduct the continuous voltage actuating testing to measure the durability of aligned CNTs/PAEK composites actuators, as shown in Figure 12. For angle-mode, it could be obtained that the recovered angles of actuators almost kept stable during the cyclic sensing test. For time mode, we could observed that the actuators finished the shape



recovery behaviors within 5s during the cyclic sensing test. The stability of angle-mode and time-mode indicated the great durability of the composite actuators and convinced the regular operation.

Figure 12 [about here]

## Conclusions

In summary, we synthesized a shape memory PAEK via nucleophilic substitution reaction, and fabricated PAEK/CNTs composites with oriented CNTs conductive paths via an electro-mixed fusion method. The composites exhibited the excellent thermal stability due to the intrinsic properties of PAEK and the incorporation of CNTs. The dispersion and orientation of CNTs in PAEK matrix were greatly affected by CNTs content, applied voltage, and current directions. Mechanical performances of composites were reinforced remarkably via the integration and orientation of CNTs in PAEK matrix. As the increasing of CNTs content, the tensile strength and Young's modulus increased gradually, whereas the elongation at break decreased. As the increasing of applied voltage, the tensile strength and Young's modulus increased. Meanwhile, the strength and modulus of composites on parallel direction were higher than that on vertical direction, concerning with the continuous and oriented arrangement of CNTs in PAEK matrix. Besides, as the increasing of CNTs content and applied voltage, the reinforcement of strength and modulus on parallel direction was more significant.

The PAEK/CNTs composites exhibited excellent heat/electric dual actuated shape memory behaviors. As for heat-actuated SME, as the increasing of CNTs content, the recovery ratio decreased. Nevertheless, it increased gradually with the increasing of applied voltage, which was attributed to the construction of thermal conductive path by continuous oriented CNTs. Besides, the recovery ratio of composites on parallel direction was almost higher than that on vertical direction, which could be concerned with the same reason. In addition, composites exhibited excellent fixity ratio which were all over 98%. As for electric-actuated SME, as the increasing of CNTs content, the recovery ratio increased due to the electrothermal effect of CNTs. As the increasing of applied voltage, the recovery ratio

increased because of the construction of conductive path. The shape recovery ratio of composites on parallel direction was always higher than those on vertical direction, which could be related to the enhancement of conductive path. Meanwhile, the conductivity of the composites on parallel direction was always slightly higher than the corresponding sample on vertical direction. Upon the applied voltage, radially aligned CNTs constructed the conductive path in PAEK matrix, which was instrumental to the thermal conductivity and electrical conductivity. Therefore, rapidly efficient heat/electric dual actuated shape memory behaviors were achieved at low triggering voltage.

In addition, we employed aligned CNTs/PAEK composites with 15 wt% CNTs as the voltage actuators due to the excellent mechanical performances, durability, rapid electric-response speed and extended applied voltage ranges. We designed the two kinds of voltage actuators (angle-mode and time-mode) to achieve the measurement of actuating actions (range from 8V to 50V). For angle-mode, we could measure the actuating actions at the range of 8V-19V, and the time-mode of voltage actuators could be utilized while the applied voltage was 20V-50V. These efficient composite voltage actuators exhibited the excellent stability and durability in continuous voltage actuating testing. We proposed a facile fabrication of an efficient radially aligned CNTs/PAEK heat/electric dual triggered shape memory composite voltage actuators which developed the exciting potential in smart actuators and electronic devices.

## Acknowledgements

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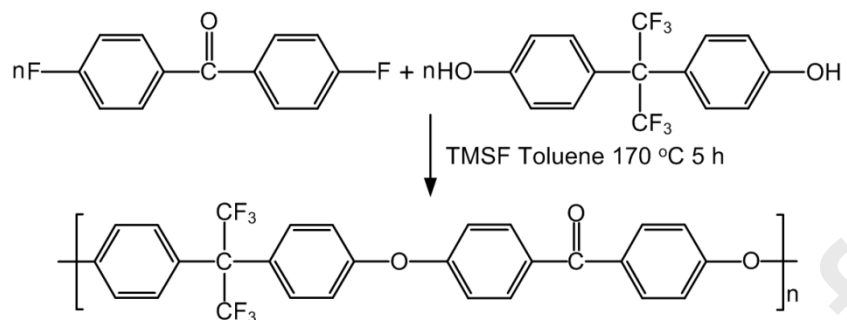
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Scheme 1. Synthetic route of shape memory PAEK

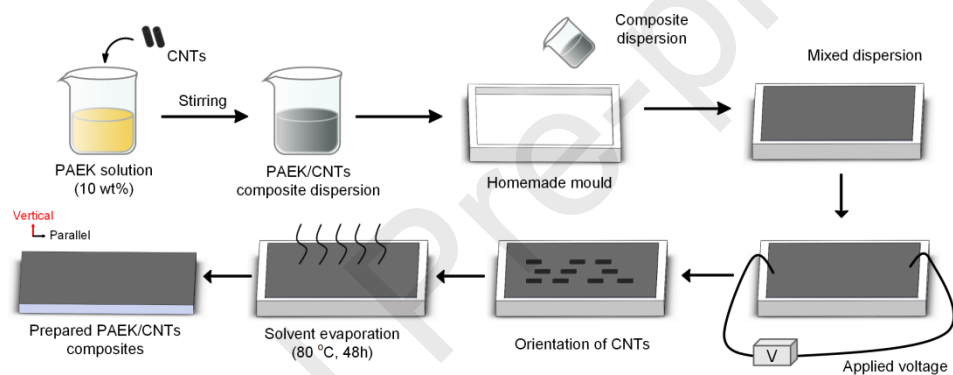
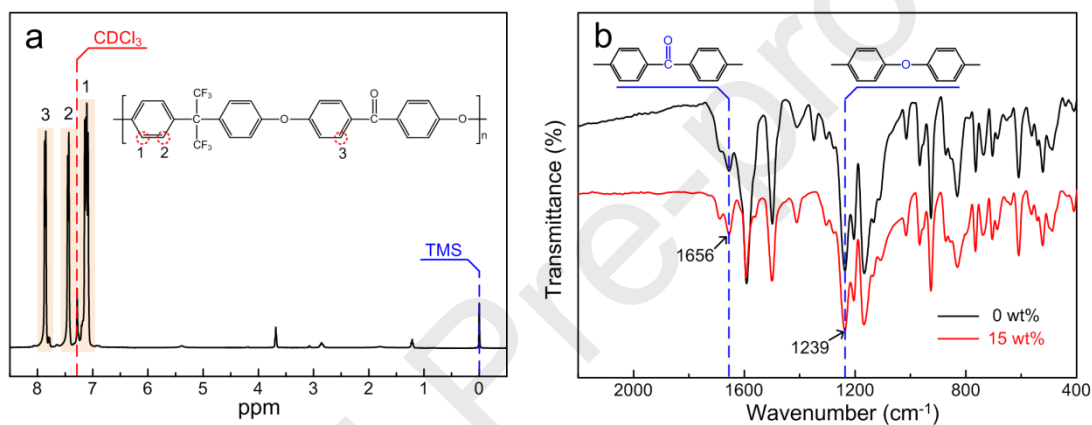


Figure 1. Fabrication process of oriented CNTs/PAEK composites

Table 1. Feed content of CNTs and applied voltages for CNTs orientation

Sample: PAEK 10V voltage	Content of CNTs			
	0 wt%	5 wt %	10 wt%	15 wt %
Sample: PAEK 10 wt% CNTs	Applied voltage for CNTs orientation			
	0V	5V	10V	15V

Figure 2. Characterization of synthesized PAEK and PAEK/CNTs composites: a  $^1\text{H}$  NMR spectra; b FTIR spectra (CNTs content of 0 wt% and 15 wt%)

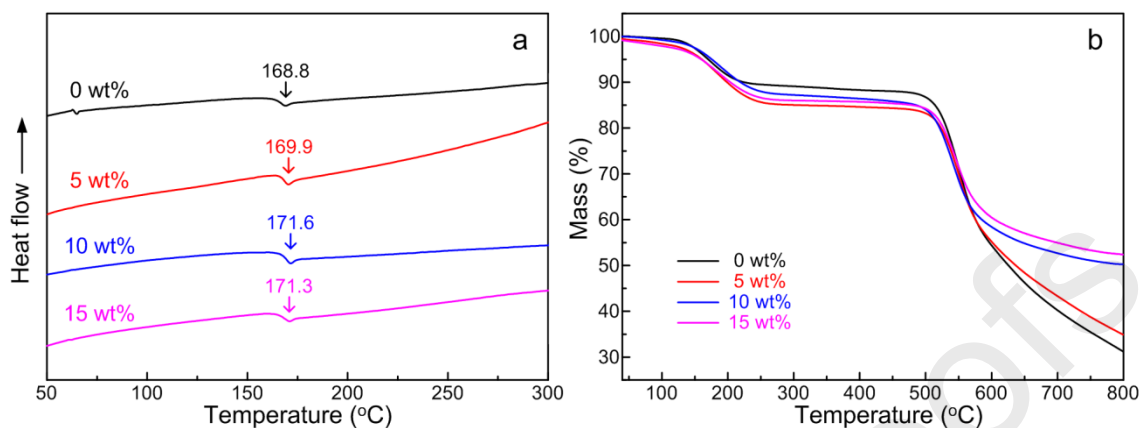


Figure 3. DSC (a) and TGA (b) curves of PAEK/CNTs composites with different CNTs content (0 wt%, 5 wt%, 10 wt%, and 15 wt%)

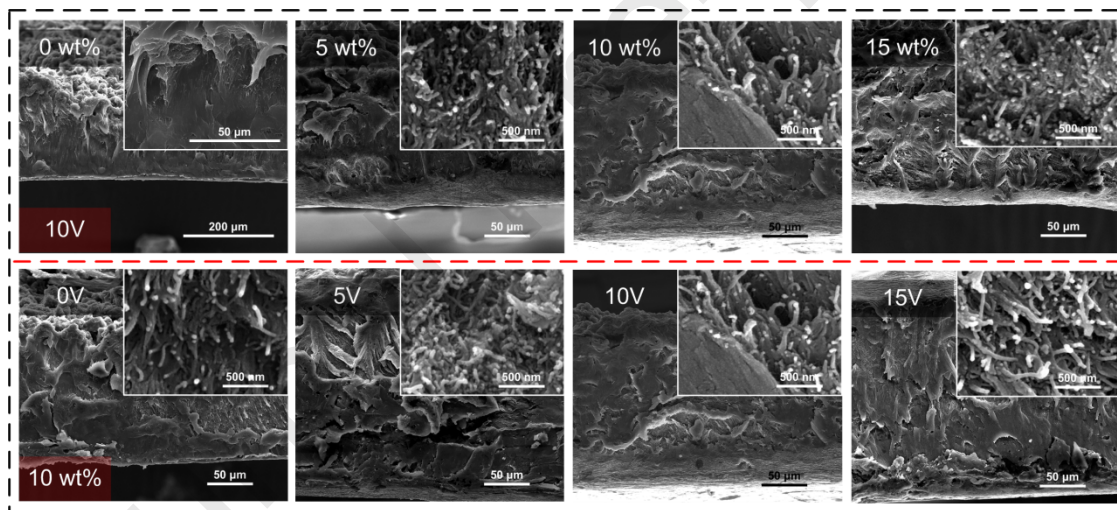


Figure 4. SEM images of PAEK/CNTs composites on parallel direction: (upper row) samples with different content of CNTs (0 wt%, 5 wt%, 10 wt%, and 15 wt%) treated by the applied voltage of 10V, and (lower row) samples of 10 wt% CNTs treated by different applied voltage (0V, 5V, 10V, and 15V)



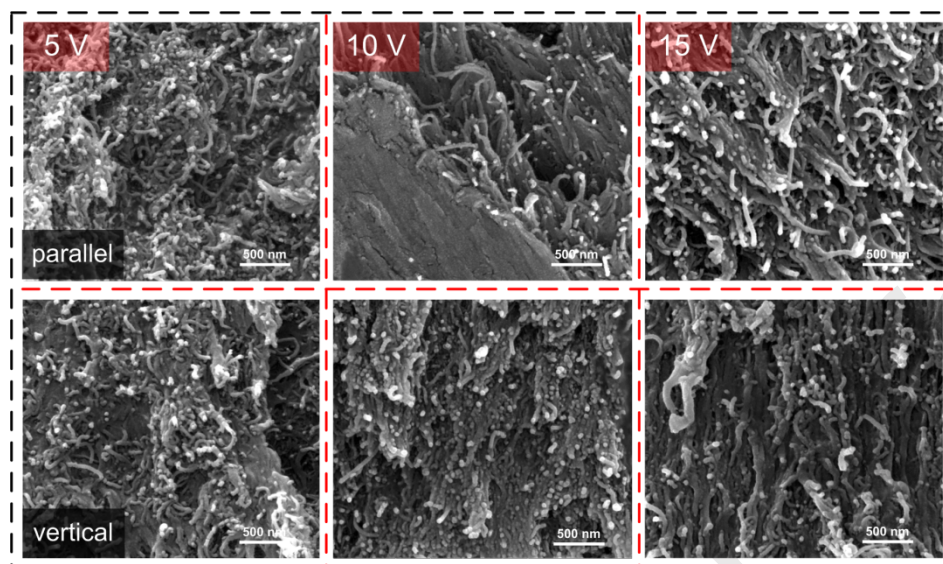


Figure 5. SEM images of PAEK/CNTs composites on parallel direction and vertical direction with 10 wt% CNTs upon different applied voltages (5V, 10V, and 15V)

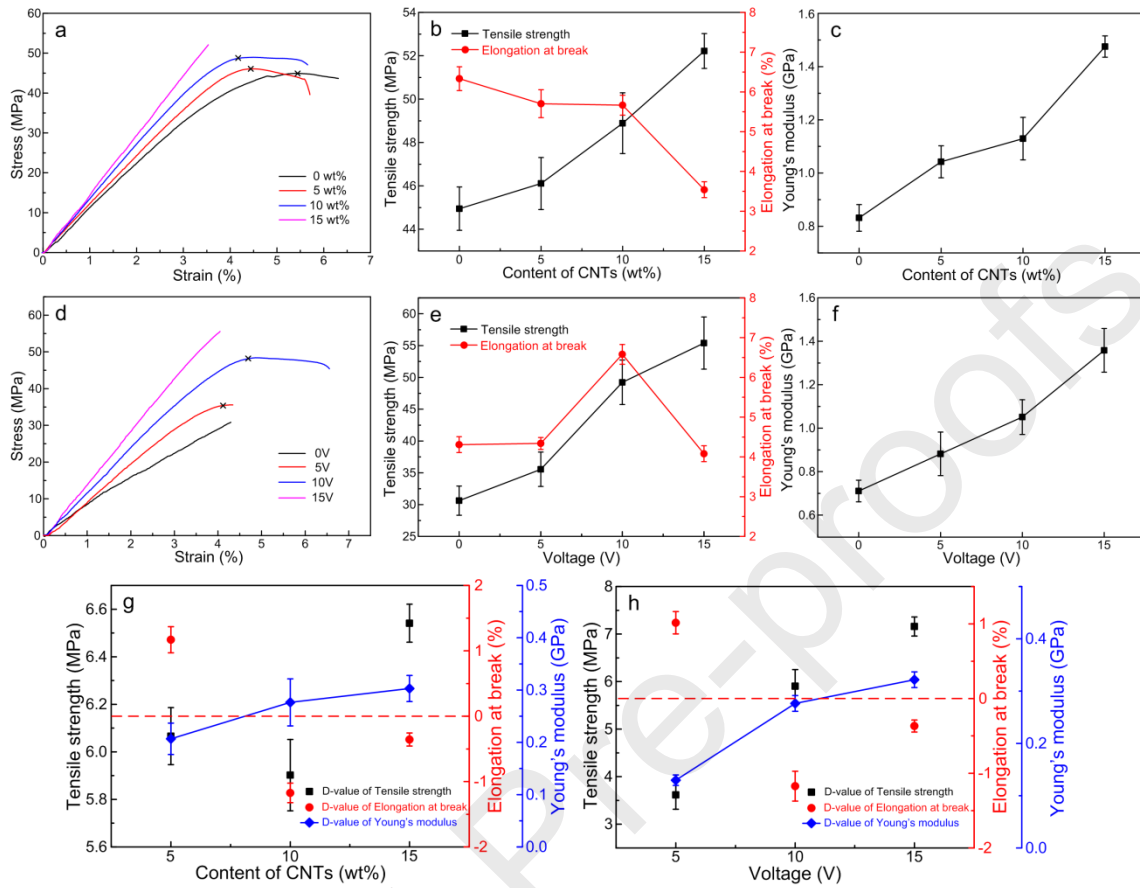


Figure 6. Static tensile test results of PAEK/CNTs composites on parallel direction and vertical direction: (a) Stress-strain curves of the composites upon voltage of 10V; (b) Tensile strength and elongation at break of the composites upon voltage of 10V; (c) Young's modulus of the composites upon voltage of 10V; (d) Stress-strain curves of the composites with CNTs content of 10 wt%; (e) Tensile strength and elongation at break of the composites with CNTs content of 10 wt%; (f) Young's modulus of the composites with CNTs content of 10 wt%; (g) D-value of mechanical properties of the composites upon the voltage of 10V between parallel and vertical directions; (h) D-value of mechanical properties of the composites with CNTs content of 10 wt% between parallel and vertical directions (a-f: the samples on parallel direction were employed for testing)

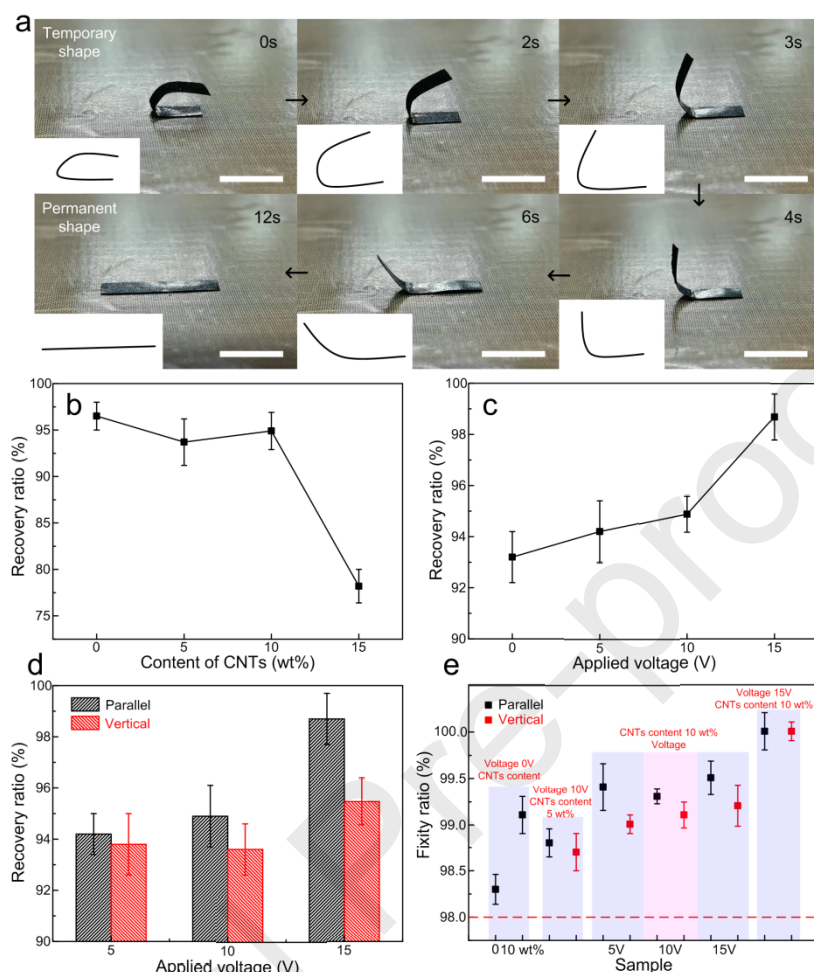


Figure 7. Heat-actuated shape memory behaviors of PAEK/CNTs composites: (a) The whole shape recovery process of the composites with CNTs content of 10 wt% upon the voltage of 10V at 181 °C ( $T_g + 10$  °C); (b) Recovery ratio of the composites upon the voltage of 10V with different content of CNTs (0 wt%, 5 wt%, 10 wt%, and 15 wt%); (c) Recovery ratio of the composites with CNTs content of 10 wt% upon different applied voltage (0V, 5V, 10V, and 15V); (d) Recovery ratio of the composites with CNTs content of 10 wt% upon different applied voltage (5V, 10V, and 15V) on parallel and vertical directions; (e) Fixity ratio of the composites with diverse content of CNTs, upon different voltage, on parallel and vertical directions (a-c: the samples on parallel direction were employed for testing, in addition that untagged scale bars of 1 cm)

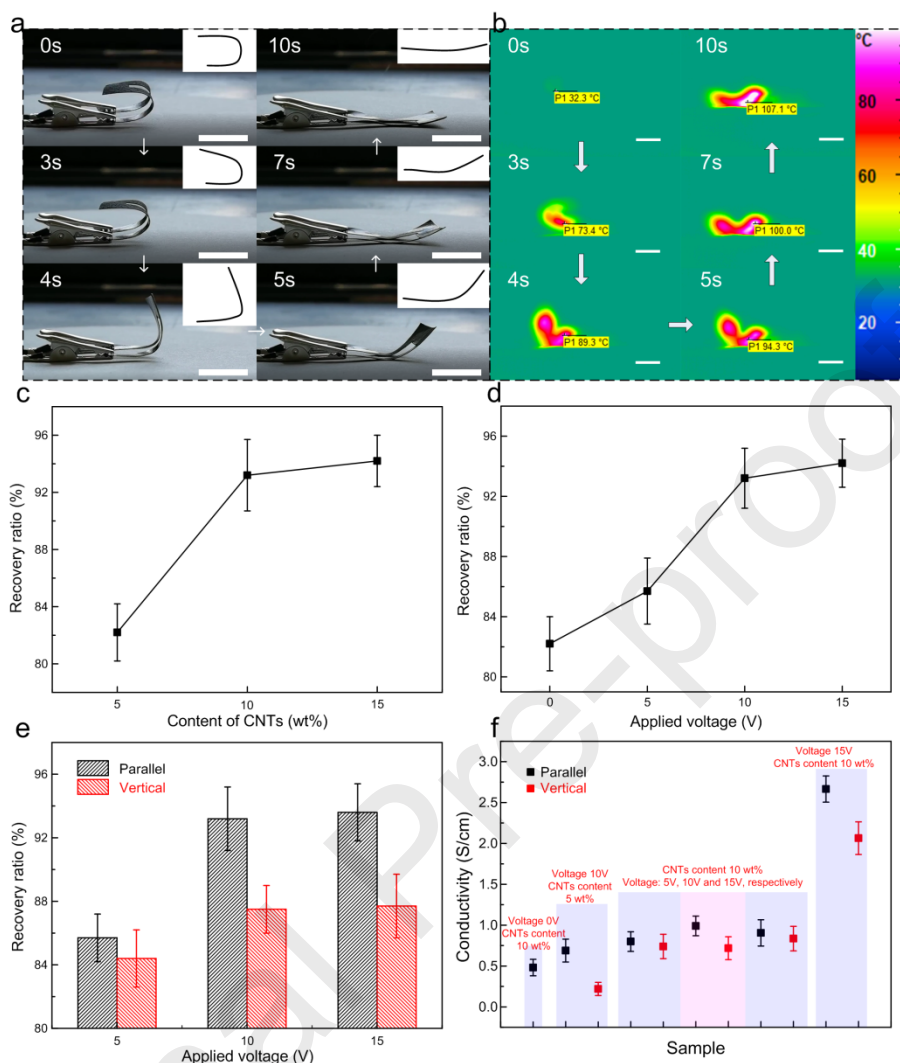


Figure 8. Electric-actuated shape memory behaviors of PAEK/CNTs composites: (a) The whole shape recovery process of the composites with CNTs content of 10 wt% and applied voltage of 10V at the triggering voltage of 40V; (b) Thermal infrared images of the whole shape recovery process; (c) Recovery ratio of the composites with different content of CNTs (5 wt%, 10 wt%, and 15 wt%) upon applied voltage of 10V; (d) Recovery ratio of the composites with CNTs content of 10 wt% upon different applied voltage (0V, 5V, 10V, and 15V); (e) Recovery ratio of the composites with CNTs content of 10 wt% upon different applied voltage (5V, 10V, and 15V) on parallel and vertical directions; (f) Conductivity of the composites with diverse content of CNTs, upon different voltage, on parallel and vertical directions (a-e: the samples on parallel direction were employed for testing, and the imposed triggering voltage was 40V, in addition that untagged scale bars of 1 cm)

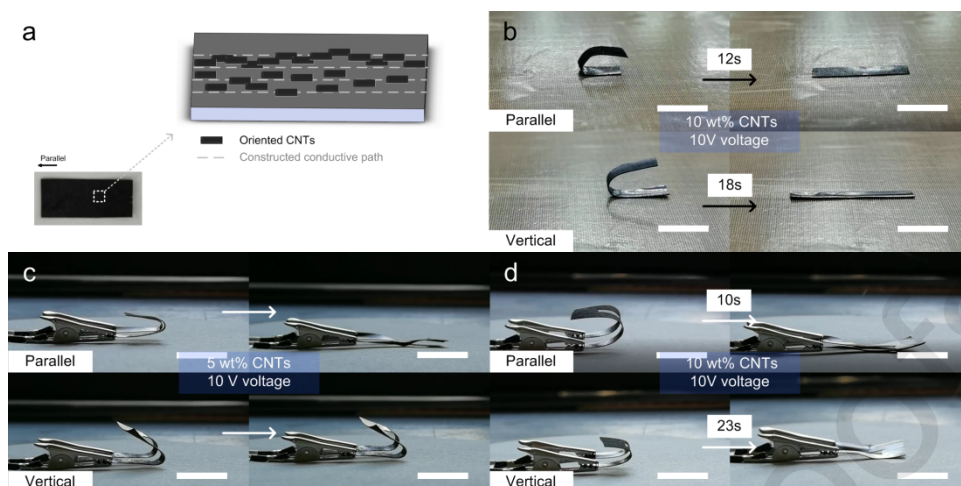


Figure 9. Efficient heat/electric dual triggered shape memory behaviors: (a) Construction of conductive path of oriented CNTs; (b) Rapid heat-triggered shape recovery behaviors; (c) Low triggering voltage; (d) Efficient electric-triggered shape recovery behaviors (triggering temperature of  $181\text{ }^{\circ}\text{C}$  ( $T_g + 10\text{ }^{\circ}\text{C}$ ), and imposed triggering voltage of  $40\text{V}$ , in addition that untagged scale bars of  $1\text{ cm}$ )

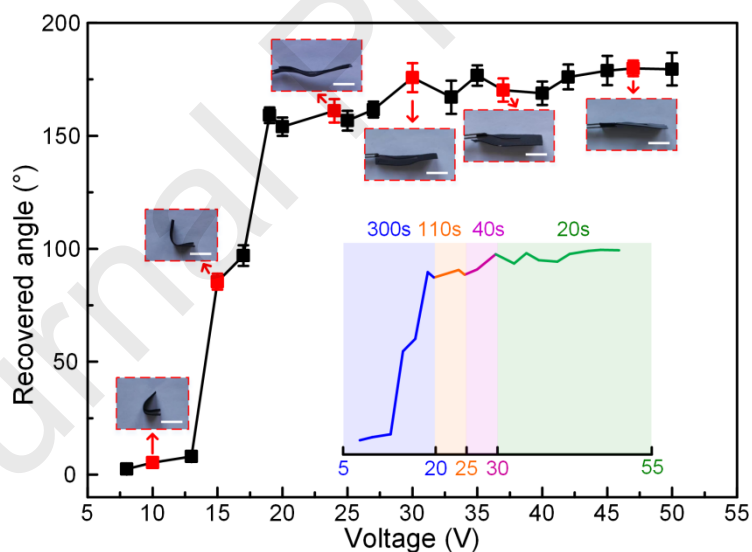


Figure 10. Recovered angles of aligned CNTs/PAEK composite actuators upon the voltage of the range from  $8\text{V}$  to  $50\text{V}$  (scale bars of  $1\text{ cm}$ )

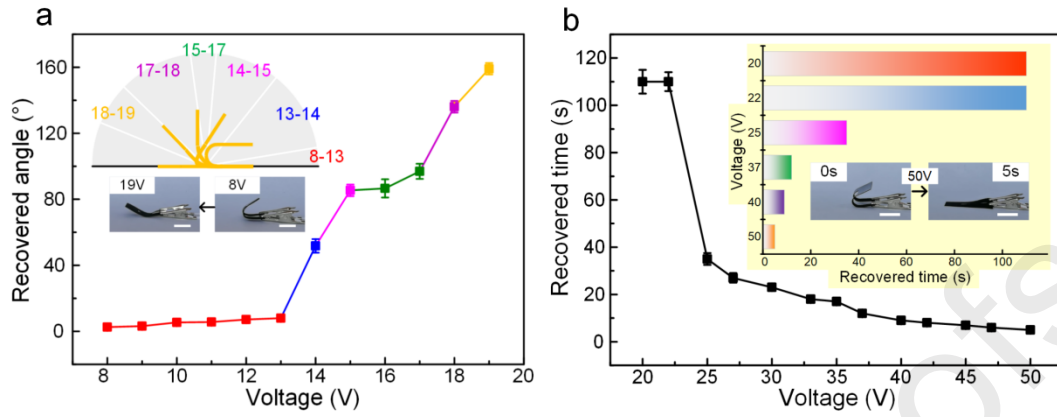


Figure 11. (a) The operation mechanism of voltage actuators-angle mode at the applied voltage with the range of 8V-19V; (b) The operation mechanism of voltage actuators-time mode at the applied voltage with the range of 20V-50V (scale bars of 1 cm)

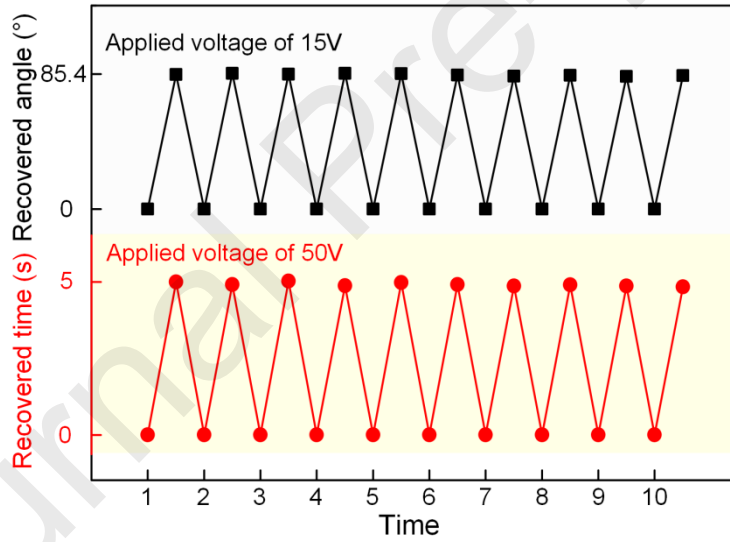


Figure 12. Continuous voltage actuating behaviors of aligned CNTs/PAEK composite actuators

Shuai Yang: Conceptualization, Methodology, Data curation, Writing-original draft, Writing-reviewing & editing.

Yang He: Supervision, Data curation, Conceptualization, Methodology, Writing-reviewing & editing.

Jinsong Leng: Conceptualization, Supervision, Resources, Funding acquisition, Project Administration, Writing-reviewing & editing.



1. We synthesized the shape memory PAEK, and fabricated oriented CNTs/PAEK composite actuators via a novel electro-mixed fusion method.
2. Composite actuators exhibited enhanced mechanical properties and excellent heat/electric dual actuated shape memory behaviors.
3. With the constructed conductive path, efficient heat/electric dual triggered shape memory effect was obtained for high recovery ratio, rapid triggered shape recovery and low triggering voltage.
4. These efficient composite voltage actuators, which exhibited the excellent stability and durability, opened door for automatic robots, engineering devices, and aerospace constructions.